[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Synthesis and Properties of Cyclobutenyl Cations

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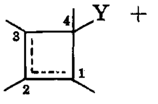
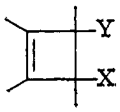
The synthesis of the pentamethyl- and the 1,2,3,4-tetramethylcyclobutenyl cations from the related halides and aluminum chloride in methylene chloride is described. The ultraviolet spectra of these cations show maxima between the absorption maxima of simple allylic and cyclopropenyl cations, demonstrating the importance of homoallylic resonance in the four-membered ring. The cross-ring resonance integral is evaluated as 0.33β. The 1,2,3,4-tetramethyl-4-chloro- and 4-bromocyclobutenyl cations have also been prepared. In contrast to benzenonium ions, none of the cyclobutenyl cations undergoes 1,2-rearrangement rapidly enough to be observed by n.m.r. spectroscopy. Whereas the cyclobutenyl halides form the cyclobutenyl cations when treated with aluminum chloride, in the presence of weaker Lewis acids they undergo rapid allylic rearrangement.

Introduction

The reaction in liquid sulfur dioxide of 1,2,3,4-tetramethyl-3,4,-dichlorocyclobutene with silver hexafluoroantimonate yields a solution of the 1,2,3,4-tetramethyl-4-chlorocyclobutenyl cation (Ia),[1,2] a stable carbonium ion. A different synthesis of this ion and the synthesis of the related pentamethylcyclobutenyl and 1,2,3,4-tetramethylcyclobutenyl cations are described below. These ions were prepared in order to determine to what extent the properties of cyclobutenyl (or homocyclopropenyl) cations, as compared with simpler allylic cations, are modified by the interaction of 2p atomic orbitals on carbon atoms 1 and 3 of the allylic system,[5] and to determine whether, as derivatives of the presumably unstable cyclobutadiene, their properties differ from those of the better known benzenonium ions.[6]



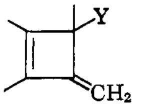


Ia, Y = Cl
b, Y = CH_3
c, Y = H
d, Y = Br

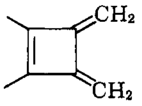
IIa, Y = CH_3, X = Cl;
b, Y = CH_3, X = Br;
c, Y = H, X = Cl;
d, Y = Cl, X = Cl
e, Y = H, X = H
f, Y = CH_3, X = CH_3
g, Y = Br, X = Br

Results

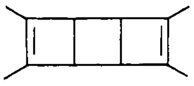
1,2,3,4,4-Pentamethyl-3-chloro(or bromo)cyclobutene (IIa or b) and 1,2,3,4-tetramethyl-3-chlorocyclobutene (IIc), required for the preparation of Ib and Ic, were synthesized as shown in Chart I. Dehydrohalogenation of 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene (IId)[7] by heating either alone or with quinoline is known[8a] to give 1,2,4-trimethyl-3-methylene-4-chlorocyclobutene (IIIa) contaminated with some of the starting material IId and the bis-dehydrohalogenated product IV.[8b] In our laboratory Id was dehydrohalogenated in dimethoxyethane (DME) with methyllithium in ether. A fraction of the product, isolated in 44% yield, consisted largely (*ca.* 85%) of IIIa contaminated by IId[9] and IV. (A forerun consisted mainly of IV and a small amount of IIIb.[11]) Reduction of IIIa with lithium aluminum hydride yields IIIc,[8a] and alkylation of IIIa with methylmagnesium iodide yields IIIb; IIIb and IIIc were easily purified by vapor phase chromatography, which separates the latter from *cis*- and *trans*-tetramethylcyclobutene (IIe) and the former from hexamethylcyclobutene (IIf) and IV. Compound IIIb was characterized by its ultraviolet maximum (ethanol) at 232 mμ (ε 14,500).[12]



IIIa, Y = Cl
b, Y = CH_3
c, Y = H



IV



V

Addition of hydrogen chloride to IIIb furnishes IIa, while IIIc yields IIc, a mixture of *cis* and *trans* isomers. Similarly, hydrogen bromide adds to IIIb to give IIb. The n.m.r. spectra of all these compounds, listed in Table I, are in accord with the structural assignments. For comparison, the n.m.r. spectrum of *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octadiene-3,7 (V)[13] is also included in

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[1] T. J. Katz, J. R. Hall, and W. C. Neikam, *J. Am. Chem. Soc.*, **84**, 3199 (1962).

[2] The preparation of stable solutions of other simple alkenyl[3] carbonium ions and unconjugated[4] carbonium ions has been described.

[3] (a) N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 1498 (1962); (b) N. C. Deno, *et al.*, *ibid.*, **85**, 2991, 2995, 2998 (1963).

[4] (a) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *ibid.*, **85**, 1328 (1963); (b) N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, **84**, 2017 (1962).

[5] (a) E. F. Kiefer and J. D. Roberts, *ibid.*, **84**, 784 (1962); *cf.* also footnote 9 in this reference; (b) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960); (c) F. F. Caserio, Jr., and J. D. Roberts, *ibid.*, **80**, 5837 (1958); (d) F. F. Caserio, Jr., S. H. Parker, R. Piccolini, and J. D. Roberts, *ibid.*, **80**, 5507 (1958); (e) E. F. Silversmith and J. D. Roberts, *ibid.*, **80**, 4083 (1958); (f) E. A. LaLancette and R. E. Benson, *ibid.*, **83**, 4867 (1961); (g) M. T. Jones, E. A. LaLancette, and R. E. Benson, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 8-13, 1963, p. 9T.

[6] (a) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6541 (1958), and earlier papers; (b) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, and W. R. Edwards, *Tetrahedron*, **4**, 178 (1958); (c) D. A. McCauley and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951); *Tetrahedron*, **5**, 186 (1959); (d) C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954); (e) G. Dallinga, E. L. Mackor, and A. A. Verijn Stuart, *Mol. Phys.*, **1**, 123 (1958); (f) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958); (g) H. C. Brown and H. W. Pearsall, *J. Am. Chem. Soc.*, **74**, 191 (1952); H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952); H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6268 (1953); (h) M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953); (i) reviewed by A. I. Shatenshtein, "Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds," Consultants Bureau, New York, N. Y., 1962, p. 130 ff.

[7] R. Criegee and A. Moschel, *Chem. Ber.*, **92**, 2181 (1959).

