

sent from the products of the photosensitized decomposition, although a single, sharp, unidentified peak at  $5.86 \mu$  was observed. Yields of 4-*t*-butylcyclohexyl chloride and  $C_2Cl_6$  were determined by g.l.c. vs. *o*-dichlorobenzene as standard. Calibration for the cyclohexyl chloride was made using authentic material pre-

pared from 4-*t*-butylcyclohexanol. *cis* and *trans* isomers appeared as separate peaks, area ratio 23:77. The thermal decomposition products showed the expected infrared absorption for the carbonate anhydride and a much lower yield of chlorides by g.l.c., although products were not determined quantitatively.

## The Photoisomerization of the 2,3-Dihydrooxepin Ring. Long-Range Coupling in Some 2-Oxabicyclo[3.2.0]hept-6-enes<sup>1</sup>

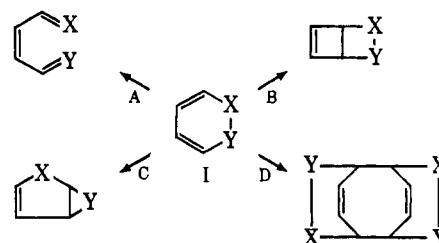
Leo A. Paquette,<sup>2a</sup> James H. Barrett,<sup>2b</sup> Robert P. Spitz,<sup>2c</sup> and Ross Pitcher

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio, and the Varian Associates Application Laboratory, Pittsburgh, Pennsylvania. Received April 23, 1965

2,3-Dihydrooxepins undergo light-induced valence tautomerism to 2-oxabicyclo[3.2.0]hept-6-enes, a previously unknown class of compounds. Chemical structure proof of the irradiation products was obtained by hydrogenolysis to 2-cyclobutylethanol, whose independent synthesis was also achieved. Double-resonance techniques have been applied to the n.m.r. spectra of the photoisomers; complete chemical shift and coupling constant assignments have been derived. The relatively large upfield shift of the vinyl proton of Va relative to Vb has been analyzed by means of a  $\cos^2$  dependence upon the neighbor-anisotropy effect of the carbon-chlorine bond.

The effect of ultraviolet irradiation on conjugated cyclic dienes has been found to vary with the particular system under study. Derivatives of 1,3-cyclohexadiene (I), for example, have been transformed into a vast array of photoproducts via ring-opening processes (A, most frequently observed),<sup>3</sup> valence-bond tautomerism reactions (B),<sup>4</sup> bond-switching mechanisms (C),<sup>5</sup> and dimerization pathways (D).<sup>6</sup> On the other hand, 1,3-cycloheptadienes have been shown<sup>7</sup> to be much more

consistent in their photochemical behavior. Valence-bond isomerization to bicyclo[3.2.0]heptenes has been observed in all instances with but one exception, namely,



the fragmentation of 3,5-cycloheptadienones to carbon monoxide and 1,3,5-hexatriene.<sup>8</sup> More recent studies with heterocyclic derivatives of this seven-membered ring system<sup>9</sup> did not give evidence of a reaction pathway other than the bridging reaction. With 1,3-cyclooctadiene, irradiation likewise effects valence isomerization to bicyclo[4.2.0]octene.<sup>10</sup> The uniform behavior in the medium-sized rings can be readily attributed to the fact that simple ring cleavage is impossible when the diene chromophore is joined at its extremities by more than two atoms.

With a desire to discover new photochemical reaction pathways of appropriate 1,3-cycloheptadienes, we have examined the irradiation of the 2,3-dihydrooxepin ring system (II). Our reasons for this choice were twofold, each based on recognition of the fact that II

(1) Part XVIII of the series on unsaturated heterocyclic systems. For part XVII, see L. A. Paquette, *J. Org. Chem.*, **30**, 2107 (1965).

(2) (a) Alfred P. Sloan Foundation Research Fellow; (b) National Science Foundation Summer Fellow, 1964; (c) undergraduate research participant, 1964.

(3) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959); D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, **1** (1960); P. de Mayo and S. T. Reid, *Quart. Rev. (London)*, **15**, 393 (1961), and additional pertinent references cited therein; E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961); E. Havinga, *Chimia (Aarau)*, **16**, 146 (1962).

(4) W. G. Dauben and R. M. Coates, *J. Am. Chem. Soc.*, **86**, 2490 (1964); H. Prinzbach and J. H. Hartenstein, *Angew. Chem.*, **74**, 651 (1962); **75**, 639 (1963); E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963).

(5) D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958); W. G. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, **81**, 4060 (1959); D. H. R. Barton, R. Bernasconi, and J. Klein, *J. Chem. Soc.*, 511 (1960); G. R. Evanega, W. Bergmann, and J. English, Jr., *J. Org. Chem.*, **27**, 13 (1962); H. Hart and A. J. Waring, *Tetrahedron Letters*, 325 (1965).

(6) L. A. Paquette and G. Slomp, *J. Am. Chem. Soc.*, **85**, 765 (1963); E. C. Taylor, R. O. Kan, and W. W. Paudler, *ibid.*, **85**, 776 (1963), and pertinent references cited in these papers.

(7) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955); O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **80**, 6685 (1958); **82**, 3642 (1960); G. Büchi and E. M. Burgess, *ibid.*, **82**, 4333 (1960); J. J. Hurst and G. W.

