

THE ATTEMPTED SYNTHESIS OF AN ELECTRON-DEFICIENT ISONITRILE

A THESIS

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THE ATTEMPTED SYNTHESIS OF AN ELECTRON-DEFICIENT ISONITRILE

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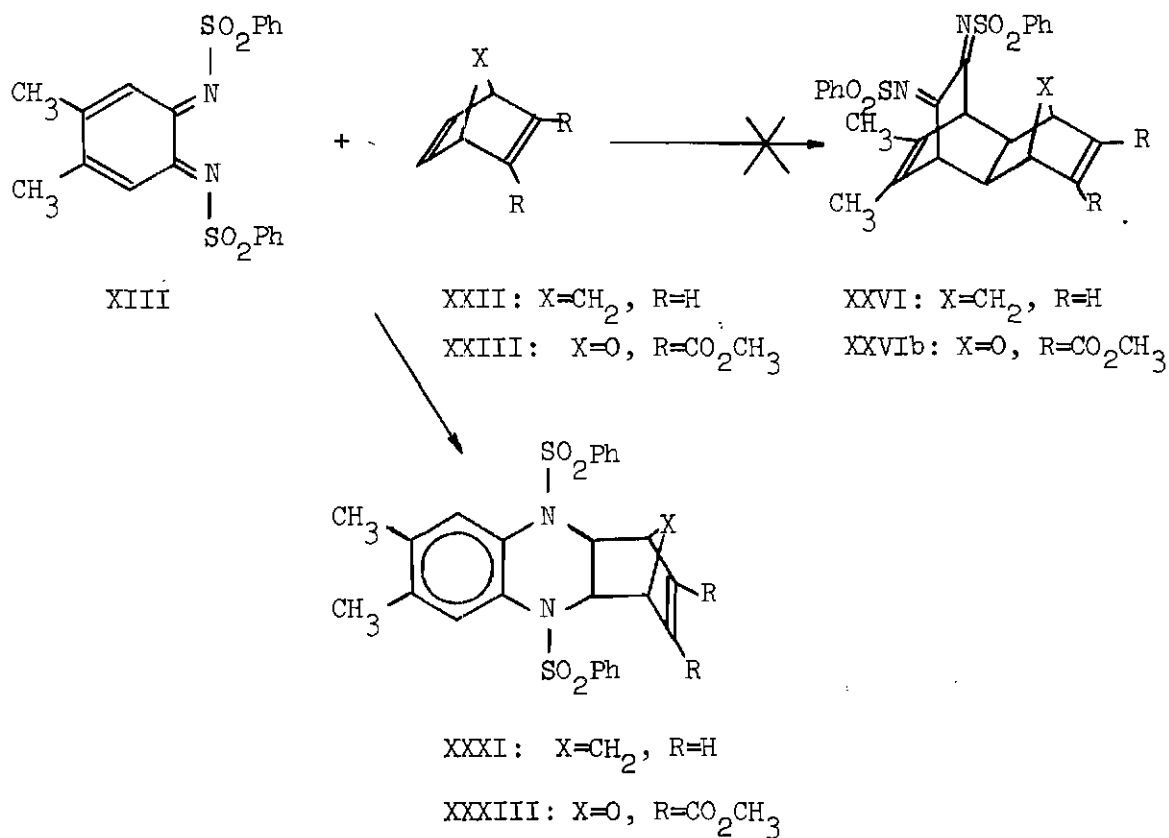
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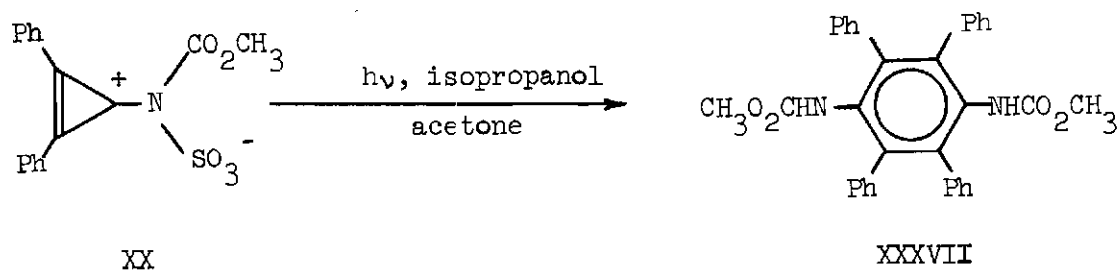
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SUMMARY

4,5-Dimethyl-o-quinone dibenzenesulfonimide (XIII) reacted with norbornadiene (XXII) and with dimethyl-3,6-epoxy-3,6-dihydrophthalate (XXIII) to give 7,8-dimethyl-5,10-dibenzenesulfonyl-1,4,4a,5,10,10a-hexahydro-1,4-methanophenazine (XXXI) and 7,8-dimethyl-2,3-dicarbomethoxy-5,10-dibenzenesulfonyl-1,4,4a,5,10,10a-hexahydro-1,4-epoxyphenazine, respectively, resulting from cycloaddition across the diazadiene system rather than the carbocyclic Diels-Alder reaction to give XXVI and XXVIb.



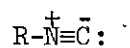
The photolysis of diphenylcyclopropene-N-carbomethoxyimine sulfonate (XX) was shown to produce N,N'-dicarbomethoxy-tetraphenyl-p-phenylenediamine (XXXVII). The mechanism proposed consisted of $[2\pi + 2\pi]$ cycloaddition, thermal rearrangement with expulsion of sulfur trioxide, and reduction by solvent.



CHAPTER I

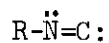
INTRODUCTION

The physical properties, such as dipole moment, of isonitriles are most consistent with the triple-bonded dipolar structure (I) (1).



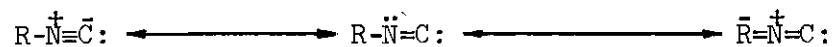
I

The first structure (II) proposed for isonitriles includes divalent character of the terminal carbon atom (2,3).



II

Isonitriles can be considered to be a hybrid of three resonance structures with structure (I) making the greatest contribution on the basis of the physical properties (1) and the fact that isonitriles usually behave as nucleophiles (4).



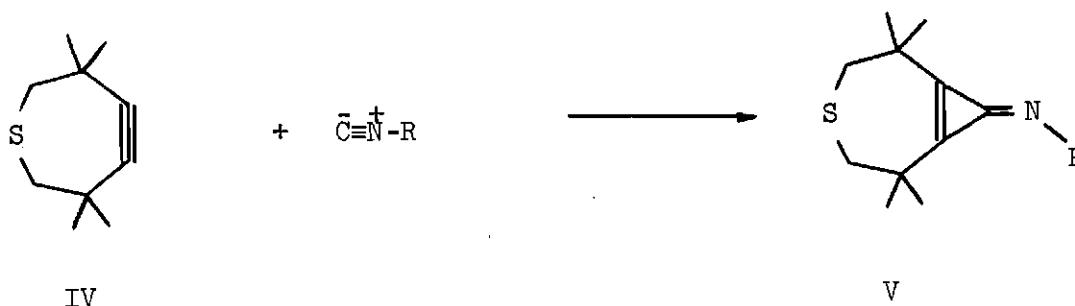
I

II

III

For isonitriles in which R is electron-withdrawing structures (II) and (III) should become more important as resonance contributors. The only isonitriles known which have electron withdrawing groups are substituted aromatic isonitriles (5,6,7).

A study (8) of the reactions of a highly strained alkyne with isonitriles to give cyclopropeneimines showed that the rates of reaction of *p*-nitrophenyl and phenyl isonitrile were, respectively, 117 and 4.7 times the rate of reaction of cyclohexyl isonitrile with 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (IV).



A sulfonyl (VI) or carbonyl (VII))isonitrile should be sufficiently electron-deficient that structures (II) and (III) are the major resonance contributors.