[8] (a) R. Criegee, *Angew. Chem. Intern. Ed. Engl.*, **1**, 519 (1962); J. Dekker, Dissertation, Köln, 1961; R. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, *Chem. Ber.*, **96**, 2362 (1963); (b) G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, **85**, 2268 (1963).

[9] The reaction mixture also contains IIg[10] formed from lithium bromide present in the methyllithium.

[10] (a) R. Criegee and K. Noll, *Ann. Chem.*, **627**, 1 (1959); (b) R. Riemschneider and D. Becker, *Monatsh. Chem.*, **90**, 524 (1959).

[11] In contrast to *n*-butyllithium, which is reported [W. Adam, *Tetrahedron Letters*, 1387 (1963)] to effect displacement of chloride, methyllithium yields little of the analogous product IIIb.

[12] Compound IIIc has its ultraviolet maximum (ethanol) at 230 mμ (ε 14,400); *cf.* ref. 8a where it is reported that $\lambda_{max}^{cyclohexane}$ 231 mμ (ε 12,500).

[13] (a) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957); (b) the compound was prepared by zinc dehalogenation of IId.

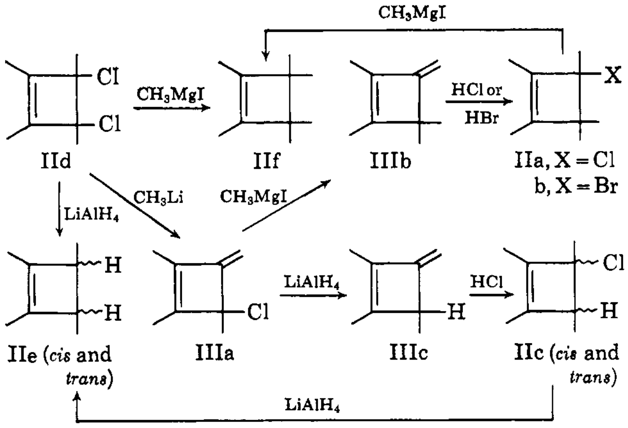
TABLE I

Compound	N.m.r. spectrum[a] Terminal methylene	Tertiary H	$CH_3-\overset{|}{\underset{|}{C}}-X$	Vinylic methyl	Saturated C-methyl
IId			8.24 (s)	8.35 (s)	
IIg			7.98 (s)	8.36 (s)	
IIIa	5.46 (m), 5.63 (m)		8.37 (s)	8.22 (m), 8.32 (m)	
IIIb	5.80 (m) (1.97)			$\underbrace{8.33\ (m), 8.42\ (m)}$ (6.05)	8.90 (s) (5.97)
IIIc	$\underbrace{5.72\ (m), 5.81\ (m)}$ (1.90)	*Ca.* 7.14 (m) (1.06)		8.27 (m), 8.44 (m) (3.17) (2.87)	8.94 [(d) J = 7.0 c.p.s.] (3.03)
IV	$\underbrace{5.52\ (s), 5.64\ (s)}$ (3.8)			8.16 (s) (6.2)	
IIf				8.59 (s) (6.17)	9.05 (s) (11.75)
V				8.57 (s)	9.06 (s)
IIe (*cis*)		*Ca.* 7.45 (m)		8.51 [(d) $J \sim 1$ c.p.s.]	9.10 [(d) J = 7.6 c.p.s.]
IIe (*trans*)		*Ca.* 8.05 (m)		8.50 [(d) $J \sim 1$ c.p.s.]	8.97 [(d) J = 6.6 c.p.s.]
IIb			8.22 (s) (3.2)	8.45 (m) (5.8)	8.72 (s), 8.96 (s) (3.0) (3.0)
IIa			8.47 (m) (8.94)		8.82 (s), 8.97 (s) (3.08) (3.03)
IIc (*cis* and *trans*)		$\underbrace{Ca.\ 7.1\ (m), ca.\ 7.5\ (m)}$ (1.09)	8.46 (m) (8.84)		$\underbrace{8.98\ (d), 8.87\ (d), J \sim 7\ c.p.s.}$ (3.05)

[a] Numbers in parentheses are the integrated areas of the peaks whose chemical shifts are listed directly above them. Chemical shifts are in p.p.m. relative to TMS as τ 10. Spectra were determined in carbon tetrachloride with TMS as an internal standard. Letters in parentheses refer to peak multiplicity: s = singlet, d = doublet, m = multiplet. The chemical shifts of IIa,b,c,d,g and IIIc were found to be the same in methylene chloride solvent.

the table. All the compounds show a characteristic double bond stretching absorption in the infrared at *ca.* 1690 cm.$^{-1}$.[10a]

CHART I



The compounds were further interrelated as follows: IIb with methylmagnesium iodide was shown to yield IIf, identical with that obtained by dimethylation of IId, and IIc on reduction with lithium aluminum hydride gave IIe (a mixture of *cis* and *trans* isomers).[10a]

The pentamethylcyclobutenyl cation (Ib) was first prepared from the pentamethylcyclobutenyl bromide (IIb) in the same way as the 1,2,3,4-tetramethyl-2-chlorocyclobutenyl cation (Ia) was from the tetramethyldichlorocyclobutene (IId), that is, by treatment with silver hexafluoroantimonate in cold (−60°) liquid sulfur dioxide[1] (see Experimental). However, there is a simpler preparation. The reaction of 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene (IId) in methylene chloride with aluminum chloride also furnishes a solution of the 1,2,3,4-tetramethyl-4-chlorocyclobutenyl cation (Ia), but unlike the sulfur dioxide solution, the methylene chloride solution is stable at room temperature. No special precautions to exclude oxygen are required. The nuclear magnetic resonance (n.m.r.) spectra of the ion prepared in the two ways are identical (Fig. 1).[14] The starting material IId is readily recovered if the carbonium ion in methylene chloride is treated with tetramethylammonium chloride in sulfur dioxide.

The pentamethyl- and 1,2,3,4-tetramethylcyclobutenyl cations are similarly prepared in methylene chloride by treating the halides IIa or b and IIc with aluminum chloride. Again, the solutions are stable at room temperature. The ions are identified by their n.m.r. spectra and by their reactions with tetramethylammonium chloride, which yield the corresponding chlorides IIa and IIc.

Also the 1,2,3,4-tetramethyl-4-bromocyclobutenyl cation (Id) is formed when 1,2,3,4-tetramethyl-3,4-dibromocyclobutene (IIg)[10a] is treated in methylene chloride with aluminum chloride. Its n.m.r. spectrum differs from that of its chloro analog.

