

18.5 mm. Practically pure *trans*-1-bromo-3-chlorocyclopentane, n_D^{20} 1.5147, and 91.7% *cis*-1-bromo-3-chlorocyclopentane contaminated by 1.9% *trans*-1-bromo-3-chlorocyclopentane and 6.4% of *cis*-1-bromo-2-chlorocyclopentane and an unknown compound were obtained. The n.m.r. spectra of the above fractions support the assignment of structure.

4-Chlorocyclopentene.—3-Cyclopenten-1-ol²³ (29.4 g.) in 85 ml. of petroleum ether was added dropwise to a mixture of phosphorus pentachloride (39 g.) and 85 ml. of petroleum ether. The temperature was maintained at -10° during the addition

(23) E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).

and allowed to slowly reach room temperature during an additional 10 hr. of stirring. The mixture was treated with ice, the organic layer washed with 10% sodium carbonate, and fractionated with a Vigreux column under reduced pressure. Pure 4-chlorocyclopentene, 2.6 g., b.p. 39° at 60 mm., was obtained. The n.m.r. spectrum was consistent with this structure. Reaction of 3-cyclopenten-1-ol with concentrated hydrochloric acid under reflux or with thionyl chloride and pyridine at 40 – 50° failed to produce 4-chlorocyclopentene.

Acknowledgment.—The n.m.r. spectra were recorded by Dr. R. King. His assistance and helpful discussions with him are gratefully acknowledged.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Photochlorination of Chlorocyclohexane and Bromocyclohexane¹

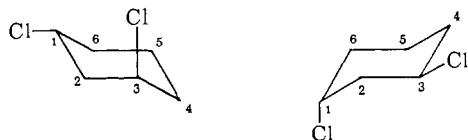
BY GLEN A. RUSSELL,² AKIHIKO ITO, AND R. KONAKA

RECEIVED JUNE 6, 1963

Bromo- and chlorocyclohexane have been chlorinated at 40 and -30° using molecular chlorine in carbon tetrachloride or carbon disulfide solution as well as *t*-butyl hypochlorite as the chlorinating agent. The seven dihalocyclohexanes have been analyzed by gas-liquid chromatography with appropriate structure proof by n.m.r. spectroscopy. A deactivating polar effect by halogen substituent was observed which became more pronounced at the lower temperature. Reaction of the β -, γ -, or δ -halocyclohexyl radical with chlorine or *t*-butyl hypochlorite gave in all instances a preferential formation of the *trans*-dihalide.

In a continuation of a study of directive effects in the chlorination of the halocycloalkanes,³ the products of chlorination of chloro- and bromocyclohexane were determined. The photochlorination of chlorocyclohexane produced the 7 expected dichlorocyclohexanes which could be separated by gas-liquid chromatography (g.l.c.). Chlorination of bromocyclohexane produced 7 isomeric bromochlorocycloalkanes in addition to *trans*-1,2-dichlorocyclohexane. Of the dichlorides, 5 were obtainable by conventional methods. For the 1,3-dichlorocyclohexanes no stereoselective syntheses could be found. By elimination, two peaks in the g.l.c. curve of the chlorination products of chlorocyclohexane could be assigned to *cis*- and *trans*-1,3-dichlorocyclohexane. These same two dichlorides were the predominant products (46 and 32% of the total dichlorides) produced in the ferric chloride-catalyzed addition of hydrogen chloride to 3-chlorocyclohexene. The dichlorides were separated from this reaction product by g.l.c. and their structures established by n.m.r. The compound with the shortest retention time in g.l.c. was assigned the *trans* structure on the basis of the spectrum given in Fig. 1. The spectrum of the isomer, considered to be *cis*-1,3-dichlorocyclohexane, is given in Fig. 2.

