

The n.m.r. spectrum showed a doublet (*ca.* 1 c.p.s.)³⁴ at 8.31 τ (allylic methyl, 6 protons), a multiplet centered at 7.70 τ (allylic methylenes, 8 protons), and a multiplet centered at 4.64 τ (2 olefinic protons). Ozonolysis of III and subsequent oxidative work-up afforded 2,5-hexanedione [bis-(2,4-dinitrophenylhydrazone), m.p. and mixture m.p. 256°³⁵] and succinic acid (m.p. and mixture m.p. 184°³⁶).

The unidentified minor products had retention times on a number of v.p.c. columns which did not correspond to those of any of the known thermal dimers^{14,15} or photodimers¹¹ of isoprene.

Kinetic Determinations.—For each kinetic run the following compounds were pipetted into a 10-ml. flask equipped with a micro reflux condenser, a thermometer inlet, and a septum-covered outlet arm: I (1.00 cc.), *n*-nonane (1.00 cc., internal standard), and *o*-dichlorobenzene (5.00 cc., solvent). The reaction flask was then partially submerged in an oil bath (550 in.³) which had been preheated to constant temperature. Temperature control was maintained by a Jumo thermometer connected to resistance heating coils and a mercury relay which served as a thermostat (H-B Instrument Co.). Control of $\pm 0.2^\circ$ was thus maintained.

(34) For similar examples of $-\text{CH}=\text{C}(\text{CH}_3)-$ coupling, see E. I. Snyder, and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962); G. S. Reddy, R. T. Hobgood, Jr., and J. H. Goldstein, *ibid.*, **84**, 338 (1962); "NMR Spectra Catalog," Varian Associates, National Press, Palo Alto, Calif., 1962, pp. 272–273.

(35) F. Nerdel, E. Henkel, R. Kayser, and G. Kannelbley, *J. prakt. Chem.*, **43**, 153 (1956).

Microliter samples, withdrawn periodically and quenched, were analyzed by v.p.c.³¹ Disappearance of I was determined by comparison to the internal standard. Previous v.p.c. analyses of I and *n*-nonane in varying ratios established the relationship between peak areas and molar amounts. The constancy of the internal standard throughout a run was demonstrated by independent experiments.³⁷

The disappearance of I over the temperature range 101–128° proved to be cleanly first order up to high conversions. The kinetic data obtained are compiled in Table II.

Effect of Additives.—Three thick-walled glass tubes were charged with identical solutions of compound I (2.0 g.) in chlorobenzene (10.0 ml.). The solutions were outgassed three times by conventional techniques and saturated with oxygen, nitric oxide, and nitrogen (control), respectively, by repeated additions of the gases to the evacuated systems. The tubes were then sealed and heated simultaneously in an oil bath for 1 hr. After cooling, the tubes were opened and analyzed by v.p.c.³¹ In each case reaction had proceeded to $87 \pm 2\%$ conversion.

Acknowledgments.—The authors are grateful to Prof. P. R. Schleyer (Princeton) and Prof. H. H. Wasserman (Yale) for helpful suggestions.

(36) M. T. Leffler and R. Adams, *J. Am. Chem. Soc.*, **58**, 1553 (1936).

(37) The importance of precise temperature control and internal standard constancy was illustrated by earlier runs in which erroneously low values were obtained for a number of the specific rate constants.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON, EUGENE, ORE.]

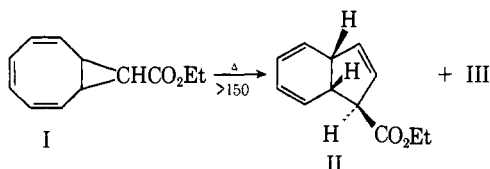
The Thermal Rearrangement of 9-Ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene

BY KARL F. BANGERT AND V. BOEKELHEIDE

RECEIVED AUGUST 19, 1963

9-Ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene (I) undergoes rearrangement at 150° giving the 9,10-dihydroindene derivative II as the main product. The structure and stereochemistry of II have been established through degradation and aromatization studies.

In the course of an investigation directed toward the preparation of the cyclononatetraene anion, we have examined 9-ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene (I) as a possible precursor. Its preparation has been previously described by Akiyoshi and Matsuda¹ and by Phillips,² who utilized the reaction of cyclooctatetraene and ethyl diazoacetate for its preparation. Although the structure of I seemed secure from the earlier work, we were interested in having material of high purity and so subjected I to vapor phase chromatography. Two products were observed, neither of which corresponded to the starting ester I. Further, when compound I was subjected to careful distillation using an efficient spinning-band column, the main product was not I but was instead an isomer. Subsequently, it was shown that I undergoes a rearrangement at temperatures above 150° giving II as the main product and another product III in minor amounts.



