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THE AROMATIZATION OF DEWAR BENZENE:
A MECHANISTIC STUDY.

Harvard University, Ph.D., 1971
Chemistry, organic

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The Aromatization of Dewar Benzene
A Mechanistic Study

A thesis presented

by

David George Shaw

to

The Department of Chemistry

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

in the subject of

Chemistry

Harvard University

Cambridge, Massachusetts

May 1971

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SUMMARY

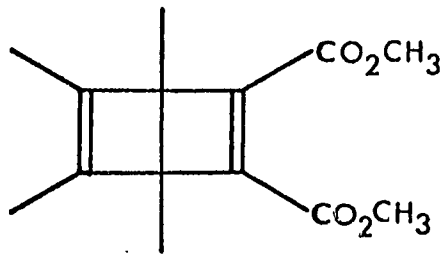
The Aromatization of Dewar Benzene

A Mechanistic Study

Professor R. B. Woodward — Harvard University

David G. Shaw — April 1971

The mechanism of the rearrangement of Dewar benzene to benzene has been studied. In the cases of 2,3-dicarbomethoxy-1,4,5,6-tetramethyl(Dewar benzene) (1) and 2,3-di-2(2-hydroxypropyl)-1,4,5,6-tetramethyl(Dewar benzene) (2) experimental data has been obtained that is consistent with the intermediacy of a diradical.



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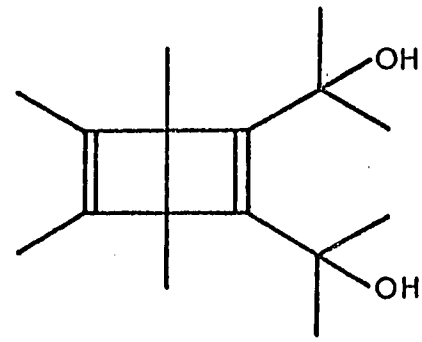

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to two very special chemists:

my father, Ralph J. Shaw

my wife, Diane L. Shaw

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ACKNOWLEDGEMENT

To study under the guidance of Professor R. B. Woodward is an inspiring, exciting and humbling experience. He will remain for me a model of intelligence, industry, patience and creative thought. Numerous other persons have helped me over the intellectual, experimental and bureaucratic hurdles that I have encountered at Harvard. I particularly want to thank Pat Confalone, Margret Currier, Gerald Dudek, Dolores Dyer, Hamper Janjigian, Robert Sitrin and most of all my wife Diane for aid, encouragement and companionship.

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CHAPTER 1
INTRODUCTION

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As the year 1965 began few organic chemists suspected that their field was at the threshold of an advance unrivaled since the development of conformational theory more than a decade earlier. Yet, in early 1965 Woodward and Hoffmann made such an advance with their recognition of the role of orbital symmetries in the determination of reaction courses [1]. Their discovery of the importance of the conservation of orbital symmetry has answered many questions, some long and carefully studied, others unasked. The principles that underlie this concept are so basic and their application so straightforward that the results now appear obvious. However, the reading of a report [2] of other workers that approached but did not master this idea testifies to the fact that it is easier to follow than to lead in thought.

Orbital symmetry considerations, as codified and extended [3,4], can be applied to every chemical reaction. "Since every elementary step in any chemical reaction is a concerted process, correlative ideas must be applicable to all reactions" [3]. Our understanding of a constantly growing list of reactions types including thermal reorganizations, cycloadditions, ring closures, solvolyses, photolyses,

---

1. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395, 2511, (1965); R. Hoffmann and R. B. Woodward, ibid., 87, 2046, 4388, 4389, (1965).
2. L. J. Oosterhoff quoted in E. Havinga and J. L. M. A. Schlatmann, Tetrahedron, 16, 151, (1961).
3. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970.
4. R. Hoffmann and R. B. Woodward, Science, 167, 825, (1970); R. Hoffmann and R. B. Woodward, Accts. of Chem. Res., 1, 17, (1968); R. Hoffmann, ibid., 4, 1, (1971); R. B. Woodward, Aromaticity, Special Publication No. 21, The Chemical Society, London, 1967, p 217; H. C. Longuet-Higgins and E. W. Abrahamson, J. Am. Chem. Soc., 87, 2045, (1965).

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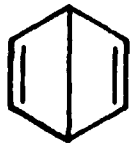
migrations, group eliminations, oxidations, reductions and extrusions has been increased by the application of this new touchstone of mechanistic chemistry.

So regiospecific and stereospecific are the predictive powers of this theory that a host of experimental organic chemists has set to work testing its predictions. To date no bona fide counter-example has been adduced. Numerous reviews of the progress in this field have already appeared[3,4,5]. So extensive has been the work in this area in the last six years and so general has been the cognizance of it in the chemical community that it is no longer necessary or even appropriate to preface an application of the principle of the conservation of orbital symmetry with a theoretical discussion. Rather we shall now proceed to describe a puzzle in chemical fact. Then we shall apply orbital symmetry considerations to that problem in order to make some predictions. Finally, we shall describe a series of experiments designed to test those predictions.

In 1866 Sir James Dewar proposed the structure (1) which now bears his name as one of several possible formulae for benzene[6].



1

Dewar represented all of his benzene formulae as planar; it is not clear that even the possibility of a non-planar representation had

---

5. among others: B. G. Odell, "Annual Reports, Section B", Vol. 66, The Chemical Society, London, 1969, p 143; J. J. Vollmer and K. L. Servis, J. Chem. Ed., 45, 214, (1968); H. Katz, ibid., 48, 84, (1971); S. I. Miller in V. Gold, "Advances in Physical Organic Chemistry", Vol. 6, Academic Press, New York, 1968, p 185; G. B. Gill, Quart. Rev., 22, 338, (1968).

6. J. Dewar, Proc. Roy. Soc. (Edinburg), 6, 84, (Nov. 1866 to May 1869).

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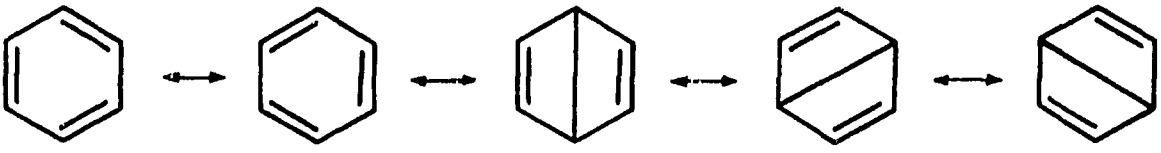
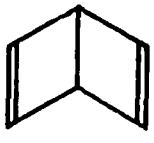
occurred to him. In those early years of chemistry, formulae[7] were not meant to be accurate three dimensional maps of molecules, but rather were intended to indicate functional behavior[8]. Dewar's representation of benzene lost favor when it was established that all six carbon atoms of benzene are equivalent[8,9].

The rise of valence bond theory resurrected Dewar benzene as a planar "resonance structure" which, along with the two Kekulé forms, contributed to the structure of benzene[10].



Recently the term Dewar benzene has acquired new meaning as a trivial name for bicyclo(2,2,0)hexa-2,5-diene (2), a non-planar compound which has an existence distinct from that of benzene.



2

To avoid the impression that (2) is a resonance form of benzene, the name "tectadiene" (Latin, tectum-roof) has been proposed[11] to replace "Dewar benzene" in its most recent usage. However, since this suggestion appears to have been universally ignored, we shall

---

7. Dewar consistently used "formula" rather than "structure".

8. V. M. Schelar in "Kekulé Centennial" Advances in Chemistry No. 61, American Chemical Society, Washington D.C., 1966, pp 169-171.

9. however, also see: C. K. Ingold, J. Chem. Soc., 121, 1133, (1922).

10. C. A. Coulson, "Valence", Second Edition, Oxford University Press, London, 1961, pp 242-245.

11. W. Schäfer and H. Hellman, Angew. Chem. Internat. Edit., 6, 518, (1967).

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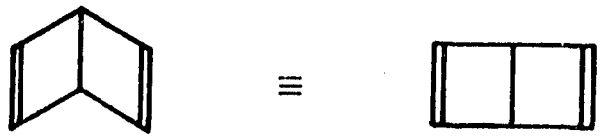
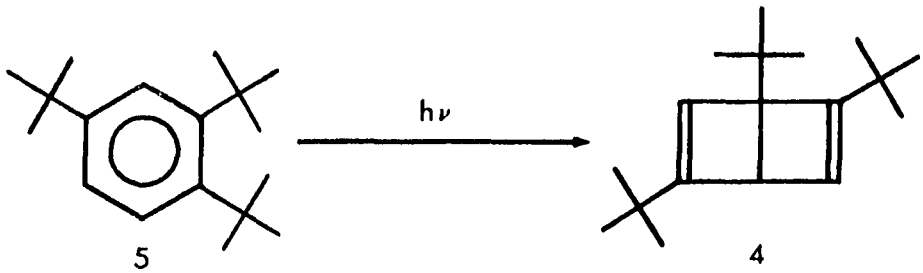
use "Dewar benzene" to denominate (2). Frequently in this dissertation we shall use the planar notation (3) to represent the nonplanar (2).



2 ≡ 3

Van Tamelen and Pappas were first to prepare a derivative of Dewar benzene. In 1962 they reported[12] the preparation of 1,2,5-tri-t-butyl(Dewar benzene) (4) by the photolysis of 1,2,4-tri-t-butylbenzene (5). A chief consideration of these workers in planning



5 4

their synthesis of a Dewar benzene was avoiding a situation in which the bicyclic compound would be converted to its aromatic valence bond isomer, a reaction which is certainly thermodynamically favored and for which they saw no obvious kinetic barrier. They reasoned that the aromatization ((4)→(5)) compared to a less encumbered analog, would be less attractive energetically because of attendant compression of the bulky vicinal groups. The moderate stability of (4) encouraged van Tamelen and Pappas to undertake the synthesis of the parent hydrocarbon (3). It must have been a pleasant if

3

12. E. E. van Tamelen and S. P. Pappas, J. Am. Chem. Soc., 84, 3789, (1962).

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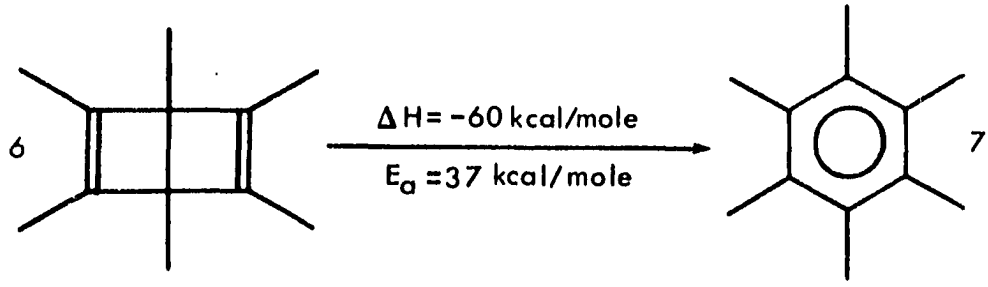
unexplained surprise to find that even (3) possesses a half life of two days at room temperature [13].

Soon several groups were preparing and studying various Dewar benzene derivatives. Table I shows those Dewar benzenes that had been prepared by the end of 1967. In particular, the enthalpy of rearrangement for the conversion of hexamethyl (Dewar benzene) (6) to hexamethylbenzene (7) was twice measured. The values determined were -62.4 ± 0.4 kcal/mole [20] and -59.5 kcal/mole [23]. Further study showed that if this rearrangement is induced thermally, the energy of activation is 37.2 kcal/mole [23].



Even though (6) contains about 60 kcal/mole of strain energy relative to (7), it is necessary to add nearly 40 kcal/mole more - to make the energy content of (6) roughly 100 kcal/mole greater than (7) - before rearrangement occurs. That orbital symmetries impose this considerable reaction barrier was noted by van Tamelen.

> What property, then, is responsible for the stability of Dewar benzene? The answer must be given in terms of bond rehybridization, including the stereo-electronic factors at work in the thermally induced ring opening of a cyclobutene to 1,3-diene. . . .
>
> In the case of cis-bicyclo(2,2,0)hexa-2,5-diene, this preferred (conrotative) mode of steroisomerization cannot operate, since an extraordinarily strained cis-cis-trans-cyclohexa-1,3,5-triene would result. In the stereoelectronically less preferred (disrotative) course of ring opening, molecular orbital symmetry preference defers to stability of the 6 π electron product,

---

13. E. E. van Tamelen and S. P. Pappas, ibid., 85, 3297, (1963); E. E. van Tamelen and D. Carty, ibid., 89, 3922, (1967).

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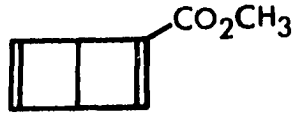
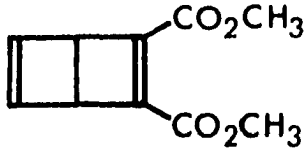
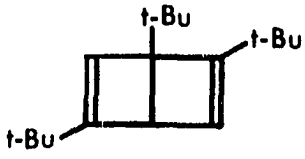
TABLE I

Dewar benzenes prepared before 1968

Compound	$T_{\frac{1}{2}}$ aromatization	Reference
	~44 hr/rt	13
	<0.5 hr/90°	14
	<1 hr/90°	15
	<0.5 hr/90°	14
	<0.25 hr/200°	12

14. L. Watts, J. D. Fitzpatrick and R. Pettit, ibid., 87, 3253, (1965).
15. G. D. Burt and R. Pettit, Chem. Commun., 1965, 517.

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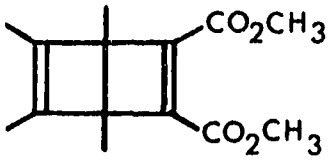
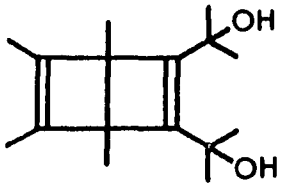
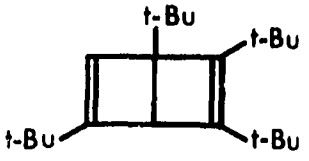
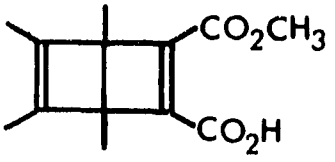
Compound	T_1 aromatization	Reference
	2 hr/98°	16
	1 hr/200°	18,19
	<0.5 hr/200°	17
	----------	16

16. R. Criegee and F. Zanker, Chem. Ber., 98, 3838, (1965).
17. E. M. Arnett and J. M. Bollinger, Tet. Letters, 1964, 3803.
18. R. Criegee and R. Askani, Angew. Chem. Internat. Edit., 5, 519, (1966).
19. R. Criegee, R. Askani and H. Grüner, Chem. Ber., 100, 3916, (1967).

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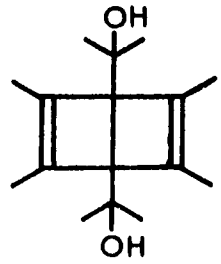
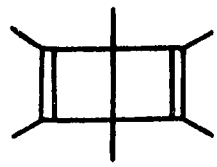
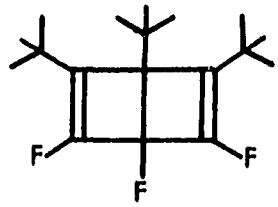
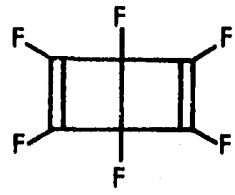
Compound	Thermal Isomerization	Reference
	----------	18
	105 hr/120° 5.5 hr/140° 2.1 hr/150°	11,20
	brief /100°	21
	<4 hr/80°	22

20. W. Schäffer, Angew. Chem. Internat. Edit., 5, 669, (1966).

21. H. G. Viehe, R. Merenyi, J. F. M. Oth, J. R. Senders and P. Valange, ibid., 3, 755, (1964).

22. G. Camaggi, F. Gozzo and G. Cevidalli, Chem. Commun., 1966, 313.

23. J. F. M. Oth, Rec. Trav. Chim., 87, 1185, (1968).

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but the transition state energy is raised and Dewar benzene enjoys comparative stabilization. [24]

This analysis, though not to be slighted in view of its early presentation, contains a flaw. It treats the correlation of Dewar benzene with benzene as if it were the correlation of a derivative of cyclobutene. This approach is correct in the correlation of bicyclo(2,2,0)hexene-2 with 1,3-cyclohexadiene.

In this latter case the symmetries of the orbitals of the saturated carbon atoms 5 and 6 do not change during the isomerization. However, in the correlation of Dewar benzene with benzene the apparent constancy of the symmetries of the orbitals of carbon atoms 5 and 6 is an artifact of the use of one Kekulé structure to represent benzene.

Certainly the pi molecular orbitals of benzene are not those of ethylene plus 1,3-butadiene. And it is by no means immediately obvious that these two sets of orbitals have the same symmetry properties. A complete analysis of this reaction must include the six pi orbitals of benzene and the related sigma and pi orbitals of Dewar benzene. These are shown in Figure 1. We have depicted the C_1 - C_4 sigma bond of Dewar benzene as being of higher energy than the pi bonds. While we suspect that this may very well be the fact of the matter, that it is so is not necessary to this analysis. It

24. E. E. van Tamelen, Angew. Chem. Internat. Edit., 4, 741, (1965).

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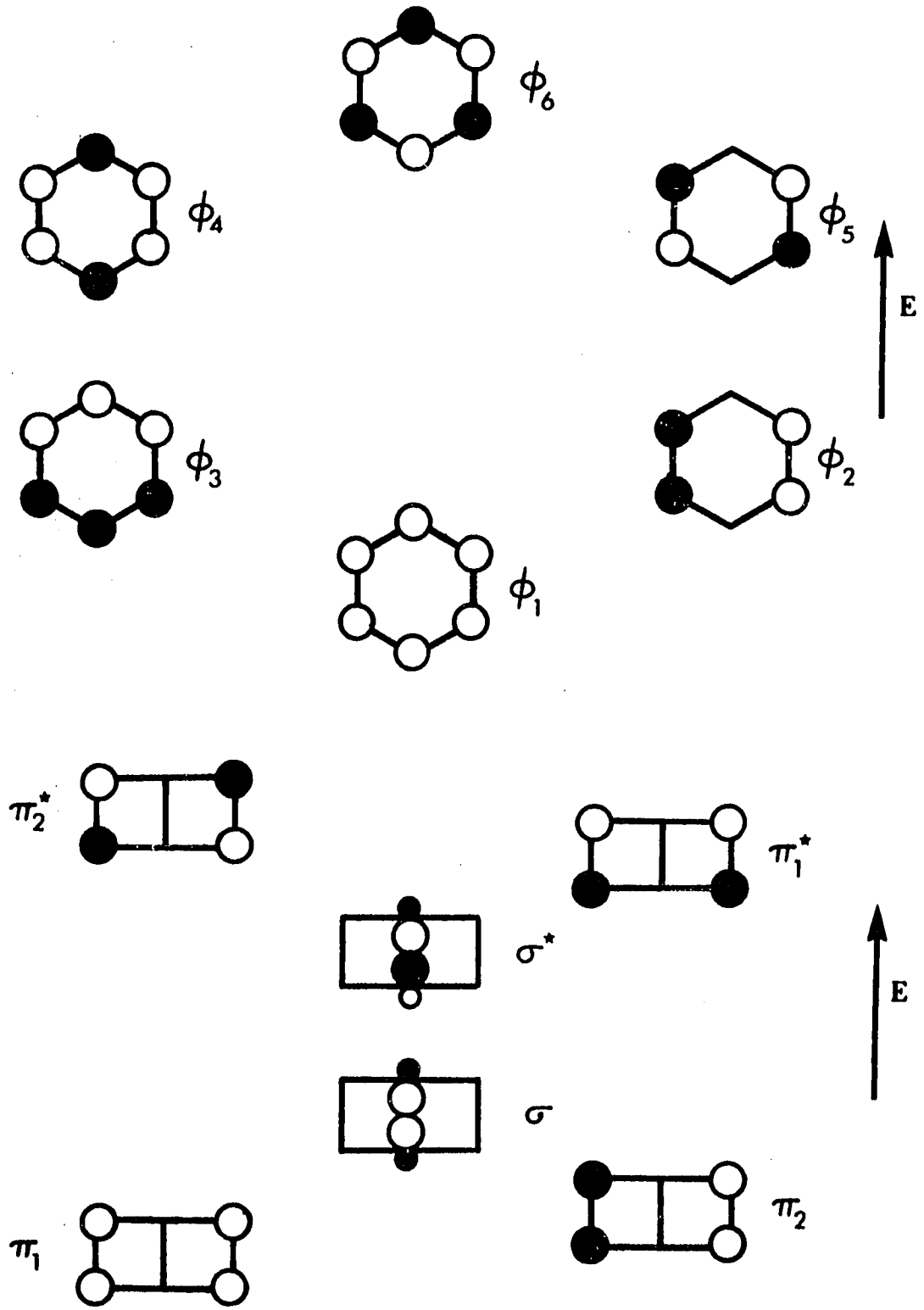

FIGURE 1

The molecular orbitals of benzene (above) and Dewar benzene (below)

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is helpful at this point to mix the orbitals of Dewar benzene in the manner shown in Figure 2[25].

Now if we break the C_1 - C_4 sigma bond of Dewar benzene with the most geometrically reasonable motion (i.e., with a disrotatory movement) we can observe the transformation of the relevant orbitals of Dewar benzene to those of benzene.

Inspection of Figure 3 reveals that the bonding orbital ($\pi_1 - \sigma$) of Dewar benzene transforms to the anti-bonding orbital ϕ_4 of benzene. This orbital symmetry relationship gives rise to the barrier to the facile conversion of Dewar benzenes to benzenes.

In this same fashion the hypothetical conrotatory cleavage of the C_1 - C_4 sigma bond of Dewar benzene can be analysed.

Figure 4 reveals that the conrotatory opening of the Dewar benzene leads to a species whose pi molecular orbitals have the nodal pattern of ground state benzene. Thus there is no symmetry-imposed barrier to this mode of aromatization[26]. However, it is this motion that, as van Tamelen has pointed out, leads to a cis, cis, trans-cyclohexatriene. Certainly this reaction course, while orbital-symmetry allowed, is rendered impossible by the strain energy that would result from a trans double bond in a six-membered ring.

This analysis rationalizes the observed moderate stability of the Dewar benzenes toward thermal aromatization. Yet this rearrangement does take place in spite of these constraints. The object of the studies described here has been to shed some light on the mechanism by which this rearrangement proceeds.

---

25. cf: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970, p 30.

26. devotees of orbital symmetry may enjoy comparing this treatment of the aromatization of Dewar benzene with the analysis of the aromatization of prismane presented in R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry"; Academic Press, New York, 1970, p 107.

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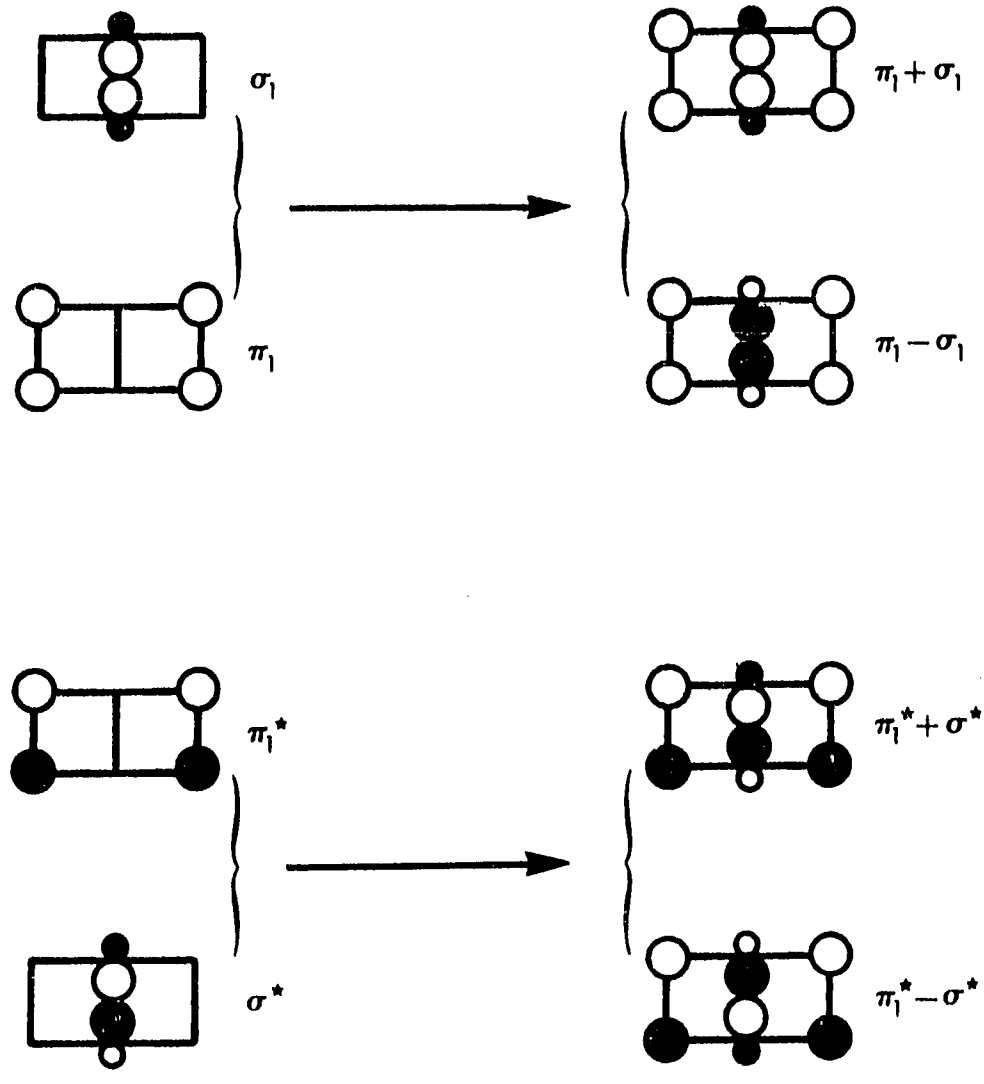

FIGURE 2

useful mixings of the orbitals of Dewar benzene

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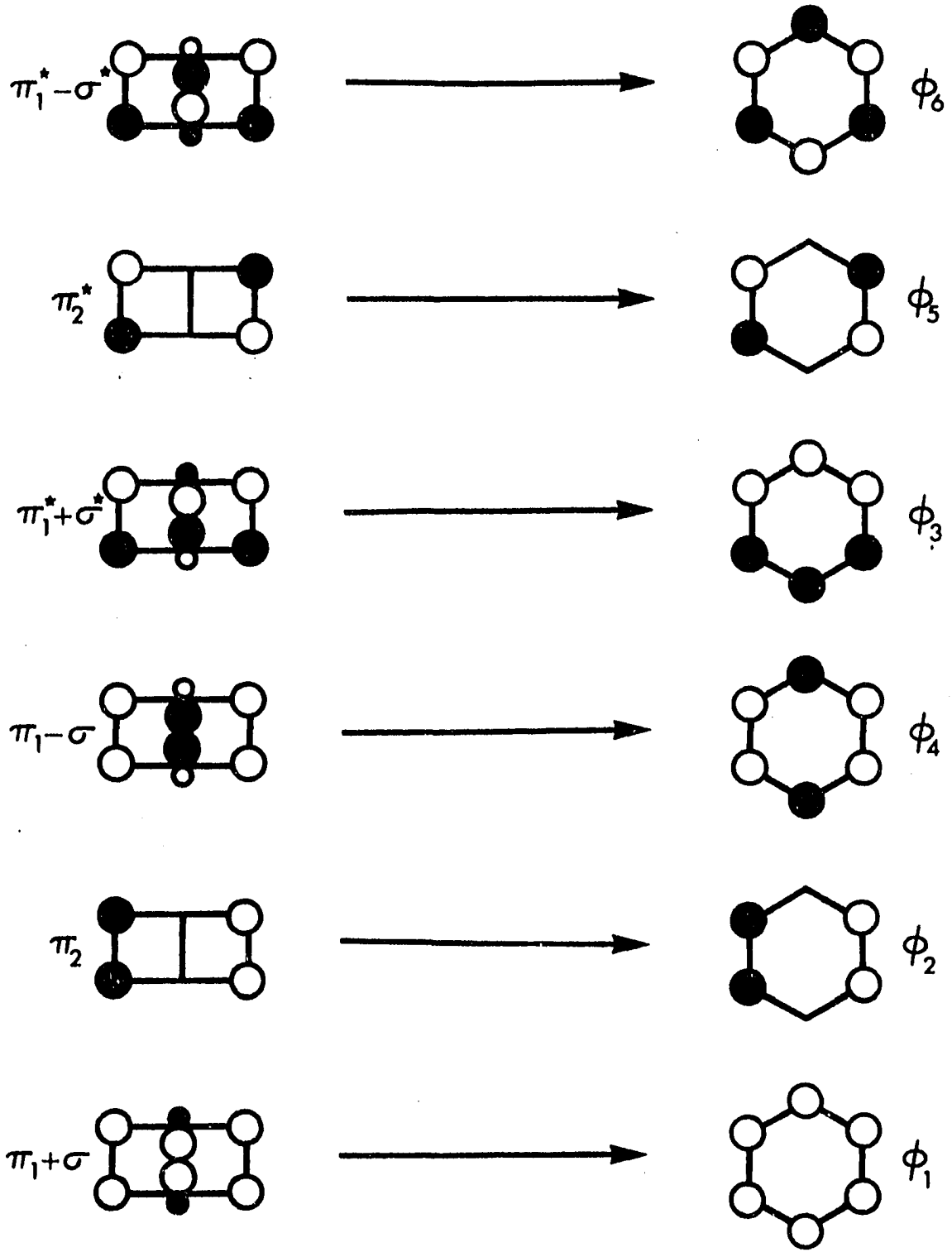

