PHOTOCHEMICAL ISOMERIZATION IN THE TETRACYCLO [4.3.0.0 ^{2,4}.0 ^{3,7}] NONA-8-ENE SYSTEM

Thesis for the Degree of Ph. D.

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Raymond Joseph Barreras

1966

This is to certify that the

thesis entitled

PHOTOCHEMICAL ISOMERIZATION

IN THE TETRACYCLO[4.3.0.$0^{2,4}$.$0^{3,7}$]NONA-8-ENE

SYSTEM

presented by

Raymond Joseph Barreras

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

William Reusch
Major professor

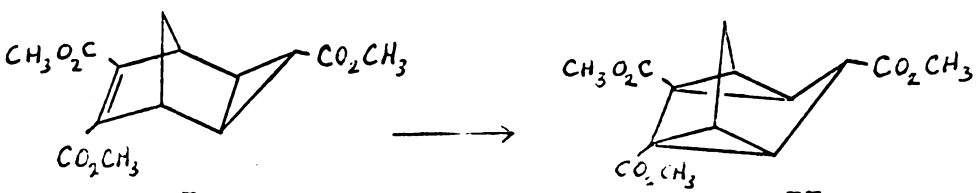
Date 11-18-66

ABSTRACT

PHOTOCHEMICAL ISOMERIZATION
IN THE TETRACYCLO[4.3.0.$0^{2,4}$.$0^{3,7}$]NONA-8-ENE
SYSTEM

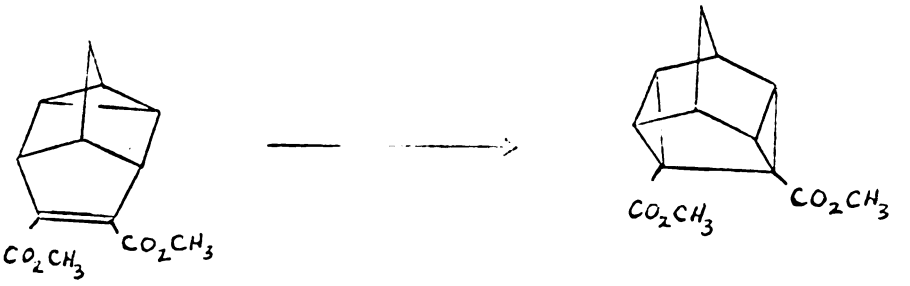
by Raymond Joseph Barreras

The first example of photochemical cyclo-addition of a cyclopropane ring to an olefin was reported by Prinzbach (I ⟶ II) (1).



I II

This investigation has disclosed a second example of intramolecular cycloaddition of a cyclopropane system to an olefin. The cycloaddition occurs readily even though the conversion of 8,9-dicarbomethoxy-tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene (III) to 3,7-dicarbomethoxypentacyclo[3.3.1.$0^{2,4}$.$0^{6,8}$.$0^{3,7}$]-nonane (IV) results in an increase in strain.



The isomerization of III to IV was effected by irradiating a dilute pentane solution (100 mg. III in 300 ml. solvent) for five hours. A 200 watt medium pressure immersion lamp (Hanovia) equipped with a Vycor filter was used to effect a 35% conversion to IV.

The structure of the pentacyclic photoproduct was deduced from mass spectral, infrared, and nuclear magnetic resonance data, and the relative thermal stability of IV. Melting at 53-4°, IV exhibited infrared absorption at 3055, 2950, 2860, 1740, 1435, 1360, 1105, and 1070 cm.$^{-1}$. The mass spectrum of IV showed a parent peak at m/e 234 and the n.m.r. spectrum has resonance at τ = 8.11, 7.40, 7.17, and 6.39 (area ratios 1:2:1:3 respectively).

The photoisomer, IV, is stable to heating to 368° but decomposes above that temperature. The tetracyclic diester, III, is thermally stable at 200° but decomposes rapidly at 300°, 368°, and 412°. The

only recoverable material is unreacted III. No trace of the photoproduct is found.

An intermolecular reaction between an olefin and a cyclopropane ring did not occur when mixtures of maleic anhydride/norcarane or cyclohexene/1,1,2,2-tetracarbomethoxycyclopropane were irradiated.

REFERENCE

1. H. Prinzbach, W. E[illegible]ch, and G. Von Veh, Ang. Chemie (Int[illegible]. Ed.), 4, 436(1965)

PHOTOCHEMICAL ISOMERIZATION IN THE TETRACYCLO[4.3.0.$0^{2,4}$.$0^{3,7}$]NONA-8-ENE SYSTEM

By

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Grateful acknowledgment is extended to the National Institutes of Health for personal financial assistance from September, 1963, to September, 1965. Appreciation is also extended to the Dow Chemical Company for a summer fellowship in 1966.

Special thanks are also extended to my wife and four children whose patience and quiet endurance has made it all possible. Finally to my parents for giving me every opportunity to advance, a warm De Colores.

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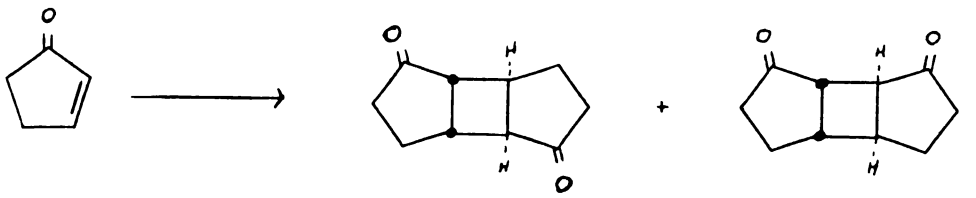
TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

LIST OF TABLES

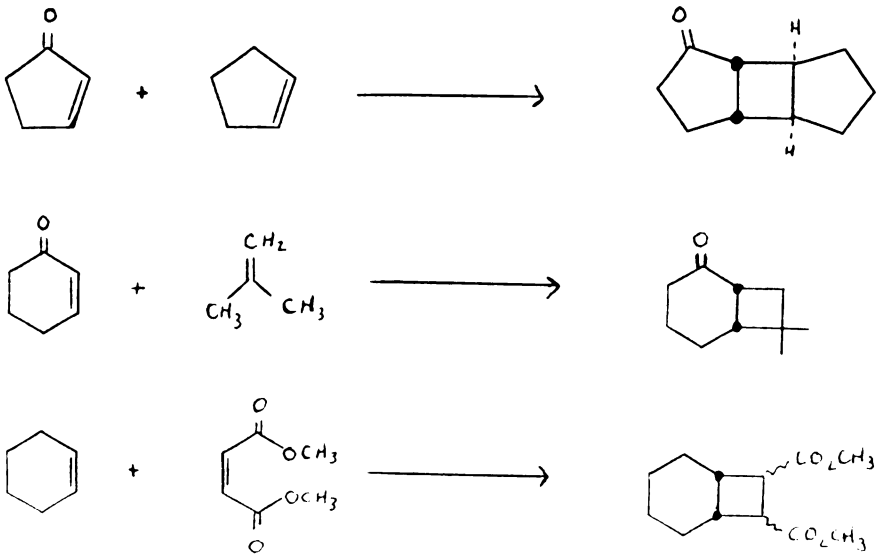
LIST OF FIGURES

It has been well known for a considerable period of time that α,β-unsaturated carbonyl compounds undergo dimerization when irradiated (1). The products are cyclobutane derivatives arising from the olefinic portions of the molecules. Sometimes a mixture of products distinguishable as head-to-head or head-to-tail dimers result (2). Further examples of such dimerization are

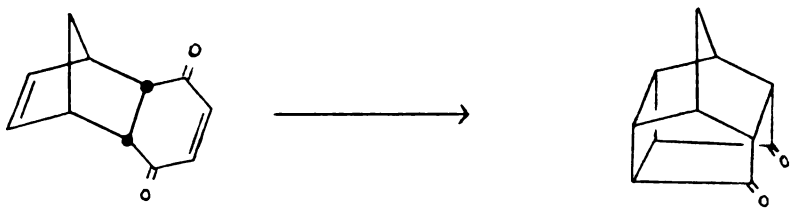


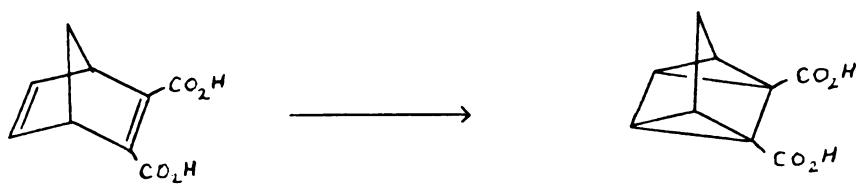
seen in the work of Griffen (3) with maleic and fumaric acids and Hammond (4) with the coumarin system.

In the presence of olefins certain α, β-unsaturated carbonyl systems undergo a similar reaction known as cycloaddition. (5,6,7)

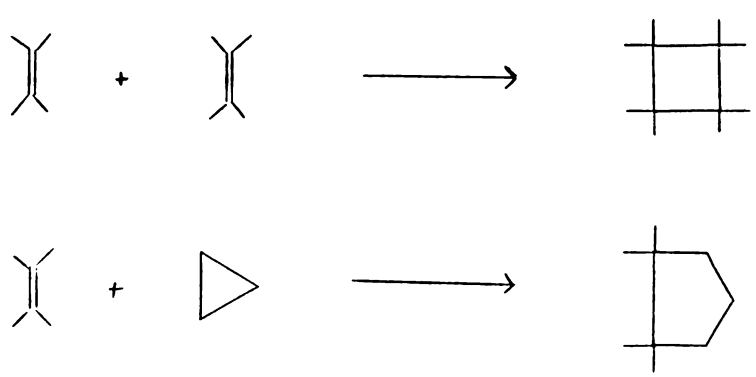


Intramolecular formation of cyclobutanes occurs even when a highly strained system results (9,10).