The main features of II were readily deduced from spectral data. In the ultraviolet, II showed absorption maxima at 282 (log ϵ 3.35), 261 (log ϵ 3.66), and 252 $m\mu$ (log ϵ 3.56) in good accord with the spectrum of 8,9-dihydroindene recorded by Vogel and Kiefer,^{3,4}

(1) S. Akiyoshi and T. Matsuda, *J. Am. Chem. Soc.*, **77**, 2476 (1955).

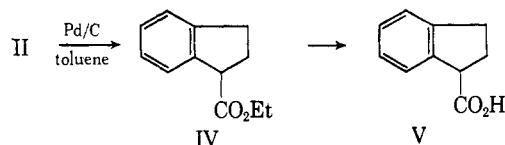
(2) D. D. Phillips, *ibid.*, **77**, 5179 (1955).

(3) E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961).

(4) We are grateful to Professor Vogel for making the details of this spectrum available to us. Through this correspondence we learned that he has also observed this same rearrangement and we are indebted to him for re-

but in sharp contrast to the starting ester I [λ_{max} 244 $m\mu$ (log ϵ 3.56)]. In the infrared the ester carbonyl of II showed a normal absorption ($\nu_{\text{C}=\text{O}}$ 1736 cm^{-1}) and the absence of conjugation was confirmed when hydrogenation of II did not affect the frequency of the carbonyl absorption. For the n.m.r. studies, the corresponding hydrazide of II proved to be most suitable and its spectrum showed clearly that the ratio of olefinic to aliphatic protons was 6:3.

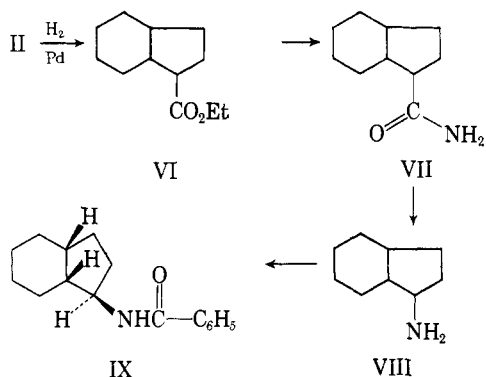
Since the spectral data were nicely compatible with a structure such as II, chemical studies were undertaken to test this hypothesis. In accord with the proposed *cis*-conjugated diene grouping, II readily underwent a Diels-Alder addition with *N*-phenylmaleimide. Further, as expected for an 8,9-dihydroindene, II was easily aromatized on heating with a 10% palladium-on-charcoal catalyst in toluene to give 1-ethoxycarbonylindane (IV), whose identity was established by hydrolysis to the known crystalline acid, 1-carboxyindane (V).



Although this evidence provided strong support for the over-all structure represented by II, it was of interest to establish the stereochemistry of the molecule as well. This was done by degradation of the corresponding saturated derivatives. As would be expected, both II and its hydrazide when subjected to hydrogenation over a palladium catalyst in ethanol absorbed 3 moles of hydrogen rapidly and cleanly,

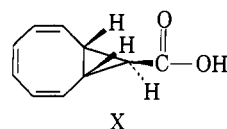
porting his work to us prior to publication (*cf.* E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, **11**, 673 (1963)).

Conversion of the saturated ester VI to the corresponding amide VII occurred smoothly in the usual manner *via* the acid and acid chloride. Hofmann degradation of the amide yielded the saturated amine VIII, whose benzoyl derivative IX melted at 130–131°. It has been shown previously by Hückel and his collaborators that reduction of *cis*-hydrindan-1-one oxime gives a mixture of the epimeric 1-amino-*cis*-hydrindanes.⁵ These, after separation, give benzoyl derivatives melting at 180 and 131°, respectively. When this result is combined with the fact that the hydrindane-1-carboxylic acid obtained as an intermediate in our sequence is definitely different from the presumably all *cis*-hydrindane-1-carboxylic acid prepared by Knowles, Kuck, and Elderfield,⁶ it can be concluded that the stereochemistry of our 1-benzoylamino-*cis*-hydrindane is correctly represented by IX. In turn, the full assignment of stereochemistry to II can be made as shown. As a final detail, the amine VIII was subjected to the Hofmann exhaustive methylation procedure and the olefin so obtained was hydrogenated. The resulting saturated hydrocarbon was shown by infrared spectral comparison to be *cis*-hydrindane.

