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University of California, Berkeley, Ph.D., 1973
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I. Synthesis and Solvolysis of Quadricyclyl-7-Carbinol
II. *Ab Initio* Studies on Bishomocubane and Related Compounds

By

John Wilmot Vinson

B.S. (Michigan State University) 1968

DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

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GRADUATE DIVISION

of the

UNIVERSITY OF CALIFORNIA, BERKELEY

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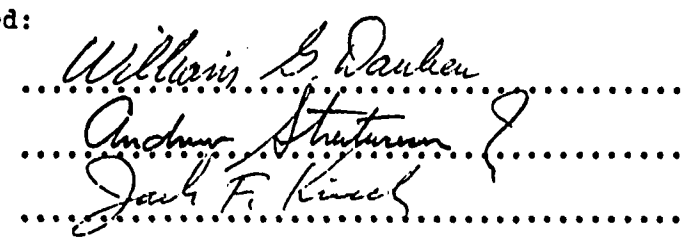

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ABSTRACT:

Part I.

The synthesis of quadricyclyl-7-carbinol (1) is described. The p-bromobenzenesulfonate and trifluromethanesulfonate esters of 1 were prepared and solvolyzed. The main product (78%) from the solvolysis of the triflate in trifluoroethanol was 2, 7-trifluoroethoxyquadricyclo[4.2.0.0^{2,8}0.^{3,5}]octane. The mechanism of the solvolysis and the interaction between strain and carbonium ion stability in this system are discussed on the basis of the results of the solvolysis.

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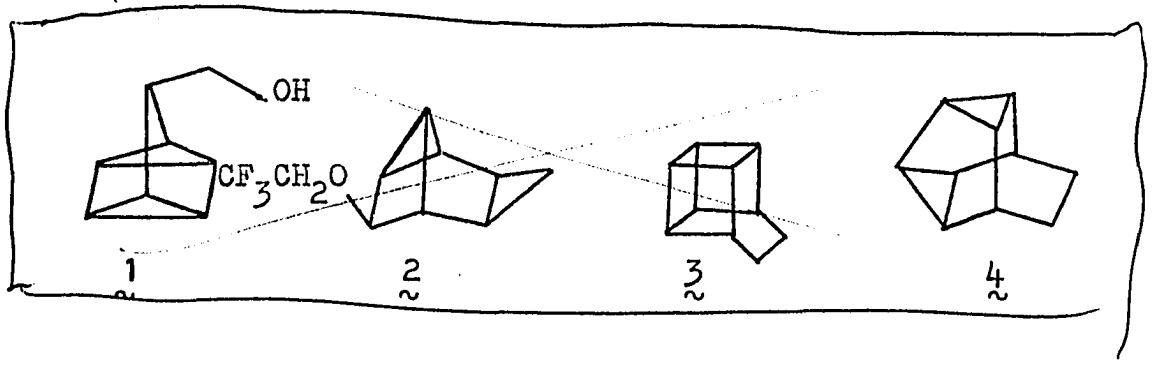

Part II.

The metal catalyzed conversion of bishomocubane (3) to pentacyclo[4.4.0.0^{2,4}0.^{3,8}0.^{5,7}]decane (4) was investigated by an ab initio molecular orbital calculation. The strained back bond (opposite the bridge) was simulated by an ethane molecule constrained in the same geometric arrangement as the carbons in 3 and 4. Electron density maps were prepared from results of the calculation. The results of the calculation are argued to

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be more consistent with a concerted mechanism for the rearrangement of 3 to 4 than with the stepwise mechanisms that have been proposed.

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Introduction

Two fields of research that have recently seen extremely rapid advances are the study of carbonium ions and the synthesis of highly strained molecules.

The concept of nonclassical ions, with positive charge delocalized over several atoms of a sigma-bonded framework, has given rise to much discussion and controversy.[1] It is now generally accepted that remote sigma bonds can participate in the ionization of suitable molecules. This participation can result in rate acceleration and molecular rearrangements.

One area of research into carbonium ion behavior has been the investigation of sequential rearrangements.[2] It is well known that an adjacent cyclopropyl ring can assist in the ionization of an alkyl halide or sulfonate ester.[3] A less investigated problem involves systems in which such a stabilized ion is generated by rearrangement. How early in the process of rearrangement does the assistance of a neighboring group take effect? This question has been touched upon in a number of systems,[4] but only rarely directly attacked. In the field of strained compounds, the availability of photochemical techniques and carbeneoid insertion reactions has made possible the synthesis of compounds which would have been considered impossible only a few years ago; compounds such as cubanes,[5] prismanes,[6] bicyclobutanes,[7] and propellanes[8]

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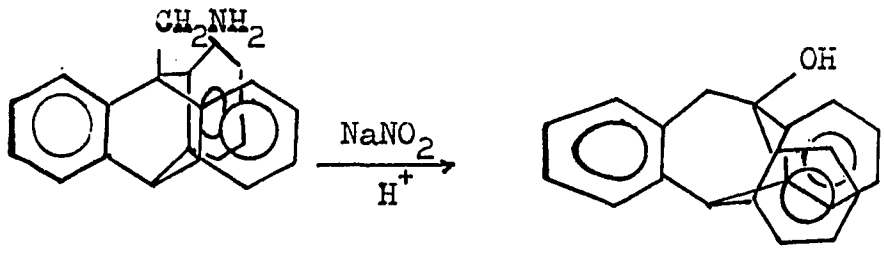
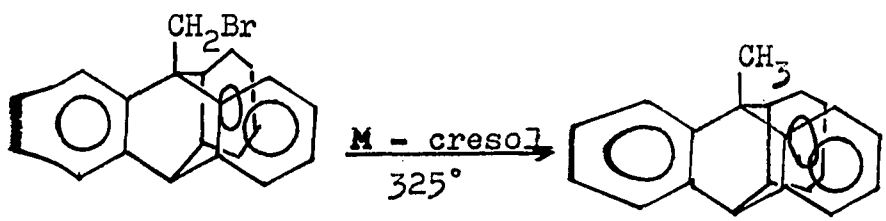
are examples of such materials.

With the widespread interest in both carbonium ions and strained molecules, it is natural to think of combining the two fields. Much work has been done on solvolysis in strained systems,[9] but the usual result has been either relief of strain[9a] or at most degeneracy.[9b] An approach that has been less thoroughly investigated is the use of carbonium ion rearrangement to incorporate strain into a molecule. Considerable energy can be released when an unstable cation rearranges to a highly stabilized one. It should be possible to salvage some of this energy in the form of new strained bonds. The rearrangement of allylcarbinyl cation to cyclopropylcarbinyl cation is an example of this kind of energy salvage, but it should be possible to apply the principle to larger systems.

Two systems in which the energy salvage concept has been investigated are the deamination of 1-aminomethyltryptic ine[10a] and the solvolysis of adamantylcarbinyl tosylate.[10c]





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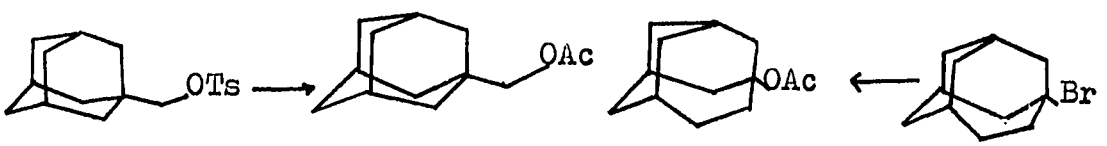
The trypticene case is not really a good example of the principle, since the final product is actually less strained than the starting material, although the intermediate bridgehead carbonium ion is highly strained. Solvolysis of trypticylcarbinyl bromide proceeds only slowly at 325° in m-cresol[10b] and yields 1-methyltrypticene, apparently by intermolecular hydride abstraction by the unrearranged cation. In contrast, deamination of the amine yields the rearranged alcohol.

In the adamantylcarbinyl system, it was shown[10c] that both



1 - OTs 1 - OAc 6% 2 - OAc 94% 2 - Br

adamantylcarbinyl tosylate (1-OTs) and 3-bromohomoadamantane (2-Br) solvolyze in refluxing acetic acid to a mixture of 6% of 1-OAc and 94% of 2-OAc. The strain energy of the homoadamantyl skeleton is estimated to be about 10 kcal/mole. The product ratio shows that the rearranged skeleton 2 is favored by 2 to 4 kcal/mole. The energy gained on rearrangement from a primary to a tertiary cation was very conservatively estimated to be approximately 16 kcal/mole;[10c] about 12 to 14 kcal of this energy has apparently been sal-

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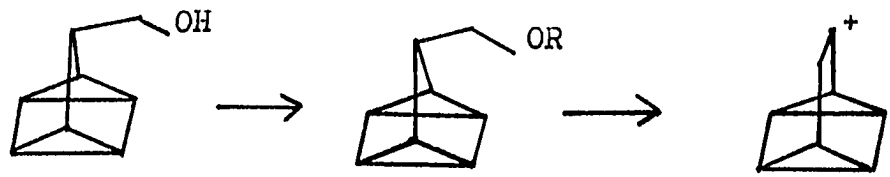
vaged in the form of skeletal strain in 2.

A compound that has the potential of providing answers to both the questions of introduction of strain by rearrangement and participation of stabilizing groups in the process of rearrangement is 3, quadricyclyl-7-carbinol (3-hydroxymethylquadricyclo [3.2.0.$0^{2,7}$.$0^{4,6}$]heptane). Solvolysis of a



3 3-OR 4

sulfonate ester of 3 would give an ion theoretically capable of a multitude of rearrangements. Of special interest is the most obvious rearrangement, a 1,2 alkyl shift. In this rearrangement a product with a highly stabilized[3] cyclopropylcarbinyl structure is formed from an unstabilized primary cation, but the rearranged structure 4 is very highly strained. A minimum of 8 kcal/mole[10c] would be gained by rearrangement from a primary to a secondary cation, and even more if the cyclopropyl ring can participate in the rearrangement step. Is the stabilization gained enough to overcome the concomitant increase in strain imposed by the rearrangement? A balance of forces is involved here, and any outcome of the solvolysis of 3-OR would be instructive. If 4 is formed (even if

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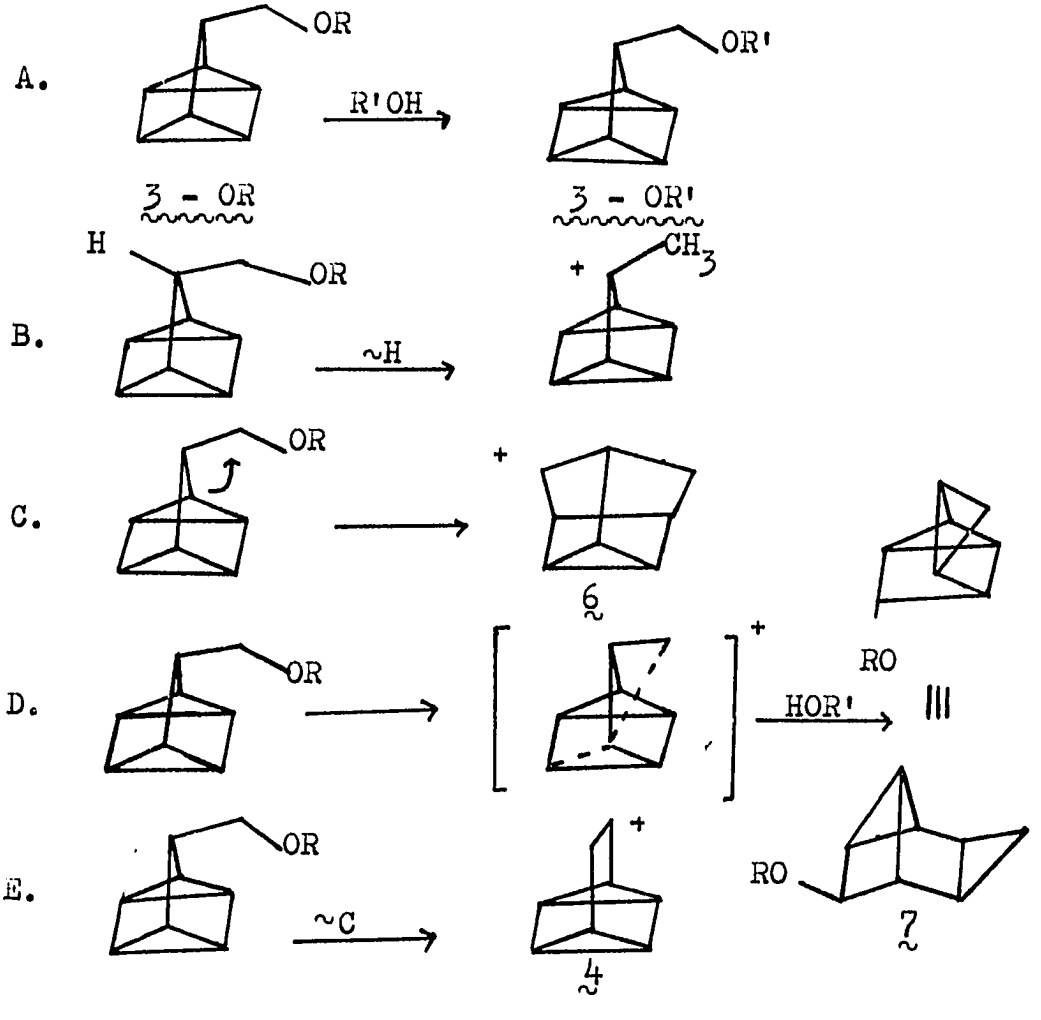
it continues to rearrange to other products) it will have been shown that a considerable amount of strain can be incorporated into a molecule by carbonium ion rearrangement. If other pathways predominate to the exclusion of rearrangement to 4, it will be clear that an otherwise favorable reaction has been obstructed by strain, forcing the molecule to adopt other, ordinarily unfavorable, ways of attaining stabilization. The synthesis and reactions of 3 are the topics of this thesis.

A variety of rearrangements are possible for the cation generated from 3, as detailed in Scheme 1.

SCHEME 1



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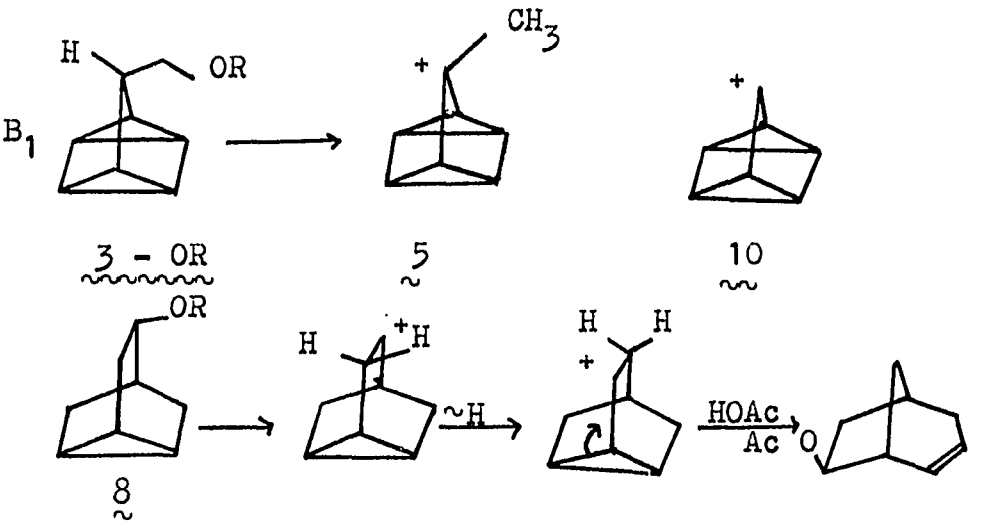
All of these reactions are known to occur in other systems. Path A, solvolysis without rearrangement, can occur by S_N2 attack of solvent or by solvent assisted S_N1 reaction. These two processes are of almost universal occurance except in such exotic non-nucleophilic solvents as fluorosulfonic acid.[11]

Path B is a hydride shift. Although hydrogen is not as effective as an alkyl group in anchimeric assistance, hydride shifts do occur, especially when much stability is gained in the process.[12] An example of such a hydride shift can be found in the solvolysis of the tricyclo[3.2.0.$0^{2,7}$]-octyl system 8. Of the product mixture, 65% is acetate 9



resulting from a hydride shift followed by opening of the cyclopropylcarbinyl cation to an allylcarbinyl system.[12] In the case of 3, the ion generated by the hydride shift would be the tertiary quadricyclyl cation 5. This cation should be even more stable than the

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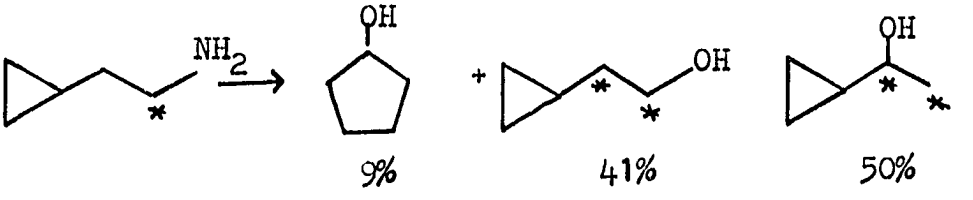
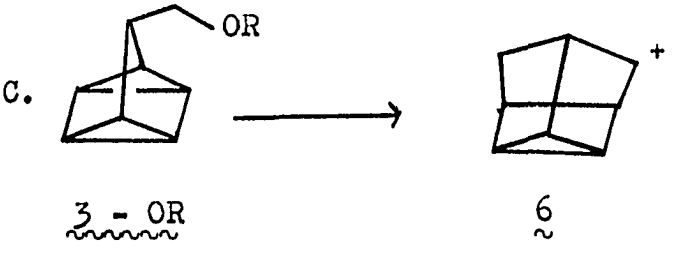
secondary quadricyclyl cation 10, which is known to be highly stabilized.[14] The hydride shift of Path B is therefore a side reaction to be considered.

Path C is an expansion from a **cyclopropylethyl** cation to a cyclopentyl cation. This type of expansion occurs to the extent of 9% in the nitrosative deamination of 2-cyclopropylethylamine, where it is accompanied by hydride shift to give 1-cyclopropyl-





3 - OR 6

ethanol and by the degenerate 1,2 cyclopropyl shift, which was detected by an isotopic labeling experiment. If this rearrangement occurs in the solvolysis of 3, cation 6 would be produced.

Path D is the rearrangement of a cyclopropylethyl cation to another cyclopropylethyl cation. Such rearrangements have been observed in a variety of compounds. In systems of favorable geometry, this type of cyclopropyl participation can lead to considerable anchimeric acceleration and rearrangement. One of the

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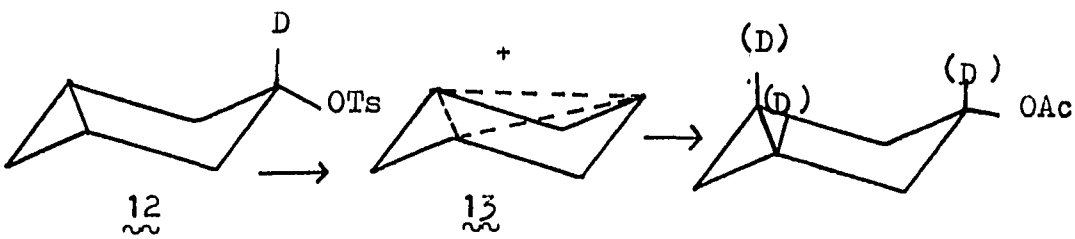
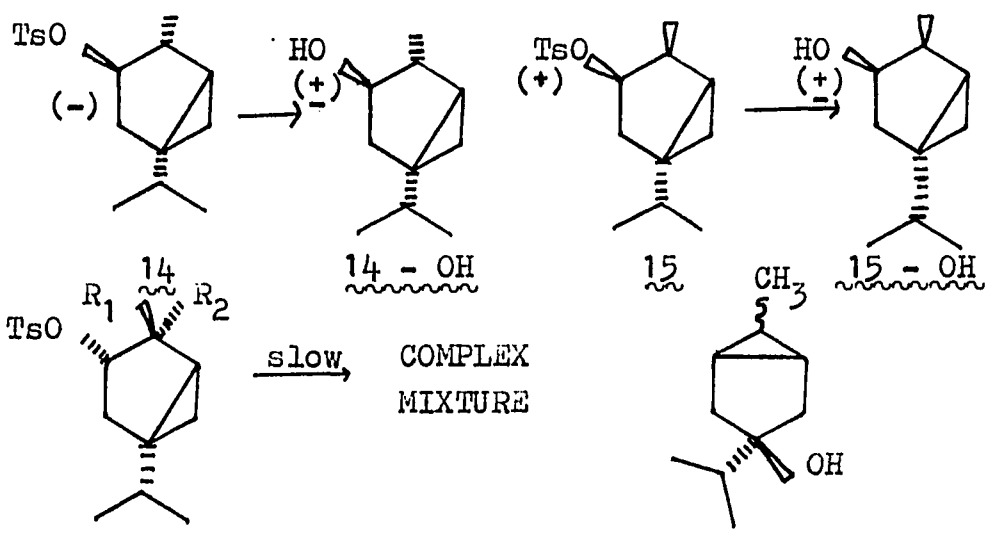
first examples of this type of participation was the solvolysis of cis-3-brosyloxybicyclo[3.1.0]hexane (12).[16] A slight acceleration of the solvolysis rate relative to cyclopentyl brosylate or the trans isomer was noted, and a deuterium label initially in the 3 position was randomly distributed among the methine positions after solvolysis. A fully delocalized tris-homocyclopropenium intermediate 13 was suggested to explain these results. Similarly, Norin[17] observed



12 13

that the hydrolysis of neothujyl and neoisothujyl toluenesulfonates 14 and 15 led to complete racemization, with the rate of solvolysis and product specificity considerably greater than the isomeric thujyl and



16 (R_1 = H, R_2 = CH_3)
17 (R_1 = CH_3, R_2 = H)

18

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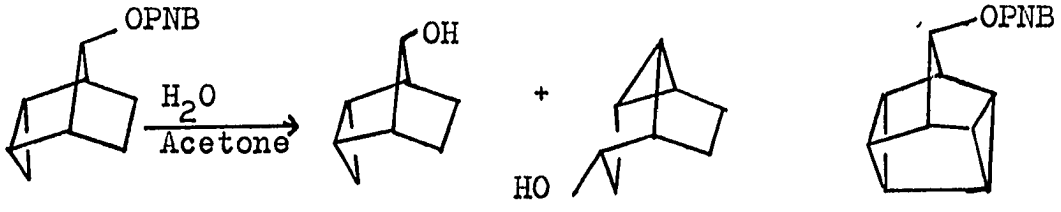
isothujyl systems 16 and 17. Interestingly, no products of structure 18 were isolated from the solvolyses even though the tertiary center might be expected to bear more of the positive charge density than the two secondary centers in the trishomocyclopropenium cation intermediate. Possibly the bulky isopropyl group hinders approach of the incoming nucleophile to such an extent that only 14-OH and 15-OH can be detected among the products.

In cases where the geometry is suitable, this type of homoconjugation of a cyclopropane ring can give strong anchimeric assistance. Two such cases are anti-endo-tricyclo-[3.2.1.$0^{2,4}$]octyl-8-p-nitrobenzoate (19)[18] and the related pentacyclo [4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl-9-p-nitrobenzoate (20).[19]



19 20

Both of these compounds exhibit solvolysis rates far greater than would be predicted from comparison with 7-norbornyl or other model systems. For instance, 19 solvolyzes in 70% aqueous acetone 1000 times faster than anti-7-norbornenyl-p-nitrobenzoate, which itself is estimated to solvolyze 10^{11} times more rapidly than 7-norbornyl deriviatives.[18] The cyclo-

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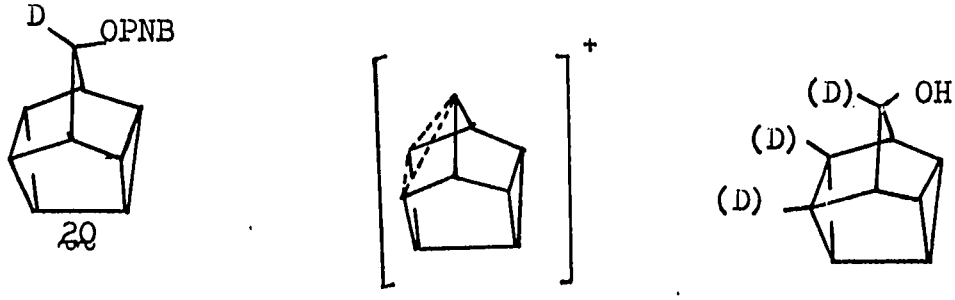
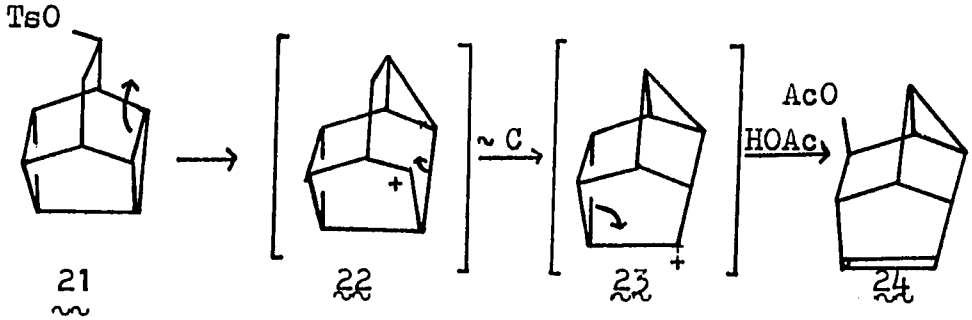
propyl ring is thus responsible for a rate enhancement of 10^{14}. The solvolysis rate of 20 is similarly enhanced, and due to the symmetry of the ion produced, complete scrambling of deuterium labels among



20

positions 2, 3, and 9 occurs during the course of the reaction.[19]

Proper geometrical orientation of the cyclopropyl ring appears to be essential for substantial rate enhancement to occur. A compound related to 20 in which the developing cation is not symmetrically centered above the cyclopropyl ring is 21, pentacyclo [4.4.0.0^{2,4}0^{3,8}0^{5,7}]decyl-9-toluenesulfonate.[20] It was found that 97% of the solvolysis product from 21 was a rearranged acetate 24, and the sequence



21 22 23 24

of rearrangements shown was invoked to explain this result. The rate of solvolysis of 21 was only

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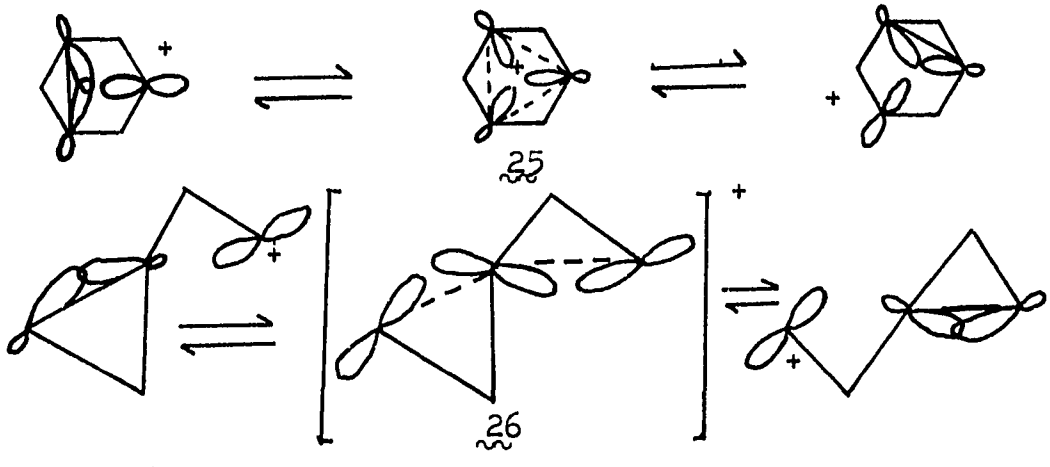
20 times that of 2-bicyclo[2.2.2]octyl tosylate, showing that the strong anchimeric assistance observed in the more symmetrical compound 20 is not as effective in the less symmetrical system 21. A puzzling feature of the mechanism shown is that the rearrangement of ion 22 to ion 23 is so efficient; inspection of models shows no obvious driving force in terms of strain relief for the rearrangement. As will be seen below, in at least one other system involving an unsymmetrical relationship between the cyclopropyl ring and the developing cationic center, a different type of interaction occurs. Instead of the adjacent bond of the cyclopropane ring opening to give an ion of type 25, one of the remote bonds interacts through its backlobe with the developing



p orbital to give an ion of type 26. Thus, there are actually two distinguishable cyclopropylethyl to cyclopropylethyl cation interconversions.

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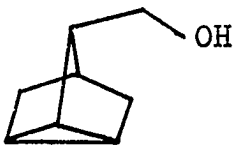
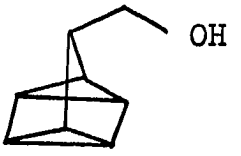
The system in which this second type of interconversion is observed is 27, 3-hydroxymethyltricyclo[3.2.0.0^{2,7}]heptane.[21,22,23] The solvolysis of deriviatives of 27 is complex, but due to the close structural relationship to the title compound

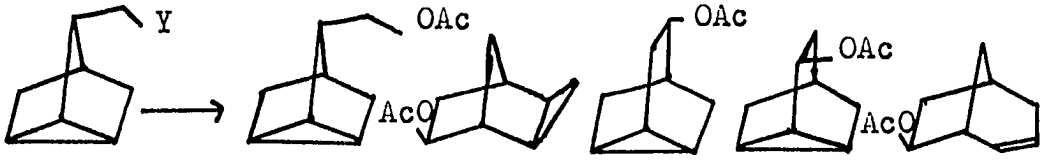


27



3

3, a discussion of the rearrangements of 27 is appropriate. Five products, 27 - 31, are observed in varying amounts in the acetolysis of 27-OTs,[21] hydrolysis of 27-OBs in dioxane-water,[21,22,23] and in the deamination of 27-NH_2.[21]



27 - Y	27 - OAc	28	29	30	31
Y = OTs $\xrightarrow[HNO_2]{AcOH}$	35.5%	37%	3%	0%	24.5%
Y = NH_2 $\xrightarrow{AcOH}$	11.5%	68%	2.5%	11.5%	6.5%

The composition of the product mixture is explained in terms of two competing rearrangements,[23] one leading to 27 and 28 and the second to 27, 29, 30, and 31. Path 1 is the example of cyclopropyl back lobe participation mentioned above. It is a major rearrangement pathway for 27; in various investigations

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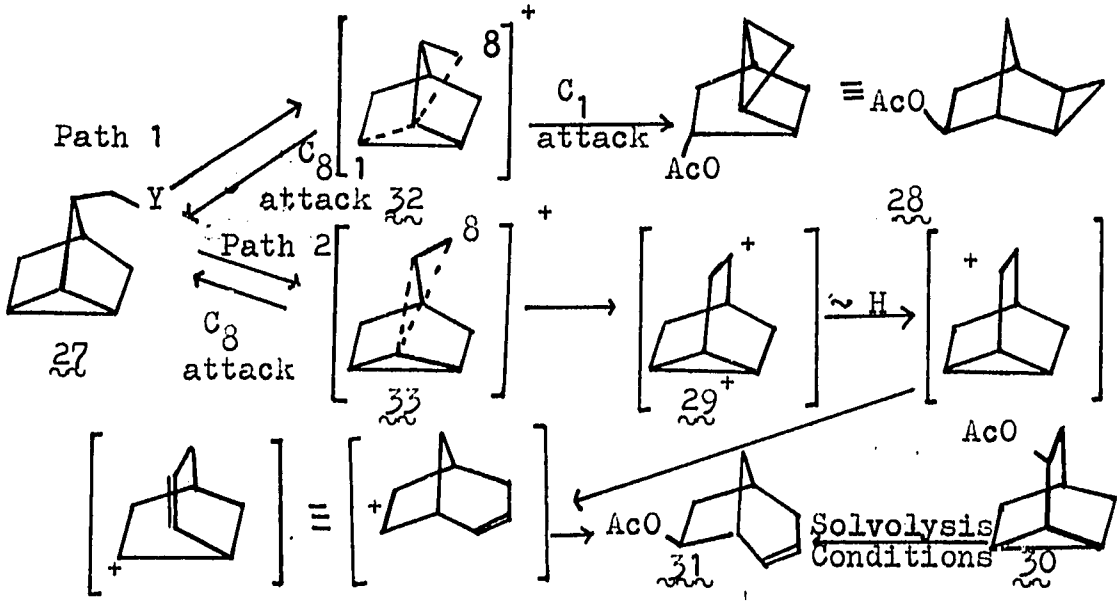
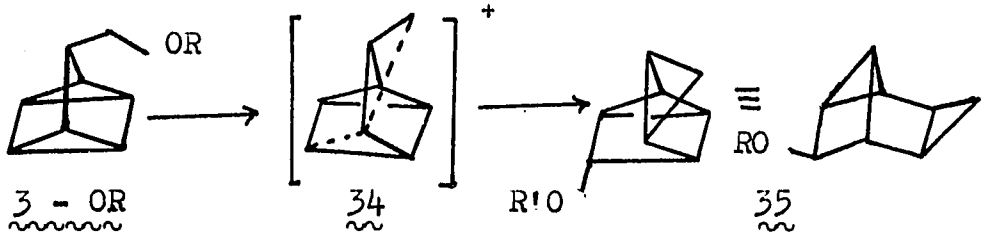
28 was found to comprise from 37% to 68% of the product mixture. The intermediate ion 32 is also

SCHEME 2



accessible from 28-OBs, solvolysis of which gives a mixture of 27, 28, and 31 in very nearly the same ratio as found in the solvolysis of 27-OBs.[22]

In the case of compound 3, a **rearrangement** similar to Path 1 for 27 would generate the tetracyclo[4.2.0.$0^{2,8}$.$0^{3,5}$]-oct-7-yl **system** 35. If the intermediate in this rearrangement is the nonclassical ion 34 it would not be expected that the second



cyclopropyl ring would be involved in stabilization

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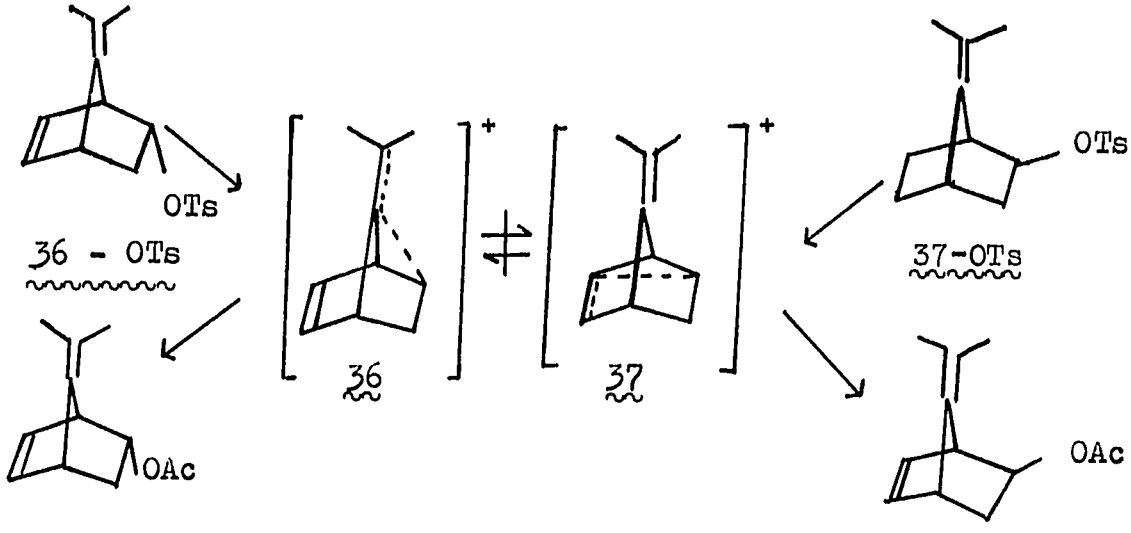
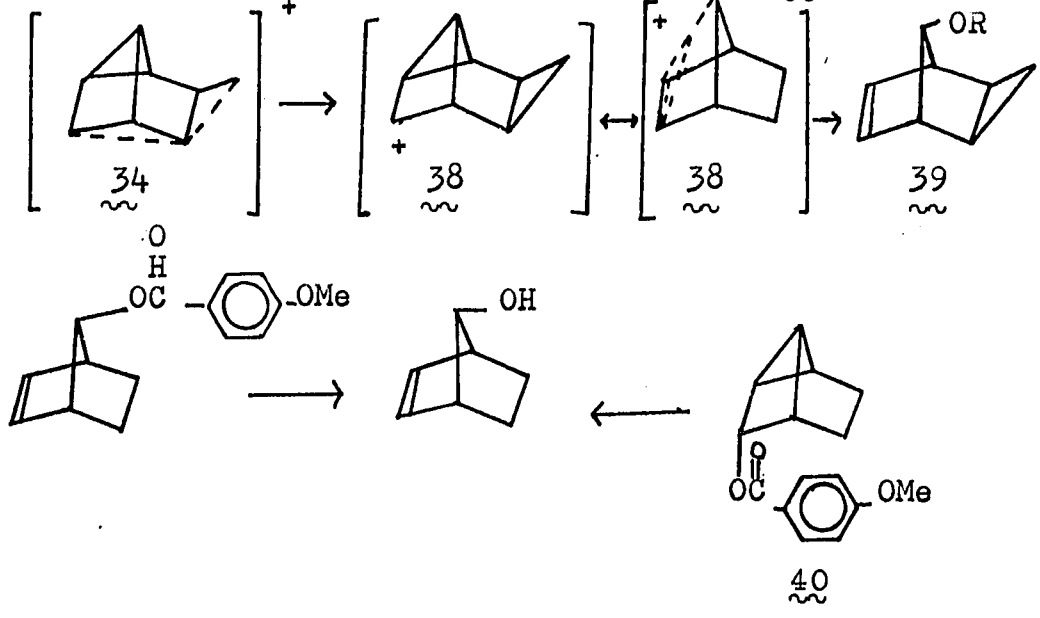
of the positive charge. An analogous case in which two nonclassical ions could, but do not, interconvert is found in the solvolyses of endo and exo-7-isopropylidene-norborneneyl-5-tosylates 36-OTs and 37-OTs. These compounds both solvolyze with complete retention of configuration,[24] indicating that there



is no leakage from ion 36 to ion 37. Similarly, ion 34 should not open to give ion 38.