The n.m.r. spectra of each of the cations Ia–d, formed in methylene chloride as described above, are presented in Fig. 1. The spectrum of the pentamethylcyclobutenyl cation consists of a peak at (τ 7.36 due to the methyls on the 1- and 3-carbons, a peak at τ 7.63 due to the methyl on carbon atom 4, and a peak at τ 8.40 due to the geminal methyls. The 1,2,3,4-tetramethylcyclo-

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[14] The n.m.r. spectrum of the ion as the hexafluoroantimonate in liquid sulfur dioxide is reported[1] to consist of three bands at τ 7.00, 7.48, and 7.58 in the intensity ratio 2:1:1. If the tropylium hexafluororantimonate used as an internal standard resonates at τ 0.67 rather than 0.55 (see Experimental), these peaks are at τ 7.12, 7.60, and 7.70.

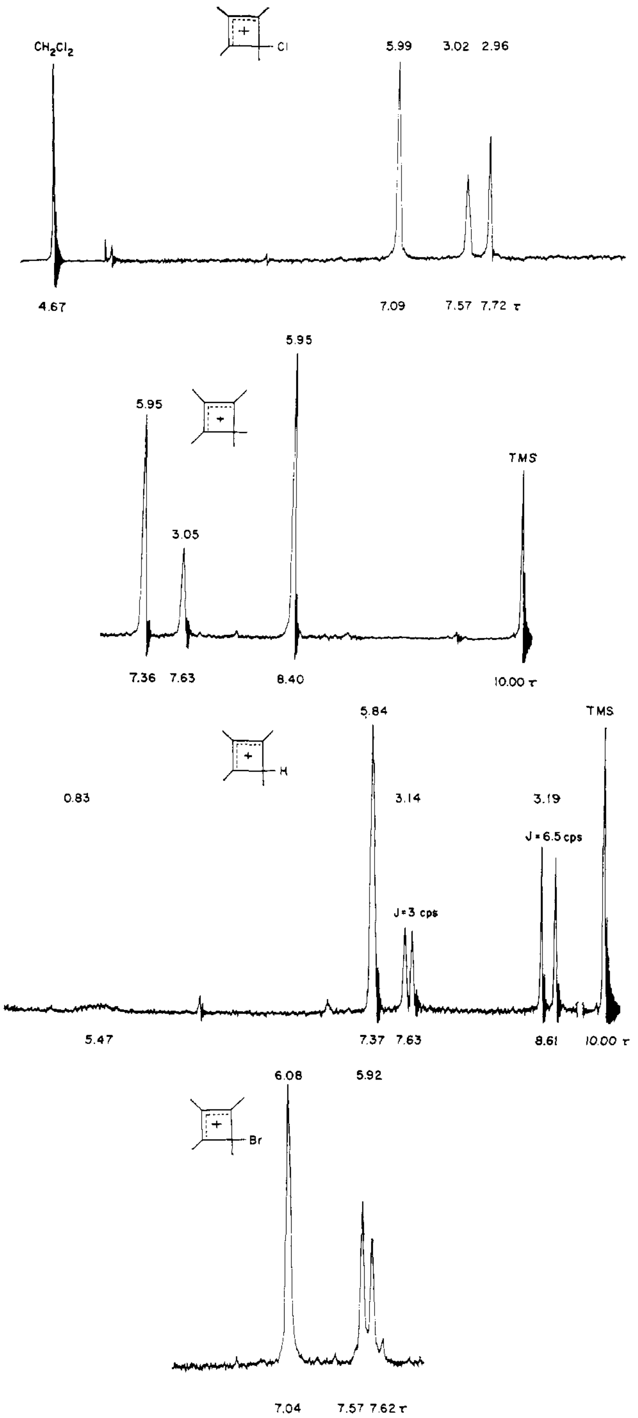

Fig. 1.—N.m.r. spectra of Ia–d as chloroaluminates in methylene chloride at 60 Mc.; TMS is the internal standard for Ib and c, while the CH_2Cl_2 is for Ia and d. Over each peak, its integrated intensity is given.

butenyl cation shows a peak at τ 7.37 due to the 1- and 3-methyls, a doublet (J = 3 c.p.s.)[15] at τ 7.63 due to the 4-methyl, a doublet (J = 6.5 c.p.s.) τ 8.61 due to the saturated C-methyl, and a broad peak at *ca.* τ 5.5 due to the single tertiary hydrogen.

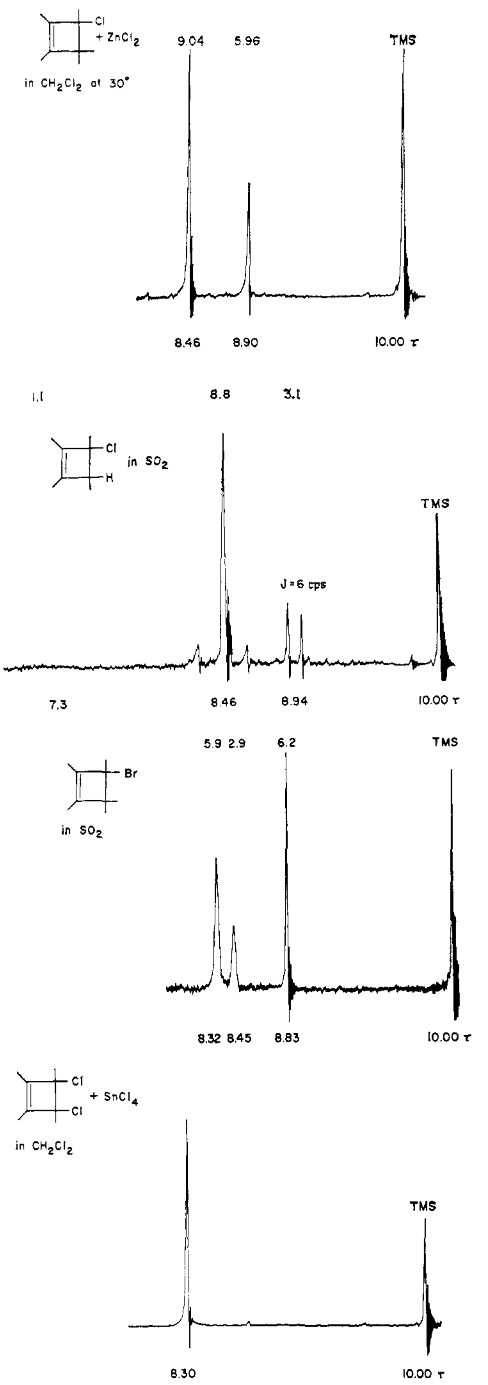

Fig. 2.—N.m.r. spectra of the cyclobutenyl halides IIa–d undergoing rapid allylic rearrangement; TMS is the internal standard in each sample: IIa in methylene chloride with zinc chloride; IIc in liquid sulfur dioxide; IIb in liquid sulfur dioxide; IId in methylene chloride with stannic chloride.