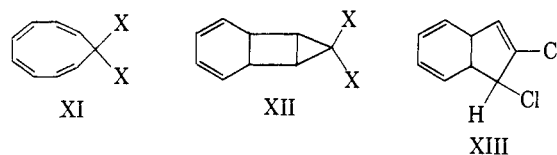


In the previous work^{1,2} on the reaction product of cyclooctatetraene and ethyl diazoacetate, no definite assignment of stereochemistry was given to I. However, Phillips suggested that there was an interaction between the triene system and the ester carbonyl in order to explain the fact that the ultraviolet absorption maximum (λ 245 $m\mu$) is abnormally low. Our examination of the n.m.r. spectra of I and its derivatives, especially the acid X, is not in agreement with this interpretation but favors instead the stereochemistry shown for X. Thus, the lone proton in the cyclopropane ring gives a triplet signal centered at 8.68 τ with a coupling constant of 4.7 c.p.s. The remaining two protons of the cyclopropane ring appear as a doublet centered at 7.88 τ and again with a coupling constant of 4.7 c.p.s. Since the work of Graham and Rogers⁷ indicates that the coupling constant for *trans*-protons of a cyclopropane ring should be about 5.68 c.p.s. whereas that of *cis*-protons should be around 8.2 c.p.s., the *trans* assignment as shown by X is clearly indicated. With regard to an explanation for the abnormal absorption in the ultraviolet, we would suggest that this is probably due to an interaction between the triene system and the cyclopropane ring rather than the ester carbonyl. Recently, Sauer and Sonnet⁸ have obtained n.m.r. evidence supporting a transannular effect between an olefinic double bond and the proton of a similarly-substituted cyclopropane ring. It is of interest that the chemical shift of our lone proton

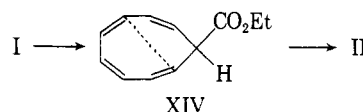
(8.68 τ) is essentially the same as that observed in their case.



In studies on the thermal rearrangement of bicyclo[6.1.0]nona-2,4,6-triene and its 9,9-dihalogen derivatives, Vogel has considered both XI and XII as probable intermediates.^{3,9} In the case of the 9,9-dichloro derivatives, which yield XIII as the final product of the rearrangement, a reaction path involving XII has been favored. However, such a reaction path seems unlikely for our 9-ethoxycarbonyl derivative since it would predict 2-ethoxycarbonyl-8,9-dihydroindene as the final product rather than structure II as observed.



Thus, a reasonable postulate for the rearrangement would be that I undergoes rupture of the cyclopropane ring to give the cyclononatetraene derivative XIV which then, by ring closure as indicated by the dotted line, would lead to the product II. It was because of this, in part, that we have been concerned with the stereochemistry of I and II. An examination of models would suggest that, if the transition from I to II, as envisioned with XIV as an intermediate, is essentially a rapid and efficient reorganization of bonding, then a molecule having the stereochemistry deduced for I should lead cleanly to a product having the stereochemistry deduced for II. At least the experimental data are consistent with postulating a simple thermal reorganization of bonding.



The minor product III from the rearrangement is a colorless, air-sensitive oil. The separation and purification of II and III by vapor phase chromatography indicates that the two products are formed in the ratio of 4 : 1. The ultraviolet absorption spectrum of III shows maxima at 307 (log ϵ 3.45), 295.5 (log ϵ 3.54), 282.5 (log ϵ 3.58), 271 (log ϵ 3.60), 262 (log ϵ 3.54), and 252 $m\mu$ (log ϵ 3.41). Also, it readily forms an adduct with tetracyanoethylene, suggesting the presence of a *cis*-conjugated diene. However, the sensitivity of III has prevented obtaining sufficient material of satisfactory purity to determine its structure.

Experimental¹⁰

9-Ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene (I) was prepared following the procedure described by Phillips² in 62% yield based on the ethyl diazoacetate employed. The n.m.r. spectrum of I shows the vinyl hydrogens of I as a split peak at 4.25 (4-protons) and 4.30 τ (2 protons). This split peak absorption in the vinyl region is typical of all the bicyclo[6.1.0]nona-2,4,6-triene derivatives we have examined.