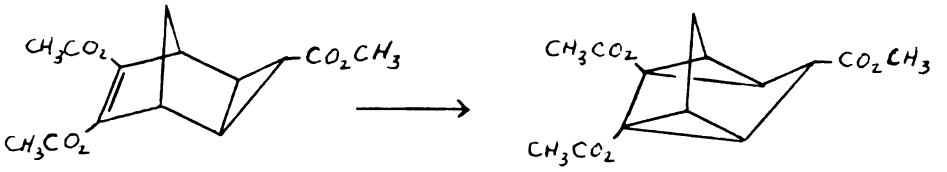


Since cyclopropane systems exhibit many properties similar to those of olefins (8), an investigation of photochemical cycloaddition reactions of three membered rings seemed worthwhile.

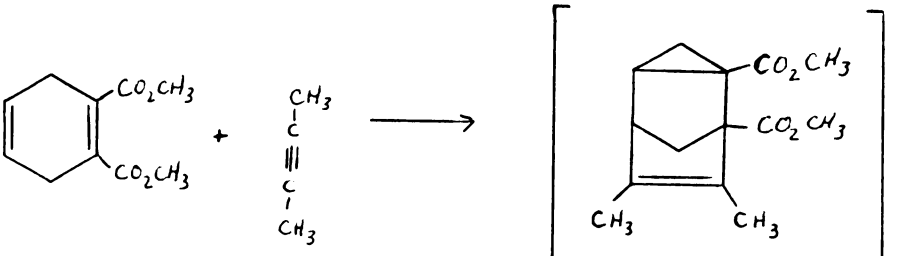


Recent reports of intramolecular photochemical rearrangement of tricyclo[3.2.1.0.^{2,4}]octene derivatives

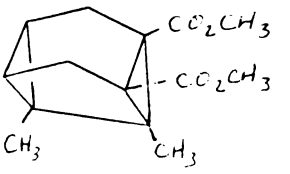
(I) to tetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane analogs (II) involve such a transformation (11,12), as must the reaction of 2-butyne with dimethyl 3,6-dihydrophthalate to give (IV) via an intermediate containing a cyclopropane ring and a double bond (III) (13,14).



I II



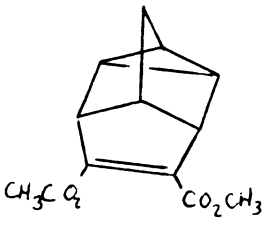
III



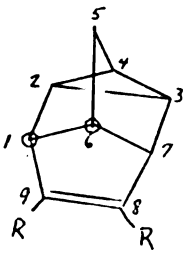
IV

RESULTS AND DISCUSSION

In order to enhance the desired cycloaddition, an intramolecular model was chosen for this study. In particular, 8,9-dicarbomethoxytetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene (V) was used, since models indicated that the olefin π-orbitals and the cyclopropane 2,3-bond overlapped well.



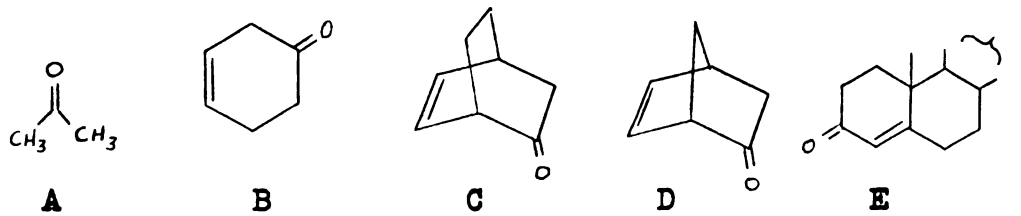
V



Synthesis of V was reported by Schrauzer and Glockner (15) and proceeded in 32% yield by reaction of dimethyl acetylenedicarboxylate with bicyclo[2.2.1]hepta-2,5-diene in the presence of a complex nickel catalyst. The 1:1 adduct was obtained in up to 50% yield by heating an equimolar mixture of diene and ester (16). In refluxing toluene the yields range from 57 to 65%.

Interactions of non-conjugated chromophores have been seen in many systems. The non-conjugated interaction

usually falls between the isolated carbonyl (A) and the conjugated carbonyl (E). The location of the absorption



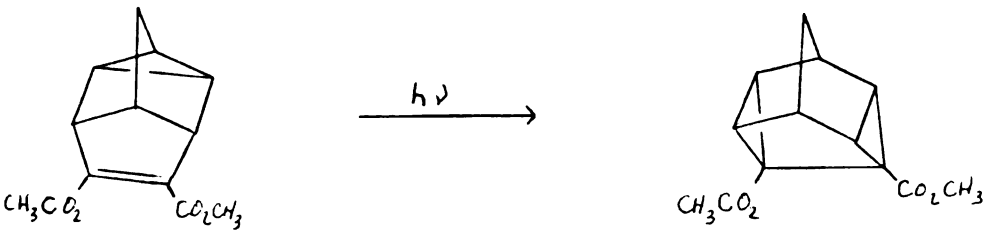
	A	B	C	D	E
λ_{max}	275	280	297	310	330
ϵ	14.1	107	107	288	

bands in the non-conjugated ketones (B-D) is related to the stereochemistry of the lone pair and π-orbitals of oxygen in relation to the π-orbitals of the carbon-carbon double bond (19). Clearly, π-orbitals will tend to interact best, when appropriately oriented with respect to each other. Thus, the shift in absorption from 297mμ to 310mμ in compounds C and D indicates a better overlap of the orbitals in the bicyclo[2.2.1]system.

The crystalline diester V, m.p. 65-66°, exhibits an absorption maximum at 244mμ(log ϵ 3.98) in the ultraviolet, indicating transannular interaction between the π-orbitals of the double bond and the bonding orbitals of the three membered ring. The significance of this interaction may be judged by comparison with dimethyl dimethylmaleate, λ_{max} 212.5mμ(log ϵ 3.95); I, λ_{max} 230mμ(log ϵ 3.83) (12) and 2,3-dicarbomethoxybicyclo[2.2.1]heptadiene, λ_{max} 237mμ (log ϵ 3.60) (10), inasmuch as the latter

two compounds undergo efficient transannular photochemical cycloaddition.

Early attempts to isomerize V led to extensive dimer formation, largely because the conditions were too severe and the concentration of substrate too high. In dilute pentane solution (100mg. V in 300 ml. solvent) a five hour irradiation led to a 35% conversion to VI. This substance, m.p. 53°, was purified by preparative v.p.c., and identified by a variety of spectroscopic measurements.



V VI

The infrared spectrum of the photoproduct, VI, (Figure 1) has bands at 3050 and 1025 cm.$^{-1}$ which can be assigned to cyclopropyl hydrogens (26). The absorption at 1735, 1235, and 1225 cm.$^{-1}$ is assigned to the carbomethoxy group and the lack of absorption in the 1700-1500 cm.$^{-1}$ region indicates the absence of a double bond (26).

