cyclohexane occurred after several hours at 179°. However, an equilibrium mixture was unaffected by this reaction.

A Dow-Corning silicone oil (No. 550) was used in the heating bath which was stirred rapidly. The temperature was controlled by a Magnaset relay-activating mercury thermometer. A high-low heating cycle gave temperature control of ±0.2° or better. Samples taken from the bath were quenched at −70°, opened, and liquid removed by hypodermic syringe for gas chromatographic analysis.

Rate constants were calculated from the kinetic data using a procedure employed previously.[46,47] $[\text{IIb}]_0/[\text{IIb}]_t$ and $\log [\text{IIb}]_0/[\text{IIb}]_t/t = k/2.303$, for example, were calculated from the amount of IIb present in the mixture at zero time and after intervals of time (t). A plot of $k/2.303$ against time was made. The intercept at zero time when only IIb was present represents the initial rate constant free from back reaction of IIa. The results of similar calculations are recorded in Table VII.

Dipole Moment Measurements.—The dielectric constants of the neat liquids were measured by M. R. Kegelman[29] using a General Radio Co. Type 716-C capacitance bridge and a Balsbaugh electrical measuring cell of 10-ml. capacity (Type 2TN-20LV) with nickel electrodes. Dissipation factors at 10 and 100 kc. were less than 0.5%. The measured ϵ' values were employed in the calculation of dipole moments listed in Table VI.

The dielectric constants for benzene solutions of the compounds at two concentrations were determined[28] by C. G. Wortz and by Naomi Schlichter using Dipolemeter Type DM 01 manufactured by the Wissenschaftlich-Technische Werkstätten, Weilheim, Oberbayern, Germany. Densities of the benzene solutions were measured by weighing 50 ml. in a volumetric flask. Molar refractions were calculated from the atomic refractions, and the polarization P_∞ extrapolated from the measured polarizations. Because the amount of the pure compounds was limited, measurements were made at only two concentrations. However, these values were checked by comparison with the moments calculated from the dielectric constants of the pure polar liquids.

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[46] H. L. Goering, J. P. Blanchard, and E. F. Silversmith, *J. Am. Chem. Soc.*, **76**, 5409 (1954).

[47] The author is indebted to Dr. E. F. Silversmith for pointing out this method of making these rate computations.

[Contribution from the Department of Chemistry of Cornell University, Ithaca, N. Y.]

Lewis Acid Induced Rapid Allylic Rearrangements of 2-Halo-3-hydroxy-2,4-dimethylcyclobutenones. An Unusually Reactive α-Haloketone[1]

By Donald G. Farnum,[2] M. Ann Tyrell Heybey, and Brian Webster

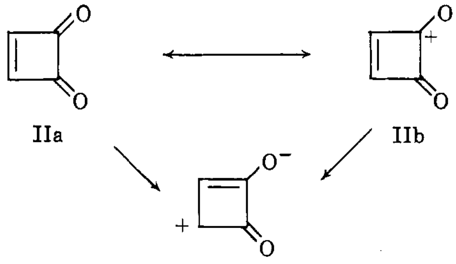
Received August 22, 1963

The n.m.r. spectrum of 3-hydroxy-2,4-dimethylcyclobutenone (X) demonstrates a long-range coupling constant of 2.5 c.p.s. through one double and four single bonds. The spectroscopic properties of X are discussed with reference to its essentially complete enolization. The sharp singlet observed for the methyl resonance in the n.m.r. spectra of 2-bromo-3-hydroxy-2,4-dimethylcyclobutenone (IX) and related compounds in the presence of Lewis acids is interpreted in terms of an allylic rearrangement taking place with a frequency of 100–200 sec.^{-1}. These observations are discussed with reference to the carbonium ion XVIII, a relative of the cyclobutadiene dication I.

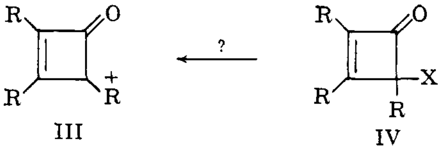
Polyhalogenated cyclobutenes and cyclobutenones have enjoyed the attention of several groups of researchers for some years.[3-8] This attention may be ascribed, in part, to an interest in the compound types as relatives or precursors of derivatives of the potentially stable cyclobutadiene dication I[7] (R = H). Thus the Blomquist group[5] and the Roberts group[4] have prepared several derivatives of cyclobutene-3,4-dione (II) and have investigated their reactions in some detail. The relationship of the π-electron system of these substances to the 2π-electron cyclobutadiene dication system has been discussed by Roberts[9] with reference to the several resonance contributors of type IIa–IIc, and has been popularized in the name "cyclobutadienoquinone."[3] Further, the preparation of stable salts of substituted cyclobutadiene dications has been attempted both by Katz[7] for I (R = CH_3) and by Freedman[8] for I (R = C_6H_5).

The possibility that there might be unusual stability associated with α-ketocarbonium ions of type III and, therefore, unusual reactivity associated with α-haloketones of type IV seemed a natural extrapolation from the above considerations. Further encouragement was afforded by the observations by Roberts that, although enol ether V, for which hydrolysis must proceed through the α-ketocarbonium ion VII,[10] is stable to prolonged heating with aqueous alcoholic acid,[11] enol ether VI, for which hydrolysis probably proceeds through the related carbonium ion VIII, is readily hydrolyzed on brief heating with this reagent. The present article is concerned with some reactions of derivatives of the haloketone IV which could lead through or to carbonium ions of type III.