FIGURE 3

the disrotatory opening of Dewar benzene

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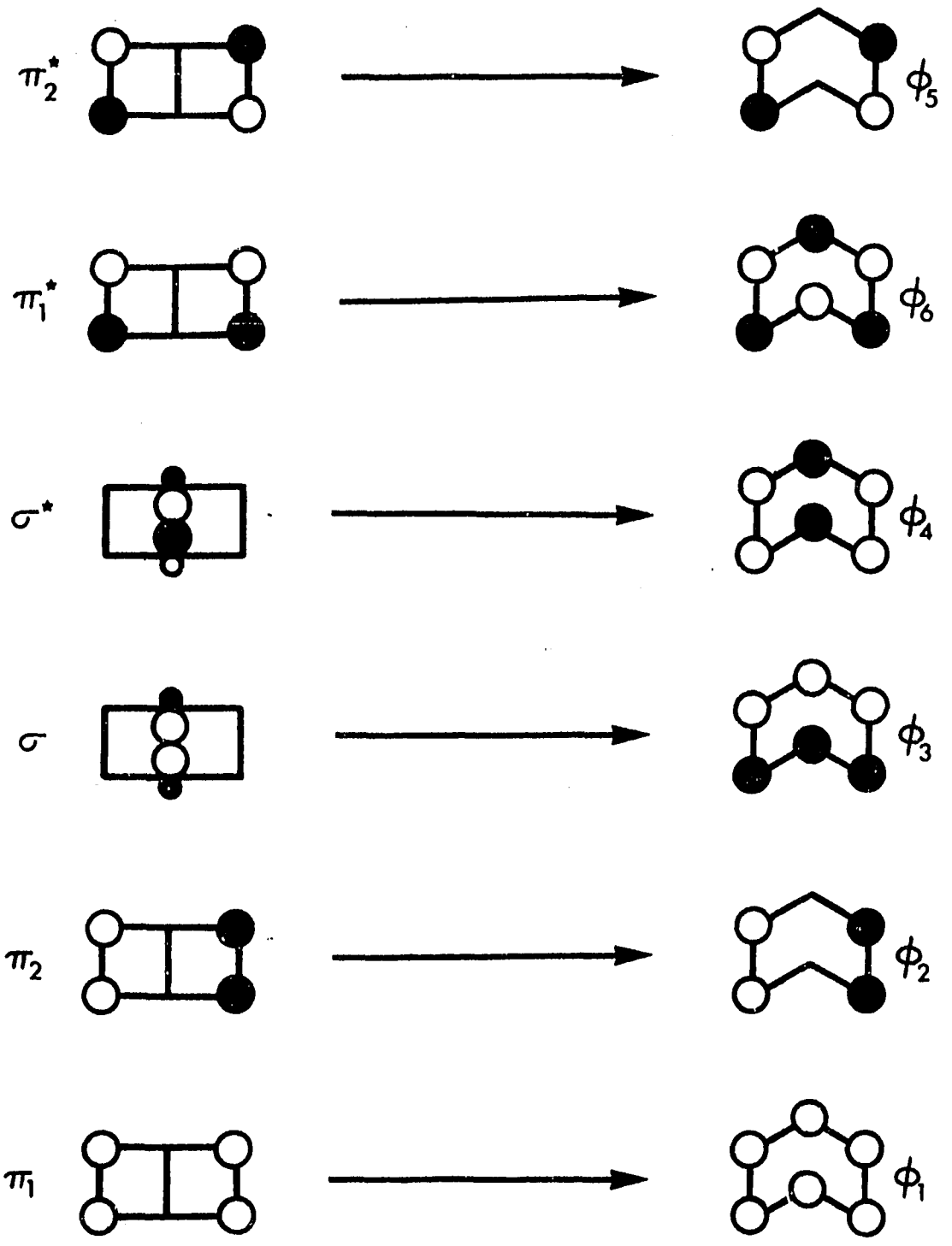

FIGURE 4

the conrotatory opening of Dewar benzene

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The situation is one of the most intriguing encountered in mechanistic studies. The anthropomorphic molecule has been completely hemmed in. All courses of action have been denied it. But when properly stimulated the crafty molecule frees itself from the trap, leaving the chemist to try to determine its escape route. In fact it may be that the barriers to escape are so nearly equal that different Dewar benzenes will choose mechanistically different paths to aromatic repose.

Perhaps the most obvious possible course for this reaction to take is the orbital symmetry-forbidden disrotatory ring opening to give an excited benzene. If enough activation energy is supplied to the Dewar benzene molecule so that its energy content (energy of activation plus strain energy relative to benzene) becomes greater than the electronic excitation energy of benzene, the symmetry-imposed barrier to the disrotatory opening disappears[27]. We have already noted that the energy of the transition state for the rearrangement of hexamethyl (Dewar benzene) is roughly 100 kcal/mole higher than the ground state of hexamethylbenzene. A rough calculation may help to decide whether this energy content of the transition state is consistent with a mechanism that involves production on an electronically excited hexamethylbenzene.

The conversion of a Dewar benzene to a benzene in either a B_{1u} or E_{1u} excited state is a symmetry-allowed process[28]. The second and third excited states of benzene have these symmetries, respectively[29]. The second electronic absorption band of hexamethylbenzene occurs at 220 nm[30]. This excited state is therefore

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27. cf: F. McCapra, Chem. Commun., 1968, 155.

28. R. Hoffmann and R. B. Woodward, Accts. of Chem. Res., 1, 22, (1968); D. Bryce-Smith and H. C. Longuet-Higgins, Chem. Commun., 1966, 594.

29. H. H. Jaffe and M. Orchin, "Theory and Application of Ultra Violet Spectroscopy", John Wiley, New York, 1962, pp 104-105.

30. R. C. Nelson and W. T. Simpson, J. Chem. Phys., 23, 1150, (1955).

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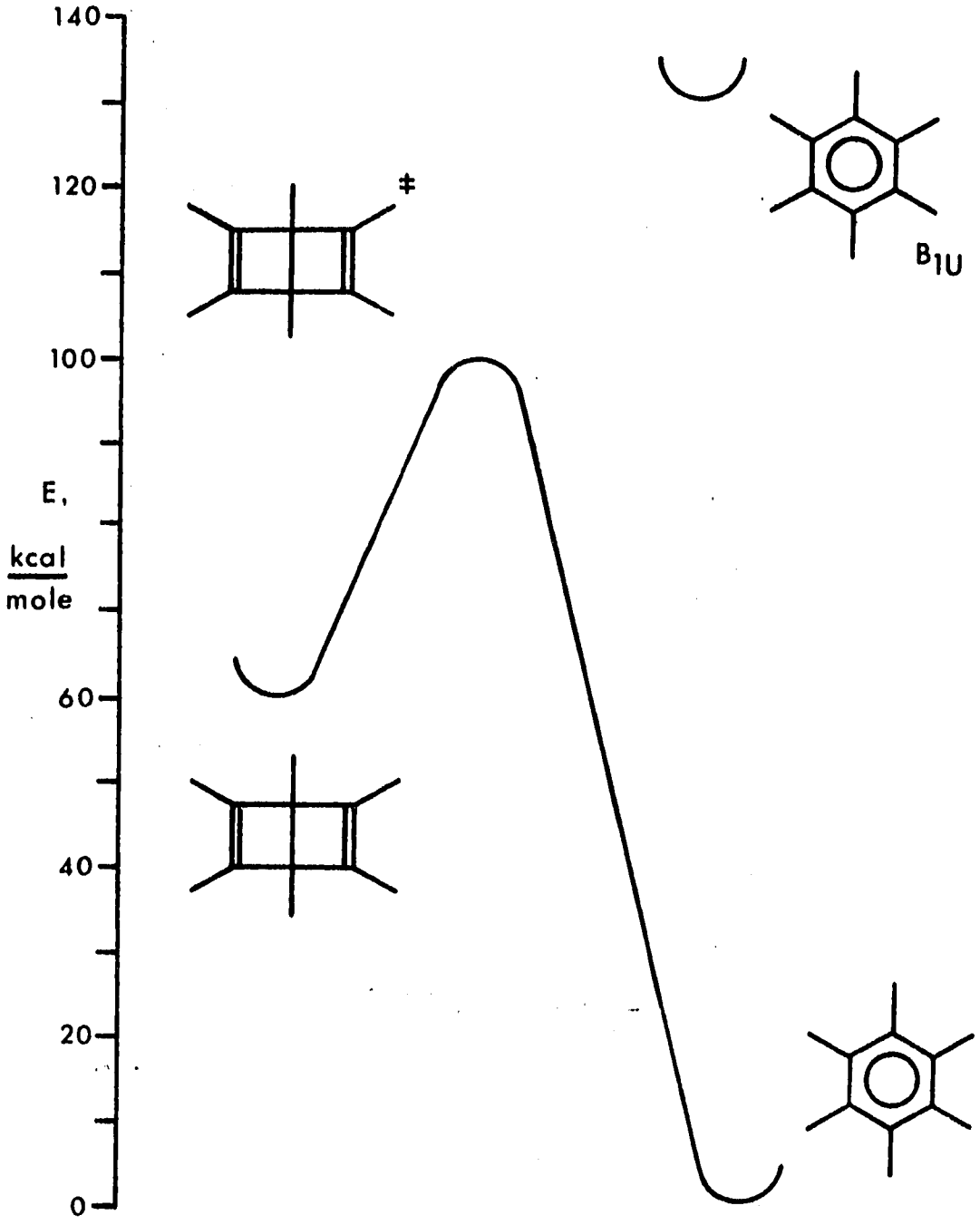

FIGURE 5

the aromatization of
hexamethyl(Dewar benzene):an energy diagram

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($E = h\nu$) 130 kcal/mole above the ground state of hexamethylbenzene. Figure 5 displays these energetic relationships.

We cannot be encouraged by these data. Clearly they imply that hexamethyl(Dewar benzene) rearranges to hexamethylbenzene by a path that does not include the B_{1u} excited state of hexamethylbenzene. Yet neither are we ever wholly convinced by thermochemical calculations of this sort. Further, this is a particular case and the generalization of quantitative data is unwise.

Two predictions follow from the above mechanism. If an electronically excited benzene is produced, it may be that such species in decaying to a ground state benzene dissipates its excitation energy by chemiluminescence[27,31]. It is also possible that an excited benzene might revert to a Dewar benzene. This must be essentially the course of reaction in the production of Dewar benzene derivatives from benzenes by photolysis[12,22]. This reversion might be observable if a Dewar benzene with a marker, such as (8) or (9), were partially aromatized. The hypothesis predicts that both (8) and (9) would be present. This is shown in Figure 6.

Another possible mechanistic path proceeds through the intermediacy of a diradical. Such a diradical might collapse directly to benzene, or, under certain conditions, might have an appreciable lifetime. We have already noted that the symmetry-allowed conrotatory ring opening of a Dewar benzene is rendered impossible by the strain of the trans double bond that such an opening produces. This strain, however, only becomes acute in the latter stages of the conrotatory movement. Initially, the conrotatory motion is facile, since it is not opposed by either steric or orbital symmetry factors. If this partial conrotatory opening takes place contemporaneously with a molecular change in conformation from boat to twist boat, a species is produced, with conservation of orbital symmetry, that resembles

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31. E. H. White, J. Wiecko and D. F. Russel, J. Am. Chem. Soc., 91, 5194, (1969).

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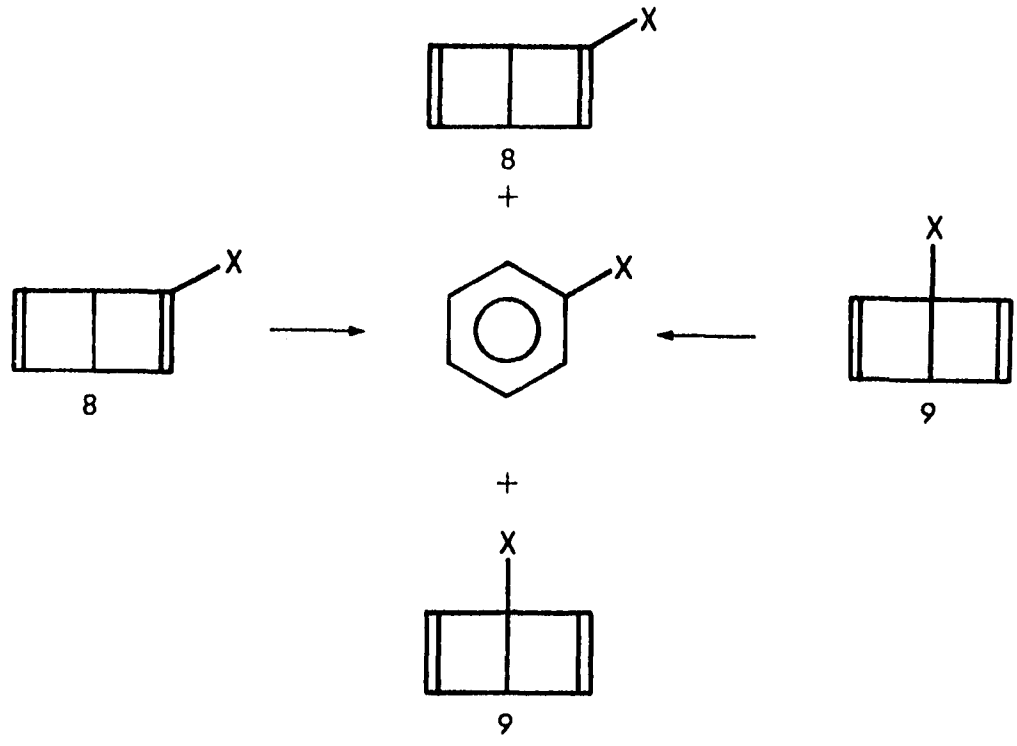

"TABLE 4

Label scrambling in a Dewar benzene

two allyl radicals bound at oblique angles to one another with sigma bonds[32] ((10)→(11)). Recently experimental evidence for the ease

10 11

32. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry"; Academic Press, New York, 1970, p 175.

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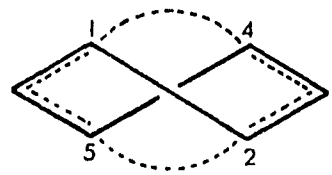
of this molecular distortion in hexamethyl(Dewar benzene) has come from an electron diffraction study of that compound's structure [33].

If some 1,4 bonding remains, symmetry demands that some 2,5 bonding develop (12). Now if this twist boat reverts to Dewar benzene,



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the sigma bond can be re-established between C_1 and C_4 or a sigma bond can be established between C_2 and C_5. This course of events is shown in Figure 7. In a properly labeled derivative this situation will lead to the same sort of scrambling as that predicted by the previous mechanism (see Figure 6). The decay of this diradical could involve the conversion of its excess energy to heat or possibly light. That is, this reaction mechanism might also result in chemiluminescence.

It is notable that this scheme does not require that the diradical (12) be long lived to produce positional scrambling. The diradical need only survive for a few molecular vibrations (on the order of 10^{-13} seconds each) so that the bonding between C_2 and C_5 becomes equivalent to that between C_1 and C_4. Such a lifetime is no longer than that of the activated complex in a reaction proceeding by a direct mechanism [34]. Thus the critical difference between these two possible modes of reaction is not the lifetime of the activated complex, but the orbital motions, conrotatory or disrotatory, that lead from reactant to activated complex. It may even be that the two mechanisms lead to one and the same activated complex.

The consideration of a mechanism involving a radical is not complete unless attention is directed to the spin state of that radical.

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33. M. J. Cardillo and S. H. Bauer, J. Am. Chem. Soc., 92, 2399, (1970).

34. R. Wolfgang, Accts. of Chem. Res., 3, 48, (1970).

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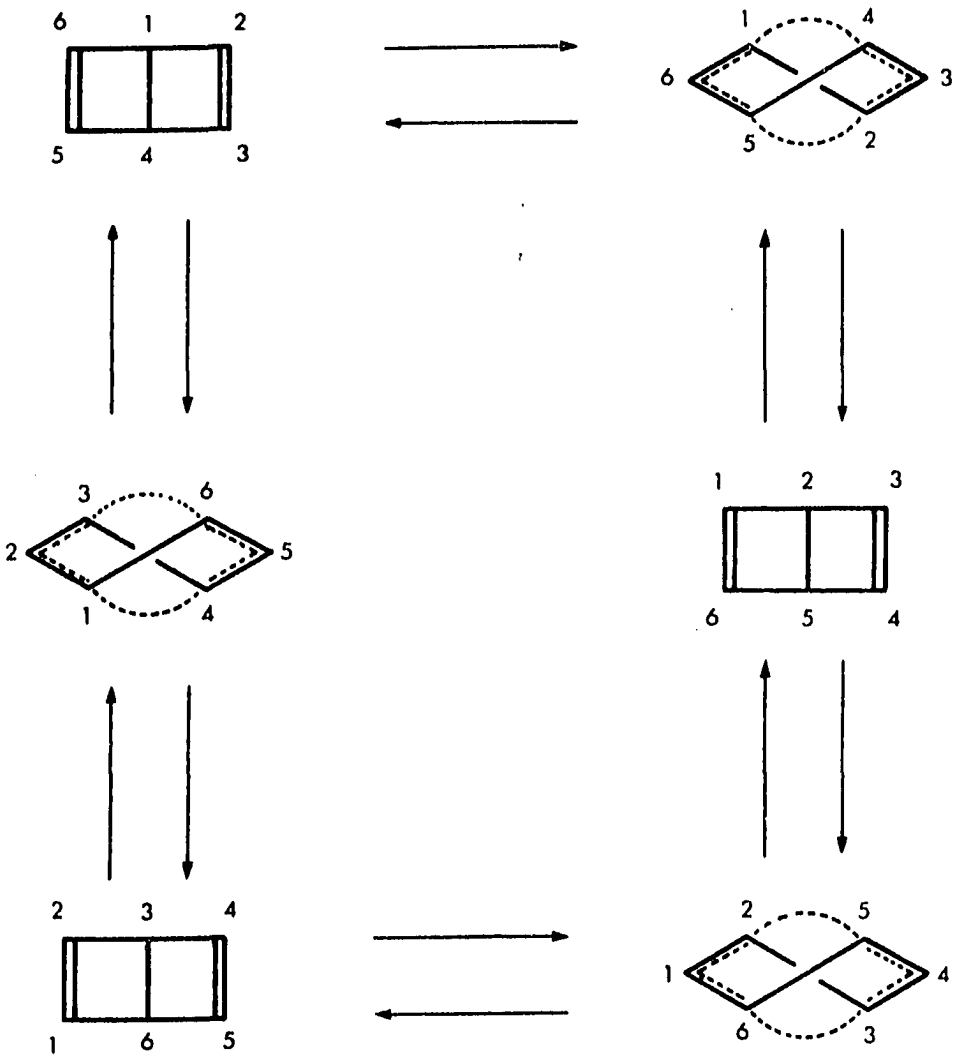

FIGURE 7

positional scrambling of carbon atoms in Dewar benzene via a diradical

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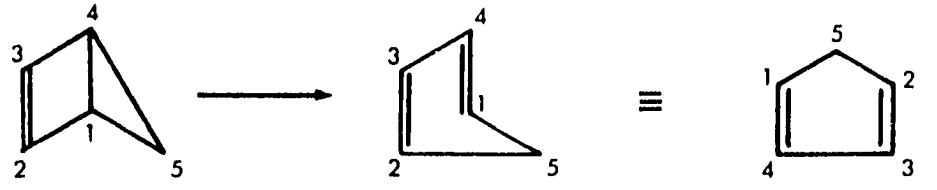
In the present context, we have proposed a mechanism that may proceed perfectly smoothly via a singlet diradical. However, we can not a priori exclude the possibility that, once formed, our hypothetical singlet diradical might decay to a triplet. We have not pursued this question: it seems more logical to determine whether some diradical is involved before considering the exact nature of that diradical. Similarily we have held in abeyance questions concerning the possibility of the conversion of the B_{1u} state of benzene to some lower triplet benzene.

A very recent report of a related reaction mechanism suggests a third possible mechanism for the conversion of Dewar benzene to benzene. Baldwin showed[35] that the isomerization of bicyclo(2,1,0)-pentene-2 to cyclopentadiene is an orbital symmetry-allowed $\sigma^2_s + \sigma^2_a$ process involving the $C_1 - C_2$ bond and the $C_4 - C_5$ bond (13).



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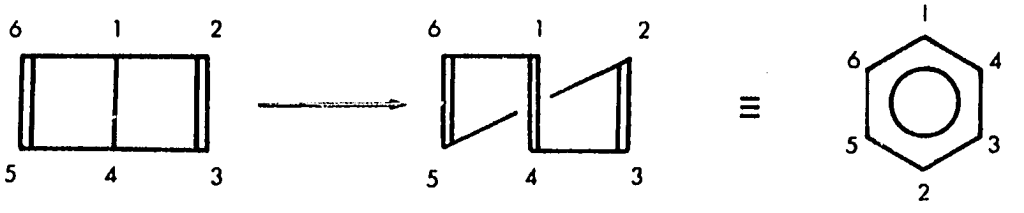
Inspection of a model shows that this reaction must proceed with inversion at either C_1 or C_4 and retention elsewhere. One can imagine an analogous mechanism for the aromatization of Dewar benzene in which the $C_1 - C_2$ and $C_4 - C_5$ sigma bonds are addends in a $\sigma^2_s + \sigma^2_a$



35. J. E. Baldwin and A. H. Andrist, Chem. Commun., 1970, 1561.

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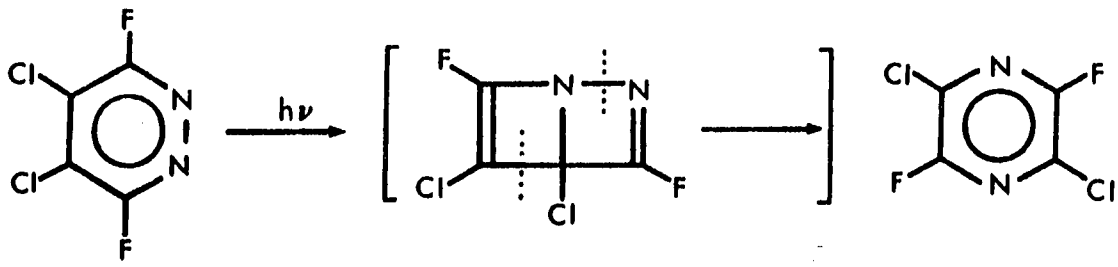
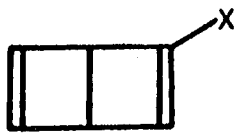
reaction or perhaps more properly a $\sigma^2_s + \sigma^2_a + \pi^2_s + \pi^2_s$ reaction.

This mechanism predicts a label scrambling in the aromatic isomer of a properly marked Dewar benzene, rather than in recovered Dewar benzene as in the two previous mechanisms. This process may be operating in a reaction recently observed by Lemal and co-workers[36a].



The possibility of the aromatization of hexamethyl(Dewar benzene) being accomplished by chemiluminescence is being investigated by Lemal[36b].

We decided to investigate the possibility of the production of scrambled Dewar benzenes in the course of aromatization. This study cannot hope to define completely the mechanistic course of this rearrangement. But it takes the next logical and necessary step toward that complete definition. The next chapter describes a series of experiments in which compounds of the type (8) are prepared, thermolized and examined for traces of (9).



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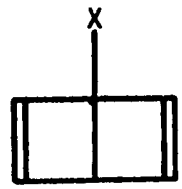

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36. a. D.W. Johnson, V. Austel, R. S. Feld and D.M. Lemal, J. Am. Chem. Soc., 92, 7505, (1970); b. D.M. Lemal, et al., Abstracts, First Northeast Regional Meeting of the American Chemical Society, Boston, Mass., October 1968, No. 45.

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CHAPTER 2
DISCUSSION

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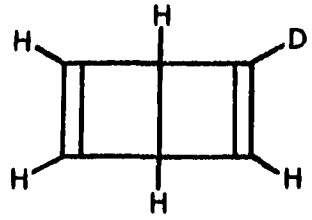
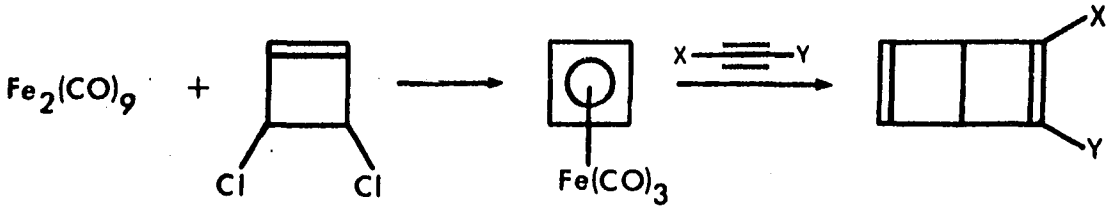
Believing in the primacy of hydrogen we first undertook the synthesis of a labeled Dewar benzene as close to the prototype as possible (14). Toward this objective we chose to make use of a



14

synthetic sequence reported by Pettit and co-workers [14,37]. By reaction of diiron enneacarbonyl (15) [38] with cis-3,4-dichlorocyclobutene (16), whose preparation from cyclooctatetraene had been developed by Nenitzescu [39], Pettit obtained the theoretically interesting cyclobutadiene irontricarbonyl (17) [40]. Decomposition of the



15 16 17 18

37. G. F. Emerson, L. Watts and R. Pettit, J. Am. Chem. Soc., 87, 131, (1965).

38. E. H. Braye and W. Hübel in "Inorganic Syntheses", Vol. 8, McGraw-Hill, New York, 1966, p 178.

39. C. D. Nenitzescu, et al., Chem. Ber., 97, 372, (1964).

40. L. Watts and R. Pettit in "The Werner Centennial", Advances in Chemistry No. 62, American Chemical Society, Washington, D.C., 1967, p 549.

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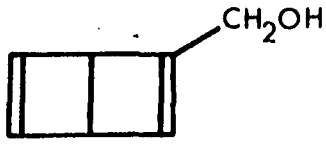
iron complex with ceric ammonium nitrate in the presence of an acetylene led to a Dewar benzene (18).