For the *trans* compound two equivalent conformations exist and if the rate of interconversion is rapid, protons attached to carbon atom 2 (as well as carbon atom 5),



should be equivalent and the hydrogen atoms at carbon atom 4 (or 6) should be nearly equivalent. In the *cis* compound the two possible conformations may not be present at equal concentrations or the preferred conformation may be essentially frozen. In any event the protons of the methylene groups should not be magnetically equivalent in the *cis* compound and a complex

spectrum should be expected. In view of this analysis, Fig. 1 obviously represents the *trans* compound and Fig. 2, the *cis* isomer. In the *trans* compound the methylene protons at the 2-position and the methine protons at carbon atoms 1 and 3 form an A_2X_2 system giving rise to a triplet (methylene protons) at $\tau = 7.81$ with $J_{AX} = 5.4$ c.p.s., while the absorption due to the methine protons centered at $\tau = 5.68$ appears to be approximately a triplet of triplets with coupling constants in the range of 5 to 5.5 c.p.s.

For the *cis* isomer the methylene protons of carbon atom 2 are non-equivalent and are strongly coupled to give approximately an AB system. The doublet centered at $\tau = 7.3$ may well be due to half of an AB system with $J_{AB} = 12.5$ c.p.s. A similar situation can be found in the spectrum of β -D-xylopyranose tetraacetate^{4a} and 6-methyl-3-piperidinol.^{4b} The peak at $\tau = 6.30$ in the spectrum for *cis*-1,3-dichlorocyclohexane is due to the methine protons. Since it is at higher field than the methine protons of the *trans* compound, it appears that the preferred conformation of *cis*-1,3-dichlorocyclohexane is the diequatorial form.⁵

It is interesting to compare the n.m.r. spectra of the 1,4-dichlorocyclohexanes with those of the 1,3-isomers. As expected, the *cis* compound now having two equivalent conformations gives the simpler spectrum. The methine peak of the *trans* compound occurs at a slightly lower field ($\tau = 5.82$) than for the *cis* compound ($\tau = 5.94$), a fact which supports the reported predominance of the diaxial conformation for *trans*-1,4-dichlorocyclohexane in carbon tetrachloride solution.⁶

The n.m.r. spectrum of all the isomeric dichlorocyclohexanes have been recorded.⁷

The bromochlorocyclohexanes formed upon chlorination of bromocyclohexane were assigned structures on the basis of retention times in g.l.c. The bromo-

(4) (a) R. V. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. Schneider, *ibid.*, **79**, 1005 (1957); (b) B. Belleau and Y.-K. Au-Young, *ibid.*, **85**, 64 (1963).

(5) Since axial protons are more shielded than equatorial protons a difference in τ -values of 0.4 is expected (L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 117. See also E. L. Eliel and M. N. Gianni, *Tetrahedron Letters*, 97 (1962)).

(6) The mole fraction of diaxial conformer is reported to be 0.75 (presumably at room temperature) on the basis of Raman spectroscopy (K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953)).

(7) A. Ito, Ph.D. Thesis, Iowa State University Library, 1963.

(1) (a) Directive Effects in Aliphatic Substitutions. XX11. (b) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) Alfred P. Sloan Foundation Fellow, 1959-1963.

(3) G. A. Russell and A. Ito, *J. Am. Chem. Soc.*, **85**, 2983 (1963).

TABLE I
PHOTOKLORINATION OF C₆H₁₁X IN CARBON TETRACHLORIDE SOLUTION

X	Temp., °C.	Dihalocyclohexanes, %								Relative reactivities, α:β:γ:δ ^a
		1,1-	<i>cis</i> -1,2-	<i>trans</i> -1,2- dichloro-	<i>trans</i> -1- bromo-2- chloro-	<i>cis</i> -1,3-	<i>trans</i> -1,3-	<i>cis</i> -1,4-	<i>trans</i> -1,4	
Cl	40	5.0	1.9	22.0	..	19.3	24.2	13.0	14.6	0.36:0.44:0.79:1.0
Cl	-30	3.7	0.4	18.4	..	23.6	24.0	14.3	15.8	.25:0.31:0.79:1.0
Br	40	5.9	^b	4.5	7.1	23.9	29.3	11.9	17.4	.40:0.20:0.91:1.0
Br	-30	3.1	^b	0.6	14.2	25.6	19.9	12.9	23.9	.17:0.20:0.62:1.0
Br ^c	-30	6.4	^b	2.6	14.0	20.6	21.1	16.7	18.6	.36:0.24:0.59:1.0
Br ^d	-30	15.6	^b	3.0	18.5	10.1	26.4	14.8	11.5	1:18:0.41:0.70:1.0