For characterization, the Diels-Alder adduct of I with dimethyl acetylenedicarboxylate was formed by heating I in a fivefold excess of dimethyl acetylenedicarboxylate overnight at 128°. After removal of the excess dimethyl acetylenedicarboxylate and

(5) W. Hückel, M. Sachs, J. Yantschulerwitsch, and F. Nerdel, *Ann.*, **518**, 155 (1935).

(6) W. S. Knowles, J. A. Kuck, and R. C. Elderfield, *J. Org. Chem.*, **7**, 374 (1942).

(7) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(8) R. R. Sauer and P. E. Sonnet, *Chem. Ind. (London)*, 786 (1963).

(9) E. Vogel, *Angew. Chem.*, **74**, 829 (1962).

(10) Analyses by F. Pascher and Microtech Laboratories. The n.m.r. spectra were determined using a Varian A-60 spectrometer, the infrared using a Beckman IR-5, and the ultraviolet using a Cary Model 11.

recrystallization of the solid from methanol, white crystals, m.p. 123–124°, were obtained.

Anal. Calcd. for $C_{15}H_{20}O_6$: C, 65.04; H, 6.07. Found: C, 64.74; H, 6.04.

The corresponding acid **X** was obtained by alkaline hydrolysis, as described by Akiyoshi and Matsuda,¹ and melted at 162–163°. Its n.m.r. spectrum showed the split vinyl peak at 4.20 and 4.25 τ . For further characterization the acid was converted to the corresponding acid chloride using thionyl chloride; this, in turn, was converted to the corresponding amide and methyl ester.

Bicyclo[6.1.0]nona-2,4,6-trien-9-carboxamide was obtained after recrystallization from methanol–water as white crystals, m.p. 194–195°, in 80% yield.

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.82; H, 6.95; N, 8.82.

9-Methoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene was obtained in 85% yield as an oil, b.p. 78–87° at 0.8 mm., which solidified on standing. Recrystallization of the solid from pentane gave white crystals, m.p. 42–43°, λ_{max} 242 $m\mu$ ($\log \epsilon$ 3.63). Passage of the methyl ester over a Carbowax column in the vapor phase chromatograph at 200° effected isomerization in the same manner as with the ethyl ester I.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.66; H, 6.99.

Thermal Rearrangement of 9-Ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene (I) to Give II and III.—A 20.0-g. sample of I was placed in a distilling flask attached to an efficient spinning-band distillation column and heated at a bath temperature of 160–180° for about 10 min. under partially reduced pressure. The pressure was then reduced to 14 mm. and the material was slowly and carefully distilled. This required about 1.5 hr. and the boiling point range was 120–130°. The crude product (15.0 g.) was then subjected to preparative vapor phase chromatography using a Carbowax column. Analytical vapor phase chromatography had indicated the presence of one main component and two minor ones. From the preparative column the ratio of the main product II to the minor product III was about 4:1. The minor product III is discussed later and the second minor component was not isolated in useful amounts. Distillation of the main product II from the preparative column gave a colorless oil, b.p. 78° at 0.5 mm.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 74.77; H, 7.34.

The **N-phenylmaleimide** adduct of II was prepared in boiling chloroform and, after recrystallization from ethanol, was obtained as white crystals, m.p. 166.5–167°.

Anal. Calcd. for $C_{22}H_{21}NO_2$: C, 72.71; H, 5.82; N, 3.85. Found: C, 72.45; H, 5.61; N, 3.55.

The **hydrazide of II** was prepared by heating a solution of 500 mg. of II and 500 mg. of hydrazine in 10 ml. of ethanol containing 0.5 ml. of water under reflux for 2 hr. The volatile solvents were removed under reduced pressure and the solid residue was recrystallized from water to give white crystals, m.p. 124–125°, λ_{max} 262 ($\log \epsilon$ 3.41) and 270 $m\mu$ ($\log \epsilon$ 3.38).

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 68.16; H, 6.86; N, 15.90. Found: C, 67.66; H, 6.81; N, 15.79.