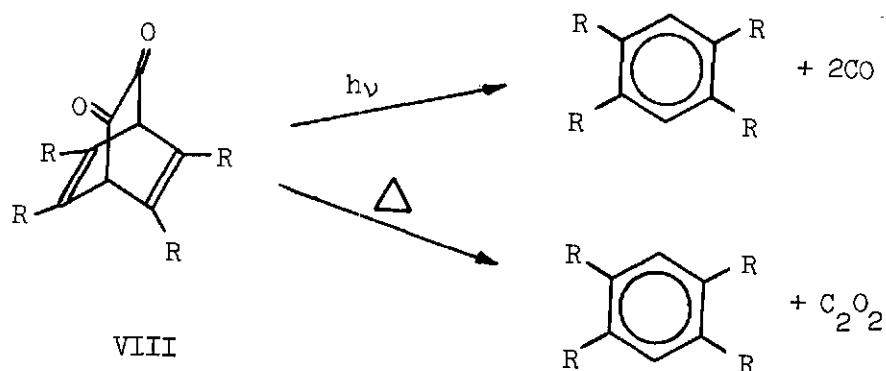
VI



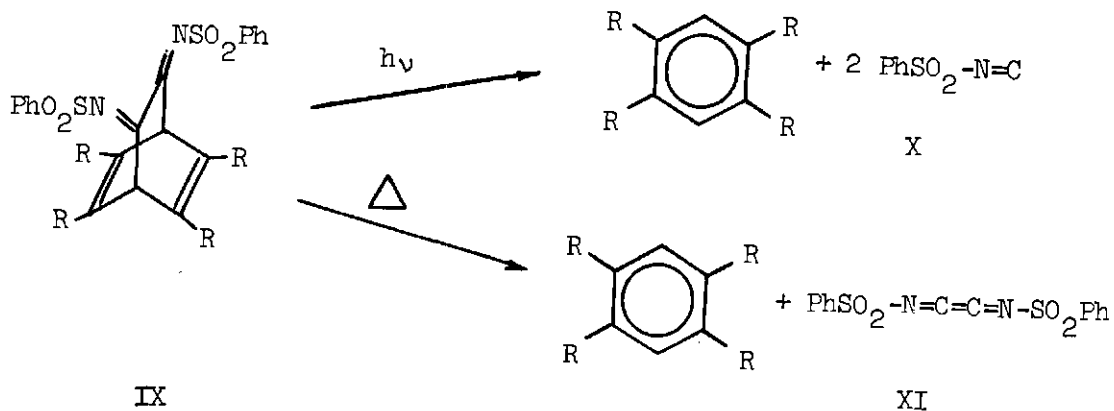
VII

The usual methods for the synthesis of isonitriles were considered unsuitable for electron-deficient isonitriles since they are predicted to have greatly enhanced reactivity due to their similarity to carbenes. Expulsion of reactive species from bridged or strained ring compounds seemed to be the most promising method.

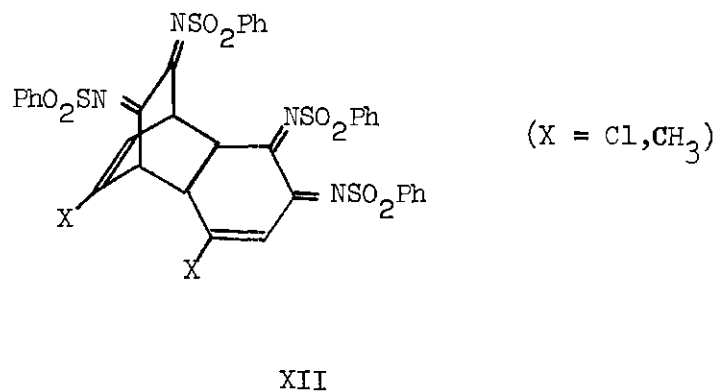
The photolysis (9) of several 2,3-diketo-[2.2.2]-bicyclo-octadienes (VIII) gave nearly quantitative yields of aromatized products after smooth evolution of carbon monoxide. Evidence for the thermal expulsion of the dimer of carbon monoxide was obtained from the mass spectra of the starting materials.



The dibenzenesulfonimide (IX) of structure (VIII) should be a suitable precursor for the photolytic generation of benzenesulfonyl isonitrile (X) and the thermal generation of its dimer (XI).

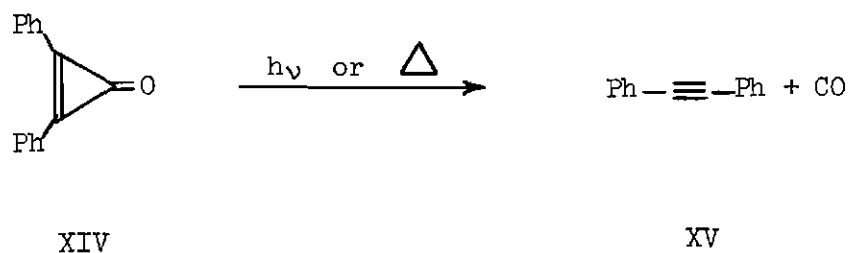


A possible route to (IX) was suggested by the postulated structures of the dimers (XII) of 4-chloro and 4-methyl-o-quinone-dibenzenesulfonimide (10).



4,5-Dimethyl-o-quinone-dibenzenesulfonimide (XIII) would not dimerize.

Pyrolysis (11) and photolysis (12) of diphenylcyclopropanone (XIV) resulted in expulsion of carbon monoxide to give diphenylacetylene (XV).

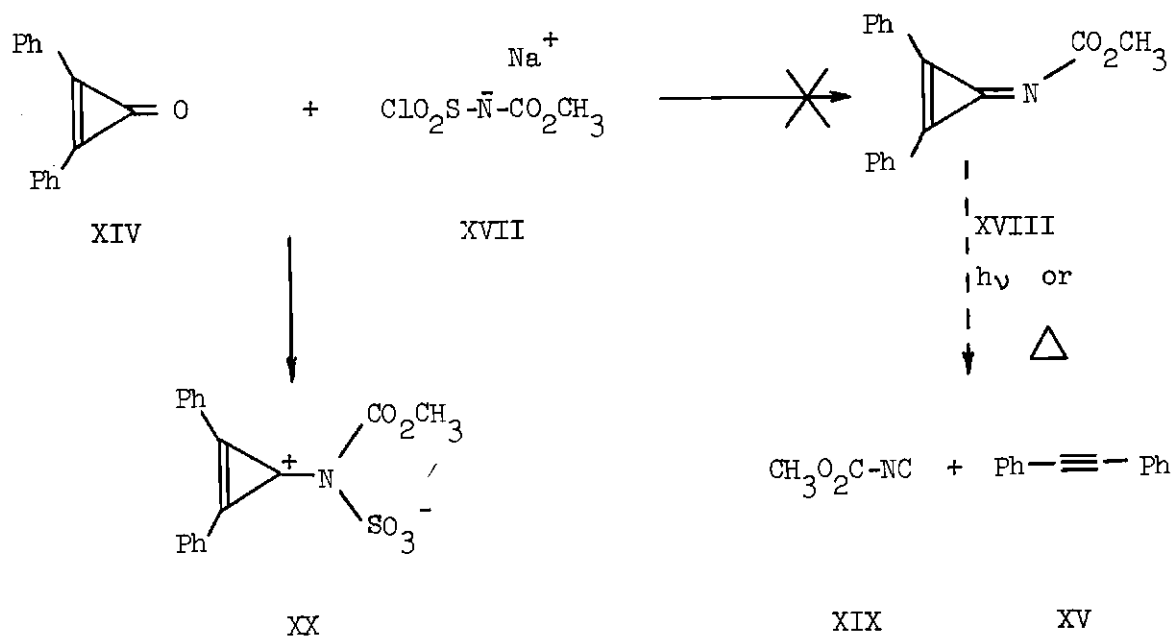


Photolysis (13) of diphenylcyclopropene-p-toluene sulfonylimine (XVI) was shown to involve cleavage of one of the carbon to carbon bonds of the cyclopropene ring to give a 1,3-diradical which then formed several products, two of which might be ascribed to p-toluene-sulfonylisonitrile.

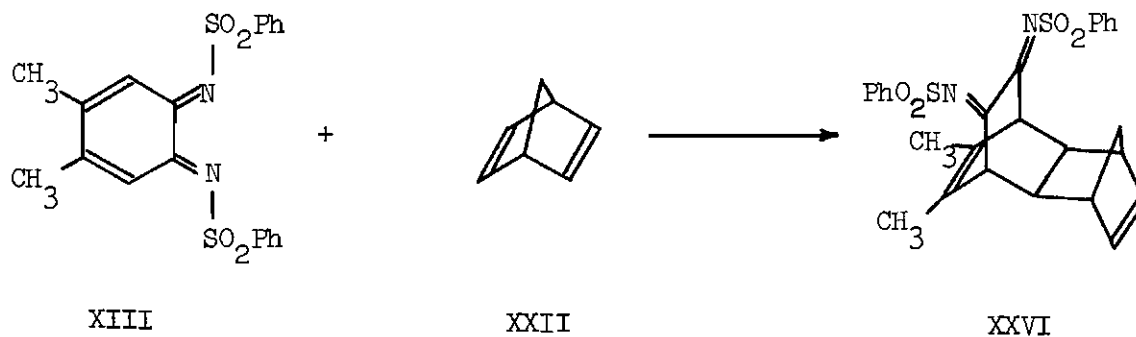
The reaction (14) of diphenylcyclopropenone (XIV) with the sodium salt of carbomethoxysulfamoyl chloride (XVII) was reported to produce diphenylcyclopropene-carbomethoxyimine (XVIII) which might be a route to carbomethoxy isonitrile (XIX). Later evidence (15) showed that the product of this reaction is diphenylcyclopropene carbomethoxyimine sulfonate (XX).