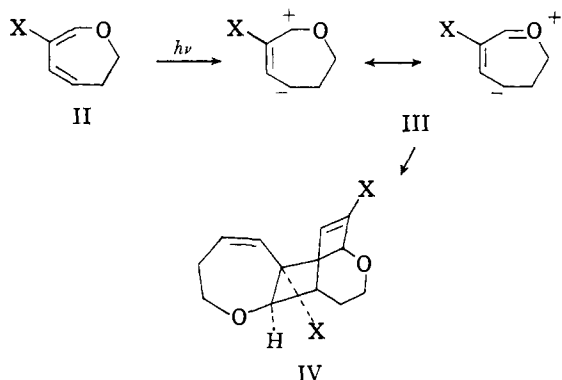
Whitham, *Proc. Chem. Soc.*, 116 (1961); *J. Chem. Soc.*, 710 (1963); W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); O. L. Chapman and D. J. Pasto, *Chem. Ind. (London)*, 53 (1961); D. J. Pasto, *J. Org. Chem.*, **27**, 2786 (1962); O. L. Chapman, H. G. Smith, and R. W. King, *J. Am. Chem. Soc.*, **85**, 803, 806 (1963); J. Rigaudy and P. Courtot, *Tetrahedron Letters*, 95 (1961); P. Courtot, *Ann. chim. (Paris)*, **8**, 217 (1963); W. G. Dauben and D. A. Cox, *J. Am. Chem. Soc.*, **85**, 2130 (1963); O. L. Chapman, H. G. Smith, and P. A. Barks, *ibid.*, **85**, 3171 (1963).

(8) (a) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *ibid.*, **84**, 1220 (1962); (b) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961).

(9) L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4092 (1964); O. L. Chapman and E. D. Hoganson, *ibid.*, **86**, 498 (1964); L. A. Paquette, *ibid.*, **86**, 500 (1964); L. A. Paquette, *Tetrahedron Letters*, 2027 (1963); G. J. Fonken, *Chem. Ind. (London)*, 1575 (1961).

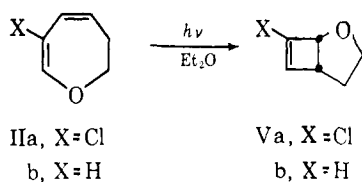
(10) S. F. Chappell, III, and R. F. Clark, *Chem. Ind. (London)*, 1198 (1962).

is a cyclic vinyl ether. First, alkyl vinyl ethers are known to react readily as dienophiles in Diels–Alder reactions<sup>11</sup>; second, this class of compounds is known to add in a facile manner to photochemically activated substrates.<sup>12</sup> It seemed plausible that a system such as II upon irradiation could give rise to the delocalized dipolar species III. Should this photoexcited state resemble the transition state characteristics of a diene moiety in a Diels–Alder reaction, then conceivably a second (unexcited) molecule of II (now acting as the dienophile) could react with III in a purely thermal process to give the unusual self-condensation



product IV (or the reverse isomer). This over-all process would *a priori* appear to be thermodynamically more favorable than the known photochemical additions of ethyl vinyl ether to 2-cyclohexenone<sup>12a</sup> and to dimethyl maleic anhydride<sup>12b</sup> which afford cyclobutane derivatives. The present paper describes the outcome of these studies.

**Chemistry.** Irradiation of 2,3-dihydro-6-chlorooxepin (IIa) in ether solution under a nitrogen atmosphere with an unfiltered 200-w. mercury arc for 4 hr. caused the total disappearance of starting material and the concomitant formation of a single photoproduct as determined by vapor phase chromatography (v.p.c.). The photoisomer, which was isolated in 81% yield, showed no ultraviolet absorption maxima above 210 m $\mu$  and possessed bands in the infrared at 3030 and 1580 cm.<sup>-1</sup>, characteristic of a cyclobutene ring.<sup>13</sup> The nuclear magnetic resonance (n.m.r.) spectrum (for discussion, see below) also displayed features which were strongly indicative of the valence tautomeric structure Va. In an identical manner, irradiation of



IIb under similar conditions gave rise after approximately 4 hr. to the photoisomer Vb in 65% yield. As in the previous example, the bicyclic nature of this photoproduct could be strongly inferred from the

(11) Yu. I. Chumakov and V. P. Sherstyuk, *Tetrahedron Letters*, 129 (1965); J. E. Pike, M. A. Rebenstorf, G. Slomp, and F. A. MacKellar, *J. Org. Chem.*, **28**, 2499 (1963); S. Julia and H. Linares, *Compt. rend.*, **252**, 2560 (1961), and pertinent references cited in these papers.

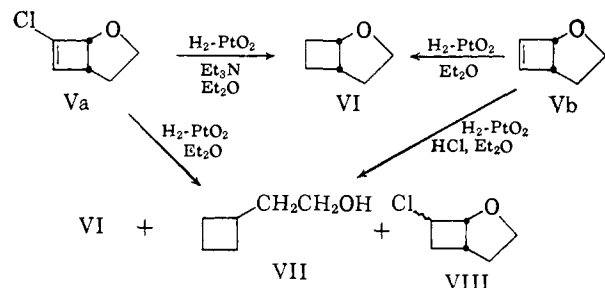
(12) (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964); (b) G. O. Schenk, W. Hartmann, S.-P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962).

(13) R. C. Lord and M. V. Evans, *J. Am. Chem. Soc.*, **79**, 2401 (1957).

available spectral data. Thus, the previously unknown 2-oxabicyclo[3.2.0]hept-6-ene system (V) can now be constructed with extreme ease.