I



IIa IIb IIc



III IV

The starting point for our investigation was the known bromoketone, 2-bromo-3-hydroxy-2,4-dimethylcyclobutenone (IX).[12] This substance was chosen

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[1] A preliminary account of some of this work has appeared in *Tetrahedron Letters*, 307 (1963).

[2] Fellow of the Alfred P. Sloan Foundation.

[3] J. D. Roberts, *Record Chem. Progr.*, **17**, 95 (1956).

[4] F. B. Mallory and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 871 (1961), and earlier papers.

[5] A. T. Blomquist and E. A. LaLancette, *ibid.*, **84**, 220 (1962), and earlier papers.

[6] J. D. Park, S. Cohen, and J. R. Lacher, *ibid.*, **84**, 2919 (1962).

[7] T. J. Katz, J. R. Hall, and W. C. Neikam, *ibid.*, **84**, 3199 (1962).

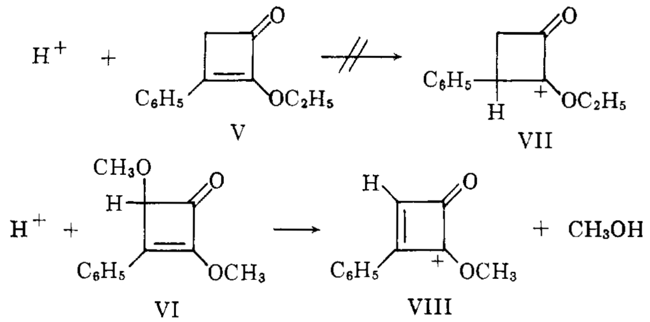
[8] H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

[9] E. J. Smutny, C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

[10] J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 169.

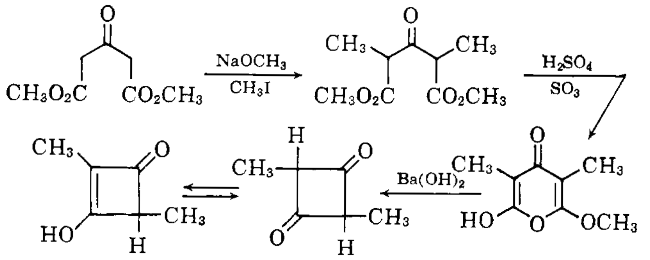
[11] E. I. Silversmith and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 4083 (1958).

[12] R. B. Woodward and G. Small, Jr., *ibid.*, **72**, 1297 (1950).



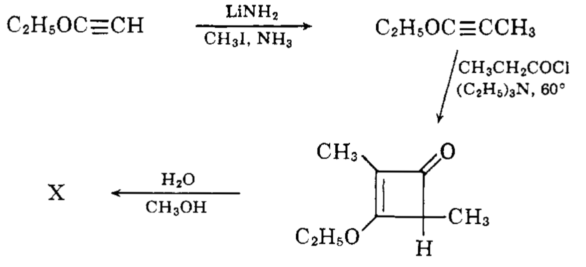
both for the practical reason of its availability, and for the less tangible reasons that the methyl groups would stabilize the anticipated carbonium ion, while the possibility of stabilization by the hydroxyl group provided added opportunity for speculation. Of the several routes available for the preparation of 3-hydroxy-2,4-dimethylcyclobutenone (X), a suitable precursor to bromoketone IX,[12-14] the one described by Woodward and Small and depicted in Chart I, though mechanistically the most obscure, proved experimentally satisfactory. The low over-all yield in this multistep procedure, however, prompted us to examine the applicability of the procedures developed by Wasserman[15a] and Hasek[15b] to the preparation of the intermediate ketone X. As depicted in Chart II, 1-ethoxypropyne was prepared in 55% yield by reaction of ethoxyacetylene with lithium amide and methyl iodide in liquid ammonia. Reaction of the product with propionyl chloride and triethylamine at 40° afforded a 60% yield (based on unrecovered ethoxypropyne) of distilled enol ethyl ether of X (infrared absorption at 5.70 and 6.15 μ; *cf.* ref. 15), which was hydrolyzed directly in aqueous methanol to give a 63% yield of ketone X. The product, 3-hydroxy-2,4-dimethylcyclobutenone (X), has already been well characterized chemically.[12-14] However, the infrared and n.m.r. spectra of the compound, determined in the present work, deserve some comment.

CHART I



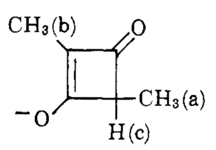
X Xa

CHART II

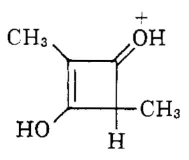


Perhaps the most unusual feature of the infrared spectrum of ketone X was the appearance of broad, creeping absorption from 3.2 to 5.5 μ and from 6.1 to 9.0 μ, with rounded peaks near 4.2 and 5.3 μ (*cf.* ref. 15b). Superimposed upon this structureless, undulating background there was an occasional sharp peak. A peak of only moderate intensity at 5.75 μ constituted the only clear evidence for carbonyl absorption in the infrared. Chloroform solutions of ketone X gave similar spectra. These characteristics seem best interpreted on the basis of the presence of the enolic form X, rather than the diketo form Xa, in the solid state and in chloroform solution. Thus, the strongly acidic[12] enolic hydroxyl would provide a source for the unusual broad absorption from 3.2 to 5.5 μ, while it has been shown that enol ethers related to X exhibit carbonyl absorption near 5.7 μ.[15] The four-membered ring diketone Xa would be expected to absorb at considerably shorter wave lengths (Conia[16] reports 5.63 μ for cyclobutanone, for example; however, see ref. 15b). This interpretation is confirmed by the n.m.r. spectra of ketone X in a variety of solvents.