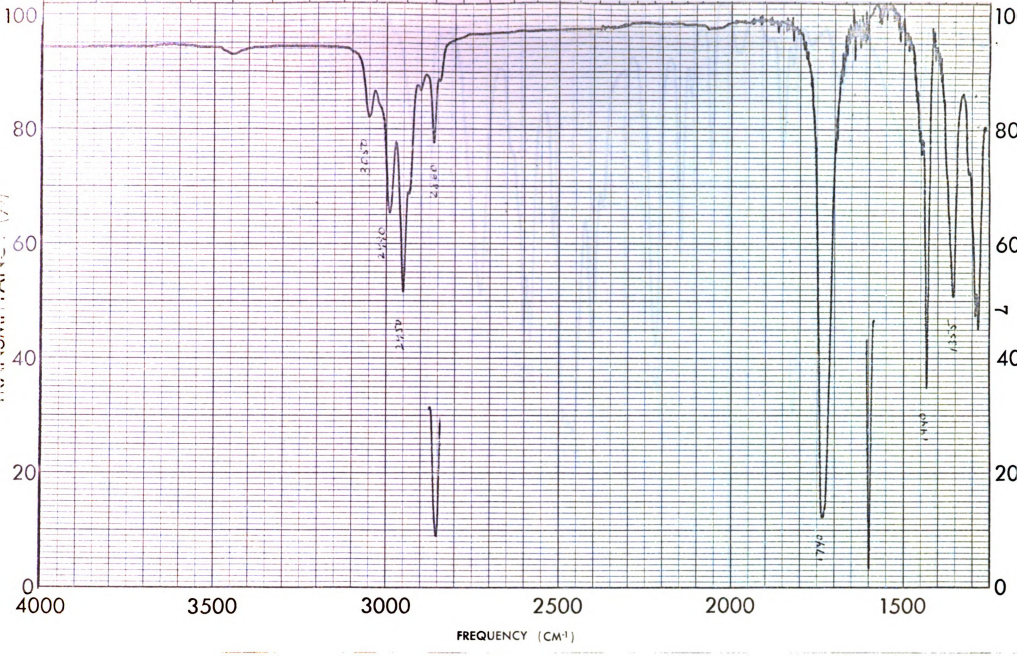


Figure 1a
Infrared Spectrum of VI

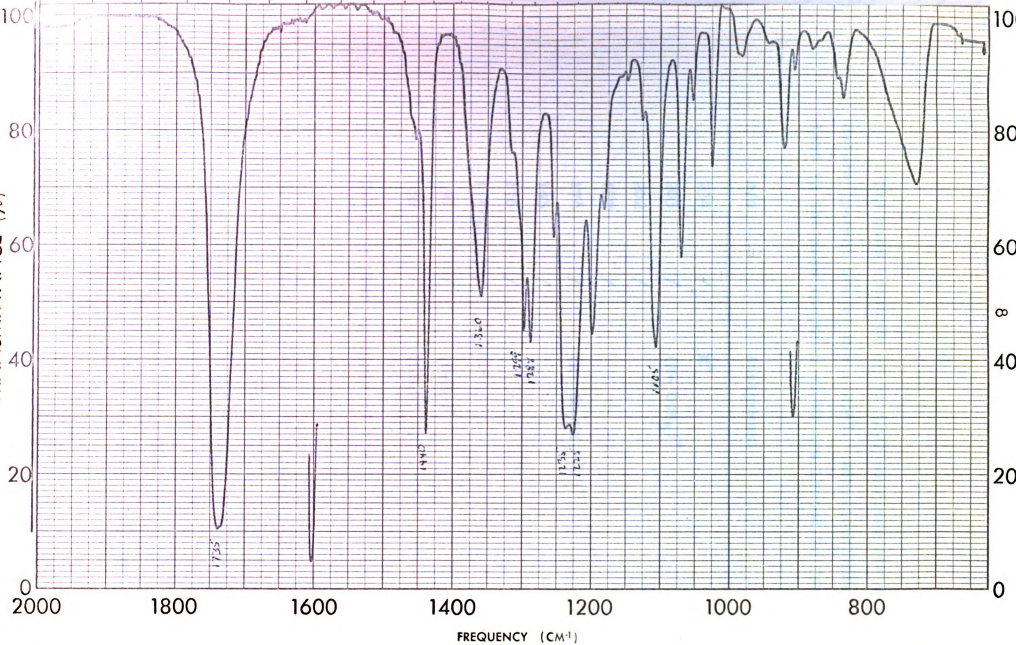


Figure 1b
Infrared Spectrum of VI

The mass spectrum of VI (20) confirms its monomeric nature (parent ion at m/e = 234). Additional prominent ions in the mass spectrum of VI are listed in Table 1.

m/e		Assignment
234	/	M^+
203	/	$(M- OCH_3)^+$
202	/	
187	/	
174	/	$(M- CO_2CH_3- H)^+$
143	/	
116	/	
115(base)	/	
91	/	$(C_7H_7)^+$
59	/	$(CH_3OC\ O)^+$

Table 1: Mass spectrum of VI

The strongest evidence for structure VI was found in the n.m.r. spectrum (Figure 2) (20), which displayed resonance signals at τ = 8.11, 7.40, 7.17 and 6.39 (area ratio 1:2:1:3 respectively). The appearance of the cyclopropyl hydrogen signal at rather low field is probably due to a combination of carbon bond angle

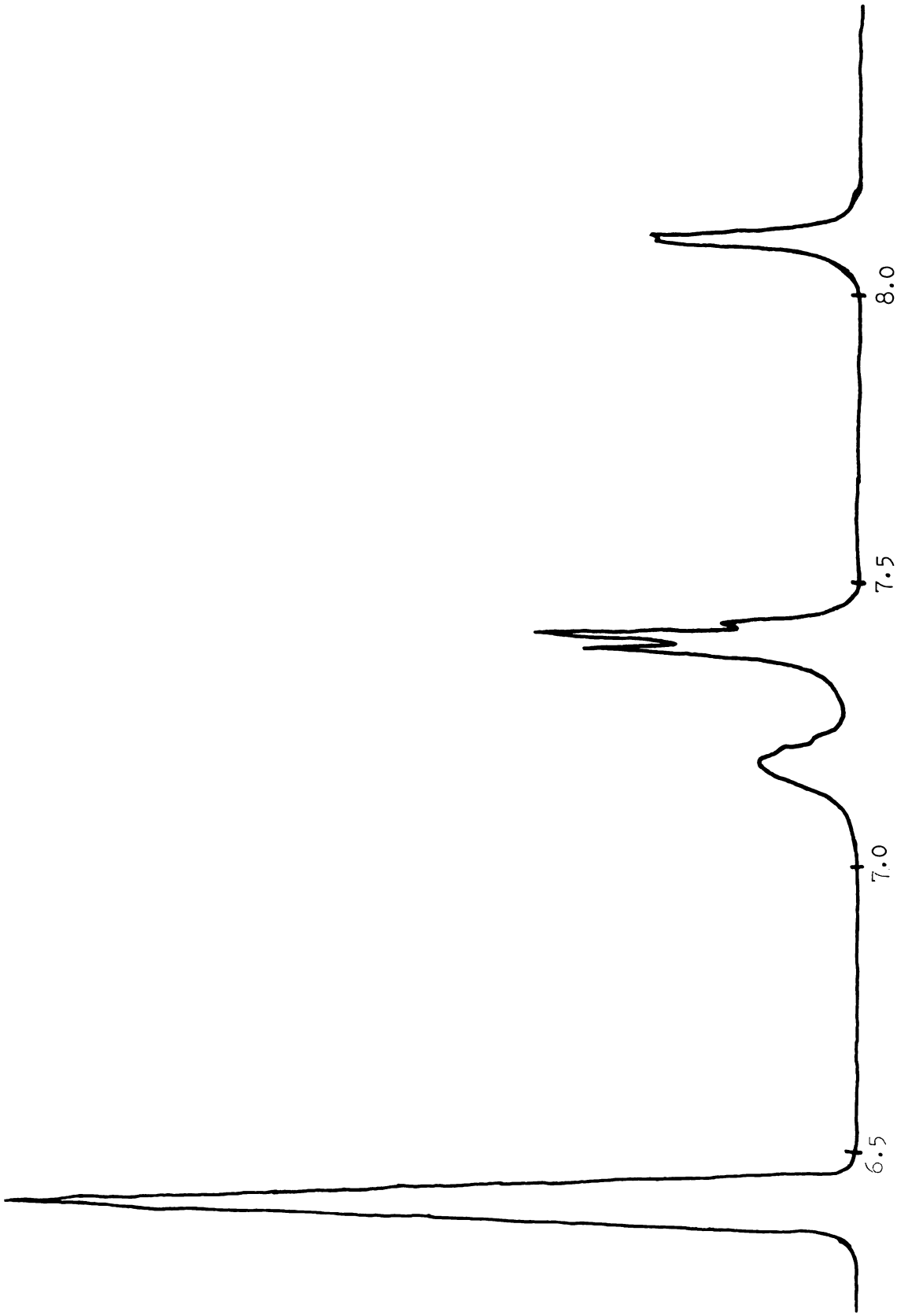


Figure 2: Nuclear Magnetic Resonance Spectrum of VI
3,7-dicarbomethoxy[3.3.1.$0^{2,4}$.$0^{6,8}$.$0^{3,7}$]nonane

constriction and electron withdrawal by the carbomethoxy substituents. Examples of these effects can be seen in other systems, such as 1-methyltricyclo[3.1.0.$0^{4,6}$]-hexane (cyclopropyl hydrogen signals at τ = 8.43 and 8.14) (21), quadricyclene (cyclopropyl hydrogen signal at τ= 8.59) (22), and 1,1,2,2-tetracarbomethoxycyclo-propane (cyclopropyl hydrogen resonance at τ= 7.82) (23).

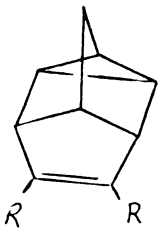
Since the low field cyclopropyl hydrogen resonance of VI conceivably reflects an increase in the acidity of these hydrogen atoms (24), base-catalyzed exchange reactions of VI were investigated. The photoproduct VI was, however, recovered unchanged from a solution of sodium methoxide and methanol-O-d after 72 hours.

To test the possibility of thermal conversion to VI, oxygen-free samples of V were heated at 200°, 306°, 368°, and 412°. Although compound V was unchanged after 19 hours at 200°, considerable darkening of the samples was observed at 306° after heating periods of 15 minutes, 1, 3, and 15 hours. An insoluble carbonaceous material was filtered off and the infrared spectrum of the soluble pyrolysate was taken. The spectrum was superimposable with that of authentic V, and v.p.c. chromatography on FFAP showed only one component, the starting material. Pyrolysis of V at 368° for 1 and 3 hours gave similar

results. Complete decomposition occurred in 15 minutes at 412°, and v.p.c. analysis showed that none of the products corresponded in retention time to either V or VI. In this higher temperature pyrolysis the carbonaceous material was again observed. No attempt was made to identify these pyrolysis products (about fifteen in number).

The photoproduct, VI, is stable at 300°, being recovered unchanged after heating for 1 and 3 hours. At higher temperatures the decomposition of VI did not include reconversion to V.

