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THE PHOTOCHEMISTRY OF AZAFULVENES

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

by

Joseph Peter Sanchez

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

Georgia Institute of Technology

June, 1972

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THE PHOTOCHEMISTRY OF AZAFULVENES

Approved:

Edward M. Burgess

Chairman

Herbert O. House

Drury S. Caine III

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SUMMARY

Although several aza- and diazafulvenes have been prepared, there has been no reported attempt to prepare triazafulvenes or diazafulvenes containing two adjacent nitrogen atoms. These would be of great interest since the photochemical expulsion of nitrogen from them would afford azatriafulvenes and triafulvenes respectively.

An approach reported for the synthesis of the heterocyclic variant of cyclopropenone, azirinone, via the decomposition of α-azidophenylketene at -30° gave only carbon monoxide and benzoitrile.

It is amusing to speculate that an analogous reaction with α-azidoallene might provide evidence for the presence of an equally interesting azatriafulvene. Since the photochemical expulsion of nitrogen from di- and triazafulvenes seemed to offer a more expeditious route to triafulvenes and azatriafulvenes, our research consisted of: (1) the preparation of suitable precursors; (2) the reaction to produce the corresponding azafulvenes; and (3) isolation and identification of the products from the subsequent photoreactions.

A series of pyrazole and triazole diphenylcarbinols and their chloro hydrochlorides has been prepared. These were converted by dehydrohalogenation with triethylamine to di- and triazafulvenes which were identified by isolation of the fulvene itself, its dimer or addition products with methanol and amines.

Irradiation of the triazafulvenes XXVII, XXXVI and XLII gave rise to a mixture of products which were isolated by column chromatography

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and identified by physical and spectral comparison with authentic samples.

The isolation of triphenylacrylonitrile (LXXXI) from the irradiation of XXXVI indicates the presence of a triphenylazatriafulvene (LXXVI) intermediate.

There is also evidence for the formation of an intermediate triphenylazete (LXXVII) from which both 2,3-diphenylquinoline (LXX) and the proposed 1,5-diazocine (XXIX) arise during photolysis of either XXXVI or XXVIII.

The photoreaction of XLII produced the dichloro analog of XXIX (XLIII), from which a complete X-ray crystallographic analysis will hopefully confirm the assigned structure.

The diazafulvenes LVIII and LXIII, although stable enough to isolate, did not evolve nitrogen upon irradiation and attempted Diels-Alder addition reactions with them as either dienes or dienophiles proved to be fruitless.

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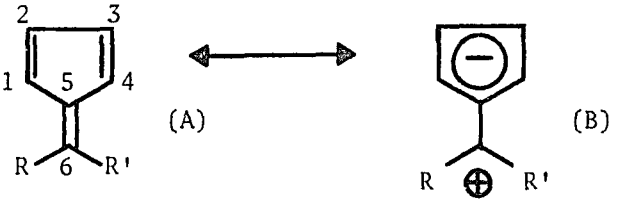
CHAPTER I

INTRODUCTION

The nature of the bonding in fulvenes can be described qualitatively as a combination of the resonance contributions of the covalent structure A and the polar structure B.



R = R' = H, Alkyl or Aryl

With the increasing electron-donating character of a substituent at carbon - 6, the polar structure B becomes more significant. This can be explained in accordance with Huckel's rule by stabilization through the cyclic conjugated system of six π-electrons. In agreement with this concept, the bond character of the fulvenes can be shifted either towards the olefinic or towards the "cyclic conjugated" character by variation of the substituents at carbon - 6.[1] It would therefore be of particular interest to see how a change in the charge distribution in the five-membered ring affects the reactions of fulvenes. Azafulvenes would be of particular interest in this respect.

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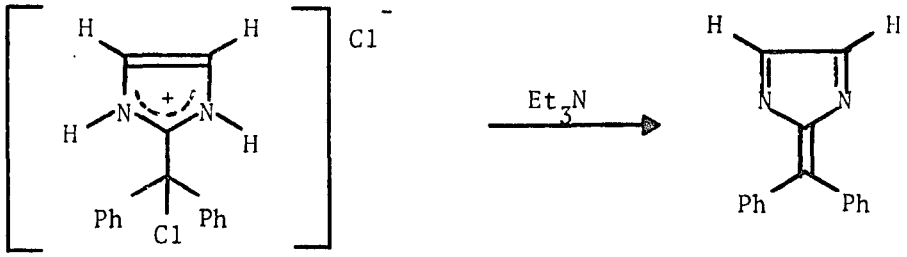
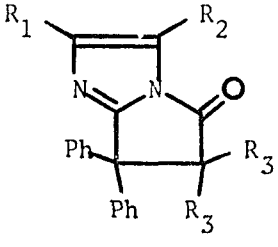
Recent synthetic efforts in the area of heterofulvenes have been successful in producing the first diazafulvene.[2] The synthesis of 6,6-diphenyl-1,4-diazafulvene (II), by Rohr and Stabb,[2] was accomplished by the dehydrohalogenation of 2-(chlorodiphenylmethyl)imidazolium chloride (I).



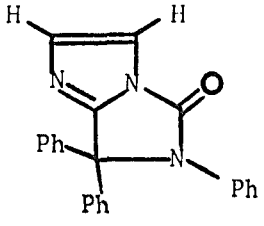
I II

By expanding this procedure to other substituted imidazoles they were able to prepare a series of diazafulvenes and study their chemistry.[3] The cycloaddition reactions of various substituted diazafulvenes with ketenes, phenyl isocyanate as well as intermolecular dimerization V, respectively, indicating the dipolar nature of the molecule (VI).

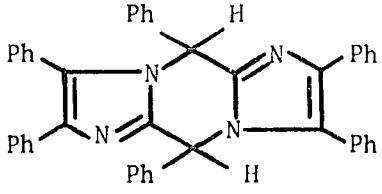


III

R_1	R_2	R_3
H	H	H
H	H	Ph
Ph	Ph	Ph
Ph	H	Ph



IV



V

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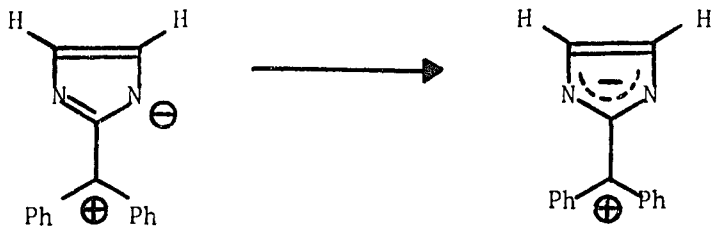
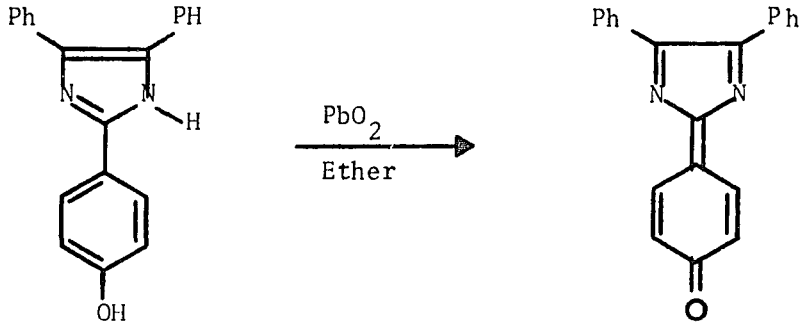


VI

The synthesis of 4-(4,5-diphenyl-2H-imidazol-2-ylidene)-2,5-cyclohexadienone (VII) was accomplished by the lead dioxide oxidation of p-4,5-diphenyl-2-imidazolyl) phenol (VIIa).[4]



VIIa VII

The structure of this product (VII) was confirmed by Hill[5] who also synthesized 2,3,6,6-tetraphenyl-1,4-diazafulvene (VIII) by two different routes; oxidation of 2-benzhydryl-4,5-diphenyl imidazole (VIIIa) with lead peroxide in benzene or dehydrohalogenation of a chloroform solution of 2-chlorodiphenylmethyl-4,5-diphenylimidazole (VIIIb) using triethylamine.

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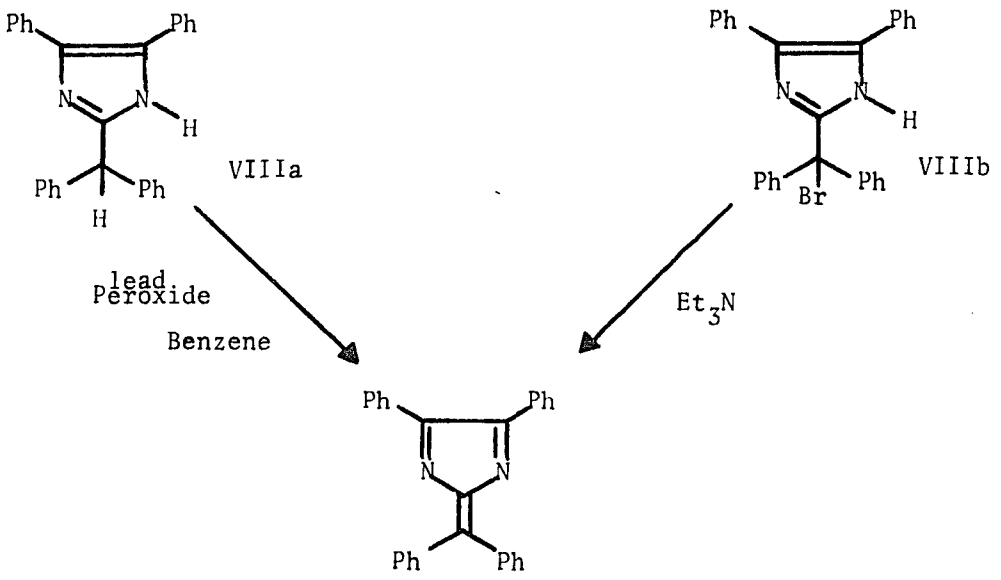
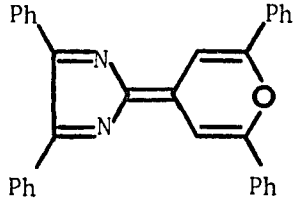


VIII

In their preparation of heterofulvalenes, Gompper and Weiss[6] reported that heating 4,5-diphenylimidazole, 4-methylthio-2,6-diphenylpyrylium perchlorate and one equivalent of sodium hydride in benzene gave IX.



IX

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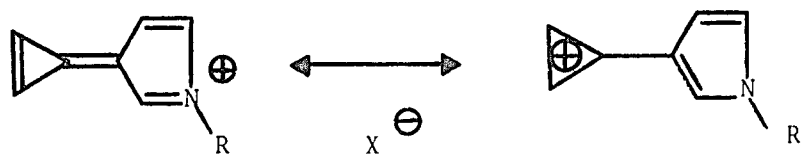
It is interesting to note that all diazafulvenes reported to date contain a stabilizing substituted imidazole nucleus and in no instance has a diazafulvene with two adjacent nitrogens been prepared.

The field of monoazafulvenes on the other hand has been explored to a greater extent. Battiste and Hill[7] have recently published the procedure for a convenient entry into the azapentatriafulvalenium system (X).



Several of these stable salts have been prepared from indole, substituted indoles and some pyrrole derivatives by the action of diphenylcyclopropenone and ethanolic hydrogen chloride on the appropriate heterocycle. The reaction evidently proceeds by electrophilic substitution by the 1-hydroxy-2,3-diphenylcyclopropenium cation produced in situ from the cyclopropenone and hydroden chloride on the most reactive position of the heterocyclic ring. Treatment of the fulvene salts with a variety of bases of low nucleophilicity in aprotic solvents produced only a fleeting color indicative of the fulvene. In some cases polymeric substances were isolated and assigned the structure XI.

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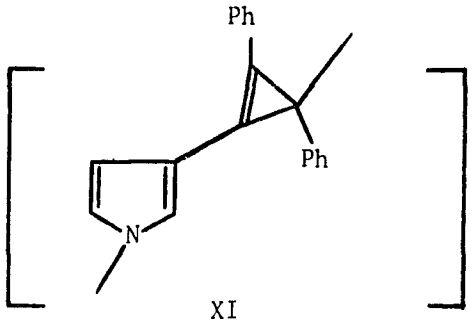
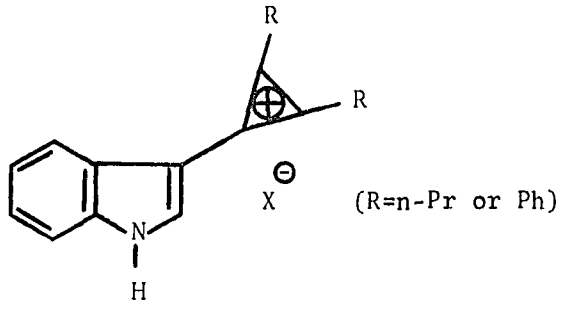


XI

It has been suggested[8] on the basis of nuclear magnetic resonance data that the fulvene derived from indole and a substituted cyclopropenium cation exists mainly as the 3-indolylcyclopropenium cation XII.



XII

Battiste and Hill[9] on the other hand present evidence based on a nuclear magnetic resonance spectral comparison of 3-benzhydrilidene-3H-indolium salts (XIV) and their common precursors (XV); and pK_R^+ values determined for XIII and for various cyclopropenium salts to suggest a more extensive delocalization of charge as represented by XIII.

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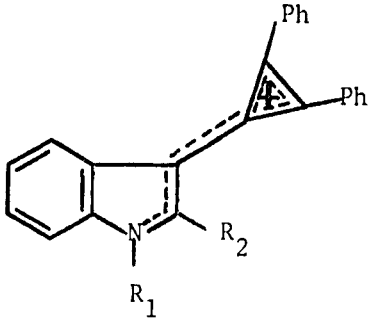
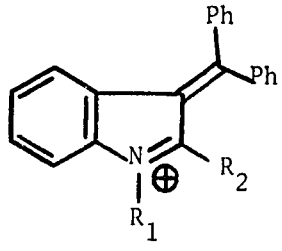
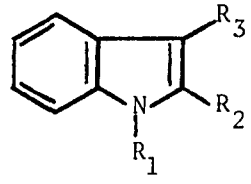


XIII

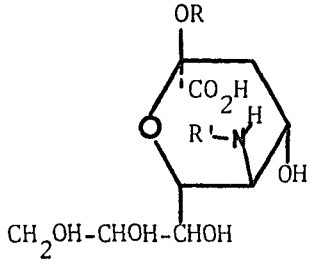


XIV



XV

In their study of the chemistry of neuraminic acid (XVI, R=R'=H) Morgan and Schunior[10] found it necessary to reinvestigate the Ehrlich reaction between XVI and p-dimethylaminobenzaldehyde (PDAB).



XVI

Previously, XVI (R'=H, R=Ac) had been demonstrated to undergo degradation in acid or base leading to pyrrole-2-carboxylic acid, which upon reacting with PDAB produces the violet color usually associated with theEhrlich reaction. The usual test requires the use of two moles of pyrrole and one mole of PDAB in ethanolic perchloric acid to give 5,5'-dicarboxy-ms-(p-dimethylaminophenyl)-2,2'-dipyrrylmethene (XVII).

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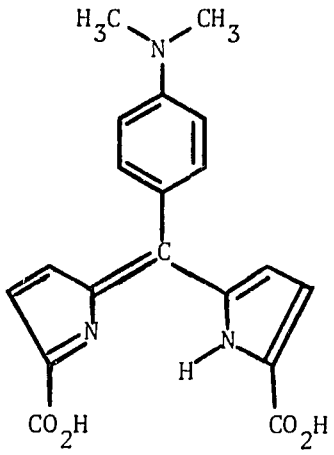
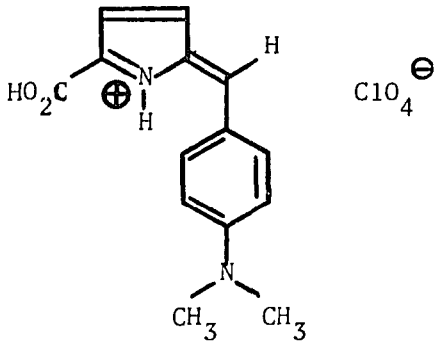


XVII

However, when the molar ratios were 1:1 a good yield of 2-carboxy-5-hydro-6-p-dimethylaminophenylazafulvene perchlorate (XVIII) was isolated as deep red needles.



XVIII

The application of this method by Castro, Tertzakian, et al.[11] led to the synthesis of a variety of substituted pyrrole fulvenes. By condensing p-hydroxybenzaldehyde (XIXa), vanillin (XIXb) or syringic aldehyde (XIXc) with 2,4-dimethyl-3-ethylpyrrole (crypto pyrrole) in ethanolic HBr, red crystalline azafulvene hydrobromides (XX) can be isolated.

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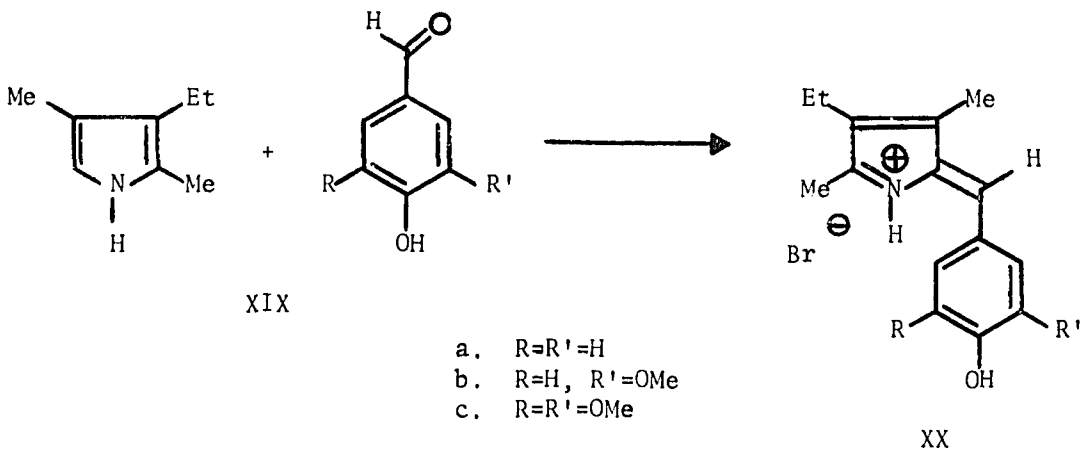
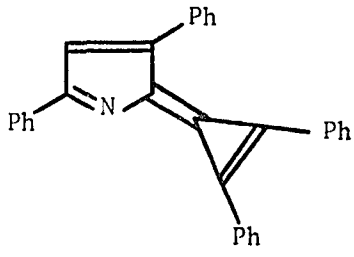


XIX

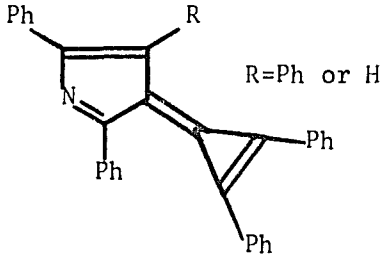
a. R=R'=H
b. R=H, R'=OMe
c. R=R'=OMe

XX

Gompper and Weiss[6] produced a series of monoazafulvenes using substituted pyrroles as the heterocycle. Di- and triphenyl pyrroles are heated with methylthiodiphenylcyclopropenylium perchlorate in glacial acetic acid or with diphenylcyclopropenone in acetonitrile to give the corresponding azatriafulvalenium salts. These are deprotonated by disopropylethylamine to give the fulvenes (XXIa-XXIb) as unstable red oils.