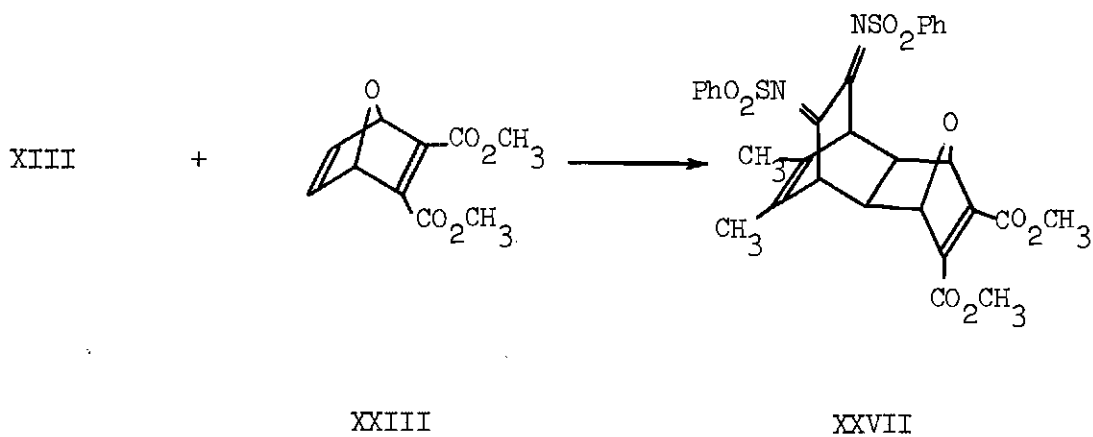
Several norbornadienone ketals have been shown to undergo thermal fragmentation with expulsion of the bridge as a carbene (16,17,18,19). The thermal fragmentation of the p-toluenesulfonylimine of a substituted norbornadienone should be a feasible route to p-toluenesulfonylisonitrile (XXI).

It was the purpose of this research to synthesize suitable precursors and to generate, trap or isolate, if possible, an electron-deficient isonitrile with sufficient contribution to the

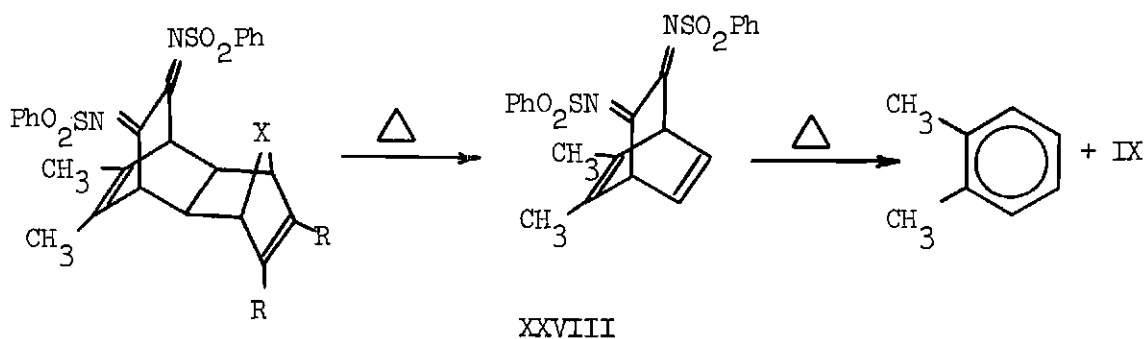


structure from resonance forms (II) and (III) to react as a carbene. The Diels-Alder reactions of (XIII) with selected dienophiles should be a feasible route to (IX). The dienophiles chosen were norbornadiene (XXII), dimethyl-3,6-epoxy-3,6-dihydrophthalate (XXIII) (20), 7,8-dicarbomethoxy-tricyclo-[4.2.2.0^{2,5}]-deca-3,7,9-triene (XXIV) (21), and dimethylacetylenedicarboxylate (XXV).

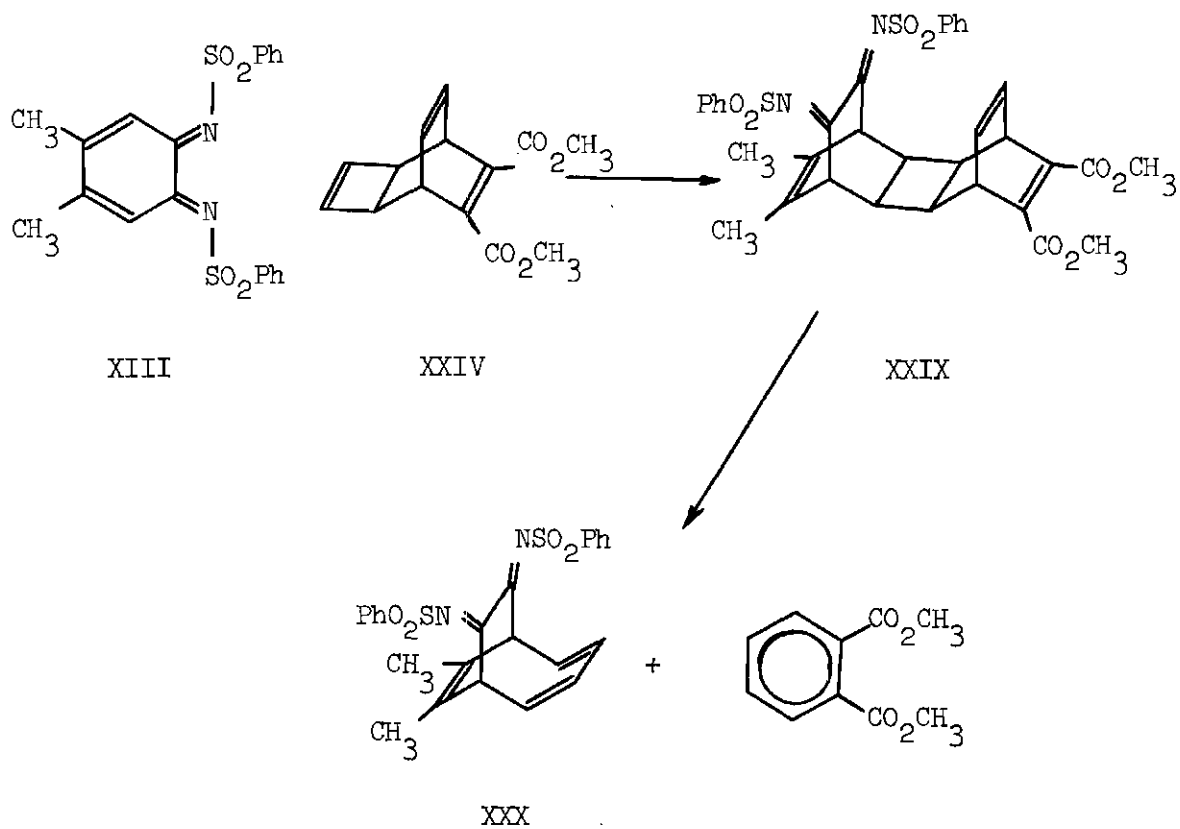




XXVI and XXVII should undergo reverse Diels-Alder reaction to give the bicyclo octadiene (XXVIII), which would result in aromatization of the residue upon capulsion of the bridge.



The first step should be quite facile for (XXVII) due to the driving force provided by formation of 3,4-dicarbomethoxyfuran.



The thermal and photochemistry of (XXX) are potentially interesting in terms of the Woodward-Hoffmann rules (22).

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

Thiophene-free benzene was distilled from sodium before use. Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Methanol and ethanol were distilled from the corresponding magnesium alkoxides.

Solvent evaporation under reduced pressure was accomplished with a Büchi Rotavapor.