The gross structural features of the n.m.r. spectra of Ib and Ic also would have been observed if what was thought to be these ions were the starting halides (IIa and IIc) undergoing rapid allylic rearrangement under the influence of the Lewis acid aluminum chloride. However, the dichloride IId would, in this case, have yielded a spectrum consisting of only one line, rather than of three as observed. Moreover, the chemical shift of each resonance line would have had to have been an average of the known chemical shifts of those lines in the halide which are averaged to produce it. Instead, the resonance lines are found at particularly low fields, as expected for the protons in a carbonium ion. Furthermore, such equilibrating mixtures are easily prepared in other ways, and their n.m.r. spectra are exactly as predicted (Fig. 2). Thus, IIa in methylene

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(15) This splitting is in excellent accord with that calculated for spin coupling through the π-electrons, assuming the methyl group to be freely rotating and the allylic hydrogen to be attached to carbon by a σ-bond parallel to the π-bond.[16]

(16) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

chloride in the presence of the weak Lewis acid zinc chloride produces, at −60°, an n.m.r. spectrum identical with that produced when the zinc chloride is absent, but consisting, at room temperature, of only two lines at τ 8.46 and 8.90 (intensity ratio 9.04 : 5.96). The 1,2,3,4-tetramethyl-3-chlorocyclobutene (IIc) behaves in exactly the same way to produce the unperturbed spectrum of IIc at −60° and the completely time-averaged spectrum at room temperature. The latter spectrum displays somewhat broadened peaks because the sample is decomposing. Similar spectra are observed even when IIa and IIc are treated in methylene chloride with only small amounts of zinc chloride, and although these n.m.r. spectra are clearly different from those of solutions of pure IIa and IIc, the infrared spectra are identical with those of the pure precursors. Excellently resolved time average n.m.r. spectra of IIa, b, and c, undergoing allylic rearrangement, are observed when the three halides are simply dissolved in liquid sulfur dioxide at room temperature (*cf.* Fig. 2).

The dichloride (IId) undergoes the allylic rearrangement less easily, and in sulfur dioxide solution its two-line spectrum is unequilibrated. In methylene chloride–zinc chloride at room temperature, it also displays a spectrum of two poorly resolved peaks (at τ 8.24 and 8.35), but at 70° these fuse into one sharp line at τ 8.30. The stronger Lewis acid stannic chloride effects this latter equilibration even at room temperature, and the same spectrum, a single line at τ 8.30, is observed whether catalytic amounts (0.06 mole per mole of IId) or excesses of stannic chloride are employed (Fig. 2). The infrared spectrum of an equimolar mixture of IId and stannic chloride in methylene chloride is identical with a composite of the spectra of its two components. Clearly, the tetramethylcyclobutadienyl dication has not been formed. The behavior of 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene is, therefore, in sharp contrast with that reported for 1,2,3,4-tetraphenyl-3,4-dibromocyclobutene, which with stannic chloride is said to yield the tetraphenylcyclobutadienyl dication.[17] Recently, other similar cyclobutenyl halides, notably 2-bromo-3-hydroxy-2,4-dimethylcyclobutenone, were reported to undergo Lewis acid-catalyzed allylic rearrangement, but not formation of macroscopic amounts of the cations that bear a resemblence to the cyclobutadienyl dication.[18]

The infrared spectra of the carbonium ions Ia–d were determined in methylene chloride solution. All had strong bands in the region from 1540 to 1340 cm.$^{-1}$, and their highest intensity maxima appeared at the following frequencies: Ia, 1475 cm.$^{-1}$; Ib, 1467 cm.$^{-1}$; Ic, 1465 cm.$^{-1}$; Id, 1465 cm.$^{-1}$. If these can be attributed to carbon–carbon stretching vibrations, their high intensity (compared to the corresponding vibrations in uncharged molecules) and their position, between the normal double and single bond stretching frequencies,[19] is noteworthy.[3]

TABLE II

ULTRAVIOLET SPECTRA OF THE CYCLOBUTENYL CHLOROALUMINATES IN METHYLENE CHLORIDE

Compound	$\lambda_{\max}^{CH_2Cl_2}$, m$\mu$	log ϵ[a]
Ia	253	3.67
Ib	245	3.46
Ic	240	3.48
Id	263	3.57

[a] The quartz cells had a path length of 0.1 mm.

The ultraviolet spectra of the ions Ia–d were determined in methylene chloride solution and are recorded in Table II. By measuring the spectra of these solutions in 0.1-mm. and 1.0-cm. path length quartz cells, Beer's law was shown to hold in the 10^{-3} to 10^{-5} concentration range.

Discussion

The ultraviolet spectra of the carbonium ions I–d are relevant to the question of how important 1,3-π-interactions are in cyclobutyl rings. The steric constraints of the four-membered ring are expected to force the ends of the allylic system into close proximity, endowing the system with cyclopropenyl[20] characteristics. An attempt to measure, kinetically, how the properties of these cyclobutenyl (homocyclopropenyl) cations are modified as a result of the 1,3-π-interaction has not, however, been easy,[5a] although Roberts has suggested that the 1,3-resonance integral be assigned a value between 0.2β and 0.5β (where β is the normal carbon–carbon 1,2-π-resonance integral).[5a,d,e]

The ultraviolet spectra of cyclobutenyl cations should sensitively probe the 1,3-π-interaction, for the lowest energy absorption maxima of normal allylic cations appear at about 300 mμ,[3] while the corresponding maximum of the dipropylcyclopropenyl cation must appear below 185 mμ.[20] This is reasonable since the HMO excitation energy for a simple allylic cation is 1.4β and for a cyclopropenyl cation 3β.[21] The observation that the pentamethylcyclobutenyl cation (Ib) has its ultraviolet maximum at 245 mμ implies that the transition energy is approximately 1.93β.[22] This, in turn, requires that, if the shift from *ca.* 300 mμ, where simpler allylic cations absorb,[3] can be attributed solely to 1,3-π-interaction (rather than, for example, to a solvent effect), then the HMO 1,3-π-resonance integral (β_{13}) must be 0.33β, in excellent accord with Robert's prediction.