Hydrolysis of II to the corresponding acid was carried out by dissolving 3.0 g. of II in 20 ml. of a 5% methanolic potassium hydroxide solution and allowing the solution to stand overnight. After removal of the methanol, the residue was acidified and the resulting oily acid was extracted with methylene chloride. The methylene chloride extract was concentrated and the residual oil distilled (b.p. 108–115° at 0.5 mm.). Since the acid could not be induced to crystallize, it was taken up in chloroform and treated with maleic anhydride to obtain a crystalline derivative for characterization. The **maleic anhydride adduct of 1-carboxy-8,9-dihydroindene**, thus prepared, was a solid which, after recrystallization from ethyl acetate, gave white needles, m.p. 204.5–206.5°.

Anal. Calcd. for $C_{11}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.11; H, 4.83.

Separation of III by Vapor Phase Chromatography.—This separation was effected using a 5-ft. column filled with Carbowax and held at 200° with a helium pressure of 40 p.s.i. The retention time of the main product II was 17.8 min. The retention time of the minor product III was 19.5 min. Traces of another product were eluted at 22.0 min., but this could never be isolated in useful amounts.

Because of the instability of III, it was used directly from the preparative column for spectral determinations and for characterization. The main features of its ultraviolet spectrum are given in the Discussion.

The **tetracyanoethylene** adduct of III was prepared in ethyl acetate. After removal of solvent, the resulting solid was recrystallized from methanol to give white crystals, m.p. 169–170°.

Anal. Calcd. for $C_{15}H_{11}N_4O_2$: C, 67.91; H, 4.43; N, 17.60. Found: C, 67.80; H, 4.70; N, 17.70.

Aromization of II over Palladium.—A mixture of 1.0 g. of II and 200 mg. of a 5% palladium-on-charcoal catalyst¹¹ in 10 ml. of toluene was boiled under reflux overnight. After removal of the catalyst and solvent, the residue remained oily and could not be induced to crystallize. Therefore, it was hydrolyzed directly by dissolving it in 10 ml. of a 10% methanolic potassium hydroxide solution and allowing the mixture to stand at room temperature overnight. After concentration of the solution the residue was dissolved in water and acidified. This gave a solid which, when recrystallized from methanol, yielded white crystals, m.p. 59–60° (lit.^{5,12} gives 59–60° as the melting point of 1-carboxyindane (V)).

1-Ethoxycarbonyl-*cis*-hydrindane (VI).—A mixture of 24.0 g. of II and 250 mg. of Adams catalyst in 200 ml. of ethanol was subjected to hydrogenation at room temperature and atmospheric pressure. Absorption of 3 moles of hydrogen was complete in 4.5 hr. After removal of the catalyst, the solution was concentrated and the residual oil distilled to give 22.5 g. (94%) of a colorless oil, b.p. 97–99° at 2.3 mm.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.30; H, 10.41.

The **hydrazide of VI** was prepared by heating a solution of VI in ethanol with hydrazine as described before for the hydrazide of II. The resulting solid was recrystallized several times from water to give white crystals, m.p. 110–111°.

When the hydrazide of II was subjected to hydrogenation, as described above for the preparation of VI, there was a rapid uptake of 3 moles of hydrogen and the resulting product, after recrystallization from water, melted at 110–111°, undepressed by admixture of the previously prepared sample of the hydrazide of VI. Also, the infrared spectra of the two samples of the hydrazide of VI were superimposable.

Anal. Calcd. for $C_{10}H_{18}N_2O$: C, 65.89; H, 9.96; N, 15.37. Found: C, 65.79; H, 9.53; N, 14.99.

***cis*-Hydrindane-1-carboxamide (VII).**—A solution of 22.0 g. of VI in 100 ml. of a 15% methanolic potassium hydroxide solution was allowed to stand at room temperature overnight. After concentration under reduced pressure, the residue was dissolved in water and acidified with 5% sulfuric acid. The oily acid, which separated, was extracted with methylene chloride and then dried by azeotropic distillation of the methylene chloride. Despite many attempts, this oil could not be induced to crystallize. Therefore, it was used directly by treating it with 60 ml. of thionyl chloride. The mixture was boiled under reflux for 2 hr. The solution was then allowed to stand at room temperature overnight before concentrating under reduced pressure. Distillation of the residual oil gave 18.5 g. (89%) of the acid chloride as a colorless oil, b.p. 108–118° at 0.1 mm. This was dissolved in ether and carefully mixed with concentrated ammonium hydroxide. The solid which separated was collected and washed carefully with water. It was then recrystallized from methanol to give 10.5 g. (64%) of white crystals, m.p. 157–158°. This amide is clearly different from the *cis*-hydrindane-1-carboxamide described by Elderfield.⁶

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 72.07; H, 10.15; N, 8.40.