XXIa



XXIb

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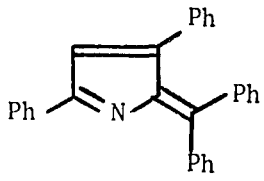
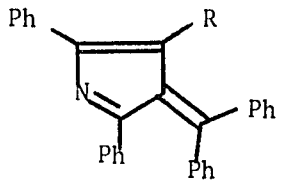
They also produced the tetra- and pentaphenyl azafulvenes (XXIIa, XXIIb) by the action of benzophenone dichloride on the appropriate pyrrole in acetonitrile at room temperature.

R=Ph or H



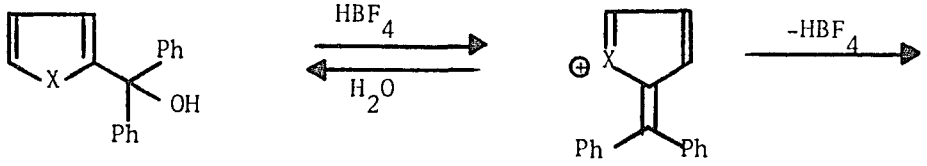
XXIIa



XXIIb

Hafner and Pfeiffer[12] prepared azafulvenes in excellent yields from indole, pyrrole, thiophene and furan by the action of ethereal fluorboric acid on the corresponding 2-diphenylcarbinols followed by deprotonation with triethylamine.

X=NH,S,O



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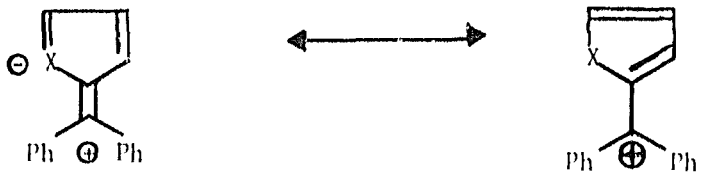

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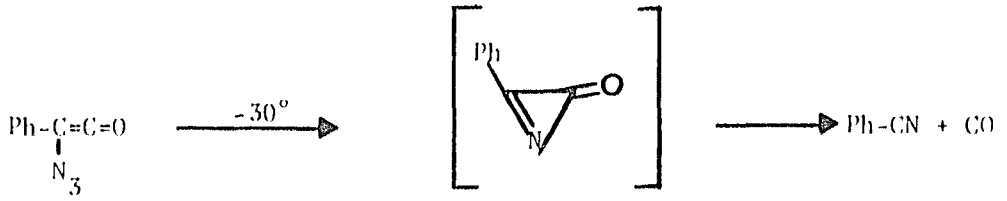

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CHAPTER II

EXPERIMENTAL

Apparatus and Techniques

Mass spectra were obtained using a Varian Model A-66 medium resolution mass spectrometer. Nuclear magnetic resonance spectra were acquired using a Varian A-60 spectrometer; deuterochloroform ($CDCl_3$) and deuterodimethylsulfoxide ($DMSO\text{-}d_6$) containing one percent of tetramethylsilane as an internal standard were used as solvents. Chemical shifts are reported in units of δ (δ=10-τ). The abbreviations s,d,t,q, and m refer to singlet, doublet, triplet, quartet and multiplet nmr signals. Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer using either 0.1 mm sodium chloride cells with chloroform as the solvent or a potassium bromide wafer. Ultraviolet spectra were recorded using one centimeter balanced cells with either 95% ethanol or tetrahydrofuran as the solvent on a Beckman DB-GT or Carey Model 14 recording spectrophotometer. Thiophene free benzene was dried by refluxing over sodium metal with the first portion of the distillate being discarded. Tetrahydrofuran was dried by refluxing 24 hrs. over sodium metal and then distilling from benzophenone ketyl. Methanol was distilled from magnesium methoxide before use. All other liquids were purified according to the procedures described by Fieser[38] and distilled prior to use. Ether, anhydrous and USP, was purchased commercially in one pound cans. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Solvent evaporation under reduced pressure

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was accomplished with a Buchi Rotavapor. A Hanovia 450 Watt high pressure mercury vapor lamp was used for irradiations. The lamp was placed in a Vycor water jacket, which was, in turn, fitted inside a Pyrex reaction vessel (Fig. 1). The resulting annular space had a capacity of about 400 ml and was filled to the neck with the solution to be photolyzed. Cold water was circulated through the water jacket during the photolysis at a rate to maintain the magnetically stirred solution at a temperature of 30°. A stream of dry helium was admitted through the frit into the reaction mixtures before irradiation. The irradiations at -78° were carried out in an apparatus similar to the one described previously except having an evacuated space between the water jacket and the reaction vessel (Fig. 2). The reaction mixture was cooled in a dry-ice/isopropanol bath prior to and during photolysis.

Experimental

5(4),α,α-Triphenyl-1,2,3-triazole-4(5)-methanol(XXIII)

A solution of phenyllithium (0.573 mole) was prepared by the addition of 90 g (0.573 mole) of bromobenzene in 100 ml of anhydrous ether on 7.9 g (1.140 mole) of lithium ribbon (containig one percent sodium metal) in 400 ml of anhydrous ether. The solution was chilled to -78° and 37.5 g (0.185 mole) of methyl 4-phenyl-1,2,3-triazole-5-carboxylate[14] was added portionwise as a solid under a nitrogen atmosphere. The mixture was allowed to warm to room temperature, then refluxed 18 hrs., cooled and decomposed using 150 ml of 5% hydrochloric acid. A fluffy white precipitate formed which was collected by filtration and dried in vacuo to yield 21 g (35%) of XXIII: mp 218-221°(dec). A sample recrys-

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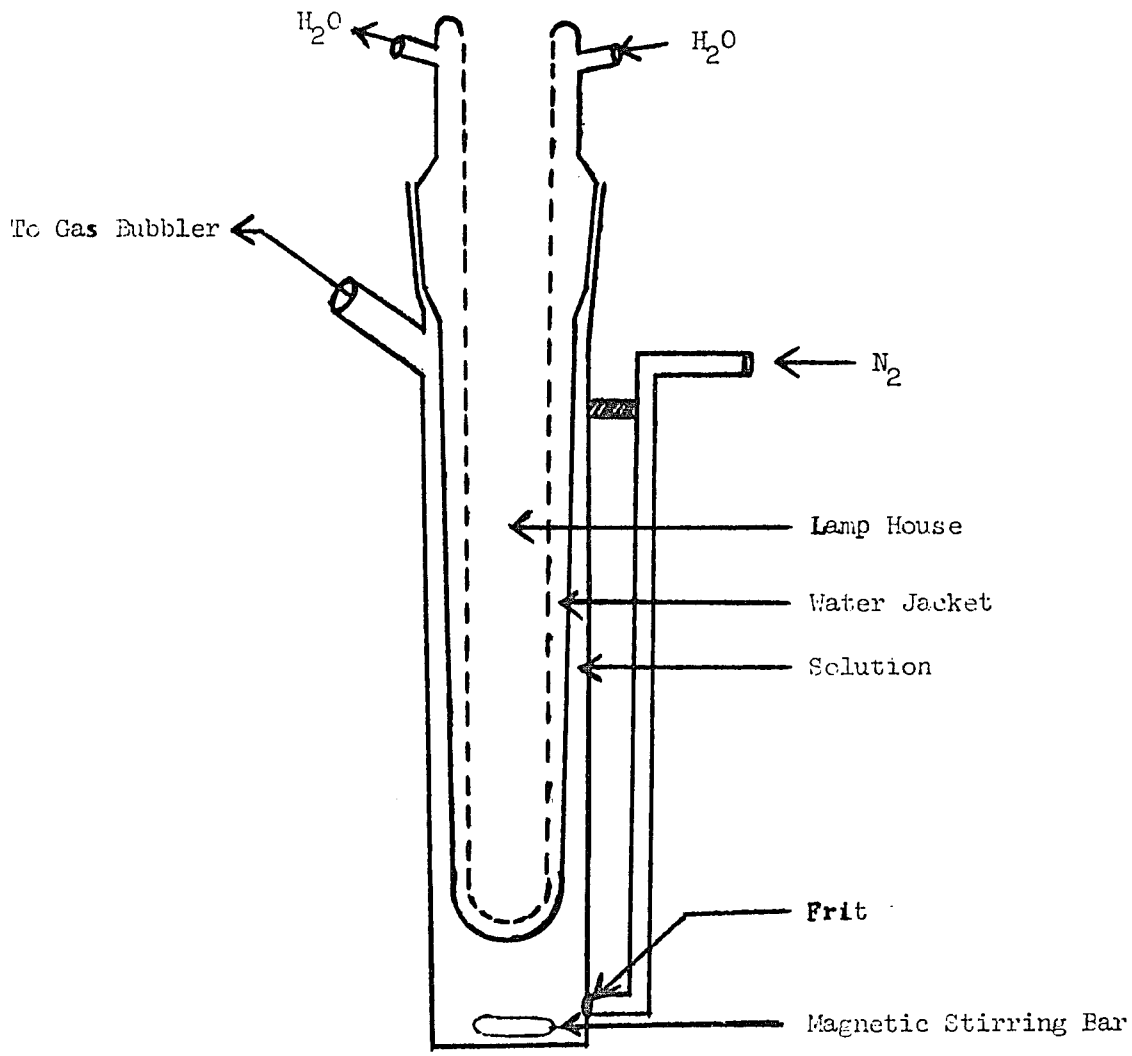

Figure 1. Photolysis Apparatus (I)

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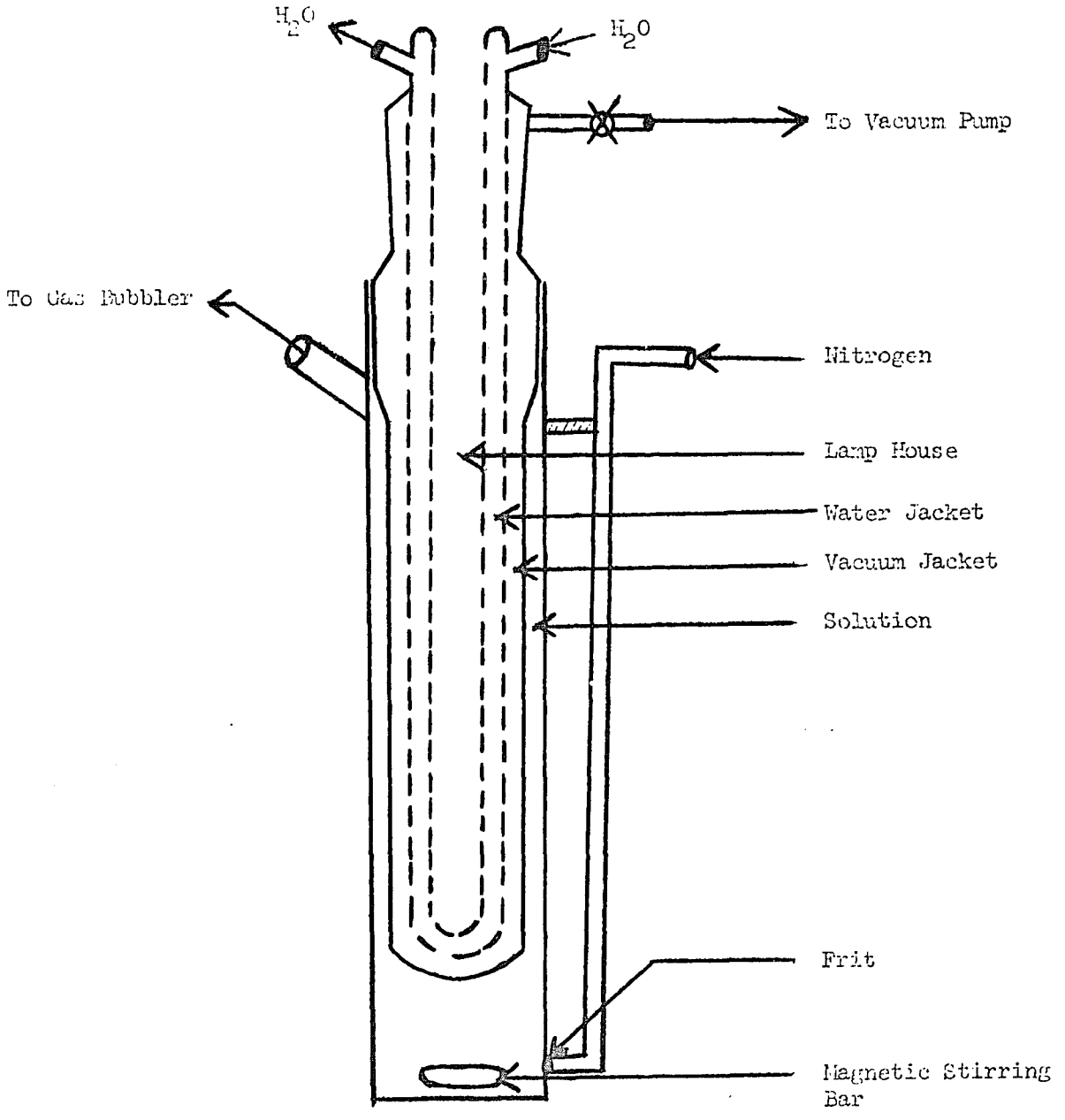

Figure 2. Photolysis Apparatus (II)

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tallized from benzene-ethanol melted at 220-221°(dec); ir (KBr) 3300 (broad O-H and N-H) cm^{-1}; nmr(DMSO-d_6) δ 7.83-6.92 (m, 15H); mass spectrum (70 eV) m/e relative intensity 327(100), and 281(67).

Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.84. Found: C, 77.19; H, 5.33; N, 12.84.

4(5),α,α-Triphenyl-1,2,3-triazole-5(4)-methanol (XXIV)

The organic layer of the above filtrate was separated, washed with water, dried ($MgSO_4$), and the solvent evaporated in vacuo. Upon diluting with pentane a fluffy white solid separated which was collected by filtration and dried to give 32 g (53%) of XXIV; mp 158-160° (dec). Recrystallization from benzene (twice) afforded an analytical sample of XXIV: mp 159-160° (dec); ir (KBr) 3320 (OH) and 3190 N-H) cm^{-1}; nmr (DMSO-d_6) δ 7.70-6.82 (m,15H); mass spectrum (70 eV) m/e (relative intensity) 327(100), 281(23) and 250(100).

Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.84. Found: C, 77.16; H, 5.36; N, 12.85.

4(5)-Phenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride(XXV)

To a solution of 40 ml of thionyl chloride in 60 ml of benzene was added 21 g (0.095 mole) of the alcohol XXIV. The mixture was stirred for 3 hr at room temperature, heated to reflux for 1 hr and then stirred at room temperature for 18 hrs. Upon diluting with anhydrous ether a solid seperated which was collected by filtration to give 24 g (66%) of XXV: mp 228-230° (dec). An additional 9 g (24%) mp 222-226° (dec) was recovered by evaporating the filtrate and diluting the residue with ether. A sample recrystallized from tetrahydrofuran-ether gave pure XXV: mp

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229-230° (dec); ir (KBr) 3270, 2340 and 1852 (N-H), 759 (C-Cl) cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 345 (7), 281 (100), 282 (100, 283 (89) and 204 (46).

Anal. Calcd for $C_{21}H_{16}ClN_3 \cdot HCl$: C, 65.97; H, 4.48; N, 10.99 Found: C, 65.90; H, 4.40; N, 11.12.

4(5)-Phenyl-5(4)-diphenylpiperidinomethyl-1,2,3-triazole(XXVI)

A solution of 1 g (0.0025 mole) of the chloro compound XXV in 200 ml of anhydrous tetrahydrofuran was chilled to -78° and treated with 0.5 g (0.005 mole) of triethylamine. There was an immediate red color and precipitate formation. The solution was filtered through Celite under a dry nitrogen atmosphere to remove 0.65 g (94%) of triethylamine hydrochloride. When the resulting clear blood-red solution was treated with 8.5 g (0.1 mole) of piperidine there resulted an immediate discharge of color. The solvent was evaporated in vacuo and the solid residue recrystallized from benzene-hexane to give 0.85 g (95%) of colorless needles of XXVI: mp 148-149°; ir ($CHCl_3$) 3410 (N-H), 2935 (C-H), 1445, 1490 and 695 cm^{-1}; nmr ($CDCl_3$) δ 7.55-6.68 (m, 15H), 3.01-2.49 (m, 4H) and 1.69-1.38 (m, 6H); mass spectrum (70 eV) m/e (relative intensity) 281 (100), 85 (29), and 84 (41).

Anal. Calcd for $C_{23}H_{26}N_4$: C, 77.06; H, 7.31; N, 15.63. Found: C, 77.24; H, 7.28; N, 15.82.