Proof of the isomeric nature of such valence tautomers is generally achieved by pyrolysis of the cyclobutene derivative at an elevated temperature, a process which regenerates the starting diene.<sup>4,7,9</sup> The uniqueness of our heterocycle prompted the selection of another means of establishing by chemical methods the correct formulation of Va and Vb. More specifically, the structure proof is based upon the well-known ready hydrogenolysis of C–Cl bonds and of allyl ethers,<sup>14</sup> and upon the existing evidence<sup>15</sup> that acid accelerates the cleavage of such C–O bonds. Furthermore, the rigid geometry of the 2-oxabicyclo[3.2.0]hept-6-ene system is such that the hydrogenolysis may be expected to be facilitated because of the relative proximity of the sites to each other.<sup>16</sup>

Initially, the molecular frameworks of Va and Vb were shown to be similar. Hydrogenation of Va in ether solution containing 1 equiv. of triethylamine<sup>17</sup> over a platinum catalyst afforded 2-oxabicyclo[3.2.0]heptane (VI) with the consumption of approximately 2 moles of hydrogen. Reduction of Vb under cus-



tomary conditions led to the absorption of 1 mole of hydrogen and gave rise to the same substance (VI), as determined by a comparison of infrared and n.m.r. spectra and retention times on v.p.c.

A repetition of the hydrogenation of Va, but in the absence of triethylamine, yielded three products which could be separated by preparative v.p.c. The most rapidly eluted substance was readily demonstrated to be VI by the usual criteria.

The second and major component (isolated yields averaged about 80%) was found to be an alcohol because of its intense infrared absorption at 3200 cm.<sup>-1</sup>. The n.m.r. spectrum of this substance was most revealing (see Experimental); from it, the specific structural assignment of 2-cyclobutylethanol (VII) could be derived, and this conclusion was confirmed by independent synthesis. Lithium aluminum hydride

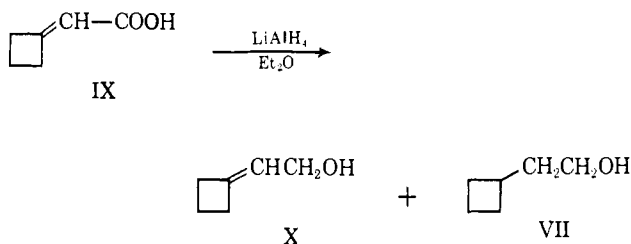
(14) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp. 12, 13.

(15) M. C. Dart and H. B. Henbest, *J. Chem. Soc.*, 3563 (1960); F. J. McQuillin and W. O. Ord, *ibid.*, 2902, 3169 (1959); W. Theilacker and H. G. Drössler, *Chem. Ber.*, **87**, 1676 (1954).

(16) Despite the evidence available which suggests that bent bicyclic molecules are hydrogenated generally from the convex face, it is evident in this case that complexing of the oxygen atom and the  $\pi$ -cloud of the double bond with the catalyst (see ref. 14, p. 19) could make approach from the concave surface quite likely. Unfortunately, these heterocycles possess no special structural features which would unequivocally permit the clarification of this point.

(17) The researchers of ref. 15 found that the presence of alkaline inorganic salts in the hydrogenation mixture greatly minimized the hydrogenolysis of hydroxyl functions. We have used triethylamine in this work as the acid scavenger with very satisfactory results.

reduction of cyclobutylideneacetic acid (IX)<sup>18</sup> gave a mixture of the unsaturated alcohol (X) and 2-cyclobutylethanol (VII) in the ratio of 4.45 to 1.0.<sup>19</sup> Catalytic hydrogenation of this mixture afforded only VII, which was identical in all respects with the previous sample. Furthermore, both liquids were independently converted to the same  $\alpha$ -naphthylurethan derivative. Thus, the presence of a cyclobutene ring in the photo-products is confirmed.



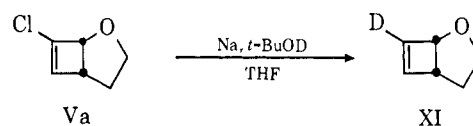
The third component of the hydrogenative process (VIII), which had the longest retention time, was formed in quite variable yield depending upon the duration of the hydrogenation experiment. That is, the longer the reaction was allowed to proceed, the smaller became the quantity of VIII. This substance has been identified as 2-oxa-7-chlorobicyclo[3.2.0]heptane (VIII) on the basis of its elemental analysis and infrared and n.m.r. spectra.

The genesis of VII from Va is very probably multicoursed. However, rupture of the heterocyclic ring can occur only while unsaturation is still present in the cyclobutane moiety; this cleavage is undoubtedly catalyzed by the hydrogen chloride liberated because of the hydrogenolysis of the C-Cl bond. Some degree of confirmation of this line of reasoning was obtained from the hydrogenation of Vb in the presence of ethereal hydrogen chloride as solvent. In a single experiment, VII and VI were obtained in a ratio of 8 to 5. The saturated 2-oxabicyclo[3.2.0]heptane (VI) did not react under similar conditions.

The irradiation of the 2,3-dihydrooxepin ring system thus leads exclusively to photoisomerization. This result suggests that the rate of intramolecular ring closure of the dipolar intermediate III (or a related species) is more rapid and thermodynamically more favorable than any possible intermolecular process.

