tremely low solubility no unambiguous spectrum for III was obtained.[10]

Finally, it should be mentioned that the observed facile conversion of the phlorin zinc complex (IV) to the chlorin V is the first of its kind and is in striking contrast to the failure of certain phlorin hydrochlorides to undergo this transformation.[11]

Acknowledgment.—We are indebted to Dr. Mendel Friedman for determining the polarographic half waves and for participating in some of the preliminary work that led to this study.

(10) The only signal recorded besides the solvent spectrum and its C-13 satellites was a sharp line at 1.95 p.p.m. at the high field side of internal benzene. The signal to noise ratio was so low that the phenyl protons would not have shown up if they exhibited the same type of splitting as they do in I. TPP-Mg dinegative ion showed the same resonance at 1.96 p.p.m. If these signals are indeed due to the identical 8 protons in III, their high shielding compared to the equivalent protons in I (−1.55 p.p.m. from benzene) must indicate a substantial loss of delocalization of the pi electrons in the dinegative ions.

(11) R. B. Woodward, *Angew. Chemie*, **72**, 651 (1960).

(12) A. P. Sloan Foundation Fellow.

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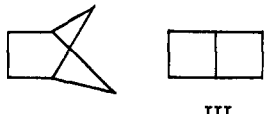
MERCURY PHOTOSENSITIZED ISOMERIZATION OF 1,5-CYCLOÖCTADIENE TO TRICYCLO[3.3.0.0^{2,6}]OCTANE

Sir:

The intramolecular addition of one olefinic group to another under the influence of light to yield an isomeric product which contains a cyclobutane ring is well known. In molecules in which the two olefinic groups have freedom to twist with respect to each other, the addition appears to be *trans* rather than *cis*. As examples, one may cite the photoisomerization of carvone to carvone camphor[1] and the mercury photosensitized isomerization of 1,5-hexadiene (I) to bicyclo[2.1.1]-hexane (II).[2] The preferential formation of II from 1,5-hexadiene rather than bicyclo[2.2.0]hexane (III) which may also be formed by the addition of the double

$CH_2{=}CHCH_2CH_2CH{=}CH_2$

I



II III

bonds led to the present investigation of the mercury photosensitized isomerization of 1,5-cycloöctadiene.

Commercial 1,5-cycloöctadiene which is predominantly the *cis,cis* material[3] was irradiated with the mercury resonance line at 2537 Å. in the presence of mercury vapor. The apparatus has been described before.[4] From the volatile fraction of the photolyzate, a compound (b.p. 125°) which constituted about 30% of this fraction was isolated. Since its molecular formula was C_8H_{12} it was isomeric to the starting material. (*Anal.*[5] Calcd. for C_8H_{12}: C, 88.82; H, 11.19. Found: C, 88.46; H, 11.19; mol. wt. 108 (mass spectrum). It showed no unsaturation in either its infrared or ultraviolet spectrum, which indicated that it was tricyclic. Pyrolysis of the compound in the vapor phase in a static system at 360–390° gave 1,5-cyclooctadiene which in turn underwent further isomerization to give 4-vinyl cyclohexene. It was inferred that the photoproduct of 1,5-cycloöctadiene was a valence tautomer that was probably formed by the mutual

(1) G. Ciamician and P. Silber, *Ber.*, **41**, 1928 (1909); G. Buchi and I. M. Goldmann, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

(2) R. Srinivasan, *J. Phys. Chem.*, in press.

(3) L. E. Craig, *Chem. Rev.*, **49**, 103 (1951).

(4) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4823 (1961).

(5) Microanalysis by Microtech Laboratories, Skokie, Illinois.

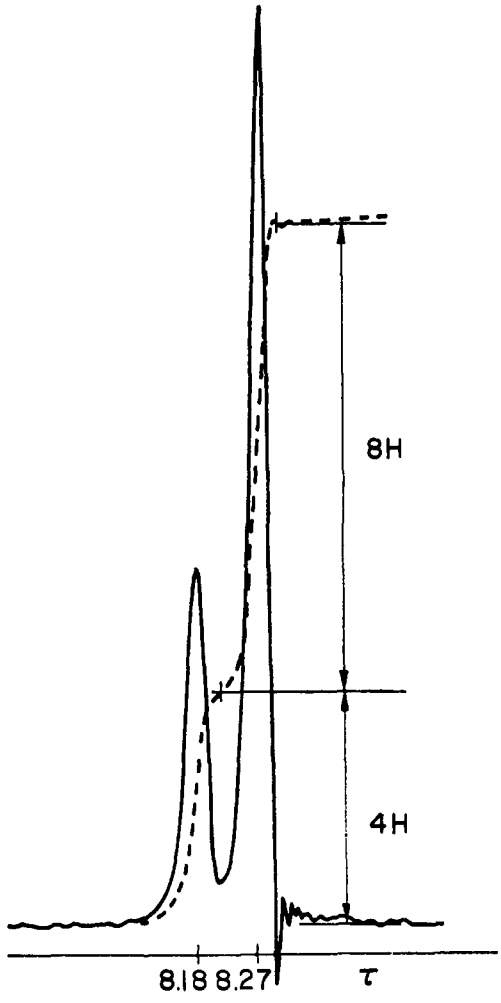


Fig. 1.—N.m.r. spectrum of tricyclo[3.3.0.0^{2,6}]octane; experimental conditions as described in text.