4(5)-Phenyl-5(4)-methoxydiphenylmethyl-1,2,3-triazole(XXVII)

A solution of 3.83 g (0.01 mole) of XXV in 250 ml of anhydrous tetrahydrofuran was cooled to -78° and treated dropwise with 2.02 g (0.02 mole) of anhydrous triethylamine during which time a deep red color developed. After stirring for 10 min the reaction mixture was

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diluted with hexane and filtered under a dry nitrogen atmosphere to remove 2.70 g (100%) of triethylamine hydrochloride. The resulting clear deep red solution was treated with 20 ml of anhydrous methanol at -78° and allowed to warm gradually to room temperature. As the reaction mixture warmed, there was a gradual discharge of color until a clear colorless solution resulted from which the solvent was evaporated in vacuo. The solid residue was crystallized from benzene/hexane to afford 3.2 g (94%) of XXVII: mp 101-102°; ir ($CHCl_3$) 3437 (N-H) and 1075 (C-O-C) cm^{-1}; nmr ($CDCl_3$) δ 7.66-6.98 (m, 15H) and 3.07 (s, 3H); mass spectrum (70 eV) m/e (relative intensity) 341 (60) and 310 (100).

Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.39; H, 5.61; N, 12.31. Found: C, 77.41; H, 5.68; N, 12.09.

Photolysis of 5(4)-Phenyl-4(5)-benzhydrylidene-4H(5H)-1,2,3-triazole (XXVIII)

A chilled solution (-78°) of 3.83 g (0.01 mole) of the chloro compound XXV in 400 ml of benzene-tetrahydrofuran (1:1) was treated with 2.02 g (0.02 mole) of triethylamine. The resulting blood-red solution (λ_{max}^{THF} 463 nm) of the fulvene was photolyzed at -78° for 5 hrs using a 450-W Hanovia high-pressure mercury discharge lamp in a Pyrex probe. The resulting colorless solution was filtered through Celite to remove 1.35 g (98%) of triethylamine hydrochloride. The solvent from the filtrate was evaporated in vacuo and the residue triturated with benzene to give 0.73 g (26%) of XXIX: mp 225-230°. After recrystallization from ethanol an analytical sample was obtained which had: mp 230-232°; λ_{max}^{EtOH} 258 nm (ϵ 42,150); $\lambda_{max}^{HCl\text{-}EtOH}$ 263 nm (ϵ 36,998); $\lambda_{max}^{con\ H_2SO_4}$ 618 nm; ir ($CHCl_3$) 1618 (C=N), 1598 (C=C), 1577 (C=C), 1492, 1448, 1125

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(broad) and 698 cm^{-1}; nmr ($CDCl_3$) δ 8.08-6.57 (m, 30H); mass spectrum (70 eV) m/e (relative intensity) 563 (50), 562 (100), 483 (6), 459 (18), 383 (21), 281 (100), 204 (48) and 178 (14).

Anal. Calcd for $C_{42}H_{30}N_2$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.55; H, 5.39; N, 4.99.

The benzene triturate was concentrated in vacuo and the residue was chromatographed on 50 g of Florisil. Upon elution with hexane 0.87 g (49%) of diphenylacetylene was isolated.[15] Elution with hexane-benzene (1:1) afforded 0.53 g (51%) of benzonitrile.[15] Further elution with pure benzene gave 0.20 g (7%) of diphenylacrylonitrile LXXI: mp 166-167° (lit mp 166-167°).[15,16] The last compound present 0.31 g (11%) was isolated by elution with benzene-chloroform (8:2 to 7:3 v/v) and was identified as 2,3-diphenylquinoline LXX: mp 90-91° (lit mp 90-91°).[15,17]

1,5,5,6,10,10-Hexaphenyl-5H,10H-ditriazolo[1,2-a:1',2'-d]pyrazine(XXX)

A solution of 2 g (0.0052 mole) of XXV in 200 ml of anhydrous tetrahydrofuran was chilled to -78° and treated with 1.05 g (0.01 mole) of triethylamine. An intense blood-red color formed during the addition of the second equivalent of triethylamine. The solution was allowed to warm to room temperature and the color faded gradually. The reaction was diluted with 200 ml of anhydrous ether and filtered through Celite to remove 1.22 g (89%) of triethylamine hydrochloride. The solvent was evaporated in vacuo to give 1.6 g (87%) of XXX: mp 277-280°; λ_{max}^{THF} 216 (ϵ 30,282); ir (KBr) 1494 and 1449 (C=C) and 895 and 698 cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 590 (15), 562 (23), 281 (100) and 204 (50).

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Anal. Calcd for $C_{42}H_{30}N_6$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.29; H, 4.93; N, 13.57.

Photolysis of XXX

A solution of 1.55 g (0.0025 mole) of the pyrazine XXX in 400 ml of benzene-tetrahydrofuran (1:1) was photolyzed for 3 hr using a Hanovia 450-W high-pressure mercury discharge lamp in a quartz probe. There was no nitrogen evolution and upon evaporating the solvent in vacuo, starting material was recovered quantitatively.[15]

Hydrolysis of XXX

To a suspension of 0.618 g (0.001 mole) of the pyrazine XXX in 200 ml of ethanol was added 50 ml of 5% hydrochloric acid. The mixture was refluxed 18 hr and the solvent evaporated in vacuo. The residue was dissolve in ether, washed with water, dried ($MgSO_4$), filtered and concentrated in vacuo. Upon diluting with pentane 0.52 g (87%) of XXIV precipitated[15] and was collected by filtration.

1-Benzyl-3-phenyl-1,2,4-triazole(XXXI)

To a magnetically stirred solution of 26.5 g (0.39 mole) of sodium ethoxide in 100 ml of ethanol was added portionwise 50.8 g (0.35 mole) of 3-phenyl-1,2,4-triazole(LXXXIV).[18] The mixture was stirred for 5 min and 66.7 g (0.525 mole) of freshly distilled benzyl chloride was added. The reaction mixture was refluxed for 1 hr and then stirred at room temperature for 18 additional hrs. The sodium chloride was removed by filtration and the filtrate concentrated in vacuo yielding an oily suspension of crystals. The oil was decanted and the solid crystallized from toluene-pentane to give 41 g (50%) of XXXI: mp 100-102°. A second crop crystallized from the oil and was removed by filtration

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affording an additional 13 g (16%) of XXXI: mp 98-100°. Recrystallization from toluene-pentane gave an analytical sample of XXXI: mp 101-102°; ir ($CHCl_3$) 2987 (C-H), 1496 (C=C), 1440 (C=C), and 695 cm^{-1}; nmr ($CDCl_3$) δ 8.32-8.03 (m, 2H), 7.94 (s, 1H), 7.53-7.00 (m, 8H), and 5.17 (s, 2H); mass spectrum (70 eV) m/e (relative intensity) 235 (100) and 91 (66).

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.54; H, 5.60; N, 17.92.

1-Benzyl-3, α,α -triphenyl-1,2,4-triazole-5-methanol(XXXII)

An 0.83 N solution of phenylithium (0.25 mole) was prepared by the action of 39.2 g (0.25 mole) of bromobenzene on 3.5 g (0.5 mole) of lithium ribbon (containing 1 percent sodium metal) in 200 ml of anhydrous ether. The mixture was cooled to -20° and treated over 1 hr with a solution of 52 g (0.22 mole) of the ester of XXXI in 200 ml of tetrahydrofuran-anahydrous ether (1:1 v/v). The mixture was stirred for 2 hrs without external cooling and a solution of 41.9 g (0.23 mole) of benzophenone in 100 ml of tetrahydrofuran was added dropwise over 1 hr. After stirring 18 hrs at room temperature, water (300 ml) was added dropwise and the resulting layers separated. The organic layer was washed with water (2 x 50 ml), dried ($MgSO_4$), filtered and the solvent evaporated in vacuo to give 49 g (53%) of XXXII: mp 118-121°.

An analytical sample of XXXII was obtained upon recrystallization from benzene and had: mp 120-122°; ir ($CHCl_3$) 3380 (OH), 3060, 3000, 1595, 1487, 1483 and 687 cm^{-1}; nmr (DMSO-d_6) δ 8.14-7.78 (m, 2H), 7.67-6.88 (m, 18H) and 5.47 (s, 2H); mass spectrum (70 eV) m/e (relative intensity) 417 (21), 326 (10), 235 (100), 182 (84), 105 (79), 91 (90).

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Anal. Calcd for $C_{28}H_{23}N_3O$: C, 80.55; H, 5.55; N, 10.07. Found: C, 80.62; H, 5.64; N, 10.08.

3(5), α,α -Triphenyl-1,2,4-triazole-5(3)-methanol(XXXIII)

A stirred solution of 47 g (0.11 mole) of the alcohol XXXII in 300 ml of liquid ammonia (-50°) was treated portionwise over 1.5 hr with 6.2 g (0.26 mole) of sodium metal. After the addition was complete, the reaction mixture was stirred 2.5 hr and quenched by the addition of 15.5 g (0.29 mole) of solid ammonium chloride. The ammonia was allowed to evaporate and the residue partitioned between ether and water. The ether layer was washed with water (2 x 100 ml), dried ($MgSO_4$), filtered and concentrated to 50 ml on a steam bath. Upon diluting with pentane, a precipitate formed, was removed by filtration, and dried in vacuo to give 21 g (58%) of XXIII: mp 228-230° (dec). The mother liquors were then evaporated to dryness to give an additional 16 g (34%) of impure XXXII. The carbinol XXXIII was recrystallized twice from toluene to afford an analytical sample which had: mp 232-233° (dec); ir (KBr) 3043 (N-H), 3263 (OH), 1490, 1468, 746 and 691 cm^{-1}; nmr (DMSO-d_6) δ 8.12-7.82 (m, 2H) and 7.58-6.82 (m, 13H); mass spectrum (70 eV) m/e (relative intensity) 327 (20), 310 (67), 209 (100), 281 (12), 250 (21), 182 (23), 178 (51), 105 (43) and 103 (44).

Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.84. Found: C, 77.22; H, 5.38; N, 12.89.

3(5)-Phenyl-5(3)-chlorodiphenylmethyl-1,2,4-triazole hydrochloride (XXXIV)

A stirred solution of 9.8 g (0.03 mole) of the alcohol XXXIII in 100 ml of anhydrous ether was saturated with dry hydrogen chloride.

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The solvent was evaporated in vacuo and the residue treated with a solution of 15 ml of thionyl chloride in 30 ml of benzene. The resulting mixture was refluxed 1 hr then stirred at room temperature for 18 hrs. Upon dilution with anhydrous ether, the crystals which formed were collected by filtration and dried in vacuo to give 10.8 g (93%) of XXXIV: mp 174-176° (dec). Two recrystallizations from tetrahydrofuran-ether afforded an analytical sample ofXXXIV which had: mp 175-177°; ir (KBr) 3300, 2380, and 1840 (NH^+), and 780 (C-Cl) cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 309 (100).

Anal. Calcd for $C_{21}H_{16}ClN_3 \cdot HCl$: C, 65.97; H, 4.48; N, 10.99. Found: C, 65.91; H, 4.54; N, 11.12.

3(5)-Phenyl-5(3)-methoxydiphenylmethyl-1,2,4-triazole(XXXV)

A solution of 3.83 g (0.01 mole) of XXXIV in 250 ml of anhydrous tetrahydrofuran was cooled to -78° and treated dropwise with 2.02 g (0.02 mole) of anhydrous triethylamine during which time a deep red-orange color developed. After stirring for 10 min at -78°, the reaction mixture was diluted with hexane and filtered under a dry nitrogen atmosphere to remove 2.58 g (94%) of triethylamine hydrochloride. The resulting clear red-orange solution was treated with 40 ml of anhydrous methanol at -78° and allowed to warm gradually to room temperature. As the reaction mixture warmed, there was a gradual discharge of color until a clear colorless solution resulted from which the solvent was evaporated in vacuo. The solid residue was recrystallized from toluene to give 2.9 g (89%) of XXXV: mp 134-135°; ir ($CHCl_3$) 3444 (N-H), 1490, 1468 and 1443 (C=C), 1100 (broad C-O-C) and 698 cm^{-1}; nmr ($CDCl_3$)δ8.28-7.92 (m, 2H),

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7.77-7.06 (m, 13H) and 3.22 (s, 3H); mass spectrum (70 eV) m/e (relative intensity) 341 (70) and 310 (100).

Anal. Calcd for $C_{22}H_{19}N_{30}$: C, 77.39; H, 5.61; N, 12.31. Found: C, 77.42; H, 5.80; N, 12.15.

Photolysis of 3(5)-Phenyl-5(3)-benzhydrylidene-5H(3H)-1,2,4-triazole (XXXVI)

A chilled solution (-78°) of 3.83 g (0.01 mole) of the chloro compound XXXIV in 400 ml of benzene-tetrahydrofuran (1:1) was treated with 2.02 g (0.02 mole) of triethylamine. The resulting red-orange solution (λ_{max}^{THF} 442 nm) of the fulvene XXXVI was photolyzed at -78° for 4.5 hrs using a 450-W Hanovia high-pressure mercury discharge lamp in a Pyrex probe. The resulting colorless solution was allowed to warm to room temperature and filtered through Celite to remove 2.62 g (92%) of triethylamine hydrochloride. The filtrate was concentrated in vacuo and the residue triturated with benzene to give 0.338 g (12%) of XXIX: mp 225-230°.[15] The benzene triturate was evaporated in vacuo and the residue chromatographed on 50 g of Florisil. Upon elution with hexane 0.85 g (48%) of diphenylacetylene was isolated.[15] Elution with hexane-benzene (1:1) afforded 0.45 g (43%) of benzonitrile.[15] Further elution with benzene gave 0.30 g (11%) of triphenylacrylonitrile LXXXI: mp 166-167° (lit mp 166-167°).[15,16] Continued elution with benzene-chloroform (1:1) led to the isolation of 1,3-diphenyl-5-diphenylmethyl-1,2,4-triazole XXXVII 0.309 g (8%): mp 188-190°.[15,19] The last compound present 0.48 g (17%) was isolated by eluting with benzene-chloroform (8:2 to 7:3 v/v) and was identified as 2,3-diphenylquinoline LXX: mp 90-91° (lit mp 90-91°).[15,17,20]

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1,3-Diphenyl-5-diphenylmethyl-1,2,4-triazole(XXXVII)

A 250 ml three-necked round-bottomed flask fitted with a reflux condensor, nitrogen inlet and pressure-equalizing dropping funnel was charged with 9.24 g (0.04 mole) of benzoyl chloride phenylhydrazone[19] and 15.44 g (0.08 mole) of diphenylacetonitrile and heated to 100°. The resulting solution was treated dropwise over 3 hrs at this temperature with a solution of 14.54 g (0.144 mole) of triethylamine in 30 ml of toluene. After the addition was complete, the reaction mixture was stirred at reflux for 18 hrs, cooled, diluted with benzene to 250 ml and the triethylamine hydrochloride removed by filtration. The organic layer was washed with water (1 x 300 ml), dried ($MgSO_4$), decolorized with Norite, filtered and evaporated in vacuo. The residue was dissolved in hot ethanol and diluted with water until turbid. After standing 18 hrs, needle-like crystals formed and were removed by filtration and recrystallized from ethanol to give 10.4 g (67%) of XXXVII: mp 188-190°; ir ($CHCl_3$) 1600 (C=N), 1498 (C=C), 1448 (C=C), 1353 and 697 cm^{-1}; nmr ($CDCl_3$) δ 8.35-8.11 (m, 2H), 7.87-6.98 (m, 18H) and 5.49 (s, 1H); mass spectrum (70 eV) m/e (relative intensity) 387 (100).

Anal. Calcd for $C_{27}H_{21}N_3$: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.72; H, 5.39; N, 10.72.

Thermolysis of XXIX

0.56g (0.001 mole) of the dimer XXIX was heated at 300° for 1 hr in a 100 ml flask. The residue was chromatographed on 15 gm of Florisil and elution with hexane-benzene (1:1 v/v) gave 0.027 g (26%) of benzonitrile.[15] Elution with benzene gave 0.059 g (13%) of pentaphenylpyridine: mp 244-245°.[15,21] Further elution with benzene

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afforded 0.326 g (58%) of the starting dimer XXIX.

2,5,5,7,10,10-Hexaphenyl-5H,10H-ditriazolo[1,2-a:1',2'-d]pyrazine (XXXVIII)

A chilled solution (-78°) of 1.91 g (0.005 mole) of the chloro compound XXXII in 200 ml of anhydrous tetrahydrofuran was treated with 1.01 g (0.01 mole) of triethylamine. The intense red-orange color formed during the addition of the second equivalent of triethylamine. The solution was allowed to warm to room temperature during which time the color faded. The reaction mixture was diluted with 200 ml of anhydrous ether and filtered through Celite to remove 1.25 g (91%) of triethylamine hydrochloride. The solvent was evaporated in vacuo to give 1.26 g (84%) of pure XXXVII: mp 291-293°; ir 1501 and 1456 (C=C), 905 and 701 cm^{-1}; mass spectrum (70 eV) (relative intensity) 590 (17), 562 (30), 281 (100), and 204 (48).

Anal. Calcd for $C_{42}H_{30}N_6$: C, 81.53; H, 4.89;; N, 13.58. Found: C, 81.23; H, 4.99; N, 13.45.

Photolysis of XXXVIII

A solution of 1.55 g (0.0025 mole) of the pyrazine XXXVIII in 400 ml of benzene-tetrahydrofuran (1:1 v:v) was photolyzed for 4 hrs using a Hanovia 450-W high-pressure mercury discharge lamp in a quartz probe. There was no nitrogen evolution and upon evaporating the solvent in vacuo, starting material was recovered quantitatively.[15]

Hydrolysis of XXXVIII

To a suspension of 0.618 g (0.001 mole) of the pyrazine XXXVIII in 200 ml of ethanol was added 50 ml of 5% hydrochloric acid. The mixture was refluxed 18 hrs and evaporated in vacuo. The residue was dissolved in ether, washed with water, dried ($MgSO_4$), filtered and concen-

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trated in vacuo to give 0.56 g (91%) of crystalline XXXIII (mp 232-233°).[15]

Methyl 4-p-Chlorophenyl-1,2,3-triazole-5-carboxylate(XXXIX)

To a suspension of 13 g (0.2 mole) of sodium azide in 175 ml of dimethylformamide at room temperature was added dropwise a solution of 39 g (0.2 mole) of methyl p-chlorophenylpropiolate[22] in 50 ml of dimethylformamide. The addition was slightly exothermic (38°) and after it was complete (1 hr) the mixture was stirred for 18 hrs at room temperature. The solvent was removed in vacuo, the residue dissolved in 550 ml of water and washed with ether. The water layer was acidified with concentrated hydrochloric acid., extracted with ether, dried ($MgSO_4$), filtered and the solvent evaporated in vacuo to give 44 g (92%) of XXXIX: mp 167-168°. Two recrystallizations from ethanol afforded the analytical sample which had: mp 170-171°; ir ($CHCl_3$) 3120 (N-H), 1730 (C=O), 1140, 1098, 1015, and 838 cm^{-1}; nmr (DMSO-d_6) δ 8.08-7.42 (m, 4H), and 3.88 (s, 3H); mass spectrum (70 eV) m/e (relative intensity) 239 (35), 237 (100), 208 (28), and 206 (79).