A Hanovia 250-watt high-pressure mercury-vapor lamp was used for irradiations. The lamp was placed in a Pyrex water jacket, which was fitted inside a Pyrex reaction vessel (Figure 1). The resulting annular space had a capacity of about 250 ml and was filled to the neck with the solution to be photolyzed. Cold water was circulated through the water jacket during the photolysis. A stream of dry nitrogen was admitted through the frit into the reaction mixtures before irradiations.

Melting points were determined on a Thomas Hoover capillary melting-point apparatus and are uncorrected. Elemental microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia.

Nuclear magnetic resonance spectra were obtained using a Varian A-60D spectrometer with tetramethylsilane as an internal standard and, unless otherwise specified, deuteriochloroform was used as solvent. Chemical shifts are reported in units of δ ($\delta=10-\tau$). The abbreviations

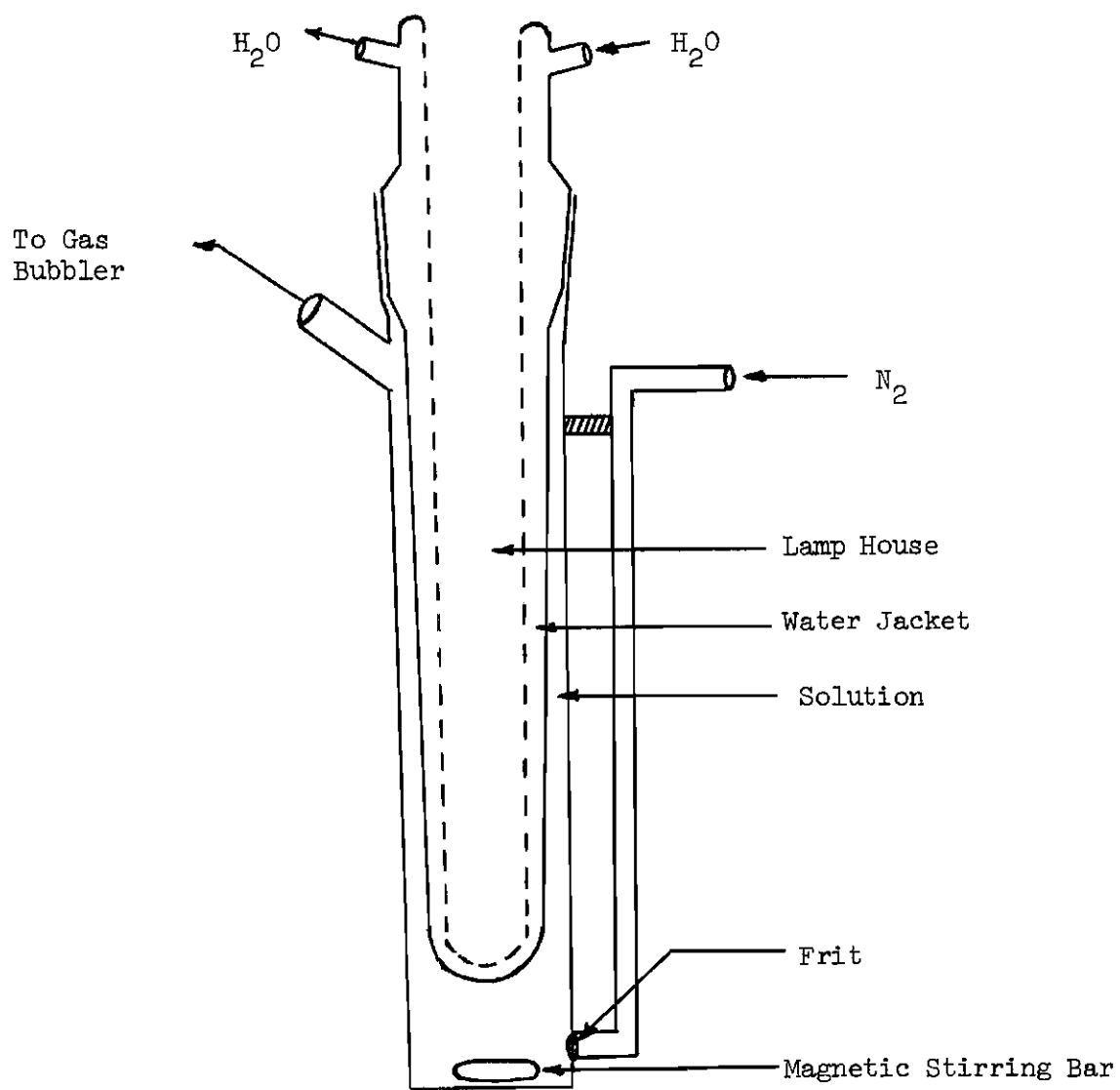


Figure 1. Photolysis Apparatus.

s, d, t, q, and m refer respectively to singlet, doublet, triplet, quartet and multiplet nmr signals.

Mass spectral data were obtained using a Varian Associates Model M-66 medium resolution mass spectrometer and a Hitachi Perkin-Elmer RMU 7L. All exact mass determinations reported agree to within 0.01 percent of the calculated value and were obtained using the Hitachi instrument.

Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer using 0.1 mm sodium chloride cells with chloroform as solvent or with KBr discs. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer using one centimeter balanced cells with 95 percent ethanol or dimethylformamide as solvent.

CHAPTER III

EXPERIMENTAL

4,5-Dimethyl-o-Quinonedibenzenesulfonimide (XIII)

Compound XIII was prepared according to the method of Adams and Winnick (10). The orange crystals had a mp 181-183°C. [lit. (10) mp 181-186°C.].

Dimethyl-3,6-Epoxy-3,6-dihydrophthalate (XXIII)

Compound XXIII was prepared according to the method of Stork (20). This compound had a bp 115°C. (1.5 mm) [lit. (20) bp 130-133°C. (2 mm)].

7,8-Dicarbomethoxy-tricyclo-[4.2.2.0^{2,5}]-Deca-3,7,9-triene (XXIV)

Compound XXIV was prepared according to the method of Reppe (21). This compound had a bp 130°C. (0.8 mm) [lit. (21) bp 149°C. (1 mm)].

7,8-Dimethyl-5,10-Dibenzenesulfonyl-1,4,4a,5,10,10a-Hexahydro-1,4-Methanophenazine (XXXI)

4,5-Dimethyl-o-quinonedibenzenesulfonimide (XIII) (10.0 g, 0.024 mole) in 100 ml of distilled norbornadiene (XXII) was refluxed until the orange color was discharged (ca. 10 min.). The excess norbornadiene was evaporated under reduced pressure. The resulting solid was crystallized from 95 percent ethanol as colorless micro-crystals (4.20 g, 34.4 percent) of the 4,5-dimethyl-o-quinonedibenzene-sulfonimide-norbornadiene adduct (XXXI): mp 253-256°C. (dec.); nmr

(CDCl₃) δ 7.4-7.9 (m, 10H) δ 7.22 (s, 2H) δ 6.20 (broad, 2H) δ 4.60 (s, 2H) δ 2.63 (broad, 2H) δ 2.20 (s, 6H) δ 1.27 (broad, 2H); ir (CHCl₃) strong absorption at 1360 and 1165 cm⁻¹ (SO₂). Exact mass determination gave 506.1328 (for C₂₇H₂₆N₂O₄S₂: 506.1334 calculated).

Anal. Calculated for C₂₇H₂₆N₂O₄S₂: C, 64.03; H, 5.14; N, 5.53; S, 12.65. Found: C, 64.14; H, 5.16; N, 5.54; S, 12.64.

7,8-Dimethyl-5,10-Dibenzenesulfonyl-1,2,3,4,4a,5,10,10a-Octahydro-1,4-Methanophenazine (XXXII)

A solution of XXXI (3.0 g, 0.0059 mole) in 250 ml of dry tetrahydrofuran was placed in a 500 ml Paar hydrogenation bottle with 0.2 g of PtO₂ catalyst and hydrogenated at 35 psi for eight hours. The solution was filtered to remove the catalyst, the solvent evaporated under reduced pressure, and the product crystallized from 95 percent ethanol as colorless microcrystals (2.7 g, 90 percent) of 4,5-dimethyl-o-quinonedibenzenesulfonimide-norbornene adduct (XXXII): mp 213-216°C.; nmr (CDCl₃) δ 7.4-8.0 (m, 10H) δ 7.23 (s, 2H) δ 4.48 (s, 2H) δ 2.21 (s, 6H) δ 2.0-2.4 (broad, 4H) δ 1.1-1.45 (broad, 6H) δ 0.7-1.0 (broad, 2H); ir (CHCl₃) strong absorption at 1355 and 1170 cm⁻¹ (SO₂). Exact mass determination gave 508.154 (for C₂₇H₂₈N₂O₄S₂: 508.149 calculated).

