Tetrahedron Letters No.7, pp. 603-607, 1967. Pergamon Press Ltd. Printed in Great Britain.

PHOTOCHLORINATION OF BICYCLO[2.2.0]HEXANE

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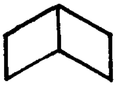
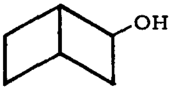
(Received 14 November 1966)

The reactions of chlorine with bicyclo[2.2.1]heptane[1] and bicyclo[2.1.1]hexane[2] have been reported to give products in which the parent ring systems are retained whereas with bicyclo[2.1.0]pentane[3] and bicyclo[1.1.0]butane[4] products derived from the parent hydrocarbons were not isolated. We wish to report here some results on the photochlorination of bicyclo[2.2.0]hexane (I) which offer (i) a clue to the role of ring strain in determining the nature of the reaction in these systems, and (ii) a practical route to the synthesis of bicyclohexyl[5] chlorides.


I



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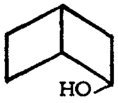

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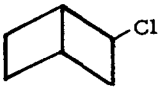
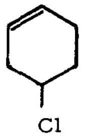


IV

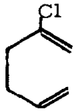
A mixture of bicyclohexane (72.6 mm) vapor and chlorine gas (15.4 mm) did not undergo any change in pressure in the dark over a 15 minute period. On exposure to ultraviolet light (> 3000 Å), a rapid reaction was observed which caused a decrease in the pressure in the system. An oily liquid condensed on the walls of the bulb. Subsequent analysis showed that the yield of hydrogen chloride, which is indicative of the extent of substitution, was 62%. The condensible materials included unreacted bicyclohexane, about 5% of 1,5-hexadiene, four monochlorides, and six higher boiling compounds which were found to be adducts of the formula $C_6H_xCl_2$.

The four monochlorides which were distributed in the ratio 2:1:1:0.2 together equaled the yield of the hydrogen chloride that was observed to be formed. Of these, the major product had the formula C_6H_9Cl (mol. weight by mass spectrometry 116, 118. Anal. Found: C, 62.04; H, 7.98; Cl, 30.54. C_6H_9Cl requires C, 61.79; H, 7.78; Cl, 30.40) and showed no unsaturation in its infrared or nmr spectra. On reduction with sodium and n-butanol it gave bicyclohexane which indicated that the ring system of the parent hydrocarbon was intact. The nmr spectrum consisted of a triplet at 5.60 τ (1H) and a complex absorption from 6.75 to 8.25 τ. The former absorption can be assigned to a proton attached to a carbon with a chlorine atom. The compound must, therefore, be 2-chlorobicyclohexane. The only monofunctional derivative of bicyclohexane that is known has been reported by McDonald and Reineke.[6] They found that in exo bicyclohexane-2-ol (II) the proton on the carbon with the substituent appeared as a triplet, while in endo bicyclohexane-2-ol (III) the same proton appeared as a multiplet. This would indicate that the major monochloride in the present instance was exo-2-chlorobicyclohexane (IV).

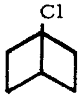
The second monochloride also had the formula C_6H_9Cl. Its nmr spectrum showed absorptions at 4.4 τ (2 protons), 5.9 τ (1 proton), and the remaining protons in a complex absorption from 7.3 to 8.2 τ. The compound obviously had olefinic protons as well as a H-C-Cl group. It was identified as 4-chlorocyclohexene (V) by comparison of its infrared spectrum with that of an authentic sample.[7]



V



VI

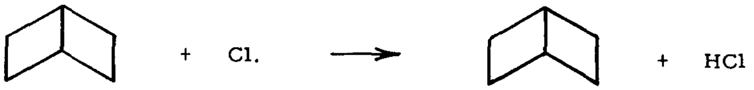


VII

The third monochloride which also had the formula C_6H_9Cl (mol. weight by mass spectrometry 116, 118. Anal. Found: C, 61.87; H, 7.83; Cl, 30.72. C_6H_9Cl requires C, 61.79; H, 7.78; Cl, 30.40) did not show any unsaturation in its infrared or nmr spectra. The latter consisted of only a complex absorption from 6.75 to 8.20 τ, which qualitatively resembled the spectrum of bicyclohexane itself.[8] The absence of a proton located in a H-C-Cl group is noteworthy. The compound decomposed readily in the vapor phase at 225° to give 93% of a product which was identified as 2-chloro-1,5-hexadiene (VI). This indicated that this monochloride was 1-chlorobicyclohexane (VII), as the formation of (VI) from (VII) would be analogous to the formation of 1,5-hexadiene during the pyrolysis of bicyclohexane (I).