Attempts have been made to prepare other derivatives of the tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene system (VII a-e). For example, V was hydrolyzed with refluxing aqueous sodium hydroxide until the oily organic



V R = R' = CO_2CH_3

VII a) R = R' = CO_2H

b) R = R' = CH_2OH

c) R = R' = CH_2OTs

d) R = R' = CH_2OAc

e) R = R' = CH_3

IX a) R = R' = C_6H_5

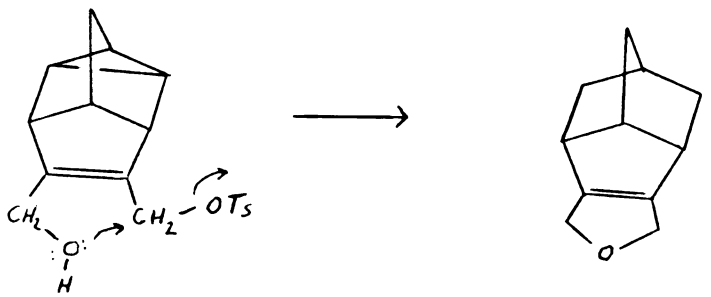
b) R = C_6H_5, R' = H

layer had dissolved and a crystalline diacid (VIIa), having oxygen-hydrogen stretching at 3000 cm.$^{-1}$ and carbonyl stretching at 1695 cm.$^{-1}$ in the infrared, was obtained. Treatment of a slurry of VIIa with diazomethane in ether gave a low yield of the starting ester, V.

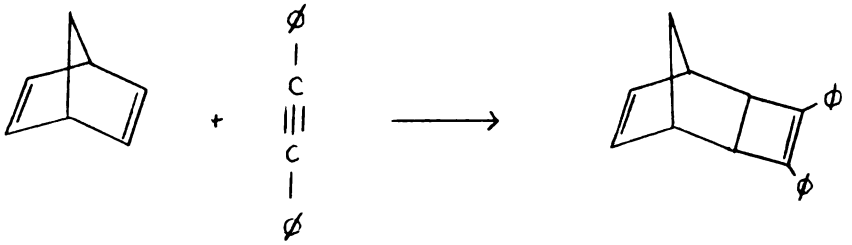
Reduction of V with excess lithium aluminum hydride gave only partial conversion to impure VIIb. This compound exhibited strong absorption in the infrared at 3350 cm.$^{-1}$ (broad, ascribed to intramolecular hydrogen-bonded hydroxyl groups), 3052, 2935, and 2860 cm.$^{-1}$. There was also weak absorption (ca. 20%) at 1720 cm.$^{-1}$, indicating some remaining carbonyl function. A semi-crystalline diacetate derivative of the diol was made by treatment of VIIb with acetic anhydride under reflux. The diacetate, VIId, had a melting point below room tmeperature and could only be recrystallized from ethyl acetate with difficulty. Infrared bands at 3050, 2915, 2851, 1740, 1370, and 1260 cm.$^{-1}$ indicated an ester structure.

As the first step in conversion of V to the deoxy compound, VIIe, via lithium aluminum hydride reduction of the ditosylate, VIIc, the diol was treated with p-toluenesulfonyl chloride. The product exhibited no hydroxyl absorption in the infrared, but also showed no

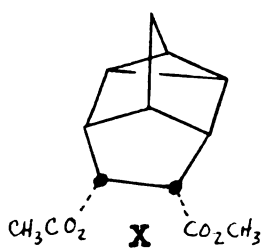
absorption characteristic of the p-toluenesulfonate group, i.e. 1230-1150 and 1440-1350 cm.$^{-1}$ (26). A possible explanation for this puzzling result involves initial formation of a mono-tosylate followed by S_n2 displacement of the tosyl group by the free hydroxyl. Such a route would lead to a dihydrofuran.



Attempts to prepare derivatives of the tetracyclo-[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene system included the reaction of bicyclo[2.2.1]hepta-2,5-diene with various substituted acetylenes. Among the acetylenes used were diphenyl-acetylene, phenylacetylene, acetylenedicarboxylic acid and 2-butyne-1,4-diol. In each case the starting materials were recovered unreacted. The work of Schrauzer and Glockner (15) on the nickel cyanide-triphenylphosphine catalyzed reactions indicates that the reaction of diphenylacetylene with bicyclo [2.2.1]hepta-2,5-diene yields a tricyclic substance rather than the expected tetracyclo derivative.



Hydrogenation of V at atmospheric pressure using a 10% palladium on charcoal catalyst yielded a dihydro-derivative, X. Inspection of models shows that the

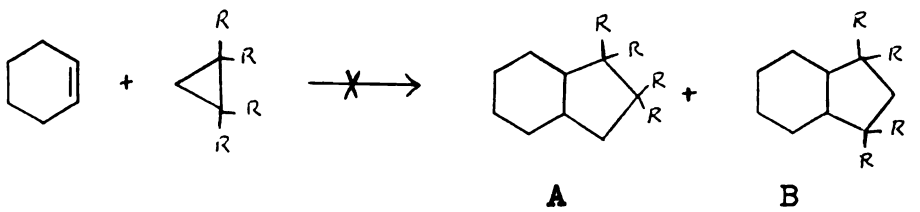


X

frontside of the molecule would be less hindered and so, although not rigorously proven, the stereochemistry of X is probably as indicated.

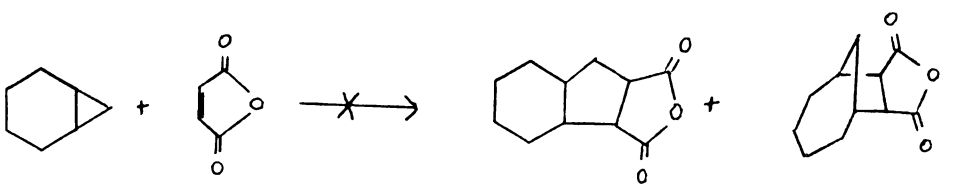
Having observed the photoreaction of an olefin and a cyclopropane ring in an intramolecular process, the investigation of several analogous intermolecular systems was undertaken. In order to minimize possible dimerization reactions, a dilute solution of the cyclopropane in the olefin or of the olefin in cyclopropane was studied.

After irradiation for 60 hours, 1,1,2,2-tetracarbomethoxycyclopropane in cyclohexene failed to give any products corresponding to a 1:1 adduct of the two reactants. Neither cyclopentane product (A and B) expected from the reaction could be detected.



A B

$R = CO_2CH_3$

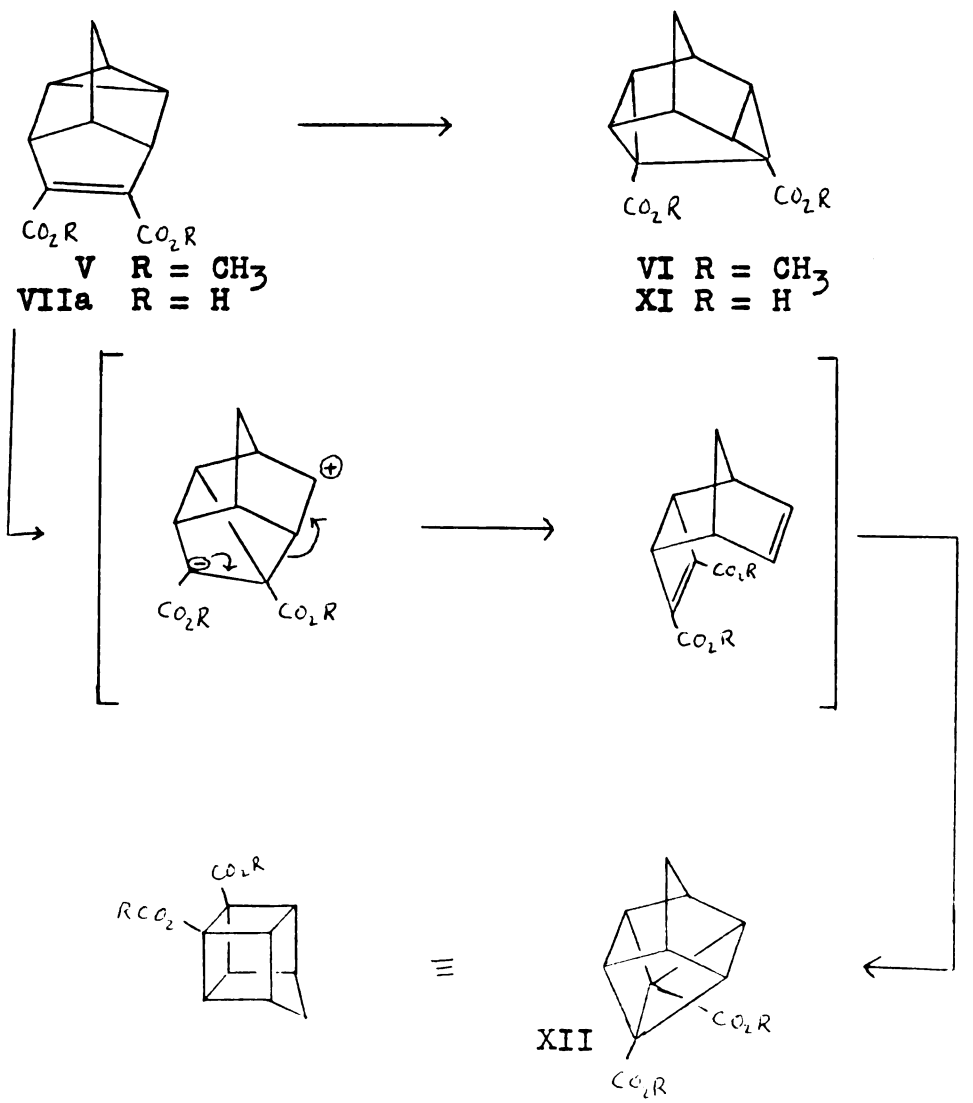


A mixture of maleic anhydride and norcarane proved to be equally unreactive when irradiated. In contrast, Schenk has reported a 95% yield of the corresponding cycloaddition between maleic anhydride and cyclohexene (25).