If the analogy between 34 and 36 does not hold, however, 34 would open to an ion of type 38. Bishomo-



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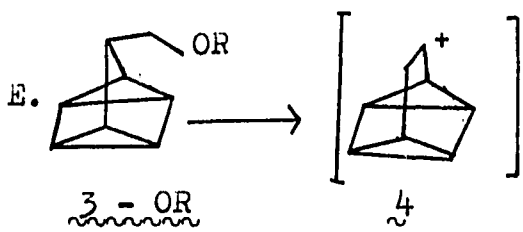
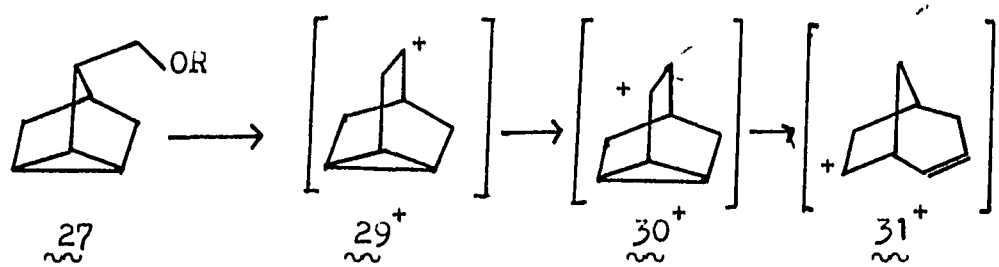
cyclopropenyl cations of this type are well known from studies of anti-7-substituted norbornenes.[25] Except under conditions in which a strong nucleophile is present,[25c] the product is uniformly the anti-7-substituted product. The same product is also obtained from solvolysis of the tricyclic isomer,[25a] for instance in the solvolysis of 40. The product from ion 38 would be 39.

The final rearrangement path open to 3 is Path E, the 1,2 alkyl shift leading to 4. This path also has an analogy in the tricyclic system 27, in which the



3 - OR 4



27 29+ 30+ 31+

cyclopropyl ring migrates to give an ion of structure 29. Ion 29 in turn rearranges to 30 by a facile hydride shift. Only 2 to 3% of acetate 29 is found in the solvolysis or deamination of derivatives of 27. Ion 30, in turn, readily rearranges to 31. Acetate 30 is in any case unstable to the solvolysis conditions,[23] and if formed would rearrange to 31.

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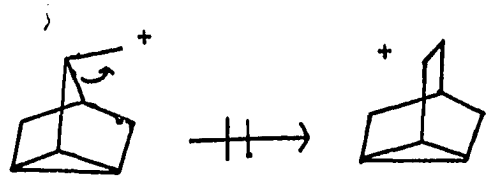
The preference for cyclopropyl migration in 27 deserves comment, since 27 could in principle rearrange directly to the cyclopropyl-conjugated ion 30 by a 1,2 shift of carbon 4. A secondary alkyl



27 30$^+$

group has a greater migratory aptitude[23,26] than a cyclopropane ring, and the rearrangement would generate the more stable of the two possible rearranged cations. In fact the rearrangement proceeds by a circuitous two-step mechanism by way of ion 29. The preference for the roundabout pathway was demonstrated[23] by an isotopic labeling experiment, and was explained by the unfavorable geometry of the transition state 41 along the reaction coordinate from 27 to 30. In ion 41 the developing p orbital on carbon 3 lies at an angle to the cyclopropane ring rather than parallel to the cyclopropane ring bonds in the favorable[3] eclipsed arrangement. Since the cyclopropyl ring is not available for conjugation during the rearrangement, its inductive effect[27] is felt instead, destabilizing the positive charge on carbon 3 rather than stabilizing it. Therefore, rearrangement to 29 occurs instead, since 29 has the

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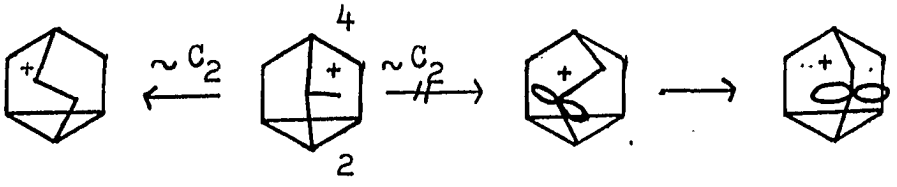
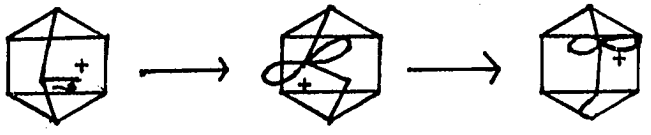


29 27^+ 41 30

advantage of being a secondary cation but lacks the disadvantage of an adjacent nonconjugated cyclopropyl ring. After 29 forms and the ring has a chance to flatten out, 30 is formed readily, since the favorable eclipsed conformation can now be attained.

The same effects would presumably apply in the rearrangement of 3 to 4. The transition state 42 in this rearrangement would be twisted in a manner similar to 41. The formation of 4 would be retarded



3 42 4

for a number of reasons. The lack of resonance stabilization felt in 41 would be equally evident in 42. In addition, the lack of flexibility introduced by the second cyclopropyl ring in 42 would cause 42 to be much more highly strained than 41. Even the

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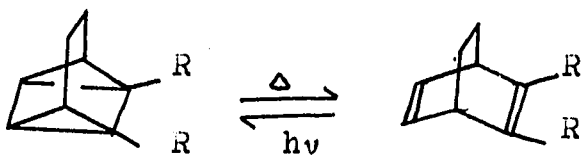
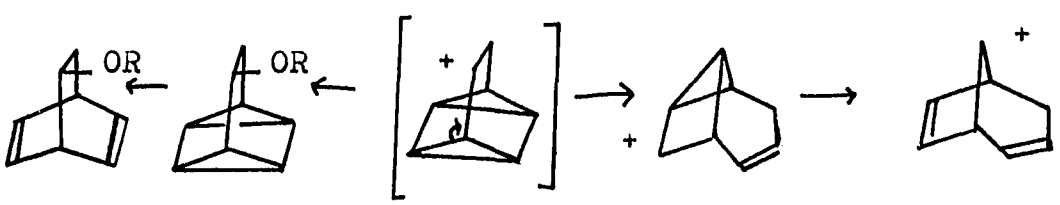
flattened-out ion 4 would be much more highly strained than the analogous ions 29 and 30. Both inspection of models and consideration of known compounds with the same skeleton lead to this conclusion. The parent hydrocarbon 43 (R = H) is not known, but derivatives in which R is an electron withdrawing



43 44

group have been prepared. Compounds of structure 43 readily rearrange to 44. For R = $COOCH_3$, for instance, the half-life of 43 at 19° is approximately 12 minutes.[28a] When R = CF_3 compound 43 is more stable; the rate of conversion of 43 (R = CF_3) to 44 (R = CF_3) has been measured to be 2.1×10^{-3} sec^{-1} at 80.5°.[28b] Therefore even if 4 should be formed and trapped by solvent, the product obtained would be 45. Alternatively, 4 or 4-OR' could undergo the same rearrangement as is found for 30. Ion 46 or even 47 could be formed in this manner. In any case, the isolated product



45 4 46 47

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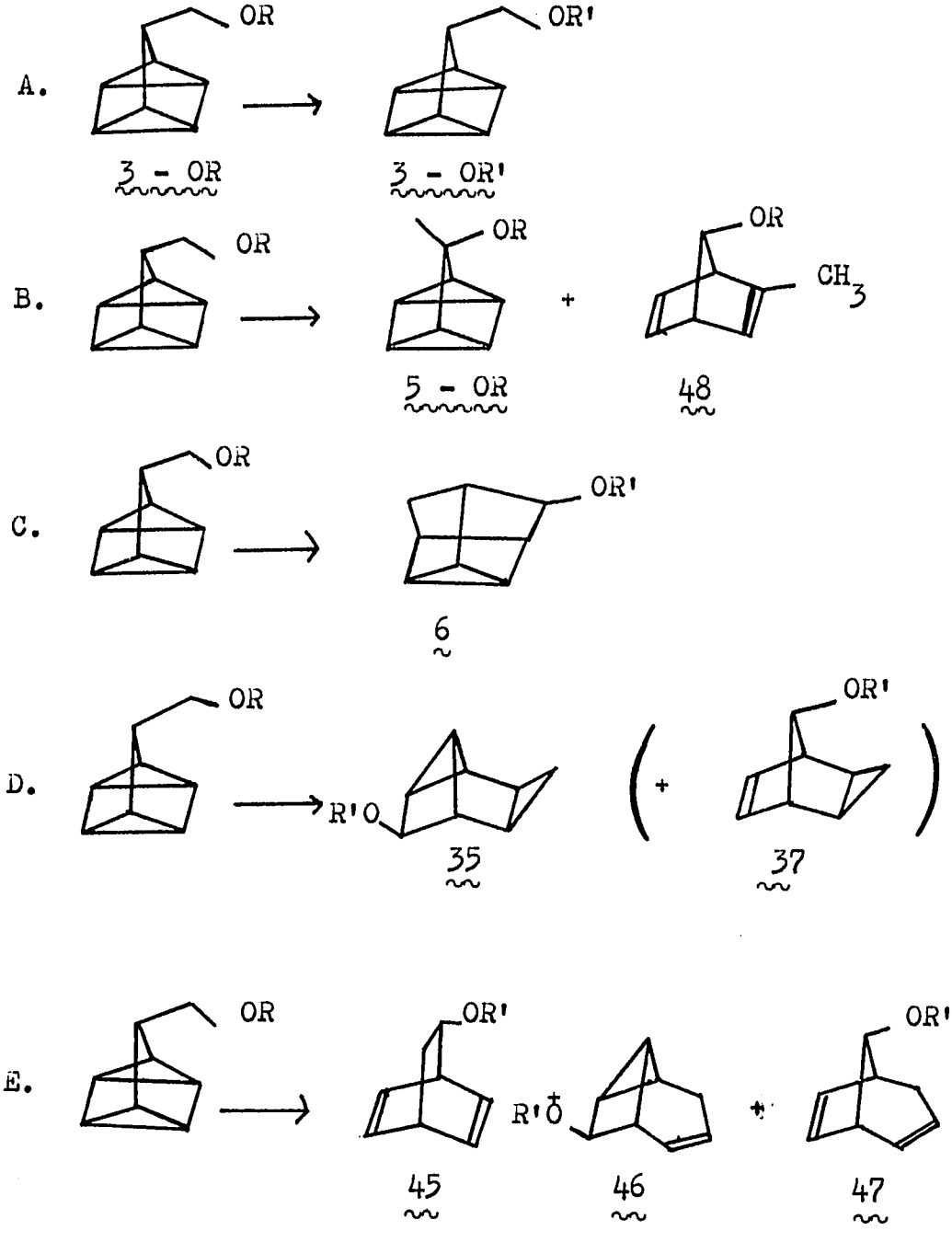
would be olefinic.

Scheme 3, an expanded version of Scheme 1, lists the products to be expected from each of the possible rearrangement pathways.

SCHEME 3



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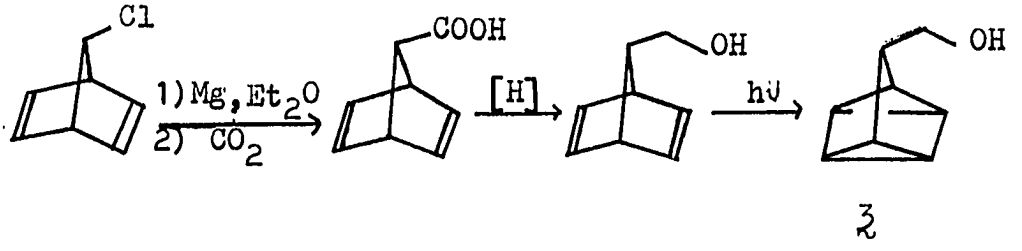
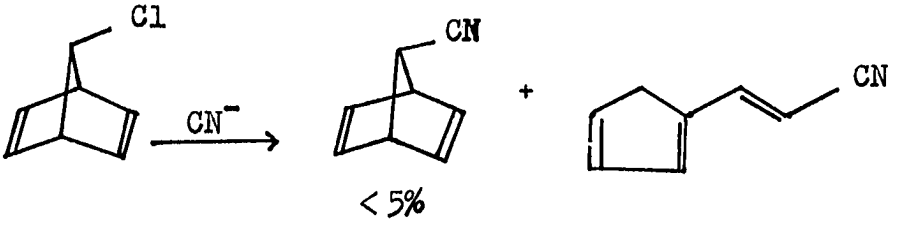
Synthesis.

The synthetic approach to quadricyclyl-7-carbinol 3 was far more arduous than had been originally anticipated. It was already known that some of the more obvious routes had severe drawbacks. For instance, a superficially attractive route would be the conversion of the known[29] 7-chloronorbornadiene to 7-norbornadiene carboxylic acid by carbonylation of the Grignard reagent, followed by reduction to the carbinol. The Grignard carboxylation has been done, however, and proceeds in less than 5% yield



3

due to extensive coupling during formation of the Grignard reagent.[30] Displacement of chloride by cyanide ion was likewise a poor reaction with both 7-chloronorbornadiene and 7-chloroquadricyclane.[30,31] The reaction of 7-chloronorbornadiene with cyanide has been investigated; the main product is 3-cyclo-



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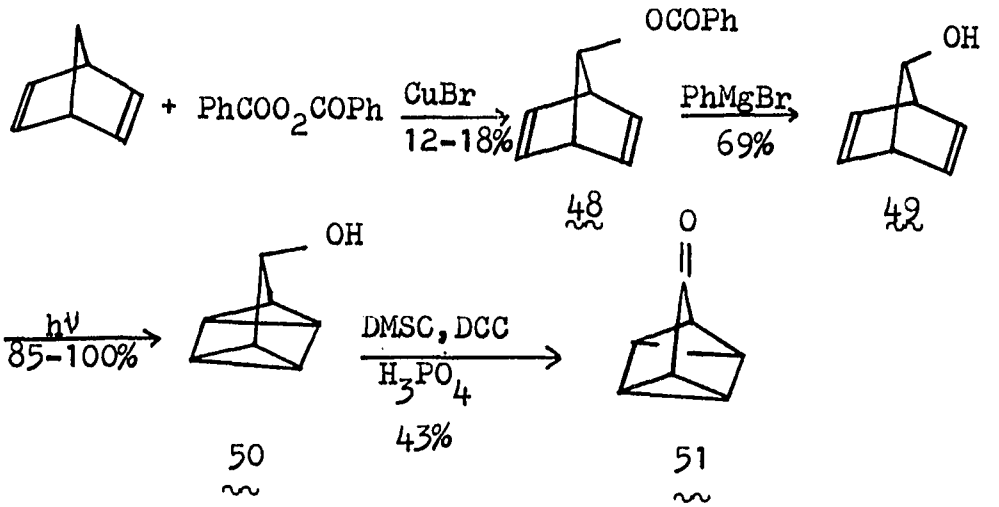
pentadienylacrylonitrile.[31] Quadricyclyl chloride is reported to give the corresponding nitrile in very low yield.[31] An additional drawback to these two routes is that a metal hydride reduction would be necessary to obtain the desired carbinol. Lithium aluminum hydride reacts with a variety of 7-substituted norbornadienes to give reduction of the syn double bond,[32] and would be expected to do the same with norbornadiene-7-carboxylate derivatives. Nucleophilic substitution reactions in general would be expected to suffer the same disadvantages.

Any route involving norbornadieneone as an intermediate would be foredoomed; if this ketone exists at all it is far too unstable to be isolated.[33] On the other hand, the isomeric ketone quadricyclanone is known.[34] Quadricyclanone was the key intermediate in the first series of reactions in the present investigation.

Quadricyclanone was prepared by the route developed by Storey and Fahrenholz,[34] with the ex-



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ception of the oxidation of quadricyclanol to quadricyclanone where the Moffitt oxidation as applied to quadricyclanol by Hoffmann and Hirsch was used.[35] In this preparative sequence, norbornadiene is allowed to react with benzoyl peroxide in the presence of cuprous chloride to give norbornadienyl-7-benzoate 48. Workup of this reaction is tedious since a solid mixture of 48 and phenyl benzoate must be distilled from the tarry product mixture and then recrystallized to obtain pure 48. Due to the sensitivity of this ester to many of the reagents ordinarily used to cleave esters, 48 must be hydrolyzed by the use of phenylmagnesium bromide. Although this method yields the desired norbornadieneol 49 in satisfactory yield (69%) the purification of the product is difficult. Any bromobenzene left from the formation of the Grignard reagent must be removed before irradiation to prevent extensive polymerization, but due to coincidental identity of boiling points the separation cannot be done by distillation and large scale column chromatography must be used to purify the alcohol. Future workers would be advised to avoid this problem either by using phenylmagnesium bromide free from bromobenzene, or by using a different Grignard reagent, or by using another route entirely. During the course of this study, 7-t-butoxynorbornadiene became commercially available, albeit at a high price, and

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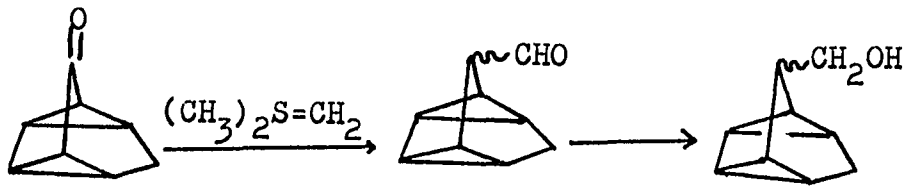
is clearly a more convenient precursor to 49 than the ester 48 since the blocking group can be readily removed in high yield under mild acidic conditions.

The irradiation of 49 to give 50 is reported[36] to fail when no sensitizer is used or when acetophenone or acetone are used as sensitizers, but when the alcohol 49 is pure and triphenylene is used as sensitizer the reaction is clean and nearly quantitative.

The Moffitt oxidation was applied to 50 by Hoffmann and Hirsch.[35] A key feature of the procedure is continuous extraction of the product mixture with pentane. The ketone is quite water-soluble and would be lost in the aqueous phase without extraction.

The first procedure investigated for the insertion of the desired carbinol group was that used by La Bel[37] in the preparation of the related carbinol 54. It was reported[37] that ketone 52 reacted with dimethylsulfonium methylide to yield the aldehyde 53, although the usual product from reaction of this ylid with a ketone is the epoxide corresponding to methylene insertion in the ketone double bond. When 51 was



52 53 54

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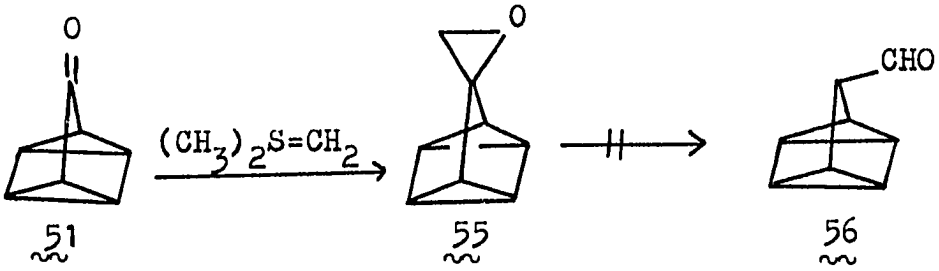
allowed to react with dimethylsulfonium methylide the product was the spiro epoxide 55. A variety of conditions were used to attempt to rearrange the epoxide 55 to the aldehyde 56. Since the analogous



51 55 56

epoxide from 52 gave aldehyde 53 from the reaction with dimethylsulfonium methylide, presumably in the presence of excess dimsyl anion, 55 was treated with dimsyl anion in DMSO. No reaction occurred. The epoxide was treated with perchloric acid in several solvents and with acidic alumina, and in all cases a complex mixture of products was obtained. No quadricyclyl-7-carboxaldehyde was obtained in any case. On the assumption that 56 might be formed, but be rapidly destroyed under the reaction conditions, the epoxide was eluted through a short column of acidic alumina directly into a solution of sodium borohydride, but again a complex mixture of products was obtained.

Two other reactions using ketone 51 which had been previously attempted without success by Chitwood[38] were reinvestigated to determine whether variation in the reaction conditions could give the desired quadricyclyl-7-carbinol.

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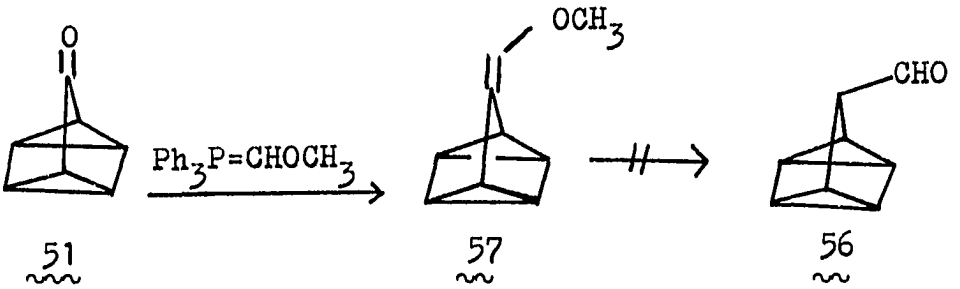
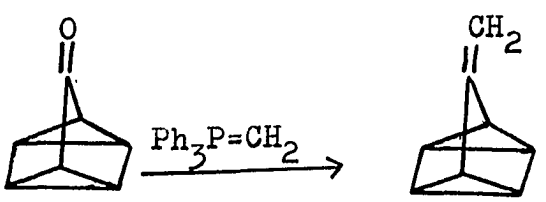
A Wittig reaction between **methoxymethylenetriphenylphosphorane**[39] and 51 gave the enol ether 57. Treatment of 57 with dilute perchloric acid in



51 57 56

aqueous dioxane, tetrahydrofuran, or ethanol gave only polymeric material. Dilute sulfuric acid in a two-phase system with ether gave a trace of an unidentified aldehyde, but no 56 could be isolated. As was apparently the case with the **epoxide** 55, conditions vigorous enough to cause any reaction were strong enough to cause extensive further rearrangement and polymerization of the acid-sensitive quadricyclane structure.

Reaction of 51 with methylenetriphenylphosphorane[40] gave 7-methylenequadricyclane 58. Due to the high volatility of 58 isolation was difficult; it was necessary to use vpc collection to obtain the olefin free from solvent.



51 58

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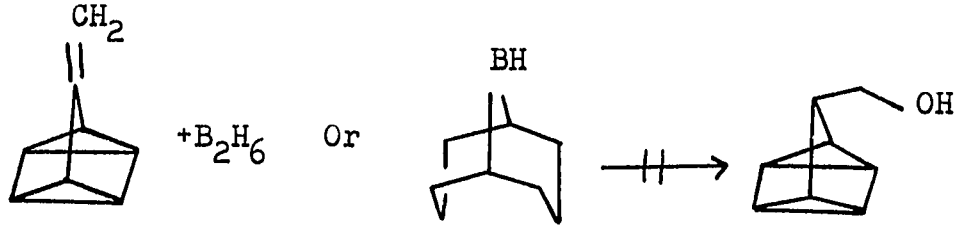
The reaction of choice for anti-Markowinkoff hydration of a double bond, as desired for 58, is hydroboration.[41] Olefin 58 was allowed to react both with diborane[41] and with the more selective[42] 9-borabicyclo[3.3.1]nonane (BBN). In both cases the



58 3

reaction was unusually slow and a complex mixture of products, not including quadricyclyl-7-carbinol, was obtained. It is difficult to rationalize this observation; if anything, 58 should be a particularly reactive olefin toward hydroboration. BBN is reported[42] to react within five minutes with ordinary olefins and within 24 hours with hindered olefins such as 2,3-dimethyl-2-butene, but with 58 the olefin had not been completely consumed after three days. The double bond in 58 is less sterically hindered than that in most disubstituted olefins due to the ring system tying back the substituents; in addition the compressed angle at the 7 carbon, shown by the unusually low carbonyl stretching frequency (1746 cm^{-1}) of ketone 51, should favor reactions which convert the 7 carbon from a trigonal to a tetrahedral center. The multiplicity of products is somewhat easier to ration-

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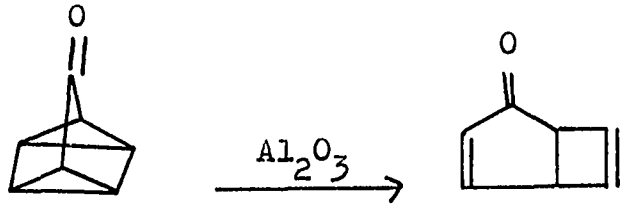
alize, since alkylboranes are known[41] to rearrange toward more stable structures. For instance, tri-3-hexylborane will rearrange thermally to tri-1-hexylborane.[41] The large amount of strain in the quadricyclane skeleton would favor rearrangement with strain relief. In addition, boranes are Lewis acids, which are known[43] to attack quadricyclanone. For example, quadricyclanone is converted to bicyclo[3.2.0]-heptadieneone 59 on contact with acidic or neutral alumina.[43] Similar rearrangements with organo-



51 59

boranes as the Lewis acid catalyst could be occuring during the hydroboration reaction, in which case the rearrangement product itself would be susceptible to hydroboration. This would explain the complexity of the the product mixture.

Since all of the reasonable routes involving quadricyclanone as the intermediate were unsuccessful a new approach was investigated. It is known[44] that norbornadienes form stable iron tricarbonyl complexes, which can readily be converted to the uncomplexed dienes by oxidation with ferric ion[45a] or ceric ion.[45b] Norbornadiene iron tricarbonyl complexes are often far

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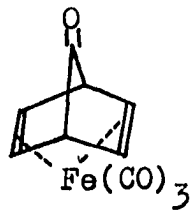
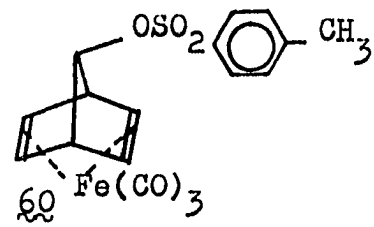
more stable than the uncomplexed compounds. Advantage has been taken of this stability in the





60

preparation of norbornadieneone iron tricarbonyl.[46] As was mentioned above, norbornadieneone has never been isolated, but the iron carbonyl complex is a readily prepared and stable compound. Similarly, 7-tosyloxynorbornadiene is very labile toward solvolysis, but 7-tosyloxynorbornadiene iron tricarbonyl has been prepared and its solvolysis investigated;[47] at the most the rate of solvolysis of the iron complex 60 was 10^{-6} times the rate of the uncomplexed compound. In fact, it is believed[47] that the rate-limiting step in the solvolysis of 60 is dissociation of the norbornadienyl tosylate from the iron, followed by rapid solvolysis of the free tosylate.

The synthetic sequence investigated in this work used tosylate 60 as the key intermediate. The reactions investigated were displacement of the tosylate in an S_N2 reaction with cyanide ion and with the lithium salt of dithiane.[48] The nitrile 63 could have been hydrolyzed to the corresponding acid and reduced to alcohol 64. Cerate ion oxidation followed by irradiation would have given quadricyclyl-7-carbinol.

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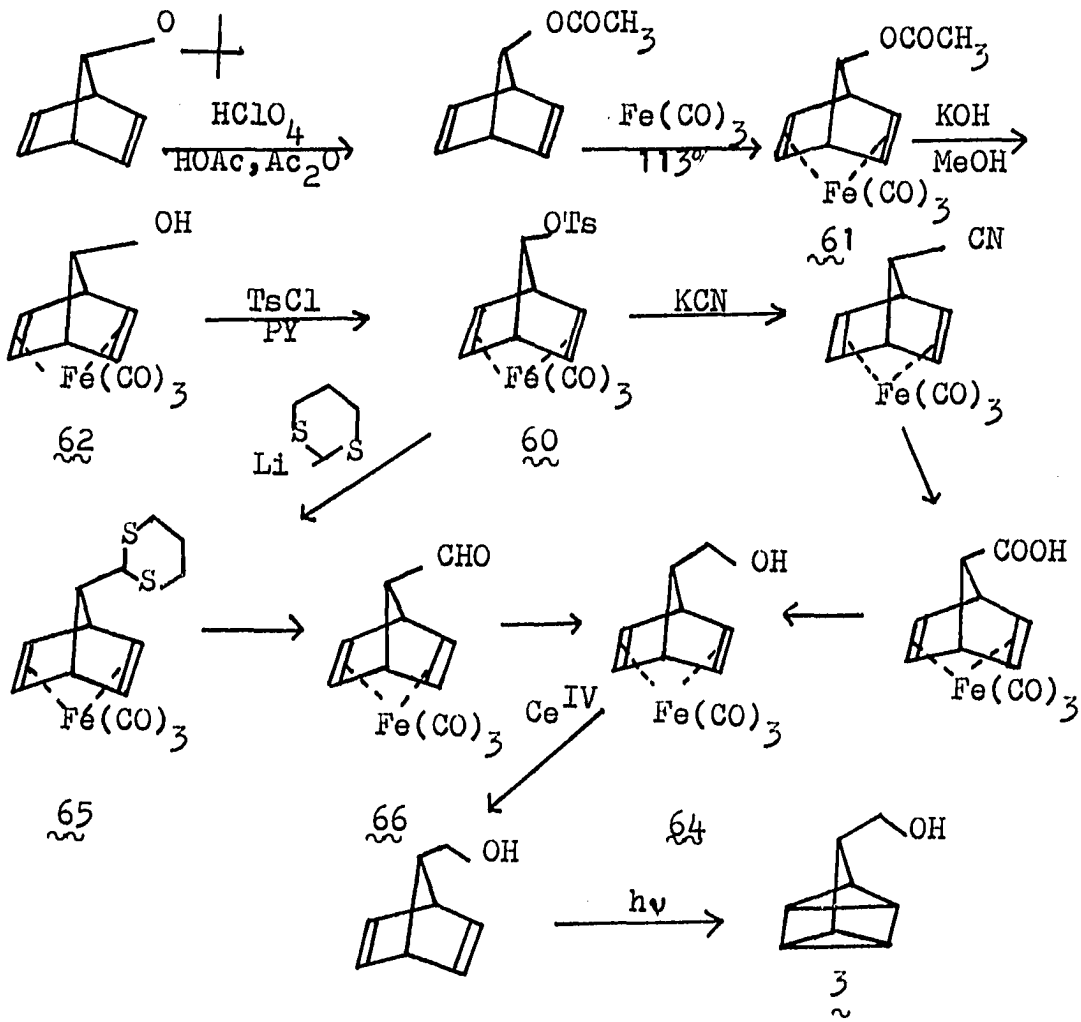
The dithiane 65 would have been hydrolyzed to aldehyde 66, which could in turn have been reduced to 64.