As will become evident in the ensuing section, the specifically deuterated 2-oxabicyclo[3.2.0]hept-6-ene (XI) was required for our n.m.r. studies. Compound XI was prepared from Va<sup>20</sup> by the use of the Gassman modification<sup>21</sup> of the Winstein dechlorination procedure.<sup>22</sup> Reaction of Va with sodium metal and *t*-

butyl alcohol-*d* in refluxing tetrahydrofuran yielded 2-oxabicyclo[3.2.0]hept-6-ene which was 85% deuterated



at position 7.<sup>23</sup> This percentage of deuterium incorporation likewise observed by Gassman<sup>24</sup> deserves comment. Because the dechlorination reaction probably proceeds *via* the formation of an intermediate vinyl carbanion and because an excess of *t*-butyl alcohol-*d* is present, 100% deuterium incorporation may be anticipated. However, in the cases investigated the chlorine atom is exchanged, on the average, by approximately 85% deuterium and 15% hydrogen. This may be a further manifestation of the high reactivity of vinyl carbanions, especially in cyclobutenes, and may arise by rapid proton abstraction from the tetrahydrofuran solvent when an alcohol molecule is not immediately available to consume the carbanionic species. The possibility that the 15% nondeuterated material is produced by a radical process cannot, however, be dismissed. Material of this deuterium content was employed in the subsequent spectral study.

*Application of Double Resonance to the 2-Oxabicyclo[3.2.0]hept-6-enes.* Unusual interest has been attached to the n.m.r. spectra of bicyclo[3.2.0]hept-6-enes as a result of the myriad of spin-spin interactions possible in this class of compounds.<sup>7-9</sup> However, the majority of the investigators have deferred serious consideration of the spectral data because of the difficulty in resolving the small coupling constants involved. Chapman and co-workers<sup>8a</sup> did undertake the examination of the n.m.r. spectrum of the parent system under conditions of high resolution; their analysis was, however, founded on certain assumptions forced upon them by the fact that the molecule is symmetrical and that therefore the two vinyl and the two allylic protons have the same chemical shifts (different for each pair) which results in a so-called "deceptively simple" spectrum.<sup>25a</sup> Proper deuterium substitution would unquestionably furnish the appropriate answers, but this has until now not been achieved.<sup>25b</sup>

The n.m.r. spectrum of Vb (Figure 1) clearly demonstrates the existence of long-range coupling. The two cyclobutene protons appear as a triplet ( $\delta$  6.12,  $J$  = 2.8 c.p.s.) and a doublet of doublets ( $\delta$  5.84,  $J$  = 2.8, 1.5 c.p.s.); the bridgehead proton  $H_d$  is seen as a triplet ( $\delta$  4.8,  $J$  = 2.8 c.p.s.), while  $H_c$  is a broad multiplet centered at  $\delta$  3.28. The remaining groups of protons are seen as complex multiplets centered at *ca.*  $\delta$  3.84 ( $H_e$ ) and *ca.* 1.50 ( $H_f$ ). The illustrated decoupled spectra (Figure 1) dramatically establish the fact that  $H_c$  and  $H_d$  are coupled with the vinylic protons, but fail to *conclusively* demonstrate which olefinic proton is responsible for a specific resonance pattern.

(23) The extent of deuterium incorporation in XI was independently deduced from its n.m.r. spectrum and from combustion measurements.

(24) The authors wish to thank Professor P. G. Gassman for informing them of certain of his results prior to publication.

(25) (a) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963); R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961). (b) After completion of this work, S. Borčić and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1056 (1965), reported the complete analysis of the n.m.r. spectrum of cyclobutene. In this work deuterium substitution was also resorted to for the purpose of spectral simplification.

(18) It is a pleasure to thank Professor Pierre Maitte for making available to us a very generous sample of IX.

(19) The conditions of this reduction were such as to lead to some saturated alcohol; for a brief discussion of the lithium aluminum hydride reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds, see ref. 14, pp. 39, 40.

(20) Attempts to convert Va to its Grignard reagent (sublimed Mg and THF) for the purpose of preparing XI by hydrolysis in deuterium oxide was unsuccessful (Va was recovered). Similar exchange reactions (with ethyl magnesium bromide) involving vinylic bromine in certain cyclobutenes containing a vinylic hydrogen or a vinylic ethoxy group have recently been reported to give rise only to mixtures of high-boiling hydrocarbons: R. Sullivan, J. R. Lacher, and J. D. Park, *J. Org. Chem.*, **29**, 3664 (1964).

(21) P. G. Gassman and P. G. Pape, *ibid.*, **29**, 160 (1964).

(22) P. Carter, R. Howe, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 914 (1965); P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, **405**, 590 (1960).