^a Per hydrogen atom. ^b Too small to measure. ^c In carbon disulfide solution. ^d *t*-Butyl hypochlorite used as chlorinating agent.

chlorides and dichlorides gave a nearly constant ratio of retention times as was observed for the bromo-chloro- and dichlorocyclopentanes.³

Results of chlorination of chloro- and bromocyclohexane are given in Table I.

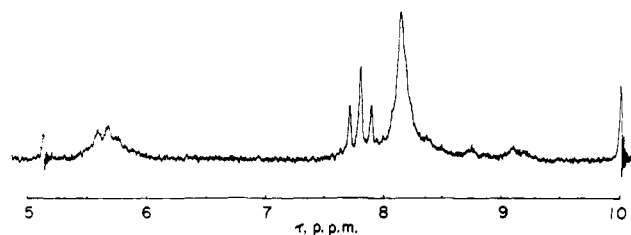


Fig. 1.—Proton magnetic resonance spectrum of *trans*-1,3-dichlorocyclohexane at 60 Mc./sec. in carbon tetrachloride. Integrated areas, $\tau = 5.4$ to 6.0, 2 units; $\tau = 7.5$ to 8.0, 2 units; $\tau = 8.0$ to 8.5, 6 units.

The chlorinations of chlorocyclohexane and bromocyclohexane show the same effects noted for the cyclopentanes³ except that there is no evidence that the bromine substituent in the cyclohexane ring has any activating influence upon β -hydrogen atoms, possibly because of geometrical considerations. Again there is a strong preference for the formation of *trans*-dihalides, a somewhat greater polar deactivation by bromine than by chlorine, and an increase in the reactivity of the 1-position when carbon disulfide is used as the solvent for photochlorination or *t*-butyl hypochlorite used as the chlorinating agent. The ratio of 2-, 3-, and 4-attack as well as the *cis-trans* ratios are essentially the same in carbon tetrachloride and carbon disulfide solution. The polar effect which deactivates the 1-, 2-, and 3-positions is more pronounced at -30° than at 40° . The ratio of *cis* and *trans* isomers resulting from 4-attack is insensitive to temperature, while the *cis*-1,3-dihalides are favored over the *trans* isomers by a decrease in temperature.

Discussion

The stereochemistry connected with the reactions of cyclohexane derivatives in free radical processes is complicated.⁸ In the present work there is first the question of axial or equatorial attack by the chlorine atom. Then there is the problem of the preferred stereochemistry of the reaction of the resulting chlorocycloalkyl radical with molecular chlorine. Intimately connected with these problems is the question of the preferred conformation of chlorocyclohexane, the intermediate chlorocyclohexyl radicals, and the resulting dichlorocyclohexanes.

In many ways the clean-cut stereospecific formation of *trans*-1,2-dichlorocyclohexane is the most difficult

(8) (a) H. L. Goering and L. L. Sims, *J. Am. Chem. Soc.*, **77**, 3465 (1955); H. L. Goering, P. I. Abell, and B. F. Aycock, *ibid.*, **74**, 3588 (1952); H. L. Goering and D. W. Larsen, *ibid.*, **81**, 5937 (1959). (b) D. G. Applequist and N. D. Werner, *J. Org. Chem.*, **28**, 48 (1963). (c) R. J. Gritter and R. J. Albert, *ibid.*, **27**, 4708 (1962). (d) F. D. Greene, C. C. Chu, and J. Wallia, *J. Am. Chem. Soc.*, **84**, 2463 (1962).