The synthesis of 60 was that of Hunt et al.[47] The overall yield of 60 from 7-t-butoxynorbornadiene was 14%. The utility of the iron carbonyl protecting group is evident in the hydrolysis of acetate 61; in the uncomplexed ester it is necessary to use a Grignard reagent to perform the same transformation.

The reaction of tosylate 60 with cyanide ion in THF or in DMF in fact did not yield nitrile 63. The

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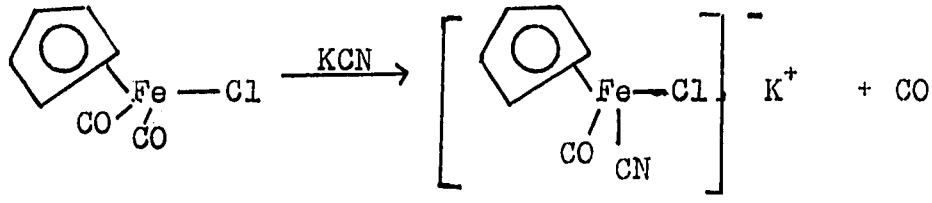
product obtained was a water-soluble material, insoluble in all organic solvents, which was presumably formed by displacement of carbon monoxide from iron by cyanide ion. Cyanide ion is known to displace carbon monoxide coordinated to iron in complexes such as dicarbonyl cyclopentadiene iron(II) chloride 67. Rearrangement or decomposition of the carbon



skeleton had apparently occured as well. The nmr spectrum of the product had four singlets which did not correspond to any signals in the norbornadiene series. Finally, cerate ion oxidation[45b] of the product failed to yield any characterizable product.

The anion of dithiane has been used to introduce an aldehyde functionality by displacement of halide.[48] The anion was prepared by treatment of dithiane with butyllithium in THF and allowed to react with tosylate 60 to prepare the thioacetal 65. The reaction proceeded slowly over several days, and the only product was a brown tar from which none of the desired product could be obtained.

After the study of the iron tricarbonyl complexes was completed, the communication by Corey,

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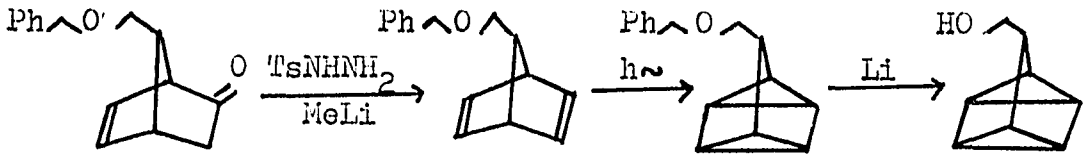
Koelliker, and Neuffer[50] describing their synthesis of prostaglandins appeared. An important intermediate in this synthesis was the ketone 68. It was apparent that 68 could also be used to prepare 3. Conversion



68 69 70 3

of the ketone functionality to a double bond could be accomplished by reaction of the corresponding tosylhydrazone with methyllithium.[51] The diene 69 could be converted to 7-benzyloxymethylquadricyclane 70 by irradiation, and 70 could be cleaved to give 3 by treatment with lithium in ammonia.[52] Acidic hydrolysis[53] and hydrogenolysis[54] are more common methods of cleaving the benzyl ether protecting group, but clearly would be unsuitable for 70; the lability of quadricyclanes to acid has already been demonstrated, and the cyclopropyl bonds of quadricyclanes are readily hydrogenated.[55] The protecting group must also be removed after irradiation rather than before, since lithium in ammonia is known to reduce one double bond in norbornadiene[56] and would be expected to do so in the case of 70 as well. This synthetic sequence is analogous to putting up a weathercock and then building a house underneath

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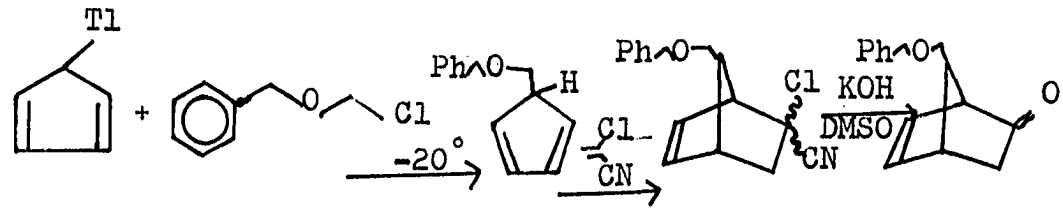
it, but it is in fact the only successful route to 3.

The original communication[50] describing the synthesis of 68 was rather sketchy in experimental details. For instance, no mention was made of the



71 72 73 74 68

route used to prepare benzyl chloromethyl ether 72. Three literature references to the compound[57,58,59] were followed in attempts to prepare 72. The procedure of Hill and Keach[57] involved passing gaseous HCl through a mixture of benzyl alcohol and aqueous formaldehyde. The preparation was unsuccessful due to decomposition on attempted distillation. Hill and Keach noted this difficulty and attributed it to the presence of benzyl chloride; however, using reagent grade benzyl alcohol known to be free of benzyl chloride, and a fourfold excess of formaldehyde so that no benzyl chloride would be formed in the reaction, no 72 could be obtained. Attempted distillation led to extensive decomposition to paraformaldehyde, benzyl alcohol, and other unidentified products.

Mamedov and coworkers[58] reported that 72 could be prepared by passing gaseous formaldehyde into

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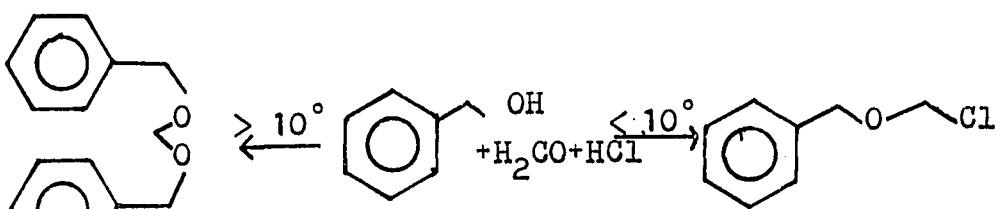
benzyl alcohol followed by gaseous HCl. Their procedure yielded an intractable emulsion of paraformaldehyde which seemed from spectral data to contain the desired chloro ether, but which could not be purified without decomposition.

At this time a preprint of a procedure to be published in Organic Syntheses[59] describing the synthesis of 72 became available. The method was essentially that of Hill and Keach with the exception that the crucial condition in the synthesis is not the presence of benzyl chloride, as Hill and Keach concluded, but the temperature of the reaction. It is essential to maintain the temperature below 10° during the addition of HCl to the mixture of benzyl alcohol and formaldehyde; otherwise the main product is dibenzylformal 75. In addition, distillation of



75 72

72 is neither necessary nor desirable. Sufficiently pure material can be obtained by passing gaseous HCl slowly into an equimolar mixture of benzyl alcohol and 37% aqueous formaldehyde, with continuous cooling in an ice-salt or ice-acetone bath. A two-phase mixture is obtained upon saturation of the solution with

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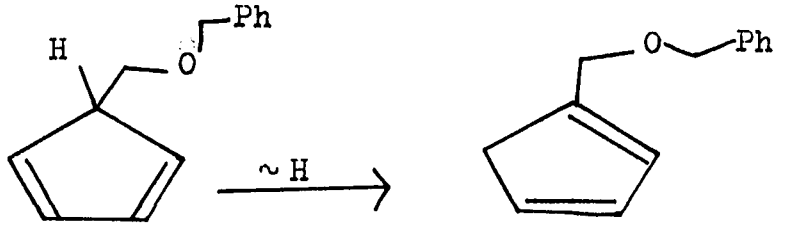
HCl. The upper layer is dried, and excess HCl is removed by rotary evaporation. The product obtained in this manner is sufficiently pure for the reaction, and distillation leads to lower yields and less pure product due to decomposition. The chloro ether is also fairly **unstable** at room temperature, and should be used immediately upon preparation.

Thallium cyclopentadienide (71) is readily prepared from cyclopentadiene, thallous sulfate, and sodium hydroxide.[60] It is unusually stable for an organothallium compound, presumably because of its crystal structure; thallium methylcyclopentadienide is pyrophoric[60] but 71 is reasonably stable in air. It should be noted that this stability is not absolute; a sample of 71 that had been stored for six weeks in a vacuum dessicator failed to react with chloroether 72.

As noted by Corey[50] **5-benzyloxymethylcyclopentadiene** 73 is a highly unstable compound. Heat, acid, or base cause prototropic rearrangement to the more stable 1-benzyloxymethylcyclopentadiene. It is therefore necessary to prepare 72, immediately allow it



73

to react with thallium cyclopentadieneide, and start

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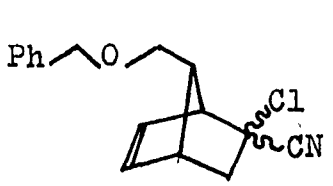
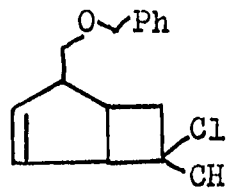
the Diels-Alder reaction of the 73 formed with α-chloroacrylonitrile without delay.

The hydrolysis of chlorocyano compound 74 to 7-benzyloxymethylnorborneneone 71 was not a very successful reaction. The Diels-Alder adduct 74 is not obtained pure from the reaction of 73 with α-chloroacrylonitrile. The impurities present included benzyl alcohol, dibenzylformal, unreacted



74



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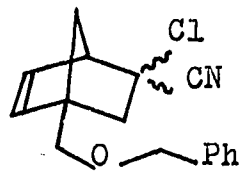

77

benzyloxymethylcyclopentadiene, bicyclo[3.2.0]heptane products such as 76 from copper-catalyzed [2+2] addition, and the Diels-Alder adduct of 1-benzyloxymethylcyclopentadiene, 77. Purification of the mixture was difficult due to the multitude of products present. Hydrolysis of the crude mixture afforded a 6.6% yield of 68 (calculated from benzyl chloromethyl ether).

A series of trial reactions were run to determine the feasibility of the later steps in the reaction sequence. Norborneneone (78) was prepared by reaction of cyclopentadiene with α-chloroacrylonitrile in refluxing benzene, followed by hydrolysis with KOH in DMSO.[61] Ketone 78 was in turn readily and quanti-

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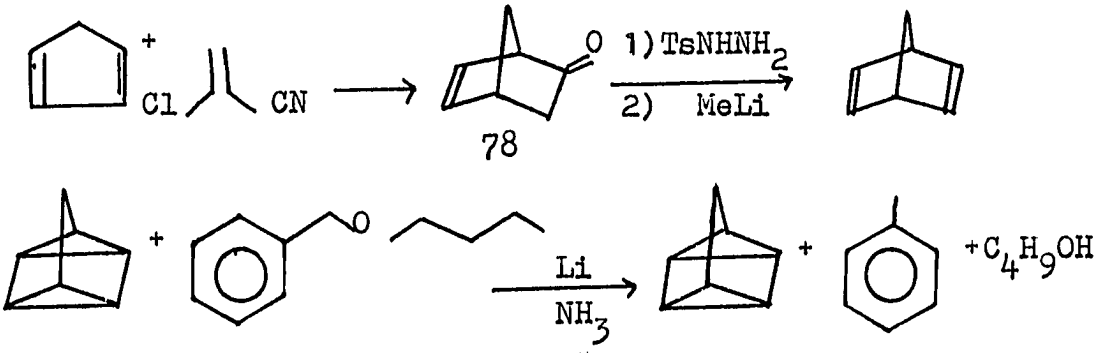
tatively converted to a crystalline tosylhydrazone by treatment with toluenesulfonylhydrazine in refluxing THF. Treatment of the tosylhydrazone with



an excess of methyllithium[51] followed by warming yielded **norbornadiene**, identified by its gas chromatographic retention time. Norbornanone tosylhydrazone reacts with sodium in aniline to give tricyclene,[62] but the analogous reaction apparantly did not occur with 78; no quadricyclane could be detected among the products.

To investigate the feasibility of the deprotection step, a sample of quadricyclane was prepared by irradiation of norbornadiene in the presence of triphenylene.[63] A mixture of quadricyclane and benzyl butyl ether was treated with a slight excess of lithium in ethylamine.[52b] The ether was cleaved to butanol and toluene, and the quadricyclane was unaffected. No tricyclane, norbornene, or other extraneous products were detected in the product mixture by gas chromatography.

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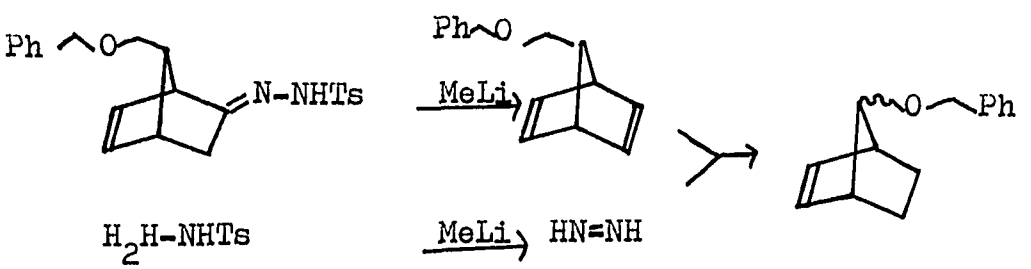
The initial preparation of 7-benzyloxymethylnorbornadiene 69 from ketone 68 was unsuccessful. An excess of toluenesulfonylhydrazine was used in the preparation of the tosylhydrazone of 68, and the tosylhydrazone could not be obtained in a crystalline state. The elimination reaction was performed in the presence of excess toluenesulfonylhydrazine; excess methyllithium was required as well due to the acidic protons on the tosylhydrazine present. The product obtained from the reaction was not the desired diene 69 but instead a mixture of syn and anti-7-benzyloxymethylnorbornenes, identified by mass spectrometry and nmr. The mechanism postulated for this conversion involves the formation of diimide from toluenesulfonylhydrazine in the presence of methyllithium, followed by reduction of the double bond of either 68 or 69 by the diimide.



It proved possible to obtain the diene 69 without isolation of the intermediate tosylhydrazone. The tosylhydrazone was prepared by refluxing equimolar amounts of ketone 68 and toluenesulfonylhydrazine in THF; benzene was then added, and THF and water were

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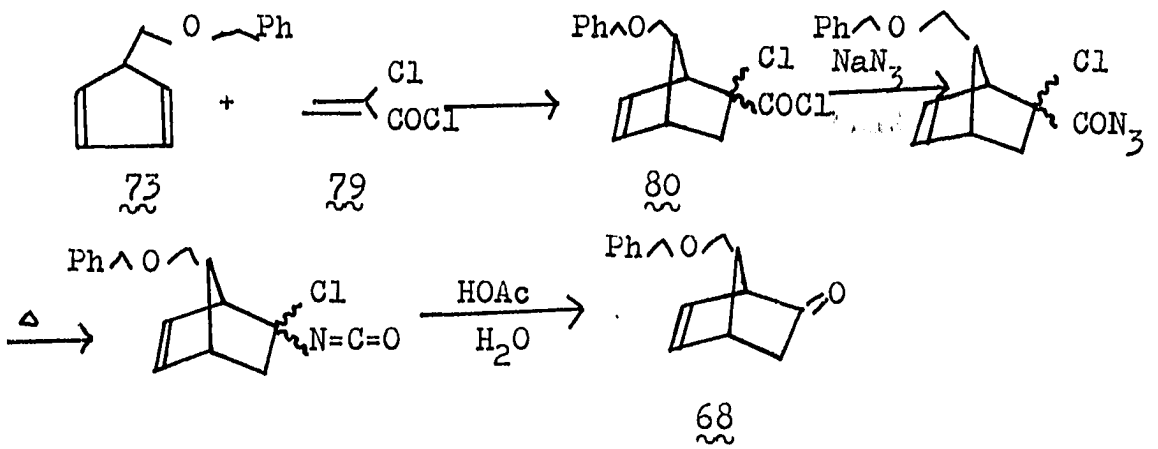
removed by azeotropic distillation. The resulting benzene solution of the tosylhydrazone was treated with two equivalents of methyllithium at reflux for 16 hours. Diene 69 was obtained in 10 - 22% yield.

A second communication on the synthesis of prostaglandins[64] demonstrated that 2-chloroacrylyl chloride 79 was a superior reagent for the preparation of ketone 68. There are two advantages to this sequence. The potent dieneophile 79 readily reacts



with a dilute ethereal solution of diene 73 at 0° without catalyst, in contrast to α-chloroacrylonitrile which requires concentration of the labile diene and assistance from the cupric tetrafluoroborate catalyst. Secondly, the Curtius degradation sequence from acid chloride 80 to ketone 68 proceeds in much better yield than the alkaline hydrolysis of chlorocyano compound 74.

2-Chloroacrylyl chloride is commercially available, but one investigation of the reaction sequence

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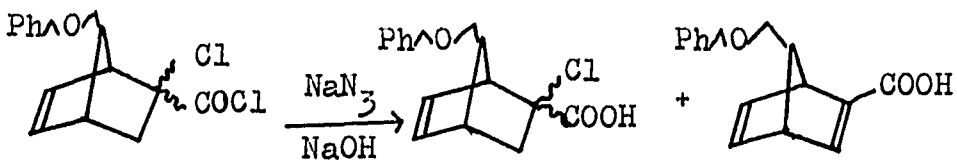
was hindered by polymerization of commercially obtained 79 during the Diels-Alder reaction. Another difficulty encountered in this investigation was the unexpected presence of sodium hydroxide in the sodium azide available from the Department of Chemistry stockroom. Hydrolysis of the acid chloride by the sodium hydroxide led to the formation of the acids



80 81 82

81 and 82 instead of the desired ketone 68.

Because of the problems encountered in the use of commercial 2-chloroacrylyl chloride, as well as its expense, it was decided to synthesize the material. Two syntheses of 79 have been reported.[65,66] The method of Marvel[65] involves reaction of 2,3-dichloropropanoyl chloride with diethylaniline at 120°. A yield of 30 - 40% is reported for this procedure, which is rather tedious and inconvenient. The second method[66] requires the use of phosgene and repeated distillations of the product. Due to the susceptibility of 79 to polymerization[65] and a reluctance to work with phosgene it was decided to attempt to prepare 79 directly by treatment of 2-chloroacrylic acid with thionyl chloride. 2-Chloroacrylic acid

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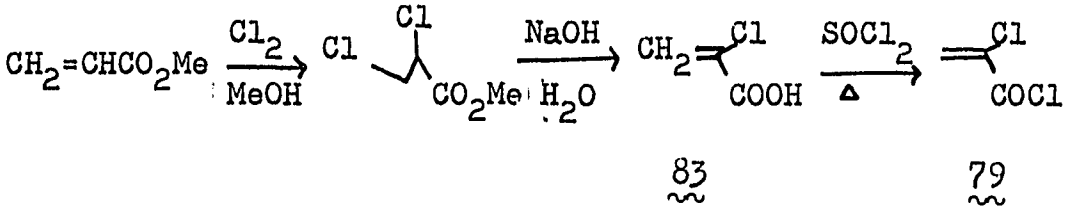

83 79

83 was prepared by basic hydrolysis and dehydrohalogenation of methyl 2,3-dichloropropanoate, itself prepared by chlorination of methyl acrylate.[65] Heating a solution of 83 in excess thionyl chloride for 24 hours afforded a 68% yield of pure acid chloride 79 after fractional distillation to remove thionyl chloride.

The acid chloride obtained in this manner was allowed to react with 5-benzyloxymethylcyclopentadiene 71 prepared as discussed above from thallium cyclopentadienide and benzyl chloromethyl ether. The cold ether solution of 71 obtained by filtration of thallous chloride was allowed to react with a slight excess of 79 at 0° for eighteen hours. The Diels-Alder adduct 80 thus obtained was isolated without purification and redissolved in dry dimethoxyethane. Reagent grade sodium azide converted 80 into the acyl azide 84, which was immediately rearranged to the isocyanate 85 by heating the solution to reflux for two hours. The isocyanate was in turn hydrolyzed directly to ketone 68 by treatment with aqueous

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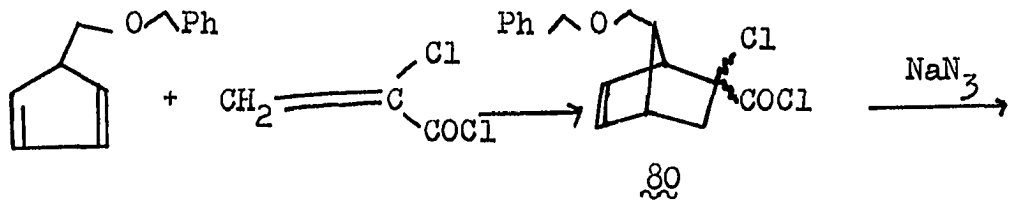
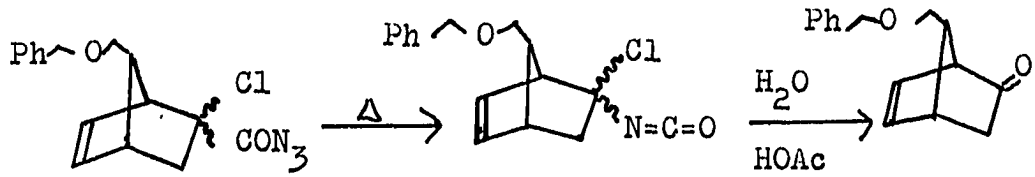


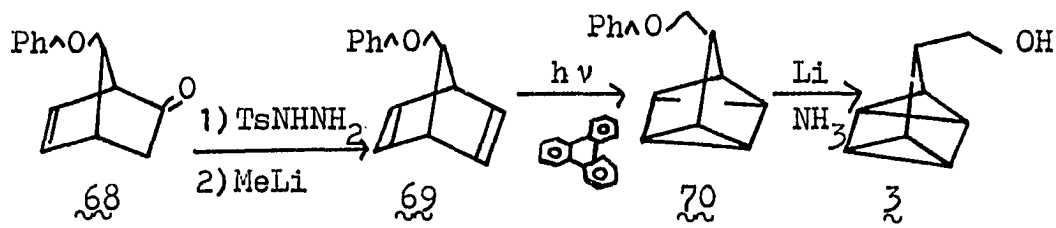
80



84 85 68

acetic acid. The overall yield of 68 from thallium cyclopentadienide was 57%, and it was possible to obtain 68 in quantity and free from impurities.

The availability of ketone 68 in pure form made it possible to improve the yield of the tosylhydrazone elimination reaction to 45%. The diene 69 thus obtained was converted to 7-benzyloxymethylquadri-



68 69 70 3

cyclane 70 in 73% yield after chromatography by irradiation in the presence of triphenylene. Quadricyclyl-7-carbinol was prepared in 43% yield by treatment of ether 70 with two equivalents of

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lithium in a mixture of liquid ammonia and THF, followed by chromatography and recrystallization. The overall yield for the sequence was 8%.

There are hazards involved in this sequence. Thallium salts are **extremely** toxic and accumulate in the body.[67] 2-Chloroacrylic acid is a strong skin irritant, and 2-chloroacrylyl chloride is reported[64] to be a potent vesicant and eye irritant. A by-product from the formation of benzyl chloromethyl ether 72 is bis-chloromethyl ether, which has been found[68] to be a powerful carcinogen, active by skin contact or inhalation. Future workers in the field should consider purchasing 7-benzyloxymethylnorborneneone 68, which became commercially available during the course of this investigation. Its high price should be balanced against the hazards of the synthetic sequence. In addition to the toxicity of some of the intermediates it should be considered that good yields were only obtained for some of the reactions after much practice.

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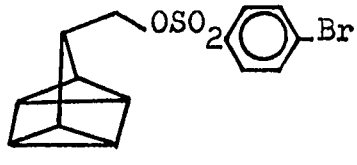
Results.

Two methods of generating the cation corresponding to 3 were investigated. It was expected that a reactive leaving group would be necessary, since 3 is a primary system and little anchimeric assistance could be expected. The two leaving groups used were the bromobenzenesulfonate, which was chosen for its reactivity[69] and so that the rate of its solvolysis could be directly compared with that of 3-brosyloxymethyltricyclane (27); and the highly reactive[70] trifluoromethanesulfonate, so that the reaction could be performed at a temperature low enough for the expected unstable products to survive the reaction conditions.



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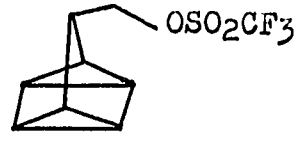

87

Brosylate 86 was prepared by the standard technique[71] of allowing the alcohol to react with bromobenzenesulfonyl chloride in pyridine. The brosylate was isolated as a crystalline solid. Acetolysis of 86 in acetate buffered acetic acid at 99.5° proceeded slowly. A very rough rate estimate was obtained by measurement of the recovered brosylate

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after 24 hours of solvolysis. The method of measurement was nmr integration of the spectrum of the recovered mixture of unreacted brosylate and products. The peak for aromatic protons at δ 7.7 was compared to the overlapping peaks for acetates at δ 2.0. The mole ratio obtained from this integration was converted to a weight ratio, which in turn was used to calculate the weight of recovered brosylate. It was assumed that the reaction followed a first-order rate law, and the rate was calculated from the rate equation:

$$\ln A = \ln A_o - kt$$

The rate calculated by this procedure should be considered a very rough estimate. No proof of first order behavior was obtained (although the solvolysis of triflate 87 discussed below gave a linear first-order rate plot). The analytical technique is subject to substantial errors, but most of the systematic errors would bias the result toward a calculated rate higher than the true rate. Incomplete recovery of brosylate, decomposition of brosylate by reactions other than solvolysis, and the presence of products lacking acetate protons would all lead to an underestimation of the amount of recovered brosylate and therefore to an overestimation of the rate. Thus, although the calculated rate constant is not a reliable estimate of the true rate, it

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is probably an upper bound of the true rate.

The value obtained from the rate calculation was 1.1×10^{-5} sec^{-1} at 99.5°. This should be compared to a rate of 0.653×10^{-5} sec^{-1} at 85° for the related brosylate 27.[22] If the assumption is made that the rate doubles for every ten degrees change in temperature, the rate of solvolysis of 86 at 85° would be $0.39 \times 10^{-5} sec^{-1}$. Evidently there is no rate acceleration in the solvolysis of 86 as compared with 27; in fact it is likely that the solvolysis rate of 86 is somewhat slower than that of 27.

The product mixture from the solvolysis of 86 was quite complex. At least ten compounds were detectable by gas chromatography. A variety of analytical gc columns were investigated, but none was successful in fully resolving the mixture. The nmr and ir spectra of the mixture were complex; the only notable features were the absence in the nmr of signals below δ0.8 and the presence of a vinyl proton multiplet at δ6.0, which integrated as one forth of the acetate signal or two-thirds of a vinyl proton per acetate group. These features are in contrast to the results of the solvolysis of the triflate discussed below.

A control experiment to determine the stability of the quadricyclane ring system to the solvolysis conditions was performed. Quadricyclyl-7-carbinol

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was exposed to the same buffered acetic acid system at 99.5° as was used for the solvolysis. After 24 hours, tlc and gc indicated that substantial decomposition had occurred. This result would suggest that the products from the solvolysis of 86 might not in fact be primary solvolysis products, but rather products of acid-catalyzed destruction of the quadricyclane ring. This observation should not, however, affect the above conclusions on the rate; if the solvolysis were in fact faster than was estimated, less brosylate would have been recovered.

The trifluoromethanesulfonate ester 87 was prepared in order to perform the solvolysis under milder conditions in which the quadricyclane system would not be attacked. It was not possible to prepare the triflate 87 by standard techniques.[71] Primary triflate esters are known[73] to alkylate amines, including pyridine, so the method used to prepare 86 would not be suitable. Trifluoromethanesulfonyl chloride was investigated as a reagent for the preparation of 87, but seemed to be fairly unreactive.

Trifluoromethanesulfonic anhydride is more reactive than trifyl chloride[73] and was used to prepare 87. Reaction of 3 with triflic anhydride in methylene chloride in the presence of a slight excess of triethylamine to scavenge the acid produced gave variable results. Apparently impurities in the

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anhydride were responsible for the formation of side products in some cases. In other cases, extensive decomposition occurred; possibly triflic acid generated in a local excess due to incomplete mixing of the reaction solution caused destruction of the product. It was determined that the method of choice for the preparation of 87 was reaction of triflic anhydride with a benzene solution of the lithium alcoholate of 7, generated with butyllithium.[74] By this means the generation of triflic acid was avoided completely. The by-product, lithium triflate, could be readily removed by centrifugation. It was not possible to purify the reactive triflate ester 87, but the crude product appeared by spectral criteria to be sufficiently pure for the solvolysis.

Acetolysis of triflate 87 at 23° in acetic acid buffered with sodium acetate was followed by nmr integration of the reaction mixture. The ^{13}C sideband of acetic acid was used as an internal standard, and the progress of the reaction was followed by the disappearance of the sharp doublet at δ 4.05, assigned to the methylene protons α to the triflate group in 87. A plot of the logarithm of the peak heights against time was linear from 40 minutes to 6.5 hours (five points); the slope corresponded to a rate of 1.79×10^{-5} sec^{-1}. Three points taken at 19.5, 24, and 30.5 hours lay on

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a line of similar slope but displaced upwards. Presumably the temperature was not adequately stable during the interval between the 6.5 and 19.5 hour points.

The acetolysis product mixture was even more complex than that from the brosylate. Twenty-five products, none of them predominant, were detectable by gas chromatography.

2,2,2-Trifluoroethanol has been used[75] as a limiting, non-nucleophilic, nonacidic solvent for solvolysis. The high polarity and low nucleophilicity of trifluoroethanol favor solvolysis with rearrangement and minimize direct displacement by solvent, while the low acidity of the solvent is valuable in preventing decomposition of sensitive substrates such as 87. Solvolysis of 87 in trifluoroethanol buffered with triethylamine yielded a more tractable product mixture than either of the acetolysis experiments. The rate of solvolysis was not measured, but the reaction was complete after 30 hours at room temperature; thus it was somewhat faster than the acetolysis. The product mixture consisted of six trifluoroethyl ethers, all of which could be resolved on analytical gas chromatography columns. It was not possible to resolve the five minor (1.7 - 7.5%) products on preparative columns, but the major (77.8%) product 88 was obtained pure.

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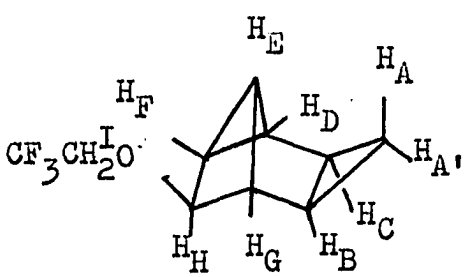
The mass spectrum of 88 showed a parent ion at m/e 204 as expected for a trifluoroethyl ether of a C_8H_9 compound. The absence of ir absorption bands in the olefinic region, together with the lack of nmr signals above δ 5, suggested that the compound must be quadricyclic. The nmr spectrum showed eight well resolved bands, all multiplets except for the sharp quartet (J = 8.8) at δ 3.41 characteristic of trifluoroethyl methylene protons. Homonuclear decoupling of the spectrum gave the pattern of couplings shown in the Table.

TABLE

Signal	Integral	Chemical Shift, δ	Coupled to Signals
A	2	0.20	B, C or D
B	1	0.92	A, C or D, G
C, D	2	1.37	A, B, E, F, G
E	1	1.80	C or D, G, H
F	1	1.86	C or D, G, H
G	1	2.88	B, C or D, E, H
H	1	4.05	G, F
I	2	3.88	Fluorine



J_{AB}, $J_{A'B}$, $J_{BC} \cong 2.8$

$J_{BG} = 1.0$

$J_{GD} = 0.4$

$J_{GH} = 3.4$

$J_{FH} = 1.8$

88 = 35-OCH_2CF_3

The spectrum is consistent with structure 35 as shown. Due to the complexity of the spectrum only a few of the coupling constants could be determined.

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Triple irradiation experiments would be necessary to completely decipher the spectrum. The coupling constants that could be assigned are listed in the Table. The other couplings could not be determined due to overlap of the signals of the two protons labeled A and the C and D protons. The only significant long-range coupling noted is the 0.4 hz coupling between protons D and G, which are in a good orientation for "W" coupling[76] to occur.