Anal. Calcd for $C_{10}H_8ClN_3O_2$: C, 50.54; H, 3.39; N, 17.58. Found: C, 50.71; H, 3.47; N, 17.57.

4(5)-p-Chlorophenyl- α,α -diphenyl-1,2,3-triazole-5(4)-methanol(XL)

To a solution of (0.31 mole of phenyllithium prepared by the action of 51.7 g (0.31 mole) of bromobenzene on 4.34 g (0.62 mole) of lithium ribbon (containing 1% sodium metal) in 300 ml of ether was added 23.8 g (0.1 mole) of the solid ester XXXIX portionwise. After the initial exothermic reaction ceased, the mixture was refluxed for 18 hrs and decomposed using 125 ml of 5% hydrochloric acid. After separating the layers, the organic layer was washed with water, dried ($MgSO_4$), filtered and the

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solvent evaporated in vacuo to give 33.6 g (96%) of XL: mp 172-175°. An analytical sample was obtained upon recrystallization once from ethanol and once from benzene which had: mp 174-175°; ir ($CHCl_3$) 3420 (O-H), 3170 (N-H), 1492 (C=C), 1448 (C=C), 1095, 1010, 840 and 704 cm^{-1}; nmr (DMSO-d_6) δ 7.79-6.93 (m, 14H); mass spectrum (70 eV) m/e (relative intensity) 363 (29), 361 (64), 317 (10), 315 (18), 286 (28) and 284 (100).

Anal. Calcd for $C_{21}H_{16}ClN_3O$: C, 69.71; H, 4.46; N, 11.61. Found: C, 69.59; H, 4.54; N,11.63.

4(5)-p-Chlorophenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole(XLI)

To a solution of 15 ml of thionyl chloride in 30 ml of benzene was added 9.05 g (0.025 mole) of the alcohol XL. The mixture was stirred at room temperature for 18 hr and then refluxed for 4 hr. Upon dilution with ether a precipitate formed which was removed by filtration and dried in vacuo to give 9.1 g (87%) of XLI: mp 245-248° (dec). Two recrystallizations from tetrahydrofuran-ether afforded the analytical sample of XLI: mp 250-252°; ir (KBr) 3310, 2520 and 1830 (N-H·HCl), 1602 (C=N), 1490 and 1443 (C=C), 750 (C-Cl) and 698 cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 345 (30), 343 (100), 268 (50) and 266 (20).

Anal. Calcd for $C_{21}H_{15}Cl_2N_3 \cdot HCl$: C, 60.52; H, 3.87; N, 10.08. Found: C, 60.47; H, 3.92; N, 10.19.

Photolysis of 4(5)-p-Chlorophenyl-5(4)-benzhydrylidene-5H(4H)-1,2,4-triazole(XLII)

A chilled (78°) solution of 4.17 g (0.01 mole) of the chloro compound XLI in 400 ml of benzene-tetrahydrofuran (1:1) was treated with 2.02 g (0.02 mole) of triethylamine. The resulting red-orange solution

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(λ_{max}^{THF} 454 nm) of the fulvene XLII was photolyzed at -78° for 3.5 hr using a 450-W Hanovia high-pressure mercury discharge lamp in a Pyrex probe. The resulting colorless solution was filtered to remove the triethylamine hydrochloride (2.43 g, 88%). The filtrate was concentrated in vacuo and the residue triturated with benzene and allowed to stand 24 hr giving 0.160 g (5%) of XLIII: mp 243-244°, which after two recrystallizations from ethanol had: λ_{max}^{EtOH} 247 nm (ϵ 36,750); $\lambda_{max}^{HCl-EtOH}$ 263 nm (ϵ 19,163); $\lambda_{max}^{H_2SO_4}$ 525 nm; ir ($CHCl_3$) 1620 (C=N), 1592 and 1485 (C=C), 1445, 1140, 1125 (broad), 1090 and 695 cm^{-1}; nmr ($CDCl_3$) δ 8.05-6.84 (m, 30H); mass spectrum (70 eV) m/e (relative intensity) 634 (21), 633 (38) 632 (82), 631 (60), 630 (100), 495 (7), 494 (10), 493 (16), 492 (14), 454 (6), 452 (13), 419 (21), 417 (46), 214 (15), 212 (40) and 178 (45).

Anal. Calcd for $C_{42}H_{28}Cl_2N_2$: C, 79.87; H, 4.47; N, 4.44. Found: C, 79.94; H, 4.52; N, 4.46.

The benzene triturate was evaporated in vacuo and the residue was chromatographed on 50 g of Florisil. Upon elution with hexane 1.17 g (66%) of diphenylacetylene was isolated.[15] Elution with hexane-benzene (1:1 v:v) afforded 0.938 g (68%) of p-chlorobenzonitrile.[15] Further elution with benzene gave 0.447 g (14%) of 1-p-chlorophenyl-2,2-diphenylacrylonitrile (LXIII): mp 142-143° (lit mp 143-144°).[15,16,23] Continued elution with benzene-chloroform (90:10 to 70:30) led to the isolation of 0.221 g (7%) of 2-p-chlorophenyl-3-phenylquinoline XLV: mp 93-95°.[15]

2-p-Chlorophenyl-3-phenylquinoline-4-carboxylic acid XLIV

To a solution of 7.35 g (0.05 mole) of isatin and 12.7 g (0.055

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mole) of 4-chloro-α-phenylacetophenone[24] in 60 ml of dry ethanol was added 12 g of sodium hydroxide in 25 ml water. The mixture was refluxed 18 hrs cooled and the solvent evaporated in vacuo. The residue was dissolved in water, washed with ether, decolorized with Norite, filtered and acidified with concentrated hydrochloric acid. The precipitate which formed was removed by filtration and dried in vacuo to give 16.5 g (92%) of XLIV: mp 305-308°. An analytical sample obtained by recrystallization from ethanol (2 times) had: mp 307-308°; ir (KBr) 3400 (OH) and 1715 (C=O) cm^{-1}; nmr (DMSO-d_6) δ 8.33-7.08 (m, 13H); mass spectrum (70 eV) m/e (relative intensity) 361 (27), 360 (48), 359 (73), 358 (92), 316 (14), 315 (23), 314 (38), 313 (35), 280 (22), 279 (84), 278 (100) and 277 (52).

Anal. Calcd for $C_{22}H_{14}ClNO_2$: C, 73.44; H, 3.92; N, 3.89. Found: C, 73.46; H, 4.04; N, 3.96.

2-p-Chlorophenyl-3-phenylquinoline(XLV)

In a 100 ml flask, 3.6 g (0.01 mole) of the acid XLIV was heated at 320° until gas evolution ceased. The residue was chromatographed over 20 g of Florisil and elution with benzene gave 2.46 g (78%) of XLV: mp 93-95°. One recrystallization from pentane afforded an analytical sample which had: mp 94-95°; ir ($CHCl_3$) 3060, 2975, 1597, 1488, 1095, 1018, 841, 701 and 597 cm^{-1}; nmr ($CDCl_3$) δ 8.33-7.10 (m, 14H); mass spectrum (70 eV) m/e (relative intensity) 317 (21), 316 (47), 315 (61) and 314 (100).

Anal. Calcd for $C_{21}H_{14}ClN$: C, 79.87; H, 4.47; N, 4.44. Found: C, 79.76; H, 4.55; N, 4.44

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Photolysis of Triphenyl-v-triazine(XLVI)

A solution of 3.09 g (0.01 mole) of triphenyl-v-triazene[25] in 400 ml of benzene-tetrahydrofuran (1:1 v:v) was photolyzed at 30° for 6 hrs using a Hanovia 450-W high-pressure mercury discharge lamp in a Pyrex probe. After concentrating in vacuo, the residue was triturated with benzene-pentane to afford yellow crystals which were removed by filtration and dried in vacuo to give 0.51 g (18%) of XXIX: mp 232-234° (after two recrystallizations from ethanol). The triturate was evaporated in vacuo and the residue chromatographed over 40 g of Florisil. Upon elution with hexane 1.21 g (68%) of diphenylacetylene was isolated.[15] Elution with hexane-benzene (1:1 v:v) provided 0.68 g (66%) of benzonitrile.[15] Continued elution with benzene-chloroform (90:10 to 70:30) gave 0.170 g (6%) of 2,3-diphenylquinoline.[15,17]

α,α-Diphenyl-1,2,3-triazole-4(5)-methanol(XLVII)

A solution of phenyllithium (0.35 mole) was prepared by the action of 55 g (0.35 mole) of bromobenzene on 4.9 g (0.7 mole) of lithium ribbon (containing 1% sodium metal) in 400 ml of anhydrous ether. The solution was cooled to 5° and 13 g (0.093 mole) of solid ethyl 1,2,3-triazole-4(5)-carboxylate[26] was added portionwise. The mixture was refluxed 18 hrs and decomposed using 125 ml of saturated aqueous ammonium chloride solution. The ether layer was washed with water, dried ($MgSO_4$), filtered and the solvent evaporated in vacuo to give 20.5 g (88%) of XLVII: mp 184-186°. One recrystallization from benzene afforded an analytical sample of XLVII: mp 185-186°; ir (KBr) 3277 (O-H), 3178 (N-H), 1658 (C=N), 1450 (C=C), 1123, 856, and 701 cm^{-1}; nmr

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(DMSO-d_6) δ 7.61 (s, 1H) and 7.52-7.04 (m, 10H); mass spectrum (70 eV) m/e (relative intensity) 251 (50), 174 (100), 105 (57) and 96 (68).

Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.21; N, 16.72. Found: C, 71.59; H, 5.27; N, 16.53.

5(4)-Chlorodiphenyl-1,2,3-triazole(XLVIII)

To a stirred solution of 40 ml of thionyl chloride in 60 ml of benzene was added portionwise 24.5 g (0.097 mole) of the solid alcohol XLVII. The mixture was stirred 1 hr during which time complete solution occurred which was followed by formation of a heavy precipitate. The reaction mixture was diluted with ether and the solid removed by filtration and dried in vacuo to give 25.8 g (84%) of XLVIII: mp 136-140°. An analytically pure sample could not be prepared as XLVIII was very moisture sensitive and could not be separated from its hydrolysis product, the alcohol XLVII. Ir (KBr) 3310, 2560 and 1845 (NH^+), 1579 (C=N), 1483 (C=C), 1443 (C=C), 750 (C-Cl) and 698 cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 233 (100), 205 (44) and 128 (24).

4(5)-Benzhydrylidene-4H(5H)-1,2,3-triazole(XLIX)

To a chilled solution (-78°) of 1.16 g (0.0037 mole) of the chloro compound XLVIII in 200 ml of benzene-tetrahydrofuran (1:1 v:v) was added 0.75 g (0.0074 mole) of triethylamine. A deep orange solution formed during the addition of the second equivalent of triethylamine but began to fade immediately at -78°. The resulting colorless solution (after 5 min) was filtered through Celite to remove the triethylamine hydrochloride (0.92 g, 91%). the filtrate was evaporated in vacuo and the residue was diluted with benzene. Upon standing 18 hrs 0.85 g (91%) of colorless crystals of XLVII (mp 184-186°) were deposited.[15]

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α,α-Diphenyl-1,2,4-triazole-3(5)-methanol(L)

A solution of phenyllithium (1.0 mole) was prepared by the addition of 157 g (1.0 mole) of bromobenzene to 14.0 g (2.0 mole) of lithium ribbon (containing 1% of sodium metal) in a total volume of 1 l of ether. The solution was chilled in an ice bath to 5° and 38.1 g (0.3 mole) of solid methyl 1,2,4-triazole-3-carboxylate[27] was added portionwise under a nitrogen atmosphere. The mixture was allowed to come to room temperature then refluxed for 18 hrs. The reaction mixture was then decomposed by the addition of 250 ml of saturated aqueous ammonium chloride solution to yield a heavy precipitate which was removed by filtration and dried in vacuo to give 32 g (42%) of L: mp 215-218°. From the filtrate, the organic layer was washed with water, dried ($MgSO_4$), filtered and the solvent evaporated in vacuo to give 11 g of triphenylcarbinol: mp 154-156°.[15] The water layers were combined and neutralized with aqueous hydrochloric acid to pH 7 after which crystals formed and were removed by filtration to give an additional 18 g (24%) of L: mp 218-220°. These two crops were combined and recrystallized from benzene to give 47 g (62%) of L: mp 221-223°. An analytical sample obtained by recrystallization from benzene melted at 222-223° and had: ir (KBr) 3380 (N-H), and 3150 (O-H) cm^{-1}; nmr (DMSO-d_6) δ 8.28 (s, 1H), and 7.82-7.03 (m, 10H); mass spectrum (70 eV) m/e (relative intensity) 251 (100), 233 (44), 174 (80), 105 (51) and 96 (38).

Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.21; N, 16.72. Found: C, 71.79; H, 5.26; N, 16.63.

3(5)-Chlorodiphenylmethyl-1,2,4-triazole(LI)

To a solution of 60 ml of thionyl chloride in 100 ml of benzene was added 38 g (0.15 mole) of the solid alcohol L portionwise. After

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the exothermic reaction ceased, the mixture was stirred 18 hrs at room temperature. The solid which formed was removed by filtration and dried in vacuo to give 33 g (73%) of LI: mp 184-187°. Two recrystallizations from tetrahydrofuran-ether afforded a pure sample of LI: mp 186-188°. An analytically pure sample could not be prepared as LI was very moisture sensitive and could not be separated from its hydrolysis product, the alcohol L. Ir (KBr) 3300, 2460 and 1890 (NH^+) and 760 (C-Cl) cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 233 (100), 205 (40) and 128 (35).

3(5)-Benzhydrylidene-3H(5H)-1,2,4-triazole(LII)

To a chilled suspension (-78°) of 3.06 g (0.01 mole) of the chloro compound LI in 300 ml of benzene-tetrahydrofuran (1:1 v:v) was added 2.02 g (0.02 mole) of triethylamine. The mixture was stirred 5 min and the resulting intense yellow solution photolyzed at -78° for 4 hrs using a Pyrex probe and a Hanovia 450-W high-pressure mercury discharge lamp. The colorless solution was filtered through Celite to remove the triethylamine hydrochloride (2.35 g 85%). The solvent from the filtrate was evaporated in vacuo yielding a gummy residue which was dissolved in benzene. Upon standing 18 hrs the solution deposited colorless crystals which were removed by filtration and dried in vacuo to give 0.75 g of L: mp 218-220°.[15] The collection of an additional 1.5 g of L: mp 217-219° brought the total yield to 89%.

5(4)-[9-Hydroxy-9-fluorene]-4(5)-phenyl-1,2,3-triazole(LIII)

To a stirred solution of 0.034 mole of o,o'-dilithiobiphenyl[28] in 100 ml of anhydrous ether was added 0.034 mole of the lithium anion of methyl 4-phenyl-1,2,3-triazole-5-carboxylate[14] as an ether suspen-

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sion. This was prepared by the addition of 20.4 ml (0.034 mole) of phenyllithium (1.66 M) to a solution of 6.9 g (0.034 mole) of the ester in 50 ml of anhydrous ether. After this suspension had been added, the mixture was refluxed for 18 hrs and then decomposed using 5% hydrochloric acid (125 ml). The organic layer was washed with water (2 x 50 ml), dried ($MgSO_4$), filtered and the solvent evaporated in vacuo yielding 6.2 g (56%) of LIII: mp 216-219°. Two recrystallizations from ether-pentane afforded an analytical sample of LIII: mp 219-220°; ir (KBr) 3210 (N-H and O-H broad); nmr (DMSO-d_6) δ 7.87-6.48 (m, 13H); mass spectrum (70 eV) m/e (relative intensity) 325 (40), 181 (54) and 152 (100).

Anal. Calcd for $C_{21}H_{15}N_3O$: C, 77.52; H, 4.65; N, 12.92. Found: C, 77.35; H, 4.75; N, 12.83

1,6-Diphenyl-5,5,10,10-bisdiphenylene-5H,10H-ditriazolo[1,2-a:1',2'-d]-pyrazine(XV)

To a stirred solution of 10 ml of thionyl chloride in 50 ml of dry benzene was added 3.25 g (0.01 mole) of the alcohol LIII. The solution was heated in order to complete solution and after 10 min a heavy precipitate formed. Heating was continued for 0.5 hr and the suspension was then stirred 18 hrs at room temperature. The reaction was diluted with dry ether, the solid removed by filtration, washed with ether and dried in vacuo to give 3 g (97%) of LIV: mp >330°; ir (KBr) 1450 (C=C), 1280, 943, 900, 745 and 700 cm^{-1}; nmr (DMSO-d_6) δ 7.81-6.98 (m, 26H); mass spectrum (70 eV) m/e (relative intensity) 279 (100).

Anal. Calcd for $C_{42}H_{26}N_6$: C, 82.06; H, 4.26; N, 13.67. Found: C, 82.14; H, 4.22; N, 13.81.