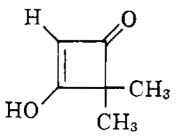
The n.m.r. spectrum of a deuteriochloroform solution of the ketone X exhibited a clean doublet at τ 8.79[17] (coupling constant of 7 c.p.s.), a closely spaced doublet at τ 8.46 (coupling constant of 2.5 c.p.s.), a weak multiplet near τ 6.5, and a singlet at τ −3.40, with area ratios approximately 3:3:1:1. In aqueous solution the spectrum was quite similar, although the peak at −3.40 was not observed, and the peak positions were slightly dependent upon the pH as shown in Table I. The close similarity of these spectra indicates the presence of similar species. Since ketone X (pK_a 2.8[12]) must be present entirely as the enolate anion XI in aqueous potassium carbonate solution, all the other solutions must contain enolate XI, enol X, or the corresponding conjugate acid XII as the only detectable tautomers present. The progressive shift of all peaks toward lower field upon increasing the acidity of the medium, as evident in Table I, is expected for the presence of increasing proportions of the protonated species X and XII in the more acidic medium. It is noteworthy that a rapid interchange of keto and enol forms such as is observed in the n.m.r. spectrum of acetylacetone[18,19] was not observed in the present case. Such a rapid interchange, had it been taking place with a frequency near 100 c.p.s. or more, would have resulted in the two methyl groups becoming indistinguishable in the n.m.r.[18]



XI



XII



XIII

Assignment of the high field doublet to the hydrogens on the methyl group attached to the saturated carbon atom (labeled (a) in formula XI) seems reasonable both by virtue of the position (for example, Wasserman[15a] has found the methyl resonance for the related enol XIII at τ 8.81), and the large coupling constant of 7.0 c.p.s. to the adjacent hydrogen. The lower field doublet then becomes assigned to the hydrogens on the vinyl methyl group (labeled (b) in formula XI), and implies a coupling constant of 2.5 c.p.s. to the far-

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(13) J. Nieuwenhuis and J. F. Arens, *Rec. trav. chim.*, **77**, 761 (1958).

(14) E. B. Reid and S. J. Groszos, *J. Am. Chem. Soc.*, **75**, 1655 (1953).

(15) (a) H. H. Wasserman and E. Dehmlow, *Tetrahedron Letters*, **No. 23**, 1031 (1962); (b) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **27**, 3743 (1962).

(16) J. M. Conia and P. Leriverend, *Compt. rend.*, **250**, 1078 (1960).

(17) The small chloroform peak from $CHCl_3$ present or added was taken as an internal reference and assigned the τ-value of 2.73 relative to tetramethylsilane (TMS) as 10.00. The relative positions of the $CHCl_3$ and TMS peaks were not changed upon addition of $SnCl_5$ or $SnCl_4$.

(18) 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. 223, 440.

(19) L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **36**, 793 (1958).

TABLE I

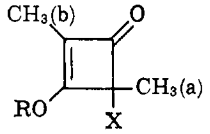
SOLVENT DEPENDENCY OF THE N.M.R. SPECTRUM OF 3-HYDROXY-2,4-DIMETHYLCYCLOBUTENONE

Solvent	Peak positions (τ-values)	Multiplicity	Coupling constant, c.p.s.
10% aq. K_2CO_3	8.98[a]	Doublet	7.0
	8.68	Doublet	2.5
	~7.0	Multiplet	
H_2O	8.90[a]	Doublet	7.0
	8.58	Doublet	2.5
	~6.6	Multiplet	
40% H_2SO_4	8.86[a]	Doublet	7.0
	8.54	Doublet	2.5
96% H_2SO_4	8.65[a]	Doublet	7.0
	8.33	Doublet	2.5
$CDCl_3$	8.79[b]	Doublet	7.0
	8.46	Doublet	2.5
	~6.5	Multiplet	
	−3.40	Singlet	

[a] τ-Values were determined against a tetramethylammonium fluoroborate internal standard taken as τ 6.87 (see Experimental). [b] See ref. 17.

removed methine hydrogen (labeled (c) in XI). In accord with this interpretation the multiplet of peaks near τ 6.5 could correspond to the methine hydrogen experiencing splitting by both sets of methyl hydrogens. Although long-range fluorine-hydrogen coupling has been well documented for small ring compounds,[20a] the observation of such a large coupling between hydrogen atoms removed by one double and four single bonds is, apparently, a rare occurrence.[20b] The authenticity of this long-range coupling was further demonstrated by determination of the n.m.r. spectrum of enol X in 10% potassium carbonate in deuterium oxide. Heating such solutions for a short time resulted in the disappearance of all resolved splitting in the n.m.r. spectrum. Two slightly broadened peaks were observed at τ 8.98 and 8.68, as expected for the removal of coupling to the methine hydrogen by deuterium substitution. Correspondingly there was no resonance in the τ 6 to 7 region ascribable to the methine hydrogen. The sluggishness of the base-catalyzed deuterium exchange of enol X (half-life near 4 hr. at room temperature) may be contrasted with the alacrity with which acetylacetone exchanges its methylene hydrogens in the presence of diethylamine[19] (half-life in the neighborhood of 10^{-3} sec. at 50°). The reluctance to form the necessary diketone intermediate Xa, already noted by Woodward,[12] and emphasized above, is again in evidence.[21]