A comparison of the methyl proton chemical shifts in the cyclobutenyl cations and in related alkenyl cations also indicates that 1,3-π-interaction is especially pronounced in the cyclobutenyl cation. Thus, the resonances of the methyl protons attached to the 1- and 3-positions of the cyclobutenyl cation appear at somewhat higher fields than those of the 1,2,3,4,4,5-hexamethylcyclopentenyl cation,[3b] for example (τ 7.36 in the former, τ 7.19 in the latter), while the methyl pro-

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[17] H. H. Freedman and A. M. Frantz, Jr., *J. Am. Chem. Soc.*, **84**, 4165 (1962). NOTE ADDED IN PROOF.—Recently this hypothesis has been disproved [R. F. Bryan, *ibid.*, **86**, 733 (1964)], but the synthesis of the dication in another way, from the dibromide and silver fluoroborate, has been claimed [H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964)]. See also D. G. Farnum and B. Webster, *ibid.*, **85**, 3502 (1963).

[18] D. Farnum, *et al.*, *Tetrahedron Letters*, 307 (1963); D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Am. Chem. Soc.*, **86**, 673 (1964).

[19] The double bond stretching frequency of the tetramethylcyclobutenes appears at 1690 cm.$^{-1}$, while single bond stretching vibrations occur at 1300 ~1100 cm.$^{-1}$ (*cf.* K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, pp. 22, 24).

[20] R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962), and references therein.

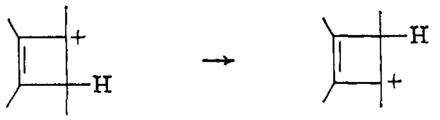
[21] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 202 ff.

[22] The transition energy was estimated from a linear plot of the frequency of the longest wave length maximum for a few simple cations against the Hückel M.O. transition energy. Figure 8.13 (p. 229) of ref. 21 was used with additional points for the hexamethylbenzenonium ion [6b] and the 1,3,5,5-tetramethylcyclohex-2-enyl cation.[3a]

tons attached to the central position of the former system appear at lower fields than in the latter (τ 7.63 *vs.* τ 7.85). These chemical shifts might be interpreted as they have been in benzenonium ions.[23] Thus we assume that a methyl bonded to an uncharged cyclobutenyl carbon atom resonates at τ 8.54, the average of the positions of the allylic methyl resonances in IIe (*cis* and *trans*), IIf, and V,[24] and assume that the shift of a methyl away from this position is proportional to the charge on the adjacent carbon atom. The proportionality constant (the sum of the shifts of the 1-, 2-, and 3-methyls from τ 8.54) is 3.27 p.p.m./unit charge.[26] Then the charge density at the 1- and 3-positions is 0.36, and at the 2-position 0.28 unit of positive charge. For the hexamethylcyclopentenyl cation (assuming the same standard of τ 8.54) the proportionality constant is 3.39 p.p.m./unit charge, and the charge densities at the 1- and 3-positions 0.40, while at the central position 0.20. The lower positive charge at the 1- and 3-positions and the higher positive charge at the 2-position of the cyclobutenyl cation suggest that resonance forms with a bond between the 1- and 3-positions are exceptionally pronounced contributors to the structure of the ion. In molecular orbital terms, the charge densities are as expected if the 1,3-π-overlap and resonance integrals were particularly large. The charge densities are about halfway between those in the simple alkenyl cation and the fully symmetrical trimethylcyclopropenyl cation, where the charge density must be one-third of a unit charge on each ring carbon atom.

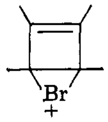
The chemical shifts in the pentamethyl- and 1,2,3,4-tetramethylcyclobutenyl cations were measured in methylene chloride using tetramethylsilane (TMS) as an internal standard. However, TMS was destroyed when it was added to the chloro- and bromotetramethylcyclobutenyl cations Ia and Id in methylene chloride, and the solvent resonance was, therefore, used as the internal standard in these cases. The validity of this procedure was checked by noting that the solvent resonance in solutions of the former cations, where TMS was used, appeared, as expected, at τ 4.67.

None of the cyclobutenyl ions prepared shows a tendency to undergo a 1,2-rearrangement (either intramolecularly or by elimination and readdition) sufficiently rapidly to cause an observable line-broadening in its n.m.r. spectrum. Thus the rearrangement reaction 1, which if it were sufficiently rapid would result in the fusion of all the methyl resonances into one, is not observed; even at 80° the ion's n.m.r. spectrum is unperturbed. In contrast, hydrogen migration occurs sufficiently readily in the related hexamethylbenzenonium ion that only one methyl resonance is observable at −30°.[27] The transition states for migration in the cyclobutenyl and benzenonium ions differ in that the former resembles a protonated cyclobutadiene and the latter a protonated benzene. The relative difficulty with which migration occurs in the cyclobutenyl cation would be understandable if the presumed instability of cyclobutadiene[28] (either steric or electronic in origin) were reflected in the transition state for the reaction. The observation might, however, also reflect the relative stability of the cyclobutenyl cation.

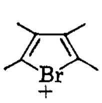


(1)

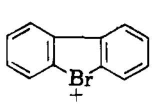
Interestingly enough, the 1,2,3,4-tetramethyl-4-bromocyclobutenyl cation, like the 1,2,3,4-tetramethyl-4-chlorocyclobutenyl cation,[1] also shows no tendency (on the n.m.r. time scale) to isomerize to either bromonium ion VI or VII. While α-bromocarbonium ions are, in other cases, unstable with respect to the corresponding bromonium ions,[29] the lack of isomerization in the present case can be attributed to the special stability of the cyclobutenyl cation Id, to the exceptional steric strain in VI, or to the energetic unfavorableness of a bromonium ion derived from cyclobutadiene. The implication that VII is unstable with respect to Id suggests that the known dibenzbromonium ion VIII,[30] in which this isomerization would entail the loss in resonance energy of two benzene rings, is not analogous to simpler, but unknown, bromonium ions, such as VII.