single result to explain in the photochlorination of chlorocyclohexane. The product is the more stable of the two isomers⁹ and exists in solution as a mixture of roughly equal parts of the 1(a),2(a) and 1(e),2(e) conformations.¹⁰ Attack of a chlorine atom on chloro-

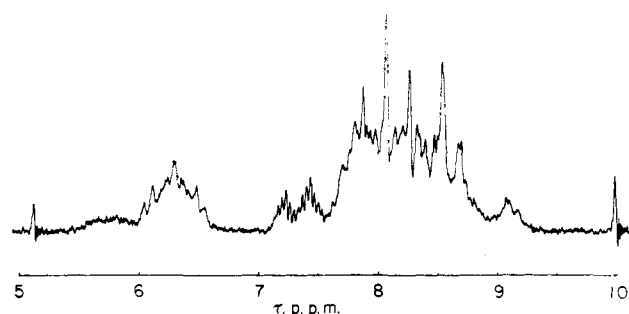


Fig. 2.—Proton magnetic resonance spectrum of *cis*-1,3-dichlorocyclohexane at 60 Mc./sec. in carbon tetrachloride. Impurity of *trans*-1,3-dichlorocyclopentane apparent at $\tau = 5.75$. Integrated areas, $\tau = 6$ to 6.6, 2 units; $\tau = 7$ to 7.6, 1 unit; $\tau = 7.6$ to 9.5, 7-8 units.

cyclohexane should produce two 2-chlorocyclohexyl radicals having conformations determined by the conformation of the chlorocyclohexane molecule attacked.¹¹



If we assume that the interconversion of the two conformations for 2-chlorocyclohexyl radical occurs no more readily than for chlorocyclohexane itself, we would have an energy barrier between conformations of about 10 kcal./mole.¹² This is certainly much greater than the free energy of activation of the reaction of an alkyl radical with molecular chlorine, a process which occurs at approximately a diffusion controlled rate. Thus, we might have expected molecular chlorine to convert each isomer into the dichloride before conformational interconversion had occurred. There appears to be a little problem in explaining only the formation of the *trans*-dichloride from the axial conformation of the radical. Attack from the "axial" side by molecular chlorine would be preferred since in the transition state for the reaction the chlorine substituent and molecular chlorine would be much farther apart than for

(9) See footnote 17, E. L. Eliel and R. V. Acharya, *J. Org. Chem.*, **24**, 151 (1959).

(10) (a) K. Kozima, K. Sakashita, and S. Maeda, *J. Am. Chem. Soc.*, **76**, 1965 (1954). (b) W. Kwestroo, F. A. Meijer, and E. Havinga, *Rec. trav. chim.*, **73**, 717 (1954).

(11) It will be assumed that carbon radicals have planar sp^2 configurations.¹⁰ Assuming rapidly interconverting sp^3 configurations would not affect the discussion materially.

(12) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 205.

attack by the chlorine atom from the "equatorial" side to yield the *cis*-dichloride. In the case of the equatorial conformation for the radical, "equatorial" attack gives the *trans* compound and "axial" attack the *cis* compound. Models indicate that equatorial attack allows the chlorine substituent and the incoming chlorine molecule to be further apart than for axial attack but the difference is not pronounced and inspection of models does not predict the complete absence of the *cis* compound, particularly when the reactivity of chlorine toward alkyl radicals is considered. It would seem most reasonable to explain the formation of *trans*-1,2-dichlorocyclohexane as being due to preferred "axial" attack on the axial conformation of the 2-chlorocyclohexyl radical. It would thus appear that: (a) the equatorial radical is not formed in the hydrogen abstraction reaction or (b) the equatorial conformer can readily interconvert to the axial conformer at a much higher rate than cyclohexane itself. Alternative (a) seems unlikely in view of the preferred equatorial conformation of the starting chlorocyclohexane and nearly identical reactivities of the hydrogen atoms toward chlorine atoms in the 2-position of chlorocyclohexane (0.44) and chlorocyclopentane (0.37) in carbon tetrachloride at 40°.