addition of the two double bonds in the molecule. Such an addition may give IV or V.

IV V

The n.m.r. spectrum of the product (carbon tetrachloride as solvent, concentration 15%; tetramethyl silane as internal standard)[6] confirmed the absence of unsaturation and consisted of two unsplit peaks located at 8.18 and 8.27 τ, respectively. The areas under these peaks were in the ratio 1:2. If the product had the structure IV, its protons may be expected to occur at less than 8 τ in common with protons on cyclobutane derivatives[7] and in bicyclo[2.2.0]hexane (III).[4,8] Further, the protons in IV, whether the molecule has a "chair" or "tub" conformation, are of three kinds of four each, which also conflicts with the observed distribution. Structure V would fit the observed spectrum well. In this structure, the molecule has only two kinds of protons which are in the ratio 4:8. The eight protons on the four methylene groups occur at nearly the same position as the methylene protons on the two carbon bridge in bicyclo[2.2.1]hexane.[4] The four tertiary protons can reasonably be expected to occur at lower τ values.

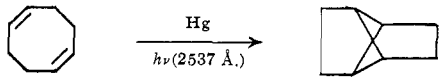
Apart from the intrinsic interest in the structure of the tricycloöctane (V), two aspects of its formation

(6) The author is deeply grateful to Drs. R. L. Hinman and E. B. Whipple of Union Carbide Research Institute, Tarrytown, N. Y., for their help in obtaining this spectrum.

(7) Catalog of NMR Spectra, Varian Associates, Palo Alto, Calif., 1962, pp. 128, 272.

(8) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, **21**, 24 (1960).

from 1,5-cycloöctadiene according to reaction 1 are worth commenting about.



(1)

One of these is the fact that although the starting material has the *cis,cis* conformation, the tricyclic product is derived from the *trans,trans* conformation. Since the over-all yield of tricycloöctane was less than 1% (the major product being a non-volatile oil) this may mean that either both the double bonds in 1,5-cyclooctadiene have to twist to a *trans* conformation in the excited state before the molecule can close to form the tricycloöctane, or only a small fraction of 1,5-cyclooctadiene molecules that may be in the *cis,trans* conformation may participate in reaction 1. A second interesting fact is that in the *cis,cis* conformation, the formation of IV could be expected to be favored. Failure to observe any IV among the products suggests that it may decompose before it can get rid of its excess energy through collisions. In contrast, pyrolysis studies suggest that V may be more stable thermally than even bicyclo[2.1.1]hexane.

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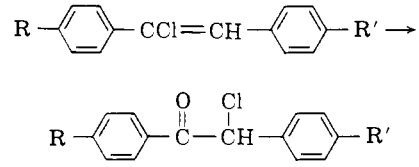
CHLORINE MIGRATION IN EPOXIDE—CARBONYL REARRANGEMENT

Sir:

Recent investigations in our laboratories into the synthesis[1,2] and chemistry[3] of α-haloepoxides have led to the observation of the novel and preferential chlorine migration in certain epoxide–carbonyl rearrangements.[4] We wish to report some of our results in this communication.

Treatment of *trans*-α-chlorostilbene[5] (Ia) with trifluoroperacetic acid in methylene chloride solution with sodium carbonate as the insoluble base[6] did not give the expected α-chloroepoxide; instead the only isolable organic product was desyl chloride (IIa, 63%). Treatment of Ia with peracetic acid also gave only IIa (67%), as did perbenzoic acid (74%).

Since the formation of IIa can be explained by either chlorine or hydrogen migration from the α-chloroepoxide (or its protonated form), several experiments were carried out to check this point. 4-Methyl-α-phenylacetophenone was prepared by the Friedel–Crafts reaction of phenylacetyl chloride with toluene (82%, m.p. 109–111°). Treatment of this ketone with phosphorus pentachloride and heating to complete dehydrochlorination afforded *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene[7] (Ib) (56%, m.p. 36–38°). When Ib was treated with trifluoroperacetic acid under the same conditions as mentioned above, a single product was isolated in 58% yield which was found to be p-methyl-α-chloro-α-phenylacetophenone (IIb, m.p. 73–74°), λ_{max} 258 mμ, ε 26,200. Also, when Ib was treated with either peracetic or perbenzoic acids, IIb was formed in 71% and 73% yields, respectively. IIb was synthesized independently in 83% yield by the treatment of *p*-methyl-α-phenylacetophenone with sulfuryl chloride.