Reaction of enol X with bromine in carbon tetrachloride afforded 2-bromo-3-hydroxy-2,4-dimethylcyclobutenone (IX), m.p. 158–160°, as reported by Woodward and Small.[12] The structure of bromoketone IX was further demonstrated by the near identity of its infrared and ultraviolet spectra with those of enol X, and by the formation of a liquid methyl ether (XIV; infrared absorption at 5.64, 6.15 μ) upon reaction with diazomethane. The reactivity of bromoketone IX was first examined by the classical silver nitrate test. Although α-haloketones are generally considered to be inert to alcoholic silver nitrate,[22] an immediate precipitate of silver bromide was obtained at 0° by the action of this reagent on α-bromoketone IX. Yet more striking was the formation of an immediate precipitate of silver bromide with anhydrous silver perchlorate in anhydrous acetonitrile, dimethyl sulfoxide, or nitromethane. Although some tertiary α-haloketones do react with aqueous alcoholic silver nitrate, the reaction often requires heating, is accompanied by rearrangement, and appears to require water or ethanol.[22,23] By contrast, the product from the reaction of bromoketone IX with aqueous silver nitrate was the "unrearranged" hydroxyketone, 2,3-dihydroxy-2,4-dimethylcyclobutenone (XV), m.p. 205–210° dec., also obtained simply by permitting an aqueous solution of bromoketone IX to stand at room temperature for 2 days. The structure of the product was demonstrated by the close similarity of its infrared and ultraviolet spectra to those of the bromoketone IX, by its reconversion to the bromoketone IX with hydrogen bromide in chloroform, and by conversion to the chloroketone XVI (m.p. 185° dec., infrared spectrum nearly identical with that of IX) with hydrogen chloride in chloroform.



IX, R = H, X = Br
XIV, R = CH_3, X = Br
XV, R = H, X = OH
XVI, R = H, X = Cl
XVII, R = CH_3, X = H

The n.m.r. spectra of the several substituted derivatives of enol X were as expected for the assigned structures. Thus, as recorded in Table II, bromoketone IX, hydroxyketone XV, and chloroketone XVI each exhibited two sharp singlets for the differently constituted methyl groups. The assignment of the lower field resonance (τ 8.18) in the spectrum of chloroketone XVI to the hydrogens on the methyl group attached to the saturated carbon (methyl group (a) in formula XVI) seems reasonable, since comparison with the similarly constituted methyl group (a) of enol X leads to a downfield shift of 0.61 p.p.m. as a result of substitution of chlorine for hydrogen. This may be compared with the expected downfield shift of 0.62 p.p.m.[24] Substitution of bromine α to a methyl group ordinarily leads to a downfield shift of 0.81 p.p.m.[24] as compared with the 0.82 p.p.m. observed for bromoketone IX. A similar assignment for each of the several electronegatively substituted derivatives of enol X also leads to consistent τ-values for the resonance of the relatively less affected vinyl methyl hydrogens (b) (see Table II).[25]

The reactions observed with these compounds, therefore, suggested an unusual facility for the acceptance of an electron deficiency at the α-carbon atom. Because of the possibility of concerted S_N2' displacement reactions such as observed by Roberts

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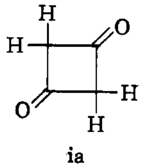
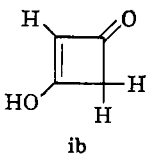
[20] (a) M. Takahashi, D. R. Davis, and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 235 (1962); (b) J. T. Pinhey, *Tetrahedron Letters*, 275 (1963), and references contained therein.

[21] This result is in contrast to that reported by Wasserman[15a] for the parent system, cyclobutane-1,3-dione (i). The single n.m.r. resonance at 6.14 τ observed for $CDCl_3$ solutions of i seems understandable only on the basis of the 1,3-diketo tautomer ia, an unlikely superposition of chemical shifts in enol tautomer ib, or a rapid equilibrium between ia and ib. It may be noted that the infrared carbonyl absorption of i in $CHCl_3$ (5.70 μ)[15a] compares closely with that of enol X (5.72 μ).



ia



ib

[22] C. L. Stevens and E. Farkas, *J. Am. Chem. Soc.*, **74**, 5352 (1952).

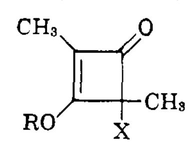
[23] A. C. Cope and E. S. Graham, *ibid.*, **73**, 4702 (1951). The observation by Cope that a bridgehead bromoketone rearranged more readily than an open chain ketone suggests the need for concerted rearrangement, and the probable absence of carbonium ion intermediates in these reactions.

[24] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959 p. 53.

[25] In the case of hydroxyketone XV the assignment is ambiguous because of the very similar chemical shifts of the methyl hydrogens.