The formation of 35 as a major product of the solvolysis is mechanistically reasonable, as discussed above; the stereochemistry of the cyclopropyl ring and the ether group are assigned by analogy to 28 from the solvolysis of 27. In order to provide firmer evidence for the stereochemistry, the shift reagent tris-(trifluoroacetylpivaloylmethano) europium[77] ($Eu(fod)_3$) was added to a chloroform solution of 87. When 60 mol % of $Eu(fod)_3$ had been added to the solution, line broadening of the signal became so severe that the spectrum was not useful, and even the trifluoroethyl methylene protons had not shifted detectably. Apparently the basicity of the triflurorethyl ether oxygen was too low for complexation to the europium ion to occur.

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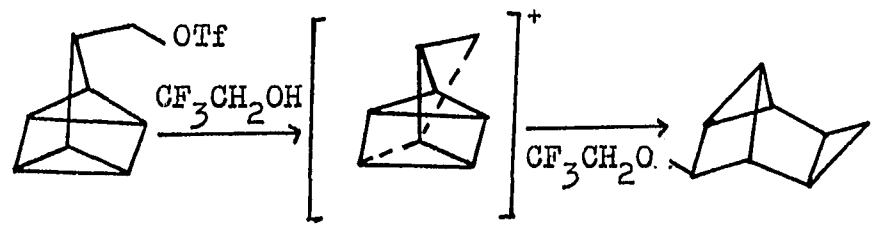
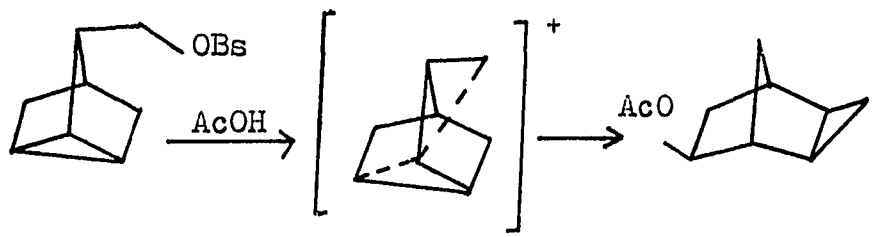
Conclusion.

The predominant product from the trifluoroethanolysis of quadricyclyl-7-carbinyl triflate 87 is 88, corresponding to Path D of Scheme 1. Participation of the back lobe of the remote cyclopropyl

D.



87 88



27 28

bond is evidently the most effective method available to 87 for assistance in ionization. This type of rearrangement is important in the solvolysis of 27, but operates to an even greater extent in 87. In addition, rearrangement by the 1,2 alkyl shift is evidently a very minor route in the solvolysis of 87. As discussed above, cation 4 would be expected to provide a variety of products, all with olefinic protons. Nmr of the crude product mixture from the trifluoroethanolysis of 87 revealed that at most

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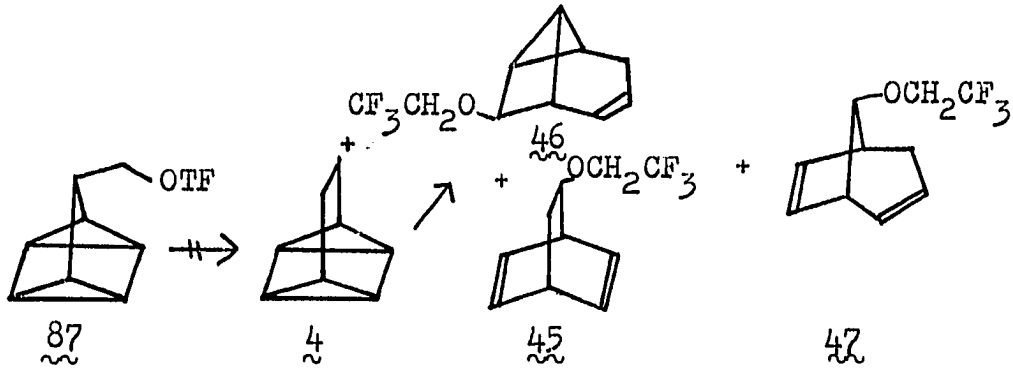
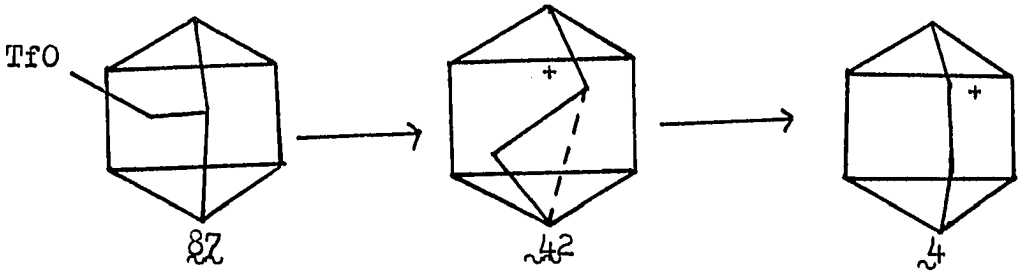
2% of the proton absorption could be attributed to olefinic protons. This suggests that the same



factors which cause 27 to rearrange to 30 by way of the circuituous mechanism outlined in Scheme 2 are also operative in the solvolysis of 87. The transition state 42 for the 1,2 shift must be so highly strained and receive so little stabilization from the adjacent cyclopropyl ring that the energy barrier for the re-



arrangement is substantially higher than the barriers to other rearrangements, in particular the rearrangement to 88.

The low rate of solvolysis of brosylate 86 is also an indication that fewer options are available to 86 than to 27. As shown in Scheme 2, 27 can ionize to either of the two nonclassical ions,

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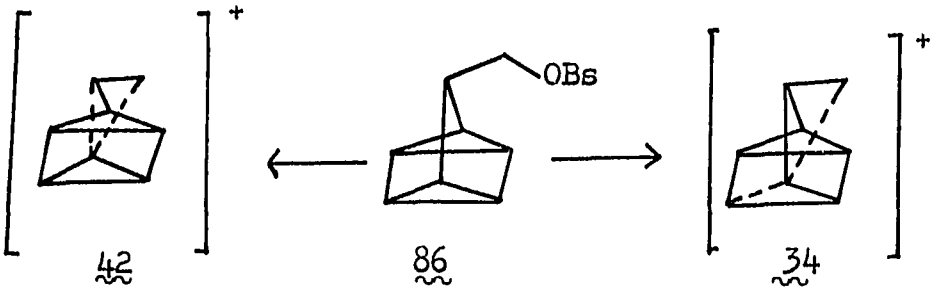
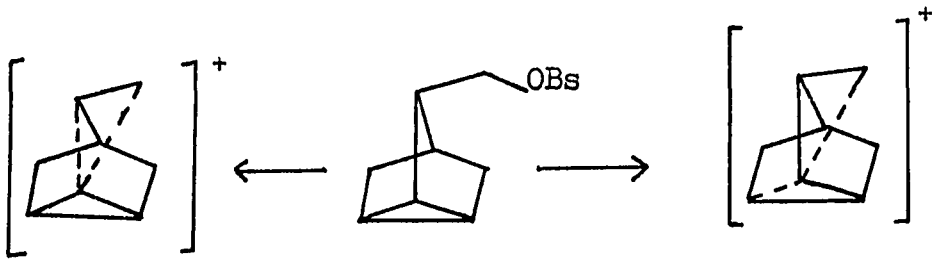


42 86 34

32 and 33. The rate of solvolysis of 27 would be the sum of the rates for these two processes. If 86 ionizes to 34 at a rate similar to that at which 27 ionizes to 32, while ionizing to 42 at a rate much slower than the rate of ionization of 27 to 33,



33 27 32

the overall rate for the solvolysis of 86 should be slower than that of 27, exactly as is observed. These rate relationships can be rationalized in terms of the relative strain of the intermediates in the tricyclic and quadricyclic cases. In the transition state 34 leading to product 88, the breaking of the bond from C_2 to C_7 relieves a portion of the strain of the quadricycane ring. In constast, ionization to 42 requires that the already highly strained fused ring system be twisted, increasing

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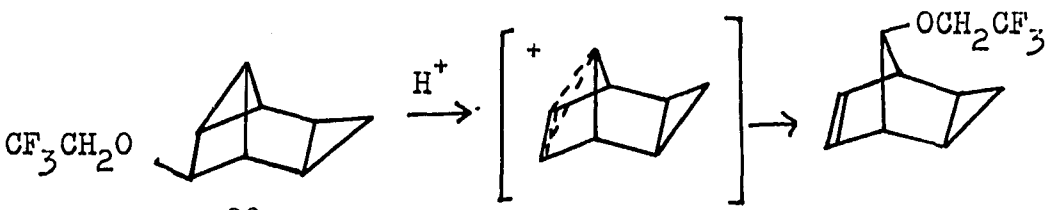
its strain even more. This twisting can be accomodated in the case of 33, but the rigidity imposed by the second cyclopropyl ring in 42 makes such twisting a highly unfavorable process. Therefore, ionization of 36 to 34 should proceed at a rate comparable to that of 27 to 32, while the ionization of 87 to 42 would be expected to be much slower than the analogous ionization of 27 to 33. The total rate of solvolysis would, therefore, be expected to be less for 36 than for 27, as observed.

The complex mixture of products obtained in the acetolyses of brosylate 86 and triflate 87 can be attributed to solvent attack both on the starting material and on the products. A multitude of products would be expected from such attack. One secondary product which might be expected from



88 37

product 88 would be the much less strained 37. Product 88 was in fact observed to slowly decompose on storage. A triplet at δ 6.0 in the nmr of the decomposed product mixture is compatible with the rearranged structure 37.

In summary, the energy salvage principle dis-

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cussed in the Introduction is not applicable in the case of quadricyclyl-7-carbinyl derivatives. The stabilization afforded by conjugation with the cyclopropyl ring is not effective in the transition state of the 1,2 rearrangement which would lead to the more highly strained cation 4. The stabilization that is obtained by conversion of a primary to a secondary cation is insufficient to overcome the increase in strain engendered by the rearrangement. With the 1,2 shift ruled out in this manner, the more obscure cyclopropyl participation to give 88 becomes the main path of rearrangement.

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Experimental Section.

7-Benzoyloxynorbornadiene.[34] In a 3 l. flask equipped with mechanical stirrer, condenser, addition funnel, and nitrogen inlet were placed 92 g (1.0 mol) of norbornadiene (Aldrich, distilled and stored under nitrogen), 500 ml of benzene, and 1.5 g (10 mmol) of cuprous bromide (MCB). A slurry of 242 g (1.0 mol) of benzoyl peroxide (MCB) in 700 ml of benzene was placed in the addition funnel and added to the moderately stirred solution at intervals over two hours. The solution was heated at reflux for two days, washed with several portions of saturated Na_2CO_3 solution and water, and stripped of solvent by rotary evaporation. The brown viscous residue was distilled, giving a forerun of phenyl benzoate and several fractions containing various amounts of 7-benzoyloxynorbornadiene. The combined solid distillates were recrystallized from ether-pentane at -78° to yield 37.6 g (0.177 mol, 17.7%) of 7-benzoyloxynorbornadiene mp 51-54° (lit.[34b] 53-54°): nmr: δ 3.70 (sextet, 2), 4.76 (br s, 1), 6.60 (t, 2), 6.72 (t, 2), 7.2-8.1 (m, 5); ir 1720, 1260; uv max ($CHCl_3$) 243 nm (ε 6600). Lit.[79] nmr: δ 3.73, 4.83, 6.62, 6.74.

Norbornadienol.[34] Phenylmagnesium bromide was prepared from 15.8 g (0.65 g-atom) of magnesium turnings and 94.3 g (0.6 mol) of bromobenzene in

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ether, using ethylene bromide to initiate the reaction. To the Grignard reagent a solution of 42.4 g (0.2 mol) of 7-benzoyloxynorbornadiene in 150 ml of ether was added. The mixture was stirred overnight and treated with an excess of saturated ammonium chloride solution. The organic layer was triturated with pentane and the precipitated triphenylcarbinol was filtered; the filtrate was distilled to yield 14.8 g (0.135 mol, 68%) of norbornadienol; bp 76-78° (50 mm): nmr: δ 2.90 (br s, 1, OH), 3.40 (septet, 2), 3.83 (br t, 1), 6.60 (m, 4): ir 3400, 3040, 2960, 1490, 1390, 1060; mass spectrum 79 (100%), 108 (parent). Lit.[79] nmr: 3.43 (septet, 2), 3.85 (1), 6.60 (t,2), 6.65 (m, 2).

Quadricyclanol.[36] A solution of 7.5 g (0.0695) of norbornadienol (chromatographed on silica gel) and 250 mg of triphenylene (recrystallized from benzene-hexane) in 750 ml of benzene (Mallinckrodt analytical grade) was flushed for 30 minutes with helium and irradiated with Vycor-filtered light from a Hanovia 450-w medium-pressure lamp. After 26 hours of irradiation, tlc (silica gel G, 50% ether-pentane) showed that essentially no norbornadienol remained. Benzene was removed by distillation at reduced pressure using a spiral-tube condenser cooled to 15° as a fractionating column. The residue was chromatographed on 100 g of silica gel to yield 5.63 g (0.52 mol, 75%) of quadricyclanol: nmr: δ 1.2-1.6 (m, 4),

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1.6-1.93 (m, 2), 4.04 (br s, 1, OH), 4.74 (t, 1): ir 3300, (br, OH), 2900. Lit.[14a] nmr: δ 1.1-1.9 (6), 4.6 (1), 2.7 (1, OH).

Quadricyclanone by Collins Oxidation. A solution of 540 mg (5.0 mmol) of quadricyclanol in 100 ml of dichloromethane was treated with 12.5 g (50 mmol) of chromium trioxide - pyridine complex (obtained from Dwight Fullerton) at 0°. A black tar formed immediately; after ten minutes, ethyl ether was added, the mixture extracted three times with satd. $NaHCO_3$, once with 2% HCl, and twice with satd. NaCl, and dried over $MgSO_4$. Tlc and gc analysis of the product indicated the presence of at least eight compounds; the nmr and ir spectra were complex. No pure ketone could be isolated from the mixture.

Quadricyclanone by Moffitt Oxidation.[35] A 5 M solution of anhydrous phosphoric acid in DMSO was prepared by carefully adding 3.13 ml (174 mmol) of distilled water to 8.25 g (58 mmol) of freshly opened phosphorus pentoxide (Mallinckrodt). The mixture was warmed until homogenous and diluted to a volume of 23 ml with DMSO (distilled from CaH_2). A solution of 5 g (46.2 mmol) of quadricyclanol and 28 g (139 mmol) of dicyclohexylcarbodiimide (Eastman) in 50 ml of DMSO was prepared under nitrogen in a 300 ml three-neck flask and 1 ml of the phosphoric acid solution was added. After twenty hours, a copious tan pre-

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cipitate had formed. The mixture was poured into 200 ml of dichloromethane and 200 ml of satd. $NaHCO_3$, stirred for two hours to destroy excess DCC, and filtered. The organic layer was dried over $MgSO_4$ and stripped of solvent by rotary evaporation, and the residue was distilled at reduced pressure. DMSO distilled at 45° (5 mm) followed by a solid at 100-107° (110 μ); the solid appeared to be DCC by nmr and ir. The distillates were combined in 200 ml of distilled water and continuously extracted for three days with pentane. The extract was concentrated to a small volume and cooled to -10°, and filtered to yield 1.24 g of white crystals of quadricyclanone. Cooling to -78° yielded an additional 0.89 g of product; the total yield was 2.13 g (19.9 mmol, 43%), mp 42-44.5 (lit. 45-47,[34] 40-42[35]): nmr: δ 1.03 (br t, 2, J = 4), 2.16 (br d, 4, J = 4): ir 2995, 2962, 2890, 1752; mass spectrum 78 (100%), 106 (parent, 40%): ^{13}C nmr: δ (C_6H_6) -89.6 (C = O), 108.2 (J_{CH} = 171), 109.5 (J_{CH} = 193). Lit.[34] ir 1746.

Anal. (8738) Calcd for C_7H_6O (106.13): C, 79.22; H, 5.70. Found: C, 78.98; H, 5.89.

7-Methylenequadricyclane Oxide. Trimethylsulfonium iodide was prepared by dissolving equimolar amounts of methyl iodide and dimethyl sulfide in ether; the resulting precipitate was recrystallized from ethanol-water. A solution of dimsyl anion was

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prepared by dissolving 101 mg (2.40 mmol) of NaH dispersion (washed with pentane to remove oil) in 5 ml of anhydrous DMSO (distilled from CaH_2) at 70°. The solution was cooled to 0° and 10 ml of THF and 520 mg (2.45 mmol) of trimethylsulfonium iodide were added. After five minutes, 212 mg (2.0 mmol) of quadricyclanone was added and the mixture was stirred at 0° for fifteen minutes, then at room temperature for an hour. Water was added and the mixture was extracted with pentane; the extract was dried over $MgSO_4$ and the volume was reduced to 15 ml with a stream of nitrogen. Cooling to -78° precipitated 57.9 mg (16%) of white crystals of 7-methylenequadricyclane oxide, mp 60-62.5°: nmr: δ 0.87 (t,2), 1.82 (m, 4), 3.10 (sh s, 2); ir (KBr) 3000, 2920, 1460, 1410, 1745 (w).

Anal. Calcd for C_8H_8O (120.13): C, 79.97; H, 6.70. Found: C, 79.4; H, 6.7.

Attempted Preparation of Quadricyclyl-7-carboxaldehyde. Aliquots of 7-methylenequadricyclane oxide were treated with a variety of reagents in attempts to cause rearrangement to the aldehyde. The conditions used were dimsyl ion in DMSO, 10% sulfuric acid in a two-phase system with ether, and elution with ether through an acidic alumina column. In all cases a mixture of several products was obtained. Since instability of the aldehyde was suspected as

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at least part of the reason for the difficulty, the effluent from the acidic alumina column was collected in a flask containing a solution of sodium borohydride in methanol. A complex mixture was obtained from which no quadricyclyl-7-carbinol could be isolated.

7-Methoxymethylenequadricyclane.[39] A suspension of 5.14 g (15 mmol) of methoxymethyltriphenylphosphonium bromide (Aldrich) in 100 ml of anhydrous ether was cooled in a Dry Ice bath under nitrogen and treated with a total of 17 ml of phenyllithium solution (Foote, approx. 1.35 M), sufficient to cause dissolution of the solid present. The orange solution was allowed to warm to room temperature and a solution of 1.02 g (9.6 mmol) of quadricyclanone in ether was added. The resulting white suspension was stirred for five hours at room temperature, filtered, washed with water and saturated NaCl, and dried over $MgSO_4$. The enol ether was not isolated in pure form, but the crude material had nmr signals at δ 3.60 (s, 3), 6.07 (s,1), and 1.2-1.8 (m). The impurity had signals in the aliphatic region partly obscuring the cyclopropyl proton signal.

Attempted Hydrolysis of 7-Methoxymethylenequadricyclane. Small aliquots of 7-methoxymethylenequadricyclane were treated with 0.005 M perchloric acid in 50% dioxane-water, 50% THF-water, 95% ethanol, and wet ether, all of which showed no reaction; and with

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0.05 M perchloric acid in the same solvents, which gave only polymeric products. An ether solution of the enol ether was stirred with 15% aqueous sulfuric acid; tlc (25% ether-pentane on silica gel G) showed slow disappearance of the enol ether spot at Rf 0.4 and a new spot at Rf 0.65. An nmr spectrum of an aliquot showed, in addition to the starting material, a peak at δ 9.83, integrating for 0.2 H relative to the enolic vinyl hydrogen. Longer reaction times led only to polymer.

Methylenequadricyclane. A suspension of 357 mg (1.0 mmol) of methyltriphenylphosphonium bromide in 10 ml of dry ether was treated with n-butyllithium (Foote) until a positive Gilman test was obtained (about 0.7 ml). A solution of 106 mg (1.0 mmol) of quadricyclanone in ether was injected and the resulting suspension was heated to reflux overnight, filtered, and dried over $CaCl_2$. Ether was removed by careful distillation through a 1' x ¼" vacuum-jacketed Vigeraux column, and pure methylenequadricyclane was obtained by vpc collection of the residue (SF96, 6' x ¼", 90°). The isolated yield was 6.4 mg (0.061 mmol, 6%) of colorless liquid: nmr: δ 1.47 (br t, 2, J = 7), 1.89 (br d, 4, J = 7), 5.00 (s, 2): ir 2980 (s), 3060 (w), 1680, 1233: mass spectrum 78 (100%), 104 (parent, 84%).

Anal. Calcd for C_8H_8: m/e 104.0625. Found:

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m/e 104.0628.

Hydroboration of 7-Methylenequadricyclane. A solution of 4 mg (38 μmol) of 7-methylenequadricyclane in 1 ml of dry ether was treated with 76 μl (380 μmol) of 5 M 9-borabicyclononane in THF (Aldrich). Vpc (6' x 1/8" SE30, 60°) was used to follow the reaction by disappearance of methylenequadricyclane at 6.8 min relative to THF at 1.1 min. No significant reaction had occurred after 4 hours. After 24 hours approximately 50% of the starting material remained; 23 μl more BBN solution was added and the mixture was left standing for two more days. About one-tenth of the original olefin was still present and tlc (50% ether-pentane on silica gel G) showed at least four products. The mixture was oxidized with 1 ml of 30% H_2O_2 and 1 ml of 6N NaOH for 5 hours and washed with satd. Na_2CO_3. Tlc and vpc (SE30, 6' x 1/8", 100°) showed no quadricyclyl-7-carbinol but instead at least six other products.

7-Acetoxynorbornadiene.[30] A solution of 15 g (0.091 mol) of 7-t-butoxynorbornadiene (Frinton) and 30 ml of acetic anhydride in 150 ml of glacial acetic acid was cooled to 0°, poured into 20.3 g (0.14 mol, 1.5 equiv) of 70% perchloric acid, and allowed to stand for one minute at 0°. The red solution was poured onto crushed ice and the mixture was extracted with methylene chloride. The extract

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was dried, concentrated, and distilled to give 11.7 g (0.077 mol, 85%) of 7-acetoxynorbornadiene, bp 70-73° (10 mm) (lit. 65° (8mm)): nmr: δ 1.95 (s, 3, $COCH_3$), 3.60 (sextet, 2), 4.45 (m,1), 6.51 (br t, 2), 6.68 (t, 2); ir 1740. Lit. ir 1740,[79] nmr: δ 3.28 (2), 3.72 (1), 6.42 (2), 6.56 (2).[79]

7-Acetoxynorbornadiene Iron Tricarbonyl.[47a] A solution of 1.5 g (10 mmol) of 7-acetoxynorbornadiene in 10 ml (approx. 50 mmol) of iron pentacarbonyl (Alfa) was heated to 113° ± 3° for six days. Tlc (silica gel G, 25% ether-pentane) was used to monitor the reaction. The black oily product was chromatographed on 10 g of alumina with ether. The solvent and excess iron pentacarbonyl were removed by rotary evaporation and the resulting red solid was recrystallized from methanol to yield 950 mg (3.29 mmol,33%) of 7-acetoxynorbornadiene iron tricarbonyl, mp 57-58° (lit.[47a] 58°): nmr: δ 1.90 (s, 3), 2.95 (m, 4, complexed vinyl), 3.42 (m,2), 4.19 (t, 1); ir 2000, 1920 (carbonyl), 1740 (acetate), 1410, 1370; mass spectrum 91 (100%), 290(parent, 10%, 4 line pattern appropriate for iron isotopes).

Anal. (3534) Calcd for $C_{12}H_{10}O_5Fe$ (290.25): C, 49.91; H, 3.23. Found: C, 49.70; H, 3.48.

Norbornadienol Iron Tricarbonyl.[47a] A saturated solution of KOH in methanol was added to 100 mg (0.34 mmol) of 7-acetoxynorbornadiene iron tricarbonyl. After one minute, water and pentane were

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added. The organic layer was dried and evaporated to yield 55 mg (0.21 mmol, 64%) of light yellow crystals, mp 92-94° (lit.[47a] 95-96.5°): nmr: δ 1.48 (br s, 1, OH), 2.92 (m, 4, vinyl), 3.02 (m,2), 3.58 (m, 1); ir 3420, 2020, 1920, 1390, 1060. Lit.[47a] nmr: δ 2.0, 2.92, 3.02, 3.28, 6.32; ir 3410, 2035, 1965, 1060.

7-Tosyloxynorbornadiene Iron Tricarbonyl.[47a] A solution of 250 mg (1.0 mmol) of norbornadienol iron tricarbonyl and 250 mg (1.3 mmol) of toluenesulfonyl chloride (recrystallized from hexane) in 3 ml of pyridine (dried over KOH) was left standing at -10° overnight. Ether was added, and the mixture was extracted with 10 ml of 1 M H_2SO_4, dried, and evaporated. The resulting orange solid was recrystallized from ether-pentane to yield 130 mg (0.32 mmol, 32%) of 7-tosyloxynorbornadiene iron tricarbonyl, mp 120-121° (dec), (lit.[47] 120°dec.): nmr: δ 2.51 (s,3), 2.82 (m,2), 3.04 (m, 2), 3.50 (m, 2), 4.05 (m, 1), 7.2-7.8 (m, 4); ir 2020, 1970, 1370, 1190, 1175; mass spectrum 91 (100%), 402 (parent, 3.3%). Lit.[47e] nmr 2.50, 2.81, 3.01, 3.45, 4.10, 7.73, 7.83; ir 2040, 1975, 1370, 1190, 1180.

Anal. (4194) Calcd for $C_{17}H_{14}O_6SFe$ (402.20): C, 50.77; H, 3.51; S, 7.97. Found: C, 50.79; H, 3.60; S, 7.81.

1,3-Dithiane.[48] A 2-l. flask equipped with condenser, mechanical stirrer, and dropping funnel was

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charged with 120 ml of glacial acetic acid, 200 ml of dichloromethane, and 6 ml of boron trifluoride etherate (MCB, distilled). A mixture of 57 g (0.5 mol) of propane-1,3-dithiol and 47 ml (42g, 0.55 mol) of dimethoxymethane (both Eastman) in a little dichloromethane was added from the dropping funnel over four hours. The mixture was stirred overnight, washed with water, and evaporated to yield white crystals of dithiane. The solid was recrystallized from methanol to yield 42.5 g (0.35 mol, 70%) of dithiane: nmr: δ2.02 (m, 2), 2.78 (t, 4), 3.78 (s, 2).

Reaction of 2-Lithio-1,3-dithiane with 7-Tosyloxynorbornadiene Iron Tricarbonyl. A solution of 300 mg (2.5 mmol) of dithiane in 10 ml of THF was cooled to -30° under nitrogen, and 2.84 ml (2.0 mmol) of butyllithium in ether (Foote, titrated, 1.42 M) was added. After 30 minutes, 804 mg (2.0 mmol) of 7-tosyloxynorbornadiene iron tricarbonyl in 2 ml of THF was added. The reaction was monitored by tlc (silica gel G, 50% ether-pentane); starting material gradually disappeared with no mobile product appearing. A similar reaction using 2.11 g (5 mmol) of the tosylate gave after seven days at room temperature a trace of unreacted tosylate and a brown gum soluble only in acetone: nmr (acetone-d_6): δ 2.4 (br s, 1), 3.3 (br s, 7), 7.3-8.0 (m,2). The product was not investigated further.

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Reaction of Potassium Cyanide with 7-Tosyloxynorbornadiene Iron Tricarbonyl. A solution of 130 mg (0.32 mmol) of 7-tosyloxynorbornadiene iron tricarbonyl in 10 ml of THF was treated with 500 mg (7.6 mmol) of potassium cyanide. The resulting suspension was stirred at room temperature for two days. Tlc (silica gel G, 50% ether-pentane and 100% ether) showed no mobile products. Saturated NaCl was added and the solution was extracted with ether and with dichloromethane; there were no extractable products. Water was removed by rotary evaporation leaving a tan solid which was insoluble in DMSO, DMF, and acetone: nmr (D_2O): δ 2.0-4.5 (band), 2.4, 3.38, 3.6, 9.05 (all br s); ir (KBr) 2020, 1970, 1940 (sh), 1370, 1190, 1175, almost superimposable on the ir of starting tosylate.

Thallium Cyclopentadienide.[60] Cyclopentadiene was prepared by distillation of its dimer (MCB) through a steamjacketed column and was stored at -78°. A solution of thallous hydroxide was prepared by dissolving 55.4 g (109.7 mmol) of thallous sulfate (Alfa) and 40 g (600 mmol) of sodium hydroxide in 150 ml of water; 33 g (500 mmol) of cyclopentadiene was added and the two-phase mixture was stirred overnight. A dense yellowish precipitate formed, which was filtered, washed repeatedly with water and ether, and dried under vacuum, yielding 56.3 g (0.209 mol, 95%) of tan powder.

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Benzyl Chloromethyl Ether: Method of Keach.[57]

A mixture of 108 g (1 mol) of benzyl alcohol and 250 g (90 g of formaldehyde, 3 mol) of 37% formaldehyde solution was cooled in ice and treated with HCl gas. The temperature of the mixture rose to 60°. After 45 minutes the solution was saturated and two phases had formed. The layers were separated, and the upper layer was dried over $CaCl_2$. Distillation of the liquid led to complete decomposition; a small amount of benzyl alcohol was collected, but the main product was a polymer of formaldehyde, which filled the entire distillation apparatus.

Benzyl Chloromethyl Ether: Method of Hamedov.[58]

A flask containing 12 g (0.4 mol) of paraformaldehyde was equipped with a nitrogen inlet and a U-shaped outlet tube leading to a second flask, cooled in ice and containing 21.6 g (0.2 mol) of benzyl alcohol. A gentle stream of nitrogen was passed over the formaldehyde as it was heated with a Meker burner to depolymerize the paraformaldehyde. When all of the formaldehyde had been transferred to the benzyl alcohol, the U tube was removed and HCl was bubbled into the mixture for 75 minutes. A white emulsion formed. The mixture was distilled at 40-53° (2mm). The distillate turned white upon standing. It was not possible to obtain a product free from polymers of formaldehyde.

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Benzyl Chloromethyl Ether.[59] A mixture of 22.5 g (0.21 mol) of benzyl alcohol and 19.1 g of 37% aqueous formaldehyde (0.23 mol) was cooled in an ice-salt (or ice-acetone) bath to below 5° and was treated with gaseous HCl. Great care was taken to maintain the temperature of the exothermic reaction below 10° at all times, as elevated temperatures led to the formation of dibenzylformal (dibenzyloxymethane). Very slow and intermittent addition of HCl at first was followed by more rapid addition; after the solution appeared to be saturated (about 90 min) HCl was passed in for an additional 45 min. Two layers were now present in the solution; the lower aqueous layer was discarded and the upper layer was dried over $CaCl_2$. Excess HCl was removed by rotary evaporation, with care to prevent water vapor from entering the flask. A clear, malodorous, somewhat lachrymatory oil weighing 31.9 g (0.2 mol, 98%) was obtained. Attempted distillation led to extensive decomposition, but the crude material seemed reasonably pure: nmr: δ 4.65 (s, 2), 5.36 (s, 2), 7.25 (s, 5). The product decomposed on standing, especially if in contact with air.

7-Benzyloxymethylnorbornenone via α-Chloroacrylonitrile.[50] A suspension of 56.13 g (0.21 mol) of 7-Benzyloxymethylnorbornenone via α-Chloroacrylothallium cyclopentadienide in 100 ml of dry ether was cooled in a Dry Ice - acetone-water slush to -20° and treated with 31.9 g (0.2 mol) of freshly prepared

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benzyl chloromethyl ether for 3.5 hr. The suspension was cooled to -50°, filtered into a chilled flask, and the residue was washed with 100 ml of cold dry ether. Ether was removed from the filtrate by rotary evaporation at 0° (ice bath). The oily yellow residue was dissolved in 71.9 g (0.82) of α-chloroacrylonitrile (MCB) and 9.86 g (0.06 mol) of $Cu(BF_4)_2$ (Alfa, dried over P_2O_5) was added. The dark mixture was stirred at 0° for 19 hr. Ether and satd. NaCl, containing some sodium tartarate, were added and the ether layer was washed, dried over $MgSO_4$, and evaporated. The residue was distilled on the Kugelrohr to give crude 5-chloro-5-cyano-7-benzyloxymethylnorbornene, which was dissolved in 200 ml of DMSO and treated with a solution of 33 g (0.5 mol) of KOH in 10 ml of water at 40° for 90 min. Water was added and the black mixture was extracted with ether. The organic layer was washed, dried over $MgSO_4$, and evaporated to yield 11.1 g of yellow oil which contained 47% 7-benzyloxymethylnorbornenone by gc (6' x 1/8" SE30, programmed 80° to 220° at 20°/min). The mixture was chromatographed on 1 kg of silica gel with ethyl acetate-hexane. A total of 3.61 g (15.8 mmol, 6.6%) of 7-benzyloxymethylnorbornenone was obtained: nmr: δ 1.85 (br s, 2), 2.62 (t of m, 1, J = 7), 2.88 (m,1), 3.10 (m, 1), 3.44 (d, 2, J = 7), 4.49 (s, 2), 5.91 (m, 1), 6.22 (d of d, 1), 7.22 (s, 5); ir 2940, 2860,

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1755, 1100; mass spectrum 91 (100%), 228 (5%, parent). Spectral data for 5-chloro-5-cyano-7-benzyloxymethyl-norbornenone: nmr: δ 2.54 (d of m, 1), 2.87 (m, 2), 3.25 (d, 2), 3.31 (m, 1), 4.38 (s, 2), 5.90 (d of d, 1), 6.19 (dof d, 1), 7.20 (s, 5); ir 2940, 2860, 2230 (w, CN), 1110; mass spectrum 91 (100%), 273 (12% parent).