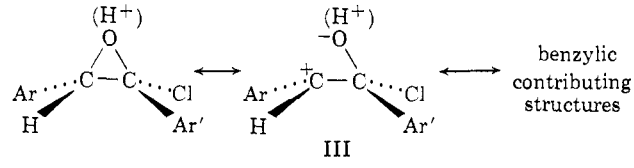
Ia, R = R′ = H
b, R = CH_3, R′ = H
c, R = H, R′ = CH_3

IIa, R = R′ = H
b, R = CH_3, R′ = H
c, R = H, R′ = CH_3

In order to complete the investigation, the other vinyl chloride, *trans*-1-chloro-1-phenyl-2-(*p*-tolyl)-ethylene (Ic), was prepared. The monobromide of *p*-xylene, from *p*-xylene and bromine under ultraviolet conditions (55%, b.p. 94–96° (12 mm.)) was treated with sodium cyanide to give the corresponding nitrile (82%, b.p. 94–96° (3 mm.), which was hydrolyzed to the corresponding acid (92%, m.p. 91–92°). Treatment with phosphorus trichloride gave *p*-tolylacetyl chloride which underwent Friedel–Crafts reaction readily with benzene to give α-(*p*-tolyl)-acetophenone (83%, m.p. 93–95°). Reaction of this ketone with phosphorus pentachloride and heating gave Ic (61%, m.p. 47–48°).

Treatment of Ic with trifluoroperacetic acid, as above, gave a product which proved to be α-chloro-α-(*p*-tolyl)-acetophenone (IIc, 53%, m.p. 73–74°[8]), $\lambda_{max.}$ 247 mμ, ε 24,500. Also, when Ic was treated with either peracetic or perbenzoic acid, IIc was isolated in 67 and 71% yields, respectively. IIc was also prepared independently by reaction of sulfuryl chloride with α-(*p*-tolyl)-acetophenone in 83% yield.

As evident from the above experiments, in every instance only that α-chloroketone was isolated which necessarily involves chlorine migration. Also, no acid chlorides or aldehydes were found which would be the result of aryl migration. There appear to be several reasonable mechanisms[9] for this rearrangement dependent upon whether the α-chloroepoxide or the intermediate protonated species is involved. The breaking of the particular C–O bond of either the epoxide or protonated epoxide leading to rearrangement is readily explained by the following contributing structures to the possible resonance hybrid of III.[10] Carbonium ion III would be of greater stability than the



III

someric one formed by breaking the other C–O bond. Such stabilization also explains why no α-chloroepoxide is isolated in our examples, whereas such is the case with 1-chlorocyclohexene.[2] In this latter example only inductive and hyperconjugative stabilization could be involved in the stabilization of intermediates.

Experiments designed to elucidate the mechanism and the steric requirements of the rearrangement are

(1) Chlorination of epoxides has been reported by C. Walling and P. S. Fredericks, *J. Am. Chem. Soc.*, **84**, 3326 (1962), and H. Gross and A. Rieche, German Patent 1,084,707 (1960).

(2) M. Mousseron and R. Jaquier, *Bull. Soc. Chim. France*, 698 (1950), have converted 1-chlorocyclohexene to the corresponding epoxide with perbenzoic acid.

(3) A. A. Durgaryan, C. A. Testanyan and R. A. Kaeryan, *Akad. Nauk S.S.S.R., Izvest. Ser. Khim. Nauk*, **14**, 165 (1961).

(4) Previous research on the epoxide–carbonyl rearrangement has been reviewed by R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(5) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

(6) W. D. Emmons and A. S. Pageno, *J. Am. Chem. Soc.*, **77**, 89 (1955).

(7) All new compounds described have given satisfactory analyses. Melting points, mixture melting points and spectra have been used to conclude structural assignments. All are in agreement with the structures given.

(8) Although the melting points of IIb and IIc are the same, their infrared spectra are quite different and their mixture melting point is appreciably depressed to 35–45°.

(9) Some of these possibilities involve chloronium ions as intermediates or transition states: J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw-Hill, New York, N. Y., 1962, pp. 148–149, has reviewed the evidence for the intermediacy of halonium ions in organic reactions.

(10) Similar structures of a hybrid have been proposed to explain the nature of the epoxide ring system (see ref. 4, pp. 739–740). Such structures should be of greater importance in the protonated epoxide to enable distribution of the charge