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3,5, α ,α -Tetraphenylpyrazole-4-methanol(XVI)

A solution of phenyllithium (0.2 mole) was prepared by the addition of 31.4 g (0.2 mole) bromobenzene to 2.8 g (0.4 mole) of lithium ribbon (containing 1% sodium metal) in 250 ml anhydrous ether. To this solution was added portionwise 13 g (0.0468 mole) of solid methyl 3,5-diphenylpyrazole-4-carboxylate.[29] The suspension was stirred for 18 hrs at reflux and decomposed with 100 ml of 5% hydrochloric acid. A solid separated and was removed by filtration to give 16.8 g of LVI: mp 207-209°. The organic layer of the filtrate was washed with water (2 x 75 ml), dried ($MgSO_4$), decolorized with Norite (2 g), filtered through Celite and evaporated in vacuo to give an additional 1.4 g of LVI: mp 208-209°. The combined yield was 18.4 g (97%) and an analytical sample of LVI obtained by crystallization from toluene and melted at 208-209°; ir (KBr) 3490 (broad O-H) and 3230 (broad N-H) cm^{-1}; nmr (DMSO-d_6) δ 12.97 (broad s, 1H), 7.52-6.61 (m, 20H) and 6.19 (s, 1H); mass spectrum (70 eV) m/e (relative intensity) 402 (40), 385 (100), and 325 (40).

Anal. Calcd for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96. Found: C, 83.29; H, 5.61; N, 7.04.

3,5-Diphenyl-4-chlorodiphenylmethylpyrazole hydrochloride(LVII)

A solution of 8.04 g (0.02 mole) of the alcohol LVI in 100 ml of tetrahydrofuran was saturated with dry hydrogen chloride. The mixture was stirred 15 min, the solvent evaporated in vacuo and the residue treated with a solution of 15 ml of thionyl chloride in 30 ml of dry benzene. After heating at reflux for 0.5 hr the mixture was stirred at room temperature for 18 hrs. The precipitate that formed was removed by fil-

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tration, washed with ether and dried in vacuo to give 6 g (66%) of LVII: mp 168-171°. A second crop crystallized affording an additional 2 g (22%) of LVII: mp 168-170°. An analytical sample obtained by crystallization from tetrahydrofuran-ether melted at 170-171°; ir (KBr) 3060, 2400 and 1850 (N-H-HCl) 1478 and 1442 (C=C) and 687 (C-Cl) cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 384 (100) and 307 (27).

Anal. Calcd for $C_{28}H_{21}ClN_2 \cdot HCl$: C, 73.52; H, 4.85; N, 6.13. Found: C, 73.50; H, 4.97; N, 6.20.

3,5-Diphenyl-4-benzhydrylidene-4H-pyrazole(XVIII)

A cooled solution (-78°) of 6 g (0.013 mole) of the chloro compound LVII in 200 ml of anhydrous tetrahydrofuran was treated with 2.6 g (0.026 mole) of triethylamine. The mixture was stirred for 10 min after the addition was complete, then diluted with iso-octane and the solid which formed was removed by filtration to yield 3.6 g (100%) of triethylamine hydrochloride. The resulting red solution was concentrated in vacuo until red needle-like crystals began to separate. The crystals were removed by filtration to give 4.7 g (94%) of LVIII: mp 155-156°; λ_{max}^{THF} 382 nm; ir ($CHCl_3$) 1540 (C=C), 1468 (C=C), 1448 (C=C), 1120 and 700 cm^{-1}; nmr ($CDCl_3$) δ 7.55-6.81 (m, 20H); mass spectrum (70 eV) m/e (relative intensity) 386 (34), 385 (100), 384 (49) and 307 (26).

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.26; H, 5.10; N, 7.13.

3,5-Diphenyl-4-methoxydiphenylmethylpyrazole(LIX)

To 10 ml of anhydrous methanol was added 0.1 g (0.00026 mole) of the fulvene LVIII resulting in an immediate color discharge. Upon standing 1 hr the solution began to deposit colorless plates which were

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removed by filtration to give 0.11 g (100%) of LIX; mp 105° (resolidifies then melts 170-172° dec); ir ($CHCl_3$) 3442 (N-H), 3190 (broad O-H), and 1078 (C-O-C) cm^{-1}; nmr ($CDCl_3$) δ 7.47-6.84 (m, 20H), 3.39 (s, 3H) and 3.20 (s, 3H); upon recrystallization from toluene-hexane; ir ($CHCl_3$) no O-H at 3190 cm_{-1}; nmr showed no signal (singlet) at 3.39 ppm; mass spectrum (70 eV) m/e (relative intensity) 416 (25), 385 (100) and 339 (15).

Anal. Calcd for $C_{29}H_{24}N_2O$: C, 83.62; N, 5.81; N, 6.73. Found: C, 83.60; H, 5.76; N, 6.59.

3,5-Diphenyl-4-aminodiphenylmethylpyrazole(LX)

A chilled solution (5°) of 0.1 g (0.00026 mole) of the azafulvene LVIII in 10 ml of anhydrous tetrahydrofuran was saturated with ammonia. The resulting colorless solution was evaporated in vacuo and the residue obtained recrystallized from ether-hexane to give 0.097 g (93%) of LX: mp 180-182°; ir ($CHCl_3$) 3442 (NH_2) and 3190 (broad N-H); nmr ($CDCl_3$) δ 7.32 (s, 2H), 7.21 (s, 1H), and 7.18-6.84 (m, 20H); mass spectrum (70 eV) m/e (relative intensity) 401 (5), 387 (100), 386 (100), 220 (31) and 181 (25).

Anal. Calcd for $C_{28}H_{23}N_3$: C, 83.76; N, 5.77; N, 10.47. Found: C, 83.55; N, 5.53; N, 10.68.

3,4 α,α -Tetraphenylpyrazole-5-methanol(LXI)

To a solution of phenyllithium (0.35 mole) prepared by the addition of 55 g (0.35 mole) of bromobenzene to 4.9 g (0.7 mole) of lithium ribbon (containing 1% of sodium metal) in 500 ml of ether was added 27.8 g (0.1 mole) of solid methyl 3,4-diphenylpyrazole-5-carboxylate.[30] After the initial exothermic reaction was complete, the mixture was re-

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fluxed 3 hrs, then stirred for 18 hrs at room temperature. The reaction mixture was decomposed by the addition of 100 ml of saturated aqueous ammonium chloride solution and the ether layer after drying ($MgSO_4$) was evaporated *in vacuo* to give 39 g (97%) of LXI: mp 150-151°; ir (KBr) 3558 (O-H), 3448 (N-H), 1492 (C=C), 1450 (C=C) and 700 cm^{-1}; nmr ($CDCl_3$) δ 7.46-7.01 (m, 20H); mass spectrum (70 eV) *m/e* (relative intensity) 402 (31), 384 (100), 325 (23) and 280 (18).

Anal. Calcd for $C_{28}H_{22}N_2O$: C, 83.55; N, 5.51; N, 6.96. Found: C, 83.47; H, 5.53; N, 6.93.

3,4-Diphenyl-5-chlorodiphenylmethylpyrazole(LXII)

A suspension of 12 g (0.03 mole) of the alcohol LXI in 300 ml of anhydrous ether was saturated with dry hydrogen chloride. During the addition there was complete solution followed by the formation of a heavy precipitate. The mixture was stirred for 30 min, the solvent evaporated *in vacuo* and the residue treated with a solution of 15 ml of thionyl chloride in 30 ml of dry benzene. After heating at reflux for 0.5 hr the resulting solution was stirred at room temperature 18 hrs. Upon diluting with ether (200 ml), a precipitate formed which was removed by filtration and dried *in vacuo* to give 13.4 g (98%) of LXII: mp 131-133°. Two recrystallizations from tetrahydrofuran-ether afforded the analytical of LXII which had: mp 134-136°; ir (KBr) 3058 and 2400 (NH^+), 1573 (C=C), 1478 (C=C), 1442, and 683 (C-Cl) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 384 (100).

Anal. Calcd for $C_{28}H_{21}ClN_2 \cdot HCl$: C, 73.52; H, 4.85; N, 6.13. Found: C, 73.64; H, 5.02; N, 5.97.

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3,4-Diphenyl-5-benzhydrylidene-5H-pyrazole(LXIII)

To a chilled solution (5°) of 4.57 g (0.01 mole) of the chloro compound LXII in 250 ml of anhydrous tetrahydrofuran was added 2.02 g (0.02 mole) of triethylamine. An intense red solution formed during the addition of the second equivalent of triethylamine. The reaction mixture was stirred 5 min at 5°, then warmed to room temperature and the solvent evaporated in vacuo. The resulting residue was dissolved in benzene and filtered through Celite under a dry nitrogen atmosphere to remove the triethylamine hydrochloride. The filtrate was concentrated in vacuo diluting with n-hexane. Red needle-like crystals formed which were removed by filtration and dried in vacuo to give 3.6 g (94%) of LXIII. Upon melting, the crystals turned to a white solid at 120-130° which then melted 179-181° (an ir of the white solid showed it to be identical to LXIV). LXII had: λ_{max}^{THF} 393 nm; ir ($CHCl_3$) 1543, 1463 and 1452 (C=C), 1134 and 698 cm^{-1}; nmr ($CDCl_3$) δ 7.74-6.91 (m, 20H), mass spectrum (70 eV) m/e (relative intensity) 385 (100), 384 (73) and 307 (34).

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.42; H, 5.22; N, 7.44.

1,2,5,5,6,7,10,10-Octaphenyl-5H,10H-dipyrazolo[1,2-a:1',2'-d]pyrazine (LXIV)

A solution of 1.12 g (.00024 mole) of the chloro compound LXII in 100 ml of dry tetrahydrofuran was cooled to 5° and treated with 0.495 g (0.0048 mole) of triethylamine. The mixture was stirred at room temperature for an additional 18 hrs. during which time the intense red color faded. The triethylamine hydrochloride was removed by filtration (0.638 g 96%). The filtrate was concentrated in vacuo and the residue

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chromatographed over 30 g of Florisil. Elution with benzene afforded 0.741 g (75%) of LXIV: mp 179-181°; ir ($CHCl_3$) 1623 (C=N), 1605 (C=C), 1475 (C=C), and 700 cm^{-1}; nmr ($CDCl_3$) δ 7.64-6.68 (m, 40H), mass spectrum (70 eV) m/e (relative intensity) 768 (100) and 384 (27).

Anal. Calcd for $C_{56}H_{40}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.24; H, 5.37; N, 7.14.

Photolysis of LXIII

To a chilled solution (5°) of 2.29 g (0.0005 mole) of LXII in 150 ml of dry tetrahydrofuran was added 1.01 g (0.01 mole) of triethylamine. The red solution was diluted with 150 ml of cold tetrahydrofuran and photolyzed 6 hrs at 5° using a 450-W Hanovia high-pressure mercury discharge lamp in a Pyrex probe. Tlc indicated no reaction and the red color still persisted.

Photolysis of LXIII

To a chilled solution (5°) of 4.57 g (0.01 mole) of the chloro compound LXII in 300 ml of dry tetrahydrofuran-benzene (1:1 v:v) was added 2.02 g (0.02 mole) of triethylamine. The reaction mixture was stirred 5 min and filtered through Celite under a dry nitrogen atmosphere to remove triethylamine hydrochloride (2.32 g 84%). The clear red solution was photolyzed at 5° using a quartz probe and a 450-W Hanovia high-pressure mercury discharge lamp. The color of the solution was discharged without noticeable gas evolution during 20 min after which the solvent was evaporated in vacuo to give 3.11 g (81%) of LXIV (mp 179-181°).[15]

α,α-Diphenyl-1H-phenanthro[9,10-c]pyrazole-3-methanol(LXV)

To a stirred solution of 52.5 ml of phenyllithium (2.3 M) in

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70:30 benzene-ether) in 100 ml of anhydrous ether was added 11 g (0.04 mole) of solid methyl 3,4-diphenylene-pyrazole-5-carboxylate,[31] After the addition was complete, the mixture was refluxed 6 hrs, stirred at room temperature for 18 hrs and decomposed using 5% hydrochloric acid (125 ml). The organic layer was washed with water, dried ($MgSO_4$), filtered and the solvent evaporated in vacuo to give 14 g (87%) of LXV: mp 168-171°. Two recrystallizations from benzene afforded an analytical sample of LXV: mp 172-173°; ir (KBr) 3410 (O-H), and 3160 (N-H); nmr (DMSO-d_6) δ 10.01-6.81 (m, 18H); mass spectrum (70 eV) m/e (relative intensity) 400 (27) and 382 (100).

Anal. Calcd for $C_{28}H_{20}N_2O$: C, 83.97; H, 5.03; N, 7.00. Found: C, 83.78; H, 5.09; N, 6.90.

3-Chlorodiphenylmethyl-1H-phenanthro[9,10-c]pyrazole(LXVI)

To a stirred solution of 20 ml of thionyl chloride in 40 ml of benzene was added 12 g (0.03 mole) of the solid alcohol LXV. The mixture was stirred 18 hrs at room temperature, then refluxed 4 hrs. The precipitate which formed was removed by filtration, washed with anhydrous ether and dried in vacuo to give 12 g (88%) of LXVI: mp 248-251°. Two recrystallizations from tetrahydrofuran-ether afforded a pure sample of LXVI: mp 250-252.° An analytically pure sample could not be prepared as LXVI was very moisture sensitive and could not be separated from its hydrolysis product, the alcohol LXV. Ir (KBr) 3250 and 2500 (NH^+) and 790 (C-Cl) cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 382 (100) and 305 (15).

Photolysis of 3-Benzhydrylidene-3H-phenanthro[9,10-c]pyrazole(LXVII)

To a solution of 2.28 g (0.005 mole) of the chloro compound LXVI

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in 400 ml of dry tetrahydrofuran-benzene (1:1 v:v) at -78° was added 1.01 g (0.01 mole) of triethylamine. The light orange solution was photolyzed at this temperature for 20 min using a Pyrex probe and a Hanovia 450-W high-pressure mercury lamp with no noticeable gas evolution. The resulting colorless solution was filtered through Celite to remove 1.27 g (92%) of triethylamine hydrochloride. The filtrate was concentrated in vacuo and diluted with benzene. Upon standing 24 hrs the solution deposited 1.8 g (95%) of LXV (mp 172-173°).[15].

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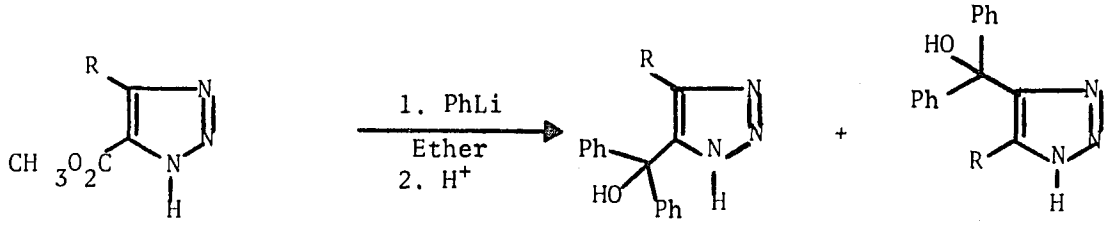
CHAPTER III

DISCUSSION OF RESULTS

The purpose of this research, as stated in the introduction, was to prepare a series of di- and triazafulvenes which would photochemically extrude nitrogen to possibly provide triafulvenes and azatriafulvenes respectively. The azafulvenes were prepared by dehydrohalogenating the corresponding chlorodiphenylmethylazoles. The chloro compounds were synthesized by the reaction of the diphenylcarbinols with thionyl chloride in benzene at ambient temperatures. Chart I outlines the three general synthetic pathways used to produce the diphenylcarbinols.

Scheme I



LXXXIIa R=Ph
b R=H
c R=p-ClC$_6$H$_5$

XXIV R=Ph
XLVII R=H
XL R=p-ClC$_6$H$_5$

XXIII

CHART I

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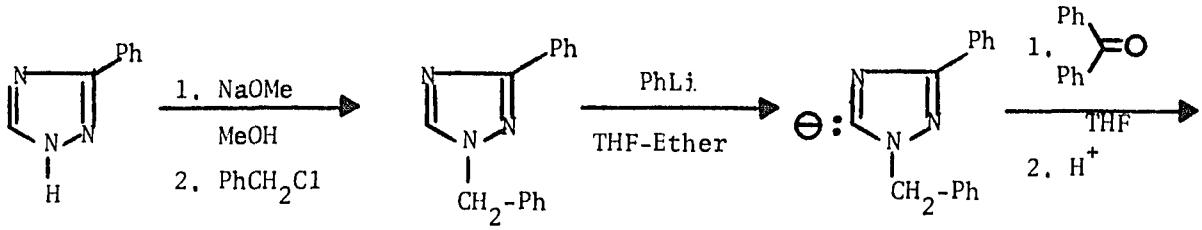
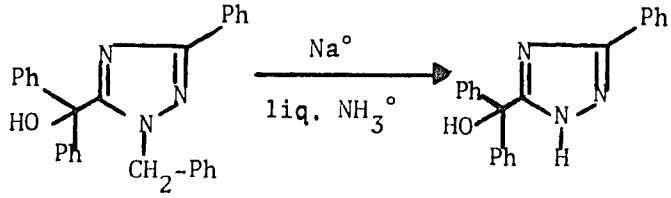
Scheme II

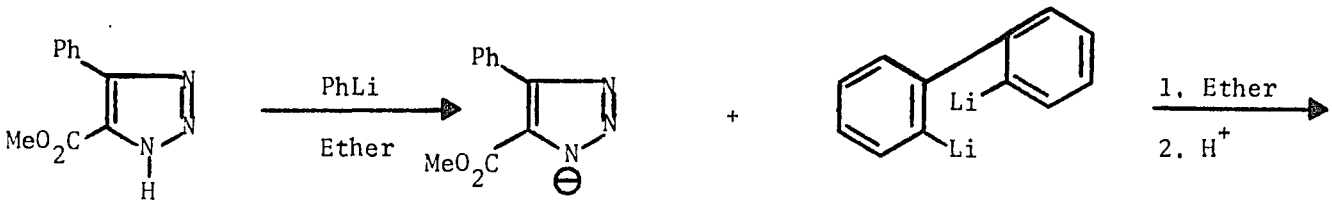


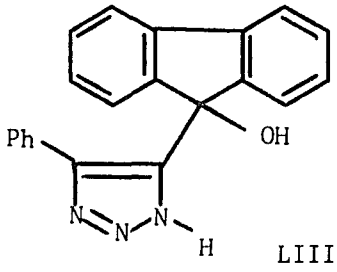
LXXXIV XXXI



XXXII XXXIV

Scheme III





LIII

Chart I. Preparation of Triazole Diphenylcarbinols.