Norbornenone.[61] Cyclopentadiene was prepared by distillation of its dimer through a steam-jacketed column, and stored at -78°. A solution of 76.2 g (0.87 mol) of α-chloroacrylonitrile (MCB) in 150 ml of benzene was placed in a 500 ml 3-necked flask with a magnetic stirrer, condenser, and addition funnel. From the funnel, 58.5 g (0.87 mol) of cyclopentadiene was added over 30 minutes. The solution was brought to reflux for three hours and stripped of solvent. A solid residue was obtained, which was melted with hot water and dissolved in 400 ml of DMSO. A solution of 143 g (2.18 mol) of KOH in 50 ml of water was added; the temperature of the mixture rose to 50° and the solution turned black. The mixture was stirred at 30° for 24 hours; ether extraction was unsuccessful due to the presence of solids. The mixture was steam distilled, yielding a yellow oil which solidified on cooling. The oil was distilled through a 6" x 3/4" glass helix column, bp 70-71° (30 mm), to yield 38.5 g (0.356 mol, 41%) of norbornenone: nmr: δ 1.77 (m, 2), 2.00 (m,2),

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2.86 (quintet, 1), 3.16 (m, 1), 6.05 (br d of d, 1), 6.49 (d of d, 1); ir (neat) 1740 (br), 1560, 3025, 2950, 2850.

Norbornadiene from Norbornenone. A solution of 10.8 g (0.1 mol) of norbornenone and 18.6 g (0.1 mol) of toluenesulfonylhydrazine in 125 ml of THF was stirred overnight at room temperature. A white solid formed, which was collected in two crops totalling 21.2 g (0.099 mol, 99%) of norbornenone tosylhydrazone, mp 188-191.5 dec: ir ($CHCl_3$) 3220, 2980, 1600 (w), 1160. A suspension of 4.24 g (20 mmol) of the tosylhydrazone in 50 ml of ether was treated with 35 ml (60 mmol) of methyllithium solution (Foote). After 48 hours 20 ml of water was added to the red solution. Vpc of the ether phase showed only peaks with the same retention time as toluene and as norbornadiene, verified by coinjection.

Stability of Quadricyclane to Ether Cleavage Conditions. A solution of 164 mg (1 mmol) of benzyl butyl ether (distilled) and 92 mg (1 mmol) of quadricyclane in 20 ml of anhydrous ethylamine (Aldrich) was treated at 0° with 14.6 mg (2.1 mg-atom) of lithium wire, cut into small pieces and hammered flat. A transient blue color formed as each piece dissolved; the color remained stable after the last addition. After one minute 50 ml of water and 50 ml of ether were added. Vpc (5' x ¼" SE30, 60°) showed peaks

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for toluene, n-butanol, and quadricyclane, and no other detectable peaks. Norbornane and norbornene were resolved from quadricyclane under these conditions.

7-Benzyloxymethylnorbornene. A solution of 840 mg (3.68 mmol) of 7-benzyloxymethylnorbornenone and 685 mg (3.68 mmol) of toluenesulfonylhydrazine (Aldrich) in 15 ml of THF was stirred at room temperature and at reflux for a total of three days. The ir band at 1745 cm^{-1} was used to monitor the reaction.[51] When it had not disappeared after three days an additional 150 mg of toluenesulfonylhydrazine was added. Finally tlc (50% ether-pentane on silica gel) showed that no ketone was left. The solution was cooled to 0° and treated with methyllithium until a positive Gilman test was obtained. The solution was left at room temperature for 7 hr, water and pentane were added, and the pentane extract was dried over $MgSO_4$ and evaporated. The residue weighed 675 mg and consisted of a mixture of products. Vpc collection (5' x ¼" SE30, 140°) of the major product gave a sample for spectra: nmr: δ 2.48 (t of m, 1), 3.25 (d, 2), 3.33 (m, 2), 4.30 (s, 2), 6.45 (t, 1), 6.73 (t,1), 7.24 (s, 5); ir 3090, 3000, 2930, 2860, 1450, 1085; mass spectrum parent 214 (calcd for diene 212).

Methyl 2,3-Dichloropropionate.[65] A solution of 225 g (2.61 mol) of methyl acrylate (MCB) and 100 ml

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of methanol was cooled in ice and treated with chlorine gas until saturated. Methanol was removed by distillation. A portion of the residue was distilled through a Vigeraux column at 75-78° (22 mm), to yield 316.4 g (1.11 mol, 42%) of methyl 2,3-dichloropropionate: nmr: δ 3.83 (s, 3), 3.2-4.6 (complex m, ABC system, 3).

2-Chloroacrylic Acid.[65] A solution of 60 g (1.5 mol) of sodium hydroxide in 500 ml of water was prepared and cooled to 50°; to it was added from a dropping funnel 130 g (0.5 mol) of undistilled methyl 2,3-dichloropropionate. The rate of addition was controlled to maintain the temperature of the exothermic reaction between 50°and 60°. The solution was stirred for 15 min until homogeneous, acidified with HCl, and extracted twice with ether. The solvent was removed and the residue was distilled, bp 70-75° (10 mm), to yield 28.3 g (0.266 mol, 44%) of 2-chloroacrylic acid, mp 50-55°. Recrystallization from hexane gave pure acid, mp 65-66° (lit.[65] 64-65°): nmr: δ 6.10 (d, 1), 6.60 (d, 1), 10.06 (s, 1); ir 2600-3300, 1710.

2-Chloroacrylyl Chloride. A solution of 70g (0.66 mol) of 2-chloroacrylic acid in 72 g (1 mol) of thionyl chloride was heated to reflux for 24 hours. Thionyl chloride and chloroacrylyl chloride were distilled away from residual acid and polymers, and fractionated through a Vigeraux column. $SOCl_2$ distilled at 78°at

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atmospheric pressure; the acid chloride distilled at 60-62° (130 mm). The total yield of pure acid chloride (purity determined by gc on a 5' x ¼" SE30 column at 60°) was 37.4 g (0.3 mol, 45%), with some more product present in the thionyl chloride fractions: nmr: δ 6.35 (d, 1), 6.85 (d, 1); ir 1780 (br), 1610.

7-Benzyloxymethylnorbornenone via 2-Chloroacrylyl Chloride.[64] 5-Benzyloxymethylcyclopentadiene was prepared as described above using 33.6 g (0.215 mol) of benzyl chloromethyl ether and 59.3 g (0.220 mol) of thallium cyclopentadienide. The ethereal filtrate was treated with 33.6 g (0.209 mol, 1.25 equiv) of 2-chloroacrylyl chloride at 0° for 18 hours. Ether was removed by rotary evaporation and the residue (primarily 5-chloro-7-benzyloxymethylnorbornene-5-carboxolyl chloride by nmr) was dissolved in dry dimethoxyethane (distilled from $LiAlH_4$) and treated with 26 g (0.4 mol) of sodium azide (Alfa reagent; technical grade was not suitable due to the presence of sodium hydroxide which hydrolyzed the acid chloride). The suspension was allowed to stand for 12 hr at room temperature and then heated to reflux for 2½ hr, until the acyl azide bands at 4.66 and 5.74 μ in the ir were replaced by isocyanate bands at 4.41 and 5.70 μ. To the dark brown solution was added 120 ml of 67% aqueous acetic acid. After two hours the ir spectrum of the mixture showed no isocyanate. Water

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and pentane were added, and the organic layer was washed with satd. NaCl, dried over $MgSO_4$ and Nuchar, and stripped of solvent. The brown residue was distilled on the Kugelrohr at 150-170° (0.4 mm), yielding 28.5 g (0.125 mol, 57%) of 7-benzyloxymethylnorbornenone. See above for spectral data.

7-Benzyloxymethylnorbornadiene. A solution of 27.8 g (0.12 mol) of 7-benzyloxymethylnorbornenone and 22.7 g (0.12 mol) of toluenesulfonylhydrazine (Aldrich) in 100 ml of THF was heated to reflux overnight. Tlc with 25% ether-pentane on silica gel G indicated the absence of ketone (Rf 0.7) and the presence of tosylhydrazone (Rf 0.05). Water and THF were removed by adding 400 ml of benzene and distilling until the head temperature reached 80°. The residue was cooled to 0° and treated with 153 ml (5.49 g of methyllithium, 0.25 mol) of 5.07% methyllithium solution (Foote). The addition was done slowly by syringe in a nitrogen atmosphere; foaming occurred during the first part of the addition. A Gilman test of the solution after all of the methyllithium had been added was positive. The orange solution was stirred under nitrogen at room temperature for 6 hr, then quenched by cautious addition of 150 ml of water. A dense solid formed which dissolved on stirring. The organic layer was separated, washed with water and satd. NaCl, filtered through $MgSO_4$, and stripped of

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solvent. The residue was distilled on the Kugelrohr to yield 10.62 g (0.05 mol, 41%) of 7-benzyloxymethylnorbornadiene: nmr: δ 2.74 (t of m, 1, bridge), 3.24 (d, 2, J = 8), 3.35 (sextet, 2, J = 2), 4.30 (s, 2), 6.45 (t, 2, J = 2), 6.70 (t, 2, J = 2), 7.14 (s, 5); ir 3080, 2980, 2970, 2850, 1080; mass spectrum 91 (100%, 145 (50%), 212 (5%, parent).

Anal. (8228) Calcd for $C_{15}H_{16}O$ (212.29): C, 84.87; H, 7.60. Found: C, 84.66; H, 7.73.

7-Benzyloxymethylquadricyclane. A solution of 10.3 g (0.048 mol) of 7-benzyloxymethylnorbornadiene and 250 mg of triphenylene in 340 ml of benzene (Mallinckrodt A.R.) was irradiated with Vycor filtered light from a Hanovia 450w lamp for a total of 5½ hr. Benzene was removed by rotary evaporation and the residue was chromatographed on 500 g of silica gel. Twelve 200 ml fractions of 10% benzene-pentane eluted 250 mg of triphenylene; three fractions of 10% ether-pentane eluted 7.468 g (35 mmol, 73%) of 7-benzyloxymethylquadricyclane: nmr: δ 1.2-1.6 (m,6), 2.74 (t of m, 1), 3.39 (d, 2), 4.40 (s, 2), 7.25 (s, 5); ir 3030, 2850, 1090.

Anal. (8246) Calcd for $C_{15}H_{16}O$ (212.294): C, 84.87; H, 7.60. Found, C, 84.61; H, 7.33.

Quadricyclyl-7-carbinol. A mixture of 500 ml of ammonia (distilled from blue sodium-ammonia solution) and 500 ml of THF with 7.25 g (34.2 mmol) of 7-benzyloxymethylquadricyclane was stirred at -78° while

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0.474 g (68.4 mg-atom, 2 equiv) of lithium wire (Lithcoa) was added in 1 cm pieces. The mixture was allowed to warm to its boiling point (Dry Ice condenser) for 90 min, at which time the lithium had been consumed. A further 50 mg of lithium gave a stable blue color. The reaction was quenched with water after 3 min. To the solution was carefully added 200 ml of water and 200 ml of ether; the condenser was removed and ammonia was allowed to evaporate for 4 hr, with occasional use of a warm water bath. The ether layer was separated and washed three times with satd. NaCl. The combined aqueous layers were continuously extracted with ether, and the two ether extracts were combined, dried, and stripped of solvent. The residue was chromatographed on 300 g of silica gel with 10-30% etherpentane. Three products were isolated. The least polar was identified as 1,2-diphenylethane (mp and mmp 51.5-52.5°, ir superimposable), yield 0.90 g (4.95 mmol, 26% based on stoichiometry 2 ether:1 diphenylethane). The next in polarity (overlapping the third) was a complex mixture of alcohols by gas chromatography. The least polar was quadricyclyl-7-carbinol, crude yield 4.013 g (32.8 mmol, 96%), which was recrystallized from pentane, yielding 1.922 g (15.9 mmol, 47%) of pure quadricyclyl-7-carbinol, mp 42-23.5°: nmr: δ 1.20-1.60 (m, 6), 2.65 (t of m, 1, J = 7), 3.56 (d, 2, J = 7), 4.26 (s, 1, variable with concentration); ir 3330, 3075,

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2920, 1230, 1030; mass spectrum 91 (100%), 122 (37%, parent).

Anal. (7370) Calcd for $C_8H_{10}O$ (122;168): C, 78.65; H, 8.25. Found: C, 78.66; H, 8.09.

7-Brosyloxymethylquadricyclane. A solution of 122 mg (1.0 mmol) of quadricyclylcarbinol and 255 mg (1.0 mmol) of bromobenzenesulfonyl chloride (Eastman) in 5 ml of pyridine was held at -10° for 16 hours. Pentane was added, pyridinium chloride was removed by filtration, and the solvent was removed. The residue was recrystallized from pentane to yield 75 mg (0.22 mmol, 22%) of 7-brosyloxymethylquadricyclane, mp 72-72.5°. The mother liquors contained unreacted alcohol, and were redissolved in pyridine and treated with more brosyl chloride. Workup as above yielded 69 mg (0.2 mmol) for a total yield of 151 mg (0.42 mmol, 42%): nmr: δ 1.2-1.8 (m, 6), 2.78 (t of m, 1), 4.00 (d, 2), 7.17 (m, 4); ir 3040, 2920, 1570, 1365 (br), 1180.

Actolysis of Brosylate. A solution of 151 mg (0.44 mmol) of brosyloxymethylquadricyclane and 30.7 mg (0.46 mmol) of sodium acetate in 5 ml of glacial acetic acid was heated to 99.5±1.5° under nitrogen in an oil bath for 24 hr. Ether was added and the mixture was extracted with satd. $NaHCO_3$. The solution was dried over $MgSO_4$ and evaporated, giving 122 mg of a complex mixture of compounds; gc (6' x 1/8" SE30, 140°) showed six ill-resolved peaks. The entire mix-

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ture was chromatographed on 10 g of silica gel. Only a partial separation into two fractions could be obtained. The first fraction, eluted with 20% ether-pentane, weighed 32.4 mg and contained 59 wt % brosylate by nmr integration. The second fraction weighed 27.1 mg and contained 37% brosylate. The recovered brosylate thus totaled 59.2 mg. This figure was used in the rate equation

$$\ln A = -kt + \ln A_0$$

to give a one-point approximation of the solvolysis rate of 1.1×10^{-5} sec^{-1} at 99.5°. Both fractions were quite complex (8 or more components) by gc. Both showed ir bands at 1740 (acetate) and the nmr of both fractions contained signals for vinyl hydrogens at δ 6.0 (m) and many overlapping signals below δ5. Due to lack of material and absence of any single major product, no further investigation could be made.

Stability of quadricyclyl-7-carbinol. In a parallel experiment to the solvolysis above, a solution of 30 mg (0.25 mmol) of quadricyclyl-7-carbinol and 30.7 mg (0.46 mmol) of sodium acetate in 5 ml of acetic acid was heated to 99.5° under nitrogen for 24 hr. Tlc (silica gel G, 30% ether-pentane) suggested that considerable decomposition had occurred: the original spot at Rf 0.55 was partially replaced by spots at Rf 0.95, 0.6, and a smear below 0.4. The alcohol was evidently not stable to the solvolysis

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conditions.

Triflic Anhydride.[73] A solution of 17.4 g (40 mmol) of barium trifluoromethanesulfonate (Minn. Mining and Manfacturing, tech.) in 75 ml of water was filtered to remove insoluble impurities and treated with 40 ml of 1 M H_2SO_4. The dense precipitate of barium sulfate was filtered and washed. Water was removed from the filtrate by rotary evaporation to yield 12.75 g of crude triflic acid hydrate. The acid was treated with 15 g of phosphorus pentoxide and heated gently with a small flame, with triflic anhydride distilling into a Dry Ice trap. Care was taken to keep triflic acid from distilling; if necessary, the distilled product was redistilled from fresh phosphorus pentoxide. Liquid nitrogen was used originally in the trap, but triflic anhydride prepared using the liquid nitrogen trap seemed to be impure, and extraneous products formed on reaction with 3. The yield of triflic anhydride was 5.1 g (34 mmol, 85%); ir 1460, 1240, 1030, with no other detectable bands. The product was stable for several days if protected from air; although a brown oil precipitated, the clear supernatant was satisfactorily pure.

Quadricyclyl-7-carbinyl Triflate. A solution of 122 mg (1.0 mmol) of quadricyclyl-7-carbinol and 111 mg (1.1 mmol) of triethylamine in 5 ml of CH_2Cl_2 was cooled to 0° and treated with 286 mg (1.01 mmol) of

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triflic anhydride, added dropwise. After one minute, pentane was added. A brown oil (presumably triethylammonium triflate) precipitated. The supernatant was evaporated to yield 261 mg (>100%) of a brown oil. The nmr of the mixture was complex, with broad absorptions from δ 0.9 to 3.6, olefinic protons at δ 6.0-6.6, and a doublet at δ 4.45 (α to triflate); ir 1830, 1720, 1410, 1220 (br).

Quadricyclyl-7-carbinyl Triflate via Anion. A solution of 221 mg (1.8 mmol) of quadricyclyl-7-carbinol in 10 ml of anhydrous benzene was cooled to 0° in the cold room and treated with 0.84 ml of 2.27 M butyllithium solution (Alfa, titrated before use). A balance had been set up in the cold room for convenience in weighing the triflic anhydride, which was so volatile and irritating that weighing or measuring at room temperature was inconvenient: 525 mg (1.9 mmol) of the anhydride was weighed into the solution with swirling. A gelatinous precipitate of lithium triflate formed within a minute, and was removed by centrifugation and washed with benzene. Benzene was removed by rotary evaporation to yield the crude, unstable triflate, which decomposed on attempted purification or on standing: nmr: δ 1.2-1.8 (m, 6), 2.95 (t of m, 1), 4.46 (d, 2); ir 3080, 2940, 1740, 1410, 1240, 1200 (br), 1140, 930 (br); mass spectrum 91 (100%), 105 (C_8H_9, 84%), 254 (parent, 21%).

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Acetolysis of Quadricyclyl-7-carbinyl Triflate. A solution of 127 mg (0.5 mmol) of crude triflate 87 was dissolved in 1 ml of 0.5 M sodium acetate in acetic acid. Nmr was used to follow the progress of the reaction. After 30 hr water and pentane were added. Gc of the pentane extract (6' x 1/8" SE30, 110°) showed at least 25 products. Nmr of the crude mixture showed overlapping singlets at δ 2.0-2.2, 4.90 (q), 6.38 (t).

Trifluoroethanolysis of 7-Quadricyclylcarbinyl Triflate. A solution of 450 mg (1.8 mmol) of crude triflate 87 and 202 mg (2.0 mmol) of triethylamine in 10 ml of trifluoroethanol was allowed to stand at room temperature for 20 hours, at which time nmr of an aliquot indicated absence of triflate (doublet at δ 4.46). Aqueous sodium bicarbonate and pentane were added, and the aqueous trifluoroethanol was extracted three times with pentane. The combined extracts were washed with satd. NaCl, dried over $MgSO_4$ and $NaHCO_3$, and stored over $NaHCO_3$ to retard decomposition. The nmr of the mixture was complex, but showed essentially no olefinic absorption. Gas chromatography (6' x 1/8" 10% Carbowax 600 - 10% KOH, 80°) indicated the presence of six products with the following retention times and percentages: 11 min, 1.7%; 13.4 min, 7.5%; 14.7 min, 1.6%; 15.9 min, 5.9%; 17.7 min, 5.4%; and 20.0 min, 77.8%. On a preparative column

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(10' x ¼" 10% Carbowax, 10% KOH, 100°) the first five compounds were not resolvable; they were collected in two fractions and the sixth compound was collected alone. Insufficient quantities of the minor components were collected for any spectra except the mass spectrum: First half of peak, 139 (100%), 91 (82%), 204 (1.4%); second half of peak, 91 (100%), 77 (79%), 78 (71%), 139 (79%), 177 (29%), 204 (21%, parent). The pure product 88 had nmr (discussed in detail in Results): δ 0.20 (m, 2), 0.92 (t of m, 1), 1.37 (m, 2), 1.80 (br s, 1), 1.86 (m, 1), 2.88 (d of m, 1), 3.41 (t, 2, J_{CH} = 8.8), 4.03 (d of d, 1); ir 3052, 3020, 2964, 2922, 2890, 1300, 1230, 1160, 1130; mass spectrum 91 (100%), 77 (90%), 78 (95%), 105 (62%), 139 (24%), 204 (1%, parent).

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Part II

Ab Initio Studies on Bishomocubane and Related Compounds

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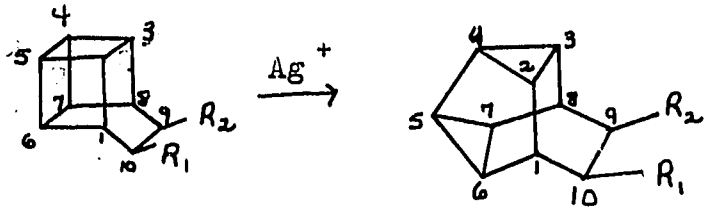
Introduction.

Metal ion **rearrangement** of strained carbon compounds have been the subject of much recent research. For instance, derivatives of pentacyclo[4.4.0.0^{2,5}0.^{3,8}0.^{4,7}]-decane (1,1'-bishomocubane, 1) react with silver ion[81] or other transition **metal** catalysts[82] to form pentacyclo[4.4.0.0.^{2,4}0.^{3,8}0.^{5,7}]decanes (dicyclopropyl compound, 2). Other systems in which this rearrangement occurs include homocubanes (i.e. 3)[83], cubane



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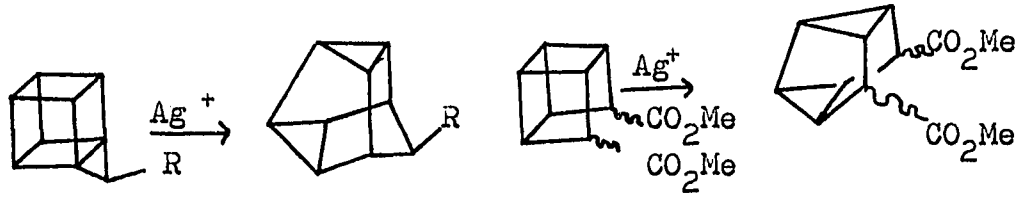
itself[84], and the secocubane diesters 4.[81,83]



3 4

Another reaction characteristic of these compounds is with complexes of rhodium to give dienes, e.g. the reaction of 1 (R_1 = R_2 = CO_2Me) with rhodium (I) tristriphenylphosphine chloride to give 5 and 6.[82,85,86] Complexes of palladium react with 1 to give mixtures of 2, 5, and 6.[82] The proportion of 2 in the product

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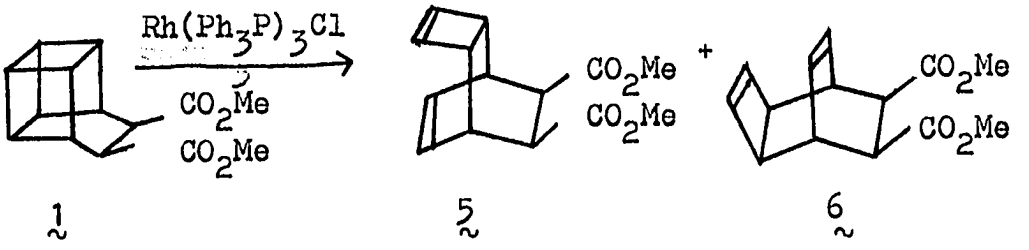
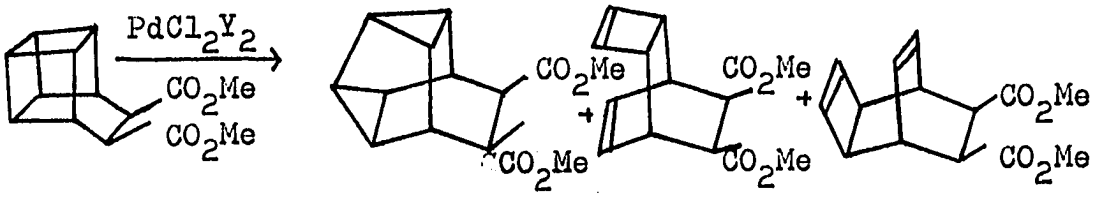
mixture has been correlated with the σ-donor and



1 5 6



1 2 5

π-acceptor properties of the ligands on the palladium ion.[82] Ligands which are good σ-donors and good π-acceptors, such as triphenylphosphine,[87] favor formation of dienes 5 and 6; those ligands which are good π acceptors but weak σ donors, such as triphenyl phosphite, favor the formation of 2. Ligands which are weak σ donors and weak π acceptors, such as benzonitrile or solvent, give 2 exclusively. These results are summarized in Table 1.[32]

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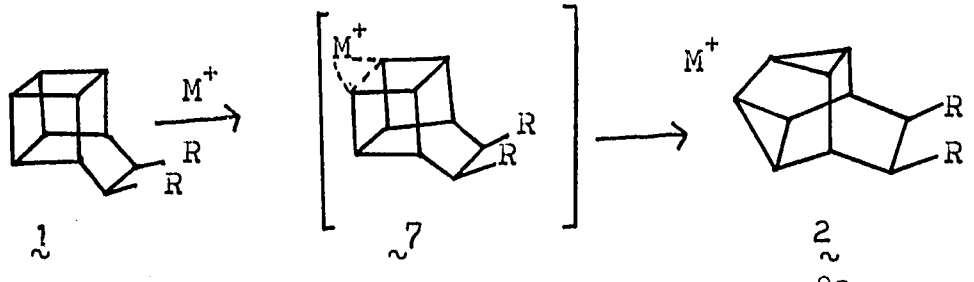
Table 1

Catalyst	% 2	% 5	% 6
$Rh(Ph_3P)_3Cl$	0	33	67
$PdCl_2(Ph_3P)_2$	41	23	35.5
$PdCl_2(Ph_3As)_2$	61.5	9.5	29
$PdCl_2(Ph_3Sb)_2$	100	0	0
$PdCl_2(P(OCH_3)_3)_2$	67	8	24
$PdCl_2(P(OPh)_3)_2$	94	2	4
$PdCl_2(PhC{\equiv}N)_2$	100	0	0
$PdCl_2$	100	0	0
$AgNO_3$	100	0	0

There has been much speculation concerning the mechanism of these reactions.[32,83,35,36] One of the mechanisms which has been suggested for the formation of 2 involves coordination of the metal to the strained "back" bond from carbon 4 to carbon 5 of 1, with the metal acting as a strong σ acceptor to yield



1 7 2

an intermediate with carbonium ion character.[82] Support for this idea comes from the relationship between the nature of the metal catalyst and the products in the reactions above. Silver is a strong σ acceptor,[83] and in other reactions it is thought to give a carbonium-ion like intermediate.[83,89,90] The results for palladium catalysts in Table 1 show an

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inverse correlation between the amount of 2 formed and the σ donor ability of the ligands on the palladium. The metal in this case is acting as a "conductor": σ donation to the metal by the ligand increaces the electron density of the metal, thus decreasing the strength with which it withdraws electrons from the hydrocarbon. Further support for the σ acceptor - carbonium ion mechanism is the solvent dependence of the product composition from the reaction of $PdCl_2(Ph_3P)_2$ with 1, shown in Table 2.[82] Solvents which stabilize carbonium ions favor the formation of 2. This result suggests that the intermediate leading to 2 has substantial charge separation in its transition state.

Table 2

Solvent	% 2	% 5	% 6
$CDCl_3$	41	23	36
CH_2Cl_2	43	20	37
$CH_3C{\equiv}N$	55	13	32
CD_3COCD_3	71	9	20
CD_3SOCD_3	85	4	11
CH_3OH	86	4	10

In order to elucidate the mechanism of the formation of 2 from 1, an ab initio molecular orbital program was used to examine the nature of bonding in 1 and 2. A calculation on the entire molecule would have been prohibitively expensive in terms of computer time: the estimated time needed for cubane (even taking advantage of its high symmetry), with a minimum basis set of STO-3G orbitals, would be eight hours of CDC 6400

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time.[91] A more modest effort was called for. The method used was to examine only the bond of interest, simulating the rest of the molecule by replacing the four carbons bound to the carbons of interest by hydrogens. The calculation was thus performed on two distorted molecules of ethane, one modeled after bishomocubane and the other after the rearrangement product 2. These molecules will be referred to as "bishomocubane-ethane" and "dicyclopropyl-ethane" respectively.

This approach seems to be new, although similar approximations have been made. The molecular-fragment approach of Christofferson[92] uses a carbon-hydrogen bond as a model for carbon-carbon bonds. In his approach, orbitals are calculated for methane and for methyl radical. These orbitals are then combined to give more complex molecules, with methane orbitals used for tetrahedral carbons and methyl radical orbitals for trigonal carbons. A carbon-carbon bonding orbital is generated by the overlap of two carbon-hydrogen bonding orbitals. Quite good results for the rotational barrier in ethane[92a] and energy levels in aromatic hydrocarbons[92b] are obtained, in spite of the extremely small basis set (one floating spherical Gaussian orbital for σ orbitals, two for π orbitals). Absolute energy differences are not well determined, as might be expected from such a crude

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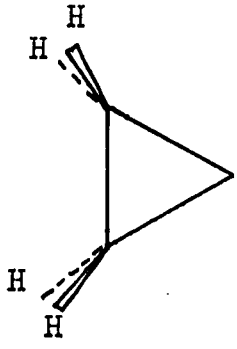
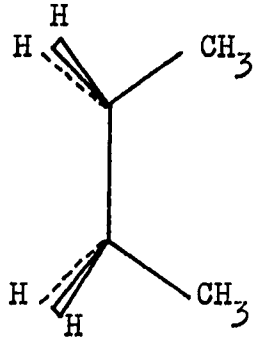
approximation. However, the method does give better energy rankings of isomeric systems than semiempirical calculations do. The ranking of energies of benzene, fulvene, trimethylenecyclopropane, and dimethylenecyclobutene by the molecular fragment method agrees with experiment and with ab initio calculations better than semiempirical calculations do.[92c]

Another justification for studying only the bond of interest can be found in a study of the orbitals of cyclopropane.[93] In this study the bentness of cyclopropane ring bonds was demonstrated, in part, by a plot of the difference in electron density between cyclopropane and a molecule of butane constrained in configuration such that carbons 2 and 3 and their hydrogens were in the same geometric arrangement as two of the carbons of cyclopropane. In this calculation the authors remark that the nature of the bonding to the hydrogens is unchanged between the two systems. This observation lends credence to the idea that the C-C bond in the simulated cage compound





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should be accurately depicted, even if the C-H bonds which simulate the rest of the cage are not.

The program used for the calculations was IBMOL4,[94] modified at Berkeley for the CDC 6400.[95] All calculations were performed using three spherical Gaussian orbitals to simulate each of a minimum basis set of Slater orbitals (the STO-3G basis). The Slater orbitals were originally those found optimal for ethane;[91] the carbon 2s and 2p orbitals and the hydrogen 1s orbitals for the "real" hydrogens were optimized. The geometry used for the bishomocubane-ethane structure was derived from an x-ray structure determination of bishomocubyl brosylate.[96] The carbon-hydrogen bond lengths to the hydrogens simulating carbons (hereinafter called "pseudocarbons") were set to 1.09 Å. The C-C-H bond angle to the "real" hydrogen was set at 135°. This is a reasonable value, since the other bonds to this carbon form almost exactly the apex of a cube; the hydrogen should be equidistant from the three other bonds. An optimization of the hydrogen bond angle in fact showed an optimal bond angle of 134.9°; 135° was used for the final calculation. The bond length of the C-H bond was optimized to 1.0877 Å.

The geometry of 2 was similarly obtained from x-ray data.[97] The optimum C-C-H angle was found to be 127.4°, but an angle of 120° was used for the final calculation. The C-H bond length to the "real" hydrogen in dicyclopropyl-ethane was also optimized, and was

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found to be 1.0769 Å. The geometry of both molecules is shown in Figure 1, and in Appendix A the geometric positions and Slater exponents of all the atoms are listed.

The energies calculated for the two molecules were -78.183386 Hartree for bishomocubane-ethane, and -78.079259 Hartree for dicyclopropyl-ethane. Clearly the calculated energies of the model compounds do not reflect the actual stability of the parent compounds. The bishomocubane-ethane model system has a lower energy than the dicyclopropyl-ethane model, whereas the bishomocubane molecule is in fact less stable than the dicyclopropyl rearrangement product. Since the rearrangement proceeds quantitatively to 2, the energy difference must be at least 5 kcal. But the energy difference calculated for the model compounds is -0.1041 Hartree or -65.5 kcal! Considering the drastic simplifications of the system this result is not unreasonable. Most of the error undoubtedly arises from the fact that only a portion of the molecule is considered. Much of the energy difference between 1 and 2 is due to strain in bonds other than the back bond which is being investigated.

It is worthwhile to dissect the energy difference between the two model systems into its components. Table 3 lists the energies of all of the molecular orbitals of both systems, along with results of a

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minimum basis set Slater orbital calculation.[100]

Table 3

Orbital	Symmetry	Bishomocubane-ethane	Dicyclopropyl-ethane
1	A_1	-11.033993	-11.012044
2	"	-1.0348226	-1.0081892
3	"	-0.62469138	-0.65040485
4	"	-0.47581567	-0.49872734
5	B_1	-11.034394	-11.012501
6	"	-0.7950107	-0.84091260
7	"	-0.47925531	-0.54436259
8	B_2	-0.59638621	-0.47084149
9	A_2	-0.38558948	-0.30954507

Energy Term	Bishomocubane-ethane	Dicyclopropyl-ethane	Eclipsed[100] ethane
E(T)	-78.183386	-78.079259	-78.98593
E(NN)	43.633907	43.122915	41.93988
E(NE)	-190.71467	-189.70929	-187.01830
E(EE)	68.897378	68.507117	66.12725

The energy difference can be partitioned into nuclear repulsion (ΔE_{NN}), nucleus - electron attraction (ΔE_{NE}), and electron - electron repulsion (ΔE_{EE}). Each ΔE term is the corresponding energy for bishomocubane-ethane minus that for dicyclopropyl-ethane. Thus, a negative value corresponds to a lower energy for bishomocubane-ethane. Note that the difference in total energy is the result of partial cancellation of much larger energy differences between the components of the energy. The largest energy difference is in the one-electron energy, ΔE_{NE}. This term is apparently responsible for an artificial lowering of

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$$\Delta E_{Total} = -0.104127$$
$$\Delta E_{NN} = +0.510992$$
$$\Delta E_{NE} = -1.00533$$
$$\Delta E_{EE} = +0.390261$$

the energy of the bishomocubane-ethane system relative to the dicyclopropyl-ethane system. This is reasonable since the bishomocubane-ethane molecule is much more compact than the dicyclopropyl-ethane molecule. The pseudocarbons are folded in toward the center of the molecule, closer to the opposite carbon, in the bishomocubane-ethane case. The electrons in the bonds to the pseudocarbons are therefore closer on the average to the positive charge on the other nuclei, and are thus more stable. In the actual molecule these pseudocarbon bonds would be between carbon and carbon, and would not be as sensitive to the proximity of nonbonded atoms.