Anal. Calculated for C₂₇H₂₈N₂O₄S₂: C, 63.78; H, 5.56; N, 5.51; S, 12.59. Found: C, 63.63; H, 5.75; N, 5.46; S, 12.70.

7,8-Dimethyl-2,3-Dicarbomethoxy-5,10-Debenzenesulfonyl-
1,4,4a,5,10,10a-Hexahydro-1,4-Epoxyphenazine (XXXIII)

4,5-Dimethyl-o-quinonedibenzenesulfonimide (XIII) (10.0 g, 0.024 mole) and 3,6-epoxy-3,6-dihydrophthalate (XXIII) (7.0 g, 0.033 mole) were dissolved in 50 ml of dry toluene and refluxed until the orange color was discharged (ca. 15 min.). The solvent was evaporated under reduced pressure and the product was crystallized from 95 percent ethanol as colorless microcrystals (8.0 g, 53.0 percent) of XXXIII: mp 188-190°C. (dec.); nmr (CDCl₃) δ 7.5-8.0 (m, 10H) δ 7.17 (s, 2H) δ 5.02 (s, 2H) δ 5.92 (s, 2H) δ 3.88 (s, 6H) δ 2.19 (s, 6H); ir (CHCl₃) strong absorption at 1745 (C=O), 1720 (C=O), 1367 (SO₂), and 1175 (SO₂) cm⁻¹. The mass spectrum showed major fragmentation ions at m/e 299, 184, 158, and 141 with no molecular ion at m/e 624.

Anal. Calculated for C₃₀H₂₈N₂O₉S₂: C, 57.69; H, 4.52; N, 4.49; S, 10.25. Found: C, 57.93; H, 4.74; N, 4.37; S, 10.05.

7,8-Dimethyl-2,3-Dicarbomethoxy-5,10-Dibenzenesulfonyl-
1,2,3,4,4a,5,10,10a-Octahydro-1,4-Epoxyphenazine (XXXIV)

A solution of XXXIII (3.0 g, 0.0048 mole) in 250 ml of dry tetrahydrofuran was placed in a 500 ml Paar hydrogenation bottle with 0.2 g of PtO₂ catalyst and hydrogenated at 35 psi for eight hours. The solution was filtered, the solvent evaporated under reduced pressure, and the product crystallized from 95 percent ethanol as metallic gray microcrystals (2.8 g, 93.3 percent) of XXXIV: mp 210-213°C.; nmr (CDCl₃) δ 7.4-8.0 (m, 10H) δ 7.15 (s, 2H) δ 5.43

(s, 2H) δ 4.49 (d of d, 2H) δ 3.79 (s, 6H) δ 3.09 (d of d, 2H)
 δ 2.18 (s, 6H); ir (CHCl₃) strong absorption at 1740 (C=O), 1360
(SO₂), and 1120 (SO₂) cm⁻¹. Exact mass determination gave 626.1355
(for C₃₀H₃₀N₂O₉S₂: 626.1393 calculated).

Anal. Calculated for C₃₀H₃₀N₂O₉S₂: C, 57.51; H, 4.83; N,
4.47; S, 10.21. Found: C, 57.24; H, 4.99; N, 4.35; S, 10.06.

Reaction of 4,5-Dimethyl-o-Quinonedibenzenesulfonimide (XIII)
with 7,8-Dicarbomethoxy-tricyclo-[4.2.2.0^{2,5}]-Deca-3,7,9-triene (XXIV)

4,5-Dimethyl-o-quinonedibenzenesulfonimide (XIII) (10.0 g,
0.024 mole) and 7,8-dicarbomethoxy-tricyclo-[4.2.2.0^{2,5}]-deca-3,7,9-
triene (XXIV) (10.0 g, 0.041 mole) were dissolved in 50 ml of dry
toluene and refluxed until the orange color was discharged (ca. 15
min.). The solvent was evaporated under reduced pressure and the
product crystallized from 95 percent ethanol as yellow microcrystals
(9.5 g, 95 percent) of 4,5-dimethyl-o-quinonedibenzenesulfonamide
(XXXV): mp 234-236°C. [lit. (10) mp 238°C.]. The mass spectrum
showed a molecular ion at m/e 416.

Reaction of 4,5-Dimethyl-o-Quinonedibenzenesulfonimide
(XIII) with Dimethyl Acetylenedicarboxylate (XXV)

4,5-Dimethyl-o-quinonedibenzenesulfonimide (XIII) (10.0 g,
0.024 mole) and dimethyl acetylenedicarboxylate (XXV) (5.0 g, 0.035
mole) were dissolved in 50 ml of dry toluene and refluxed until the
orange color was discharged (ca. 15 min.). The solvent was evaporated
under reduced pressure and the product crystallized from 95 percent
ethanol as yellow microcrystals (9.6 g, 96 percent) of 4,5-dimethyl-

o-quinonedibenzenesulfonamide (XXXV): 235-236°C. [lit. (10) mp 238°C.].
The mass spectrum showed a molecular ion at m/e 416.

Diphenylcyclopropenone (XIV)

Diphenylcyclopropenone was prepared according to the method of Breslow (11). The white crystals had a mp 115-118°C. [lit. (11) mp 119-120°C.].

Carbomethoxysulfamoyl Chloride (XXXVI)

Compound XXXVI was prepared according to the method of Burgess and Taylor (23). The colorless needles had mp 69-70°C. [lit. (23) mp 70-71°C.].

Diphenylcyclopropene Carbomethoxyimine Sulfonate (XX)

Compound XX was prepared according to the method of Burgess and Williams (14,15). The white solid had mp 195-197°C. (dec.) [lit. (14) mp 195-197°C. (dec.)].

N,N'-Dicarbomethoxy-Tetraphenyl-p-Phenylenediamine (XXXVII)

A suspension of diphenylcyclopropene-carbomethoxyimine sulfonate (XX) (16.0 g, 0.047 mole) in 250 ml of dry isopropanol containing 5.0 ml of dry acetone was irradiated for 12 hours using a 250-watt Hanovia lamp. The solvent was then evaporated under reduced pressure. The resulting solid was triturated in 95 percent ethanol, filtered, and the residue washed with water to give a white solid (1.3 g, 10.6 percent) mp 345-350°C. (dec.); nmr (DMSO-d₆) δ 7.05 (broad, 20H) δ 2.05 (s, 6H); ir (KBr) strong absorption at

1700 cm^{-1} ($\text{C}=\text{O}$). Exact mass determination gave 528.2071 (for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_4$: 528.2049 calculated).

Anal. Calculated for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_4$: C, 77.27; H, 5.35; N, 5.30. Found: C, 77.04; H, 5.40; N, 5.32.

Degradation of N,N'-Dicarbomethoxy-Tetraphenyl-p-Phenylenediamine (XXXVII)

Reaction of XXXVII with LiI

N,N'-Dicarbomethoxy-tetraphenyl-p-phenylenediamine (XXXVII) (0.8 g, 0.0015 mole) and anhydrous lithium iodide (5.0 g, 0.037 mole) were dissolved in 50 ml of dry dimethylformamide under nitrogen and refluxed for eight hours. This mixture was then poured into water and the resulting solid collected, titrated with benzene, and extracted with hydrochloric acid. The aqueous extract was neutralized to give a precipitate which was collected and crystallized from 95 percent ethanol to give yellow microcrystals (0.4g): mp 325°C . Thin-layer chromatography on silica gel with benzene-5 percent ethanol as solvent showed only one compound present, but the mass spectrum had ions at m/e 484, 470, 438, 426, 412, and 178. These results indicate that the product is a mixture of several compounds. All attempts to separate them failed. Exact mass determination gave 470.153 (for $\text{C}_{32}\text{H}_{26}\text{N}_2\text{O}_4$: 470.199 calculated).

Oxidation with Lead Tetraacetate

The mixture of compounds (0.3 g) resulting from reaction of XXXVII with LiI and lead tetraacetate (3.0 g) were dissolved in glacial acetic acid and heated almost to boiling. This mixture

was then extracted with benzene. The benzene extract was washed with water, dried over anhydrous magnesium sulfate, filtered, and the benzene evaporated under reduced pressure. The resulting solid was chromatographed on silica gel and elution with benzene gave two products. The first fraction was tetraphenylquinone (0.2 g) (XL): mp 295°C . [lit. (24) mp $311-315^{\circ}\text{C}$.]; ir (CHCl_3) strong absorption at 1650 cm^{-1} (quinone $\text{C}=\text{O}$). The mass spectrum had ions at m/e 412, 384, and 356. Both spectra were identical with those of authentic tetraphenylquinone (24).