The lack of reactivity of the two systems may be attributed to an entropy effect, whereby the olefin and cyclopropane never achieve the proper orientation to allow the necessary interaction to occur. Alternatively,

the energy initially absorbed by the chromophore may be lost by collision with solvent molecules prior to reaction.

After our structure proof in this system was completed a communication reporting a similar photochemical isomerization appeared in Chemical Communications (27).



The n.m.r. spectrum of the photoacid sodium salt (XI) is reported to have absorptions at τ = 6.73, 7.07, and 7.65 which agree well with the spectrum of the photoester, VI (resonance peaks at τ= 7.17, 7.40, and 8.11. Multiplicity and peak area ratios are the same in both compounds.)

These authors reported a mixture of liquid products upon irradiation of the ester, V, while this work indicates a clean isomerization to one photoproduct, VI. That the photoproduct has structure VI instead of the alternately proposed structure XII is best evidenced by the thermal stability of the photoisomer and some preliminary x-ray data cited in the communication (27). Structure XII has two four-membered rings which would be expected to be thermally unstable.

EXPERIMENTAL

Melting points were determined on a Koefler hot stage. Infrared spectra were recorded on a Perkin-Elmer Model 237B, Double-beam grating spectrophotometer, and the ultraviolet spectra were taken on a Beckman DB spectrophotometer. The nuclear magnetic resonance spectra were determined in carbon tetrachloride solution using a Varian Associates, A-60, spectrometer and a Varian Associates, HR-100, high resolution spectrometer. Vapor phase chromatography analyses were made using an Aerograph, A-90-P, gas chromatograph with a 0.25 in., 6-ft. column of FFAP on Chromasorb G. Micro-analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan, and by Micro-Tech Laboratories, Skokie, Illinois.

8,9-Dicarbomethoxytetracyclo[4.3.0.0^{2,4}.0^{3,7}] nona-8-ene, V

A solution of bicyclo[2.2.1] hepta-2,5-diene (9.2 g., 0.1 m.) and dimethyl acetylenedicarboxylate (5.1 g., 0.036 m.) in 12 ml. toluene was refluxed for 20 hours. The toluene was removed from the amber solution under reduced pressure and the dark residue was vacuum distilled at 1 mm. and yielded a clear liquid, b.p. 118-120°, which solidified on standing, m.p. 59-60°. The yield of this 1:1 adduct was 4.8 g., 0.02 m., 57%. Crystallization from pentane gave a white crystalline material, m.p. 65-66°, λ_{max} 244 mμ, log ε 3.98; $\nu_{max}(CCl_4)$ 3060, 2990, 2945, 2860, 1720, 1615, 1440, 1340, 1225, 1160, 1090 cm.$^{-1}$ (Fig. 3); τ = 6.31 (6H-singlet), 7.05 (2H-broad multiplet), 7.82 (1H-broad multiplet), 8.20 (1H-broad doublet), 8.41 (4H-broad multiplet) (Fig. 4).

Analysis: Calc. for $C_{13}H_{14}O_4$: C, 66.64%; H, 6.02%

Found: C, 66.31%; H, 5.93%.

3,7-Dicarbomethoxypentacyclo[3.3.1.0^{2,4}.0^{6,8}.0^{3,7}]nonane, VI

Photoisomerization of V was accomplished by irradiating a solution of 100 mg. V and 300 ml. pentane with a 200 watt medium pressure immersion lamp (Hanovia) equipped with a vycor filter. The solution was irradiated for five hours at room temperature, evaporated on a Rinco flash evaporator, and the resulting oil was