A related reason for the energy difference is an artificial destabilization of the dicyclopropyl-ethane compound. The bonds in the pseudocyclopropane rings cannot be formed properly with hydrogens; the bonding in cyclopropane depends on a high p (or even d)[93] contribution to the bonding orbital from both carbons. The single 1s orbital on the pseudocarbons cannot contribute any p character to the bond; as a result, all of the bend of the 60° bond angle between the two pseudocarbons must be accomodated by rehybridization at one carbon, rather than shared rehybridization at

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both carbons as in the case of the actual molecule. This excessive need for rehybridization is reflected in the fact that the angle as calculated below between the internuclear axis and the orbital comprising the bond to each pseudocarbon is 31°, as compared with 18° in cyclopropane.[93] The electrons in the psuedocarbon bonds are thus not pointing directly toward the psuedocarbon nucleus; this raises the E_{NE} for the dicyclopropyl-ethane system. Since the angle is less acute in bishomocubane-ethane, the problem is not as severe; thus the relative energy of the two systems is not correctly calculated.

It should be noted that the difference in energy between the two systems is due mainly to the approximations involved in the representation of carbons by hydrogens. The energy difference does not even reflect the relative strain of the two carbon-carbon bonds, much less the energy difference between the parent compounds $\underset{\sim}{1}$ and $\underset{\sim}{2}$. Nonetheless, there is no reason to expect that the nature of bonding between the two carbons is inaccurately depicted. Even though no reliable conclusions can be drawn from the energy results, the other properties of the carbon-carbon bond of interest should still be useful.

The bond angle calculation mentioned above was based on the POPOL population analysis programs,[94,95] which generated localized orbitals from the calculated

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symmetry orbitals by the Boys method.[98] One definition of bond bentness is the angle between the bonding orbital and the internuclear axis. The direction of each bonding orbital from the carbon atom was defined as a vector, the components of which were the coefficients of the p_x, p_y, and p_z orbitals. The internuclear vector was known from the coordinates of the atoms. The bentness of the bond by this criterion was the angle between these vectors, from the formula:

$$\cos\theta = \vec{B}\cdot\vec{N} / |\vec{B}|\,|\vec{N}|$$

where $\vec{B}$ is the orbital vector and $\vec{N}$ the internuclear vector. The angles calculated are shown in Table 4, together with the normalized direction vectors $\vec{B}/|\vec{B}|$ and $\vec{N}/|\vec{N}|$.

Table 4

		θ
Bishomocubane-ethane:		
C-C	$\vec{B}$ = (-0.31349, 0.0, 0,94959)	
	$\vec{N}$ = (0.0, 0.0, 1.0)	18°
C-H	$\vec{B}$ = (0.76359, 0.0, 0.64576)	
	$\vec{N}$ = (0.70704, 0.0, 0.70704)	4°
C-ΨC	$\vec{B}$ = (-0.56450, 0.81397, 0.14281)	
	$\vec{N}$ = (-0.68825, 0.72527, 0.01722)	11°
Dicyclopropyl-ethane:		
C-C	$\vec{B}$ = (-0.5534, 0.0, 0.99874)	
	$\vec{N}$ = (0.0, 0.0, 1.0)	3°
C-H	$\vec{B}$ = (0.83675, 0.0, 0.54759)	
	$\vec{N}$ = (0.86606, 0.0, 0.50000)	3°
C-ΨC	$\vec{B}$ = (-0.43176, 0.87750, 0.20876)	
	$\vec{N}$ = (-0.81122, 0.50000, 0.30326)	31°

It should be noted that the bonds to the real

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hydrogens are essentially straight, with 4° and 3° of bend for bishomocubane-ethane and dicyclopropyl-ethane respectively. The bonds to the pseudocarbons are bent 11° for bishomocubane-ethane and 31° for dicyclopropyl-ethane as mentioned above. Most importantly, the C-C bond in the bishomocubane-ethane structure is bent 18°, while the corresponding bond in the dicyclopropyl-ethane structure is bent only 3°.

The hybridization of the C-C bonds in the two structures, also obtained from program POPOL, is fairly similar. In the bishomocubane-ethane system the C-C bonding orbitals are $sp^{2.20}$, corresponding to 31% s character; in the dicyclopropyl-ethane case the hybridization is $sp^{1.85}$, with 35% s character. In both cases the bonds to the pseudocarbons have high p character: $sp^{3.39}$ or 22% s character for bishomocubane-ethane, and $sp^{4.76}$ or only 17% s character for dicyclopropyl-ethane. The p orbitals are heavily involved in bonding to the pseudocarbons, as would be expected from the compressed angles that these bonds form. The high p character leaves less p character for the central bond.

The composition of the bonding orbitals in terms of the contribution of individual atomic orbitals is another method of examining the nature of bonding in the system. The C-C bonds in both systems have a zero contribution from the p_y orbital, as is required by

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symmetry: the p_y nodal plane is a molecular symmetry plane. Both bonds also have a large p_z component along the direction of the internuclear axis. However, the p_x component, which is perpendicular to the bond and in the symmetry plane of the molecule, is twenty times larger for the bishomocubane-ethane structure than for the dicyclopropyl-ethane structure: the contribution of the p_x orbital in the former case is 0.065764, while in the dicyclopropyl-ethane structure the p_x contribution is only 0.003213. This high p_x character is observed in the bishomocubane-ethane molecule in spite of the fact that more p_x character is needed for bonding to the pseudocarbons in bishomocubane-ethane than is needed for dicyclopropyl-ethane. The pseudocarbons in dicyclopropyl-ethane lie more out from the ends of the molecule, and the p_z orbital can be used for bonding, while in bishomocubane-ethane the pseudocarbons lie almost in the nodal plane of the p_z orbital, and the bonding must be shared between the p_x and p_y orbitals. Thus even though the bishomocubane-ethane structure has less p_x contribution to spare, the system is most stable with a substantial amount of p_x contribution to the C-C bond. This p_x character can be can be regarded as a π component of the C-C bond, as shown. This is merely another way of looking at the bentness of the bond, but as discussed below, is relevant to the reactivity of the system.

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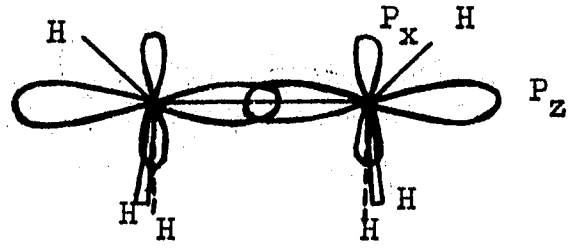

The most straightforward and intuitive criterion for the bentness of a bond is an electron density map. Program IBPLOT is part of the Berkeley IBMOL package,[95] and was used to generate plots of the electron density distribution in bishomocubane-ethane and dicyclopropylethane. The details of the plot programs are contained in Appendix B. The two types of plots used were the three-dimensional perspective plot and the contour plot of electron density. Two cross-sectional planes through the molecule were investigated: the xz plane containing the carbons and the "real" hydrogens, and the xy plane perpendicular to the center of the C-C bond.

Figures 2-9 are examples of three-dimensional perspective plots; figures 10-17 are contour plots of the total electron density and the electron density of C-C bonding orbital. It can be seen that the [illegible] differences in bentness of the bond are more evident in the contour plots than in the three-dimensional

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plots. A variety of view angles were investigated for the latter, but the bend so clearly evident for bishomocubane-ethane in the contour plots, for instance in Figures 10 and 12, remained unimpressive in the 3D plots. The view angle for Figures 2-9 is from an altitude of 20° and an azimuth of 135°; the carbon atoms are located in the tall peaks, the hydrogens in the small peaks to the left of and behind the carbons. As can be seen in Figures 2 and 3, the core electron density dominates the map to such an extent that subtleties such as bond bending are concealed. The plots of the logarithm of electron density, Figures 4 and 5, likewise show little of interest. More useful are Figures 6 and 7, which are plots of the valence electron density, the electron density contributed by all the orbitals except the carbon 1s orbitals. The most useful of the perspective plots are Figures 8 and 9, which show the density of the sum of symmetry orbitals 2 and 4, (see Table 3). These two symmetry orbitals have the most carbon-carbon bonding character; the remainder of the symmetry orbitals are either carbon 1s combinations or primarily localized on C-H bonds. The ridge of electron density in Figure 9, the dicyclopropyl-ethane case, lies along the line between the two carbon peaks; in Figure 8 the ridge is clearly displaced outward toward the left. In other words, the bond is bent outward.

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The contour plots in Figures 10-17 allow a clearer view of the bond bending. The lines on Figures 10 and 11 connect the carbons and hydrogens; the dotted lines are the projections on the xz plane of the pseudocarbon bonds. The scale and orientation of the molecules are the same for Figures 12 and 13. In Figures 14-17 the lines are projections on the xy planes of the bonds to hydrogen (to the right) and to the pseudocarbons. The intersection of the lines defines the C-C bond axis, which is perpendicular to the plane of the paper in these plots.

Figures 10 and 11 show the total electron density in the xz plane. The bend of the bishomocubane-ethane bond in Figure 10 is clearly visible, as is the straightness of the dicyclopropyl-ethane bond in Figure 11. Figures 12 and 13 show the density in the localized C-C bonding orbital. Again the maximum electron density is clearly located outside of the internuclear axis in bishomocubane-ethane, Figure 10, and along the internuclear axis in dicyclopropyl-ethane, Figure 11.

Figures 14 and 15 are plots of the total electron density in the xy plane perpendicular to the center of the bond axis. Again in the case of bishomocubane-ethane, Figure 14, the center of electron density is clearly outside the internuclear axis, and the outermost contours of low electron density reach out farther from the molecule than in the case of

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dicyclopropyl-ethane, Figure 15. Finally the density of the localized C-C bonding orbital shows the same trend in Figures 16 and 17.

There is one final method by which the bentness of the bond in bishomocubane-ethane can be visualized. Part of the output from IBPLOT is a listing of the grid of density values to be plotted. From this output it is possible to find the x-coordinate of maximum electron density along any given value of the z-coordinate - the ridge crest, so to speak. To find the point of maximum electron density, five points at x = -0.30, -0.15, 0.0, 0.15, and 0.30 Bohrs were taken at z values from 0.0 to 1.20. The bond is symmetrical, so only half of it needs to be calculated. At each z value a parabola was fitted to the five points by the method of least squares, using program PLS.[99] The maximum of the this parabola was taken as the point of maximum electron density. The locus of these maxima, the crest of the electron density ridge, is plotted in Figure 18.

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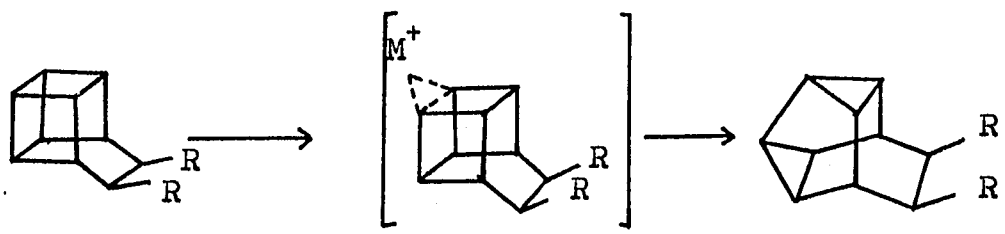
Conclusion.

The most obvious conclusion that can be drawn from the calculations is that the back bond in bishomocubane is quite strongly bent outward, while the back bond in its rearrangement product 2 is essentially straight. The electron cloud extends substantially further from the body of the molecule of 1 as a consequence of this bending. In addition, the electron density at the center of the bond in the bishomocubane system is slightly higher than that at the center of the dicyclopropyl bond.

Structure 1 can be viewed as having a bulging, accessible electron cloud, which could readily be attacked by an electrophilic metal ion. In contrast, the dicyclopropyl system back bond is straight and not as readily attacked.

Three mechanisms have been proposed to explain the conversion of 1 to 2.[82,83,84] The differences in the proposed mechanisms are the nature and fate of the intermediate 7. One line of reasoning is that 7



1 7 2

is an oxidative insertion intermediate.[83,84] In the

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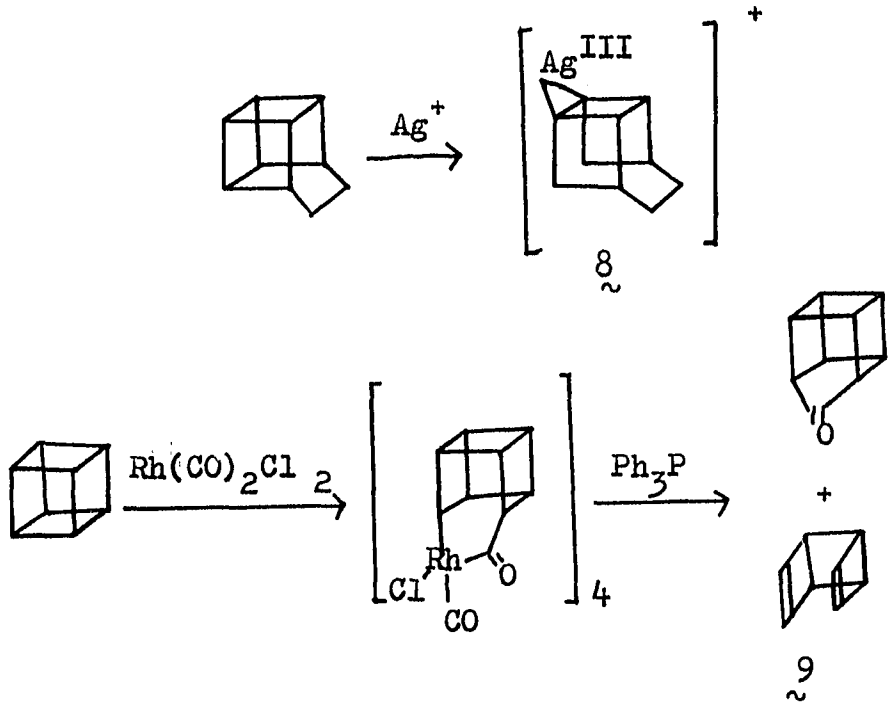
process of an oxidative insertion the metal is formally oxidized; silver would be converted to a sigma-bonded silver (III) ion in 8. An oxidative insertion intermediate is observed with rhodium carbonyl dichloride dimer in its reaction with cubane.[6a] The product formed in this reaction, after treatment of the intermediate with triphenylphosphine, is homocubanone, in addition to the tricyclooctadiene 9. The mechanism invoked by Halpern[4,6a] for the formation of 9 involves



formation of the oxidative insertion product 8 followed by opening to the carbonium ion 10 and rearrangement to 11 by a cyclobutyl - cyclopropylcarbinyl rearrangement, as shown for cubane. By this mechanism, however, the strained, bent back bond of bishomocubane

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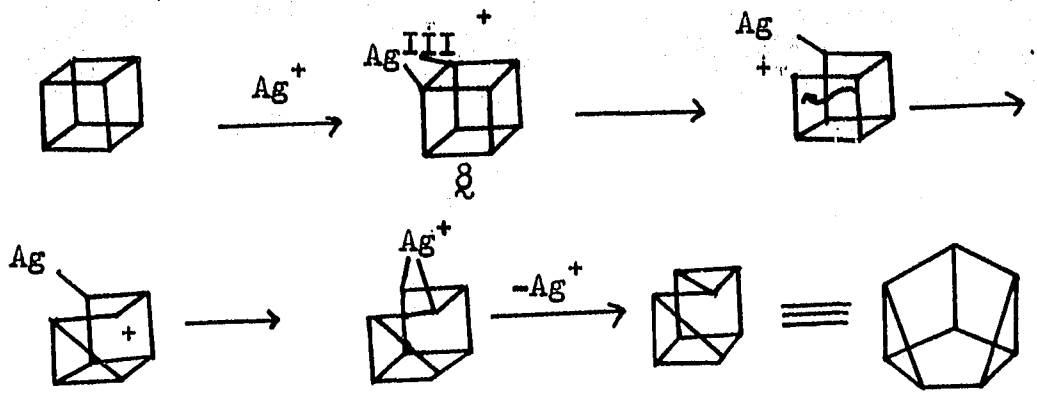
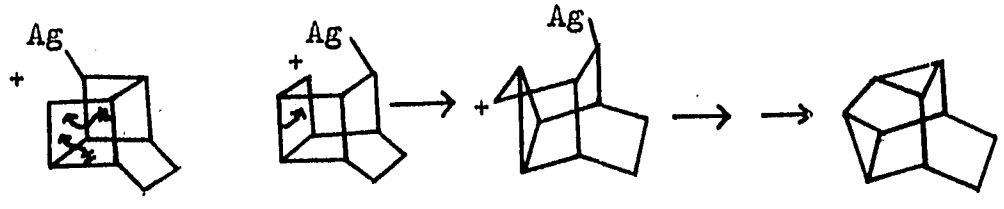


8

would not be the one attacked. Attack on the back bond would lead to intermediate carbonium ion 12; no



12 2

cyclobutyl - cyclopropylcarbinyl rearrangement in 12 can lead to the observed product. In order to obtain 2 by this mechanism, one of the side bonds must be attacked. Attack on the side bonds is less plausible than initial attack on the back bond because the side bonds in bishomocubane are substantially less strained than the back bond.

A second mechanism which involves the intermediacy of the oxidative insertion product 8 is that proposed by Paquette.[83,85] Here the key intermediate is the metallo carbonium ion 13. Metallo carbonium

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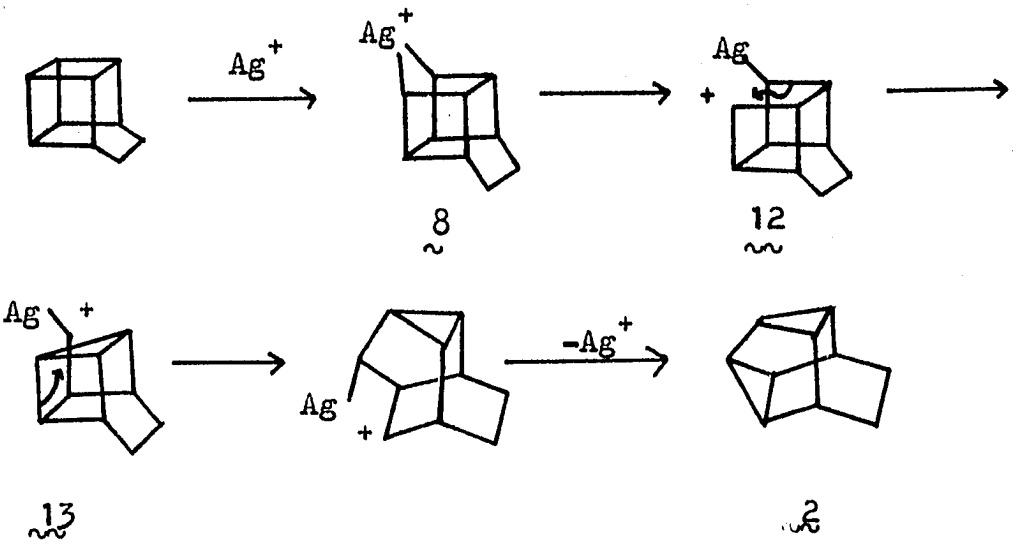
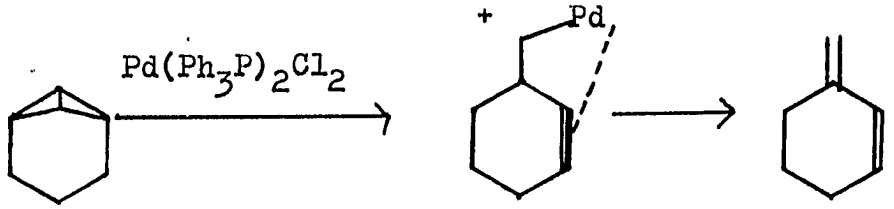
ions have been postulated and observed in the rearrange-



13 2

ment of bicyclobutanes with palladium and with silver. For instance, tricyclo$[4.1.0.0^{2,7}]$ heptane 14 is converted to methylenecyclohexane by way of intermediate 15, observed by nmr.[89] The difficulty with this



14 15

mechanism is that two 1,3 carbonium ion shifts are required.

The final mechanism[2,3] is simply a concerted switch of bonds in an electron deficient intermediate such as 7, which has not opened to an oxidative insertion species such as 8. The intermediate 7 would be

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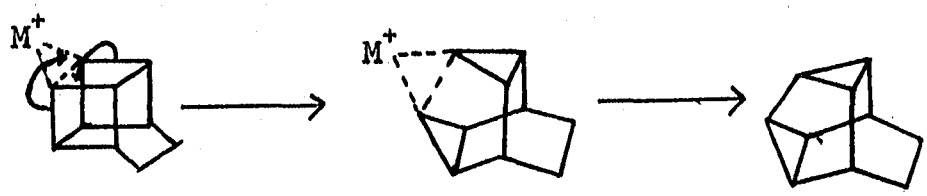
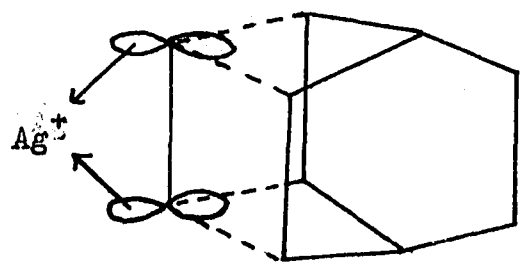


7 2

characterized by electron withdrawal primarily from the p_x orbitals which make the back bond bent and accessible to the electrophile. This withdrawal would have the effect of weakening the side bonds and facilitating the concerted switch to give structure 2. In 2 the p_x orbitals are now more strongly involved in bonding to the other carbons and less strongly directed outward; the silver ion would be less tightly bound and would dissociate.



The results from the calculations are certainly consistent with this concerted mechanism. The extent of p_x contribution to the bending of the C-C

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bond in 1 and the near absence of such contribution in 2 support the suggestion that the side bonds in 1 could be weakened by coordination of an electrophilic metal ion to the back C-C bond. The overall strain relief caused by the rearrangement would be abetted by the improved bonding available to the p_x orbitals in 2 as compared with 1. The concerted double rearrangement can also be viewed as a 90° rotation of the two carbons of the back bond relative to the bicyclo[2.2.2]-octane system making up the rest of the molecule. The coordination of the metal ion makes the rearrangement possible by weakening the side bonds by electron withdrawal through the back-bond carbons.

The two nonconcerted mechanisms are not ruled out by the calculations; a case could easily be made for 7 simply being a transition state in the opening of 1 to the oxidative insertion intermediate 8. The calculations provide no information on this or later stages of the first two mechanisms. However, the objectionable features of the two stepwise mechanisms and the reasonableness of the concerted mechanism suggest that the latter may be more valuable than has been previously supposed.

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APPENDIX A

Geometry

Bishomocubane-ethane

Center	x	y	z
C 1	0.	0.	1.4078731
C 2	0.	0.	-1.4078731
H 3	1.4539540	0.	2.8618270
H 4	1.4539540	0.	-2.8618270
H 5	-1.4189858	1.4952990	1.4438353
H 6	-1.4189858	1.4952990	-1.4438553
H 7	-1.4189858	-1.4952990	1.4438553
H 8	-1.4189858	-1.4952990	-1.4438553

Dicyclopropyl-ethane

Center	x	y	z
C 1	0.	0.	1.408818
C 2	0.	0.	-1.408818
H 3	1.763046	0.	2.426713
H 4	1.763046	0.	-2.426713
H 5	-1.672505	1.030865	2.033938
H 6	-1.672505	1.030865	-2.033938
H 7	-1.672505	-1.030865	2.033938
H 8	-1.672505	-1.030865	-2.033938

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Slater Exponents

Basis Orbital	Center	Type	- Exponents - Bishomocubaneethane	Dicyclopropylethane
1	C 1	1s	5.70	5.70
2	C 1	2s	1.7360	1.7382
3	C 2	1s	5.70	5.70
4	C 2	2s	1.7360	1.7382
5	H 3	1s	1.1962	1.2026
6	H 4	1s	1.1962	1.2026
7	H 5	1s	1.17	1.17
8	H 6	1s	1.17	1.17
9	H 7	1s	1.17	1.17
10	H 8	1s	1.17	1.17
11	C 1	$2p_x$	1.7360	1.7382
12	C 2	$2p_x$	1.7360	1.7382
13	C 1	$2p_y$	1.7360	1.7382
14	C 2	$2p_y$	1.7360	1.7382
15	C 1	$2p_z$	1.7360	1.7382
16	C 2	$2p_z$	1.7360	1.7382

Symmetry orbitals

Symmetry Number	Symmetry	Orbital Number	Composition
1	A_1	1	$C_1 1s + C_2 1s$
		2	$C_1 2s + C_2 2s$
		3	$H_3 1s + H_4 1s$
		4	$H_5 1s + H_6 1s + H_7 1s + H_8 1s$
		5	$C_1 2p_x + C_2 2p_x$
		6	$C_1 2p_z - C_2 2p_z$
2	B_1	1	$C_1 1s - C_2 1s$
		2	$C_1 2s - C_2 2s$
		3	$H_3 1s - H_4 1s$
		4	$H_5 1s - H_6 1s + H_7 1s - H_8 1s$
		5	$C_1 2p_x - C_2 2p_x$
		6	$C_1 2p_z + C_2 2p_z$
3	B_2	1	$H_5 1s + H_6 1s - H_7 1s - H_8 1s$
		2	$C_1 2p_y + C_2 2p_y$
4	A_2	1	$H_5 1s - H_6 1s - H_7 1s + H_8 1s$
		2	$C_1 2p_z - C_2 2p_z$

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APPENDIX B

Plotting Parameters

View Altitude - 60°

View Azimuth - 135°

View Distance - 20 radii (75 Bohrs)

Grid Density - 1 line = 0.15 Bohr

Grid size:

Figures 2 - 13: 51 x 51 grid lines (7.5 x 7.5 Bohrs)

Figures 14 - 17: 41 x 41 grid lines (6.0 x 6.0 Bohrs)

Contour Intervals:

Figures 10, 11:

0.03 0.10 0.20 0.23 0.25 0.27 0.30 0.50 2.50 10.0

Figures 12, 13:

0.001 0.003 0.01 0.03 0.10 0.20 0.30 0.50 2.50 10.0

Figures 14, 15:

0.01 0.03 0.10 0.16 0.20 0.23 0.25 0.26

Figures 16, 17:

0.001 0.003 0.01 0.03 0.10 0.20 0.22 0.25

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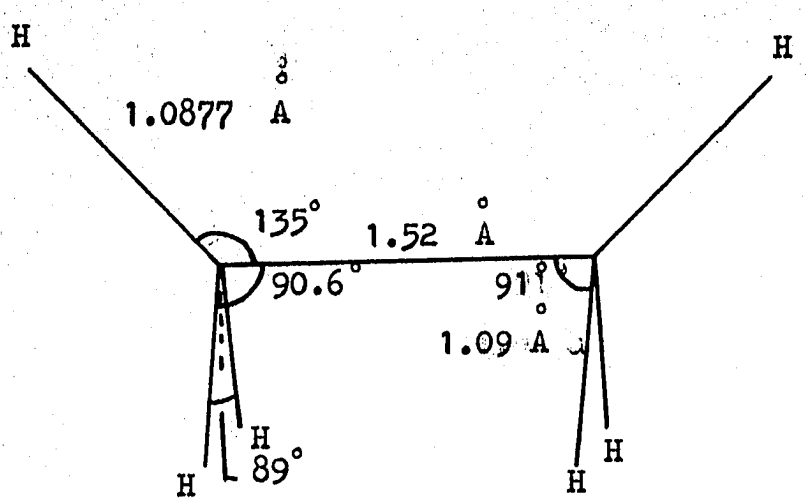
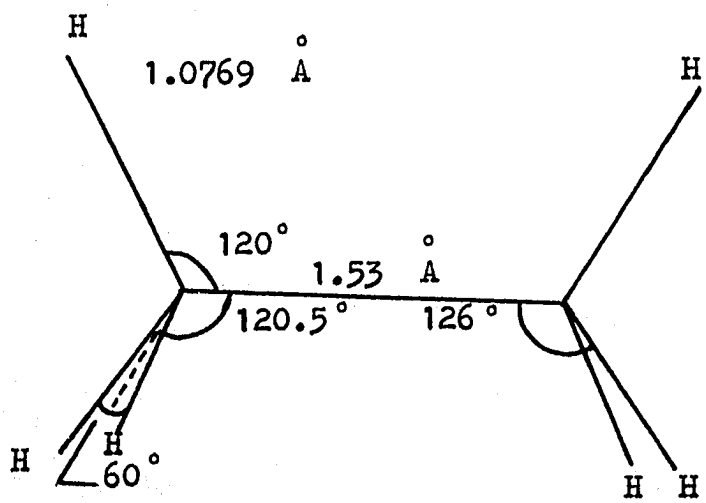
FIGURE 1



Bishomocubane-ethane



Dicyclopropyl-ethane

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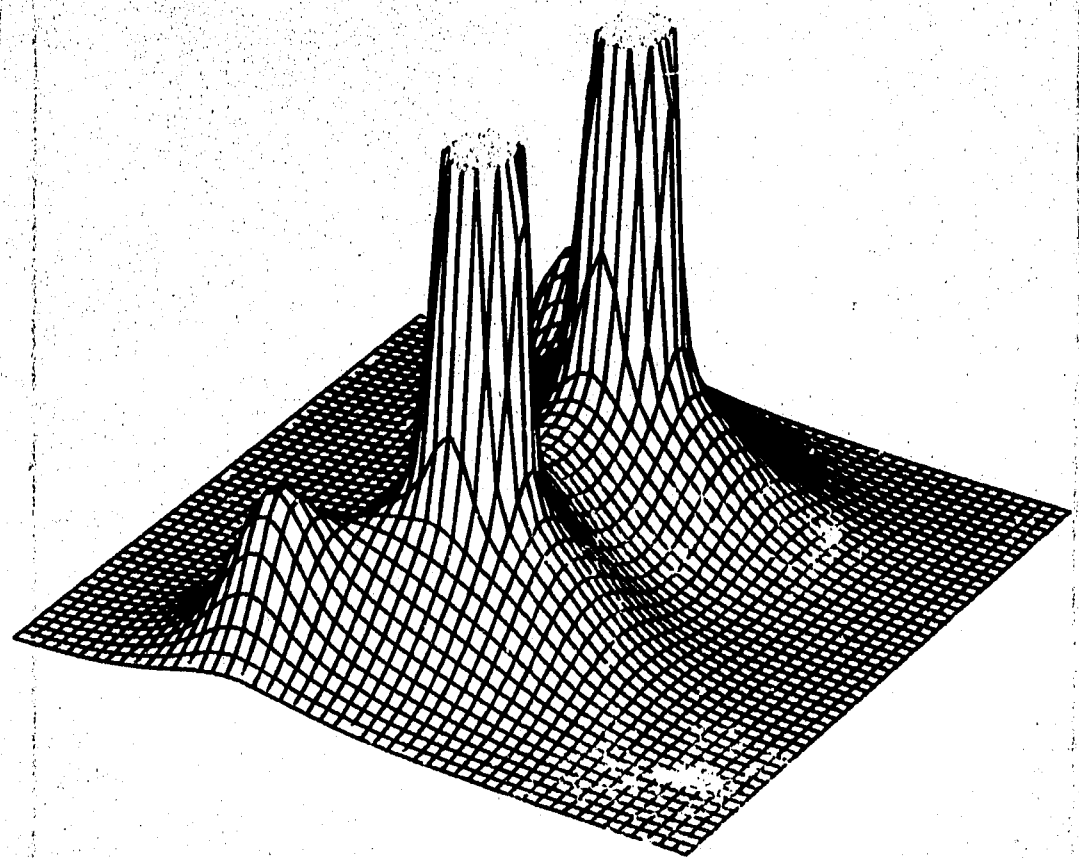
FIGURE 2