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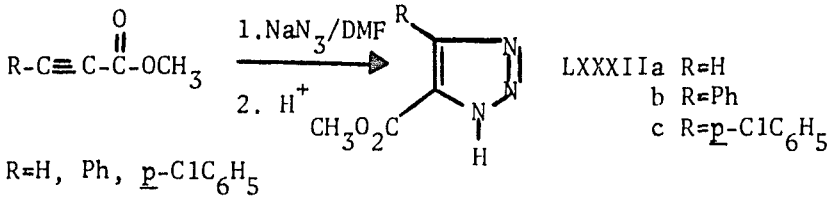
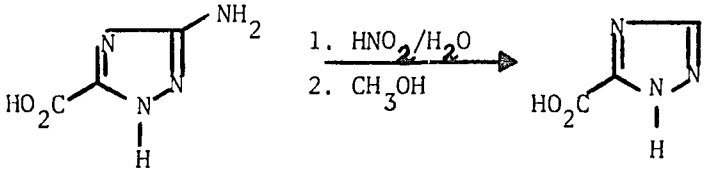
The 1,2,3-triazole esters LXXXIIa, LXXXIIb and LXXXIIc (Scheme I) were prepared by the cycloaddition of the corresponding propiolate esters to an azide ion in dimethylformamide followed by acidification.



The 1,2,4-triazole ester LXXXIII was synthesized by diazotiation followed by reduction of the corresponding amino acid which was prepared by the method of Cipens and Grinshtein.[27]



The synthesis of the carbinols XXXIV and LIII are outlined in Schemes II and III.

The physical and spectral properties of the diphenylcarbinols and the chloro hydrochlorides derived by treatment with thionyl chloride are summarized in Table I.

The dehydrohalogenation was accomplished by treating tetrahydrofuran solutions of the chloro hydrochlorides previously described with triethylamine at -78°. The triazafulvenes XXVIII, XLIX, XXV, LII, and

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Table 1. Physical and Spectral Properties of the Triazole Diphenylcarbinols and their Chloro Hydrochlorides.

Compound	mp	Characteristic infrared absorbances
Diphenylcarbinols:		
XXIV	159-160°	KBr - 3320 (O-H), 3190 (N-H) cm^{-1}
XXIII	220-221°	KBr - Broad O-H and N-H 3300 cm^{-1}
XLVII	185-186°	KBr - 3277 (O-H), 3178 (N-H) cm^{-1}
XL	174-175°	$CHCl_3$ - 3420 (O-H), 3170 (N-H) cm^{-1}
XXXIII	232-233°	KBr - 3263 (O-H), 3143 (N-H) cm^{-1}
LIII	219-220°	KBr - broad O-H and N-H 3210
L	222-223°	KBr - 3380 (O-H), 3150 (N-H) cm^{-1}
Chlorohydrochlorides:		cm^{-1}
XXV	229-230°	KBr - 3270, 2340 and 1852 ($\overset{+}{N}$-H), 759 (C-Cl)
XXXIV	175-177°	KBr - 3300, 2380 and 1840 ($\overset{+}{N}$-H), 780 (C-Cl)
XLI	250-252°	KBr - 3310, 2520 and 1830 ($\overset{+}{N}$-H), 750 (C-Cl)
XLVIII	136-140°	KBr - 3310, 2560 and 1845 ($\overset{+}{N}$-H), 750 (C-Cl)
LI	186-188°	KBr - 3300, 2460 and 1890 ($\overset{+}{N}$-H), 760 (C-Cl)

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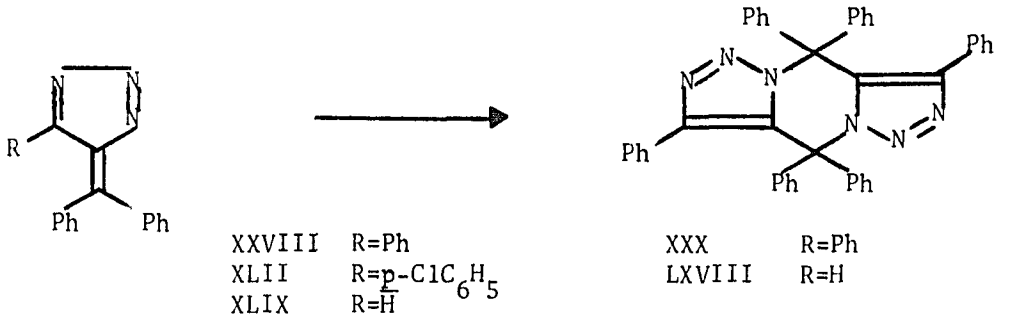
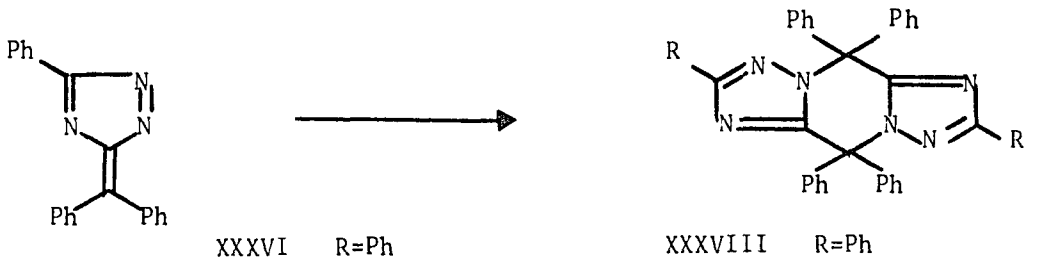
LIV were unstable at room temperature and immediately dimerized to the photochemically inert 5H,10H-ditriazolo(1,2-a:1',2'-d)pyrazines[3,32] XXX, LXVIII, XXXVIII, LXIX and LV.



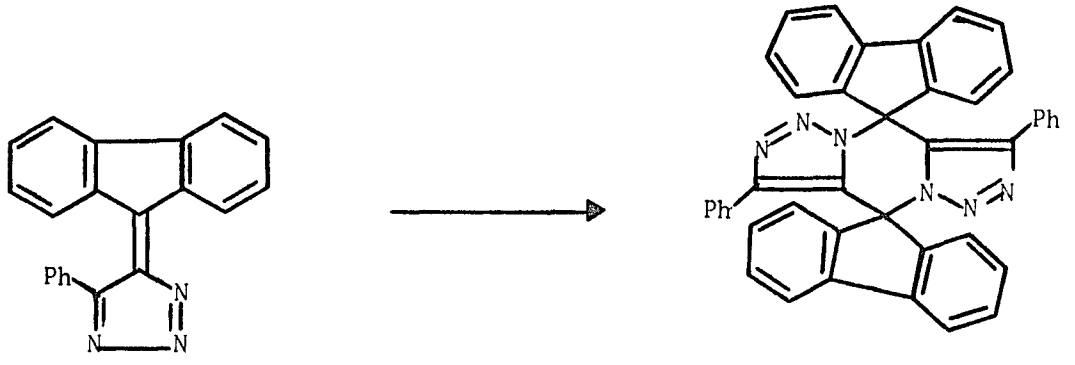
XXVIII R=Ph
XLII R=p-ClC$_6$H$_5$
XLIX R=H

XXX R=Ph
LXVIII R=H



XXXVI R=Ph
LII R=H

XXXVIII R=Ph
LXIX R=H



LIV LV

Chart IV. Preparation of Triazafulvene Dimers.

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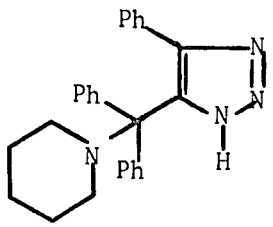
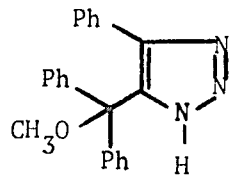
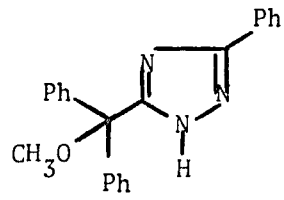
The pyrazines were isolated in all cases except LXVIII and LXIX (R=H) which hydrolyzed spontaneously on exposure to moisture to the diphenylcarbinols XLVII and L. The pyrazines XXX and XXXVIII (R=Ph) could also be hydrolyzed to the corresponding carbinols by heating with hydrochloric acid in ethanol and water and this is offered as a partial structure proof. The fulvenes XXVIII and XXXVI were further characterized by their reaction with methanol to give the ethers XXVII and XXXV and with piperidine to give the adduct XXVI.



XXVI



XXVII



XXXV

Benzene-tetrahydrofuran solutions (1:1 v:v 0.025 M) of XXVIII (λ_{max}^{THF} 463 nm), XXXVI (λ_{max}^{THF} 442 nm) and XLII (λ_{max}^{THF} 454 nm) were stable at -78° for periods > 8 hrs. Irradiation of the previously described solutions of XXVIII and XXXVI afforded a mixture of products from which diphenylacetylene,[15] benzonitrile,[15] 2,3-diphenylquinoline(LXX), triphenylacrylonitrile(LXXI) and a yellow crystalline dimer of constitution $(C_{21}H_{15}N)_2$ (XXIX) were isolated. 1,3-Diphenyl-5-diphenylmethyl-1,2,4-triazole was also isolated as one of the photoproducts from XXXVI (Chart III and Table II).

2,3-Diphenylquinoline(LXX) was prepared by decarboxylation of 2,3-diphenylcinchoninic acid which was prepared by the method of Pfitzinger.[17]

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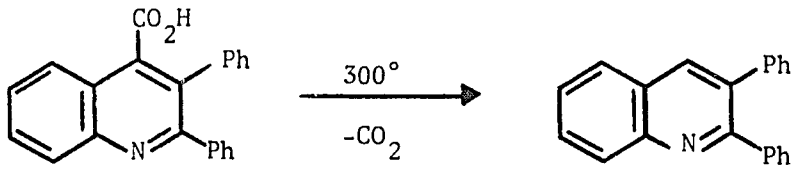
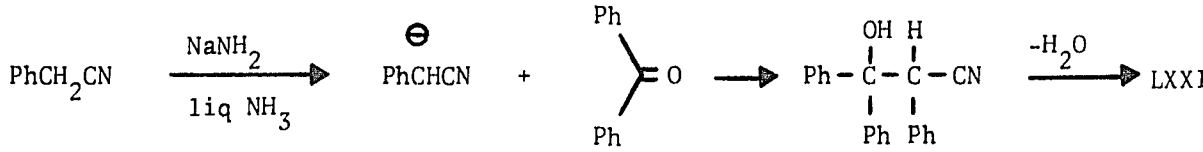
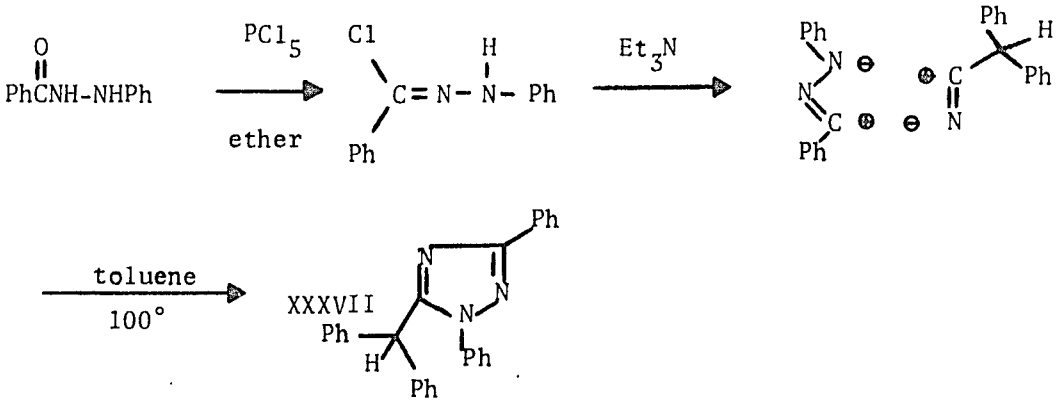


Triphenylacrylonitrile (LXXI) was prepared by the aldol condensation of phenylacetonitrile with benzophenone.



An unequivocal synthesis of XXXVII was carried out using the method of Huisgen et. al.[19] which involved the addition of the nitrile ylid (LXXXIV) to diphenylacetonitrile. The ylid was prepared by dehydrohalogenating benzoylchloride phenylhydroazone with triethylamine.



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The hexaphenyl-1,5-diazocine structure XXIX has been assigned to the dimer pending a complete X-ray crystallographic analysis on the dichloro analog (XLIII) produced by the irradiation of XLII. This structural assignment is based in part on the observation that thermolysis of XXIX at 300° gives only benzonitrile and pentaphenylpyridine. Structural symmetry can be inferred from the mass spectrum (70 eV) which displayed major ions at m/e 562 ($C_{42}H_{30}N_2^+$), 281 ($C_{21}H_{15}N^+$) and 204 ($C_{21}H_{15}N^+-C_6H_5$). Other spectral data obtained on XXIX includes ir ($CHCl_3$) 1618 (C=N), 1598 (C=C), and 1577 (C=C); nmr ($CDCl_3$) δ 8.08-6.57 (m, 30H); λ_{max}^{EtOH} 258 nm (ϵ 42,150), $\lambda_{max}^{EtOH\cdot HCl}$ 263 nm (ϵ 36,998) and the formation of a cation in con sulfuric acid with λ_{max} 618 nm.

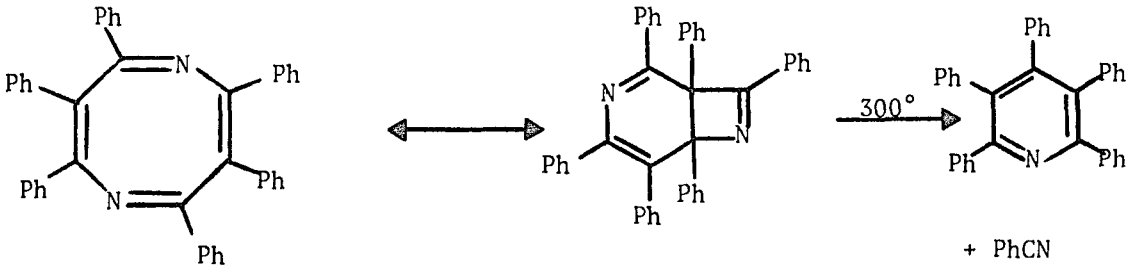

Chart V. Thermal Products of XXIX.

The mechanism for the formation of XXXVII can be explained by the cis-addition of a photo-excited benzene molecule to the fulvene(XXXV) in a $\pi^2_s + \pi^6_s$ cycloaddition reaction to give LXXII. Subsequent bond reorganization followed by a suitable hydrogen shift gives the product XXXVII.

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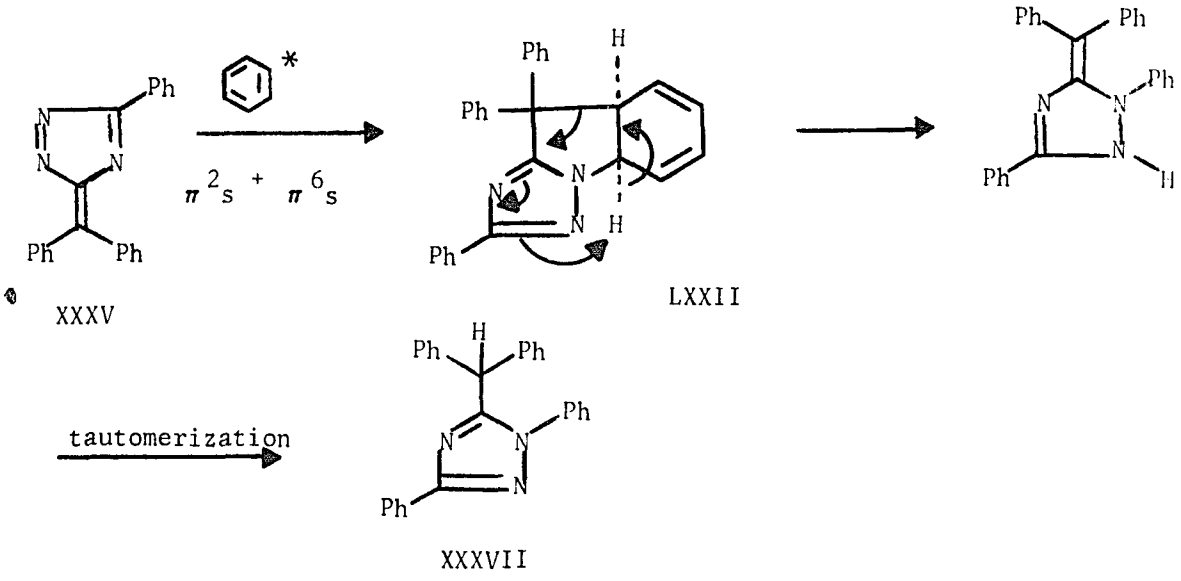
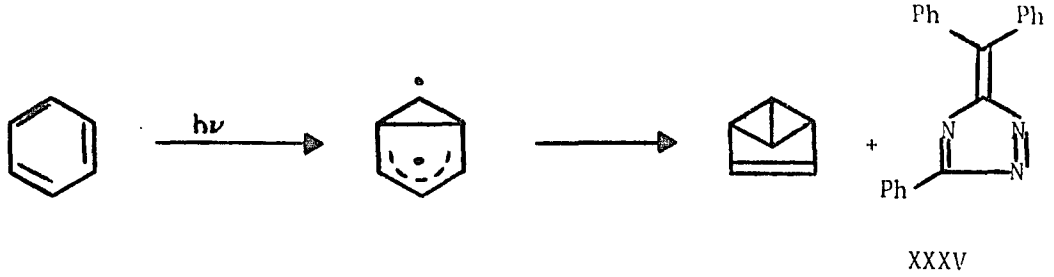


Chart IV. Mechanism for the Formation of 1,3-Diphenyl-5-diphenylmethyl-1,2,4-triazole.

An alternative mechanism involves the formation of benzvalene which adds to the fulvene in a $\pi^6_s + \pi^2_s$ cycloaddition reaction to give LXXIX followed by bond reorganization to also give XXXVII.