From its ir and nmr spectra, and its hydrolysis to tetraphenylquinone, the structure of the second compound is presumed to be N-carbomethoxy-tetraphenylquinone monoimine (XLI) (0.05 g) mp 205°C . (dec.); ir (CHCl_3) strong absorption at 1650 (quinone $\text{C}=\text{O}$) and $1710\text{ (CO}_2\text{CH}_3\text{) cm}^{-1}$; nmr (CDCl_3) δ 7.18 (s, 20H) δ 1.27 (s, 3H).

Pyrolysis of Diphenylcyclopropene Carbomethoxyimine Sulfonate (XX)

Diphenylcyclopropene carbomethoxyimine sulfonate (XX) (2.6 g, 0.008 mole) was pyrolyzed in 50 ml of refluxing diglyme under nitrogen using a bubbler containing 2,4-dinitrophenylhydrazine solution. Formaldehyde-2,4-dinitrophenylhydrazone collected from the bubbler was crystallized from 95 percent ethanol as yellow crystals: mp $158-159^{\circ}\text{C}$. [lit. (25) mp 166°C .]. A mixture of this product with authentic material showed no depression of the melting point. The diglyme solution was filtered to give a crude solid which was washed with water and crystallized from dimethylformamide-benzene as light tan microcrystals (0.1 g) mp $251-252^{\circ}\text{C}$. (dec.); ir (KBr) 1830 cm^{-1} .

The mass spectrum indicated that the product was a dimer of diphenylcyclopropeneimine (M^+ , m/e 410). This material could not be obtained sufficiently pure for structure determination.

CHAPTER IV

DISCUSSION OF RESULTS

It was the purpose of this research to attempt to synthesize an electron-deficient isonitrile. Several routes have been investigated with no success.

The reaction of 4,5-dimethyl-o-quinonedibenzene-sulfonimide (XIII) with norbornadiene (XXII) gave a 1:1 adduct resulting from $[4\pi + 2\pi]$ cycloaddition across the nitrogen atoms rather than the carbocyclic Diels-Alder reaction, which would have resulted in structure XXVI, (see Figure 2).

The structure of adduct XXXI was established from the nmr spectrum, which had a two proton singlet at δ 7.22, and hydrogenation to give compound XXXII having a two proton singlet at δ 7.23. Absorption of only one mole of hydrogen means that there was only one non-aromatic double bond. The mass spectrum of XXXII is much simpler than that of XXXI with peaks at m/e 508, 367, 299, and 226.

Reaction of XIII with XXIII also gave a 1:1 adduct via the heterocyclic Diels-Alder reaction, (see Figure 3).

Adduct XXXIII showed a two-proton singlet at δ 7.17 in the nmr spectrum, two carbonyl absorptions at 1745 and 1720 cm^{-1} in the infrared spectrum, and absorbed only one mole of hydrogen. The hydrogenated product had a two-proton singlet at δ 7.15 in the nmr spectrum and showed only one carbonyl absorption at 1740 cm^{-1} in

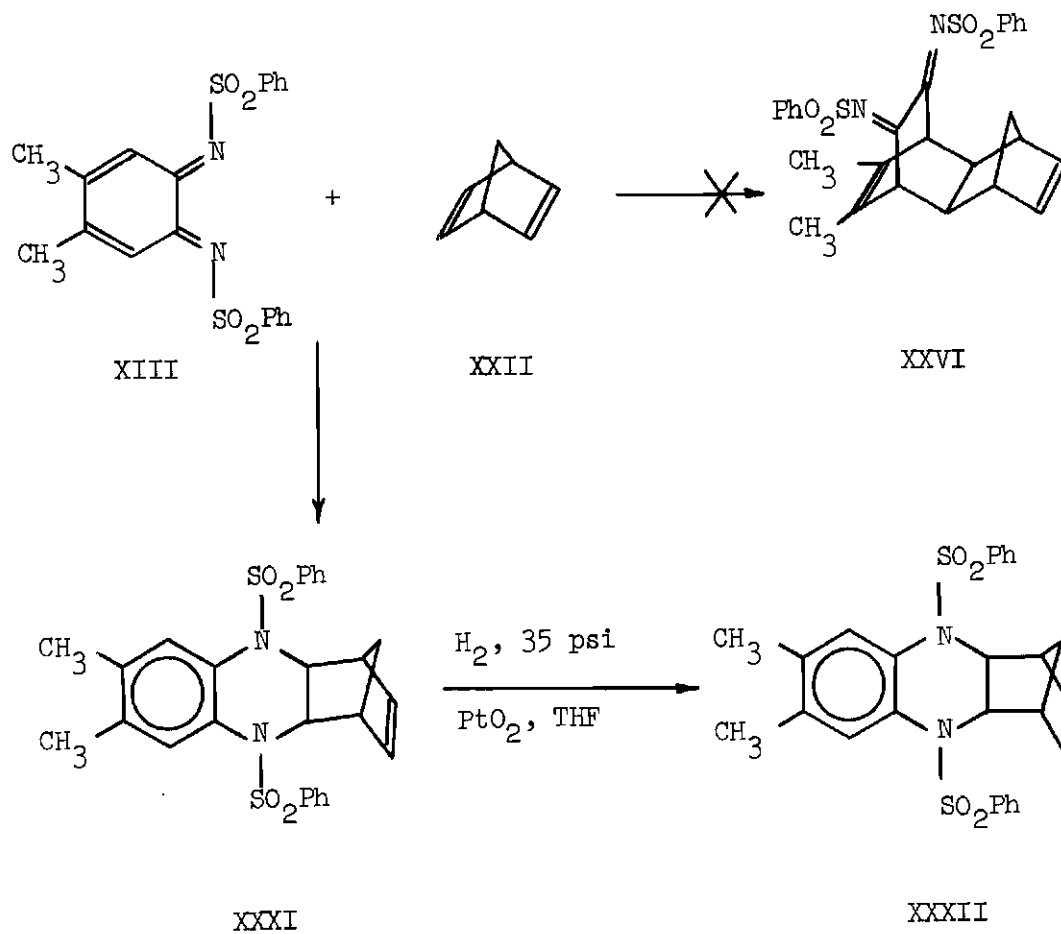


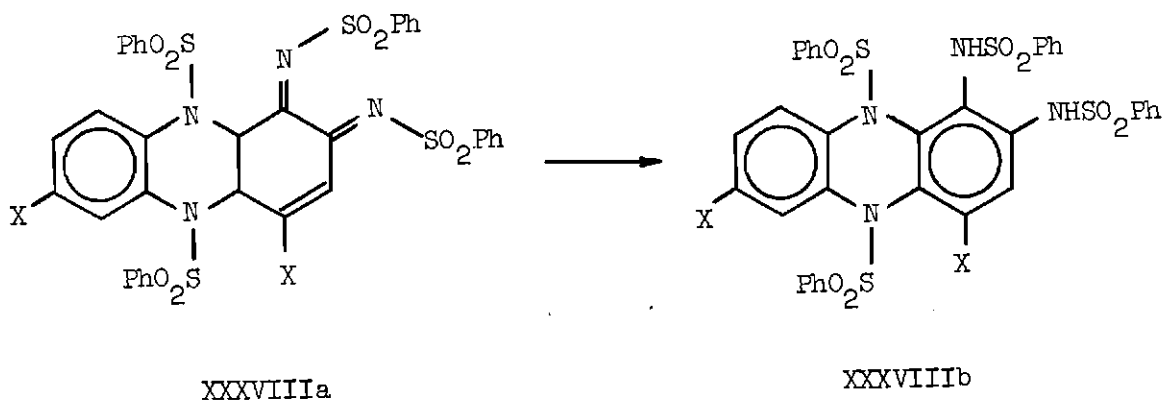
Figure 2. Reaction of XIII with Norbornadiene.

the ir spectrum. The reasons for the two carbonyl absorptions in the ir spectrum of XXXVIII are not known. One possibility is that the compound is a mixture of stereoisomers.