BISHOMOCUBANE, ALL ORBITALS

ELECTRON DENSITY

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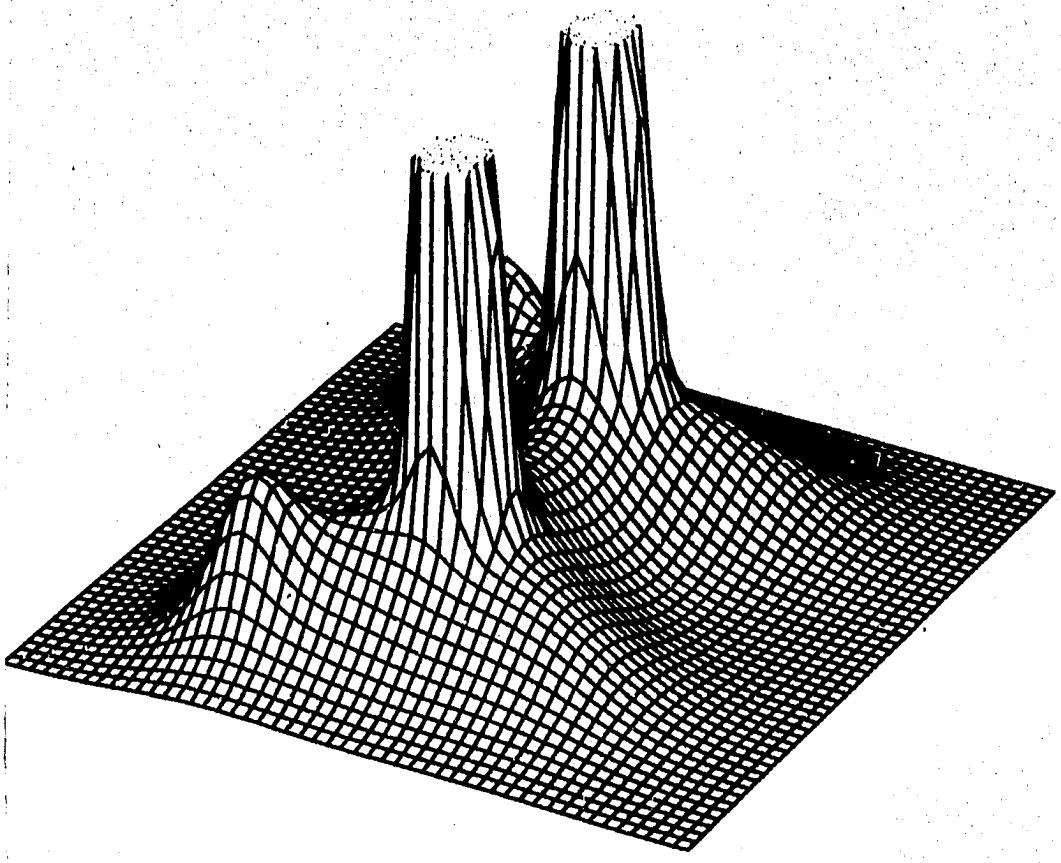
FIGURE 3



DICYCLOPROPYL, ALL ORBITALS

ELECTRON DENSITY

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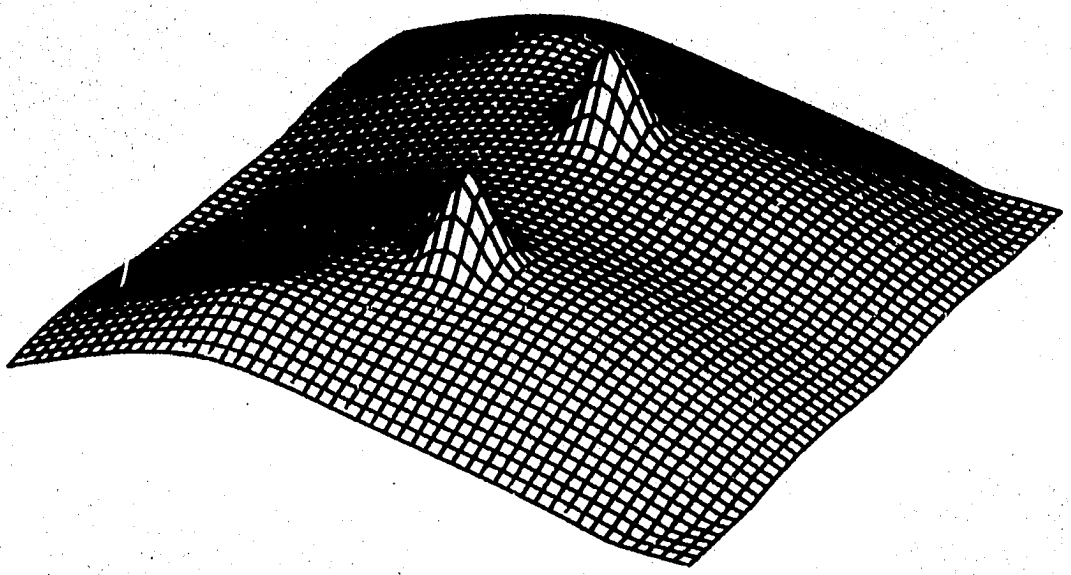
FIGURE 4



BISHOMOCUBANE, ALL ORBITALS

LOG ELECTRON DENSITY

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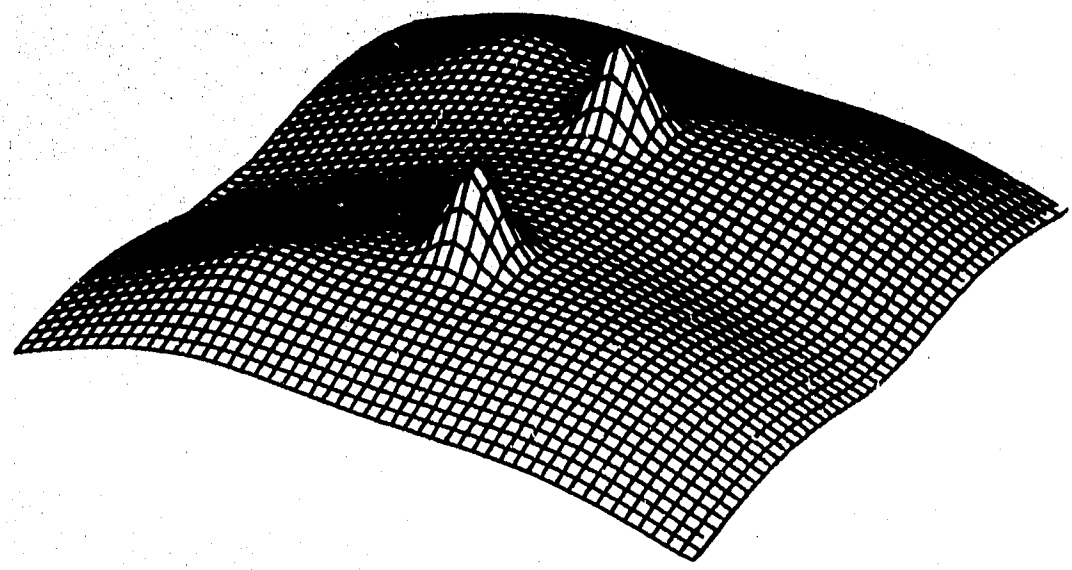
FIGURE 2



DICYCLOPROPYL, ALL ORBITALS

LOG ELECTRON DENSITY

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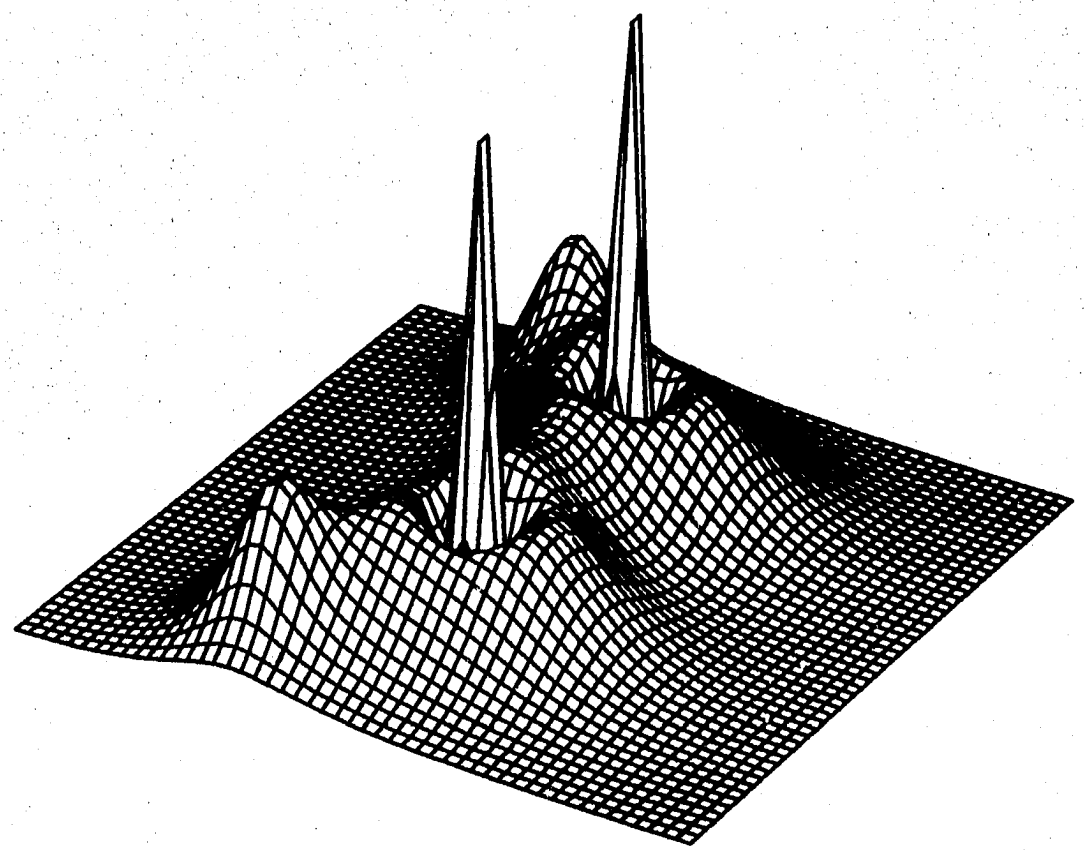
FIGURE 6



BISHOMOCUBANE, VALENCE ORBITALS

ELECTRON DENSITY

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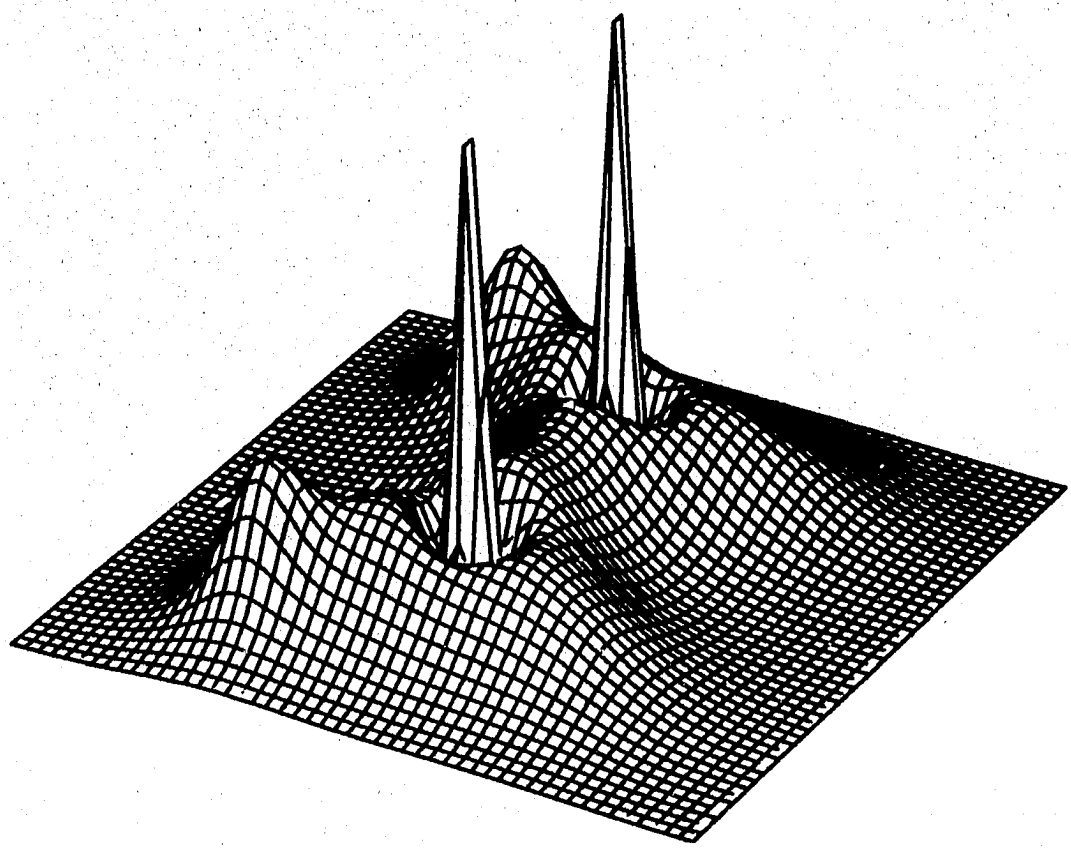
FIGURE 7



DICYCLOPROPYL. VALENCE ORBITALS

ELECTRON DENSITY

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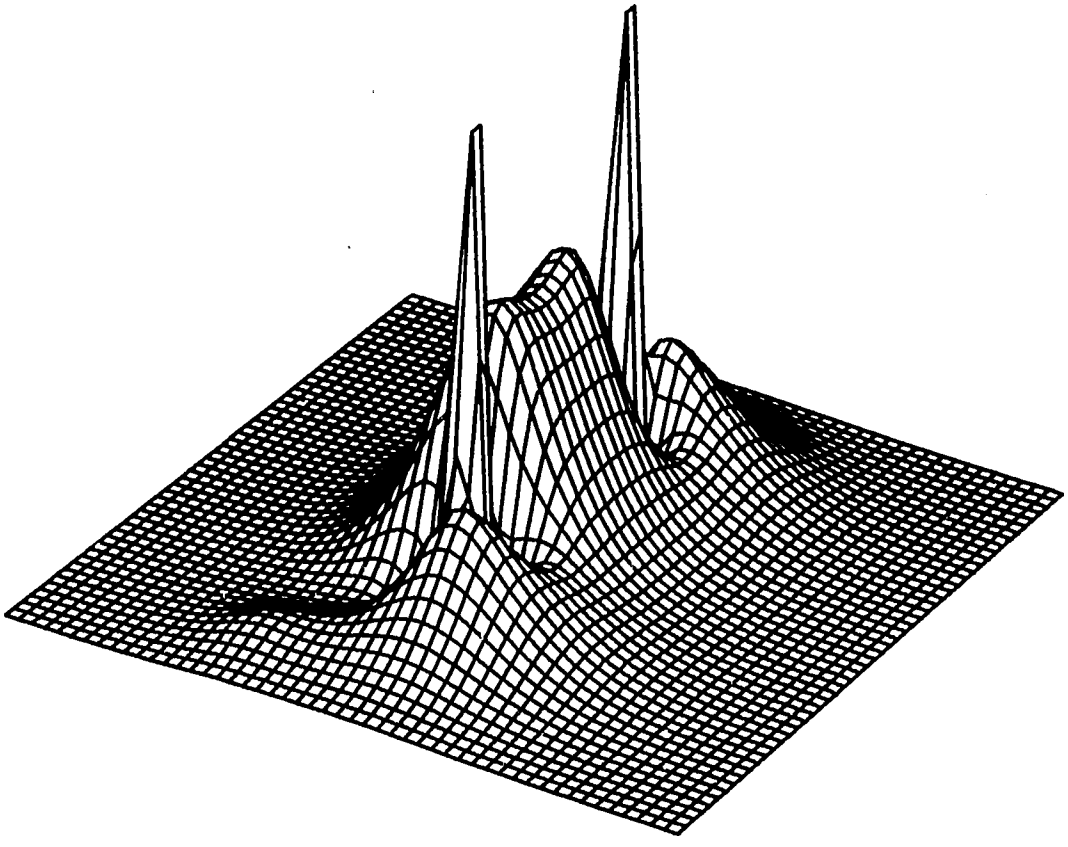
FIGURE 8



BISHOMOCUBANE, ORBITALS 2 AND 4

ELECTRON DENSITY

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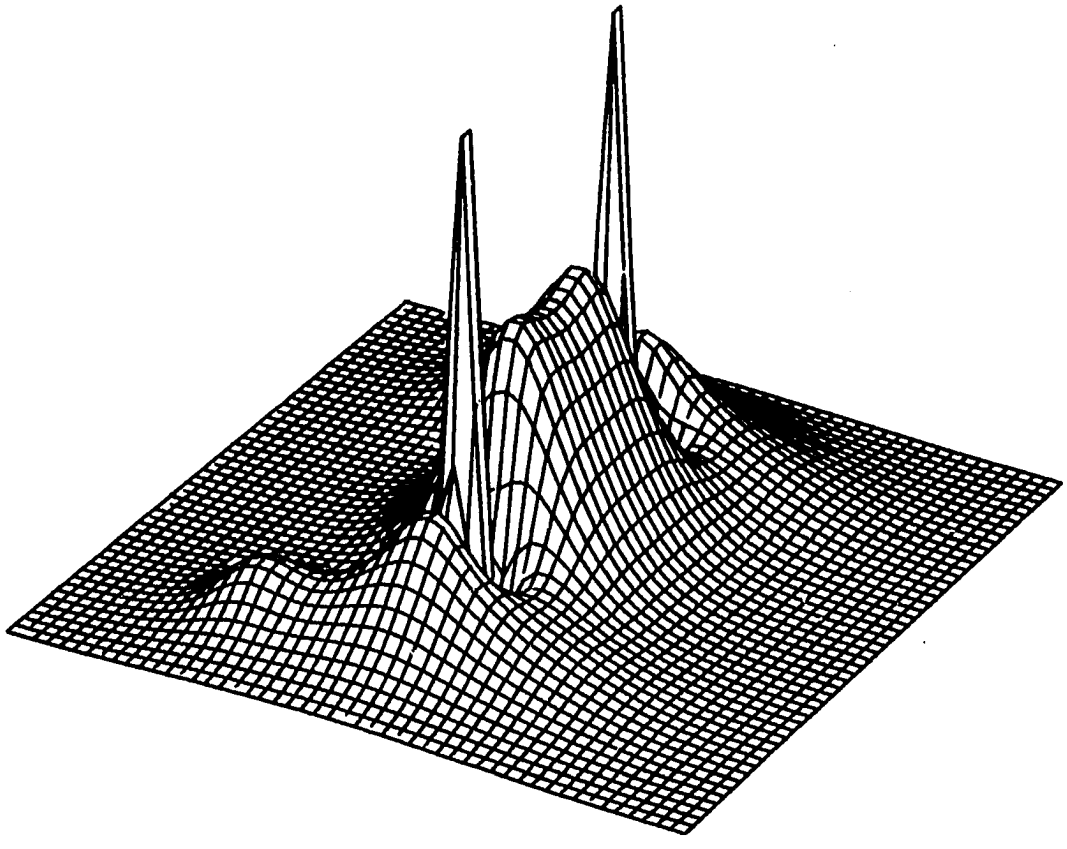
FIGURE 9



DICYCLOPROPYL, ORBITALS 2 AND 4

ELECTRON DENSITY

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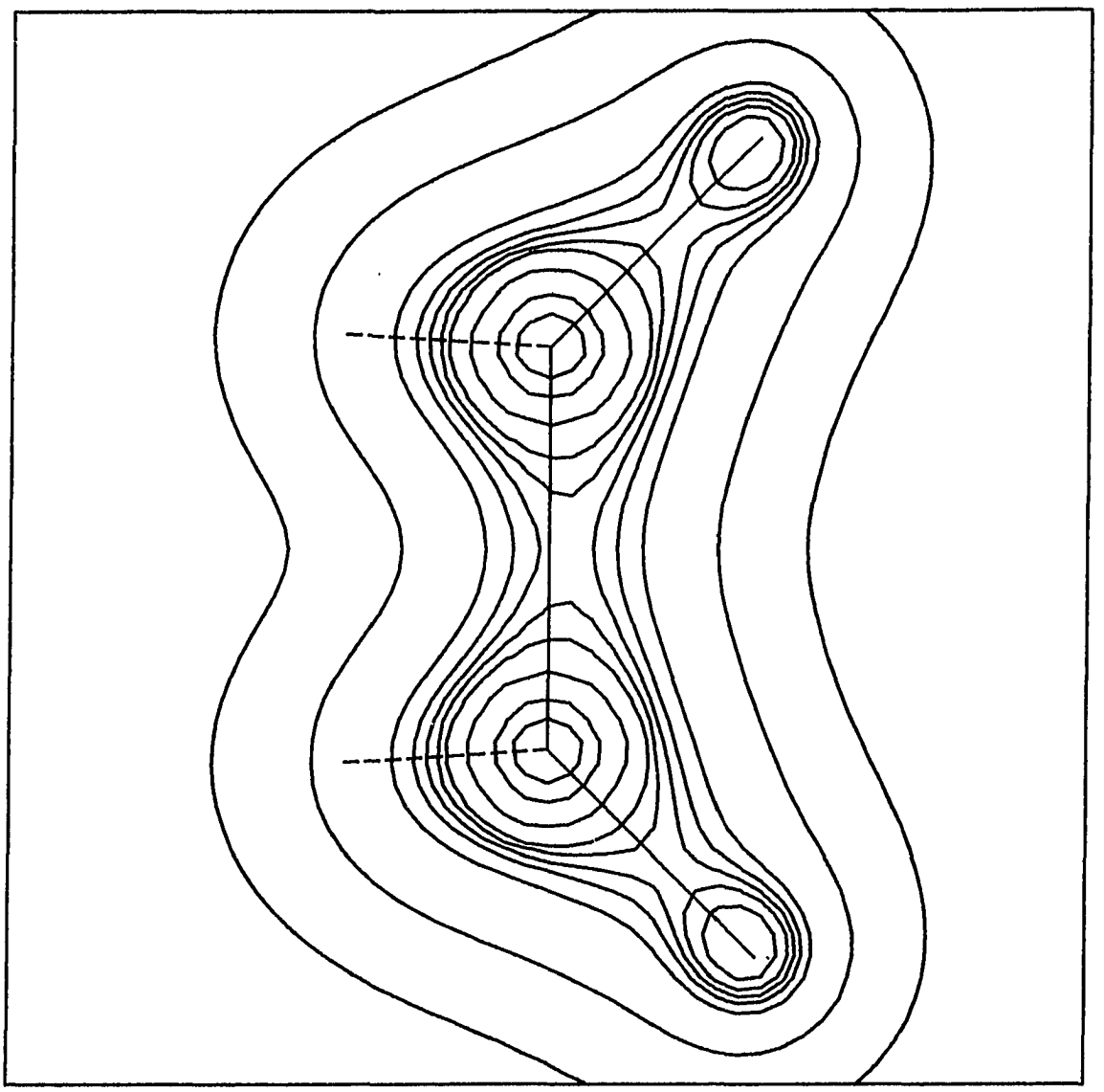
FIGURE 10



BISHOMOCUBANE, ALL ORBITALS

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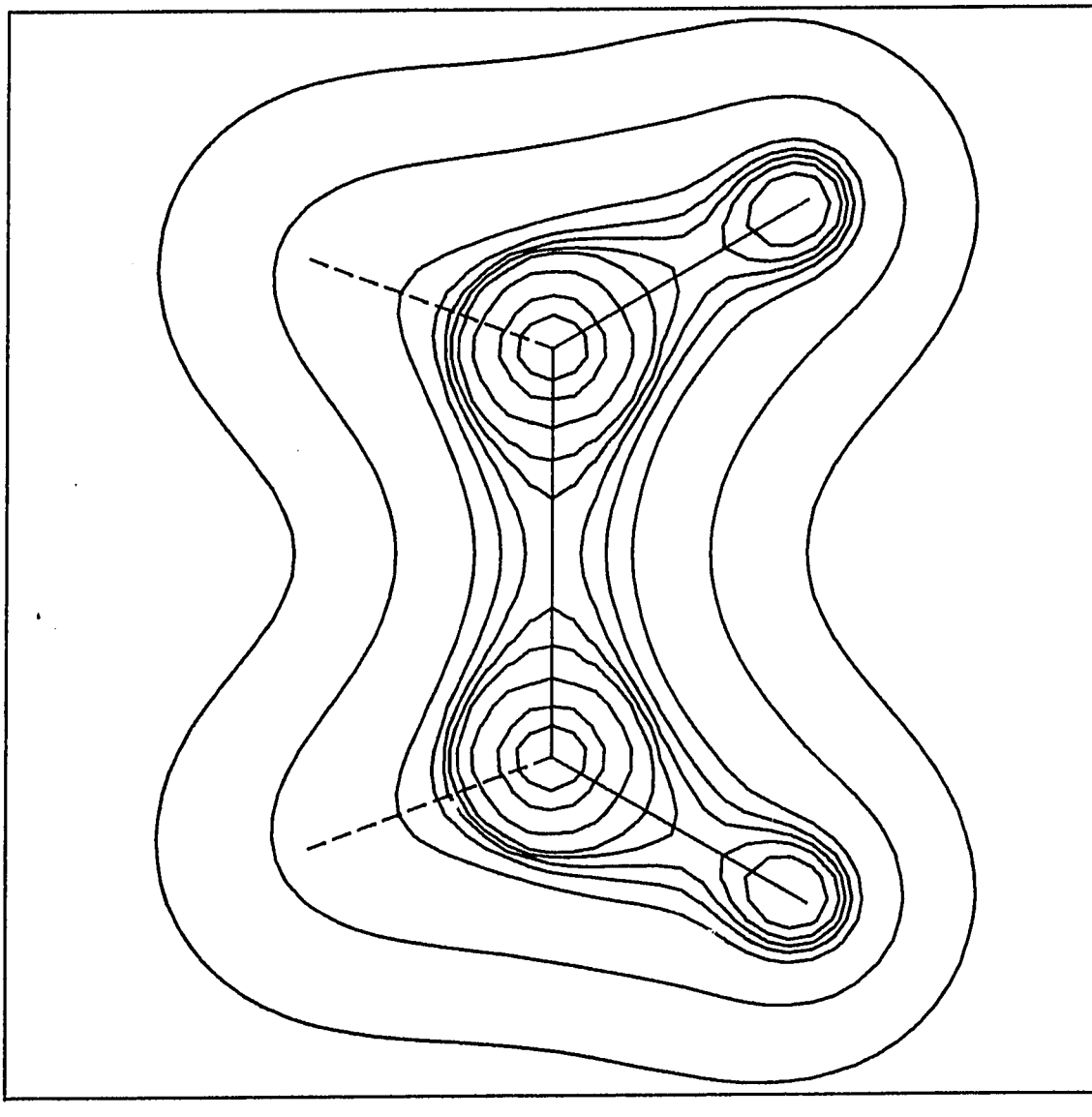
FIGURE 11



DICYCLOPROPYL, ALL ORBITALS

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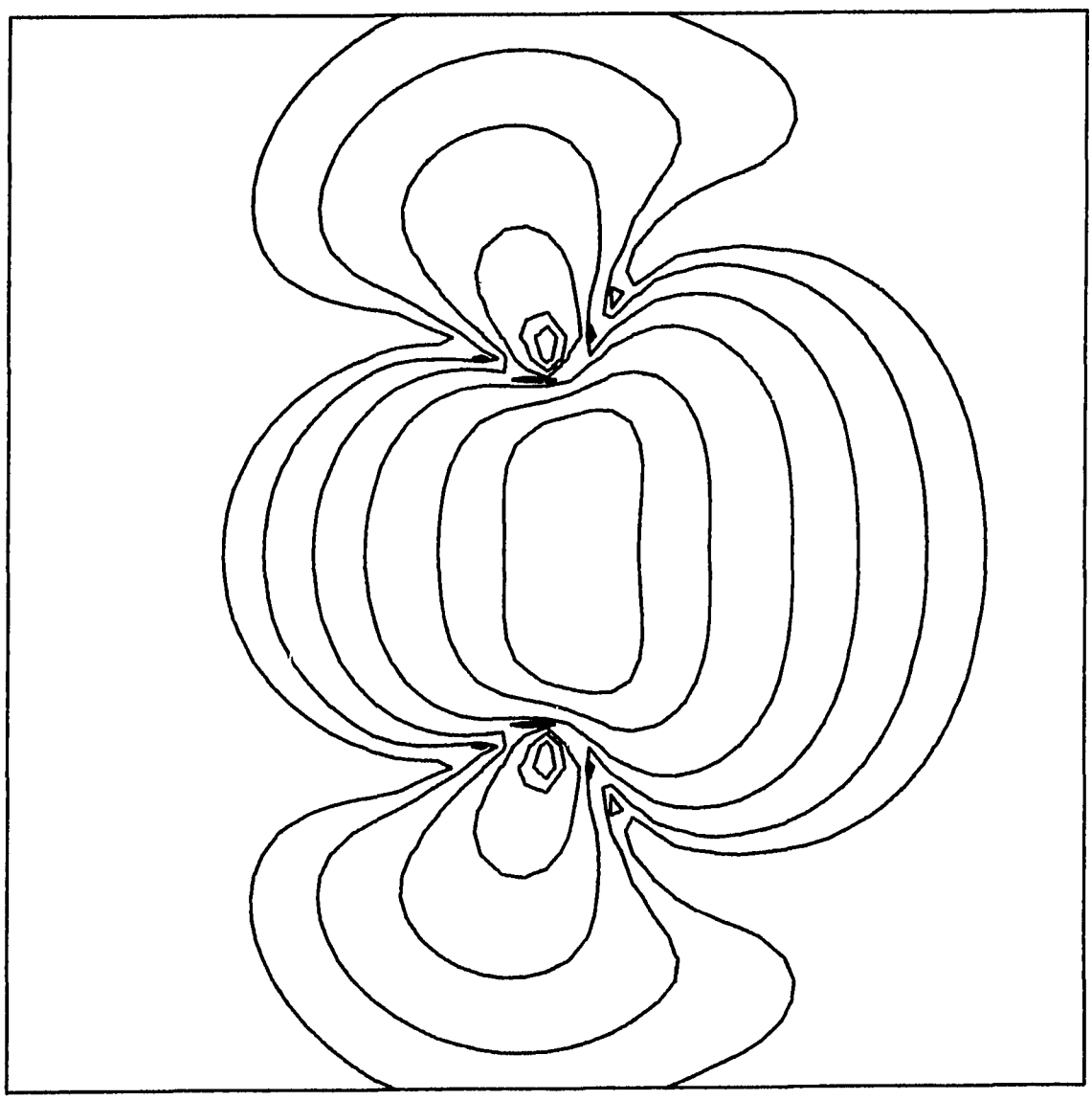
FIGURE 12



BISHOMOCUBANE, ORBITAL 2

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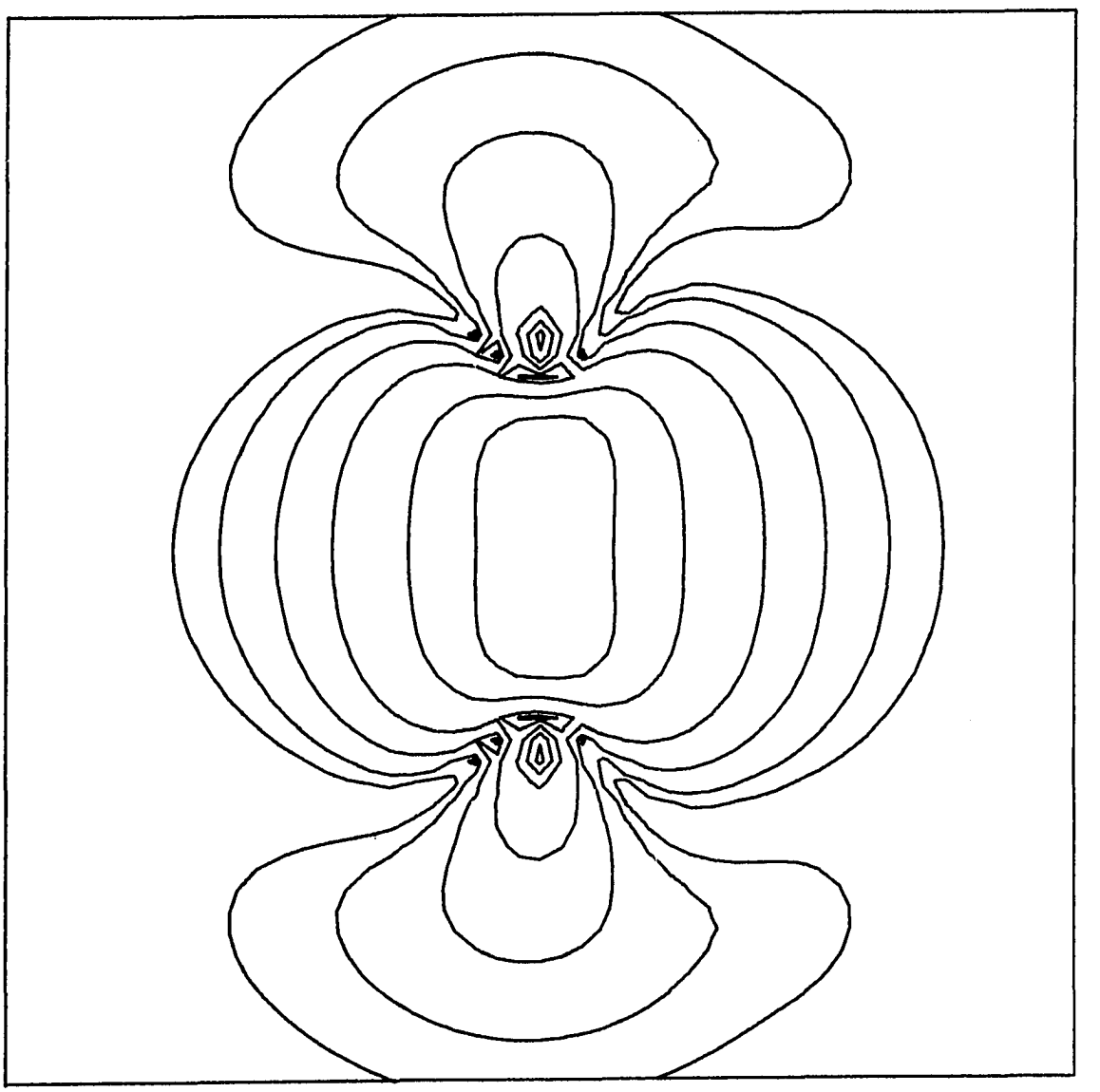
FIGURE 13