VI



VII



VIII

The observations that were made on the Lewis acid-catalyzed rearrangements of the cyclobutenyl halide IId are of two kinds. In the presence of the strong Lewis acid *aluminum chloride in methylene chloride* the tetramethyl-4-chlorocyclobutenyl cation is formed, but at room temperatures undergoes no 1,2-chlorine migration. In the presence of the weaker Lewis acid stannic chloride in methylene chloride the chlorine atoms rapidly migrate between all four ring carbon atoms. The former observation requires that the migration of chlorine in the presence of the weak Lewis acid not proceed through the formation of the chlorocyclobutenyl cation followed by intramolecular migration of the remaining chlorine. There are two remaining possibilities. The migration occurs when the dichloride is treated with the weaker Lewis acid either because the conjugate acid of the weaker Lewis acid rechlorinates the carbonium ion rapidly or because the weaker acid forms no carbonium ion, the migration occurring concertedly. The migration does not occur by exchange of chlorine between the chlorocyclobutenyl cation (Ia) and the dichlorocyclobutene (IId), for when these are combined they are rapidly destroyed. This observation also implies that the reaction between aluminum chloride and the dichlorocyclobutene succeeds only because it is so rapid.

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(23) C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961).

(24) The choice of reference is slightly different from that in ref. 23, where τ 8.43 was chosen by correcting the resonance of toluene for the ring current effect. However, the ring current effect is derived, for example, from the observed shift of the toluene resonance from that of α-phellandrene,[25] and the choice of an allylic methyl resonance in a compound related to the cyclobutenyl cation was therefore preferred. There is, in any case, little difference between the two choices.

(25) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(26) This is significantly different from the 4.75 p.p.m. found by MacLean and Mackor[23] for the methylbenzenonium ions and might suggest that the procedure is invalid.

(27) (a) C. MacLean and E. L. Mackor, *Discussions Faraday Soc.*, **34**, 165 (1962); (b) G. A. Olah, "The Friedel Crafts Reaction," Vol. 1, John Wiley–Interscience Publishers, New York, N. Y., 1963.

(28) Reference 21, p. 261.

(29) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 148 ff., 214 ff.

(30) R. B. Sandin and H. J. Hay, *J. Am. Chem. Soc.*, **74**, 274 (1952).

When the dichloride IId or the dibromide IIg is treated in methylene chloride with an excess of aluminum chloride only one chlorine atom ionizes. Only the cyclobutenyl cations Ia and Id are detectable in these solutions by n.m.r. spectroscopy; no evidence of the tetramethylcyclobutadienyl dication can be found.

Solutions of the pentamethyl or 1,2,3,4-tetramethylcyclobutenyl cation in methylene chloride containing triphenylmethane exhibit n.m.r. spectra that are a superposition of their components. Thus, the cyclobutenyl cations do not abstract a hydride ion from triphenylmethane.

Experimental

Infrared spectra were determined using a Perkin–Elmer Model 421 spectrophotometer, ultraviolet spectra using the Cary Model 14, and n.m.r. spectra using the Varian A-60 spectrometer. The Perkin–Elmer Model 154 vapor fractometer with thermistor detector was used for all analytical and preparative vapor phase chromatograms (v.p.c.). All the v.p.c. columns were 6 ft. × 0.25 in. o.d. packed with 20% of a stationary phase on firebrick. Melting points are uncorrected. The infrared spectra of the carbonium ions were determined in NaCl cells. Other infrared spectra of solutions where Lewis acids were present were determined in Irtran cells.

1,2,4-Trimethyl-3-methylene-4-chlorocyclobutene (IIIa).—To a stirred refluxing solution of 80 g. (0.447 mole) of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (IId) dissolved in 400 ml. of 1,2-dimethoxyethane (DME), 315 ml. of a 1.7 *M* solution of methyllithium in ether (0.535 mole) was added dropwise, under nitrogen, over a 2-hr. period. After addition was complete, most of the DME was removed by distillation. Pentane (150 ml.) was added to the residue, and the mixture was filtered free of the lithium salts. The filtrate was distilled and two fractions were collected: (1) b.p. 44–54° (30 mm.), 8.1 g.; the v.p.c. on di-*n*-decyl phathalate showed this fraction to be a mixture of 21% DME, 8.5%IIIb, and 70.5% IV; (2) b.p. 54–62° (30 mm.), 28.4 g.; the n.m.r. spectrum showed that this fraction consisted of approximately 85% IIIa and 15% IV and IId.

1,2,4,4-Tetramethyl-3-methylenecyclobutene (IIIb).—To a stirred solution of 0.38 mole of CH_3MgI in 600 ml. of ether, 27 g. (0.19 mole) of IIIa (fraction 2) was added at a rate that maintained a gentle reflux. After addition was complete, the mixture was refluxed further for 2 hr. The excess CH_3MgI was destroyed with water, the mixture was filtered free of magnesium salts, and the water layer was extracted three times with 100-ml. portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered, and distilled, yielding 9.3 g. (40%) of IIIb, b.p. 45–47° (60 mm.), contaminated by 10% of IV and IIf. The product was readily purified by v.p.c. at 93° on a di-*n*-decyl phthalate column.

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.64; H, 11.58.

Hexamethylcyclobutene (IIf).—To a stirred solution of 0.28 mole of CH_3MgI in 250 ml. of ether, 10.0 g. (0.056 mole) of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (IId) was added at a rate that maintained a gentle reflux. After addition was complete, the mixture was refluxed for 2 hr. The excess CH_3MgI was destroyed with water, the mixture filtered free of magnesium salts, and the water layer was extracted three times with 50-ml. portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered, and then distilled, yielding 4.9 g. (63%) of hexamethylcyclobutene (IIf), b.p. 53–55° (50 mm.), contaminated with approximately 3–4% of IIIb. The compound was readily purified by v.p.c. at 93° on a di-*n*-decyl phthalate column.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.80; H, 13.16.

1,2,4-Trimethyl-3-methylenecyclobutene (IIIc).[8a]—To a stirred suspension of 8.3 g. (0.21 mole) of $LiAlH_4$ in 300 ml. of ether, 43 g. (0.30 mole) of IIIa[31] was added dropwise at a rate that maintained a gentle reflux. After addition was complete, the mixture was refluxed for 18 hr. The excess $LiAlH_4$ was destroyed under a nitrogen atmosphere with water. The mixture was filtered free of salts and the water layer was washed three times with 100-ml. portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered, and distilled through a 20-cm. Vigreux column, yielding 15.6 g. (48%) of IIIc, b.p. 36–38° (45 mm.), contaminated by 25% of *cis*- and *trans*-1,2,3,4-tetramethyl cyclobutene (IIe). Compound IIIc was readily purified by v.p.c. at 71° on a dimethyl sulfolane column. Its ultraviolet maximum in cyclohexane and in ethanol appeared at 230 mμ (log ϵ 4.13, 4.16, respectively).