TABLE II

PROTON N.M.R. CHEMICAL SHIFTS OF SOME CYCLOBUTENONES



Compound	R	X	Solvent	Acid	Peak position[a] (τ-values)
XVI	H	Cl	$CDCl_3$	None	8.18, 8.36
				$SbCl_5$	7.92
XIV	CH_3	Br	$CDCl_3$	None	5.78, 8.11, 8.29
				$SbCl_5$	5.23, 7.78
IX	H	Br	CD_3COCD_3	None	8.24, 8.48[e]
			$CDCl_3$	$SnCl_4$	8.12
XV	H	OH	H_2O	None	8.48, 8.59
			96% H_2SO_4		8.02
X	H	H	$CDCl_3$	None	8.46,[b] 8.79[c]
			$CDCl_3$	$SbCl_5$	8.13,[b] 8.46[c]
			$CDCl_3$	$SnCl_4$	8.31,[b] 8.64[c]
			H_2O	None	8.58,[b] 8.90[c]
			96% H_2SO_4		8.33,[b] 8.65[c]
XVII	CH_3	H	$CDCl_3$	None	6.05, 6.8[d] 8.52,[b] 8.99[c]
				$SbCl_5$	5.64, 5.9[d] 8.20,[b] 8.59[c]
IX	H	Br	96% H_2SO_4		7.83, 8.14
XVI	H	Cl	96% H_2SO_4		7.99, 8.14

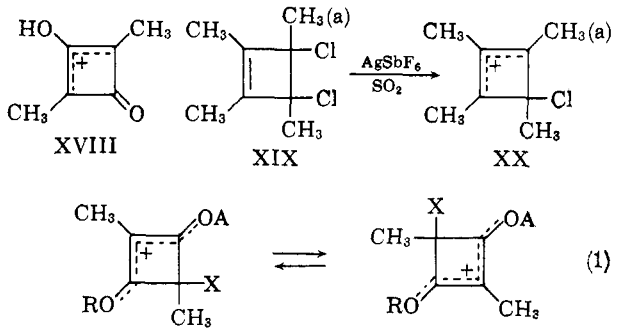
[a] For $CDCl_3$ solutions see ref. 17; for H_2O and H_2SO_4 solutions see Table I, *footnote a*. [b] Doublet, coupling constant 2.5 c.p.s. [c] Doublet, coupling constant 7.0 c.p.s. [d] Weak multiplet. [e] The low solubility of bromoketone IX in $CDCl_3$ prevented a satisfactory determination of its n.m.r. spectrum in that solvent although a broad envelope near τ 8.17 was observed at high amplitudes.

in closely related systems,[26] however, it could not be concluded with certainty that the α-keto carbonium ion XVIII (Chart III) was involved. Furthermore, the question of the relative effectiveness of the double bond and the closed π-system in stabilizing the possible intermediate could not be answered. We, therefore, undertook an investigation of the n.m.r. spectra of a number of derivatives of enol X under conditions which might lead to the formation of detectable amounts of the carbonium ion XVIII in order to obtain more decisive evidence bearing upon its stability.

From the numerous data in the recent literature[7,27] it was clear that carbonium ion XVIII would exhibit n.m.r. absorption for the methyl hydrogens at considerably lower τ-values than would the covalent compounds. The formation of appreciable amounts of the carbonium ion from covalent compounds such as XVI would, therefore, be evidenced in the n.m.r. as the replacement of the two different methyl resonances observed for the covalent compounds by a single resonance peak at lower field for the two equivalent methyl groups of carbonium ion XVIII. Reference to the data presented in Table II shows that just this kind of behavior is, in fact, observed when the haloketones IX, XIV, and XVI are treated with the Lewis acids antimony pentachloride or stannic chloride in deuteriochloroform solution, or when the hydroxyketone XV is dissolved in 96% sulfuric acid.[28] In each case a sharp *single* peak appears in the n.m.r. spectrum, shifted 0.26 to 0.57 p.p.m. downfield from the *two* peaks observed in the absence of added acid.

Although the n.m.r. spectra of these solutions are thus qualitatively in accord with the presence of the carbonium ion XVIII, a comparison with numerical data from the literature reveals the inadequacy of this hypothesis alone to explain the observed small magnitudes of the downfield shifts. Thus, Katz[7] finds the proton resonance for the terminal methyls on the cyclobutenyl cation XX (methyl group (a) in formula XX, Chart III) at τ 7.0 in liquid sulfur dioxide solution—a shift of 1.27 p.p.m. downfield from that at τ 8.27 for the corresponding covalent chloride XIX in carbon tetrachloride solution (methyl group (a) in formula XIX, Chart III). Deno[27] reports a τ-value of 6.93 for similarly constituted methyl groups on allylic carbonium ions. An estimate of the value expected for the methyl proton n.m.r. absorption in keto carbonium ion XVIII can be reached in the following way. A comparison of keto carbonium ion XVIII with chlorocarbonium ion XX (see Chart III) suggests that two major factors would be expected to contribute to a difference in the proton resonance for the terminal allylic methyl groups: (1) the substitution of a carbonyl group in XVIII for the methyl chlorocarbinyl group in XX, (2) the substitution of a hydroxyl group on the central carbon atom of the allylic system of XVIII for the methyl group in XX. The first effect can be estimated to cause a downfield shift of less than 0.1 p.p.m. by a comparison of the resonance of methyl group (a) for chloroketone XVI (τ 8.18) with that for the dichlorocyclobutene XIX (τ 8.27).[7,29] The effect of the second factor is more difficult to assess. However, a crude estimate can be obtained by a comparison of the n.m.r. spectrum of a sulfuric acid solution of enol X (see Table II), which presumably contains its conjugate acid XII, with that of a liquid sulfur dioxide solution of the Katz cyclobutenyl cation XX[31]

CHART III



XII, R = A = X = H
XXI, R = H, X = Cl, A = $SbCl_5^-$
XXII, R = X = H, A = $SbCl_5^-$
XXIII, R = A = H, X = OSO_3H

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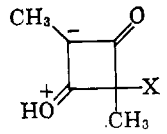
(26) M. C. Caserio, H. E. Simmons, Jr., A. Johnson, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3102 (1960); Y. Kitahara, M. C. Caserio, F. Scardiglia, and J. D. Roberts, *ibid.*, **82**, 3106 (1960); E. F. Jenny and J. Druey, *ibid.*, **82**, 3111 (1960).