In our hands this reaction sequence provided Dewar benzenes (18) only if X and Y or both were strongly electron withdrawing. Thus we found that decomposition of the iron complex (17) in the presence of either acetylene itself or 2-butyne led to tricyclo(4,2,0,$0^{2,5}$) octa-3,7-diene (19) but no detectable bicyclic material. Similarily, decompo-

19

sition of (17) in the presence of propargyl alcohol or propargyl acetate did not prove to be synthetically useful for the preparation of the Dewar benzene derivatives (20) or (21) respectively. However, if the decomposition of (17) were carried out in the presence of propargyl



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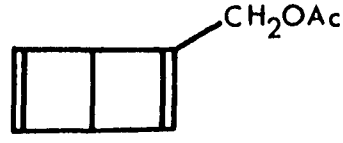

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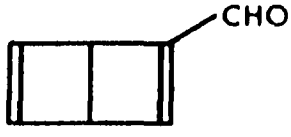
aldehyde or dimethyl acetylenedicarboxylate, 2-aldehydo (Dewar benzene) (22) or 2,3-dicarbomethoxy (Dewar benzene) (23) respectively was formed.



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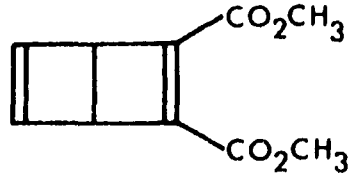

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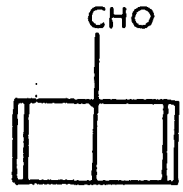
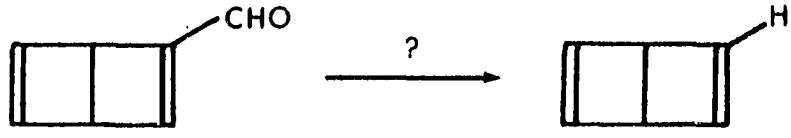
The aldehyde (22) drew our attention for two reasons. In nuclear magnetic resonance spectroscopy the chemical shift of the aldehyde proton is known to vary in response to even slight changes in chemical environment[41]. Thus the presence of 1-aldehydo (Dewar benzene) in mixture with its isomers benzaldehyde and 2-aldehydo (Dewar benzene) quite probably is detectable by NMR spectroscopy. A potentially



even more useful attribute of the aldehyde group is the ease with which it can be decarbonylated by tris(triphenylphosphine) chlororhodium[42]. In favorable cases this reaction proceeds in good yield at room temperature. Double bonds are not hydrogenated or isomerized under the reaction conditions. We hoped to bring about the reaction:



41. L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, New York, 1959, p 57.

42. K. Ohno and J. Tsuji, J. Am. Chem. Soc., 90, 99, (1968); M. C. Baird, C. J. Nyman, and G. Wilkinson, J. Chem. Soc. (A), 348, (1968).

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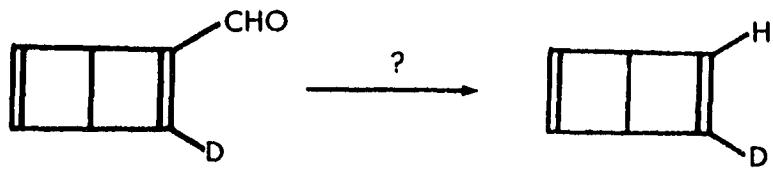
or more purposefully:



This last reaction necessitates the preparation of the propargyl aldehyde d_1 (23a). It is only necessary to protect propargyl aldehyde[43] from base decomposition as the dimethyl acetal before generating the anion[44] which can be neutralized with D_2O to obtain (25).

$$DC\equiv CCHO$$

23a

However, 2-deutero (Dewar benzene) was never prepared. We obtained 2-aldehydo (Dewar benzene) (22) and identified it by its NMR and IR spectra and by its rearrangement to benzaldehyde. All attempts to purify the crude (22) either through conversion of the aldehyde to the phenylhydrazone, azine or semicarbazone, or by preparative thin layer chromatography, only hastened decomposition.

We were able to study the thermal decomposition of the crude 2-aldehydo (Dewar benzene) at room temperature. The aldehyde region of the NMR spectrum of the crude reaction product showed resonances corresponding to propargyl aldehyde, 2-aldehydo (Dewar benzene) and benzaldehyde. If the spectrum were redetermined periodically over the course of several hours, the 2-aldehydo (Dewar benzene) resonance was seen to diminish and the benzaldehyde resonance to enhance while the propargyl aldehyde resonance remained constant. No new or transient resonances were detected.

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43. J. C. Sauer in "Organic Syntheses", Coll. Vol. IV, John Wiley, New York, 1963, p 813.

44. E. J. Corey, R. B. Mitra and H. Uda, J. Am. Chem. Soc., 86, 490, (1964).

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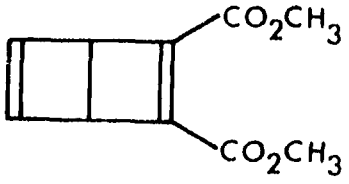
We turned our attention from the all too readily reactive aldehyde (22) to the diester (23) which we hoped would prove more manipulable.



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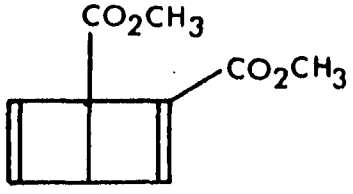
The crude diester (23) was purified by thin layer chromatography. From this treatment a fraction could be obtained whose chief constituent was the diester (23). By subjecting this material to a second chromatographic separation a sample of substantial purity could be obtained in great enough quantity to be useful for rearrangement study.

We can, with a good degree of confidence, make qualitative predictions about the ways in which the NMR spectrum of the isomeric Dewar benzene (24) might differ from that of (23). For reference



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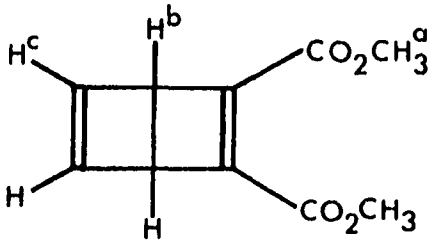
we give the chemical shifts of the resonances of (23). The proton in



a = 3.78 δ

b = 3.98 δ

c = 6.58 δ

the 3-position of (24) will be shifted downfield relative to the protons in the 5- and 6-positions of (23) by the electron withdrawing influence of the carbomethoxy group in the 2-position of (24). A rough estimate

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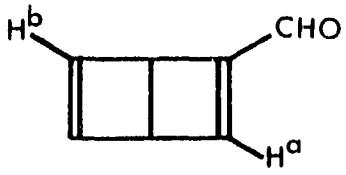
of this shift can be obtained by comparison of the shifts in the 3- and 6-positions of the aldehyde (22). Thus the proton in the 3-position



a=7.22 δ

b=6.64 δ

of the diester (24) can be expected to resonate slightly below 7 δ. This is a region of the spectrum vacant of any obscuring peaks. The protons in the 5- and 6-positions of the diester (24) can also be expected to be shifted downfield relative to (23) by the influence of the carbomethoxy group in the 1-position of (24). These shifts will be of lesser magnitude than that of the 3-proton, however. The appearance of any new resonances in the carbomethoxy region might well be obscured by the large resonances already appearing there.

With these predictions in mind we proceeded to the experimental test. Inspection of NMR spectra taken during the isomerization of 2,3-dicarbomethoxy (Dewar benzene) (23) to dimethyl phthalate revealed no evidence for the production of 1,2-dicarbomethoxy (Dewar benzene) (24).

In selecting another Dewar benzene derivative for study, our attention was drawn to 2,3-dicarbomethoxy-1,4,5,6-tetramethyl (Dewar benzene) (25). This compound and others obtainable from it through

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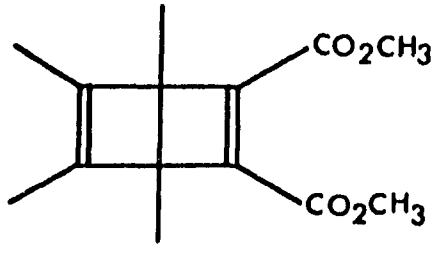

reactions of its ester groups offer two distinct advantages over the less fully substituted Dewar benzenes previously studied. First these hexa-substituted compounds have notably higher activation energies

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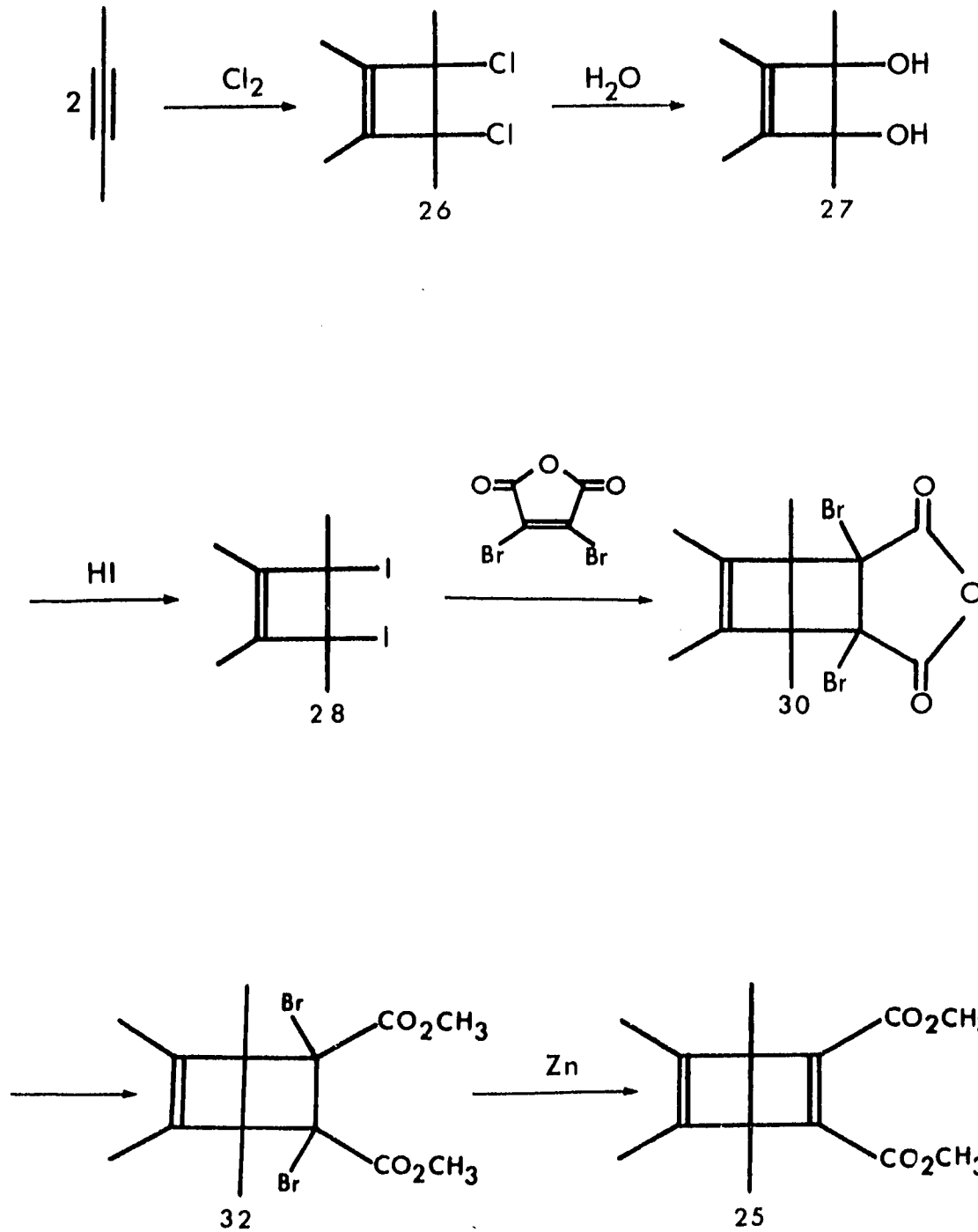

FIGURE 8

the synthesis of a Dewar benzene

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for aromatization than the mono-or di-substituted derivatives. This results in their having half lives of months rather than hours at room temperature. We planned to make use of this additional time to carry out more effective purification procedures. Second, we hoped that the close packing of substituents about the ring system would favor torsions that produce skewing as the 1,4-bond ruptures during aromatization. Such skewing of the boat-shaped Dewar benzene favors production of a diradical that may lead to scrambling.

Criegee and co-workers have developed in detail a sequence that converts butyne-2 to the diester (25). This sequence is outlined in Figure 8. The chlorination of butyne-2 to give the versatile intermediate 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (26) has been described in "Organic Syntheses" [45]. Aqueous tetrahydrofuran converts the dichloride (26) to the diol (27) [46]. Treatment of this diol (27) with hydriodic acid gives the unstable diiodide (28) [46] which is immediately allowed to react with dibromomaleic anhydride [47] in the presence of mercury to give the tricyclic bromoanhydride (30) [16]. Esterification of (30) first with sodium methoxide followed by acid and then with diazomethane produces the dibromodiester (32) [16]. Debromination of (32) with zinc-copper couple [48] to give the desired diester (25) completes the synthetic sequence [16]. Following these procedures, we were easily able to prepare the diester (25) in quantities on the order of a gram.

Although Criegee described (25) as "eine schön kristallisierte Substanz vom Schmp. 32-33°" [16], it remained in our hands always a clear viscous oil. On occasion the debromination of the ester (32) did yield a crystalline substance. After our hope that we had at last

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45. R. Criegee in "Organic Syntheses", Vol. 46, John Wiley, New York, 1966, p 34.

46. R. Criegee, H. Kristinsson, D. Seebach and F. Zanker, Chem. Ber., 98, 2331, (1965).

47. O. Diels and M. Reinbeck, ibid., 43, 1274, (1910).

48. R. Smith and H. Simmons in "Organic Syntheses", Vol. 41, John Wiley, New York, 1961, p 72.

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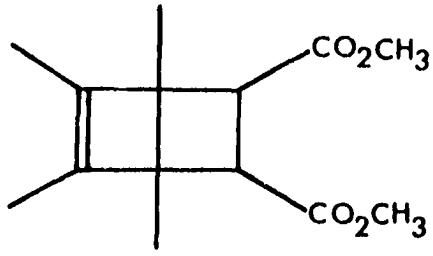
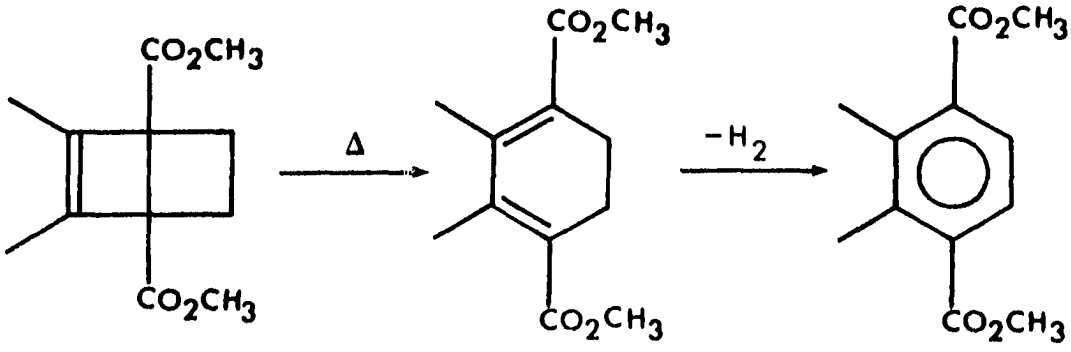
prepared (25) in the crystalline state proved groundless, we identified the crystalline substance as cis-3,4-dicarbomethoxy-1,4,5,6-tetramethyl-bicyclo(2,2,0)hexene-5 (33).

33



This dihydrodiester is in its own right an interesting compound that may be capable of undergoing numerous rearrangements. We took a short diversion to investigate its behavior on thermolysis. Experimental analogy for one mode of thermal rearrangement of (33) can be found in Seebach's study[49] of the thermolysis (34). The



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possibilities for variation on this theme must be evident. The intermediate cyclohexadiene is particularly ripe for a variety of transformations.

The diester (33) proved to be remarkably stable to heat. But, when heated at 225° for one hour in pyridine-d_5, change was evident. All traces of (33) had vanished. At least three new substances were present. But none of them was the phthalate (35).

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49. D. Seebach, Chem. Ber., 97, 2953, (1964).

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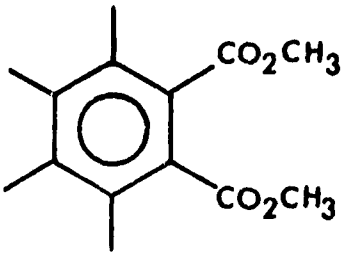
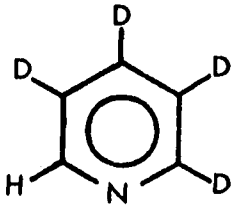


35

Furthermore, inspection of the NMR resonances due to traces of pyridine-d_4 in the solvent, showed an unmistakable enhancement of the resonance of 2,3,4,5-tetradeuteropyridine (36). This suggests the intermediacy of hydrogen radicals[50]. We pursued this matter no further, but returned to the problem that we had set for ourself.



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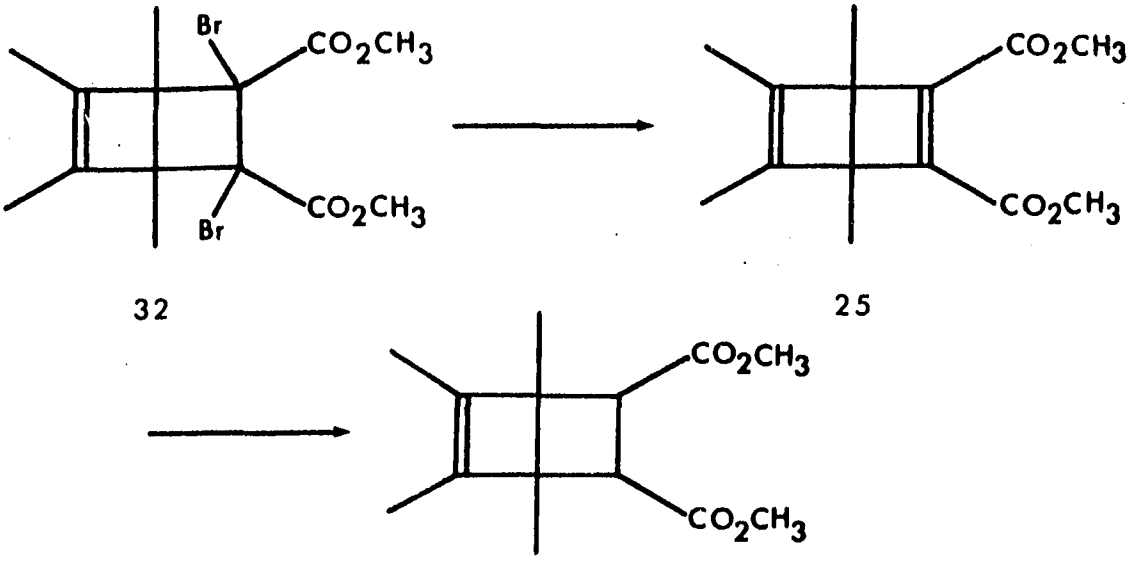
We found that from a mixture of the esters (25) and (33) crystalline



32 25 33

50. R. A. Barnes in E. Klingberg ed., "Pyridine and Its Derivatives", Interscience, New York, 1960, pp 12-26 and references therein.

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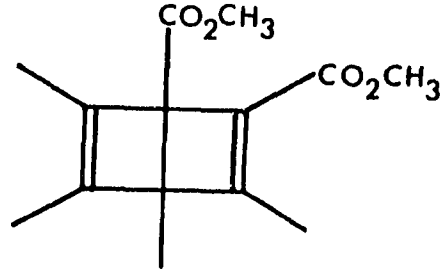
(33) could be isolated free of (25), but that the oil (25) could not be isolated free of (33) even by chromatography. Further study of the zinc debromination of (32) revealed that the reduction which leads to (33) does not set in until the conversion of (32) to (25) is complete. Since the dibromide (32) and the Dewar benzene (25) are readily separable by thin layer chromatography, pure (25) could easily be obtained if the debromination were stopped slightly short of completion.

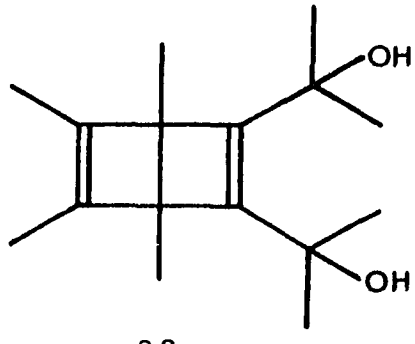
A sample of chromatographically pure (25) in pyridine-d_5 was sealed into an NMR tube. NMR spectra taken during thermolysis at 115° clearly showed a set of small transient resonances whose chemical shifts are consistent with the structure (37). We attempted to prepare (37) independently by the photolysis of dimethyl tetramethyl-



37

phthalate (35). No Dewar benzene could be detected in this reaction mixture. It must also be noted that if thermolysis were carried out on an impure sample of (25), no evidence of an intermediate could be observed.

We turned our attention to the preparation of 2,3-di-2-(2-hydroxypropyl)-1,4,5,6-tetramethyl (Dewar benzene) (38) hoping that the added bulkiness of its ring substituents in the 2- and 3-positions might serve



38

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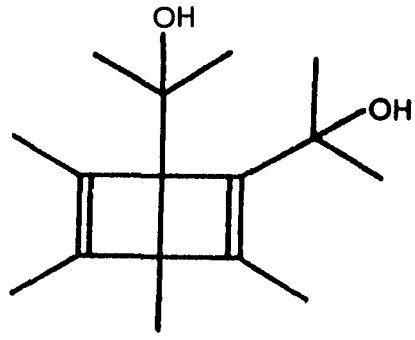
to promote positional scrambling. The diol (38) is readily available from the diester (25) by the use of methylmagnesium iodide [19].

There is reason to believe that (38) may be thermodynamically less stable than its isomer (39). The photolysis of 1,2,4-tri-t-



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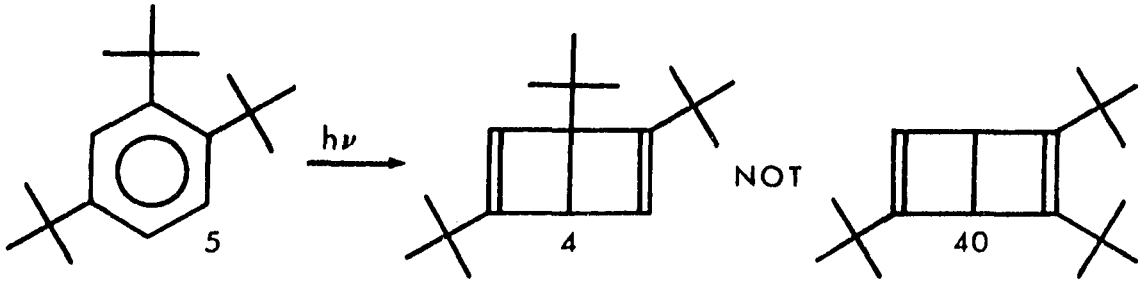
butylbenzene (5) produces 1,2,5-tri-t-butyl (Dewar benzene) (4), not



2,3,5-tri-t-butyl (Dewar benzene) (40). Wiltzbach, Kaplan and Den Besten have made a comprehensive study of this reaction [51]. Gas chromatographic and nuclear magnetic resonance analysis of a photostationary mixture resulting from prolonged irradiation of (5) revealed the presence of (4), (5), (41), (42), and (43) but did not detect any (40). It is notable that the Dewar benzene (44) was also absent from the photostationary mixture. Inspection of our model (see below) showed that the 3,5-substitution pattern leads to greater crowding of the t-butyl groups than does the 1,2 pattern.

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51. K. E. Wiltzbach and L. Kaplan, J. Am. Chem. Soc., 87, 4004, (1965); I. E. Den Besten, L. Kaplan and K. E. Wiltzbach, ibid., 90, 5868, (1978)

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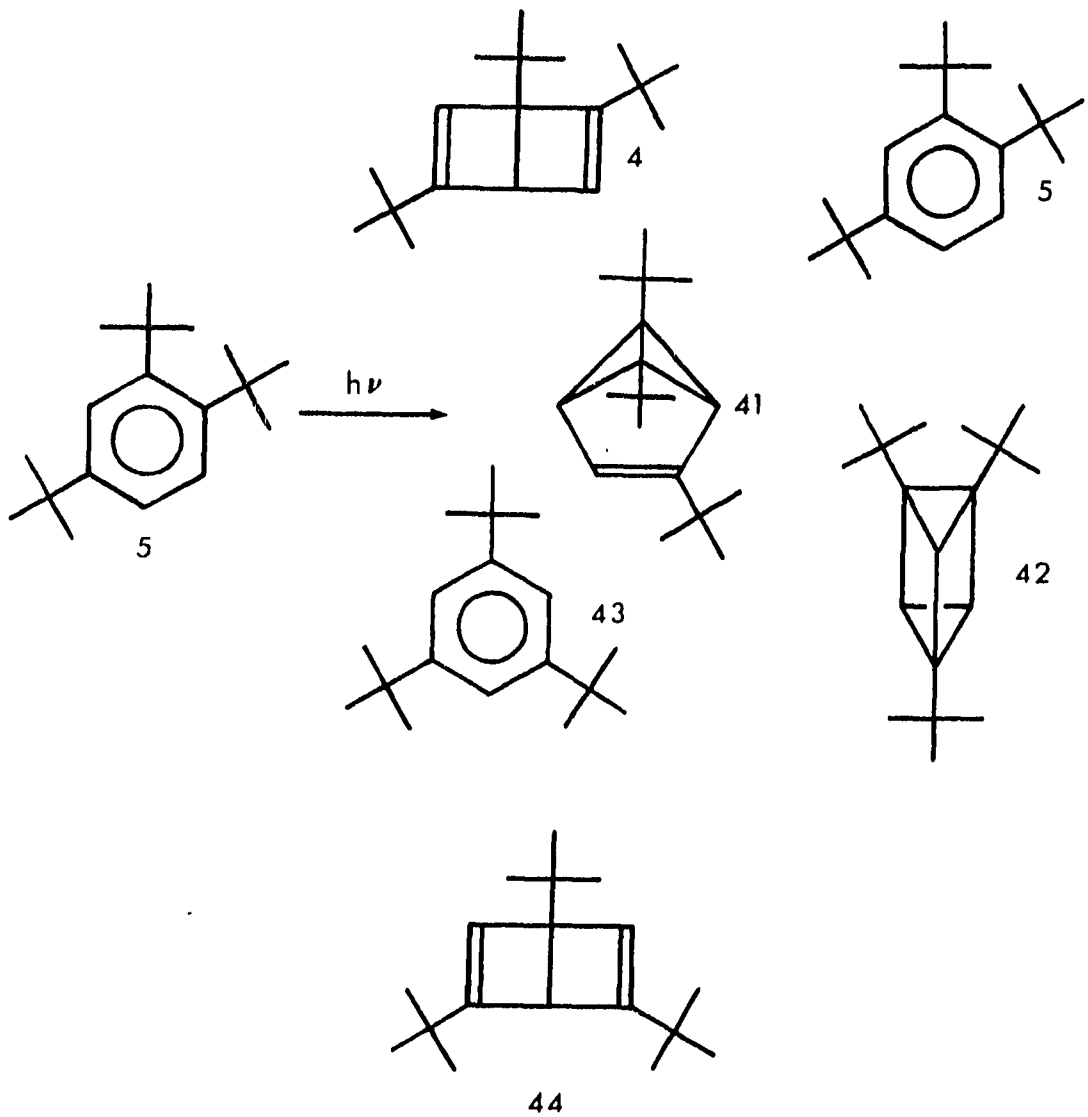

Nenitzescu and co-workers have found[52] that under the influence of bisbenzonitrile palladium dichloride, t-butylacetylene is transformed to the Dewar benzene palladium dichloride complex (45) to the exclusion of complexes with other alkyl substitution patterns. The formation of Dewar benzene ring systems with the 1,2,4 substitution pattern by two reactions that are undoubtedly mechanistically distinct strongly suggests that the observed pattern is thermodynamically favored.

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52. C. D. Nenitzescu, et al., Chem. Ber., 102, 3996, (1969).