Hofmann Degradation of VII.—To a solution of 2.0 g. of VII in 30 ml. of a 10% aqueous sodium hydroxide solution there was added 1 ml. of bromine with stirring. When the solution was stirred overnight at room temperature, a crystalline solid separated. The mixture was then warmed to 75° causing the solid to redissolve, and an oil separated. The oil was extracted with methylene chloride, dried, and concentrated. Distillation of the residue gave 450 mg. of the amine VIII as a colorless oil, b.p. 120–150° at 12 mm. This was taken up in ether; aqueous 10% sodium hydroxide and then benzoyl chloride were added. After the mixture was shaken vigorously, crystals began to separate from the ether layer. The ether was removed by evaporation and the solid was collected. Recrystallization of the solid from methanol gave white crystals, m.p. 130–131° (Hiickel, *et al.*,⁵ give 131° for the one stereoisomer of 1-benzoylamino-*cis*-hydrindane; for the epimeric 1-benzoylamino-*cis*-hydrindane, they give 180° as the melting point.)

Conversion of VIII to *cis*-Hydrindane.—The preparation of the crude amine VIII was carried out as described before starting with 2.0 g. of the amide VII. The amine VIII was dissolved in 5 ml. of 90% formic acid, 4.0 ml. of formalin (37%) was added, and the mixture was boiled under reflux for 12 hr. Then, 4 ml. of concentrated hydrochloric acid was added and the mixture was concentrated under reduced pressure. The solid residue was dissolved in a small amount of water, made basic with sodium hydroxide, and extracted with chloroform. Concentration of the chloroform gave an oily residue which was treated directly

(11) R. Mozingo, Procedure C, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 686.

(12) M. Tiffeneau and A. Orelthoff, *Bull. soc. chim. France*, [4] 27, 782 (1920).

with excess methyl iodide. An exothermic reaction occurred giving a semicrystalline mass. This was dissolved in water, the aqueous solution was extracted with ether, and then an aqueous solution of sodium perchlorate and perchloric acid was added. The crystals that separated from the aqueous solution were collected and recrystallized from water to give 1.4 g. of *N,N,N*-trimethyl-*cis*-hydrindane-1-ammonium perchlorate as white crystals, m.p. 218–220°.

Anal. Calcd. for $C_{12}H_{24}NO_4Cl$: C, 51.14; H, 8.58; N, 4.97. Found: C, 50.49; H, 8.29; N, 4.89.

A solution of 1.2 g. of the perchlorate in 20 ml. of a 20% aqueous potassium hydroxide solution was heated at 120° for 2 hr. The cold solution was extracted with ether and the ether extract was carefully concentrated. The residual oil was dissolved in ethanol, 100 mg. of a 5% palladium-on-charcoal catalyst¹¹ was added, and the mixture was subjected to hydrogenation at room temperature and atmospheric pressure. There was a rapid up-

take of 61 ml. of hydrogen indicating the presence of 320 mg. (61%) of olefin. After removal of the catalyst, the solution was carefully concentrated. Vapor phase chromatography of the residue using a Carbowax column was carried out and the main component was collected and examined in the infrared using carbon tetrachloride as solvent. The infrared spectrum thus obtained agreed very closely with that given for *cis*-hydrindane¹³ and was different from that of *trans*-hydrindane.¹⁴

Acknowledgment.—We are indebted to the National Science Foundation for support of this work. Also, we wish to thank the Badische Anilin and Soda Fabrik A. G., Ludwigshaven A. Rhein, for a generous supply of cyclooctatetraene.

(13) American Petroleum Institute Tables of Infrared Spectra, No. 1647.

(14) American Petroleum Institute Tables of Infrared Spectra, No. 1648.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

Conjugation Effects in Phenylcyclopropanes

BY ALAN L. GOODMAN¹ AND RICHARD H. EASTMAN

RECEIVED JULY 22, 1963

The ultraviolet absorption spectrum of phenylcyclopropane has previously been interpreted as evidence that the cyclopropane ring electrons interact with those of the benzene ring to form a conjugated system. It has now been shown, using rigid model compounds, that the steric relationship between the cyclopropane and benzene rings is of little consequence spectroscopically.

The ability of the cyclopropane ring to enter into conjugation with a neighboring unsaturated system has been the subject of a number of recent investigations.² However, few of these have been concerned with ascertaining the steric requirement necessary for such interaction to occur.