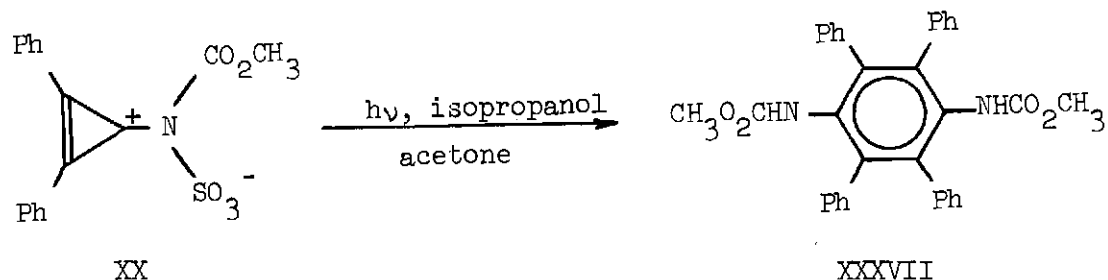
These cycloaddition reactions were not unexpected since they are predicted to be symmetry-allowed by the Woodward-Hoffmann rules of orbital symmetry conservation as $[4\pi + 2\pi]$ cycloaddition reactions (22). Cycloaddition in this manner would also be predicted from thermodynamic considerations due to the driving force provided by aromatization of the ring. Several examples of Diels-Alder addition to 1,4-diazadiene systems have been reported (26).

The reactions of XIII with XXIV and with dimethyl acetylenedicarboxylate (XXV) resulted in the reduction of XIII to 4,5-dimethyl-O-phenylenediamine dibenzenesulfonamide (XXXV) in quantitative yield.

The structures of XXXI and XXXVIII suggests that the structures of the dimers of 4-chloro- and 4-methyl-O-quinonedibenzenesulfonimides (10) should also be the heterocyclic Diels-Alder adduct XXXVIII.



The photolysis of diphenylcyclopropene-carbomethoxyimine sulfonate (XX) resulted in the formation of a dimer which was shown to be N,N'-dicarbomethoxy-tetraphenyl-p-phenylenediamine (XXXVII). The spectra, exact mass, and elemental analysis were consistent with this structure. The most convincing evidence was provided by degradation to tetraphenyl-p-quinone whose ir and mass spectra were identical with those of authentic material.



The reaction of XXXVII with excess lithium iodide in refluxing dimethylformamide gave a complex mixture of products which could not be separated. The mass spectrum of the mixture indicated the presence of two compounds resulting from the loss of one (XXXIXa) and two (XXXIXb) carbomethoxy groups and two additional compounds resulting from reaction of these two with methyl iodide to give (XXXIXc) and (XXXIXd), (see Figure 4).

Oxidation of this mixture with lead tetraacetate gave two compounds which were separated by chromatography. The first product was shown to be tetraphenyl-p-quinone (XL) by comparison with authentic material. The structure of the second product could only be suggested by its infrared spectrum and the fact that it is hydrolyzed in acid

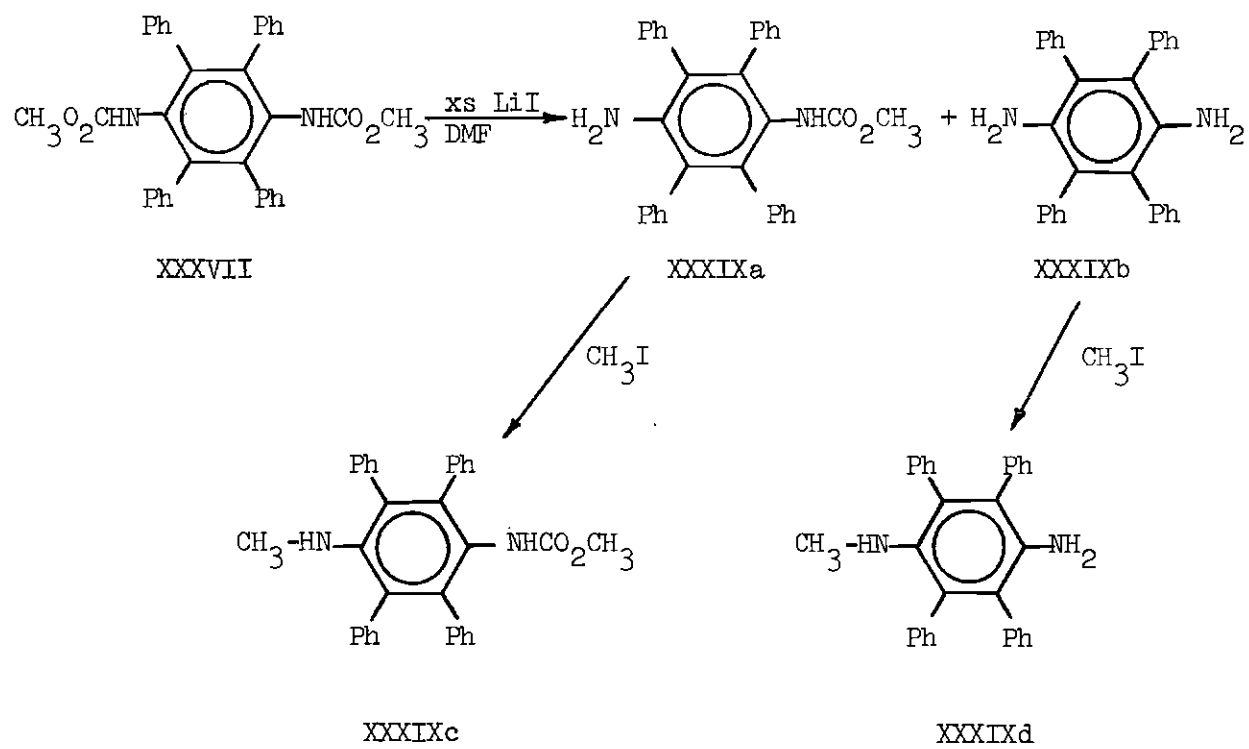
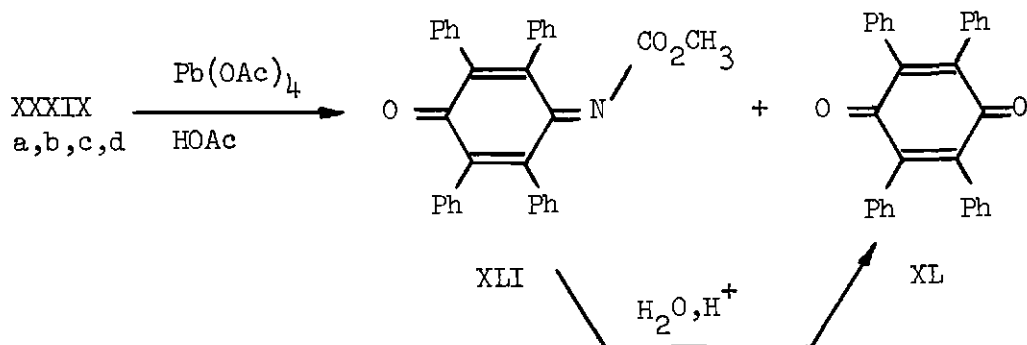


Figure 4. Reaction of XXXVII with LiI.

to XL.



The photodimerization of diphenylcyclopropene carbomethoxyimine sulfonate (XX) may be visualized as proceeding via $[2\pi + 2\pi]$ cycloaddition, thermal rearrangement with simultaneous expulsion of sulfur trioxide, and, finally, reduction by the isopropyl alcohol used as solvent, (see Figure 5). This mechanism is supported, in part, by the reported photodimerizations of three 1,2-diphenyl cyclopropenes which formed dimers via $[2\pi + 2\pi]$ cycloaddition to give tricyclohexanes. These products rearranged thermally to give the corresponding 1,4-cyclohexadienes (27).

Pyrolysis of diphenyl cyclopropene carbomethoxyimine sulfonate (XX) resulted in evolution of formaldehyde and a product which appears to be a dimer of diphenylcyclopropeneimine. An absorption band in the infrared spectrum at 1830 cm^{-1} indicates that the structure contains a cyclopropene ring. The evidence cited and some speculation results in Figure 6.