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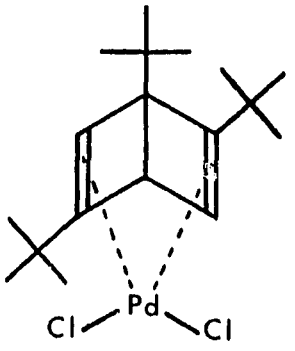

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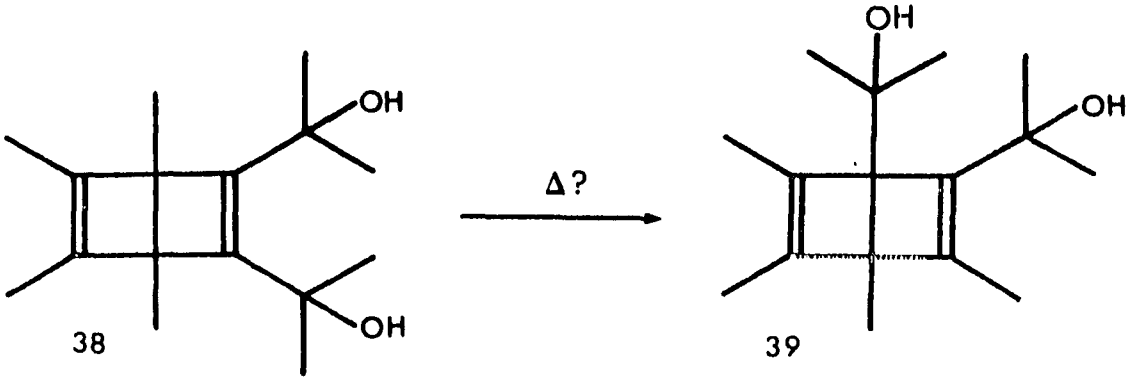
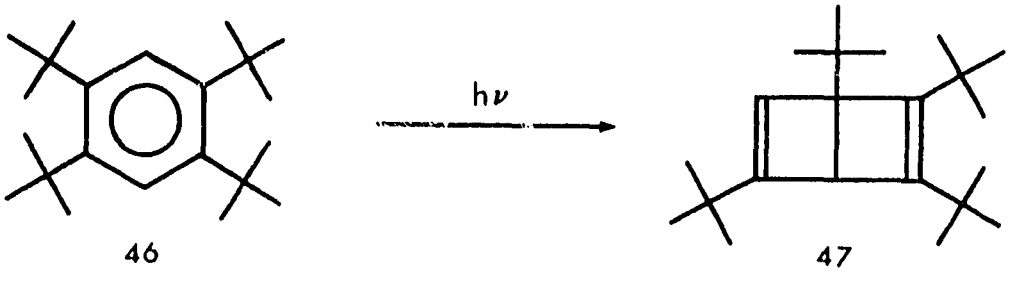
The application of the above already imperfect model to the isomerization ((38)→(39)) is further obscured by the fact that the



38 39

photolysis of o-di-t-butyl-benzene gives no Dewar benzene but rather a mixture of m- and p-di-t-butylbenzenes [53]. Another experimental fact that emphasizes the complexity of the situation is ((46)→(47)) [17]. In the related case of the photochemical conversion of



46 47

53. A. W. Burgstahler, P. L. Chien and M. O. Abdel-Rahman, J. Am. Chem. Soc., 86, 5286, (1964); K. Kirk, PhD Thesis, University of Wisconsin, 1963 quoted in E. E. van Tamelen, Angew. Chem. Internat. Edit., 4, 741, (1965).

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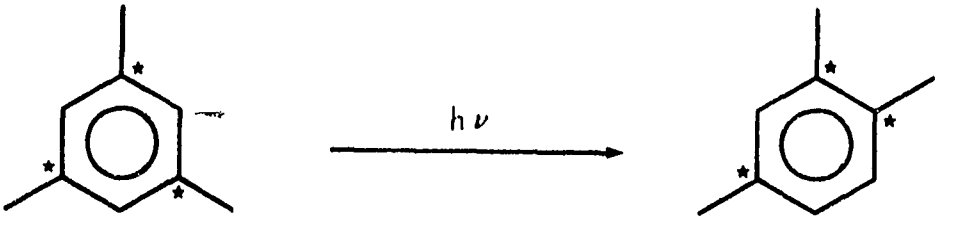
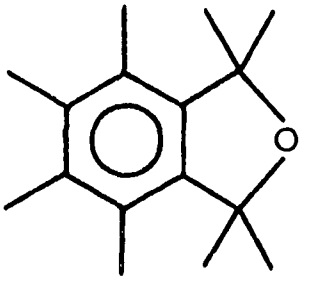
mesitylene (48) to 1,2,4-trimethylbenzene (49), labeling studies[54] have shown that the alkyl migration is accompanied by transposition



of ring carbon atoms. This finding suggests the intermediacy of a valence bond isomer of trimethylbenzene.

Greater confidence in the stability of (39) vis a vis (38) came from the construction of scale models using the molecular dimensions determined for hexamethyl (Dewar benzene)[33]. These models indicate that there is less crowding in (39) than in (38).

The aromatization of the diol (38) is complicated by concomitant dehydration. The product observed is that of both reactions (50). We sought to preclude this cyclodehydration by converting the diol (38) to the dimethyl ether (51). Attempts to bring about this reaction with



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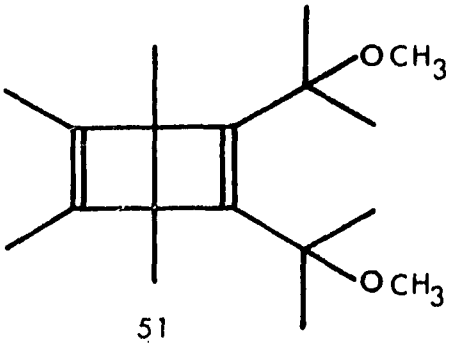

51

either trimethyloxonium fluoroborate or with diazomethane and aluminium chloride[55] failed. Steric hinderance must account for the inertness of (38) to these two potent methylating reagents. In light

54. L. Kaplan, K. E. Wiltzbach, W.G. Brown and S. S. Yang, J. Am. Chem. Soc., 87, 675, (1965).

55. E. Müller, R. Heischkeil and M. Bauer, Ann., 667, 55, (1964).

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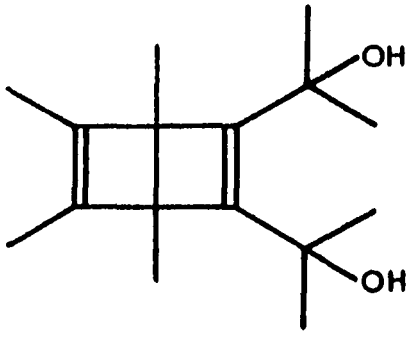
of these results and after viewing our model, we elected not even to attempt any reaction of the diol that involved backside attack on the alcohol.

Rather we proceeded to carry out thermal rearrangement studies on the diol (38) since there is good evidence that aromatization to the diol (52) preceeds the dehydration that gives (50).



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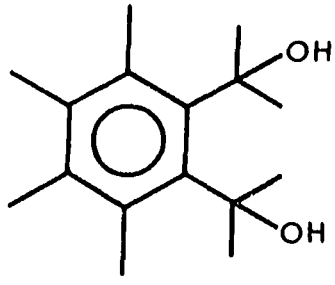

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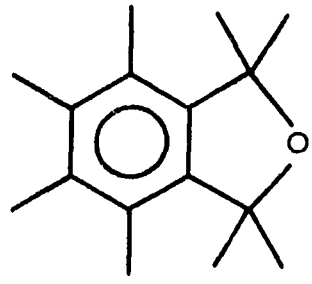

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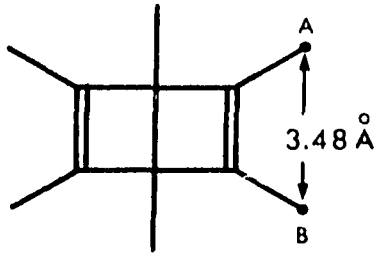
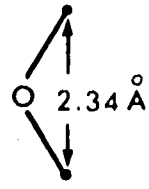
The distance between carbon atoms A and B in hexamethyl (Dewar benzene) is 3.48Å [33] while the distance between carbon atoms in dimethyl ether, an unstrained ether, is only 2.34Å [56]. Carbon atoms





A and B are simply too far apart to be easily linked by a single oxygen atom. This geometric constraint accounts for the fact, first noted by Criegee [16] and confirmed by our own work, that the tricyclic bromoanhydride (30) cannot be debrominated to the corresponding Dewar benzene (53) by conditions that readily convert the dibromodiester (32) to the Dewar benzene diester (25). The carbon atoms in the 2- and 3-positions of (30) are unable to rehybridize from sp^3 to

56. K. Kimura and M. Kubo, J. Chem. Phys., 30, 151, (1959); L. Pauling and L. O. Brockway, J. Am. Chem. Soc., 57, 2684, (1935).

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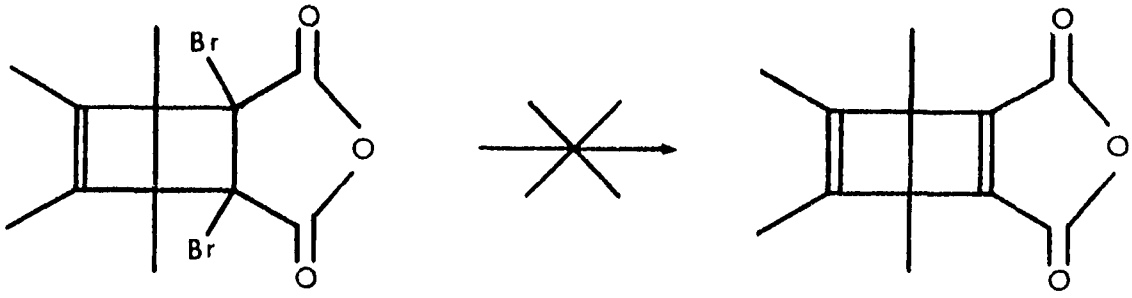
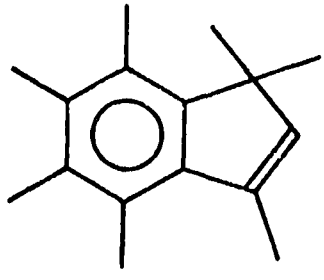


30 53

sp^2 because of the increase in interior angles that would accompany this change.

Direct experimental evidence that aromatization precedes dehydration in (38) comes from a pair of experiments performed by Criegee and co-workers [19]. These workers found that if the aromatic diol (52) (obtained by photolysis of (38)) is subjected to the conditions that cause (38) to aromatize and dehydrate, the diol (52) is dehydrated to (50). Further, it was found that treatment of (38) with p-toluenesulfonic acid in benzene resulted in the loss of two moles of water and the formation of the heptamethylindene (54). From these data



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Criegee concluded that aromatization must precede dehydration in the thermal rearrangement of (38).

NMR spectra taken during the thermolysis of chromatographically pure (38) contained a set of transient resonances whose chemical shifts were consistent with the isomeric Dewar benzene (39). It was not possible to isolate the substance that gave rise to these transient resonances. If this thermolysis were carried out on less pure samples of (38), no transients were observed.

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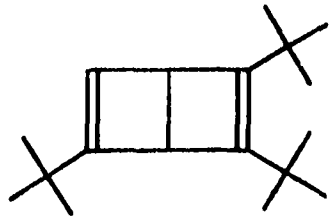
Hoping to prepare a Dewar benzene in which positional scrambling would occur to a degree that would make it unmistakable, we sought to prepare a compound more closely modeled after (40). Toward this end we proposed a variation on a pair of reactions recently reported



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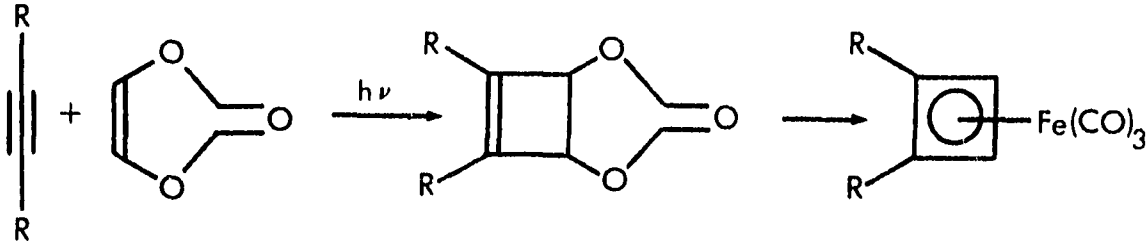
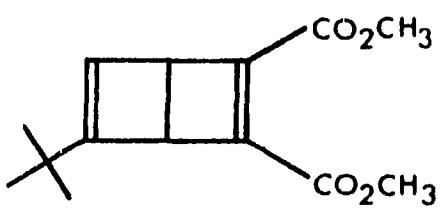
by Grubbs [57].



This sequence not only offers a route to cyclobutadiene irontricarbonyl shorter than that of Pettit [14,37,40], but also provides a means of incorporating alkyl substituents in the process. We hoped to prepare the Dewar benzene (55) by the reaction of the iron complex (56) with dimethyl acetylenedicarboxylate.



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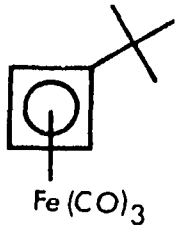

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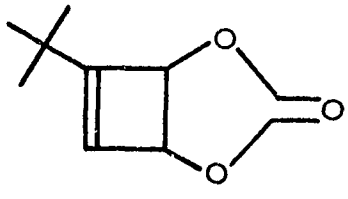

57

To date we have prepared the carbonate (57). Attempts to convert this material to the corresponding irontricarbonyl complex would be welcomed.

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57. R. H. Grubbs, J. Am. Chem. Soc., 92, 6693, (1970).

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CHAPTER 3
EXPERIMENTAL

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General Experimental Procedures

Infrared spectra were taken on a Perkin-Elmer model 137. Routine nuclear magnetic resonance (NMR) spectra were obtained with a Varian T-60 spectrometer; all isomerizations were monitored with a Varian HA-100 NMR spectrometer. Chemical shifts are given in ppm (δ) from tetramethylsilane (TMS), which was used as an internal standard. Mass spectra were obtained with an AEI model MS-9. Gas chromatographic separations were performed using a Varian-Aerograph model 1520-B. Melting points were measured on a Kofler hot stage microscope and are uncorrected. Spinning band distillations were carried out using a Nester-Faust 18-inch column with a platinum band.

The phrase "anhydrous diethyl ether" indicates Mallinckrodt analytical reagent grade diethyl ether from a freshly opened can. The silica gel used in thin and preparative layer work was PF_{254} "for preparative layer chromatography" from E. Merck. Where the eluting agent is a mixture of solvents, the proportions are given on a volume basis.

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Preparation of diiron enneacarbonyl (15)[38]

A solution of iron pentacarbonyl (50 ml, 73 grams, 0.37 mole, K & K) in glacial acetic acid (100 ml) was prepared in a pyrex flask. This was placed in a Rayonet photochemical reactor fitted with 16 lamps whose peak output is at 3750 Å. Provision was made for continuous purging with argon and for stirring. After approximately 12 hours irradiation a crop of bright orange platelets of (15) was collected by vacuum filtration of the photolysed solution. The orange solution was quickly returned to the reactor and purged with argon. If the photolysis solution was exposed to the air for more than five minutes, it took on a deep green hue. The collected crystals were quickly washed twice with absolute ethanol and then once with anhydrous diethyl ether, sucked dry and placed in a vacuum desiccator. Two more crops were collected at 12 hour intervals.

Yield: 42.5 grams; 61%.

An attempt to purify an aged sample of (15) was unsuccessful[38].

This reaction and all other reactions using iron carbonyls should be carried out in a hood as these compounds are particularly toxic to the lungs if vapors or dusts are inhaled[58].

Preparation of 3,4-dichlorocyclobutene (16)[39]

A solution of cyclooctatetraene (40 grams, 0.4 mole, BASF) in carbon tetrachloride (40 ml) was prepared under an atmosphere of nitrogen. Chlorine gas was introduced with vigorous stirring below the level of the liquid. The temperature of the reaction was held below 20° with an ice/water bath. Chlorine was added continuously until the rapid, exothermic uptake of gas ceased

58. N. I. Sax, "Dangerous Properties of Industrial Materials", Third Edition, Reinhold, New York, 1968, p 842.

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(ca. two hours). The sharp end point color change reported by Nenitzescu was not observed. The pale tan product was shaken with anhydrous potassium carbonate and then filtered into a flask containing dimethyl acetylenedicarboxylate (30 grams, 0.4 mole, Aldrich). The resultant solution was refluxed for three hours. The solvent was removed at the rotary evaporator. The resulting light brown oil was pyrolysed at 200° and distilled through a spinning band column in one operation. With the still pot at 200°, distillate was collected (bp = 35-110°/15 mm). This crude distillate was redistilled to give, after a forerun of cyclooctatetraene, 9.2 grams of the dichloride (16) boiling 66-68°/58 mm. Frequently this fractionation was complicated by the presence of trans,trans-1,4-dichlorobutadiene (bp = 60°/58 mm) which tended to solidify in the column head. The yield in this preparation was quite variable, ranging over 0-30%.

Physical Data
3,4-dichlorocyclobutene (16)

OBSERVED	LITERATURE
IR (neat)	IR (neat)[39]
3000	3000
1280	1300
1230	1250
1190	1200
1110	1120
1000	1010
910	910
NMR ($CDCl_3$)	NMR (neat)[59]
5.17 (t, 1, J = 1 Hz)	5.22 (t, 1, J = 1 Hz)
6.26 (t, 1, J = 1 Hz)	6.30 (t, 1, J = 1 Hz)
BP	BP[59]
66-68°/58 mm	79-80°/58 mm

59. S. Monti and R. B. Woodward, unpublished observations.

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Preparation of cyclobutadiene irontricarbonyl (17)[40]

A mixture of diiron enneacarbonyl (44 grams, 87 mmole), cis-3,4-dichlorocyclobutene (5.3 grams, 43 mmoles) and n-pentane (acid-washed and distilled under argon) was stirred and heated to 30° for five hours under an argon atmosphere. The cooled reaction mixture was then filtered under argon by gravity to remove suspended solids. The dark mud that remained in the reaction flask was washed several times with degassed pentane and these washings added to the filtrate. Care was taken since the residue was usually pyrophoric. At the rotary evaporator the pentane was removed from the filtrate leaving a dark red (or occasionally green) oil. This dark oil was promptly distilled using a one-piece micro still. After a forerun of orange iron pentacarbonyl (bp = 40°/15 mm), pale yellow cyclobutadiene irontricarbonyl (bp = 90-100°/15 mm) was collected.

Yield : 1.03 grams; 12%.

This reaction and all other reactions using iron carbonyls should be carried out in a hood since these compounds are particularly toxic to the lungs if vapors or dusts are inhaled[58].

Physical Data
cyclobutadiene irontricarbonyl (17)

OBSERVED	LITERATURE[37]
IR (neat)	IR
2070	2055
1960	1985
NMR (CCl_4)	NMR
3.90 (s)	3.91 (s)

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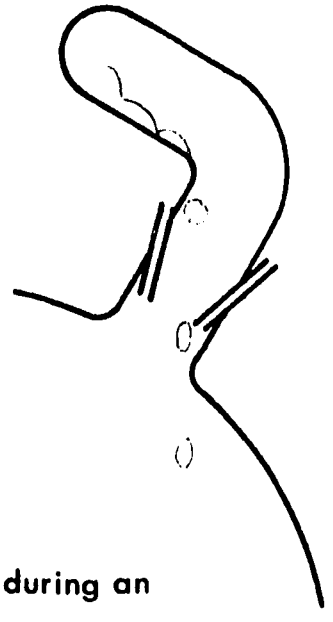
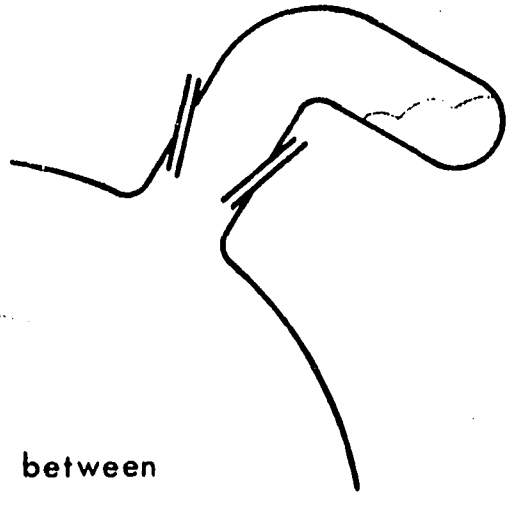
Preparation of 2-aldehydo (Dewar benzene) (22) [14]

A solution of cyclobutadiene irontricarbonyl (300 mg, 1.5 mmoles) and propargyl aldehyde [43] (0.61 ml, 600 mg, 11 mmoles) in methanol (20 ml, distilled under argon) was prepared under argon. Since propargyl aldehyde is a powerful lachrymator and since it is used in excess, it was convenient to measure it by volume (in a syringe) rather than by weight. Ceric ammonium nitrate (2.5 grams, 4.5 mmoles) was added to the stirred, 0° solution in small portions. To facilitate this operation an "L" shaped reservoir was fashioned from 10 mm id pyrex tubing. One end of this tube bore a 14/20 standard taper male joint; the other was sealed. In use, the solid to be added was placed in the closed end of the reservoir and the joint fitted to one of the slanted side necks of the three neck reaction flask. To make an addition the base of the "L" was rotated upward and tapped lightly if necessary to get the powder moving.



during an addition



between additions

This apparatus proved much more effective for small scale work than the commonly cited gooch tubing Erlenmeyer flask arrangement. The addition was made over a period of one hour. When

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the addition was complete the orange reaction mixture was allowed to warm to room temperature, diluted with water and extracted with pentane (acid washed and distilled). The pentane extract was dried with magnesium sulfate and concentrated with the rotary evaporator. Thin layer chromatography of the partially concentrated extract (on silica, eluted three times with petroleum ether/diethyl ether, 10/1) showed the aldehyde (22) $R_f = 0.53$, benzaldehyde $R_f = 0.59$, and only very small slower moving spots. If the chromatographed aldehydes were developed with 2,4-dinitrophenylhydrazine spray, (22) appeared red-brown while benzaldehyde appeared orange. After concentration was complete, NMR and TLC showed a much higher proportion of impurities. Samples of (22) isolated by preparative layer chromatography (same system) underwent substantial decomposition before they could be studied.

This reaction and all other reactions using iron carbonyls should be carried out in a hood since these compounds are particularly toxic to the lungs if vapors or dusts are inhaled [58].

Physical Data
2-aldehydo (Dewar benzene) (22)

OBSERVED		
IR (CCl_4)		
1690		
1650		
NMR (CCl_4)		
4.00 (s, 1)	6.56 (s, 1)	9.64 (s, 1)
4.01 (s, 1)	6.63 (s, 1)	
6.00 (s, 1)	7.45 (s, 1)	
$T_{1/2} \sim 3$ hrs/30°		

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Preparation of 2,3-dicarbomethoxy (Dewar benzene) (23) [14]

A solution of cyclobutadiene irontricarbonyl (250 mg, 1.2 mmoles), dimethyl acetylenedicarboxylate (0.55 ml, 850 mg, 6.0 mmoles, Aldrich) and methanol (20 ml, distilled under argon) was prepared under argon. Provision was made for addition of ceric ammonium nitrate (2.0 grams, 3.6 mmoles). The reaction mixture was chilled with an ice/water bath and stirred during the addition of the salt over a one hour period. The resulting orange solution was diluted with water and extracted with pentane. This extract was dried with magnesium sulfate and concentrated at the rotary evaporator. Thin layer chromatography (on silica, eluting with petroleum ether/diethyl ether 3/1) showed two spots (R_f = 0.4 and 0.2) The faster moving spot was shown to be identical with that obtained from dimethyl acetylenedicarboxylate. The crude material was subjected to preparative layer chromatography (silica, four elutions with petroleum ether/diethyl ether 10/1). The faster band was determined by TLC to be dimethyl acetylenedicarboxylate. The slower band (65 mg) was determined by NMR to be slightly impure 2,3-dicarbomethoxy (Dewar benzene). This material was rechromatographed (silica, one elution with petroleum ether/diethylether 3/1) to give a clear, colorless oil that was immediately taken up in a minimal amount of chloroform-d and transferred to an NMR tube for thermal rearrangement study.

Physical Data
2,3-dicarbomethoxy (Dewar benzene) (23)

OBSERVED	LITERATURE [14]
NMR ($CDCl_3$)	NMR
3.80 (s, 3) 3.99 (s, 1) 6.59 (s, 1)	3.75 (s, 3) 3.98 (s, 1) 6.61 (s, 1)
$T_{1/2}$: 2 hrs/30°	$T_{1/2}$ < 0.5 hr/90°

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Preparation of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (26)

This material was prepared by the method of Criegee[45]. The butyne used was either obtained commercially (Farchan) or prepared by the method of Stoll and Rcuve[60]. To prepare butyne-2 by this method in quantities over 50 grams was laborious.

Physical Data
3,4-dichloro-1,2,3,4-tetramethylcyclobutene (26)

OBSERVED	LITERATURE[61]
IR (CCl_4)	IR
3000	3000
1690	1690
1430	1430
1360	
1060	
1040	
NMR ($CDCl_3$)	NMR
1.63 (s, 1)	1.85 (s, 1)
1.80 (s, 1)	2.01 (s, 1)
MP	MP
56-57°	57-58°

Preparation of trans-3,4-dihydroxy-1,2,3,4-tetramethylcyclobutene (27)[46,61]

To a stirred solution of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (123 grams, 0.68 mole) in tetrahydrofuran (500 ml), water (200 ml) was added dropwise over a period of one hour. Stirring was continued at room temperature for two additional hours. The tetrahydrofuran was then removed at the rotary evaporator. The resulting aqueous solution was neutralized with potassium car-

60. M. Stoll and A. Rouve, Helv.Chem. Acta., 21, 1542, (1938).
61. R. Criegee and G. Louis, Chem. Ber., 90, 417, (1957).

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bonate and finally extracted several times with cyclohexane. On concentration and cooling of this solution, 20.0 grams of fluffy, iridescently white crystals of (27) were obtained.

After several attempts to bring about further crystallization from solution failed, the concentrated mother liquors, now a dark paste, were transferred to a sublimator. After tedious removal of residual solvent, sublimation at 60°/0.1 mm produced 60 grams of oily white solid.

The NMR spectrum of the sublimate showed singlets of equal intensity at δ = 1.20 and 1.60, the locations of resonances in the NMR spectrum of the trans-3,4-dihydroxy-1,2,3,4-tetramethylcyclobutene crystallized from cyclohexane. In addition the spectrum of the sublimate showed a pair of singlets at δ = 1.17 and 1.50. These latter peaks were equal in intensity to one another, but each somewhat less intense than the pair assigned to the trans diol.

The tentative identification of the sublimate as a mixture of cis and trans diols was confirmed by its transformation to the diiodide (29) in yield comparable to that of the crystalline trans diol.

Total yield: 80 grams; 80%.

Physical Data
trans-3,4-dihydroxy-1,2,3,4-tetramethylcyclobutene (27)

OBSERVED	LITERATURE[46]
IR (KBr)	
3300-3500	
3000	
1430	
1360	
1170	
1090	
1040	

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Physical Data

trans-3,4-dihydroxy-1,2,3,4-tetramethylcyclobutene (27) (Cont.)

OBSERVED	LITERATURE[46]
NMR ($CDCl_3$)	
1.27 (s,1) 1.57 (s,1)	
MP (from cyclohexane)	MP
90-91°	90-91°

Preparation of 3,4-diiodo-1,2,3,4-tetramethylcyclobutene (28)[46]

A solution of 3,4-dihydroxy-1,2,3,4-tetramethylcyclobutene (17.3 grams, 0.122 mole) in chloroform (100 ml) was cooled to -20° with a dry ice/carbon tetrachloride bath. After the stirred solution had been purged with nitrogen, a mixture of nitrogen and anhydrous hydriodic acid (Matheson) was passed into the reaction vessel for a few minutes. Additional portions of hydriodic acid diluted with nitrogen were added at 15 minute intervals for two hours. A positive flow of nitrogen was maintained between additions. During the reaction period the temperature was held at -20°. Unreacted hydriodic acid was blown from the reaction vessel with nitrogen and the reddish solution allowed to warm to room temperature. The water present was removed with sodium sulfate. The dried solution was filtered and concentrated at the rotary evaporator. The resulting red oil was dissolved in acetone (100 ml) by heating on the steam bath. On cooling with dry ice/acetone, crystals formed. These were isolated on a sintered glass funnel, washed with cold diethyl ether (10 ml) and sucked dry using dental dam. This diiodide was used immediately to prepare the tricyclic bromoanhydride (30).