DICYCLOPROPYL, ORBITAL 2

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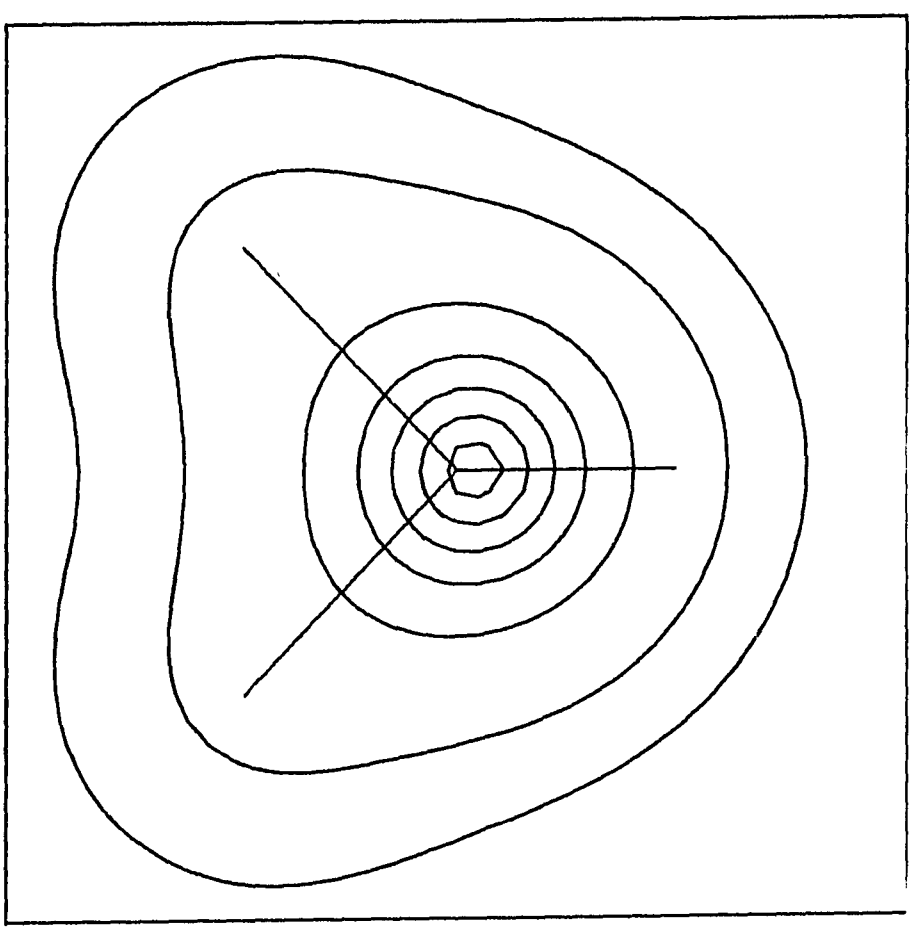
FIGURE 14



BISHOMOCUBANE, ALL ORBITALS

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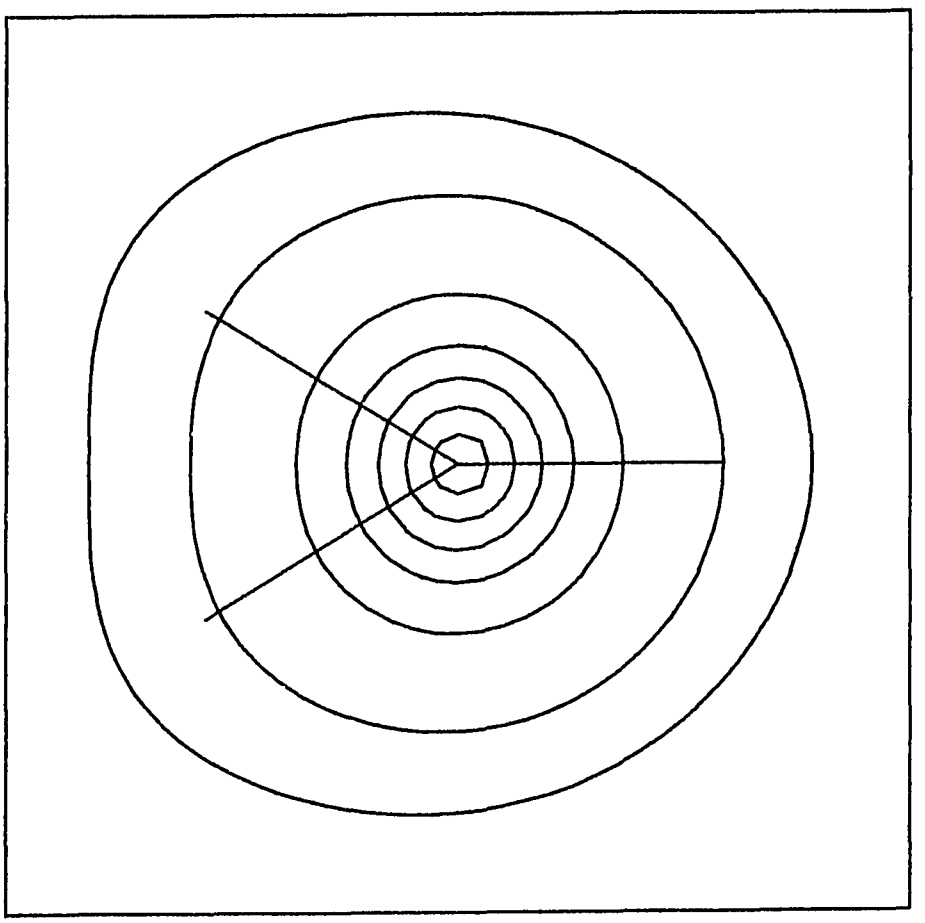
FIGURE 15



DICYCLOPROPYL, ALL ORBITALS

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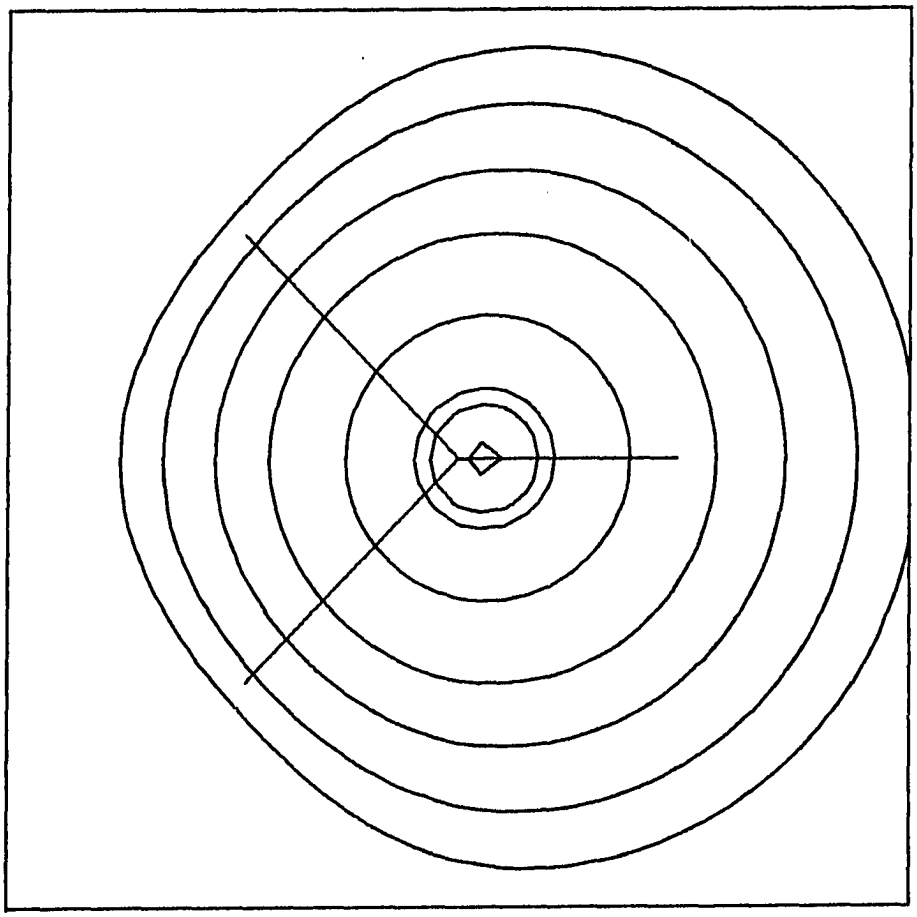
FIGURE 16



BISHOMOCUBANE, ORBITAL 2

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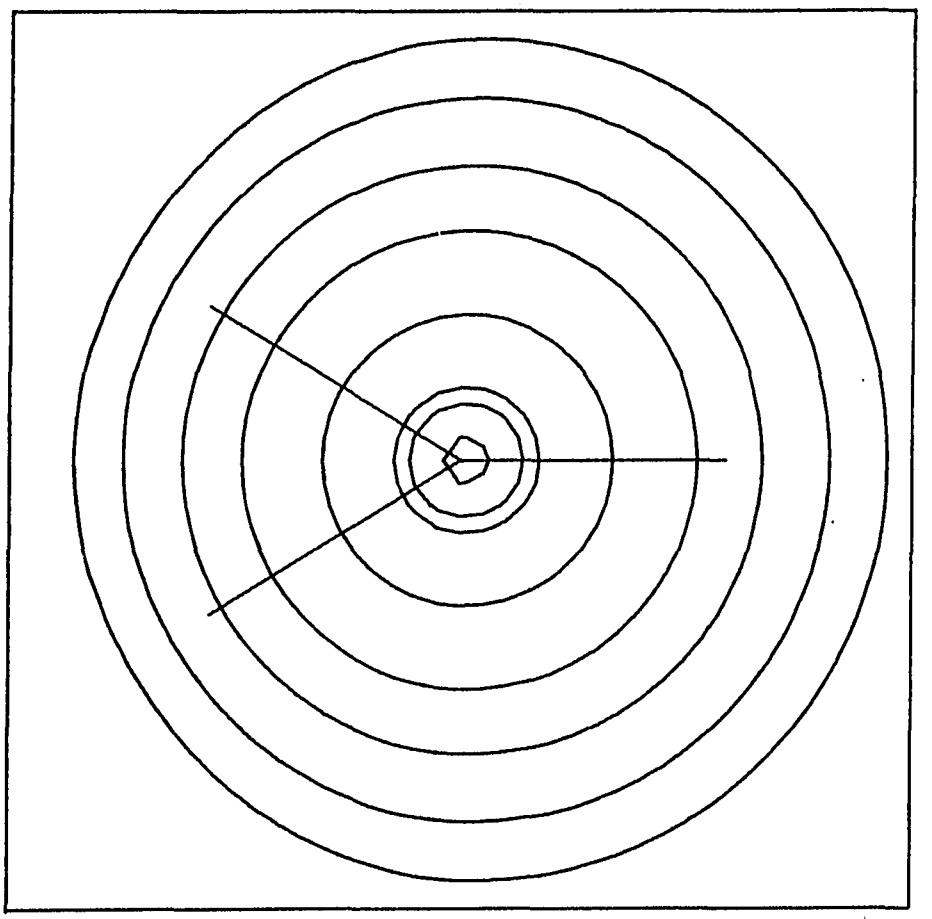
FIGURE 17



DICYCLOPROPYL, ORBITAL 2

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FIGURE LEGEND 18

Bishomocubane-ethane		Dicyclopropyl-ethane	
1.20	4.3×10^{-5}	1.20	5.52×10^{-5}
1.05	3.5×10^{-4}	1.05	1.16×10^{-4}
0.90	5.9×10^{-3}	0.90	4.41×10^{-3}
0.75	3.54×10^{-2}	0.75	7.75×10^{-3}
0.60	7.45×10^{-2}	0.60	3.71×10^{-3}
0.45	9.85×10^{-1}	0.45	4.43×10^{-3}
0.30	1.12×10^{-1}	0.30	7.19×10^{-3}
0.15	1.11×10^{-1}	0.15	10.10×10^{-3}
0.00	1.18×10^{-1}	0.00	9.00×10^{-3}

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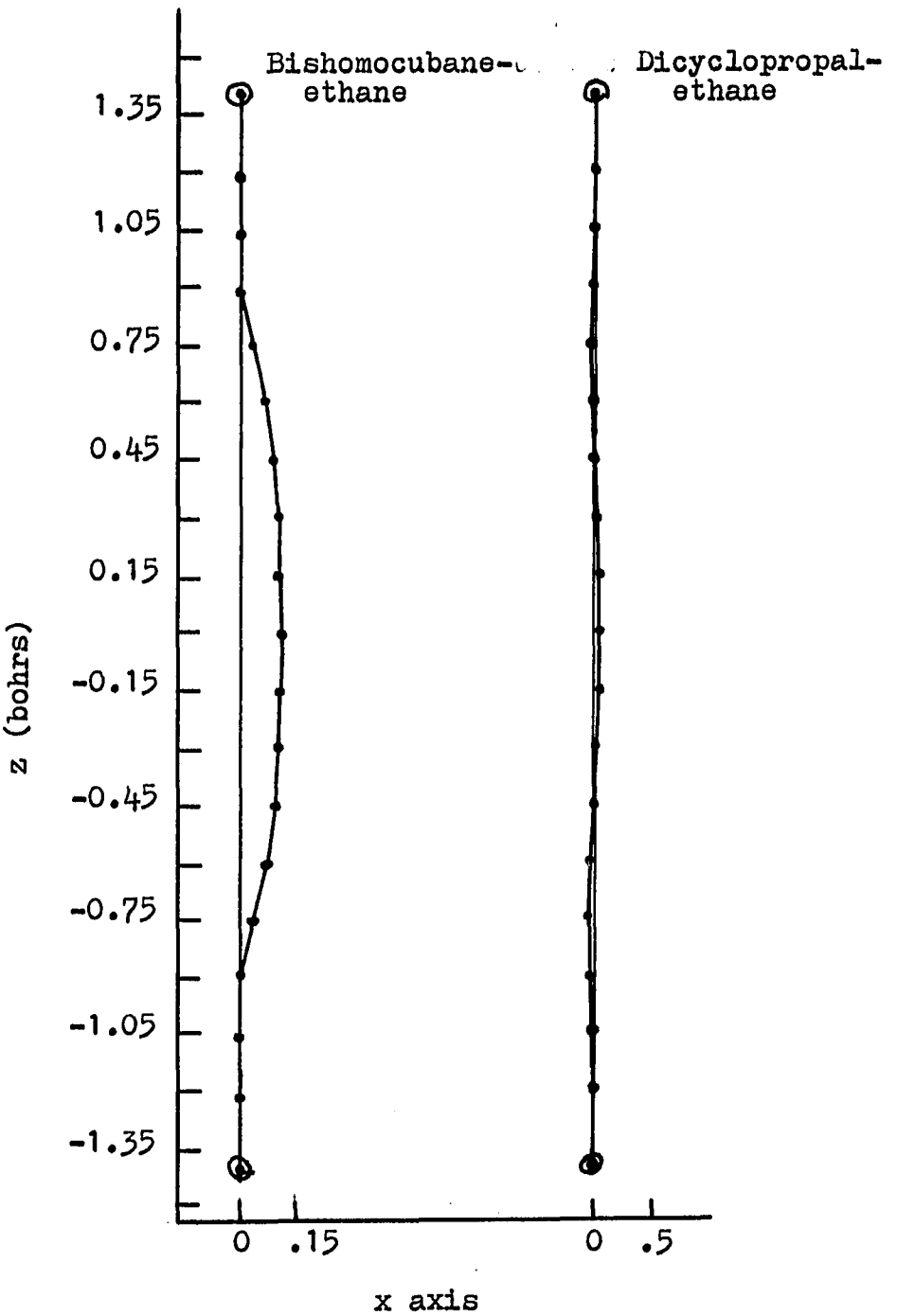
FIGURE 18



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Bibliography.

1. a. S. Winstein, Anita H. Lewin, and K. C. Pande, J. Amer. Chem. Soc., 85, 2324, (1963).

b. D. Bethell and V. Gold, in "Carbonium Ions: An Introduction", pp. 261-271, Academic Press, New York, 1967.

c. S. Winstein, in "Carbonium Ions", ed. by G. E. Olah and P. von R. Schleyer; Ch. 22. New York, Interscience, 1968.

2. a. W. G. Dauben and J. L. Chitwood, J. Amer. Chem. Soc., 90, 3835 (1968).

b. J. A. Berson, in "Molecular Rearrangements", ed. by Paul de Mayo, Interscience, New York, 1963.

3. a. H. G. Richey, Jr., in "Carbonium Ions", ed. by G.A. Olah and P. von R. Schleyer; Vol. 3, Ch. 25. New York, Interscience 1968.

4. a. Charles F. Wilcox and H. D. Banks, J. Amer. Chem. Soc., 94, 8231, 8232 (1972).

b. J. Simonsen and L. N. Owen, "The Terpenes", Vol. 2, Cambridge University Press, Cambridge, Eng., 1949.

5. a. P. E. Eaton and T. W. Cole, Jr., J. Amer. Chem. Soc., 86, 3157 (1964).

b. P. E. Eaton and T. W. Cole, ibid., 962.

6. a. H. G. Viehe, R. Merenyi, S. F. M. Oth, J. R. Saunders, and P. Valange, Angew. Chem., 76, 922 (1964).

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b. K. E. Wilzbach and Louis Kaplan, J. Amer. Chem. Soc., 87, 4004 (1965).

7. a. R. Srinivisan, J. Amer. Chem. Soc., 85, 4045 (1963).

b. I. Haller and R. Srinivisan, J. Chem. Phys., 40, 1922 (1963).

c. D. M. LeMal, F. Menger, and G. W. Clark, J. Amer. Chem. Soc., 85, 2529 (1963).

8. a. K. B. Wiberg and G. J. Burgmaier, J. Amer. Chem. Soc., 94, 7396 (1972).

b. K. B. Wiberg, J. Burgmaier, Kei-Wei Shen, J. LaPlaca, C. Hamilton, and D. Newton, J. Amer. Chem. Soc., 94, 7402 (1972).

c. D. Ginsberg, Acc. Chem. Res., 2, 121 (1969).

d. D. Ginsberg, ibid., 5, 249 (1972).

9. a. Wolfgang Lotsch and Andrew S. Kende, Angew. Chem. Intern. Ed., 10, 559 (1971).

b. Ronald E. Leone and Paul von R. Schleyer, Angew. Chem. Intern. Ed., 9, 860 (1970).

c. W. G. Dauben and Dale L. Whalen, J. Amer. Chem. Soc., 88, 4739 (1966).

10. a. S. J. Cristol and D. K. Pemelle, J. Org. Chem., 35, 2357 (1970).

b. James W. Wilt and P. Malley, J. Org. Chem., 37, 2781 (1972).

c. J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. Fort Jr., J. J. Harper, and R. D. Nichols, J. Amer. Chem. Soc., 88, 4475 (1966).

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11. I. L. Reich, A. Diaz, and S. Winstein, J. Amer. Chem. Soc., 91, 5637 (1969).

12. J. A. Berson, D. Wege, G.M. Clarke, and R. G. Bergmann, J. Amer. Chem. Soc., 91, 5594 (1969).

13. J. A. Berson, Dieter Wege, George M. Clarke, and Robert G. Bergmann, J. Amer. Chem. Soc., 91, 5601 (1969).

14. a. H. G. Richey and Niel C. Buckley, J. Amer. Chem. Soc., 85, 3057 (1963).

    b. P. R. Story and S. R. Fahrenholz, J. Amer. Chem. Soc., 86, 527 (1964).

15. George F. Cartier and Stanley C. Bunce, J. Amer. Chem. Soc., 85, 932 (1963).

16. a. S. Winstein, E. C. Friedrich, R. Baker, and Y. Liu, Tetrahedron Suppl., 8 (II), 621 (1966).

    b. S. Winstein and J. Sonnenberg, J. Amer. Chem. Soc., 83, 3235, 3244 (1961).

17. Torbjörg Norin, Tet. Letters, 1964, 37.

18. a. M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, J. Amer. Chem. Soc., 89, 1954 (1967).

    b. H. Tanida, T. Tsuji, and R. Irie, J. Amer. Chem. Soc., 89, 1953 (1967).

19. R. M. Coates and J. K. Kirkpatrick, J. Amer. Chem. Soc., 90, 4162 (1968).

20. W. G. Dauben and C. H. Schallhorn, J. Amer. Chem. Soc., 93, 2254 (1971).

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21. a. R. R. Sauers and J. A. Beisler, Tet. Letters, 1964, 2181.

b. R. R. Sauers and J. A. Beisler, J. Org. Chem., 32, 569 (1967).

22. K. B. Wiberg and George R. Wenzinger, J. Org. Chem., 30, 2278 (1965).

23. a. J. A. Berson, Dieter Wege, G. M. Clarke, and R. G. Bergmann, J. Amer. Chem. Soc., 91, 5601 (1969).

b. Idem., J. Amer. Chem. Soc., 90, 3240 (1968).

c. J. A. Berson, Robert A. Bergmann, and George M. Clarke, ibid., 3236.

24. C. H. DePuy, I. A. Ogawa, and J. C. MacDaniels, J. Amer. Chem. Soc., 82, 2397 (1960).

25. a. S. Winstein, M. Shavatsky, C. Norton, and R. B. Woodward, J. Amer. Chem. Soc., 77, 4183 (1955).

b. Idem., J. Amer. Chem. Soc., 78, 592 (1956).

c. Jean Lhomme, Arthur Diaz, and S. Winstein, J. Amer. Chem. Soc., 91, 1548 (1969).

d. J. J. Tufariello and R. J. Lorence, J. Amer. Chem. Soc., 91, 1546 (1969).

e. Leo A. Paquette and Gerald Zon, J. Amer. Chem. Soc., 94, 5096 (1973).

26. Personal communication from Cyril Tang.

27. Baren R. Ree and J. C. Martin, J. Amer. Chem. Soc., 92, 1660 (1970).

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28. a. H. Prinzbach, W. Eberbach, and G. Philipossian, Angew. Chem. Inter. Ed., 7, 887 (1968).

b. H. Prinzbach, G. Philippossian, and U. Scheidegger, Helv. Chim. Acta, 53, 857 (1960).

c. Robert S. Lin, Tet. Letters, 1969, 1409.

d. S. F. Nelson and J. P. Gillespie, Tet. Letters, 1969, 3259.

e. S. F. Nelson and J. P. Gillespie, ibid., 5059.

29. a. S. Winstein and C. Ordronneau, J. Amer. Chem. Soc., 82, 2084 (1960).

b. P. R. Story and M. Saunders, J. Amer. Chem. Soc., 84, 4876 (1962).

c. H. C. Brown and H. M. Bell, J. Amer. Chem. Soc., 85, 2324 (1963).

d. G. Wittig and J. Otten, Tet. Letters, 1963, 601.

30. a. H. Tanida and Y. Hata, J. Org. Chem., 30, 977 (1966).

b. H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, J. Org. Chem., 30, 2259 (1965).

31. G. W. Klumpp and F. Bickelhaupt, Tet. Letters, 1966, 865.

32. a. Boris Franzus and E. I. Snyder, J. Amer. Chem. Soc., 85, 3902 (1963).

b. Idem., J. Amer. Chem. Soc., 87, 3423 (1965).

33. a. S. Yankelevitch and B. Fuchs, Tet. Letters, 1967, 4945.

b. C. F. H. Allen, Chem. Rev., 62, 653 (1966).

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33. c. P. G. Gassmann, D. H. Aue, and D. S. Patton, J. Amer. Chem. Soc., 86, 4211 (1964).

34. a. P. R. Story and S. R. Fahrenholz, J. Amer. Chem. Soc., 86, 1270 (1964).

b. H. Tanida and T. Tsuji, J. Org. Chem., 29, 849 (1965).

35. a. R. W. Hoffmann and R. Hirsch, Liebigs Ann. Chem., 727, 222 (1969).

b. K. E. Pfitzner and J. G. Moffatt, J. Amer. Chem. Soc., 87, 5661 (1965).

36. Private communication from James L. Chitwood.

37. Private communication from F. Barlow and N. A. La Bel.

38. a. E. J. Corey and M. Chaykovski, J. Amer. Chem. Soc., 87, 1353 (1961).

b. R. K. Bly and R. S. Bly, J. Org. Chem., 28, 3165 (1963).

39. a. J. G. Levine, J. Amer. Chem. Soc., 80, 6150 (1958).

b. G. Wittig and M. Schlosser, Chem. Berichte, 94, 1373 (1961).

40. G. Wittig and U. Schoellkopf, Org. Syn., 40, 66 (1961).

41. H. C. Brown, "Hydorboration", W. A. Benjamin, New York, 1962.

42. H. C. Brown and Evord F. Knights, J. Amer. Chem. Soc., 91, 5281 (1968).

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43. P. R. Story and S. A. Fahrenholz, J. Amer. Chem. Soc., 87, 1623 (1965).

44. a. R. Pettit, J. Amer. Chem. Soc., 81, 1266 (1959).

b. K. G. Ihrman and T. H. Coffield, U. S. Pat. Off. #3,093,671.

c. R. L. Collins and D. Pettit, J. Amer. Chem. Soc., 85, 2332 (1963).

d. R. Pettit, G. F. Emerson, and J. E. Mahler, J. Chem. Ed., 40, 175 (1963).

e. R. Pettit, Adv. Organometall. Chem., 1, 165 (1955).

45. a. G. F. Emerson and R. Pettit, J. Org. Chem., 29, 3620 (1964).

b. L. Watts, J. D. Fitzpatrick, and R. Pettit, J. Amer. Chem. Soc., 87, 3253 (1965).

46. J. M. Landesberg and J. Siekowski, J. Amer. Chem. Soc., 93, 972 (1971).

47. a. D. F. Hunt, C. P. Lillya, and M. D. Rausch, J. Amer. Chem. Soc., 90, 2561 (1968).

b. Idem., Inorg. Chem., 8, 446 (1969).

48. a. E. J. Corey and D. Seebach, Angew. Chem. Intern. Ed., 4, 1075 (1965).

b. E. J. Corey and Dennis Crouse, J. Org. Chem., 33, 298 (1968).

c. E. J. Corey, D. Seebach, and N. R. Jones, J. Org. Chem., 33, 300 (1968).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

49. a. T. S. Piper, F. A. Cotton, and G. Wilkenson, J. Inorg. Nucl. Chem., 1, 165 (1955).

b. K. K. Joshi, P. L. Dawson, and W. H. Stubbs, J. Organometall. Chem., 1, 51 (1963).

50. a. E. J. Corey, Urs Koelikker, and Jörg Neuffer, J. Amer. Chem. Soc., 93, 1489 (1971).

See also:

b. E. J. Corey, N. A. Weinshenhr, T. K. Schaaf, and W. Huber, J. Amer. Chem. Soc., 91, 5675 (1969).

c. D. A. Evans, W. L. Scott, and L. K. Truesdale, Tet. Letters, 1972, 121.

d. Hans Krieger, Suomen Kemistilehti, B 36, 68 (1963).

51. J. Seeman, Ph.D. thesis, University of California, Berkeley, 1970.

52. a. Elmer J. Reist, Victor J. Bartuska, and Leon Goodman, J. Org. Chem., 29, 3725 (1964).

b. K. B. Wiberg and J. G. Pfeiffer, J. Amer. Chem. Soc., 92, 553 (1970).

53. a. W. Baker and N. C. Brown, J. Chem. Soc., 1948, 2303.

b. M. Bodanszky and V. du Vigneaud, Nature, 183, 1324 (1959).

c. John P. Marsh, Jr. and Leon Goodman, J. Org. Chem., 30, 2491 (1965).

54. W. H. Hartung and R. Siminoff, Org. Reactions, 7, 263 (1961).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

55. W. G. Dauben and R. L. Cargill, Tetrahedron, 15, 197 (1961).

56. B. R. Ortiz de Montellano, B. A. Loving, T. C. Shields, and P. D. Gardner, J. Amer. Chem. Soc., 89, 3365 (1967).

57. Arthur J. Hill and D. T. Keach, J. Amer. Chem. Soc., 48, 257 (1926).

58. Shamkhal Mamedov, M. A. Avanesyan, and B. M. Alieva, Obshch. Khim., 32, 3635 (1961).

59. Org. Syn., in preparation.

60. a. H. Meister, Angew. Chem., 69, 533 (1957).
b. F. A. Cotton and L. T. Reynolds, J. Amer. Chem. Soc., 80, 272 (1958).

61. D. K. Freeman, D. M. Balls, and D. G. Brown, J. Org. Chem., 33, 2211 (1968).

62. Hans Krieger, S. E. Masar, and H. Ruotsalainen, Suomen Kemistilehti, B 39, 237 (1966).

63. Private communication from James Chitwood.

64. E. J. Corey, T. Ravindranathan, and S. Terashima, J. Amer. Chem. Soc., 93, 4326 (1971).

65. C. S. Marvel, J. Dec, H. G. Cooke Jr., and J. C. Cowan, J. Amer. Chem. Soc., 62, 3495 (1940).

66. M. Seefelder, German Patent #1,167,819 (1964); Chem. Abstr., 61, 1761 (1964).

67. E. C. Taylor and A. McKillop, Acc. Chem. Res., 3, 338 (1970).

68. Org. Syn., in preparation.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

69. S. Winstein, E. Grunwald, and L. L. Ingraham, J. Amer. Chem. Soc., 70, 821 (1948).

70. a. A. Streitweiser, Jr., C. L. Wilkins, and E. Kiehlmann, J. Amer. Chem. Soc., 90, 1598 (1968).

b. Tah Mun Su, W. F. Sliwinski, and P. von R. Schleyer, J. Amer. Chem. Soc., 91, 5386 (1969).

c. R. C. Bingham, W. F. Sliwinski, and P. von R. Schleyer, J. Amer. Chem. Soc., 92, 3471 (1970).

71. S. Winstein and R. Heck, J. Amer. Chem. Soc., 78, 4801 (1956).

72. F. Daniels and R. A. Alberts, "Physical Chemistry", 3rd ed., Wiley and Sons, New York (1966).

73. Gramstad and Hazeldine, J. Chem. Soc., 1957, 4096.

74. L. Fieser and M. Fieser, "Reagents for Organic Synthesis", vol. 1, p. 1079; John Wiley and Sons, New York, 1967.

75. W. S. Trahanovsky and Michael P. Doyle, Tet. Letters, 1968, 2155.

76. a. A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, Tet. Letters, 1964, 233.

b. J. W. Feeney and L. H. Sutcliffe, in "High Resolution NMR Spectroscopy", vol. 1, p. 174; Pergamon Press, New York (1965).

77. a. J. R. Campbell, Aldrichimica Acta, 4, 55 (1971).

b. R. von Ammon and R. D. Fischer, Angew. Chem. Intern. Ed., 11, 675 (1972).

78. Personal communication from Cyril Tang.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

79. E. I. Snyder and Boris Franzus, J. Amer. Chem. Soc., 86, 1166 (1964).

80. P. R. Story, J. Org. Chem., 26, 287 (1961).

Bibliography, Section II.

81. W. G. Dauben, C. H. Schallhorn, and Dale L. Whalen, J. Amer. Chem. Soc., 93, 1446 (1971).

82. W. G. Dauben and A. J. Kielbania, J. Amer. Chem. Soc., 93, 7345 (1971).

83. L. A. Paquette, Acc. Chem. Res., 4, 280 (1971).

84. L. Cassar, P. E. Eaton, and J. Halpern, J. Amer. Chem. Soc., 92, 6366 (1970).

85. a. L. A. Paquette and J. C. Stowell, J. Amer. Chem. 92, 2584 (1970).

b. Idem., J. Amer. Chem. Soc., 93, 2459 (1971).

86. L. Cassar, P. E. Eaton, and J. Halpern, J. Amer. Chem. Soc., 92, 3515 (1970).

87. a. F. A. Cotton, Inorg. Chem., 3, 702 (1964).

b. R. P. Stewart and P. M. Treichel, Inorg. Chem., 7, 1942 (1968).

c. C. A. Tolman, J. Amer. Chem. Soc., 92, 2953 (1970).

d. G. Henrici-Olivé and S. Olivé, Angew. Chem. Intern. Ed., 10, 105 (1970).

88. H. W. Quinn and J. H. Tsai, Adv. Inorg. Chem. Radiochem., 12, 217 (1969).

89. P. G. Gassmann and T. J. Atkins, J. Amer. Chem. Soc., 93, 4597 (1971).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

90. M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, J. Amer. Chem. Soc., 93, 4611 (1971).

91. Personal communication from Peter Owens.

92. a. R. E. Christofferson, J. Amer. Chem. Soc., 93, 4104 (1971).

b. R. E. Christofferson, J. Chem. Phys., 54, 239 (1971).

c. R. E. Christofferson, Chem. Phys. Letters, 3, 419 (1969).

93. H. Marsmann, J. B. Robert, and J. R. Van Wazar, Tetrahedron, 27, 4377 (1971).

94. Enrico Clementi, "Special IBM Technical Report: IBMOL", IBM Research Laboratories, San Jose, Cal. (1966).

95. Peter Owens, Ph.D. Thesis, University of California, Berkeley, 1971.

96. a. W. G. Quarles, Ph.D. Thesis, University of California, Berkeley.

b. LRL Report UCRL 19906.

97. a. C. H. Schallhorn, Ph.D. Thesis, University of California, Berkeley, 1969.

b. W. G. Dauben, M.A. Buzzolini, C. H. Schallhorn, and D. L. Whalen, Tet. Letters, 1970, 787.

98. S. F. Boys, Quantum Theory At., Mol., and Solid State, 1966, 253.

99. Obtained courtesy of Dr. A. Streitweiser

100. R. M. Pitzer and W. N. Lipscomb, J. Chem. Phys., 39, 1995 (1963).

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