Anal. Calcd. for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.55; H, 11.15.

Preparation of 1,2,3,4,4-Pentamethyl-3-bromocyclobutene (IIb).—The preparation was performed on a vacuum manifold at a pressure of *ca.* 3 μ. Anhydrous HBr (0.041 mole) was added to 3.80 g. (0.0311 mole) of IIIb at −78°. The mixture was kept at −78° for 30 min., after which it was slowly warmed to room temperature. The excess HBr was then pumped off at −78°. The product was evaporatively distilled twice at room temperature to yield 5.92 g. (94%) of pure IIb that melted at *ca.* 9°.

Anal. Calcd. for $C_9H_{15}Br$: C, 53.21; H, 7.44; Br, 39.34. Found: C, 53.32; H, 7.48; Br, 39.46.

Methylation of IIb.—To a solution of 1.63 g. (0.010 mole) of CH_3MgI in 15 ml. of ether, 0.300 g. (0.00148 mole) of IIb was added, and the mixture was refluxed for 2 hr. The excess CH_3MgI was destroyed with water, the mixture was filtered free of magnesium salts, and the water layer was extracted three times with 10-ml. portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered, and most of the ether was then removed by distillation. The remaining solution (~0.5 ml.) was purified by v.p.c. on a di-*n*-decyl phthalate column at 93°. The only product obtained besides ether was 0.076 g. (36%) of hexamethylcyclobutene (IIf), identical in all respects (v.p.c. retention time, infrared, n.m.r.) with the sample of IIf prepared as above.

1,2,3,4,4-Pentamethyl-3-chlorocyclobutene (IIa).—In a manner analogous to that used to prepare IIb, 0.0060 mole of anhydrous HCl was added to 0.685 g. (0.00562 mole) of IIIb. Pure IIa was obtained in 84% yield (0.751 g.) and melted at *ca.* −15°.

Anal. Calcd. for $C_9H_{15}Cl$: C, 68.12; H, 9.53; Cl, 22.35. Found: C, 68.29; H, 9.72; Cl, 22.12.

***cis*- and *trans*-1,2,3,4-Tetramethyl-3-chlorocyclobutene (IIc).**—As above, 0.046 mole of anhydrous HCl was added to 4.50 g. (0.0416 mole) of IIIc. Pure IIc was obtained in 92% yield (5.50 g.). The n.m.r. spectrum showed it to be a 1:1 mixture of the *cis* and *trans* isomers.

Anal. Calcd. for $C_8H_{13}Cl$: C, 66.42; H, 9.06; Cl, 24.51. Found: C, 66.51; H, 9.11; Cl, 24.53.

Reduction of IIc with $LiAlH_4$.—To a stirred suspension of 0.076 g. (0.0020 mole) of $LiAlH_4$ in 10 ml. of ether 0.290 g. (0.0020 mole) of IIc was added. The mixture was refluxed overnight. The excess $LiAlH_4$ was decomposed with water (under a nitrogen atmosphere), the mixture was filtered free of salts, and the water layer was washed three times with 10-ml. portions of ether. The combined ether extracts were dried over $MgSO_4$ and filtered, and most of the ether was removed by distillation. The remaining solution (~1 ml.) was purified by v.p.c. on a di-*n*-decyl phthalate column at 74°. The only products obtained, besides ether, were 0.005 g. (3%) of *trans*-1,2,3,4-tetramethylcyclobutene and 0.040 g. (17%) of *cis*-1,2,3,4-tetramethylcyclobutene. They were identical in all respects with the known isomers (v.p.c. retention time, infrared, n.m.r.) prepared according to the method of Criegee and Noll.[10a, 32]

General Method for the Preparation of the N.m.r. Samples of the Cyclobutenyl Cations (Ia,b,c,d) in CH_2Cl_2.—Anhydrous $AlCl_3$ (0.00053 mole) was weighed into an n.m.r. tube which was then covered with a rubber serum bottle cap. The tube was cooled in a Dry Ice–acetone bath, and a solution of 0.00050 mole of the halide IIa, b, c, d, or g in 0.35 ml. of methylene chloride was rapidly injected. The tube was shaken in the air and cooled only as necessary to keep it from heating above room temperature. After all the $AlCl_3$ had dissolved, the samples (except for Id) could be stored at room temperature.

Preparation of the Pentamethylcyclobutenyl Hexafluoroantimonate (Ib) in Liquid SO_2.—Anhydrous $AgSbF_6$ (0.0015 mole) was put into the open end of a U-tube fitted at one end with a ground glass joint for connection to the vacuum manifold and at the other with a sintered glass disk and n.m.r. sample tube. The tube was evacuated to a pressure of 10^{-6} mm. and 3 ml. of

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(31) This sample of IIIa contained no IV; the only impurity present was IIg.

(32) The procedure was modified in that equimolar amounts of the dichloride IId and lithium aluminum hydride were used.

liquid SO_2 was distilled in; IIb (0.203 g., 0.0010 moles) was distilled into the mixture, which was cooled in a liquid nitrogen bath. The U-tube was sealed closed and warmed to −78° with vigorous shaking. The solution was filtered at −60° into the n.m.r. tube which was then fused off. The n.m.r. spectrum was determined at −60°; decomposition set in at temperatures above −30°. The spectrum consisted (from lower to higher fields) of three singlets of relative intensity 6.2:3.1:5.7 spaced 0.2 and 0.7 p.p.m. apart. Calibration by replacement of the sample tube with one containing TMS in SO_2 showed the absolute peak positions to be *ca.* τ 7.5, 7.8, 8.5. Relative to internal tropylium hexafluoroantimonate at τ 0.67, the peaks appear at τ 7.47, 7.68, and 8.39.

General Method for the Determination of the Ultraviolet Spectra of Ia,b,c, and d.—The methylene chloride was purified as follows. It was washed with concentrated H_2SO_4, neutralized with aqueous ammonia, washed with water, and dried over $CaCl_2$ and then KOH. It was refluxed over $AlCl_3$ overnight and distilled immediately prior to use. The carbonium ions were prepared in methylene chloride solution in the way described above for the preparation of the n.m.r. samples. The ultraviolet spectra were determined in 0.1-mm. and 1.0-cm. quartz cells.