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Yield: 23 grams; 52%.

Preparation of dibromomaleic anhydride (29)[47]

Dibromomaleic acid (100 grams, 0.36 mole, Eastman) was added in small portions to acetyl chloride (150 ml) containing two drops of sulfuric acid. Immediately a brisk evolution of gas began. After the reaction was complete, acetic acid and excess acetyl chloride were removed at the rotary evaporator. The crude crystals were sublimed at 80°/0.1 mm. This gave 90.5 grams (97% of theory) of hard yellow crystals melting 118-119°.

Physical Data
dibromomaleic anhydride

OBSERVED	LITERATURE[47]
IR (KBr)	
1870	
1780	
1600	
1225	
1175	
930	
MP	MP
118-119°	118-119°

Preparation of 2,3-dibromo-1,4,5,6-tetramethylbicyclo(2,2,0)hex-5-ene-endo-cis-2,3-dicarboxylic acid anhydride (30)[16]

A mixture of freshly prepared 3,4-diiodo-1,2,3,4-tetramethylcyclobutene (23 grams, 0.064 mole), mercury (63 grams, 0.32 gram atom), dibromomaleic anhydride (31 grams, 0.12 mole) and anhydrous diethyl ether (200 ml) was stirred for 36 hours under nitrogen with enough vigor to form small droplets of

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mercury. During this time a fine green solid formed. The reddish ether solution was filtered and the green residue transferrred to a flask in which it was refluxed in tetrahydrofuran (100 ml) for five minutes. The tetrahydrofuran was decanted. The extraction of the residue was repeated three more times. The ether solution and the combined tetrahydrofuran extracts were placed in a refrigerator for 12 hours. From these cooled solutions 7.4 grams of the tricyclic bromoanhydride (30) were isolated. The combined mother liquors were concentrated to dryness and taken up in tetrahydrofuran. This led to a second crop of (30).

Yield: 11.3 grams; 48%.

Physical Data
2,3-dibromo-1,4,5,6-tetramethylbicyclo (2,2,0)hex-5-ene-endo-cis-2,3-dicarboxylic acid anhydride (30)

OBSERVED	LITERATURE[16]
IR (KBr)	IR ($CHCl_3$)
3000 1860 1790 1680 1430 1370 1200 980- 920	1865 1790 1670
NMR ($CDCl_3$)	NMR ($CDCl_3$)
1.35 (s, 1) 1.62 (s, 1)	1.36 (s, 1) 1.61 (s, 1)
MP	MP
161-162°	161-163°

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Preparation of 2,3-dibromo-1,4,5,6-tetramethylbicyclo(2,2,0)hex-5-ene-endo-cis-dicarboxylic acid dimethylester (32) [16]

To a flask containing sodium methoxide (1.7 grams, 31 mmoles) in methanol (50 ml) was added in one portion tricyclic bromo-anhydride (30) (11.3 grams, 31 mmoles). The resultant solution was stirred at room temperature for ten minutes. The solvent was then removed at the rotary evaporator. The crude sodium salt of the half ester (31) was taken up in water (50 ml) and precipitated by the addition of 2 N sulfuric acid (50 ml). The crude half ester was then extracted into diethyl ether. The pale tan ether extract was dried with sodium sulfate and chilled to 0^{o}. An ether solution of diazomethane was added until no further evolution of gas was observed. Removal of ether at the rotary evaporator gave crude diester (32) which was used without purification.

Yield: 10.8 grams.

Physical Data
2,3-dibromo-1,4,5,6-tetramethylbicyclo
(2,2,0)hex-5-ene-endo-cis-dicarboxylic acid dimethylester (32)

OBSERVED	LITERATURE [16]
IR (KBr)	IR
2960 1730 1675 1420 1360 1220 - 1240	1740 1675
NMR ($CDCl_3$)	NMR (CCl_4)
1.35 (s, 1) 1.62 (s, 1) 3.75 (s, 1)	1.33 (s, 1) 1.58 (s, 1) 3.68 (s, 1)
MP (crude)	MP
$90-97^{o}$	104^{o}

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Preparation of 2,3-dicarbomethoxy-1,2,5,6-tetramethyl (Dewar benzene) (25)[16]

A mixture of the dibromo diester (32) (250 mg) and freshly prepared zinc copper couple[48] (200 mg) in anhydrous diethyl ether (10 ml) was stirred and heated at reflux for 50 minutes. After the reaction mixture had cooled to room temperature, solids were removed by filtration. The filtrate was washed with 0.2 M hydrochloric acid, water, and saturated sodium chloride solution, then dried. The dry ether solution was concentrated to a tan oil at the rotary evaporator. On heating at 120° for three hours the diester (25) was converted to a crystalline solid. The identity of this solid was determined by NMR (observed : δ = 3.77 and 2.26 in the ratio 1:2 in CCl_4 ; literature : δ = 3.75 and 2.20 in the ratio 1:2 in CCl_4) and, after preparative layer chromatography (on silica, eluted three times with diethyl ether/petroleum ether 1/10) and recrystallization from n-heptane, melting point (observed : 126-127°; literature : 127°) to be dimethyl tetramethylphthalate.

Purification of the crude Dewar benzene (25) was effected by preparative layer chromatography (silica, four elutions diethyl ether/petroleum ether 1/10). Under these conditions (25) has an R_f = 0.4 while the dibromide (32) has an R_f = 0.5. From this procedure 2,3-dicarbomethoxy-1,4,5,6-tetramethyl (Dewar benzene) free of impurities as judged by TLC and NMR was obtained.

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Physical Data
2,3-dicarbomethoxy-1,4,5,6-tetramethyl
(Dewar benzene) (25)

OBSERVED	LITERATURE
IR (thin film) 3000 1740 1710 1630 1430 1300 1260 1240 1220 990	
NMR ($CDCl_3$) 1.30 (s, 1) 1.65 (s, 1) 3.82 (s, 1)	
MP oil	MP[16] 32-33°
$T_{1/2}$ ~ 17 min/115°	$T_{1/2}$: 2 hrs/98°

Preparation of 2,3-di-2(2-hydroxypropyl)-1,4,5,6-tetramethyl (Dewar benzene) (38)[19]

A stock methylmagnesium iodide solution was prepared using amounts of diethyl ether and methyl iodide calculated to yield a 2 M solution. Magnesium turnings were used in 10% excess of the theoretical amount. This reagent, when stored in a serum capped brown glass bottle, was active for several months.

A solution of 2,3-dicarbomethoxy-1,4,5,6-tetramethyl (Dewar benzene) (71 mg, 3 mmole) in anhydrous diethyl ether (10 ml)

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under argon was cooled to -30° in a dry ice/carbon tetrachloride bath. To this solution 2 M methylmagnesium iodide solution (4 ml) was added in one portion. After 15 minutes stirring, the solution was allowed to warm to room temperature. The solution was then heated at reflux for 15 minutes under argon. After the solution cooled to room temperature, decomposition of excess Grignard reagent and hydrolysis were brought about by the addition of saturated aqueous ammonium chloride. The resulting two-phase system was extracted three times with diethyl ether. The combined ether extracts were dried with sodium sulfate and concentrated at the rotary evaporator. The crude oil was promptly subjected to purification by preparative layer chromatography (silica, eluted two times with petroleum ether/diethyl ether 2/1). Using this system, the diol (38) has an $R_f = 0.1$ per elution. NMR showed that the crystals obtained from this treatment contained some impurities. Therefore the partially purified diol was rechromatographed using four elutions with the same solvent absorbent system. NMR now showed pure diol (38). This material was recrystallized once from n-heptane to give long, perfectly white needles. This crystalline material was used in thermolysis study.

Physical Data
2,3-di-2(2-hydroxypropyl)-1,4,5,6-tetramethyl
(Dewar benzene) (38)

OBSERVED	LITERATURE[19]
IR (KBr)	IR (CCl_4)
3400	
3000	
1680	1680
1650	1640
1430	
1370	
1350	
1260	
1200	
1160	

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Physical Data
2,3-di-2(2-hydroxypropyl)-1,4,5,6-tetramethyl
(Dewar benzene) (38) (Cont.)

OBSERVED	LITERATURE[19]
NMR (pyridine-d_5)	NMR (pyridine)
1.10 (s, 1)	1.19 (s, 1)
1.37 (s, 1)	1.46 (s, 1)
1.45 (s, 1)	1.54 (s, 1)
1.54 (s, 1)	1.61 (s, 1)
($CDCl_3$)	($CDCl_3$)
1.16 (s, 1)	1.12 (s, 1)
1.34 (s, 1)	1.31 (s, 1)
1.40 (s, 1)	1.37 (s, 1)
1.63 (s, 1)	1.60 (s, 1)
MP	MP
136-137°	136-137°
$T_{1/2} \sim 40$ min/200°	$T_{1/2}$: 1 hr/200°

Preparation of 2,3-dicarbomethoxy-1,4,5,6-tetramethylbicyclo (2,2,0)hexene-5 (33)

In a flask were placed dibromodiester (32) (9.8 grams, 23 mmoles), freshly prepared zinc-copper couple[48] (10 grams), and anhydrous diethyl ether (200 ml). This mixture was stirred vigorously at reflux for fifty minutes. The ether solution was filtered into a separatory funnel where it was extracted with 0.2 N HCl, water and finally saturated aqueous sodium chloride. This extracted solution was dried with sodium sulfate and concentrated at the rotary evaporator. The resulting yellow oil was subjected to molecular distillation (0.1 mm/bath temperature 90°). This yielded a pale yellow oil which deposited white crystals on standing at 0°.

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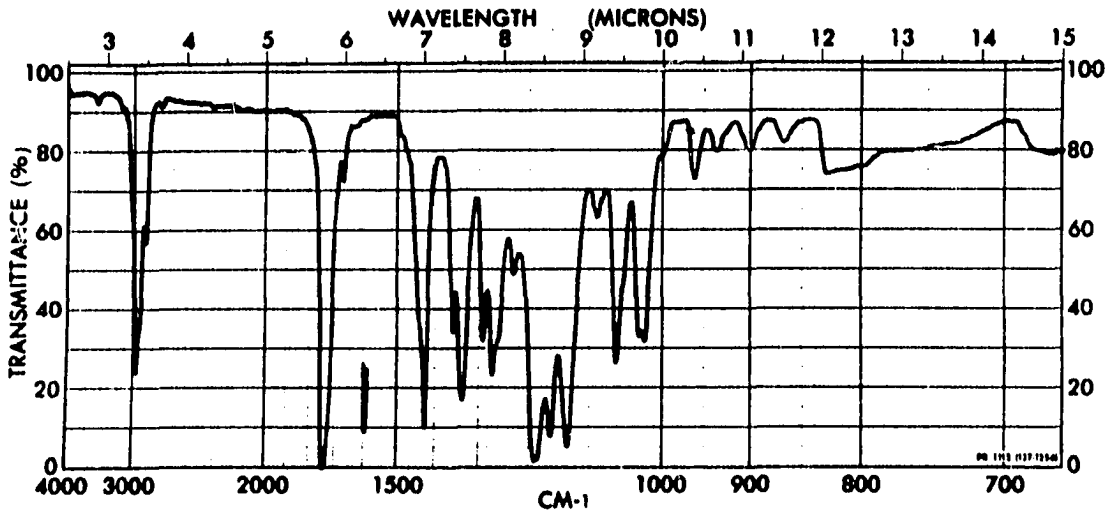
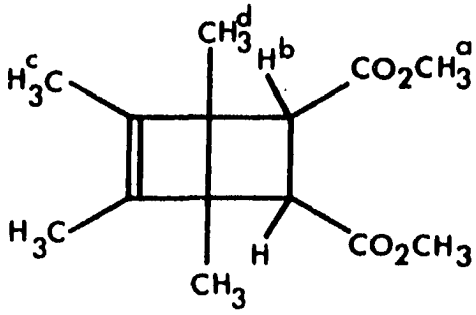




$H^a = 3.56\ \delta$

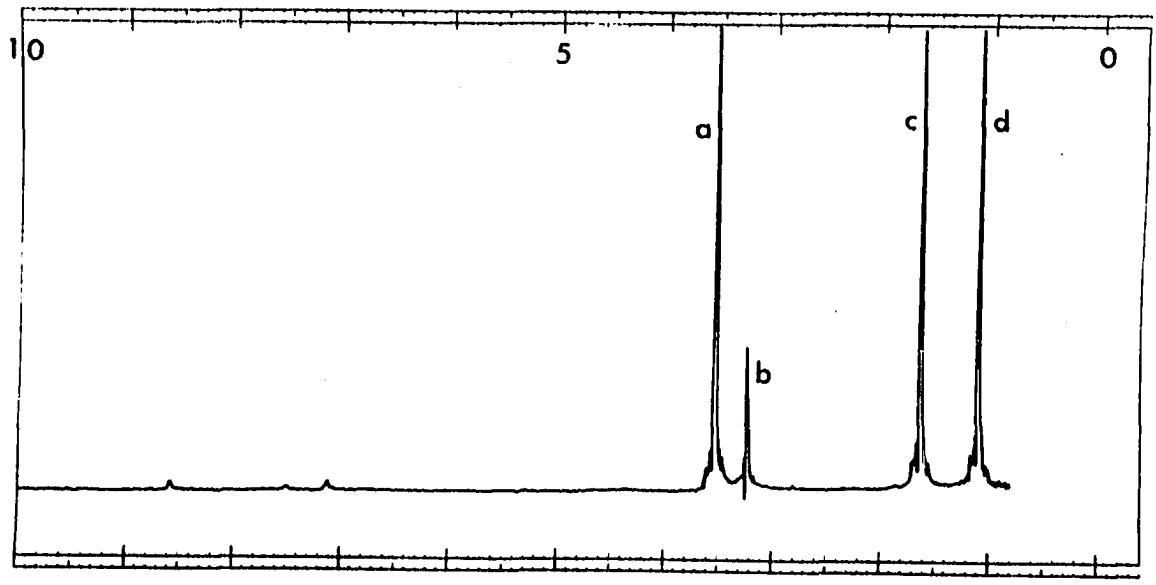
$H^b = 3.25\ \delta$

$H^c = 1.65\ \delta$

$H^d = 1.10\ \delta$

NMR in pyridine-d_5

IR in CCl_4



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These crystals were isolated by filtration and recrystallized from acetone/water. Large prismatic crystals which melted 58-60° formed at -40°.

Yield of oil and crystals: 3.0 grams.

The identity of this compound was established by NMR, IR, and mass spectra and by mass spectrometric determination of exact mass.

Exact Mass:

Calculated ($C_{14}H_{20}O_4$) : 252.1361

Observed : 252.1351

Mass Spectrum:

M/e	ra
252	8
193	29
161	15
149	30
134	45
133	56
119	35
108	100
105	23
93	24
91	30
77	26
59	32
53	15

Preparation of 1-t-butyl-cis-3,4-carbonyldioxycyclobutene-1 (57)[57]

A well-type photochemical reactor was charged with acetone (200 ml, freshly distilled under nitrogen), vinylene carbonate (2.0 grams, 23 mmoles, Aldrich) and t-butylacetylene (10.0 grams 122 mmoles, Farchan). The resulting solution was cooled with water flowing in the lamp's quartz cooling jacket, stirred and purged with nitrogen for one hour. Photolysis (Hanovia 450 watt medium pressure mercury lamp) was then begun. The reaction was monitored by the replacement of the infrared car-

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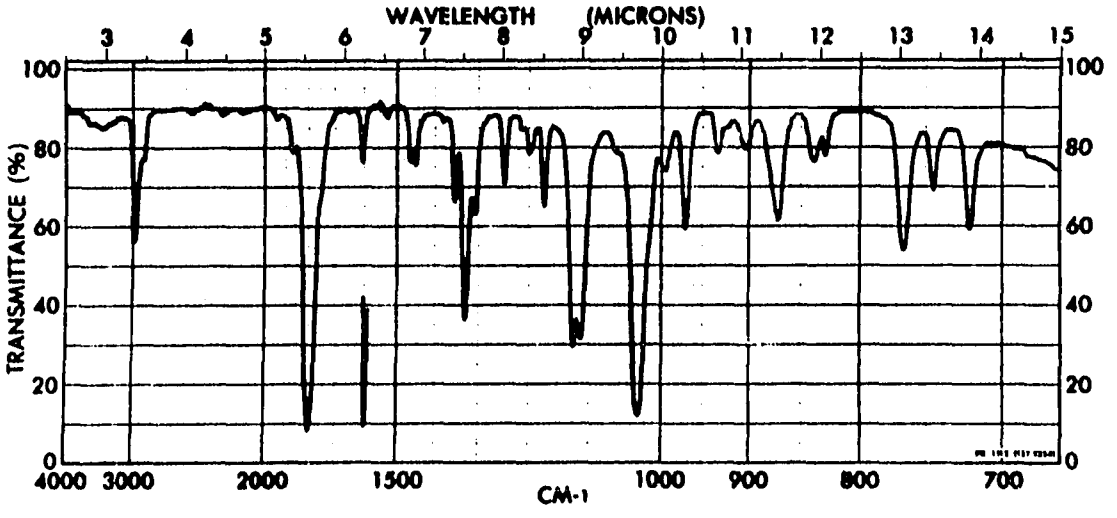
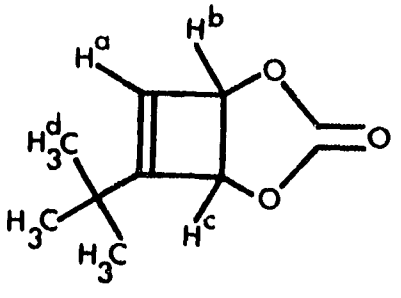




$H^a = 6.30\ \delta$

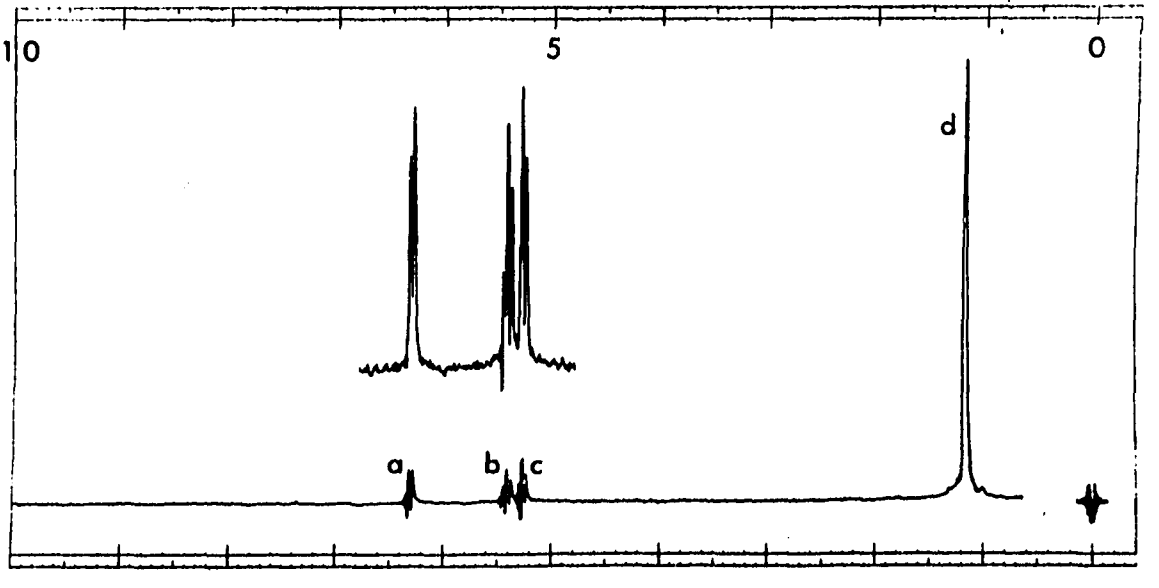
$H^b = 5.42\ \delta$

$H^c = 5.27\ \delta$

$H^d = 1.18\ \delta$

NMR in $CDCl_3$

IR of neat liquid



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bonate absorption of vinylene carbonate at 1840 cm^{-1} with that of the cyclobutene carbonate (57) at 1800 cm^{-1}. After two hours the reaction was complete. The clear solution was transferred to a flask for solvent removal at the rotary evaporator. A fine white solid (vinylene carbonate dimer [62]) was removed from the resulting yellow oil by filtration. The solution was distilled to give pale yellow cyclobutene carbonate (57) that boiled 136-137°/ 1 mm. For analytical purposes, clear, colorless oil could be obtained by gas chromatography (12 ft. x 1/4 in., 15% DEGS on Cromosorb S; oven temperature 170°).

Yield: 2.37 grams, 60%.

The identity of this compound was established by NMR, IR, and mass spectra and by combustion analysis.

Combustion Analysis :

	C	H
Calculated ($C_9H_{12}O_3$) :	64.27	7.19
Observed :	64.00	7.27

Mass Spectrum :

M/e	ra
109	100
81	22
67	16
57	41
55	24
53	22
44	15
43	68
41	56

Thermolysis of 2-aldehydo(Dewar benzene) (22)

Experimental :

A sample of 2-aldehydo (Dewar benzene) was taken up in a minimal amount of carbon tetrachloride and transferred to an NMR tube. The tightly capped tube was stored at -40° until the re-

62. W. Hartmann, ibid., 101, 1643, (1968).

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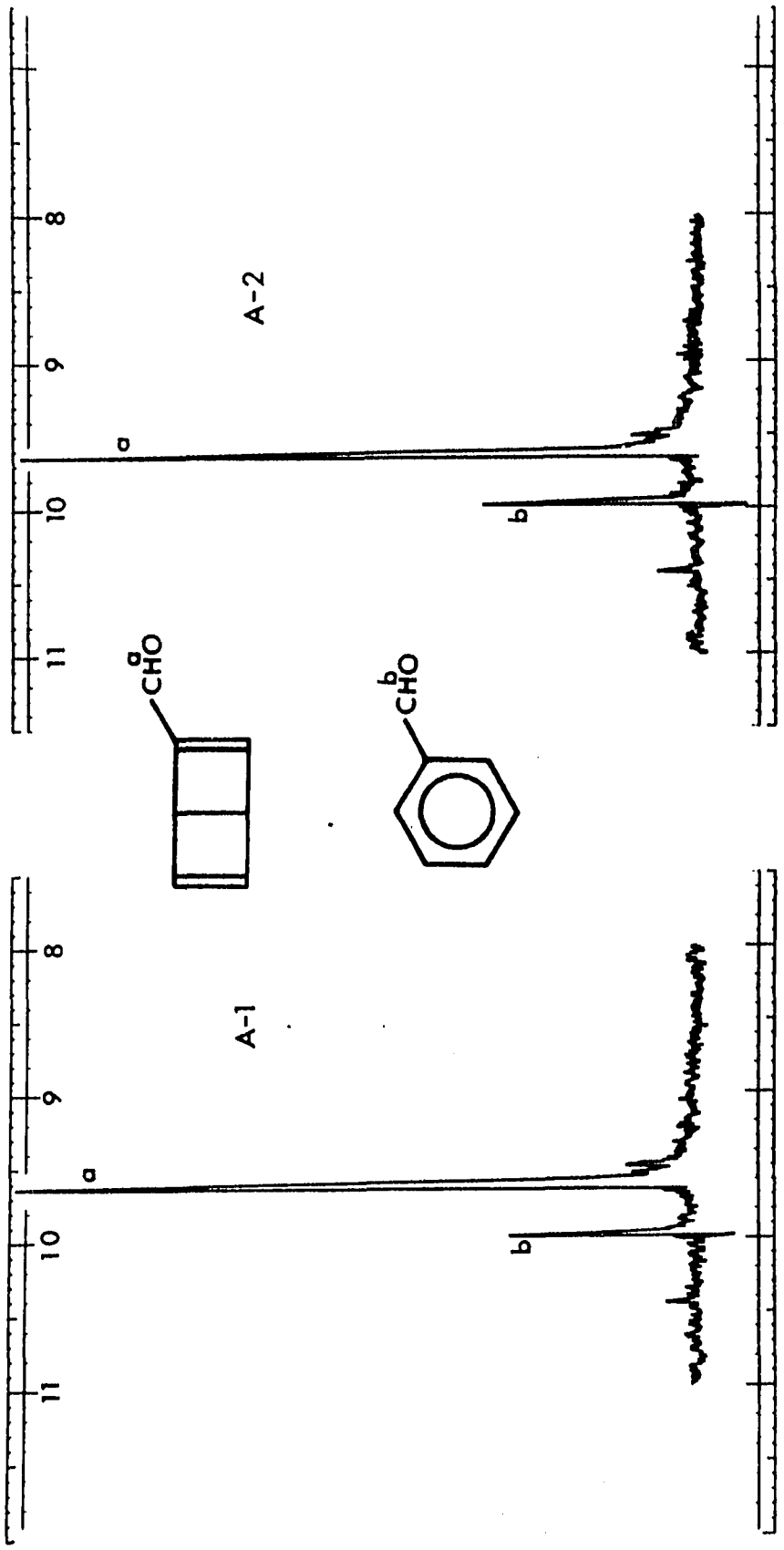

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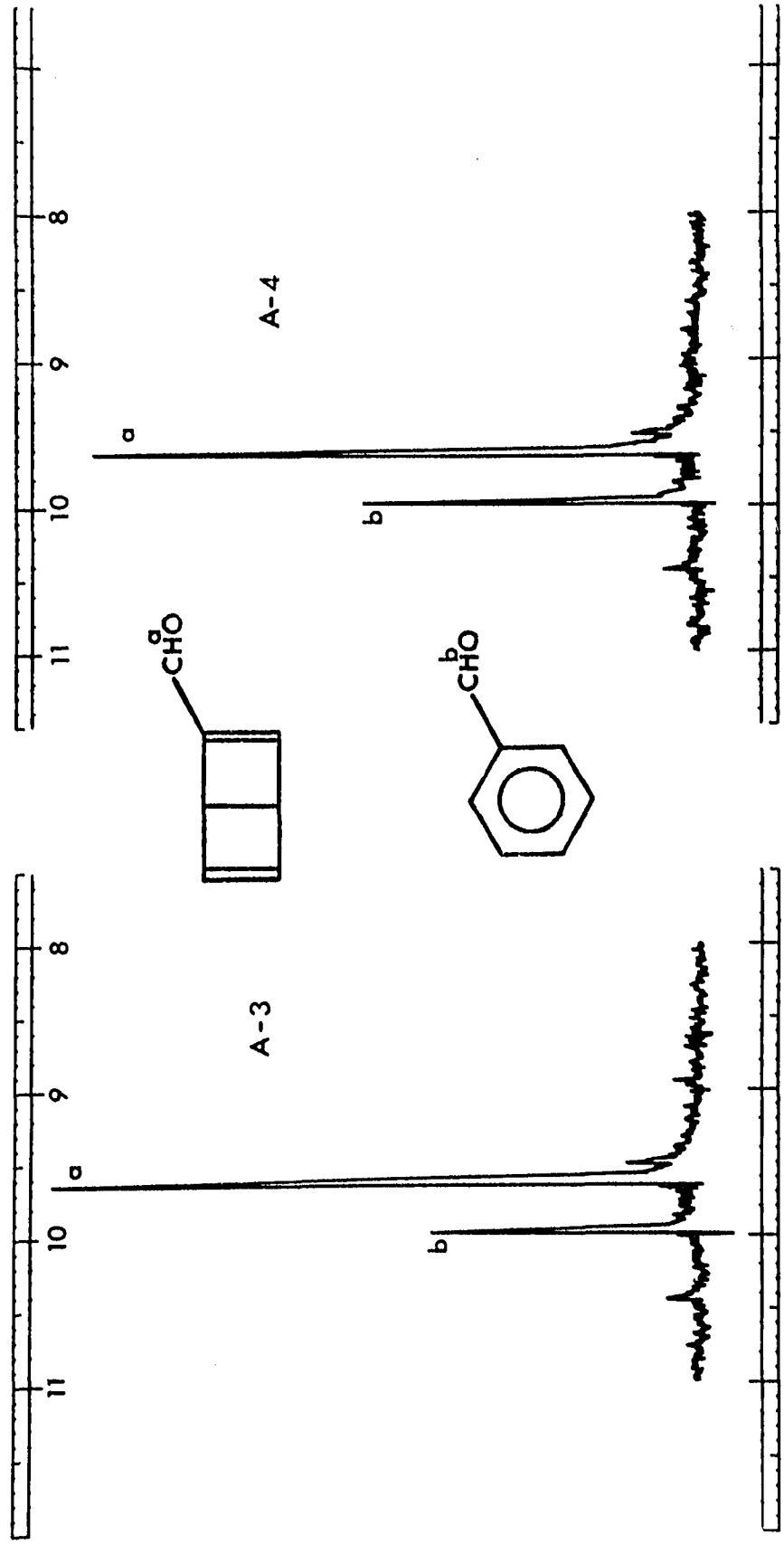

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arrangement was to begin. The sample was brought to room temperature and placed in the probe of the NMR spectrometer. After initial optimization of the spectrum, the spectrometer controls were left untouched and the sample was not removed from the probe. Nine spectra were taken at 30-minute intervals (spectra A-1 to A-9). Another spectrum (A-10) was taken of the same solution five days later.