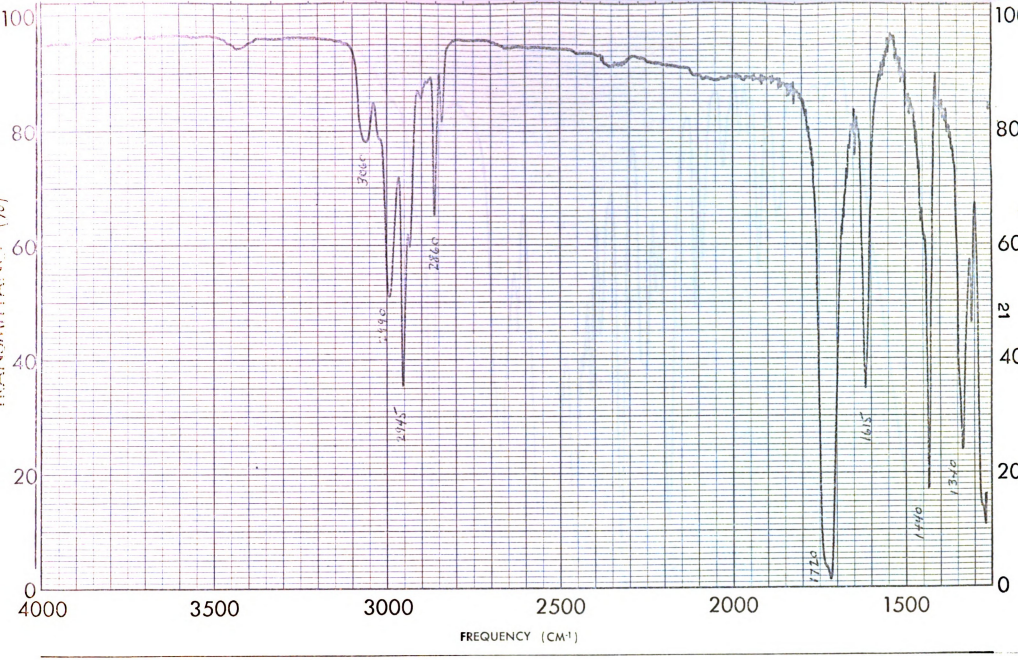


Figure 3a
Infrared Spectrum of V

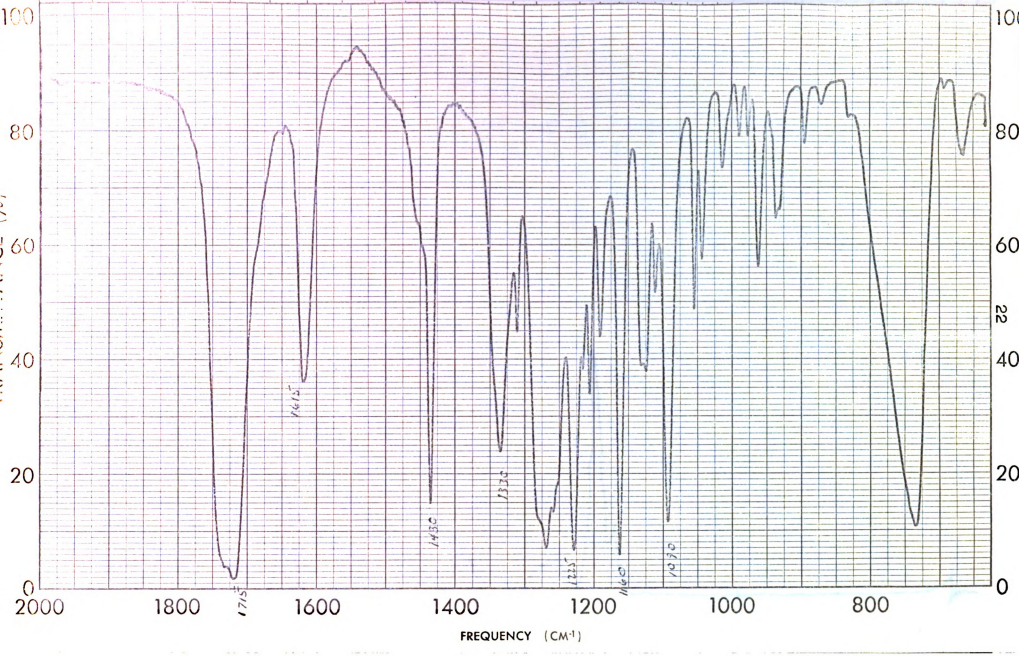


Figure 3b
Infrared Spectrum of V

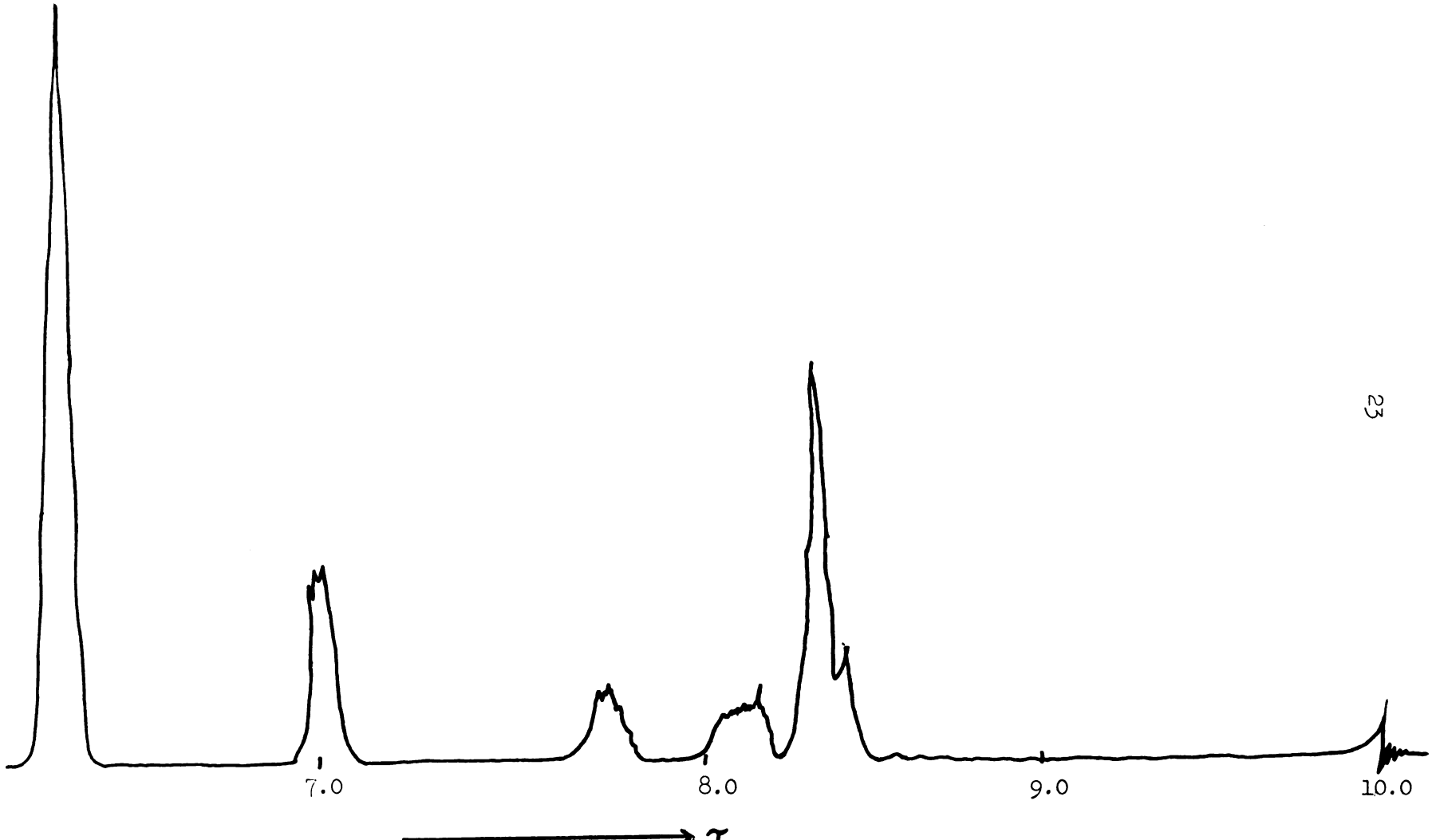


Figure 4: Nuclear Magnetic Resonance Spectrum of V
8,9-dicarbomethoxytetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene

dissolved in benzene and separated by vapor phase chromatography. Two peaks appeared in the chromatogram. The first peak (65%) was collected and found to be identical to V in every respect (m.p., i.r., and n.m.r.). The second peak (35%) solidified upon cooling in the collection tube and melted at 53-4°. The infrared spectrum showed absorption at 3055, 2950, 2860, 1740, 1435, 1360, 1105, and 1070 $cm.^{-1}$ (Fig. 1). The mass spectrum of VI showed a parent peak at m/e 234 (Table 1) and the n.m.r. spectrum had resonance at τ = 8.11, 7.40, 7.17, and 6.39 (area ratios 1:2:1:3 respectively) (Fig. 2).

Analysis: Calc. for $C_{13}H_{14}O_4$: C, 66.64%; H, 6.02%
Found: C, 66.48%; H, 6.33%.

When photolysis was carried out in a more concentrated solution (e.g., 200-900 mg.) or for times exceeding five hours, several secondary reactions occurred which led to the formation of dimers. Their structures were not determined but evidence of their dimeric character came from the retention times on the gas chromatograph. After irradiation for nineteen hours a one gram solution of V in pentane showed several peaks at retention times of 1.1-1.3 hours.

Tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene-8,9-dioic acid, VIIa

To a 0.1 g. (0.00043 m.) 8,9-dicarbomethoxy-tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene was added 5 g. sodium hydroxide and 50 ml. water. The mixture was refluxed for two days, during which time the oily organic material had gone into solution. Upon cooling and acidification with dilute hydrochloric acid, a white flocculent precipitate formed. Extraction with ether gave the diacid, VIIa, in 80% yield, m.p. 217-9°. The n.m.r. showed resonance at τ = 6.77, 7.73, 8.02, and 8.33 with area ratios of 2:1:1:4 respectively. (The spectrum was run in hexadeuteroacetone with tetramethylsilane as an internal standard. A quintuplet at τ = 7.95 is correct for acid hydrogens partially exchanged for deuteriums in the hexadeuteroacetone.) (Figure 5).

Method II

An alternate method of synthesis of the diacid, VIIa, is from bicyclo[2.2.1]hepta-2,5-diene and acetylenedicarboxylic acid. A solution of 2.73 g. (0.025 m.) acetylenedicarboxylic acid and 2.78 g. (0.31 m.) bicyclo[2.2.1]hepta-2,5-diene in 20 ml. toluene and 5 ml. 95% ethanol was heated under reflux

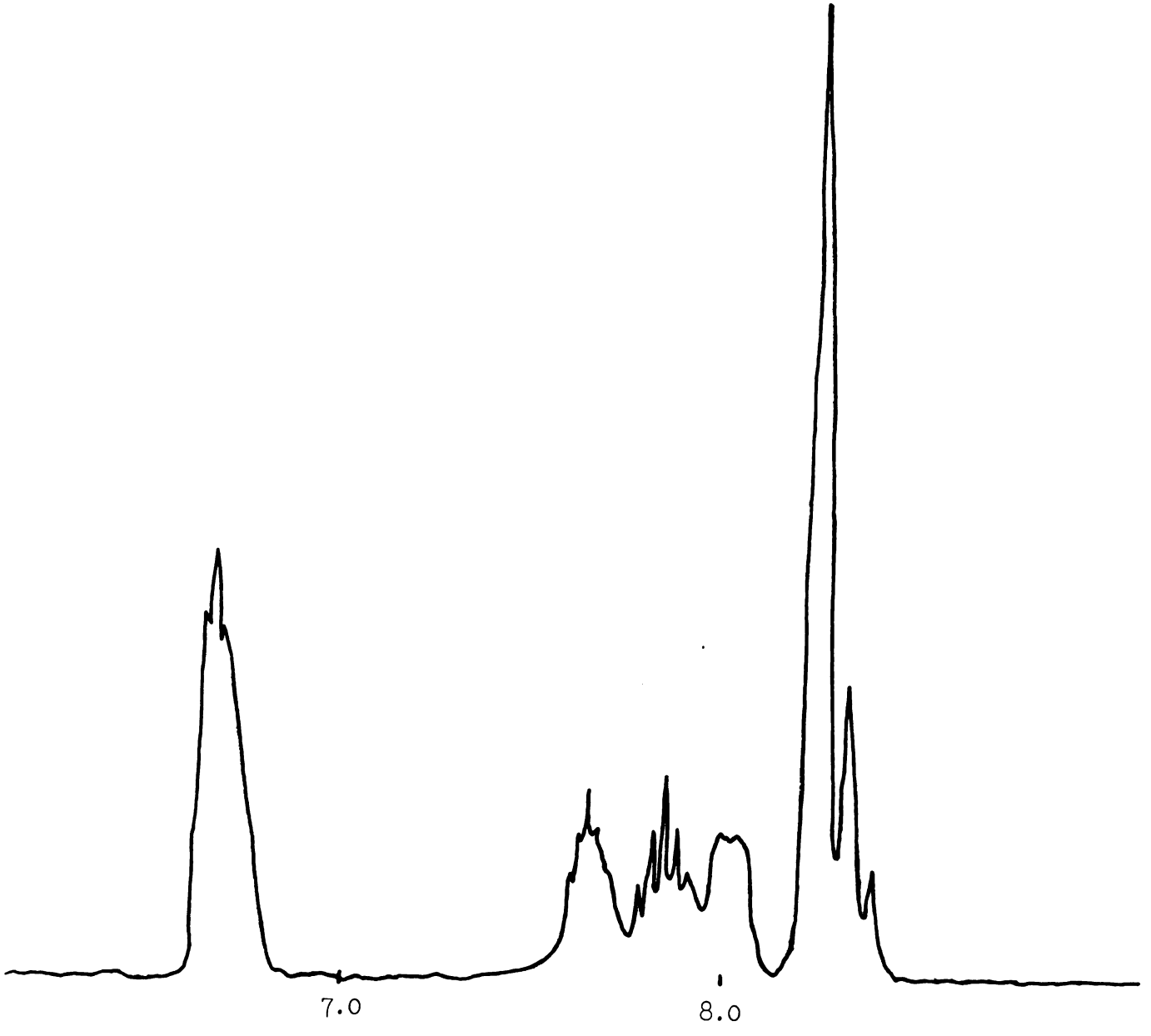


Figure 5: Nuclear Magnetic Resonance τ Spectrum of VIIa
Tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene-8,9-dioc acid

for two days. After cooling to room temperature, the reaction mixture was evaporated to remove the solvents. No 1:1 adduct could be isolated from the remaining yellow oil. Thin-layer chromatography showed no less than nine spots, one of which corresponded to the diacid derived from the diester, V, upon hydrolysis. No further attempt was made to use this route synthetically.