The idea that cyclohexyl radicals have but little conformational stability and that the "trans"-1(a),2(a) transition states are preferred is not in disagreement with the exclusive formation of *trans*-1,2-dibromide in the Hunsdiecker reaction of the silver salt of *trans*-1,2-cyclohexanedicarboxylate^{8b,9} or in the selective *trans* addition of hydrogen bromide to the 1-halocyclohexenes.^{8a} Bridged intermediates in the formation of 1,2-dihalocyclohexane would appear to be excluded by the observations that optically active 1-bromocyclohexyl radicals form optically active *trans*-1,2-dibromocyclohexane with little if any loss of optical activity.^{8b}

Attack of a chlorine atom at the 3-position of chlorocyclohexane produces the 1,3-dichlorides with a *cis* to *trans* ratio of 0.80, whereas in chlorocyclopentane the *cis,trans*-1,3-dichlorocyclopentanes are formed in a ratio of 0.67 in carbon tetrachloride at 40°.³ Models indicate that in the axial 3-chlorocyclohexyl radical that "axial" attack to give the *cis*-dihalide must be difficult because of the proximity of the chlorine substituent and the incoming chlorine molecule. All other transition states involving "equatorial" attack on the axial conformer and "axial" or "equatorial" attack on the equatorial conformer of the radical appear to be reasonable. Of the three reasonable transition states, two predict the *trans* product and one predicts the *cis* product. The predominance of the *trans* product is thus explained but it is not obvious why the *cis-trans* ratios are so nearly equivalent for the cyclopentyl and cyclohexyl systems.

trans-1,4-Dichlorocyclohexane is also preferred over the *cis* isomer. In fact the *cis-trans* ratio for products from 4-attack is not materially different from the *cis-trans* ratio for the products of 3-attack although in the hydrogen abstraction reaction by a chlorine atom there is a substantial polar effect in the 3-position but none in the 4-position. It may be that in the formation of 1,3-dichlorides polar considerations in the transition state for reaction with molecular chlorine lead to the less stable *trans* isomer whereas in the formation of 1,4-dichlorides all considerations lead to the most stable isomer, the *trans*-1,4-dichloride.

Experimental

Analytical Procedure.—The general details of the methods employed have already been described.³

Analyses of the chlorination products utilized a combination of 2.2-m. polyphenyl ether, 20% on Chromosorb W, column and

TABLE II
RELATIVE RETENTION TIMES OF DIHALOCYCLOHEXANES

Isomer	—Packed column, 135° ^a —		—Golay column, 100° ^b —	
	Dichloride	Bromo- chloride	Dichloride	Bromo- chloride
1,1-	1.0 ^c	2.22	1.0 ^c	1.35 ^d
<i>trans</i> -1,2-	1.75	2.92	1.32 ^d	1.85
<i>trans</i> -1,3-	1.98	3.44	1.45	2.16
<i>trans</i> -1,4-	2.13	3.78	1.49	2.26
<i>cis</i> -1,3-	2.25	3.96	1.54	2.36
<i>cis</i> -1,4-	2.61	4.60	1.77	2.78
<i>cis</i> -1,2-	2.76	..	1.79	..

^a 2.2-m. polyphenyl ether (20%) and 1.5-m. diisodecyl phthalate (10%) in series. ^b 300 ft. × 1/16 in. copper column treated with polypropylene glycol. ^c Actual retention times 8–9 min. ^d Not resolved.

a 1.5-m. diisodecyl phthalate, 10% on Chromosorb W, column at 135° as well as a 300 ft. × 1/16 in. copper Golay column treated with polypropylene glycol at 100°. The relative retention times of the isomeric dichloro- and bromochlorocyclohexanes are given in Table II.