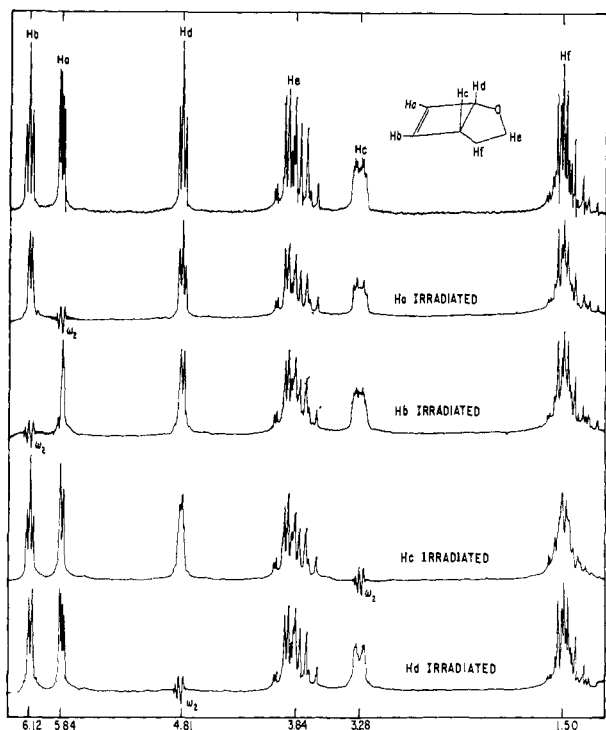


Figure 1. 100-Mc. n.m.r. spectra of Vb in carbon tetrachloride ( $\delta$ -units).

The n.m.r. spectrum of monodeuterated XI (Figure 2) resolved this dilemma. The replacement of  $H_a$  by deuterium (85% exchange) greatly diminished the absorption at  $\delta$  5.84; therefore  $H_b$  must resonate at the lower field position ( $\delta$  6.12). When  $H_d$  was saturated with an external field, the  $H_b$  doublet collapsed to a singlet (note that the small amount of residual  $H_a$  is unaffected). This result substantiates the fact that the allylic coupling  $J_{BD}$  in 2-oxabicyclo[3.2.0]hept-6-ene (Vb) corresponds to 2.8 c.p.s.; further examination of Figures 1–3 reveals that the other allylic coupling ( $J_{AC}$ ) is interestingly only 1.5 and that the vinylic coupling  $J_{AB}$  is 2.8 c.p.s. These data are in agreement with the well-established fact<sup>26</sup> that allylic protons oriented for efficient overlap with the  $\pi$ -orbitals of a double bond are ideally positioned to transmit spin information *via* the  $\pi$ -electron system to the vinyl substituent three carbons removed. There is little obvious coupling (*i.e.*, less than 0.5 c.p.s.) between  $H_a$ – $H_d$  and  $H_b$ – $H_c$ . A logical conclusion derivable from this information is that the dihedral angle between the planes defined by  $H_a$ – $C_7$ – $C_1$  and  $H_d$ – $C_1$ – $C_7$  approximates  $90^\circ$ .<sup>27</sup>

The decoupled spectra of Va (Figure 3) in general bear out the same conclusions as above. It should be noted that in these spectra slight inflections and broadening in both the doublet and triplet were observed indicating that there may be more small couplings present, on the order of less than 0.5 c.p.s.

Of particular interest in the above spectra is the observation that  $H_b$  in Va ( $\delta$  5.98) resonates at higher field than the same proton in Vb ( $\delta$  6.12). The causative factors for this phenomenon cannot lie predominantly in the inductive properties and electronegativity of the

(26) For leading references, see L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4096 (1964).

(27) F. A. L. Anet, *ibid.*, **84**, 671 (1962).

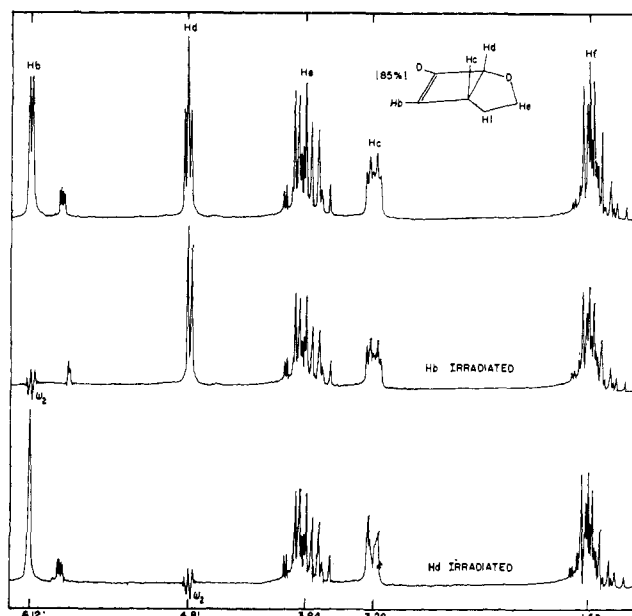
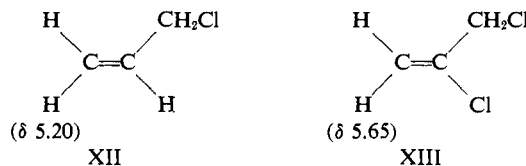


Figure 2. 100-Mc. n.m.r. spectra of XI in carbon tetrachloride ( $\delta$ -units).