8,9-Dicarbomethoxytetracyclo [4.3.0.$0^{2,4}$.$0^{3,7}$]nonane, X

A solution of 0.234 g. (0.001 m.) 8,9-dicarbomethoxytetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$] nona-8-ene in 100 ml. ethyl acetate was stirred in a 125 ml. round bottom flask fitted with a condenser and a three-way stopcock, having one outlet leading to a vacuum system and one to a balloon of hydrogen gas. Palladium on charcoal (0.1 g., 10%) was added and the system evacuated until the ethyl acetate started to boil. Hydrogen was allowed to enter and the evacuation-filling process repeated three times. The reaction mixture was then stirred for five hours. The catalyst was removed by filtration and the resulting clear solution was evaporated. Crystallization was effected from ethanol, yielding a product melting at 57°. The infrared of this material showed bands at 3055, 2950, 2870, 1745,

1435, 1350, 1315, 1235, 1190, and 1170 cm.$^{-1}$ (Fig. 6). The n.m.r. showed absorbance at τ = 6.38 (singlet), 6.89 (broad triplet), 7.75, 8.17, 8.49, and 8.74 (all broad multiplets) with area intensity 6:2:1:1:2:3 respectively (Fig. 7).

8,9-Dihydroxymethyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]nona-8-ene, VIIb

A slurry of 0.4 g. lithium aluminum hydride and 0.24 g. (0.001 m.) 8,9-dicarbomethoxytetracyclo-[4.3.0.0^{2,4}.0^{3,7}]nona-8-ene in 70 ml. ether was heated under reflux for 1.5 hours. The excess hydride was destroyed by careful addition of ethyl acetate. A solution of saturated aqueous ammonium chloride (25 ml.) was then added. The reaction mixture was filtered and the filtrate extracted with ether. Some additional product was also obtained by washing the collected precipitates with portions of ether. Evaporation of the solvent from the combined extracts yielded an oil, the infrared spectrum of which still showed a weak carbonyl absorption at 1720 cm.$^{-1}$.

Upon treatment with excess acetic anhydride in pyridine the infrared absorption band at 3350 cm.$^{-1}$ present in the diol disappeared. The product from this reaction, presumably the diacetate, exhibited a typical ester odor and showed acetate absorption at

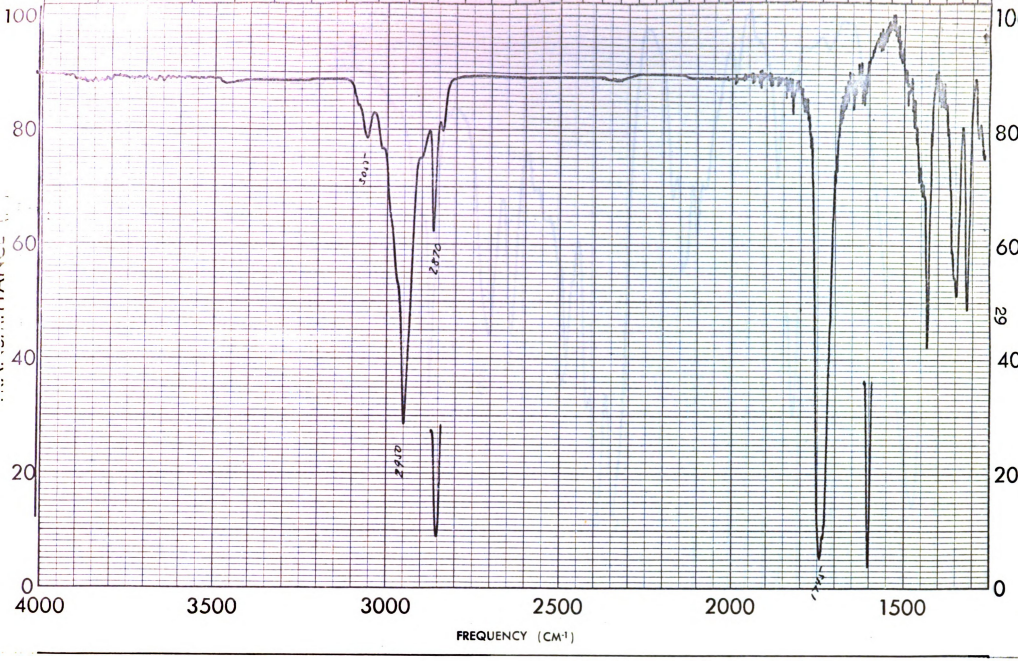


Figure 6a
Infrared Spectrum of X

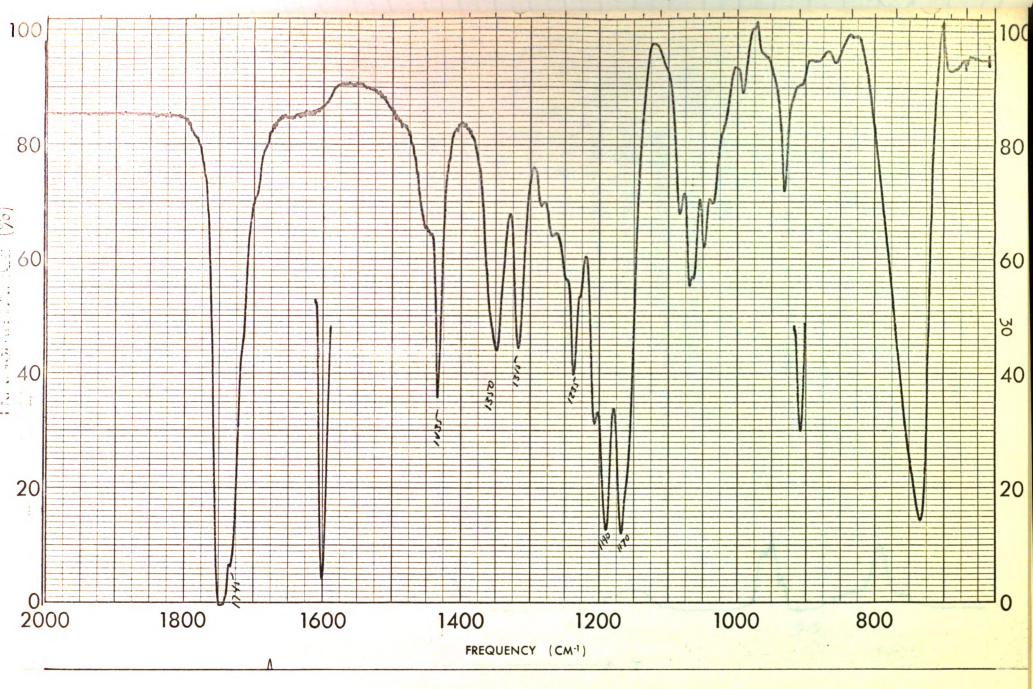


Figure 6b
Infrared Spectrum of X

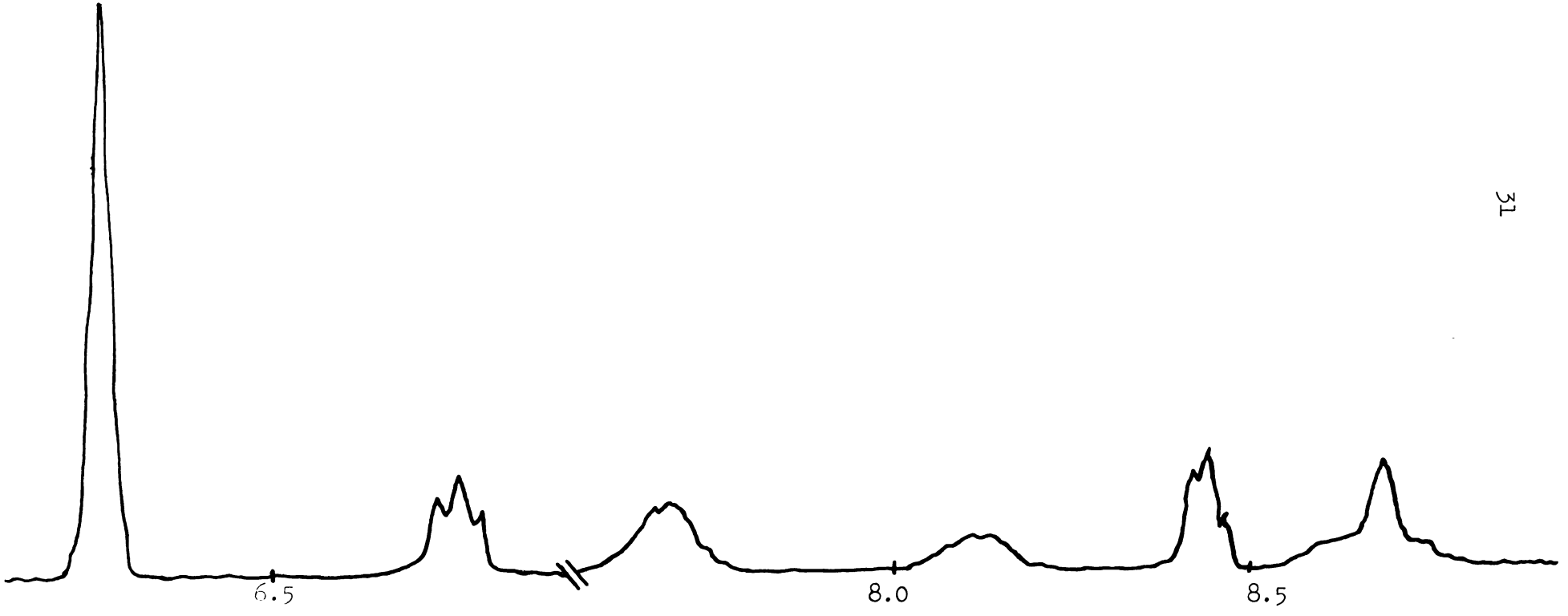


Figure 7: Nuclear Magnetic Resonance Spectrum of X

8,9-dicarbomethoxytetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane

1740 and 1260 cm.$^{-1}$ in the infrared. The diester was a non-crystalline material which formed small crystals from a cold solution of ethyl acetate; however, these melted below room temperature.