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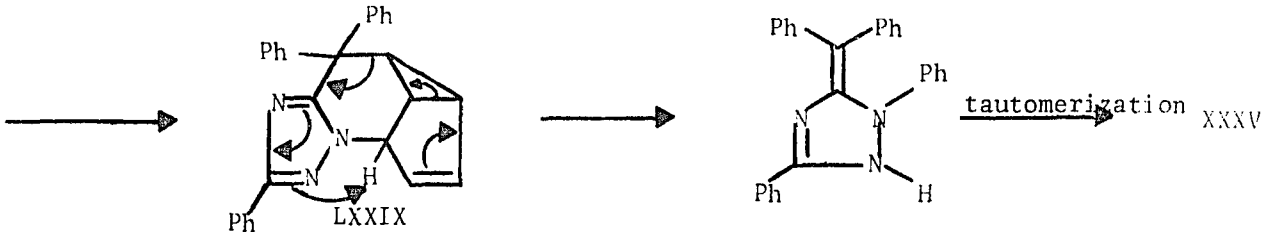
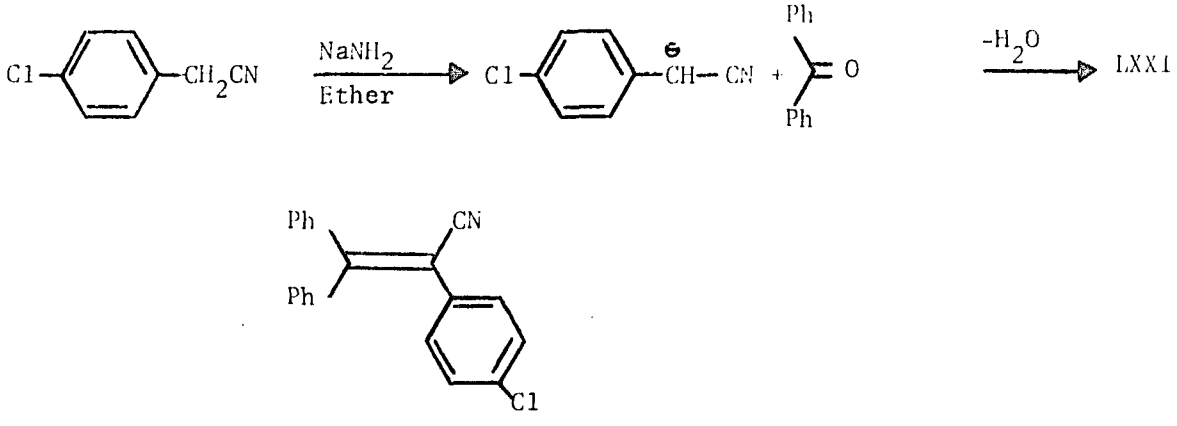


Chart IV. Mechanism for the Formation of 1,3-Diphenyl-5-diphenylmethyl-1,2,4-triazole.

The synthesis and irradiation of XLII was undertaken to produce an analog of XXIX which would contain a heavy atom suitable for X-ray crystallographic analysis. In addition to the formation of the desired dimer of $C_{21}H_{14}ClN$(XLIII), the isolation of p-chlorobenzonitrile, diphenylacetylene, 1-(p-chlorophenyl)-2,2-diphenylacrylonitrile(LXXIII) and 2-(p-chlorophenyl)-3-phenylquinoline(XLV) (Chart III and Table II) afforded additional information concerning the probable mechanism of the reaction.

10(p-chlorophenyl)-2,2-diphenylacrylonitrile(LXXIII) was prepared by the Aldol condensation of p-chlorophenylacetonitrile with benzophenone using sodium amide in ether.[16,23]



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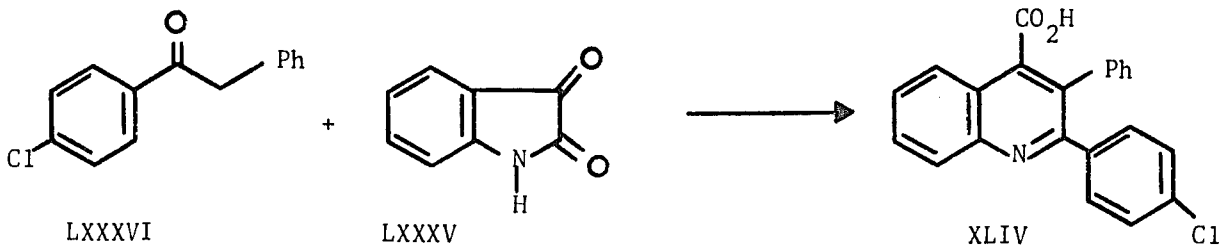
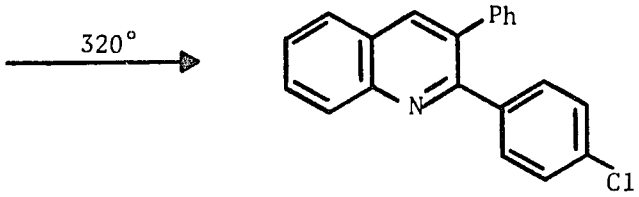
2-(p-chlorophenyl)-3-phenylquinoline (XLV) was prepared by decarboxylation of the heretofore unknown 2-(p-chlorophenyl)-3-phenylcinchonic acid XLIV which was in turn prepared by the general method of Pfitzinger.[17] Isatin (LXXXV) was condensed with 4-chloro-α-phenylacetophenone[24] LXXXVI in alcoholic sodium hydroxide followed by acidification.



LXXXVI LXXXV XLIV



XLV

It would be difficult to rationalize the formation of some of the same products from two structurally diverse fulvenes (XXVIII and XXXV) without invoking several common intermediates. The appearance of diphenylacetylene, benzonitrile and p-chlorobenzonitrile is readly explained by the cleavage of the intermediate diradicals LXXIVa, LXXIVb and LXXV with the rearrangement of the 1,1-diphenylethylene carbene to

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diphenylacetylene.

The genesis of triphenylacrylonitrile (LXXI) and 1-(p-chlorophenyl)-2,2-diphenylacrylonitrile (LXXIII) can be explained by a simple rearrangement (1,2 phenyl shift) of the diradicals LXXIVa and LXXIVb respectively. However, the formation of LXXI from the diradical LXXV cannot readily be explained without the intervention of triphenyltriazafulvene LXXVIa. Chart II outlines the interconversions of the diradicals and offers a plausible mechanism for the formation of the substituted acrylonitriles.

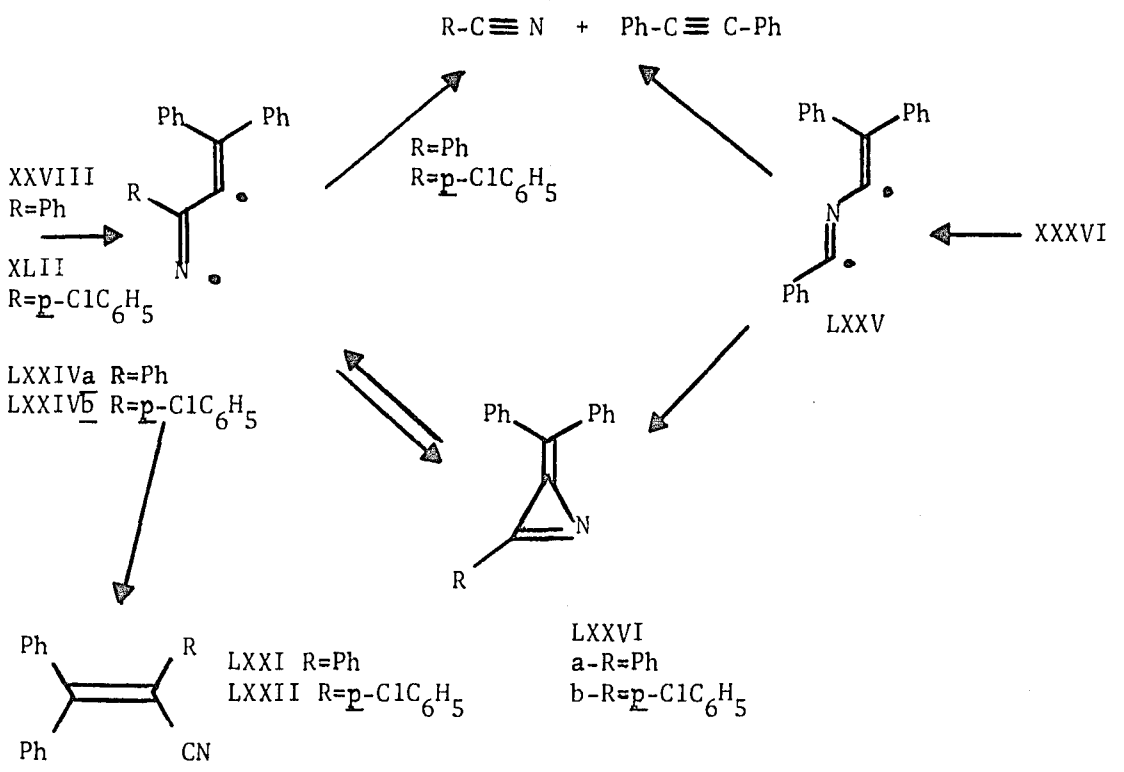

Chart II. Interconversion of Diradicals from the Photolysis of 1,2,3- and 1,2,4-Triazafulvenes.

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Chart III. Photolysis Products from 1,2,3- and 1,2,4-triazafulvenes and Triphenyl-v-triazine.

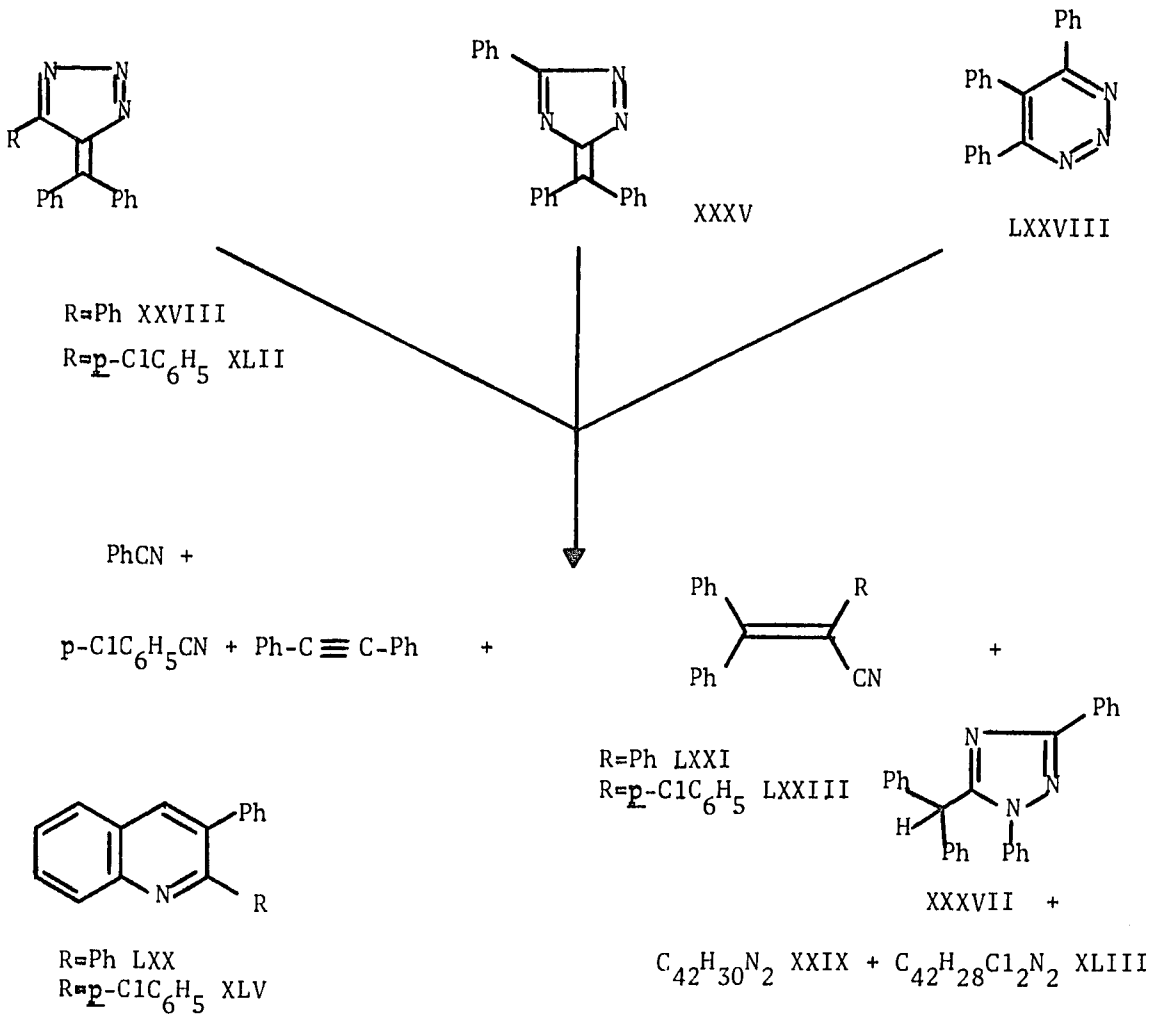

Table 2. Percent Yield of Photoproducts

Compd.	PhCN	p-ClC$_6$H$_5$CN	Ph-C≡C-Ph	70	45	71	73	37	29	43
XXVIII	51	--	49	11	--	7	--	--	26	--
XXXVI	43	--	48	17	--	11	--	8	12	--
XLII	--	68	66	--	7	--	14	--	--	5
LXXVIII	66	--	68	6	--	--	--	--	18	--

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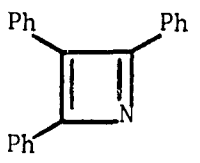
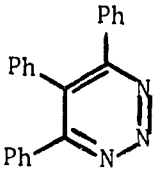
The formation of the dimers (XXIX and XLII) and the substituted quinolines (LXX and XLV) as photoproducts probably represents a further transformation of an intermediate triphenylazete LXXVII.



LXXVII



LXXVIII

Both species can be formed from LXXIV or LXXV by phenyl migration and closure.

The hypothesis that XXIX, XLIII, LXX and XLV are derived from either LXVII or LXXX exclusively is supported by a reexamination of the photochemistry of triphenyl-v-triazine [25] LXXVIII. Irradiation of LXXVII in benzene-tetrahydrofuran solution (1:1 v:v 0.0025 M) at 30° for 5 hrs gave in addition to the previously reported benzonitrile and diphenylacetylene, both XXIX and LXX (Chart III and Table II). The $\pi^2_s + \pi^4_s$ dimerization of LXXVII followed by electrocyclic opening would give XXIX.

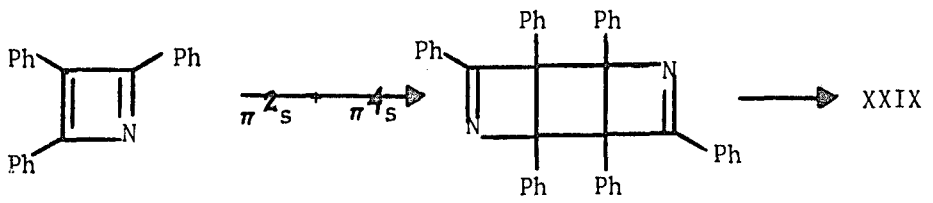


Chart VII. Mechanism for the Formation of XXIX.

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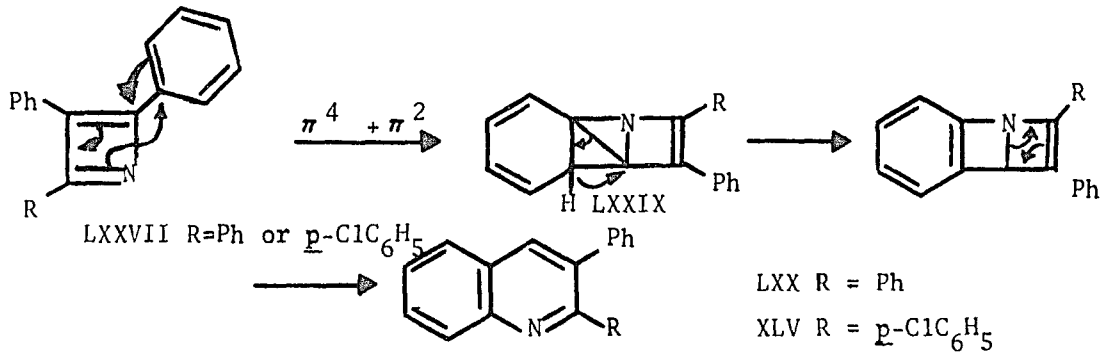
The mechanistic process for the conversion of LXXVII to LXX can be compared to an analogous sequence for the transformation of tetraphenylcyclobutadine to 1,2,3-triphenylnaphthalene.[32] A $\pi 4 + \pi 2$ intramolecular cyclization of LXXVII to LXXIX followed by suitable hydrogen shift and bond reorganization leads to the formation of LXX.



A second mechanistic consideration involves the cyclization of LXXXVII to the intermediate LXXXI which then undergoes a rearrangement to give LXX.

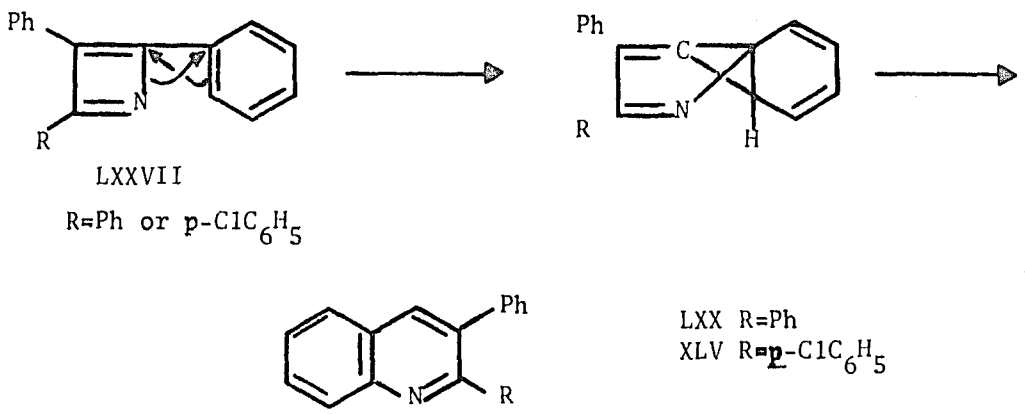


Chart VIII. Mechanisms for the Formation of the Substituted Quinolines.