Results :

Spectrum A-1 shows resonances at $\delta = 9.64$, 9.98, and 10.44. These resonances correspond to 2-aldehydo(Dewar benzene), benzaldehyde, and propargyl aldehyde, respectively. An unidentified resonance is also present at $\delta = 9.50$. Examination of spectra A-1 through A-9 shows a steady decay of the resonance at $\delta = 9.64$ and an enhancement of that at $\delta = 9.98$, while those at $\delta = 9.50$ and 10.44 remain unchanged. No evidence for any transient species is seen. Spectrum (A-10) shows complete aromatization of the Dewar benzene but no change in the other two resonances.

Thermolysis of 2,3-dicarbomethoxy(Dewar benzene) (23)

Experimental :

A sample of twice-chromatographed 2,3-dicarbomethoxy(Dewar benzene) in chloroform-d was placed in the probe of the NMR spectrometer. After initial optimization of the spectrum, the controls were left untouched. The spectrum was scanned without removing the sample from the probe at 30-minute intervals for four and one half hours (spectra B-1 to B-9). Another spectrum was obtained after an additional four hours at room temperature.

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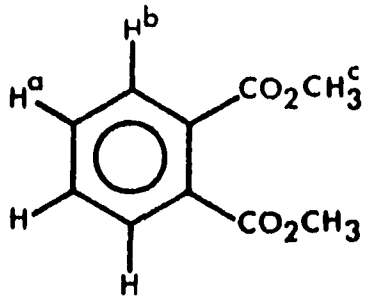
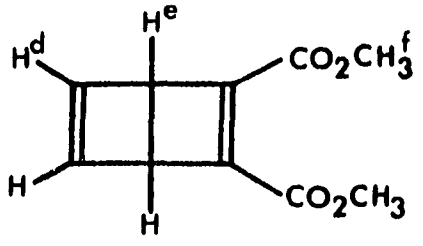
Results :

Spectrum B-1 shows resonances corresponding to 2,3-dicarbomethoxy (Dewar benzene) (δ =3.80, 3.99 and 6.59) and dimethyl phthalate (δ = 3.89 and 6.7). Three additional resonances in the spectrum (δ = 3.32, 3.65 and 6.32) are tentatively identified as 1,6-dicarbomethoxytetracyclo(4,4,0, $0^{2,5}$,$0^{7,10}$)deca-3,8-diene [63]



H^a } 7.6
H^b }

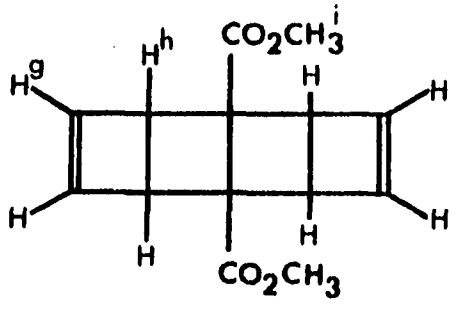
H^c = 3.89



H^d = 6.59

H^e = 3.99

H^f = 3.80



H^g = 6.32

H^h = 3.32

H^i = 3.65

The sequence of spectra B-1 to B-10 shows a steady decay of the Dewar benzene derivative together with an enhancement of the aromatic isomer. No change in the intesity of the other peaks is seen. No new or transient resonances are observed.

63. R. Pettit, Chem. and Engn. News, 43, No. 34, 38, (1966).

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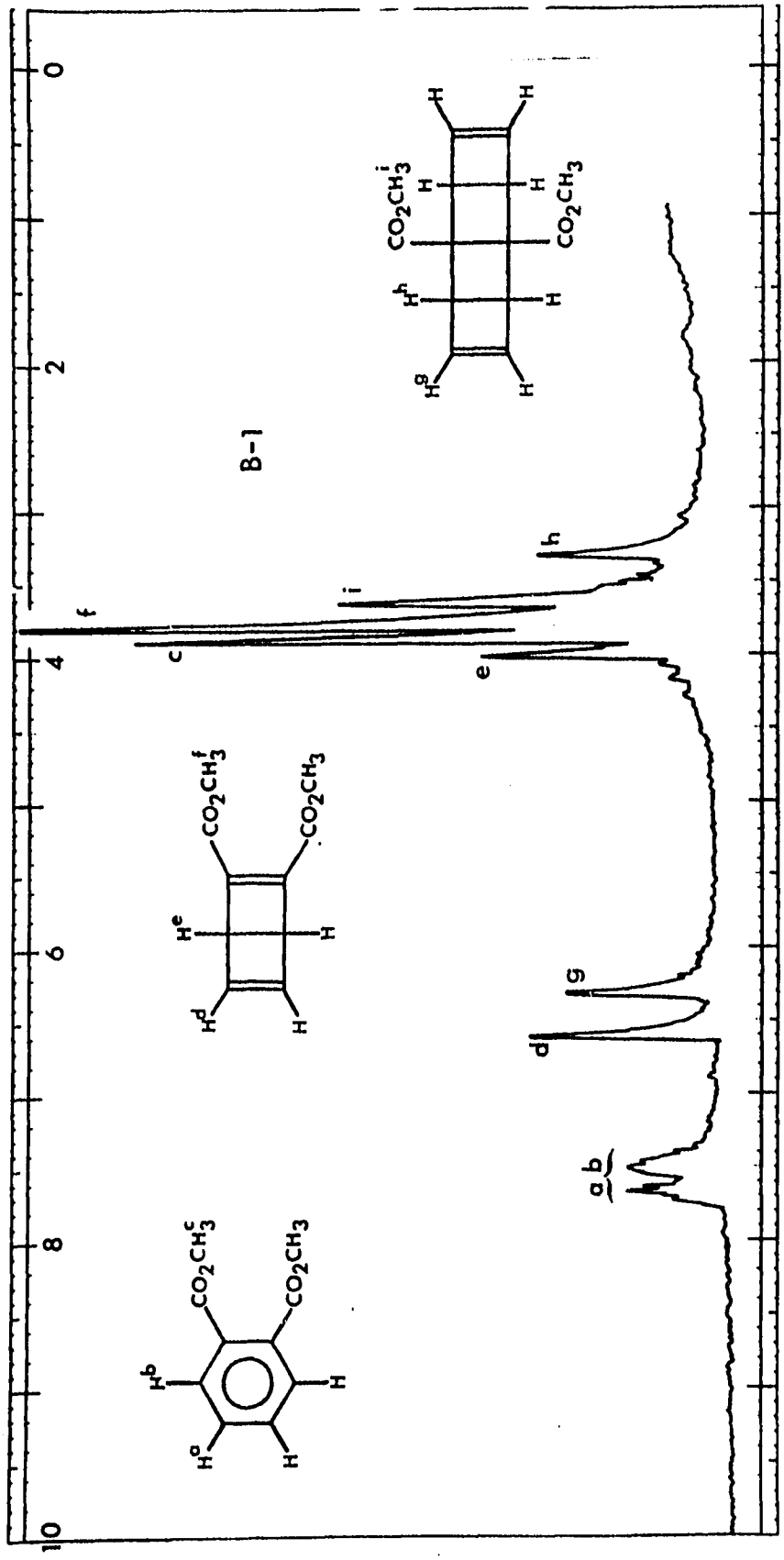

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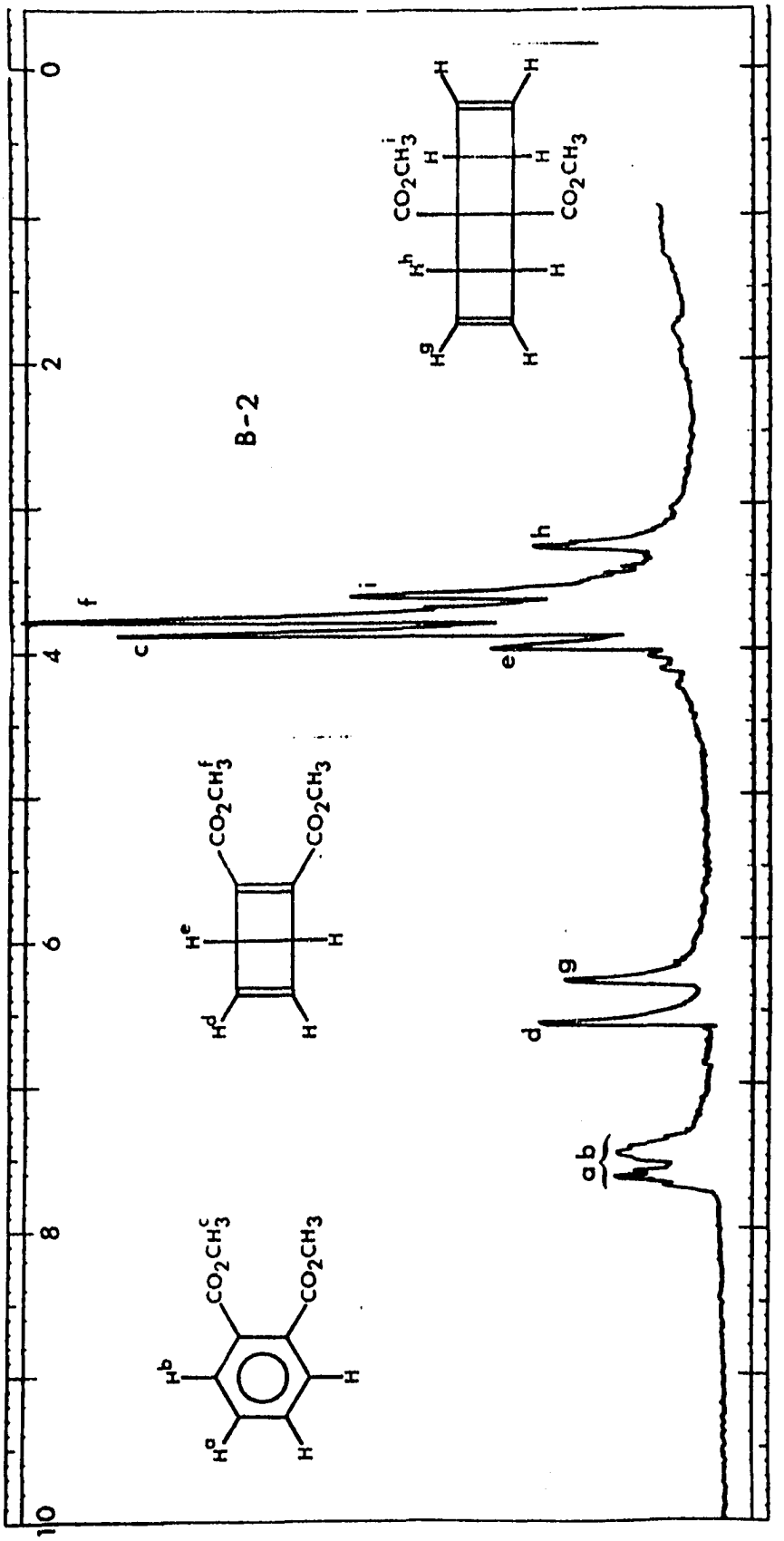

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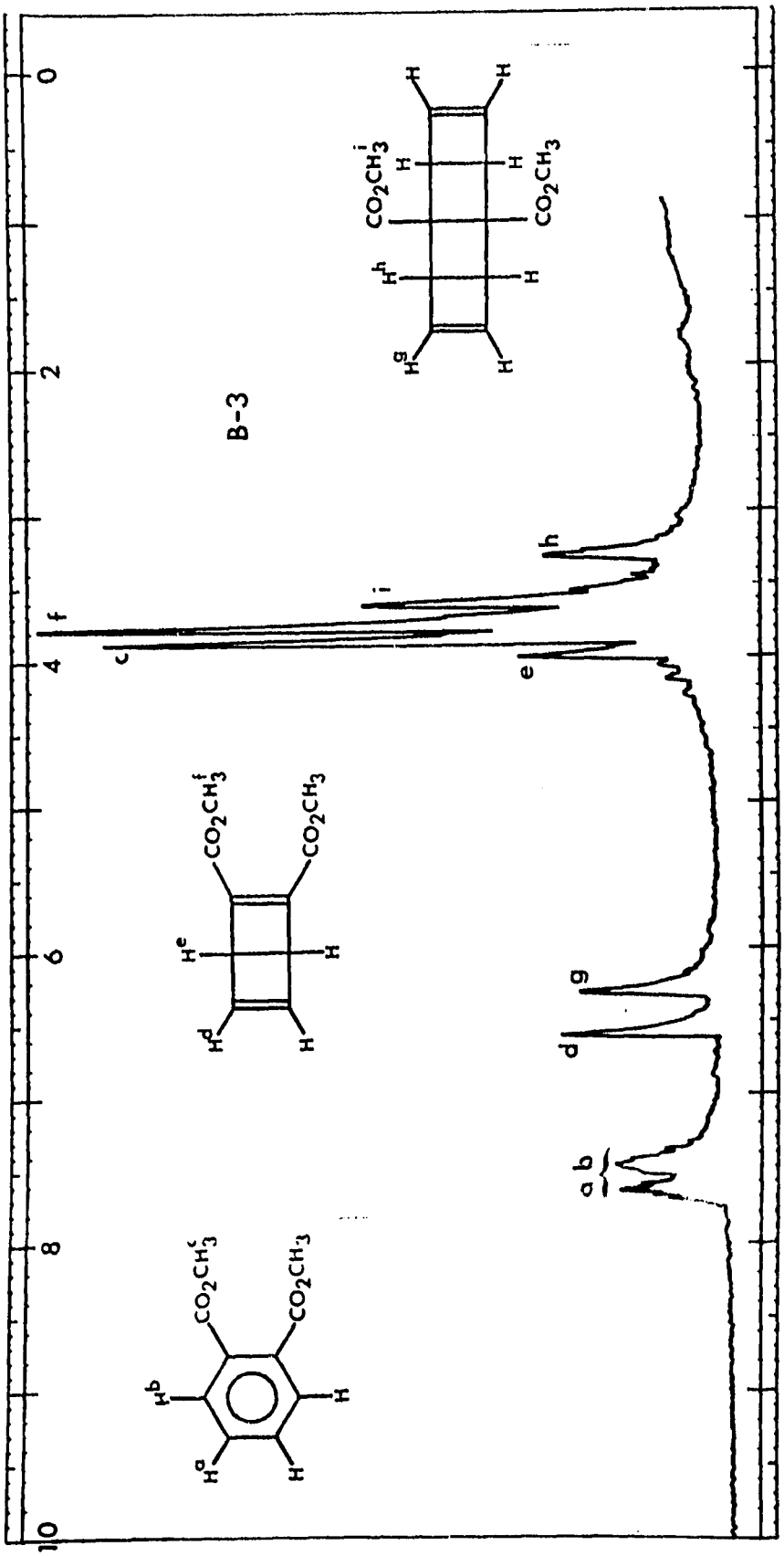

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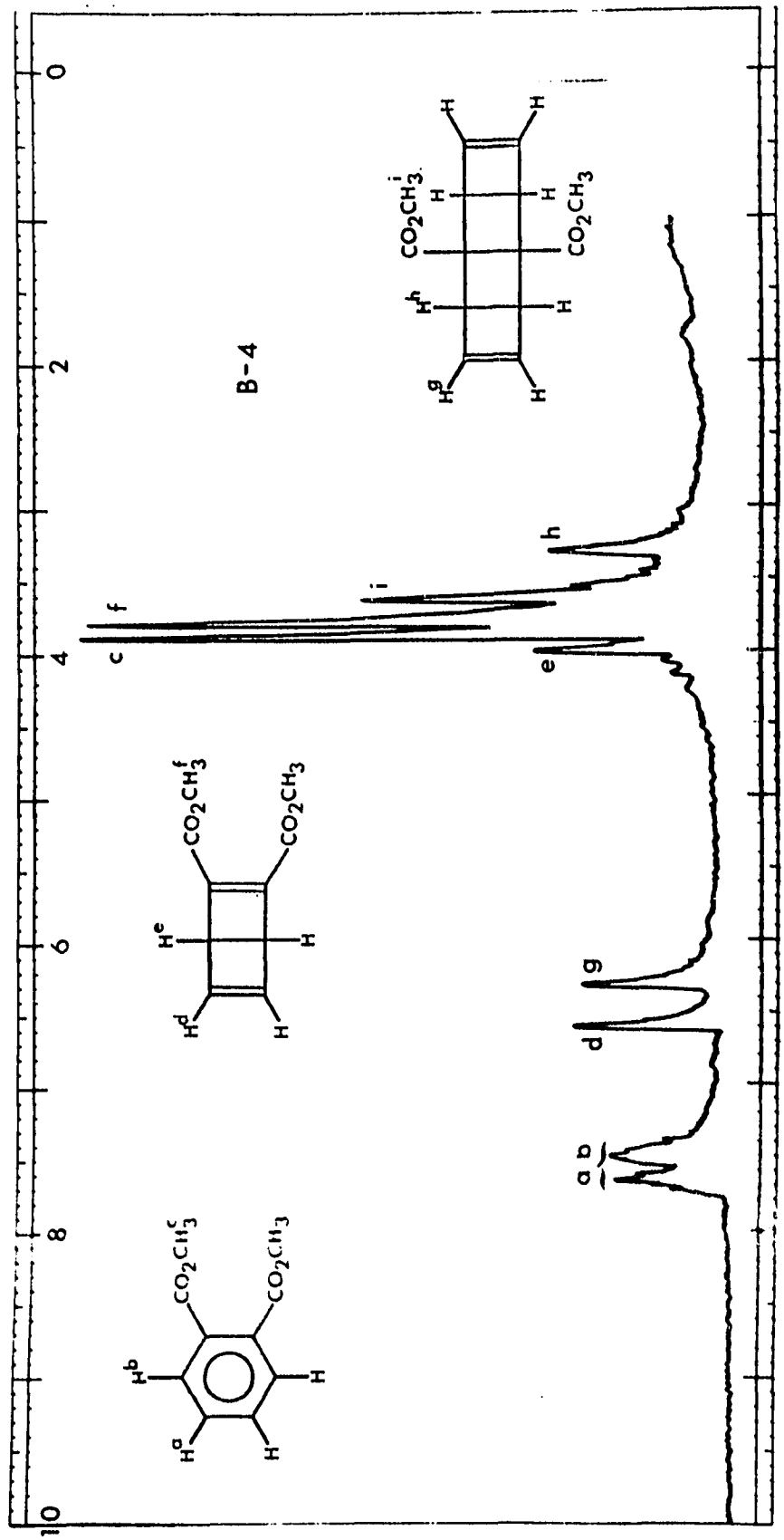

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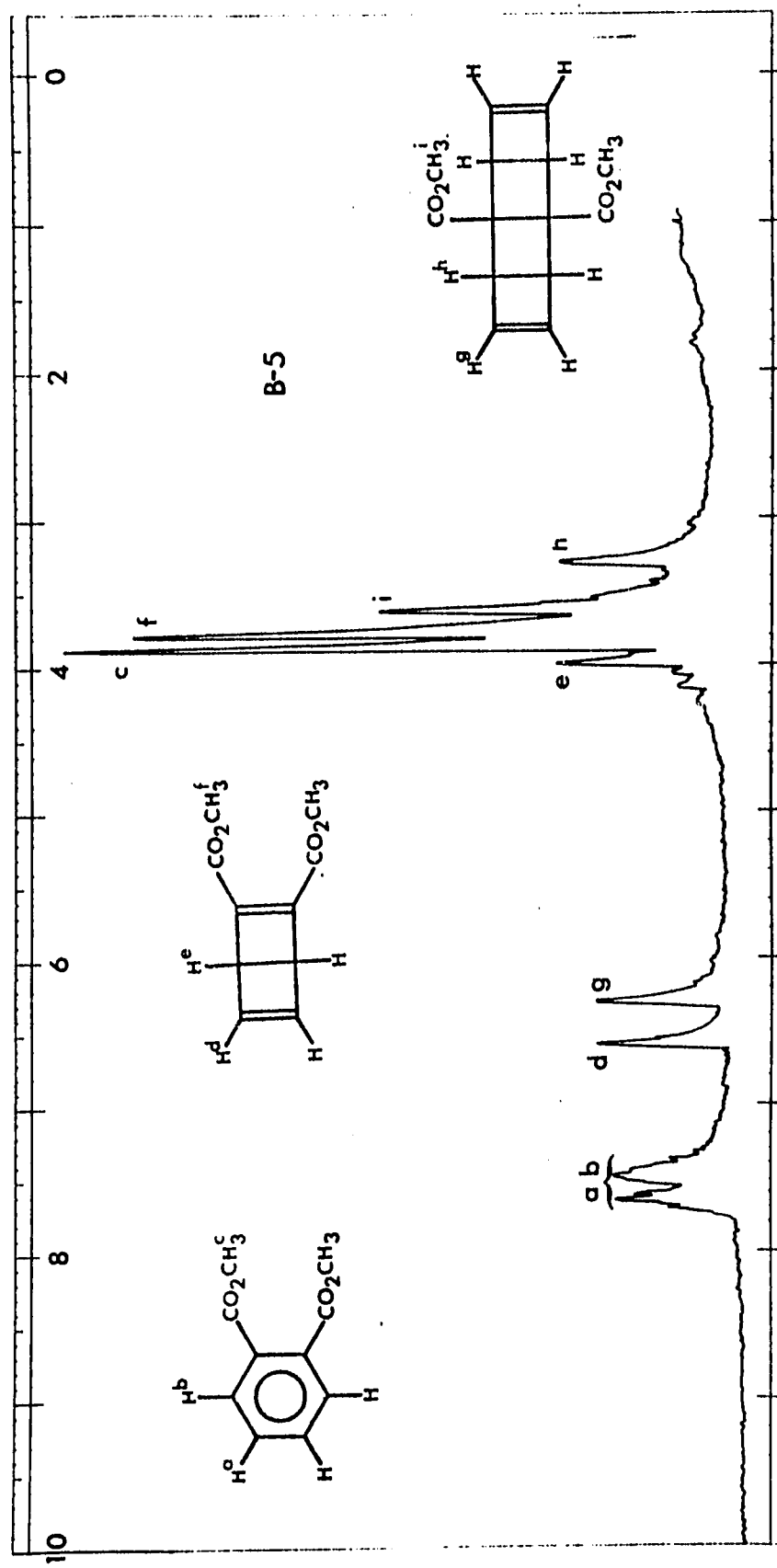

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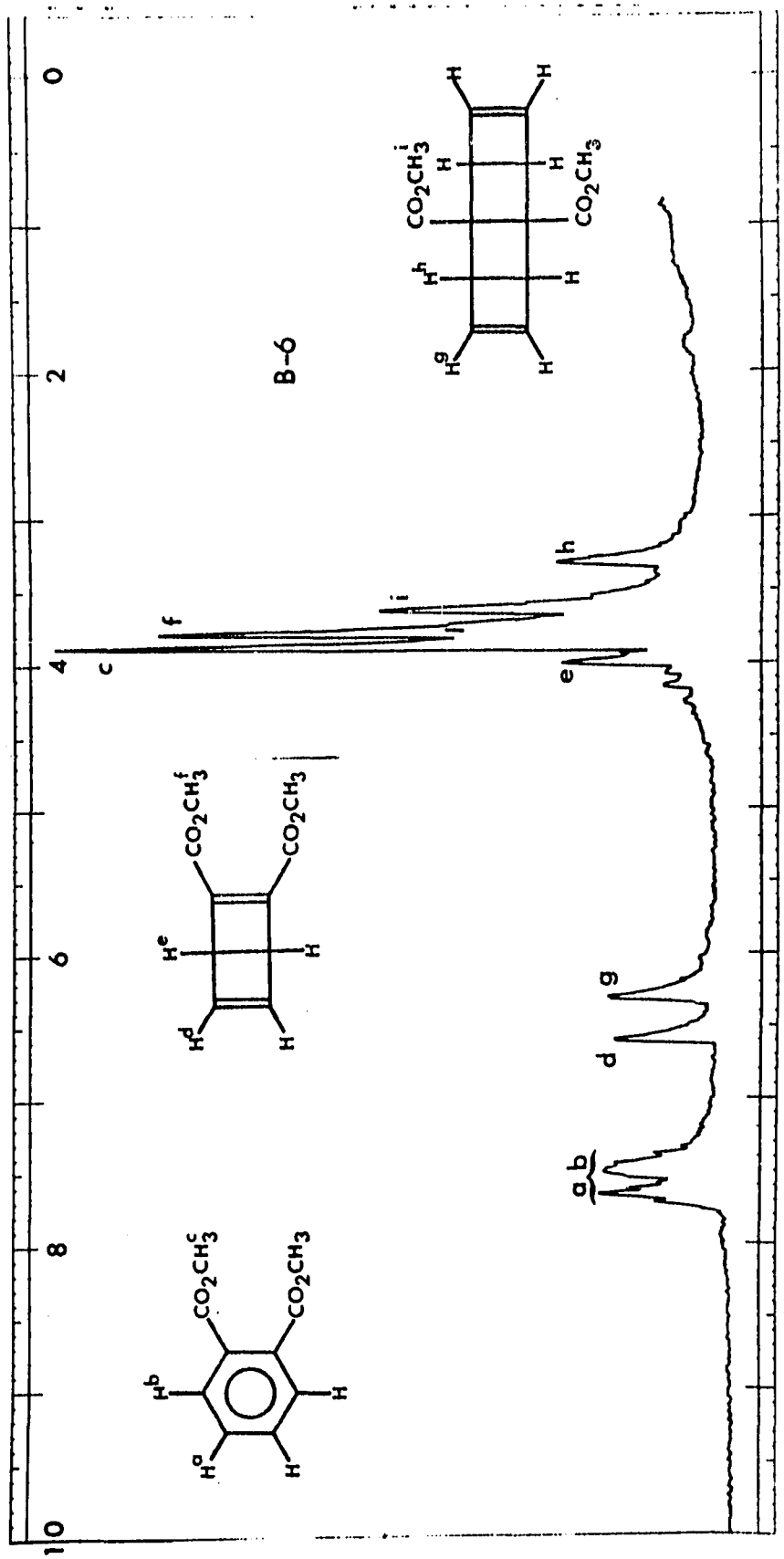