Method II

An alternate preparation of 8,9-dihydroxymethyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]nona-8-ene was attempted utilizing a reaction similar to that employed in the preparation of the tetracyclic ester, V. A solution of 8.6 g. 2-butyne-1,4-diol and 9.2 g. bicyclo[2.2.1]hepta-2,5-diene in 15 ml. dimethylsulfoxide was heated under reflux for two days. Vacuum distillation at 4 mm. yielded the bicycloheptadiene in a forerun, dimethylsulfoxide as the major distillate, and residues which were essentially unreacted 2-butyne-1,4-diol. Further preparations were not attempted.

Attempted synthesis of 8,9-dimethyltetracyclo-[4.3.0.0^{2,4}.0^{3,7}]nona-8-ene, VIIe

A sample of the impure 8,9-dihydroxymethyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]nona-8-ene (0.1 g., 0.00043 m.) was dissolved in 5 ml. pyridine and 2 g. of p-toluenesulfonyl chloride in 5 ml. pyridine was added. The

mixture was heated under reflux for two hours. After cooling to room temperature, 25 ml. of water was added and the aqueous solution was extracted twice with ether. The ether was washed with a 10% sodium bicarbonate solution and twice with water. The organic layer was dried over sodium sulfate and evaporated, yielding a colorless oil. Except for carbon-hydrogen absorption, the infrared spectrum of this oil showed no absorptions ascribable to the expected tosylate, VIIc. The p-toluenesulfonate grouping is known to have absorption in the infrared at 1230-1150 and 1440-1350 $cm.^{-1}$ (26). Absorption was lacking in these regions.

The oil was dissolved in ether and 0.2 g. lithium aluminum hydride was added. The reaction mixture was allowed to remain at room temperature for several days, at which time the excess hydride was destroyed by adding ethyl acetate. Except for a slight increase of O-H absorption in the infrared, presumably due to reduction of any residual carbonyl present after the first reduction, the infrared spectrum was essentially the same as that prior to reduction.

Attempted synthesis of 8-phenyl-[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene, IXb

Phenylacetylene (30.6 g., 0.3 m.) and bicyclo-[2.2.1]hepta-2,5-diene (27.6 g., 0.3 m.) were refluxed for twelve hours. The initially light yellow solution turned a deeper yellow and finally a rich amber red. Upon distillation of the reaction mixture, only unreacted starting materials were recovered.

Attempted synthesis of 8,9-diphenyltetracyclo-[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene, IXa

A solution of 2 g. (0.02 m.) bicyclo[2.2.1]hepta-2,5-diene and 0.32 g. (0.002 m.) diphenylacetylene (tolan) in 5 ml. toluene was refluxed for 19 hours. Upon flash evaporation of the volatile components, a creamy yellow powder was obtained. Recrystallization from pentane gave quantitative recovery of the diphenylacetylene.

When the reaction was repeated in the absence of toluene at the temperature of refluxing bicyclo [2.2.1]-hepta-2,5-diene (approximately 150°) no adduct was observed.

Pyrolysis of 8,9-dicarbomethoxytetracyclo-[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene

In the pyrolysis experiments the glass vials were prepared in the following manner.

Pyrex tubing (8 mm. O.D.- 4 mm. I.D.) was cut into 20 cm. lengths and placed in a bath of nitric acid for 5 hours. The tubes were rinsed thoroughly with distilled water and covered with ammonium hydroxide for 30 minutes. After rinsing well with distilled water, they were placed in a drying oven at 120° for 7 hours. The tubes were then sealed and stored in a desiccator.

Samples of compound V (ca. 100 mg.) were degassed, sealed under nitrogen, and heated in an aluminum block furnace at 200°, 302°, 368°, and 412° for various lengths of time. The temperature was controlled to ± 2°C. After 19 hours at 200° a sample of V was completely unchanged. The clear, colorless liquid solidified upon cooling to room temperature, and its infrared spectrum was identical with that of the unheated V.

Upon heating to 302° for 15 minutes, 1, 3, and 15 hours, each of the samples became quite dark and discolored. At the longer reaction times dark, chunky flakes of carbonaceous material formed. After cooling, the vial was broken and the organic material dissolved

in benzene. Vapor phase chromatographic analysis of these benzene solutions exhibited one peak at the retention time of the starting material in each case. Infrared spectra of the samples in CCl_4 were identical to those of V.

At 368°, samples heated for 15 minutes and 1 hour again exhibited decompostion. The soluble organic material again proved to be the starting ester V.

Pyrolysis of V at 412° also led to extensive decomposition, but v.p.c. analysis of the soluble components showed a complex mixture of products, none of which corresponded to the starting diester, V, or to the photoproduct, VI. No attempt was made to identify these substances.

Pyrolysis of 3,7-dicarbomethoxypentacyclo-[3.3.1.$0^{2,4}$.$0^{6,8}$.$0^{3,7}$]nonane, VI

Photoisomer, VI, remained essentially unchanged when heated to 300°. At higher temperatures the decomposition did not involve conversion to the starting diester, V.

Deuterium Exchange of 8,9-dicarbomethoxytetracyclo-[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene, V

A mixture of 145 mg. (0.00062 m.) V, 56 mg. sodium methoxide and 30 ml. methanol-O-d (80% d) was heated under reflux for 20 hours. The reaction mixture was cooled, added to 30 ml. heavy water (99% d), and the aqueous layer extracted with pentane. After drying over sodium sulfate, the pentane solvent was evaporated, yielding a white solid. The infrared and n.m.r. spectra of this material were identical to that of the starting material, V.

Deuterium Exchange of 3,7-dicarbomethoxypentacyclo-[3.3.1.$0^{2,4}$.$0^{6,8}$.$0^{3,7}$]nonane, VI

After 72 hours of warming on a steam bath, a mixture of 40 mg. VI and 48 mg. sodium methoxide in 30 ml. methanol-O-d (80% d) was cooled, poured into deuterium oxide (99% d), and extracted with ether. The solid material recovered proved to be identical to the photoproduct, VI.

After 3 weeks of sitting at room temperature a 20 mg. sample of VI in a solution of deuteromethanol/ sodium methoxide was also recovered unchanged. The infrared and n.m.r. spectra were taken to make comparisons for possible incorporation of deuterium. The results were negative.

Irradiation of Maleic Anhydride and Norcarane

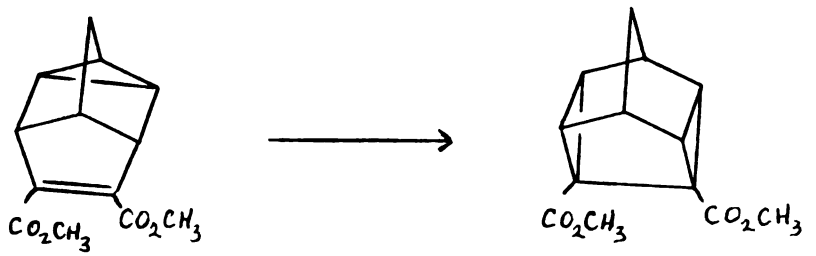
Irradiation of a solution of 35 mg. maleic anhydride in 1 ml. norcarane (bicyclo[4.1.0]heptane) for two hours in a vycor test tube using a 250 watt medium pressure mercury lamp led to no observable products. Analysis was by vapor-phase chromatography.

Irradiation of 1,1,2,2-tetracarbomethoxycyclopropane and cyclohexene

Irradiation of solutions of 45 mg. 1,1,2,2-tetracarbomethoxycyclopropane in 3 ml. cyclohexene for from 1 to 60 hours in quartz test tubes using a 250 watt medium pressure mercury lamp led to no observable products. Analysis was by vapor-phase chromatography.

SUMMARY

This investigation has disclosed a second example of intramolecular cycloaddition of a cyclopropane system to an olefin. The cycloaddition occurs readily even though the conversion of 8,9-dicarbomethoxy-tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nona-8-ene (V) to 3,7-dicarbomethoxypentacyclo[3.3.1.$0^{2,4}$.$0^{6,8}$.$0^{3,7}$]-nonane (VI) results in an increase in strain.



V VI

The structure of the pentacyclic photoproduct was deduced from mass spectral, infrared, and nuclear magnetic resonance data, and the relative thermal stability of VI.

The photoisomer, VI, is stable to heating to 368° but decomposes above that temperature. The tetracyclic diester, V, is thermally stable at 200°

but decomposes rapidly at 306°, 368°, and 412°. The only recoverable material is unreacted V. No trace of the photoproduct is found.

An intermolecular reaction between an olefin and a cyclopropane ring did not occur when the reactants were maleic anhydride/ norcarane or cyclohexene/ 1,1,2,2-tetracarbomethoxycyclopropane.

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