Products of chlorination of chlorocyclohexane were analyzed using the packed column except for the 1,1-dichloride which appeared to undergo decomposition. The concentration of this isomer was obtained from the peak areas observed with the Golay column at 100° using *trans*-1,2-dichlorocyclohexane as the reference. Area ratios were equated with mole ratios. Products of the chlorination of bromocyclohexane were treated in a similar fashion except that the analysis for 1-bromo-1-chlorocyclohexane using the Golay column was complicated by the presence of *trans*-1,2-dichlorocyclohexane which could not be separated from 1-bromo-1-chlorocyclohexane. The concentration of *trans*-1,2-dichlorocyclohexane was measured with the packed column by use of an experimental calibration factor involving *trans*-1,2-bromochlorocyclohexane as the standard. By use of a separately determined calibration factor (again relative to *trans*-1,2-bromochlorocyclohexane) the peak area expected for *trans*-1,2-dichlorocyclohexane was estimated for the analysis using the Golay column and the concentration of 1-bromo-1-chlorocyclohexane obtained by difference from the analysis using the Golay column.

1,1-Dichlorocyclohexane.—Material prepared from the reaction of phosphorus pentachloride and cyclohexanone¹³ had a b.p. of 66.8–67.8° at 20 mm., *n*_D²⁰ 1.4812. It was found by g.l.c. to be 93.2% pure.

***trans*-1,2-Dichlorocyclohexane.**—Reaction of cyclohexene with chlorine¹⁴ gave a fraction, b.p. 80.0–80.1° at 20 mm., *n*_D²⁰ 1.4908, which was 97.1% pure by g.l.c.

***cis*-1,2-Dichlorocyclohexane.**—*trans*-2-Chlorocyclohexanol was prepared by the method of Newman and VanderWerf¹⁴; b.p. 80.0–86.5° at 15 mm., *n*_D²⁰ 1.4849. Reaction with hydrochloric acid gave *cis*-1,2-dichlorocyclohexane, b.p. 115–116.3° at 50 mm., *n*_D²⁰ 1.4951, that was found to be 87% pure by g.l.c.

***cis*- and *trans*-1,3-Dichlorocyclohexane.**—An attempt to prepare the corresponding dichlorides from a mixture of *cis*- and *trans*-1,3-cyclohexanediol (K and K Laboratories) by thionyl chloride and pyridine was unsuccessful while reaction with phosphorus pentachloride gave mainly *trans*-1,2-dichlorocyclohexane.

3-Chlorocyclohexene,¹⁵ b.p. 79–81° at 84 mm., *n*_D²⁰ 1.4882, was placed in a Carius tube and 3.4 g. of hydrogen chloride and 0.15 g. of anhydrous ferric chloride were added at liquid nitrogen temperature. After 10 days at –10° the reaction mixture was taken up in hexane, washed with water, and dried over calcium chloride. By g.l.c. the dichlorocyclohexanes formed were found to be 6% *trans*-1,2-, 32% *trans*-1,3-, 11% *trans*-1,4-, 46% *cis*-1,3-, and 5% *cis*-1,4-. A second experiment employing gallium(III) chloride gave essentially the same ratio of chlorides in low over-all yield. Distillation using a 30-cm. Dufton column gave the dichlorocyclohexanes, b.p. 95–105° at 37 mm., in 2% yield. Most of the *trans*-1,4-dichlorocyclohexane was removed by freezing the mixture at –80° followed by decantation of the liquid. The isomeric 1,3-dichlorocyclohexanes were isolated by preparative g.l.c. using a 1.5-m. diisodecyl phthalate column (10% on Chromosorb W) and 2-m. polyphenyl ether column (20% on Chromosorb W) in series.

***cis*- and *trans*-1,4-Dichlorocyclohexane.**—Twenty grams of a mixture of *cis*- and *trans*-1,4-cyclohexanediol (K and K Laboratories) and 86 ml. of concentrated hydrochloric acid were heated in a Carius tube at 100° for 7 hr.^{10b} An upper layer of oil gradually separated. The oil was taken up in ether, washed, and

(13) B. Carroll, D. G. Kubler, H. W. Davis, and A. M. Whaley, *J. Am. Chem. Soc.*, **73**, 5382 (1951).