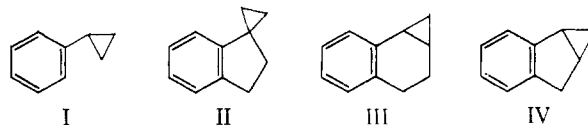
Walsh^{3a} predicted for interaction that the plane of the cyclopropane ring should be perpendicular to the plane of the unsaturated side chain; his model was used by Music and Matsen^{3b} to predict the ultraviolet absorption maximum of phenylcyclopropane from molecular orbital calculations. Experimental evidence was given by Cromwell⁴ in the case of the *cis* and *trans* forms of arylarylethylenimines and ethylene oxides to the effect that a rather critical orientation of the three-ring atoms and the adjacent p-orbital bearing carbon atom must be met for appreciable conjugation to occur. Fuchs and Bloomfield^{5a} have provided kinetic evidence for a pronounced geometrical bias in the transmission of electronic effects by the cyclopropane ring, whereas the equilibrium studies of Trachtenberg and Odian^{5b} showed the cyclopropane system to be inferior to a two-carbon saturated chain in such transmission.

Kosower and Ito,^{6a} in the cases of the two cyclopropyl ketones spiro[4.2]heptan-1-one and bicyclo[3.1.0]hexan-2-one, predicted and found the spiroketone to absorb at longer wave lengths than the fused ring ketone. They interpreted their data as supporting the importance of the geometrical factor for which

evidence had earlier been reported by Cromwell.^{2,4} The ultraviolet spectra of compounds derived from natural products where the cyclopropyl ring is a γ -substituent on an α,β -unsaturated ketone have also been interpreted to correspond to changes in the overlapping of the electrons of the ring and the double bond in the excited state.^{6a,b}

Striking differences in the position of maximum absorption were observed in a series of substituted *trans*-2-phenylcyclopropanecarboxamides by Perold.⁷ According to Walsh's theory,³ for maximum conjugative interaction the hydrogen atom on that carbon atom of the cyclopropane ring which is bonded to the aromatic nucleus must lie in the plane of the benzene ring. If bulky groups such as methyl are substituted in the position *ortho* to the cyclopropyl substituent, the rings might be expected to twist out of conjugation. Perold⁷ reports that 2-*o*-tolylcyclopropanecarboxamide possesses no measurable band near 220 m μ , while the corresponding *m*- and *p*-tolyl compounds have absorption maxima at 225 m μ (log ϵ 3.96) and 226 m μ (log ϵ 4.12). On the other hand, *trans*-1-methyl-2-phenylcyclopropanecarboxamide has its absorption maximum at 220 m μ (log ϵ 4.0), and the corresponding *trans*-2-phenyl-3,3-dimethyl compound has a maximum at 218 m μ (log ϵ 4.01). The bathochromic shifts relative to the *o*-tolyl compound were taken by Perold⁷ to correspond to the appearance of a complete chain of conjugation from the phenyl group through the cyclopropane ring to the amide. It seemed likely that it was the phenylcyclopropane chromophore that was being affected.⁸

The relative ease of shifting the position of the absorption maximum in Perold's amide series suggested that a possibility existed for semiquantitative measure-



(1) This material is taken from the Dissertation of Alan L. Goodman offered in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Stanford University. National Science Foundation Pre-doctoral Fellow, 1959–1960; Du Pont Fellow, 1961–1962.

(2) For leading references see: M. T. Rogers and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 843 (1946); R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955), and earlier papers; R. S. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957); G. W. Cannon, A. A. Santilli, and P. Shenian, *ibid.*, **81**, 1660 (1959); R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *J. Org. Chem.*, **27**, 733 (1962).

(3) (a) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); (b) J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5256 (1950).

(4) See N. H. Cromwell, F. H. Schumacher, and J. I. Adelfang, *ibid.*, **83**, 974 (1961), for a bibliography of the extensive work in this field.

(5) (a) R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963); (b) E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4081 (1958).

(6) (a) E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962); (b) G. Buchi and H. J. E. Loewenthal, *ibid.*, 280 (1962).

(7) G. W. Perold, *J. S. African Chem. Inst.*, **6**, 22 (1953); **8**, 1 (1955); **10**, 11 (1957); *Chem. Abstr.*, **48**, 4314c (1954); **50**, 6326d (1956); **52**, 1074i (1958).

(8) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947).