(27) N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, *ibid.*, **84**, 1498 (1962).

(28) Dilution of the sulfuric acid solutions of hydroxyketone XV with ice regenerated the n.m.r. doublet of the hydroxyketone.

(29) The contrasting small upfield shift of 0.01 p.p.m. observed for the vinyl methyls (b) (8.35 and 8.36) leads one to suspect a compensating upfield shift of about 0.1 p.p.m. brought about by the hydroxyl group as depicted in resonance contributor ii. A similar upfield shift is observed for the β-olefinic protons of some enol ethers.[30]



ii

(30) Reference 24, p. 62.

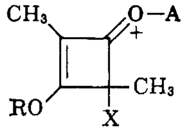
(31) It has been observed by C. F. Wilcox and D. Nealy that sulfuric acid solutions of the dichloride XIX exhibit a single n.m.r. peak at τ 7.43, very near the weighted average (τ 7.26) of the three peaks observed by Katz for carbonium ion XX in liquid sulfur dioxide.[32] Thus, there seems to be, at most, only a small solvent effect on the *chemical shifts*, and a comparison of

(see Chart III). The proton resonance for the methyl group on the central carbon atom of allylic carbonium ion XII, subjected to the electron-donating effects of two hydroxyl groups, appears at τ 8.33 while that for the central methyl group in allylic carbonium ion XX, subjected to the electron-donating influence of two methyl groups, appears near τ 7.5.[7] Thus an upfield shift of 0.8 p.p.m. is effected by the two hydroxyls. It seems certain that the effect of the single hydroxyl group substituted on the central carbon atom of allylic carbonium ion XVIII will be considerably less than 0.8 p.p.m. It also seems certain that it will be considerably greater than the 0.1 p.p.m. shift observed for the covalent chloroketone XVI (see footnote 29). An upfield shift of 0.2 to 0.6 p.p.m. is probably a good estimate for the expected range of the effect of this substituent. The net upfield shift expected for the methyl resonance in keto carbonium ion XVIII as compared with cyclobutenyl cation XX is, then, 0.1 to 0.5 p.p.m. This leads to an expected τ-value for the methyl resonance in keto carbonium ion XVIII of 7.1 to 7.5—well below the 7.8 to 8.1 actually observed. An alternative explanation for the observed singlet in the n.m.r. spectra of the haloketones IX, XIV, and XVI in the presence of Lewis acids, and the hydroxyketone XV in sulfuric acid, must therefore be sought.

The hypothesis of an antimony pentachloride complex of the haloketones, such as XXI in which the methyl groups appear equivalent in the n.m.r. because of a rapid (100 to 200 sec.$^{-1}$)[18] allylic chloride migration as depicted in eq. 1 (Chart III), is also qualitatively in accord with the data. That it also provides a reasonable quantitative fit with the downfield shifts actually observed can be shown by an examination of the shifts brought about in the n.m.r. spectrum of enol X in the presence of acids. For example, as shown in Table II, both methyl resonances in deuteriochloroform solutions of the enol X are shifted downfield by 0.33 p.p.m. upon addition of excess antimony pentachloride.[33] These solutions most probably contain the oxonium complex XXII, and therefore a similar shift would be expected for the conversion of chloroketone XVI to the related complex XXI. The average of the downfield shifts observed for the two methyl groups of chloroketone XVI upon addition of antimony pentachloride (0.26 and 0.44 p.p.m.) is 0.35 p.p.m.—remarkably close to the 0.33 p.p.m. shift observed for enol X. An alternative method of presenting these data is given in Table III. Here the expected position of the n.m.r. absorption for a rapidly equilibrating Lewis acid complex of the electronegatively substituted derivatives of enol X is calculated from the observed n.m.r. spectrum of the Lewis acid complex of enol X, and the expected shift in the methyl resonances[34] upon substitution of the appropriate electronegative group for the α-hydrogen.

TABLE III

CALCULATED AND OBSERVED CHEMICAL SHIFTS FOR LEWIS ACID COMPLEXES OF SOME HYDROXYCYCLOBUTENONES



R	X	A	Chemical shift (τ-values) Calcd.[a]	Chemical shift (τ-values) Obsd.
H	H	$SbCl_6^-$		8.30[a]
H	Cl[b]	$SbCl_5^-$	7.94	7.92
H	H	H		8.49[a]
H	OSO_3H[c,d]	H	8.18	8.02
H	H	$SnCl_4^-$		8.47[a]
H	Br[b]	$SnCl_4^-$	8.00	8.12
CH_3	H	$SbCl_5^-$		8.23
CH_3	Br[b]	$SbCl_5^-$	7.76	7.78

[a] Calculated average of the chemical shifts of the methyls. [b] Values for the expected downfield shift taken from ref. 24, p. 53. [c] Assumed substituent upon solution of alcohol XV in 96% sulfuric acid. [d] Value for the expected downfield shift taken from a comparison of the methyl resonances of ethyl alcohol (τ 8.58) and *n*-hexyl alcohol (τ 9.11) in 96% sulfuric acid.