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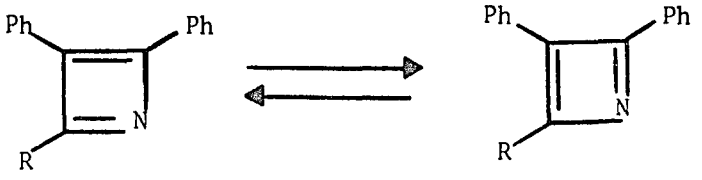
It is interesting to note that the only qinoline isolated from the irradiation of XLII is XLV. There is no evidence to indicate the presence of 2,3-diphenyl-6-chloroquinoline which would arise if the $\pi 2 + \pi 4$ cyclization that takes place involved the p-chlorophenyl group. From this observation it can be implied that the isomerization of LXXVII to LXXXX is not occurring.

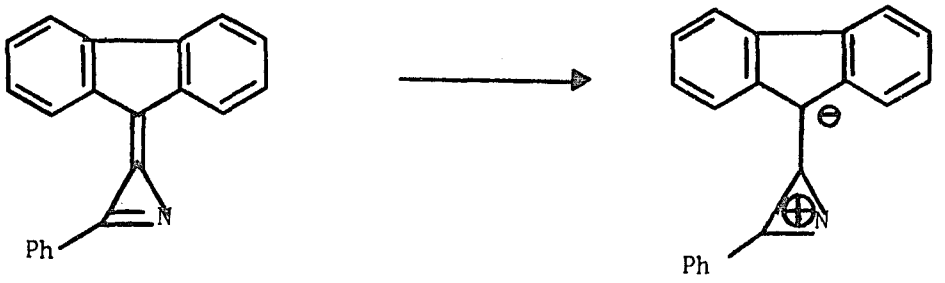


LXXVII LXXXX

R=Ph or p-ClC_6H_5

Since one of the postulated intermediates of the photoreactions was the triphenyltriazafulvene LXXVI, the fluorenol LIII was prepared in the hope that resonance stabilization by the fluorene ring would lead to the isolation of LXXXI.

LXXX



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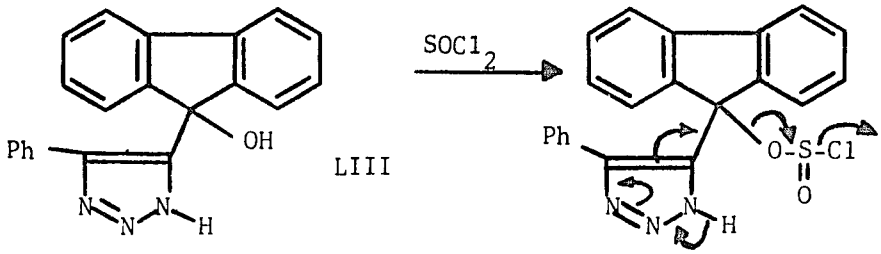
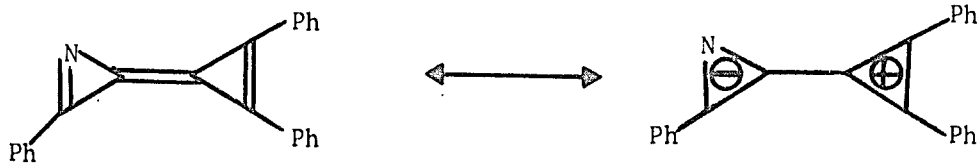
However, the reaction of LIII with thionyl chloride in order to prepare the chloro precursor led to the isolation of a chlorine free product melting >330° whose structure was established as the fulvene dimer LXXXI ($C_{42}H_{26}N_6$). The ir had no absorbance above 1500 cm^{-1} and the nmr showed only aromatic proton resonances. This coupled with the mass spectrum (70 eV) m/e 279 ($C_{21}H_{13}N^+$) and the fact that acid hydrolysis gave only the starting alcohol LIII substantiates this assignment. A similar dimerization has been reported in the case of α,α-diphenyl-tetrazole-5-methanol.[33]



LIII

LXXXI

Battiste and Hill[7] have reported a convenient method for preparing azapentatriafulvalenium ions in high yield. Since the cyclopropenyl ring is electron-withdrawing, it would provide an excellent substituent for stabilizing an azatriafulvene LXXXII.



LXXXII

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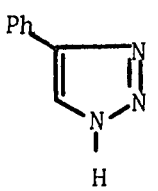
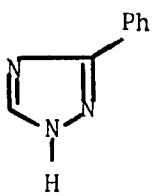
The isomeric triazoles LXXXIII and LXXXIV were prepared by decarboxylation of their corresponding acids. However, when these triazoles were dissolved with an equimolar amount of diphenylcyclopropenone in methylene chloride at 0° and the mixture reacted with anhydrous hydrogen chloride gas, no cyclopropenyl adduct could be isolated. Since the original work was carried out using indole and substituted pyrroles which both have electron rich 3-positions, it is evident that the introduction of additional nitrogen atoms into the ring diminishes the susceptibility to electrophilic attack by the cyclopropenyl cation.

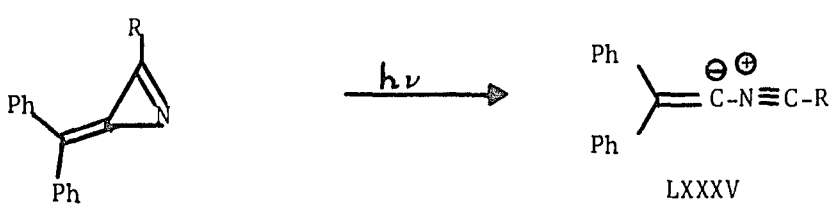


LXXXIII



LXXXIV

Padwa has recently shown[34] that azirines are photochemically transformed into their corresponding nitrile ylids which can be trapped from the reaction mixture with several electron-deficient olefins. Since azatriafulvenes are analogous to azirines, they might also be rearranged photochemically to the corresponding nitrile ylids LXXXV.



LXXXV

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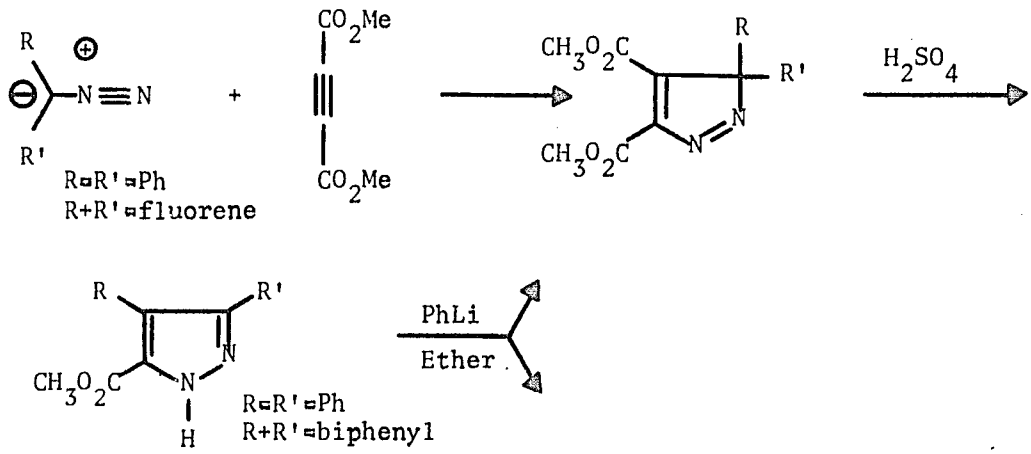
Attempts to trap LXXXV with a series of reagents including furan, acrylonitrile, methanol and diisopropylamine were unsuccessful. In some cases, the addition of the trapping agent so changed the polarity of the medium that the increased rate of dimerization of the fulvenes was the only reaction observed.

Unsuccessful attempts[35,36] have been made to prepare the much sought after tetraphenyltriafulvene LXXXVI.

LXXXVI

The preparation and irradiation of 1,2- or 3,4-diazafulvenes appeared to offer a facile entry into this system. The necessity of phenyl substitution on the azafulvene ring for stabilization has been pointed out previously in the case of the azatriafulvenes. Therefore, the two initial diazafulvenes prepared were LVIII and LXIII which synthesized from their esters by the same sequence of reactions as the triazafulvenes.

The pyrazole esters LXXXVII.[30] LXXXVIII[31] and LXXXIX[29] were prepared by an acid catalyzed rearrangement of the corresponding



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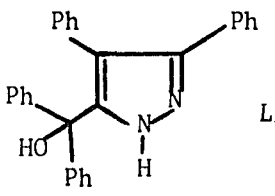
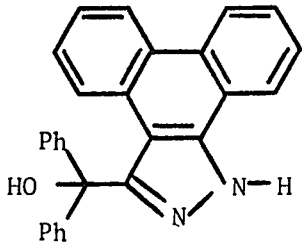


LXI



LXV

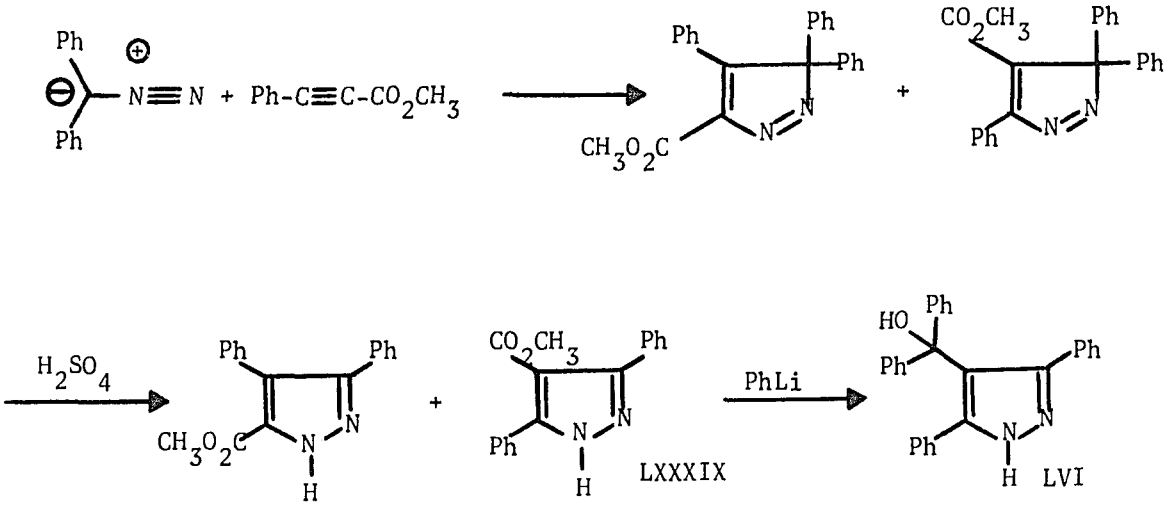


Chart XI. Preparation of Pyrazole Disphenylcarbinols.

The physical and spectral properties of the diphenylcarbinols and the chloro hydrochlorides derived from them are summarized in Table III.

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Table 3. Physical and Spectral Properties of the Pyrazole Diphenylcarbinols and their Chloro Hydrochlorides.

Compound	mp	Characteristic infrared absorbances
Diphenylcarbinols:		
LVI	208-209°	KBr - 3490 (O-H), 3230 (N-H) cm^{-1}
LXI	150-151°	KBr - 3558 (O-H), 3448 (N-H) cm^{-1}
LXV	172-173°	KBr - 3410 (O-H), 3160 (N-H) cm^{-1}
Chlorohydrochlorides:		cm^{-1}
LVII	170-171°	KBr - 3060, 2400 and 1850 ($\overset{+}{N}$-H), 687 (C-Cl)
LXII	134-136°	KBr - 3058, and 2400 ($\overset{+}{N}$-H), 683 (C-Cl) cm^{-1}
LXVI	250-252°	KBr - 3250 and 2500 ($\overset{+}{N}$-H), 790 (C-Cl) cm^{-1}

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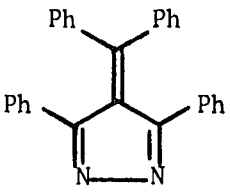
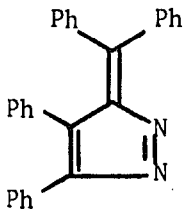
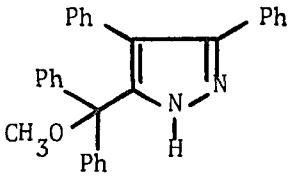


LVIII

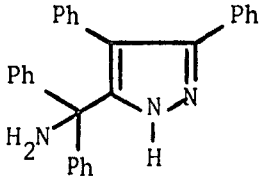


LXIII

Unlike the triafulvenes, LVIII and LXIII were not only stable in solution at 5° but could be isolated and characterized. The azafulvene LVIII was further characterized by conversion to the corresponding ether LIX with methanol and the amine LX with ammonia.



LIX



LX

Photolysis of LXIII at 5° for 6 hrs in tetrahydrofuran (0.0015 M) using a Pyrex probe led to the recovery of unchanged starting material. When a quartz probe was substituted under the same conditions, the color was discharged in 20 mins without noticeable gas evolution and the product isolated was identical to that from the thermal dimerization of the fulvene in tetrahydrofuran at 25°. The mass spectrum (70 eV) displayed major ions at 768 ($C_{56}H_{40}N_4^+$) and 384 ($C_{28}H_{20}N_2^+$) from which the pyrazine structure LXIV can be inferred by analogy with the triafulvenes.

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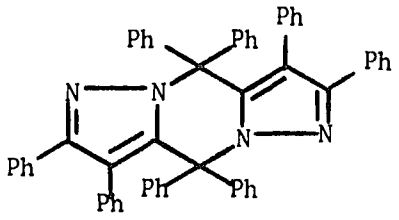
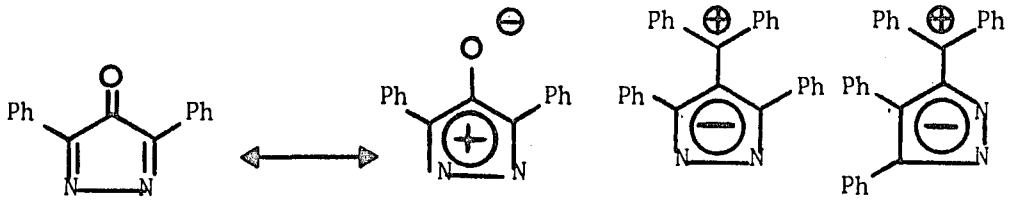


LXIV

Photolysis of LVIII under the previously described conditions yielded only unchanged starting material.

Diels-Alder addition reactions of LVIII and LXIII with n-phenylmaleimide, norbornadiene, 4-phenyl-1,2,4-triazoline-3,5-dione, diphenylcyclopropene, 2,3-dimethylbutadiene, dimethyl acetylenedicarboxylate and 1-diethylamino-1-propyne afforded only unchanged or hydrolyzed starting materials upon work up.

This result may seem unexpected since the somewhat analogous 2,5-diphenyl-3,4-diazacyclopentadienone undergoes the Diels-Alder reaction as a dienophile, in moderate yields, adding to electron-rich dienes.[37] However, when the resonance structures are compared, it is evident that LVIII and LXIII have greater charge separation than LXXVII.



LXXVII LVIII LXIII

Photolysis of LXVII with loss of nitrogen would lead to the benzhydrylidene analog of the unknown phenanthrocyclopropenone system LXXVIII.

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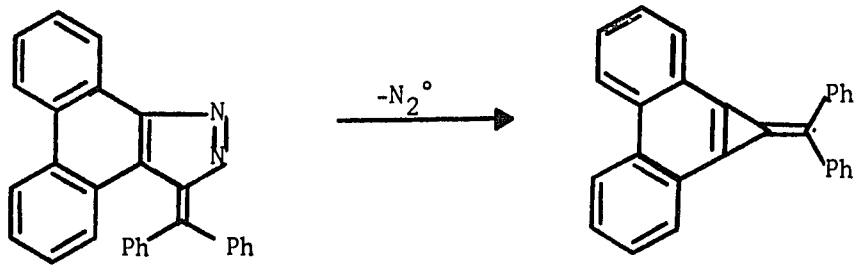

LXVII LXXXVIII

The photolysis of LXVII did not lead to noticeable nitrogen evolution but the fulvene solution was decolorized after 20 min of irradiation and the starting alcohol was isolated quantitatively. This product probably arises from hydrolysis of the intermediate fulvene dimer during isolation.

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CHAPTER IV

CONCLUSIONS

A series of pyrazole and triazole diphenylcarbinols and their chloro hydrochlorides has been prepared. These were converted by dehydrohalogenation with triethylamine to di- and triazafulvenes which were identified by isolation of the fulvene itself, its dimer or addition products with methanol and amines.

Irradiation of the triazafulvenes XXVII, XXXVI and XLII gave rise to a mixture of products which were isolated by column chromatography and identified by physical and spectral comparison with authentic samples.

The isolation of triphenylacrylonitrile (LXXXI) from the irradiation of XXXVI indicates the presence of a triphenylazatriafulvene (LXXVI) intermediate.

There is also evidence for the formation of an intermediate triphenylazete (LXXVII) from which both 2,3-diphenylquinoline (LXX) and the proposed 1,5-diazocine (XXIX) arise during photolysis of either XXXVI or XXVIII.

The photoreaction of XLII produced the dichloro analog of XXIX (XLIII), from which a complete X-ray crystallographic analysis will hopefully confirm the assigned structure.

The diazafulvenes LVIII and LXIII, although stable enough to isolate, did not evolve nitrogen upon irradiation and attempted Diels-Alder

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addition reactions with them as either dienes or dienophiles proved to be fruitless.

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VITA

Joseph P. Sanchez was born January 20, 1942 in Wakefield, Michigan. He received the Bachelor of Science Degree in Chemistry in 1965 from the Detroit Institute of Technology. Following his graduation he was employed as an Assistant Research Chemist with Parke-Davis and Company at its research center in Ann Arbor. He entered the Georgia Institute of Technology to begin graduate study in organic chemistry in September, 1968.

He is married to the former Karen M. Poikey and they have two sons Scot Andrew (born October 9, 1970) and Brian Michael (born August 24, 1971).

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