The last monochloride was not identified as it was both a minor product and difficult to separate from (V). The same mixture of monochlorides was observed to be formed when photochlorination was carried out in carbon tetrachloride solution.

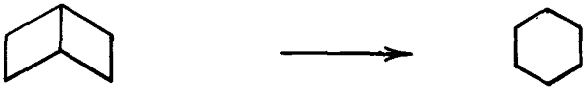
These results leave no doubt that bicyclohexane can undergo substitution by chlorine. The formation of 2-*exo*-chlorobicyclohexane is predictable on the basis of a simple free-radical scheme such as:



(1)

(2)

The substitution is on the less hindered side of the molecule which would be consistent with the pattern seen in bicyclo[2.2.1]heptane.[1] The formation of 4-chlorocyclohexene can be explained if the radical that is formed in (1) is postulated to rearrange:



(3)

Such a rearrangement is entirely analogous to the formation of the norbornenyl radicals from the nortricyclyl radical in the photochlorination of nortricyclene.[9]

The formation of 1-chlorobicyclohexane is remarkable, as substitution at the bridgehead has not been reported to occur to a significant extent in bicyclo[2.2.1]heptane or bicyclo-[2.1.1]hexane.[10] It is noteworthy that this compound appears to be the first example of a simple 1-substituted bicyclohexane.

The strain energy in bicyclo[2.1.0]pentane is known to be approximately the sum of its two component small rings. It is a reasonable guess that the strain energy in bicyclohexane is also equal to the sum of the strain energies in two cyclobutane rings and hence nearly equal to that of bicyclo[2.1.0]pentane. The formation of 1- and 2-chlorobicyclohexanes in the present study would indicate that the bicyclohexyl radical shows an appreciable life (*ca.*, 10^{-9} sec) that allows it to undergo bimolecular collisions even at 90 mm pressure. The failure of bicyclo[2.1.0]pentane to undergo a similar free-radical substitution may be due to its greater reactivity towards addition which, in turn, may be due to the presence of a cyclopropane ring.

ACKNOWLEDGMENT

The authors wish to thank Drs. N. Poutsma and E. B. Whipple of the Union Carbide Research Institute, Tarrytown, New York, for valuable advice and criticism.

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2. R. Srinivasan and F. I. Sonntag, J. Am. Chem. Soc., submitted for publication.
3. R. T. La Londe, *ibid*, 87, 4217 (1965).
4. K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, Tetrahedron 21, 2749 (1965).
5. The term bicyclohexane without any numbering will hereafter refer to bicyclo[2.2.0]-hexane.
6. R. N. McDonald and C. E. Reineke, J. Am. Chem. Soc. 87, 3020 (1965); Tetrahedron Letters, 2739 (1966).
7. This material has been prepared by Dr. M. Poutsma according to the procedure of F. S. Birch, R. A. Dean, and H. J. Hunter, J. Org. Chem. 23, 1026 (1958).
8. R. Srinivasan, J. Am. Chem. Soc. 83, 4923 (1961).
9. M. Poutsma, *ibid*, 87, 4293 (1965).
10. It has been observed that the dimer of acenaphthene is chlorinated preferentially at the bridgehead position.[11] This system is also made up of a cyclobutane ring rigidly fused to two cyclopentane rings. More recently (J. Am. Chem. Soc. 88, 4437 (1966)), Wiberg

and Connor have reported that bicyclo[1.1.1]pentane undergoes preferential chlorination at the 1-position. A referee has suggested that both the CH and CH_2 positions may be deactivated by bond angle deformation and that the normal tendency for tertiary to be more reactive than secondary may be reappearing.

11. H. Shechter, private communication.