From the data presented in Table III it seems clear that the *keto carbonium ion XVIII is not present in appreciable amounts* in the systems investigated, although its presence in small concentrations as an intermediate in the rapid allylic rearrangement depicted in eq. 1 (Chart III) is not excluded. This apparent reluctance of ketocarbonium XVIII to be formed as compared with the chlorocyclobutenyl cation XX may find an explanation, in part, in the poor ionizing ability of the chloroform solvent. The importance of a solvent effect in deuteriochloroform solutions is confirmed by the observation that deuteriochloroform solutions of the dichlorocyclobutene XIX in the presence of stannic chloride give a singlet in the n.m.r. at τ 8.24. This may be compared with the spectrum in the absence of stannic chloride, which exhibits peaks at τ 8.25 and 8.40. Thus there is little, if any, of the chlorocyclobutenyl cation XX present in these solutions, although there is a rapid allylic rearrangement resulting in equivalence of the methyls. This solvent effect cannot be the only important factor, however, since appreciable ionization of the dichlorocyclobutene XIX to the chlorocyclobutenyl cation XX takes place in 96% sulfuric acid,[31,32] while there can be, at best, some 25% of the ketocarbonium ion XVIII in equilibrium with the covalent sulfate in 96% sulfuric acid solutions of hydroxyketone XV.[35] Furthermore, *bromoketone IX is completely resistant to solvolysis in 96% sulfuric acid* over several days at room temperature as evidenced by the unchanged appearance of the two singlets in the n.m.r. at τ 7.83 and 8.14. It must be concluded that any special stability associated with the closed π-electron system of ketocarbonium ion XVIII as compared with chlorocyclobutenium ion XX is more than compensated by the increased electronegativity of the protonated carbonyl function in complex XVIII, as compared with the methyl and chlorine substituents in dichlorocyclobutene XIX.

Alternative methods for the preparation of salts of ketocarbonium ion XVIII, and the possibility of its intermediacy in the rapid allylic rearrangements encountered in this work, are under investigation.

Experimental[36]

Determinations of the n.m.r. spectra were accomplished with a Varian A-60 60-Mc. spectrometer. Spectra taken in deuteriochloroform solution were referenced against the internal chloroform present (or added in small amount) and independently

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sulfuric acid and sulfur dioxide solutions is probably justified.

(32) C. F. Wilcox, private communication.

(33) The assignment of the methyl resonances is unequivocal by virtue of the near constancy of the coupling constants for each methyl to the methine hydrogen.

(34) The shift in the vinyl methyl resonance was estimated to be one-sixth that for the methyl attached to the saturated carbon. This factor was reached on the basis of a comparison of the relative shifts of the two methyl groups upon substitution of the hydrogen in enol X by the chlorine in chloroketone XVI.

(35) This number is obtained from the data in Table III and the maximum estimated τ-value for the methyls in ketocarbonium ion XVIII (7.5). Thus the observed chemical shift (τ 8.02) falls downfield from the calculated value for the rapidly equilibrating complex XVIII (τ 8.18) by one-quarter the distance to the calculated value for ketocarbonium ion XVIII.

(36) Melting points and boiling points are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories.

determined to be 2.73 on the τ-scale with TMS as an internal reference. This was necessary in order to avoid the deterioration of the TMS reference peak observed in some samples with added antimony pentachloride. It was demonstrated that the separation of the chloroform and TMS peaks in deuteriochloroform solution was unchanged immediately after the addition of antimony pentachloride or stannic chloride. Aqueous and acidic solutions were referenced against internal tetramethylammonium fluoroborate (TMA, Chemicals Procurement Laboratories, Inc., College Point 56, N. Y.). The chemical shift of TMA in aqueous solution was determined to be 6.87 ± 0.02 p.p.m. on the τ-scale in several determinations against acetonitrile (τ 7.98) and dioxane (τ 6.30) as internal standards.[37] Furthermore, the separation between the peak characteristic of TMA and that of tropylium fluoroborate remained at 5.93 ± 0.01 p.p.m. in water, 50% aqueous sulfuric acid, and 96% sulfuric acid. It should be noted that, although the TMA resonance appears broadened in acetonitrile and can be resolved into a triplet, it appears as a quite sharp singlet in aqueous mixtures.

Samples for n.m.r. determinations were made up by mixing the components near 0° and running the spectra within 30 min. whenever Lewis acids or sulfuric acid were present. The spectra were determined at room temperature, however.

2,4-Dimethyl-3-hydroxycyclobutenone (X). (a) **By the Procedure of Woodward and Small.**[12]—Dimethyl acetonedicarboxylate (200 g., 1.15 moles) was condensed with methyl iodide (332 g., 2.37 moles) and sodium methoxide [from sodium (52.8 g., 2.29 g.-atoms) and methanol (520 ml.)] to give dimethyl α,α'-dimethylacetonedicarboxylate (182 g., 78%). The α,α'-dimethyl derivative (162 g., 0.80 mole) was added dropwise with stirring to a mixture of concentrated and fuming sulfuric acid (600 g. containing 7–8% free SO_3)[38] at 5–6°. After standing at room temperature overnight the solution was diluted with ice (900 g.), which precipitated 3,5-dimethyl-6-methoxy-2,4-pyronone (50 g., 37%). The pyronone (25 g., 0.17 mole) was washed free of acid, dried, and added to a hot suspension of barium hydroxide octahydrate (150 g., 0.36 mole) in water (150 ml.). After 2 hr. excess barium was removed by precipitation with carbon dioxide followed by filtration. The filtrate was evaporated almost to dryness, acidified with a little concentrated hydrochloric acid, and the remaining moisture removed under reduced pressure. The 2,4-dimethyl-3-hydroxycyclobutenone (X, 3.59 g., 22%) was extracted from inorganic material with hot benzene. It had m.p. 129–131° (lit.[12] 130–131°); infrared: λ_{max} (Nujol) 4.2 (w), 5.75 (m), 6.8 (s), 7.7 (s) μ; ultraviolet: λ_{max} (EtOH) 252 mμ, ϵ 1.6 × 10^4.