chlorine atom which predict a significant downfield shift<sup>28</sup>; allyl chloride (XII) and 2,3-dichloro-1-propene (XIII), for example, illustrate the commonplace downfield shift of a vinyl proton observed upon the intro-



duction of neighboring vinyl chlorine atom. The effect must be the result of the carbon-halogen bond anisotropy. We have fitted our data to the equation

$$\Delta\sigma = \frac{\chi}{3R^3} (1 - 3 \cos^2 \gamma)$$

developed by Pople, Schneider, and Bernstein,<sup>29</sup> where  $\Delta\sigma$  is expressed in p.p.m. ( $\delta$ -units),  $\chi$  is the atomic susceptibility (of chlorine in this particular case),<sup>30</sup>  $R$  is the distance from the proton to the center of the carbon-halogen bond, and  $\gamma$  is the internal angle made by this line. Figure 4 illustrates the molecular diagrams of the vinyl regions of XIII and Va, respectively, as derived from Dreiding models. These line tracings indicate that  $\gamma_{\text{XIII}} = 64^\circ$  and  $\gamma_{\text{Va}} = 39.5^\circ$ , and therefore for XIII  $[1 - 3(\cos 64^\circ)^2] = +0.427$  and for Va  $[1 - 3(\cos 39.5^\circ)^2] = -0.245$ . A change in sign is obvious, and this phenomenon can be qualitatively correlated with the observed changes in the direction of the vinyl proton chemical shift. Quantitative substantiation of this  $\cos^2$  approximation can be obtained as follows.

(28) For a recent demonstration of this phenomenon in the adamantane system and pertinent references to the subject matter, see R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

(29) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 176–178.

(30) The assumption is made that the change in the magnetic susceptibility ( $\chi$ ) of the chlorine atom in the molecules discussed herein is negligible with respect to the change in magnitude of other values.

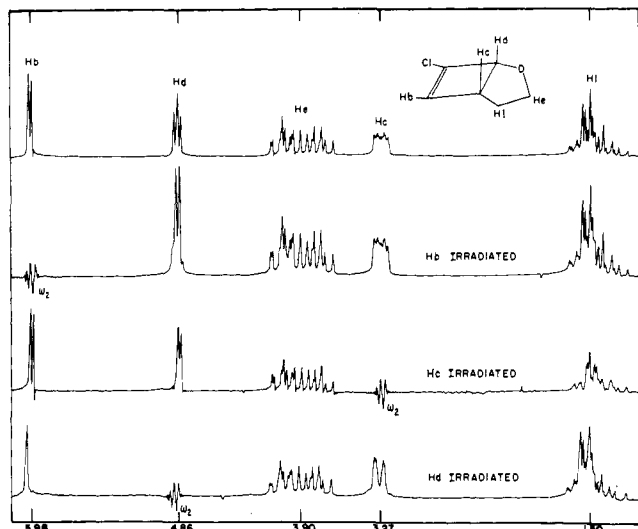


Figure 3. 100-Mc. n.m.r. spectra of Va in carbon tetrachloride ( $\delta$ -units).

$$\frac{\Delta\sigma_{\text{XIII}}}{\Delta\sigma_{\text{Va}}} = \frac{R_{\text{Va}}^3(1 - 3 \cos_{\text{XIII}}^2 \gamma)}{R_{\text{XIII}}^3(1 - 3 \cos_{\text{Va}}^2 \gamma)} = \frac{(2.92)^3(+0.427)}{(2.32)^3(-0.245)} = -3.51$$

Since  $\Delta\sigma_{\text{XIII}} = \delta 0.45$  (see above), then

$$\Delta\sigma_{\text{Va}} = -\frac{0.45}{3.51} = \delta -0.128 \text{ (calcd.)}$$

$$\Delta\sigma_{\text{Va}} \text{ (obsd.)} = \delta -0.14$$

The correspondence between the calculated and observed chemical shift differences is excellent. The present work appears to be the first application of the  $\cos^2$  dependence of the proton chemical shift to the neighbor-anisotropy effect of a C-X bond (X being chlorine in this case); if this result is of true significance, it indicates the validity of the approximation<sup>29</sup> and suggests many applications in the prediction of chemical shifts.

### Experimental<sup>31</sup>

**Photoisomerization of 2,3-Dihydro-6-chlorooxepin (IIa).** 2-Oxa-7-chlorobicyclo[3.2.0]hept-6-ene (Va). A solution<sup>32</sup> of 16.2 g. (0.124 mole) of 2,3-dihydro-6-chlorooxepin (IIa)<sup>33</sup> in 300 ml. of anhydrous ether was

(31) Melting points and boiling points are uncorrected. The infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer fitted with a sodium chloride prism. The microanalyses were determined by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The deuterium analysis (falling-drop method) was performed by J. Nemeth, Urbana, Ill. The v.p.c. analyses were obtained with an Aerograph A-90P gas chromatograph using one of the following columns: A, 10 ft.  $\times$  0.25 in. stainless steel packed with 20% Carbowax 20M on firebrick at 150°; B, 5 ft.  $\times$  0.25 in. stainless steel packed with 20% Silicone SF-96 on firebrick at 120°. Helium was used as the carrier gas and percentage compositions reported refer to the relative areas observed for the different components. N.m.r. spectra other than those illustrated in Figures 1-3 were recorded on a Varian A-60 spectrometer using dilute carbon tetrachloride solutions. The decoupled spectra were obtained on a Varian HA-100 spectrometer operating in the frequency-sweep mode; an audio frequency oscillator (HP 200 CD) was employed to supply the saturating field.

(32) Dissolution of IIa which had been kept at 0° for more than 48 hr. after redistillation often gave a cloudy ethereal solution. Because irradiation of this suspension proved very unsatisfactory, the impurities should be removed by suction filtration through a pad of magnesium sulfate prior to photolysis.