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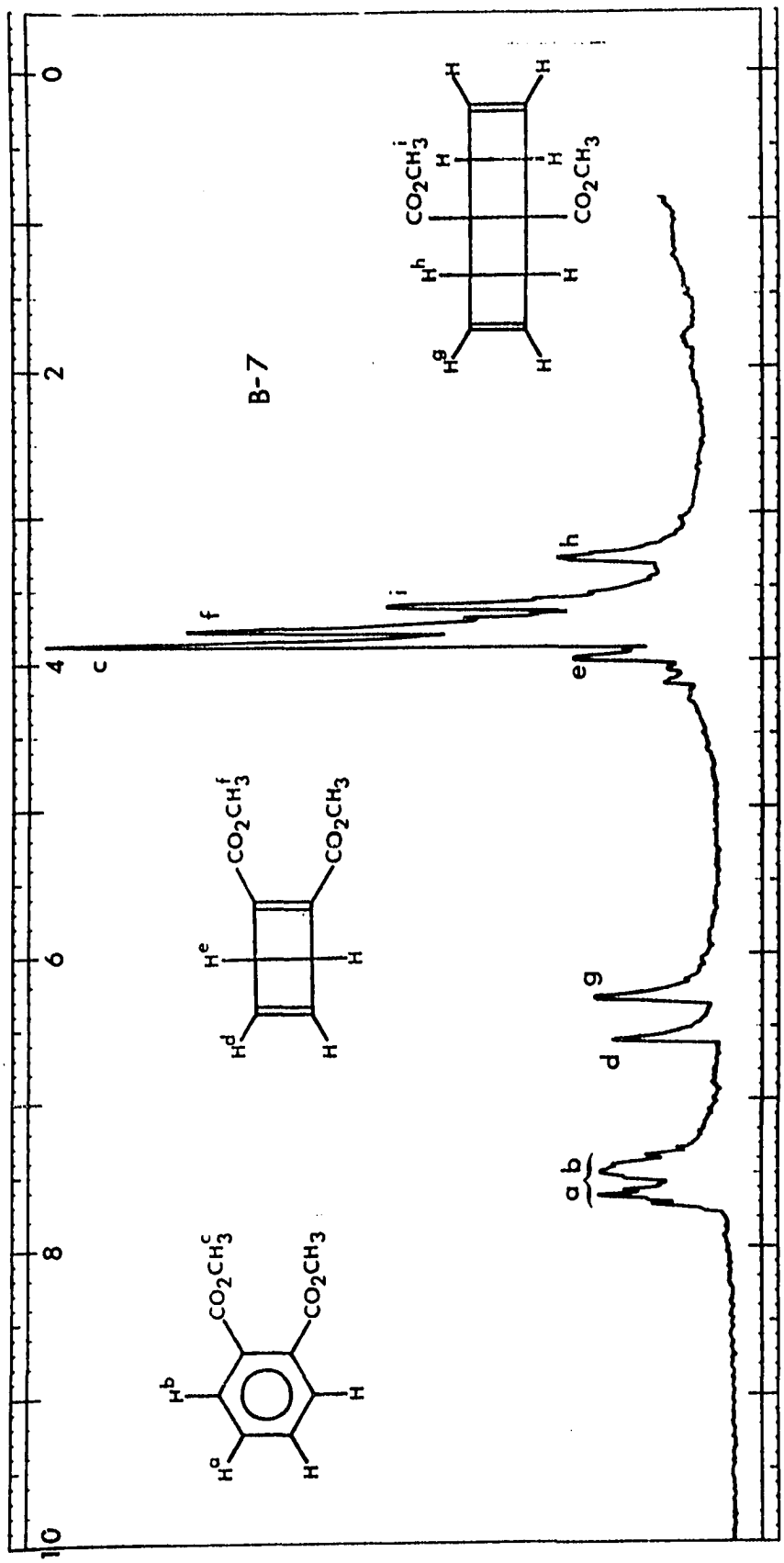

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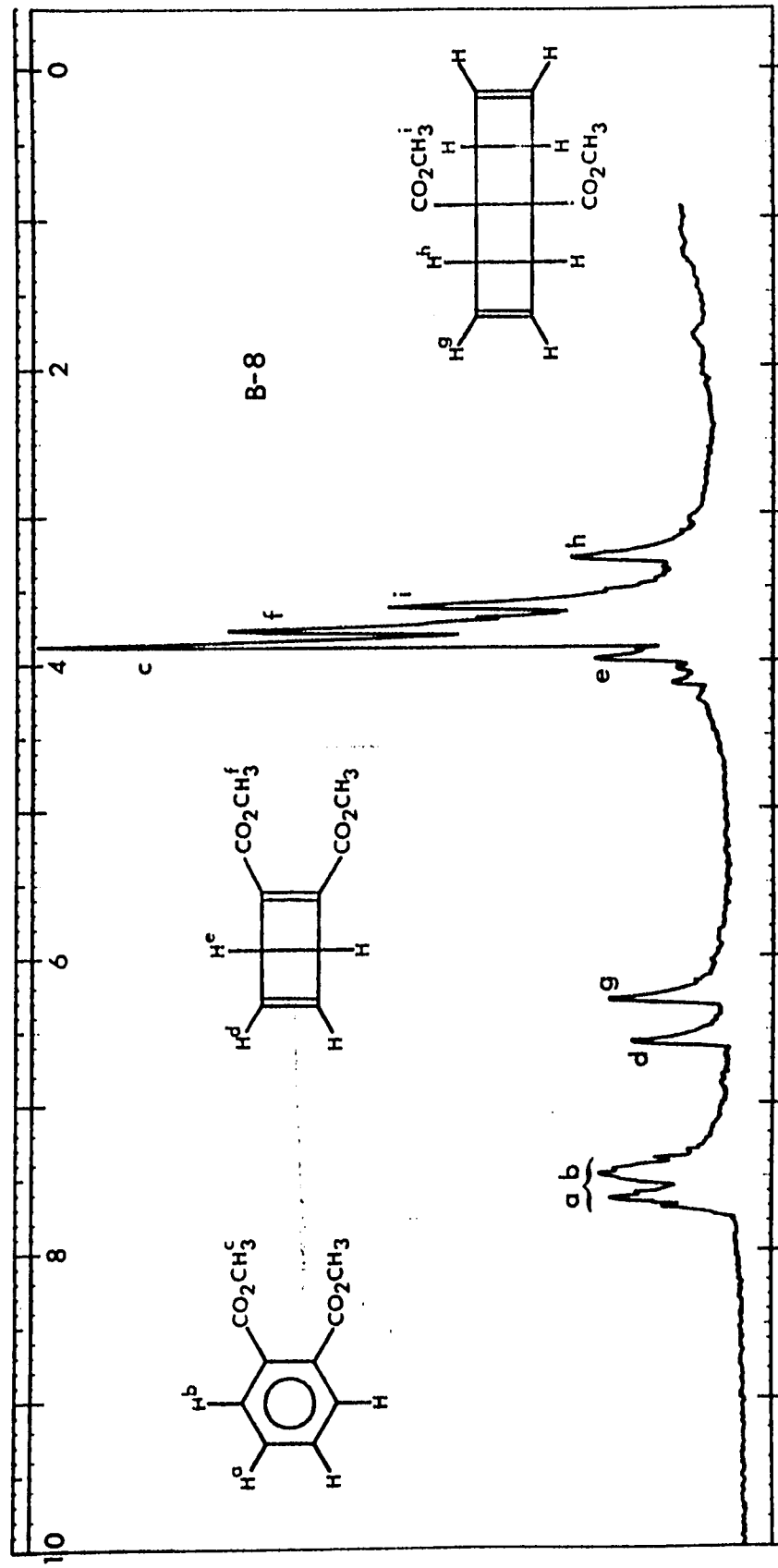

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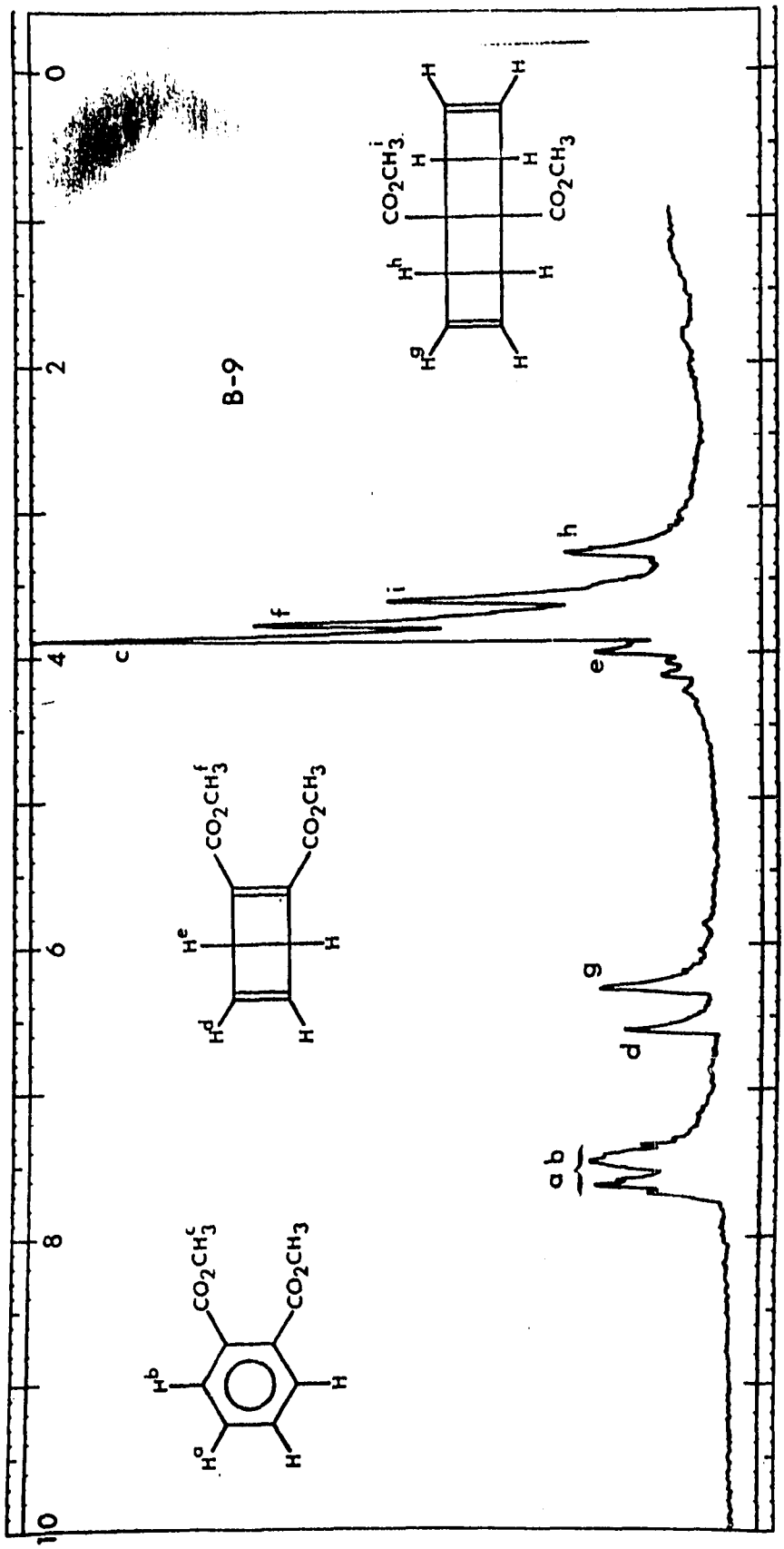

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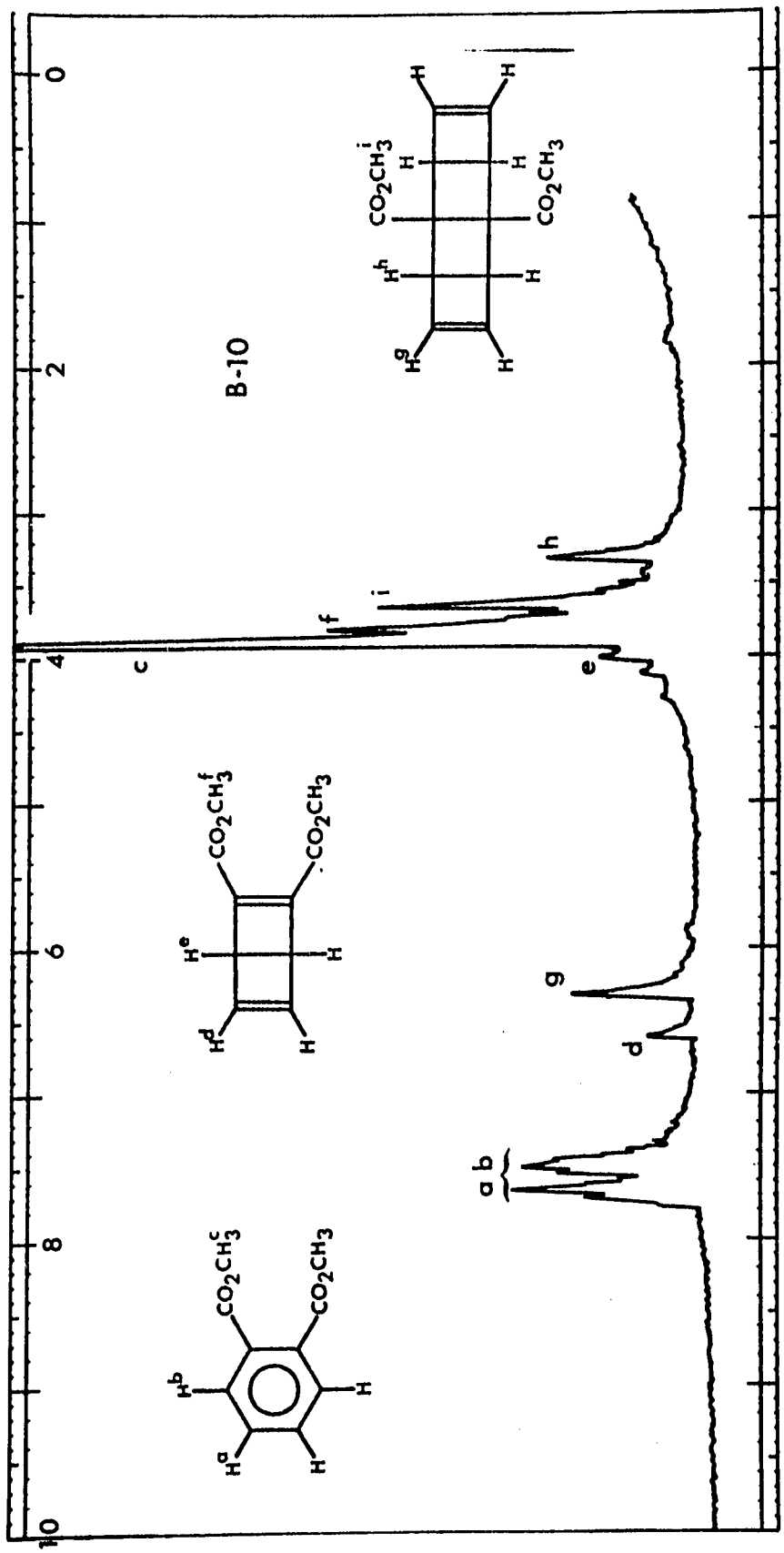

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Thermolysis of 2,3-dicarbomethoxy-1,4,5,6-tetramethyl (Dewar Benzene) (25)

Experimental :

Ten milligrams of chromatographically pure diester (25) were taken up in a minimal amount of pyridine-d_5 containing a few percent TMS. This solution was transferred to an argon filled, thick-walled NMR tube. After the TMS concentration was checked, the tube was sealed with a torch. Thermolysis was carried out in a preheated Carius oven at 115°. NMR spectra C-1 through C-6 were taken according to the plan summarized in the table.

SPECTRUM	SWEEP WIDTH (Hz)	MINUTES AT 115°
C-1	1000	0
C-2	1000	10
C-3	1000	20
C-4	1000	30
C-5	1000	90
C-6	1000	190

Results :

Spectrum C-1 is that of 2,3-dicarbomethoxy-1,4,5,6-tetramethyl (Dewar benzene). Spectrum C-2 shows partial rearrangement to dimethyl tetramethylphthalate (35) (resonances at δ = 2.04, 2.25 and 3.87). A further, much more interesting aspect of C-2 is the three smaller resonances at δ = 1.87, 3.67 and 3.71. The appearance of these resonances and the broadening of the bases of the resonances at δ = 1.30 and 1.65 are consistent with the formation of the diester (37). The subsequent spectra (C-3 to C-6) show a steady decay of the diester (25) and the minor resonances of spectrum C-2 together with an enhancement of the aromatic isomer (35).

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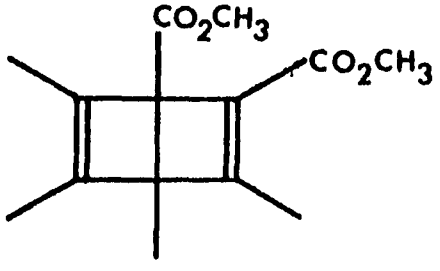
We can consider various possibilities for the identity of the species that give rise to the transient resonances. The transience of these resonances shows that they are not due to any aromatic material. Neither can these peaks be assigned to a prismane derivative. No dicarbomethoxyprismane has non-equivalent methyl ester groups (as observed at 3.67 and 3.71). Also the transient resonance at 1.87δ is at too low a field for a methyl group attached to a prismane ring[19]. This resonance at 1.87δ is reasonably assigned to a methyl group attached to an unsaturated carbon atom α to an electron withdrawing group. Such a methyl group might be either in the 3- or 6-position of the scrambled Dewar benzene (37).



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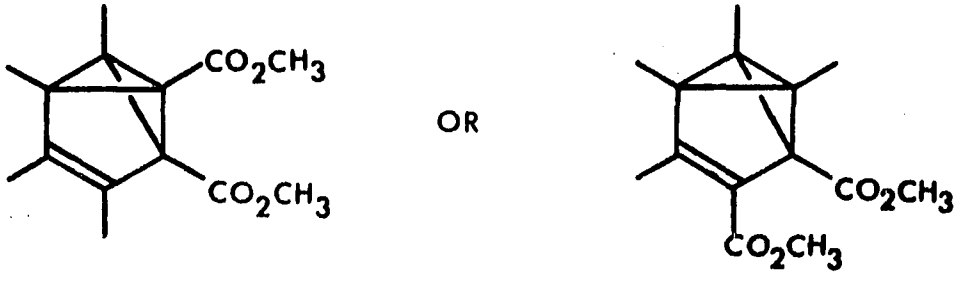
A dicarbomethoxytetramethylbenzvalene cannot be excluded since such a compound can contain non-equivalent ester groups and a methyl group attached to an olefinic carbon atom. It is even



possible that some adduct between the Dewar benzene (25) and pyridine has formed. The assignment of the three small peaks to the scrambled Dewar benzene (37) is consistent with, but not uniquely demanded by the available data.

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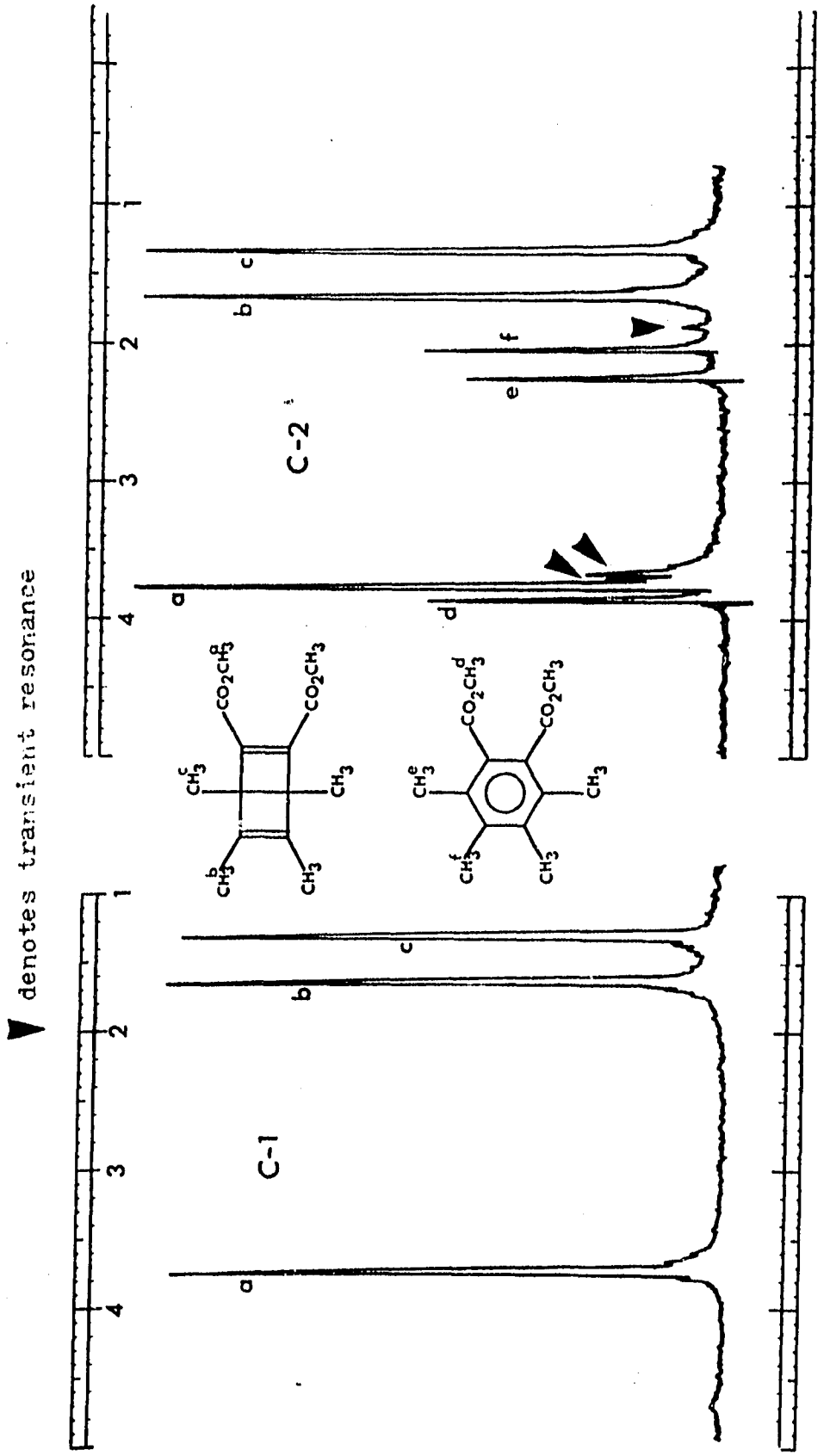

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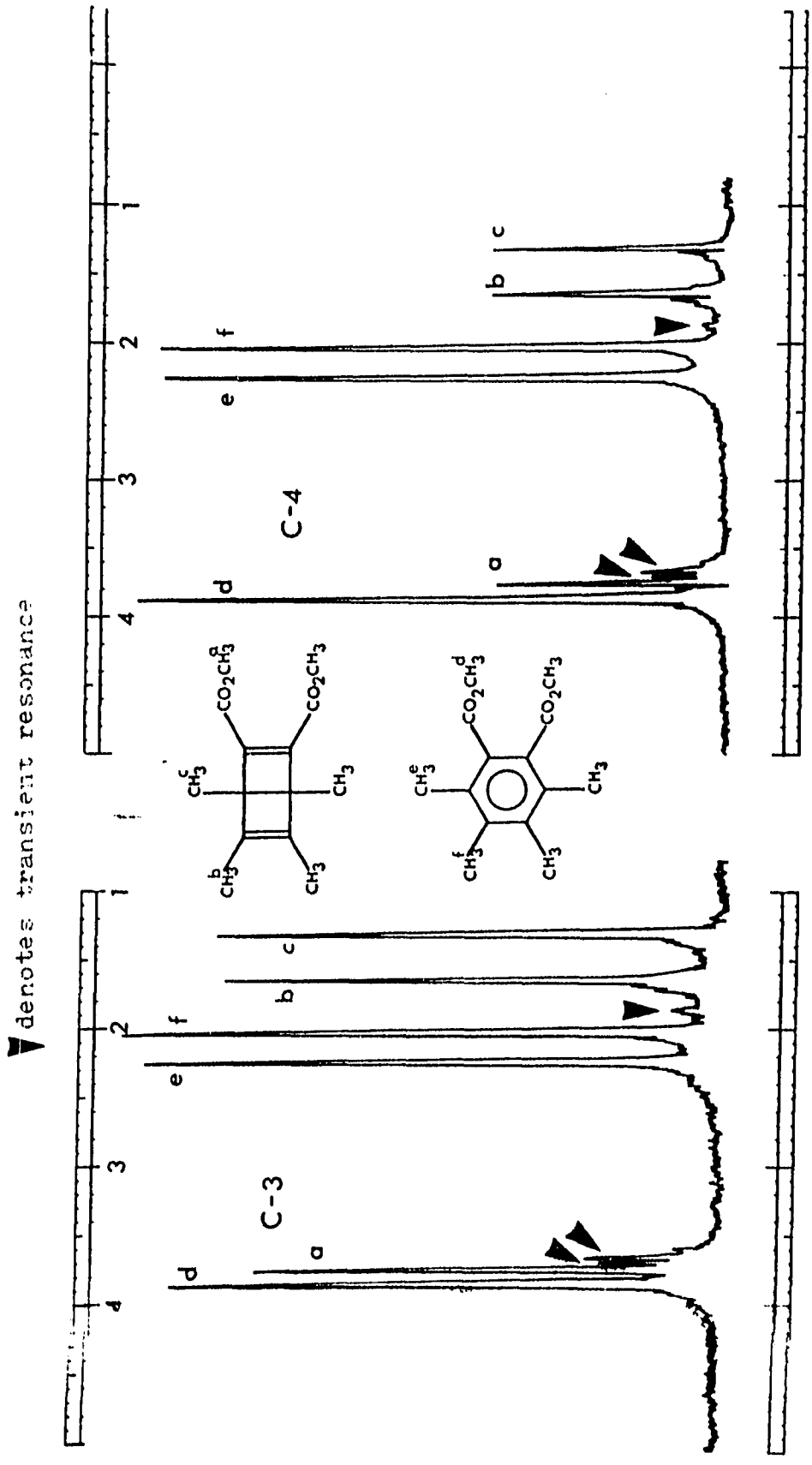

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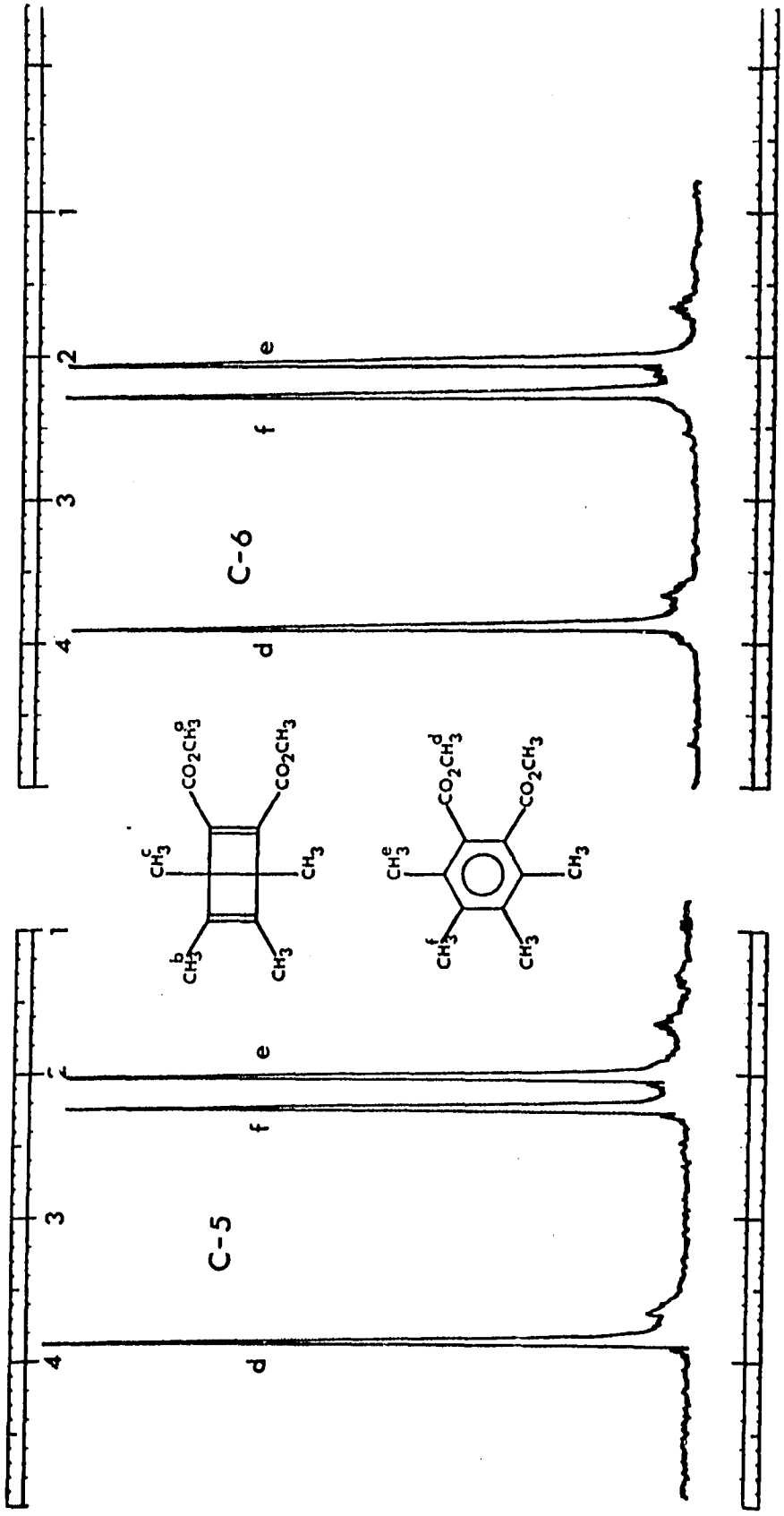

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Thermal rearrangement of 2,3-di-2-(2-hydroxypropyl)-1,4,5,6-tetramethyl (Dewar benzene) (38)

Experimental :

A sample of (2.6 mg) of the Dewar benzene (38) was taken up in a minimal amount of pyridine-d_5. About 10% TMS was added and the resulting solution was transferred to an argon filled thick-walled NMR tube. After checking the TMS concentration, the tube was sealed with a torch. Thermolysis was carried out in a preheated Carius oven at 200°. NMR spectra were taken before and periodically during the thermolysis. Spectra (D-1 to D-7) were taken according to the plan summarized in the table.