(14) M. S. Newman and C. A. VanderWerf, *ibid.*, **67**, 233 (1945).

(15) C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

dried over anhydrous sodium sulfate. The ether was evaporated and the oil gradually cooled to -20° . Crystals grown during this period were separated by filtration. The crude *trans*-1,4-dichlorocyclohexane (3.0 g.) was recrystallized from ethanol to yield 1.3 g. of pure material, m.p. 102.0–102.8°. The filtrate was distilled using a Todd column packed with glass helices to give a fraction, b.p. 90.5–91.5° at 17 mm., n_D^{20} 1.4947, that was shown by g.l.c. to be 93% pure *cis*-1,4-dichlorocyclohexane.

***trans*-1-Bromo-2-chlorocyclohexane.**—The method of Goering and Sims was employed utilizing the reaction of hydrogen chloride

in chloroform solution with 24.6 g. of cyclohexene and 50 g. of *n*-bromosuccinimide.^{8a} Distillation gave 41 g. of material, b.p. 69–70° at 8 mm. Rectification in a Todd column packed with glass helices gave 93.3% *trans*-1-bromo-1-chlorocyclohexane (64.5%), b.p. 60° at 2.6 mm. No major impurities were revealed by g.l.c.

Acknowledgment.—The n.m.r. spectra were recorded by Dr. R. King. His assistance and helpful discussions with him are gratefully acknowledged.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

Carbonium Ions. XI. Nuclear Magnetic Resonance Spectra of the Aliphatic Alkenyl Cations¹

BY N. C. DENO, HERMAN G. RICHEY, JR., NORMAN FRIEDMAN, JAMES D. HODGE, JOHN J. HOUSER, AND CHARLES U. PITTMAN, JR.

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The nuclear magnetic resonance spectra of nine cyclopentenyl cations, six cyclohexenyl cations, and three linear alkenyl cations are presented. The areas of the bands correspond to values predicted from the structures of the ions. The positions of the bands (such as H or CH₃ on the central carbon of the allylic system or hydrogens on the carbon α to the allylic system) are invariant with structure and serve to identify these ions, either when present in complex mixtures or when produced from complex reactions. The kinetics of decomposition of carbonium ions is discussed with the view of directing attention to the critical choice of conditions necessary to achieve chemical stability.

Introduction

The discovery that the 1,3,5,5-tetramethylcyclohexenyl cation is stable in 96% H₂SO₄² opened the way to a direct study of the properties of a variety of aliphatic alkenyl (allylic) cations. Among the strictly hydrocarbon cations (excluding those with substituents such as hydroxy, chloro, etc.), chemical stability sufficient for n.m.r. studies has been achieved only with cations in which the terminal positions of the allylic system were completely alkylated. This paper presents the n.m.r. spectra of such ions. The papers immediately following will describe rearrangements, hydrogen–deuterium exchanges, ultraviolet spectra, and equilibrium studies.

Experimental

The n.m.r. spectra were recorded on a Varian A-60 instrument. The field was adjusted with an ethyl bromide sample until the resolution was between 0.005 and 0.02 parts per million (p.p.m.). The viscosity of 96% H₂SO₄ prevents the resolution obtainable in more mobile solvents. Nevertheless, the spectra were beautiful in their simplicity and examples are shown in Fig. 1–5.