Quenching of Carbonium Ion Ia with Tetramethylammonium Chloride.—To a stirred suspension of 1.34 g. (0.010 mole) of $AlCl_3$ in 5 ml. of CH_2Cl_2 at −78°, 1.79 g. (0.010 mole) of IId was rapidly added. After warming to room temperature, the solution was syringed dropwise into a stirred solution of 2.2 g. (0.020 mole) of tetramethylammonium chloride in *ca.* 30 ml. of liquid SO_2 at −78°. The SO_2 was allowed to boil away. Pentane was added to the residue and the mixture filtered. The filtrate on evaporation left 1.49 g. of a yellow solid, m.p. 51–53°, which sublimed (45° at 15 mm.) to give 1.43 g. (80%) of IId, m.p. 56–57° (lit.[7] m.p. 57°), identical (mixture m.p., infrared, n.m.r.) with a known sample.

Quenching of Ib.—Compound Ib was prepared in 3 ml. of methylene chloride from 0.134 g. (0.0010 mole) of $AlCl_3$ and 0.203 g. (0.0010 mole) of IIb. The methylene chloride was evaporatively distilled at 10^{-6} mm. and the residue was then pumped on at 10^{-6} mm. for 30 min. Sulfur dioxide (3 ml.) was subsequently distilled in at −78°. From a side arm attached to the reaction vessel 0.22 g. (0.002 mole) of tetramethylammonium chloride was rapidly added to the stirred SO_2 solution at −78°. The solution was warmed to −30° and most of the SO_2 was removed by evaporative distillation at 10^{-6} mm. The very small amount of liquid remaining was evaporatively distilled at room temperature into another flask, which was then allowed to stand at room temperature and atmospheric pressure to permit the last traces of SO_2 to escape. To ensure complete removal of the SO_2, the remaining liquid was warmed to *ca.* 50° for 1 min. Subsequent evaporative distillation of the liquid at 10^{-6} mm. afforded 0.091 g. (57%) of pure (infrared, n.m.r.) 1,2,3,4,4-pentamethyl-3-chlorocyclobutene (IIa).

Quenching of Ic.—The procedure was the same as for Ib. The carbonium ion (0.0010 mole) was prepared in methylene chloride and quenched with 0.22 g. (0.002 mole) of tetramethylammonium chloride to yield 0.096 g. (66%) of pure (infrared, n.m.r.) *cis*- and *trans*-IIc.

Treatment of the Cyclobutenyl Halides with $SnCl_4$ and $ZnCl_2$.—The n.m.r. samples were prepared in methylene chloride using the same techniques employed for preparing the n.m.r. samples of the carbonium ions using $AlCl_3$. Only in the case of IIc was it necessary to store the reaction mixture at −78°. The other mixtures could be warmed to room temperature.

Recovery of IId from a Mixture of IId and $SnCl_4$.—The technique was the same as for quenching Ia. A mixture of 0.895 g. (0.005 mole) of IId and 0.650 g. (0.025 mole) of $SnCl_4$ in 5 ml. of methylene chloride was added to 1.1 g. (0.010 mole) of tetramethylammonium chloride in 25 ml. of liquid SO_2 at −78°. Pure IId (m.p., mixture m.p., infrared, n.m.r.) was obtained, after sublimation, in 84% yield.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KYOTO GAKUGEI UNIVERSITY, FUSHIMI-KU, KYOTO, JAPAN]

Molecular Rotations of Methylcyclohexanols in Relation to Their Structures

BY SHUKICHI YAMANA

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The PM method, a modification of the Kirkwood method[1] of computing optical rotatory power, is shown to be applicable to the methylcyclohexanols.

In 1956, Whiffen[2] studied the molecular rotation of optically active substances such as derivatives of cyclohexane and tetrahydropyrane, using monochromatic (sodium D line) plane polarized light, and concluded that the predominant optical effect was contributed by the adjacent substituents of the chair form of these molecules. Indeed, he proposed a new method of computing optical molecular rotation. It should be noted, however, that Whiffen's method is only a first approximation; that is, in some cases the smaller rotation effects of more widely separated substituents account for the major part of the optical activity.

According to Kirkwood,[1] the rotation is caused by the dynamic coupling effect between any two members of unit groups in the molecule. Studies[3] by the author suggest that Kirkwood's theory must be modified for carbohydrates. This modified method of calculating molecular rotation is called the PM method[4] and has been used successfully for carbohydrates,[5–7] polyhydroxycyclohexanes,[8] and menthol-like compounds.[9] This article is a study of the applicability of the PM method to methylcyclohexanols.

The basic relationship of the PM method is

$$[M]_{\mathrm{D}}{}^{20} \equiv \sum_{\mathrm{i} \neq \mathrm{k}} [\mu]_{\mathrm{D}}{}^{20}{}_{\mathrm{obs(ik)}} \qquad (1)$$

But $[\mu]_{\mathrm{D}}{}^{20}{}_{\mathrm{obs(ik)}}$ is the partial molecular rotation contributed by the dynamic coupling effect between the groups i and k, and therefore

$$[\mu]_{\mathrm{D}}{}^{20}{}_{\mathrm{obs(ik)}} = \zeta_{\mathrm{i}}\zeta_{\mathrm{k}}[\mu]_{\mathrm{D}}{}^{20}{}_{\mathrm{calcd(ik)}} \qquad (2)$$

In this equation ζ_{i} and ζ_{k} are characteristics of i and k,

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(1) W. W. Wood, W. Fickett, and J. G. Kirkwood, *J. Chem. Phys.*, **20**, 561 (1952).

(2) D. H. Whiffen, *Chem. Ind.* (London), 964 (1956).

(3) S. Yamana, *Bull. Chem. Soc. Japan*, **30**, 203 (1957).

(4) Reference *17 in the previous paper.[5]

(5) S. Yamana, *Bull. Chem. Soc. Japan*, **31**, 558 (1958).

(6) S. Yamana, *ibid.*, **30**, 207, 920 (1957); **31**, 564 (1958); **35**, 1269, 1421, 1950 (1962); **36**, 473 (1963).

(7) S. Yamana, *ibid.*, **30**, 916 (1957).

(8) S. Yamana, *ibid.*, **33**, 1741 (1960); **34**, 1212 (1961).

(9) S. Yamana, *ibid.*, **34**, 1414 (1961).