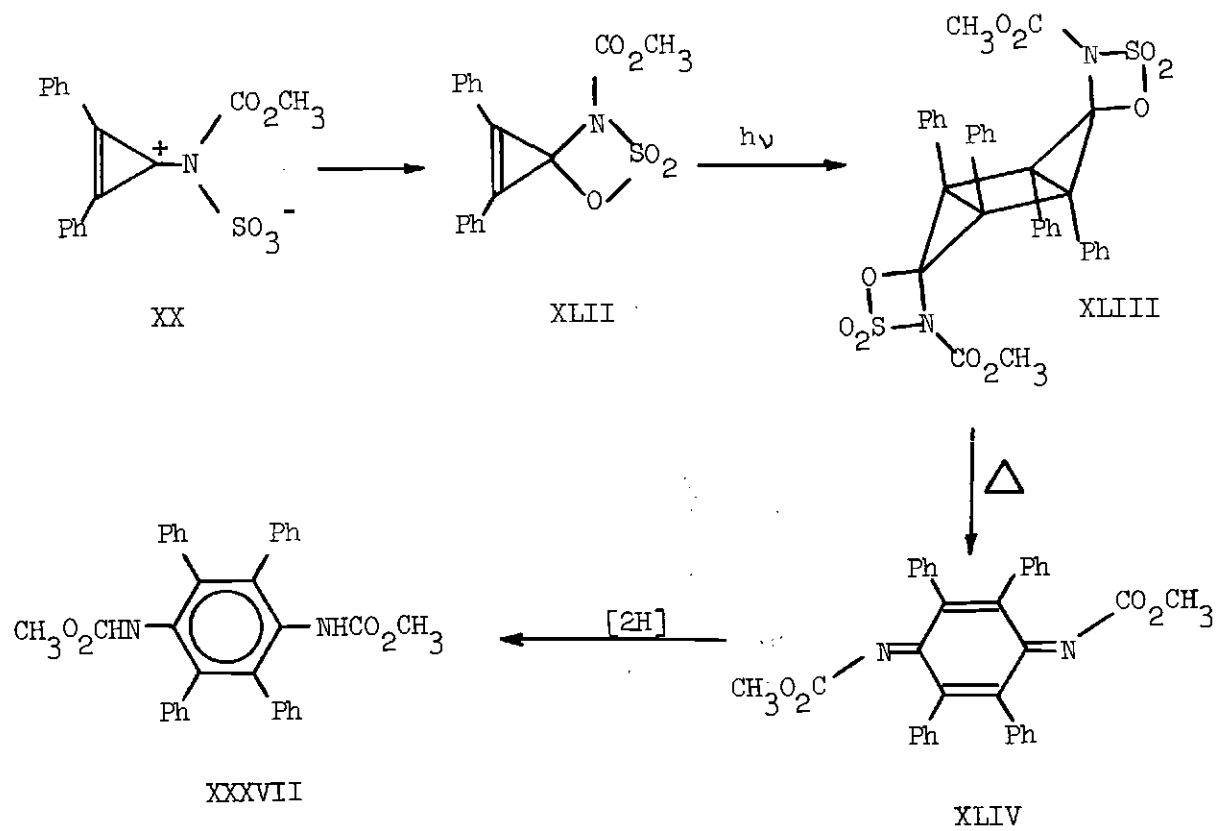


Figure 5. Proposed Mechanism of Photolysis of XX.

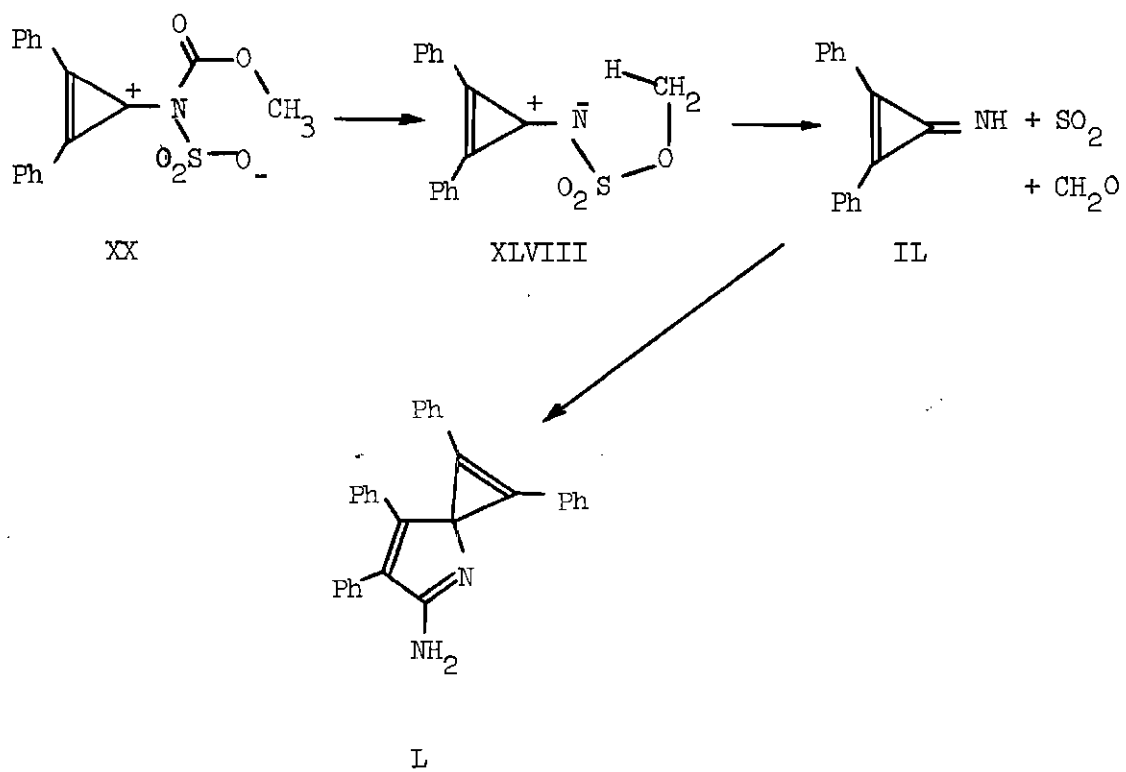
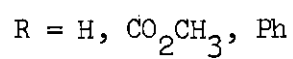
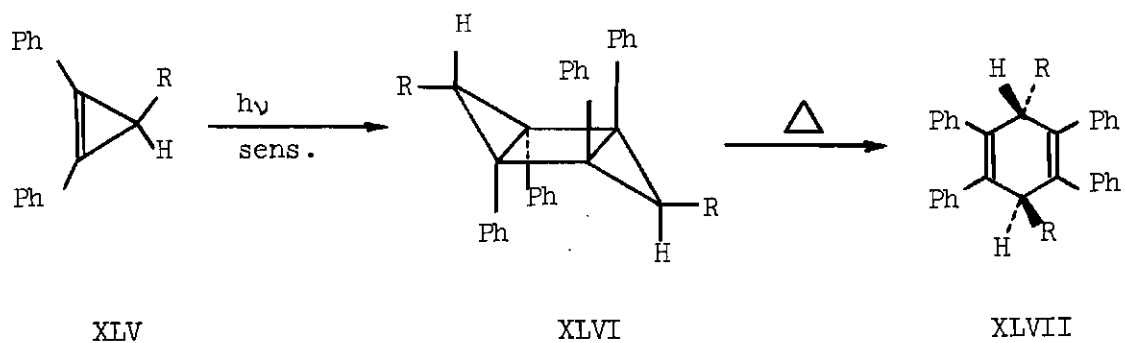
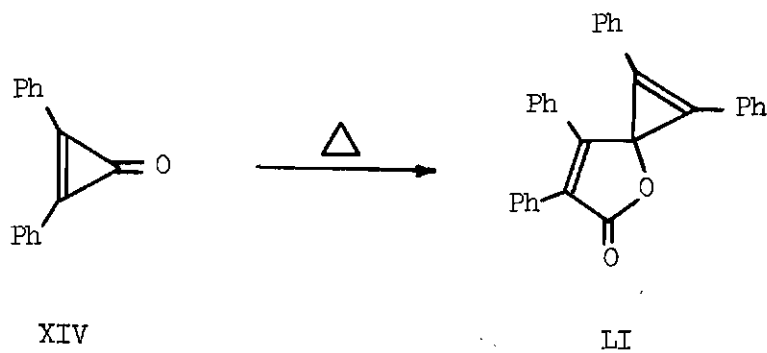


Figure 6. Proposed Mechanism of Pyrolysis of XX.



The last step of this proposed mechanism is analogous to the thermal dimerization of diphenylcyclopropenone (11).



CHAPTER V

CONCLUSIONS

Compound XIII was found to react as a diazadiene system in those reactions which gave adducts. When no adducts were obtained, XIII was reduced to the aromatic diamide.

The photolysis of XX resulted in dimer XXXVII by a process for which a three-step mechanism is proposed. The pyrolysis of XX evolved formaldehyde and resulted in the proposed structure L.

No electron-deficient isonitriles were synthesized or generated from any of the methods tried.

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VITA

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He is married to the former Harriett Edwina Lay and has two daughters.