The positions of the bands in the n.m.r. spectra in 96% H₂SO₄ were calibrated by reference to (CH₃)₄N⁺Cl[−] as an internal standard (suggested by Prof. P. S. Skell and Miss Josephine de Luis). These positions are presented in Table I and are expressed as the difference in p.p.m. relative to (CH₃)₄Si. Clearly, the actual numbers depend entirely on the value chosen for the difference between (CH₃)₄Si and (CH₃)₄N⁺. A value of 3.10 p.p.m. was used, the silane at higher field, and this is based on a measured difference of 3.10 p.p.m. between (CH₃)₄N⁺ and (CH₃)₃Si(CH₂)₂SO₃H in 96% H₂SO₄ coupled with an assumed difference of zero between (CH₃)₄Si and (CH₃)₃Si(CH₂)₂SO₃H.³

This choice is not free from objection. The difference between (CH₃)₄N⁺ and (CH₃)₃Si(CH₂)₂SO₃H was 3.19, 3.17, 3.12, and 3.10 in 0, 50, 83, and 96% H₂SO₄. The latter two values were independently confirmed by Miss de Luis. An indirect comparison between (CH₃)₄N⁺ and (CH₃)₄Si was accomplished using a precision coaxial n.m.r. tube. The (CH₃)₄N⁺ was in solution in 96% H₂SO₄ in the inner tube and a 1% solution of (CH₃)₄Si in CCl₄ was in the outer tube. Appropriate corrections were made for the magnetic susceptibilities of the solvents.⁴

This method gave a difference of 2.94 p.p.m. A direct comparison between (CH₃)₄N⁺Cl[−] and (CH₃)₄Si was accomplished in methanol and in trifluoroacetic acid giving the differences 3.28 and 3.29, respectively. Obviously, we are plagued with minor discrepancies and can only emphasize that a value of 3.10 p.p.m. was chosen for the difference between (CH₃)₄N⁺ and (CH₃)₄Si in 96% H₂SO₄.

Neither (CH₃)₄Si, (CH₃)₃Si(CH₂)SO₃H, nor (CH₃)₃SO₃H⁵ are suitable calibration standards in sulfuric acid. (CH₃)₄Si is both insoluble and unstable, (CH₃)₃Si(CH₂)SO₃H rapidly decomposes, and (CH₃)₃SO₃H exhibits variation in band position from 70 to 96% H₂SO₄.

The alkenyl cations were produced by adding the dienes to 96% H₂SO₄. Polymerization could be minimized by adding the diene through a capillary tube or as a fine film to the periphery of vigorously stirred H₂SO₄ at 0°. The syntheses of the dienes are described under the titles of the cations which they generated because in most cases the cations were better characterized than the dienes. We anticipate making a better characterization of these dienes at a later date and particularly to compare the composition of dienes when prepared by acid-catalyzed equilibration and by quenching of the cations in alkali. Most distillations were conducted using a Nestor–Faust spinning band column.

1-Alkyl-3-methylcyclopentenyl Cations.—2,5-Hexanedione was cyclized to 3-methyl-2-cyclopenten-1-one.⁶ The three dienes were made by treating this ketone with methyl, ethyl, and isopropyl Grignard reagents. The Grignard products were hydrolyzed with a small excess of hydrochloric acid. The dienes were isolated by distillation, and no attempts were made to separate the components of the diene mixtures. The three diene mixtures have been reported (methyl,⁷ ethyl,⁸ and isopropyl⁹), but in each case were prepared by other methods. The yields by the Grignard method were 44, 31, and 28%. No attempt was made to achieve optimum yields.

1-Alkyl (or Phenyl)-3,5,5-trimethylcyclohexenyl Cations.—The four dienes were prepared by addition of methyl, ethyl, isopropyl, and phenyl Grignard reagents to isophorone (3,5,5-trimethyl-2-cyclohexen-1-one). The Grignard products were hydrolyzed with saturated aqueous NH₄Cl. The dienes were isolated by distillation. The intermediate allylic alcohols can dehydrate in either of two directions to produce an endocyclic or a half exocyclic diene. The n.m.r. spectra of the methyl and ethyl derivatives showed that both dienes were present and in nearly equal amounts. This is particularly evident in the *gem*-dimethyl bands which were well resolved for the two dienes and had equal areas. The b.p. of each diene mixture agreed with reported values.¹⁰

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