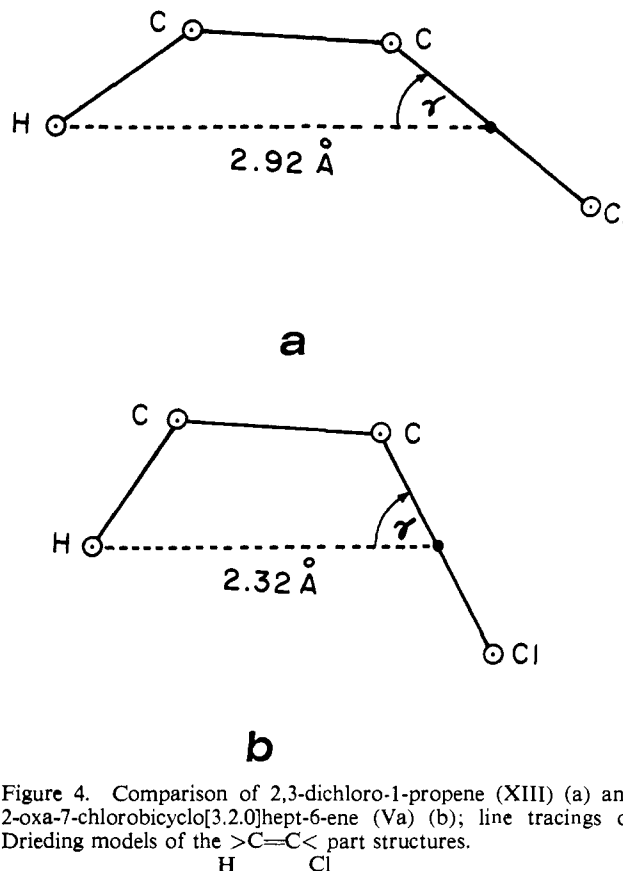


Figure 4. Comparison of 2,3-dichloro-1-propene (XIII) (a) and 2-oxa-7-chlorobicyclo[3.2.0]hept-6-ene (Va) (b); line tracings of Drieding models of the  $>\text{C}=\text{C}<$  part structures.

irradiated at room temperature in a nitrogen atmosphere with an immersion-type Hanovia unfiltered 200-w. lamp. The progress of the reaction was followed by vapor phase chromatography (column A)<sup>31</sup>; after 4 hr. the reaction was complete. The ether was carefully evaporated on a steam bath through a 2-ft. Vigreux column. The remaining liquid was distilled to give 13.1 g. (81.0%) of a colorless liquid, b.p. 49-50° (14 mm.),  $n_{\text{D}}^{26}$  1.4855.

A sample purified by preparative v.p.c. (column A) was subjected to analysis.

*Anal.* Calcd. for  $\text{C}_6\text{H}_7\text{ClO}$ : C, 55.19; H, 5.41; Cl, 27.16. Found: C, 55.11; H, 5.55; Cl, 26.75.

**Photoisomerization of 2,3-Dihydrooxepin (IIb).** 2-Oxabicyclo[3.2.0]hept-6-ene (Vb). A solution of 6.79 g. (0.07 mole) of 2,3-dihydrooxepin (IIb)<sup>33</sup> in 300 ml. of anhydrous ether was irradiated as above. Samples of the reaction mixture were subjected to v.p.c. (column A)<sup>31</sup> during the course of the reaction, and after 4 hr. and 20 min. no starting diene remained. The ether was carefully removed by distillation through a 2-ft. Vigreux column. The remaining liquid was rectified to give 4.42 g. (65.0%) of colorless Vb, b.p. 59-60° (130 mm.),  $n_{\text{D}}^{24}$  1.4451.

*Anal.* Calcd. for  $\text{C}_6\text{H}_8\text{O}$ : C, 74.97; H, 8.39. Found: C, 74.42; H, 8.30.

**Hydrogenation of 2-Oxa-7-chlorobicyclo[3.2.0]hept-6-ene (Va).** A. With Triethylamine. 2-Oxabicyclo[3.2.0]heptane (VI). A solution of 2.11 g. (16.2 mmoles) of Va and 1.64 g. (16.2 mmoles) of triethylamine in 15 ml. of anhydrous ether was hydrogenated over pre-

(33) E. Schweizer and W. E. Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960).

reduced platinum at atmospheric pressure. Two equivalents of hydrogen was absorbed. The triethylamine hydrochloride and catalyst were removed by filtration and the solution was distilled. There was obtained 0.96 g. (60.7%) of VI as a colorless liquid, b.p. 66–69° (126 mm.),  $n_{27}^{20}D$  1.4468.

*Anal.* Calcd. for  $C_6H_7O$ : C, 73.43; H, 10.27. Found: C, 73.37; H, 10.40.

*B. Without Triethylamine.* A solution of 1.36 g. (10.4 mmoles) of Va in 10 ml. of anhydrous ether was hydrogenated over prerduced platinum at atmospheric pressure. After 3 equiv. of hydrogen had been absorbed, the hydrogenation was stopped, the solution was filtered, and the ether was carefully removed. The remaining liquid was analyzed by v.p.c. (column A)<sup>31</sup> and was found to consist of three components in the ratio of 1:9:1 (actually varying ratios were obtained; see Discussion section). The three constituents were separated by preparative v.p.c. (column B).<sup>31</sup>

The most rapidly eluted material was found to possess the same retention time as 2-oxabicyclo[3.2.0]heptane (VI). In addition, its infrared and n.m.r. spectra were superimposable upon those of an independently synthesized sample.