SPECTRUM	SWEEP WIDTH (Hz)	MINUTES AT 200°
D-1	1000	0
D-2	250	0
D-3	250	30
D-4	250	50
D-5	250	80
D-6	250	110
D-7	1000	110

Results :

Spectra D-1 and D-2 are that of the Dewar benzene (38). It should be noted that each hydroxypropyl group contains a pair of diastereotopic methyl groups. Spectrum D-3 shows the formation of the aromatic ether (50) (resonances at δ = 1.63, 2.11 and 2.19) at the expense of (38). D-3 also shows the appearance of transient minor resonances at δ = 1.28, 1.52 and 1.57.

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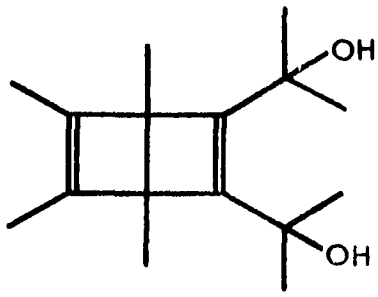

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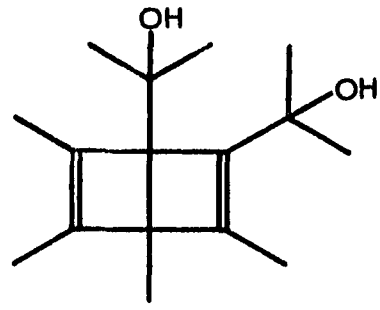

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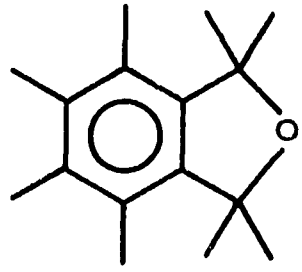
These minor resonances are consistent with the structure (39). Specifically, the peak at δ = 1.28 can be assigned to the bridgehead (4-position) methyl group of (39). The assignment of the



50

remaining lower field minor resonances is not nearly so clear cut. The remaining methyl groups of (39) are all expected (using (38) as a model) to occur in the range of 1.5δ to 1.7δ. Even if an NMR spectrum of pure (39) were available, complete assignment would be difficult.

Spectra D-4 and D-5 show the decay of the minor resonances and those assigned to (38). Spectra D-6 and D-7 show the aromatic ether (50) and an additional broad resonance at δ = 2.13.

The possibility that the minor resonances observed in D-3 are due to the compounds (52), (58) or (59) can be excluded since the reported NMR spectra of these compounds in pyridine do not coincide with the observed resonances. We cannot, however, rule out the possibility that the minor resonances are due to a benzvalene or a pyridine adduct. Further, because of

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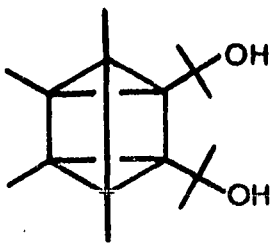

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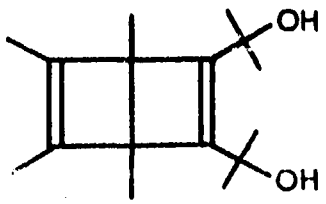

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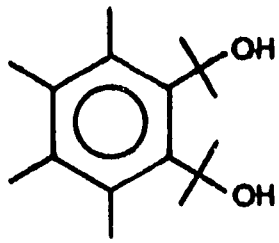

52

the broad resonance at δ = 2.13 that appears at the conclusion of this thermolysis, we cannot even be certain that the minor resonances represent a material that is ultimately converted to the aromatic ether (50). These data are consistent with, but do not conclusively establish the production of the scrambled Dewar benzene (39) during the thermolysis of (38).

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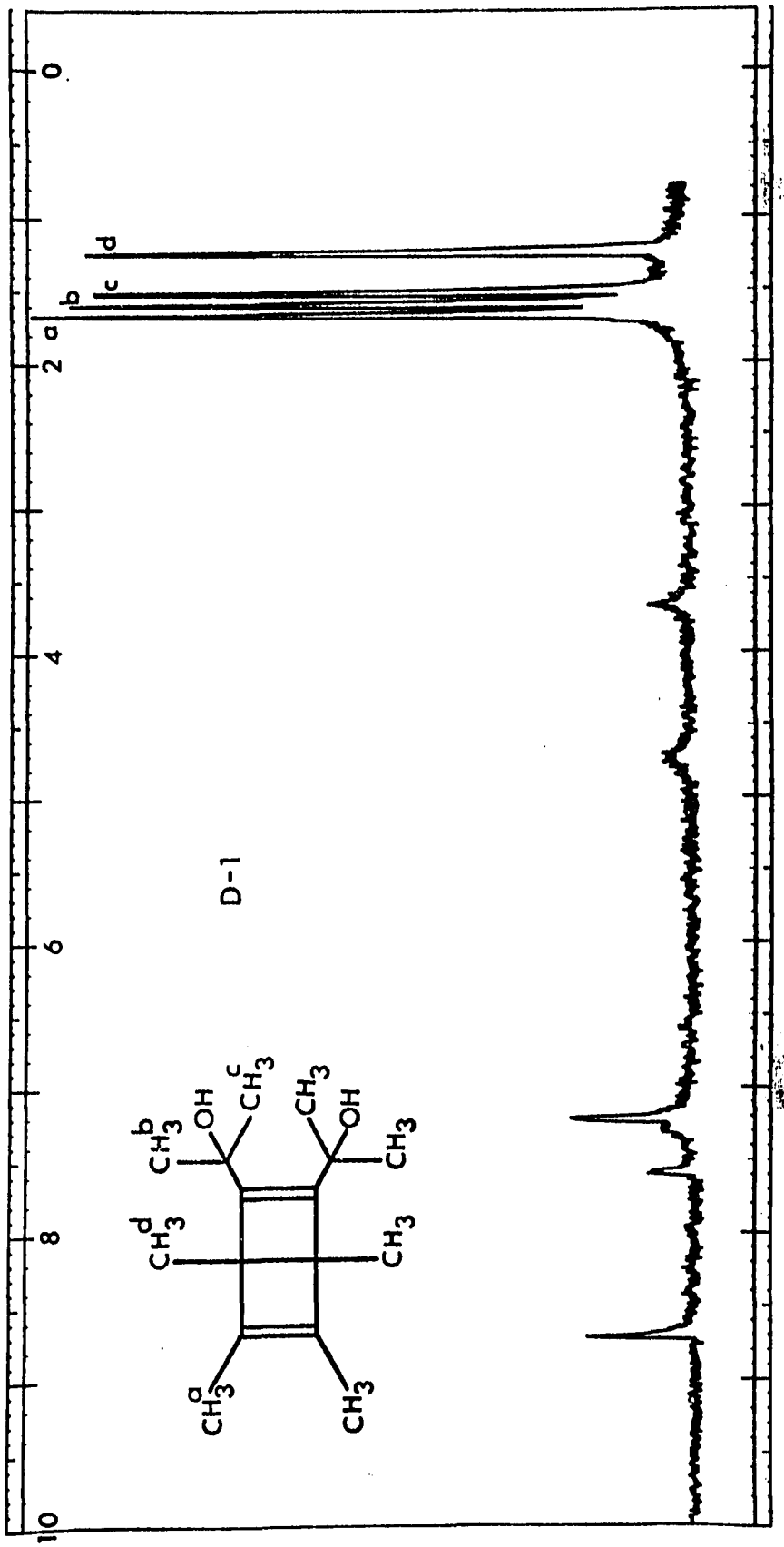

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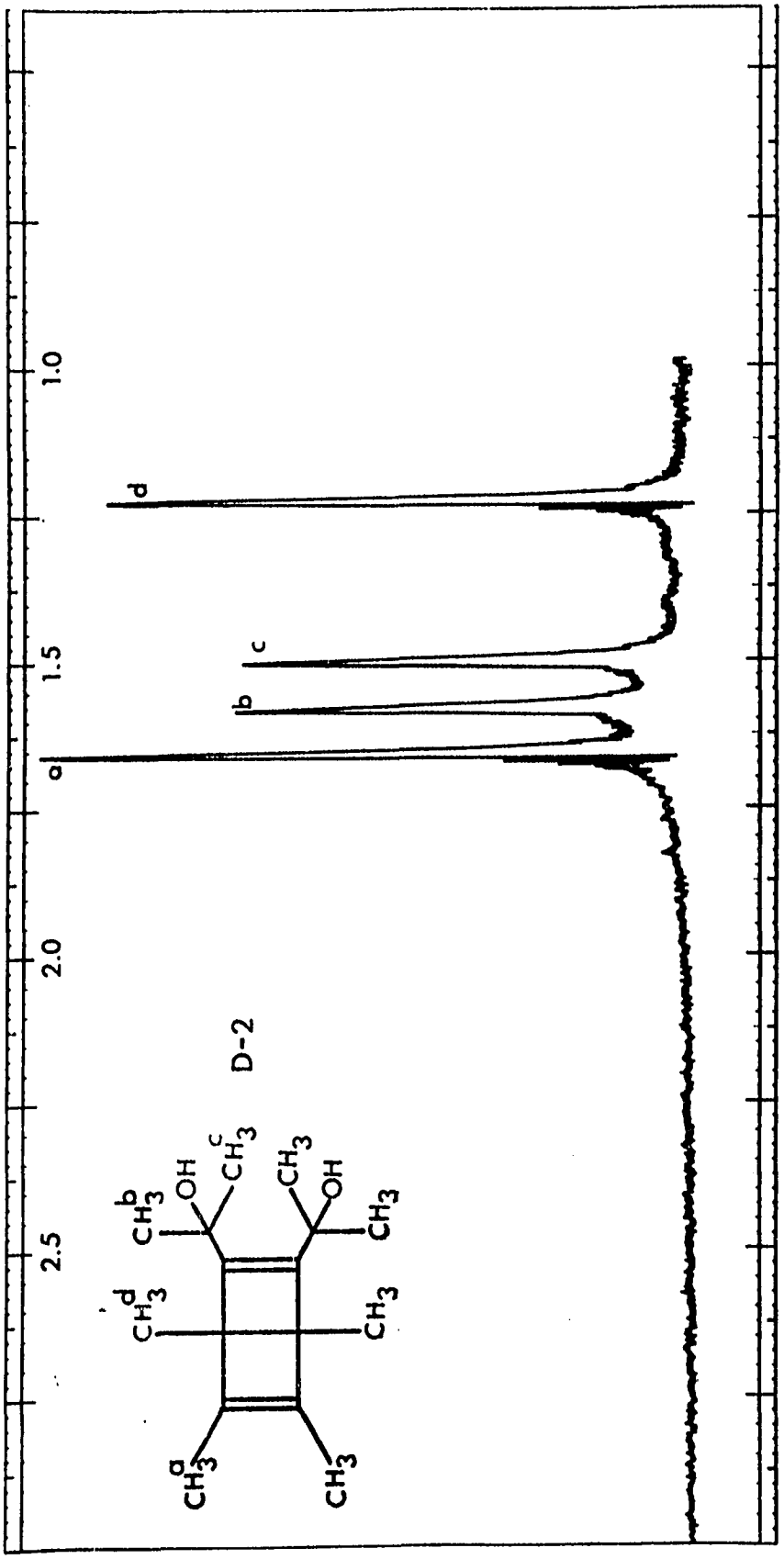

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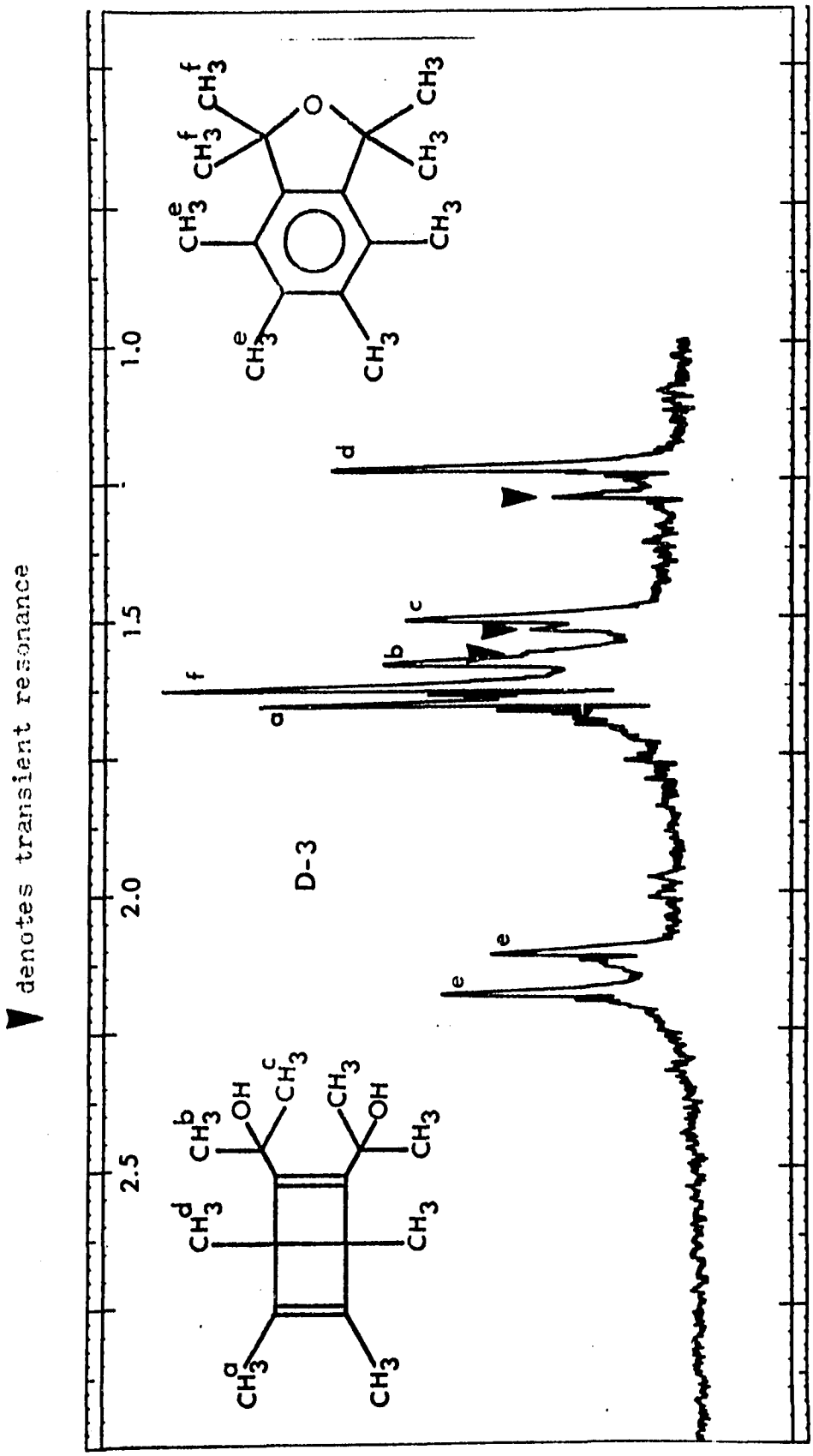

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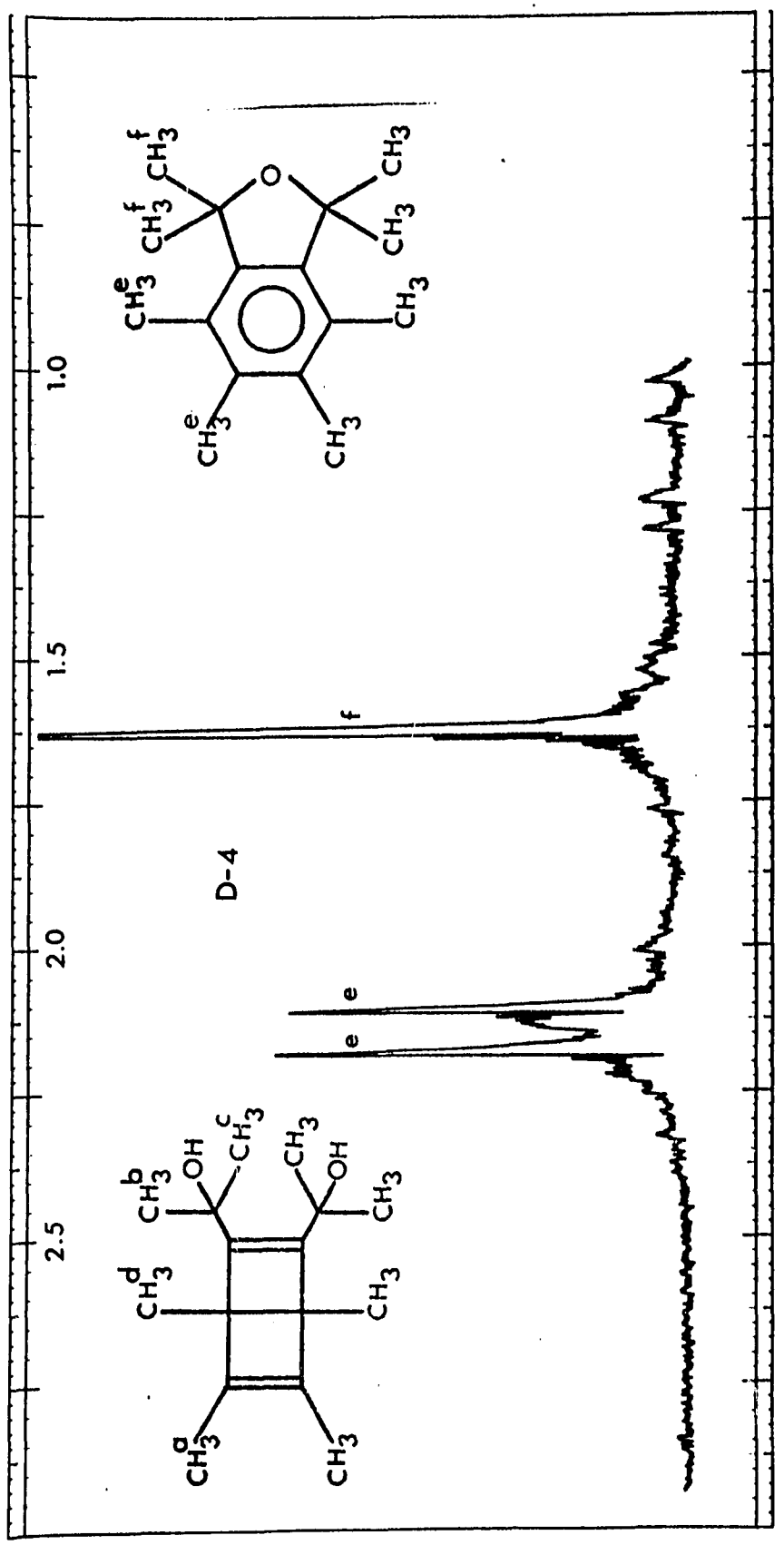

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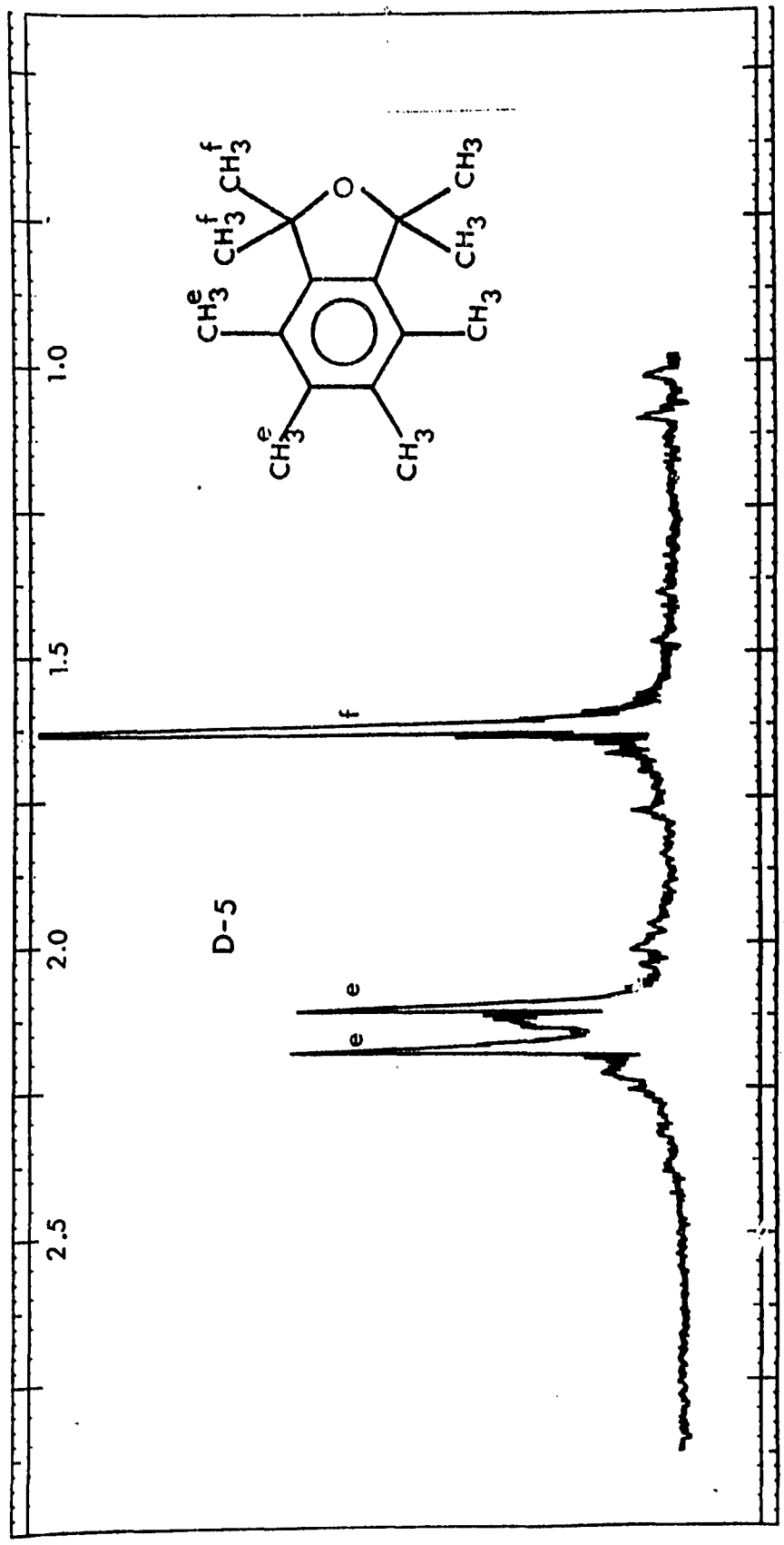

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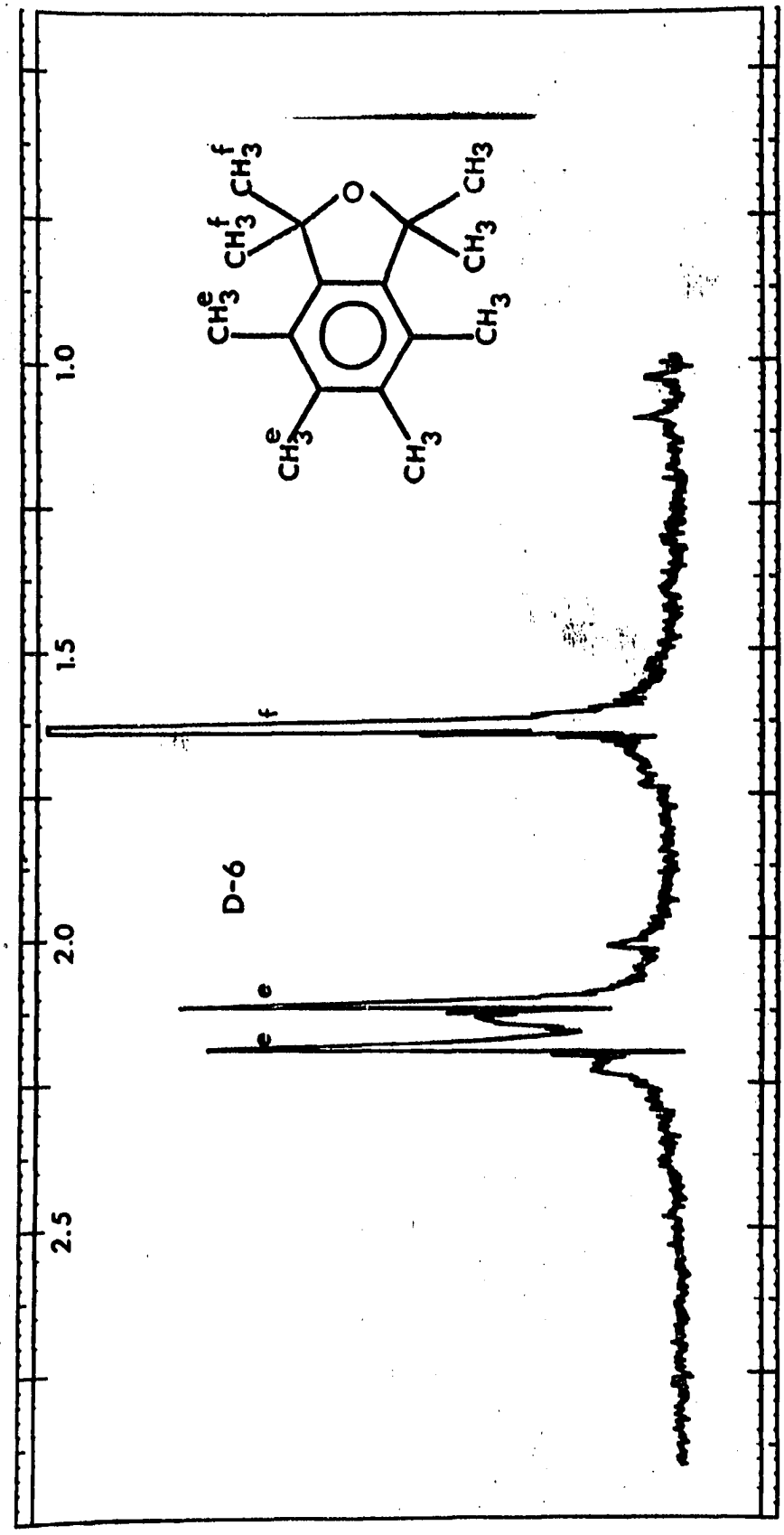

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