The second component (0.81 g., 79.5%) was found to be an alcohol,  $n_{25}^{20}D$  1.446, identical in all respects with an authentic sample of 2-cyclobutylethanol (VII) (see below).

The sample had broad n.m.r. absorption at *ca.*  $\delta$  1.70 (9 H, cyclobutyl-CH<sub>2</sub>-), a triplet ( $J = 6.4$  c.p.s.) at 3.43 (-CH<sub>2</sub>-O-), and a broad singlet at 4.37 (-OH). The latter peak was greatly diminished in magnitude when D<sub>2</sub>O was introduced into the n.m.r. tube.

*Anal.* Calcd. for  $C_6H_{12}O$ : C, 71.95; H, 12.08. Found: C, 71.44; H, 12.10.

This alcohol was readily converted to an  $\alpha$ -naphthylurethan, m.p. 80.5–81°.

*Anal.* Calcd. for  $C_{17}H_{19}NO_2$ : C, 75.81; H, 7.11; N, 5.20. Found: C, 75.81; H, 7.35; N, 4.88.

The least rapidly eluted substance was characterized as 2-oxa-7-chlorobicyclo[3.2.0]heptane (VIII) by virtue of its elemental analysis and infrared and n.m.r. spectra.

*Anal.* Calcd. for  $C_6H_9ClO$ : C, 54.35; H, 6.84. Found: C, 54.29; H, 6.89.

#### *Hydrogenation of 2-Oxabicyclo[3.2.0]hept-6-ene (Vb).*

*A. In Neutral Medium.* A solution of 1.44 g. (0.015 mole) of Vb in 15 ml. of anhydrous ether was hydrogenated over prerduced platinum catalyst. When 0.015 mole of hydrogen was absorbed, the catalyst was separated by filtration, the solvent was carefully evaporated, and the residue was distilled. There was isolated 1.28 g. (90.5%) of 2-oxabicyclo[3.2.0]heptane (VI) as a colorless liquid, b.p. 60–61° (100 mm.),  $n_{27}^{20}D$  1.4469. This material was identical by the usual criteria with the sample of VI prepared above.

*B. In Acidic Solution.* To 10 ml. of ethereal hydrogen chloride containing about 200 mg. of prerduced platinum catalyst was added 1.00 g. (0.01 mole) of Vb. The mixture was hydrogenated at room temperature and atmospheric pressure until the uptake of hydrogen ceased. The catalyst was separated by filtration and the solvent was evaporated.

The residue was submitted to v.p.c. (column A)<sup>31</sup> and showed the disappearance of the starting material and the appearance of two new peaks. These peaks corresponded in retention times with those of VII and VI, respectively, in the ratio 8:5.

#### *Synthesis of Authentic 2-Cyclobutylethanol.*

*A.* To a stirred slurry of 0.67 g. (17.8 mmoles) of lithium aluminum hydride in 30 ml. of anhydrous ether was added in small portions 2.0 g. (17.8 mmoles) of cyclobutylideneacetic acid (IX).<sup>34</sup> The mixture was refluxed for 3 hr., cooled, and treated dropwise with 0.67 ml. of water, 0.67 ml. of 30% sodium hydroxide, and 2.0 ml. of water, in that order. The resulting solid was filtered and washed thoroughly with ether. The ether was removed and the residue was distilled to give 1.0 g. (55%) of a colorless liquid, b.p. 72–81° (15 mm.). V.p.c. (column A)<sup>31</sup> of the product indicated a two-component system in the ratio of 4.45:1.0 which is derived from the presence of X and VII, respectively (see below).

*B.* The above mixture (1.0 g., 0.01 mole) was dissolved in 10 ml. of ether and was hydrogenated over a prerduced platinum catalyst at room temperature and atmospheric pressure. The usual work-up gave a colorless oil, a small sample of which was submitted to v.p.c. The major peak observed in part A above had disappeared and only one peak corresponding to the minor peak above was observed. The entire sample was purified by preparative v.p.c. (column A)<sup>31</sup>; the 2-cyclobutylethanol afforded infrared and n.m.r. spectra identical with those of the material isolated above. The  $\alpha$ -naphthylurethan derivative melted at 81.0–81.2°.

*2-Oxabicyclo[3.2.0]hept-6-ene-7d (XI).* To a refluxing solution of 75 ml. of tetrahydrofuran and 13 ml. of *t*-butyl alcohol-*d* containing 6.4 g. (0.278 g.-atom) of sodium metal cut into small pieces was added a solution of 5.0 g. (0.038 mole) of Va in 20 ml. of tetrahydrofuran over a 30-min. period. The solution was refluxed for 4 hr. and allowed to cool to room temperature. The liquid was decanted from the solids which were washed with petroleum ether (b.p. 60–80°). Water (200 ml.) was added slowly to the combined liquid and washings and the resulting solution was extracted with three 50-ml. portions of petroleum ether. The combined extracts were washed with two 50-ml. portions of water and one 250-ml. portion of saturated sodium chloride solution; this organic solution was then dried, filtered, and concentrated to approximately 10 ml. The concentrated residue was submitted to preparative v.p.c. (column A)<sup>31</sup> and there resulted a colorless oil, shown to be XI.

*Anal.* Calcd. for  $C_6H_7DO$ : 12.5 atom % excess D. Found: 10.60 atom % excess D, *i.e.*, 84.8% deuterated.

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(34) H. Normant and P. Maitte, *Bull. soc. chim. France*, 1424 (1960).