The over-all yield of X from dimethyl acetonedicarboxylate was 6.3%.

(b) **From Propionyl Chloride and 1-Ethoxypropyne.** (i) **1-Ethoxypropyne.**—In a 1-l. 3-necked round-bottomed flask fitted with a mechanical stirrer, dropping funnel, and Dry Ice condenser were placed liquid ammonia (500 ml.) and a crystal or two of ferric nitrate. To the mixture was added small pieces of lithium wire (8.75 g., 1.25 moles) and after the blue color had completely disappeared, ethoxyacetylene (70 g., 1.0 mole) was added with stirring over a period of 20 min. Next, methyl iodide (173 g., 1.25 moles) was added dropwise as quickly as practical in view of the vigorous exothermic reaction. This was followed by ether (100 ml.) and the mixture was stirred for a further 3 hr., after which ammonium chloride (15 g., 0.28 mole) was introduced, the Dry Ice condenser changed for a water-cooled condenser, and the liquid ammonia left to evaporate slowly overnight. After all the ammonia had evaporated, water (250 ml.) was added and the liquid layers were separated. The aqueous layer was extracted with ether and the extracts were combined with the separated organic layer. After drying over sodium sulfate the solution was distilled on an efficient fractionating column to yield ethoxypropyne (52.5 g., 55%), b.p. 90–92° at atmospheric pressure (lit.[39] 88–90.5°).

(ii) **2,4-Dimethyl-3-ethoxycyclobutenone.**—A mixture of propionyl chloride (9.25 g., 0.1 mole) and 1-ethoxypropyne (4 g., 0.048 mole) was added dropwise with vigorous stirring to a mixture of triethylamine (10 g., 0.1 mole) and ethoxypropyne (6 g., 0.071 mole) at 60° over a period of 10 min.[40] Dry ether (25 ml.) was added and the mixture filtered free of precipitated triethylamine hydrochloride (13.2 g., 98%). The filtrate was distilled and unchanged ethoxypropyne (5.7 g., 0.068 mole) recovered.

The infrared spectrum of the residue (7.8 g.) contained peaks characteristic of the β-lactone dimer of methyl ketene together with those characteristic of the enol ethyl ether of X. It was subjected to a pressure of 0.05 mm. at room temperature overnight. This resulted in the removal of the lactone dimer (0.8 g.) isolated from the cold traps and identified by infrared comparison with an authentic sample.[41] Pure 2,4-dimethyl-3-ethoxycyclobutenone (4.3 g., 60% based on unrecovered ethoxypropyne) was obtained by distillation. It had b.p. 97–98° (11 mm.) [lit.[42] 102° (12 mm.)]. A tarry residue (2.7 g.) remained in the distillation flask.

(iii) **Hydrolysis of the Enol Ethyl Ether of X.**—The ethyl ether obtained above (4.3 g., 0.031 mole) was dissolved in 70% aqueous alcohol (15 ml.) to which 2 or 3 drops of concentrated hydrochloric acid had been added. After standing at room temperature overnight the mixture was evaporated under reduced pressure leaving a crystalline solid in a yellowish oil. The solid was washed with cold benzene and proved to be almost pure 2,4-dimethyl-3-hydroxycyclobutenone (X) (2.2 g., 63%), m.p. 133–134°, alone or on admixture with the product from the Woodward–Small procedure. The over-all yield of X based upon unrecovered ethoxypropyne was 38%.

2-Bromo-2,4-dimethyl-3-hydroxycyclobutenone (IX).—To dimethylhydroxycyclobutenone (X) (1 g., 8.9 mmoles) suspended in carbon tetrachloride (20 ml.) was added a solution of bromine (0.15 g., 9.4 mmoles) in the same solvent (10 ml.). The solution became clear and after a very few minutes hydrogen bromide began to be evolved while a white precipitate began to separate. After 30 min. the mixture was almost colorless and the precipitate was filtered. The crude bromo compound IX (1.5 g., 88%) was crystallized twice from ethyl acetate. It had m.p. 158–159° (lit.[12] 158°); infrared: λ_{max} (Nujol) 4.3 (w), 5.72 (m), 6.8 (s), 7.7 (s), 13.1 (w), 14.4 (s) μ; ultraviolet: λ_{max} (Et_2O) 228 mμ, ϵ 1.27 × 10^4.

Anal. Calcd. for $C_6H_7O_2Br$: C, 37.73; H, 3.70; Br, 41.84. Found: C, 37.88; H, 3.82; Br, 41.43.

The bromine atom in compound IX was found to be very labile and could be replaced easily by hydroxyl (see below). Solutions of IX in water, anhydrous alcohol, anhydrous acetonitrile, dimethyl sulfoxide, or nitromethane gave immediate precipitates with silver nitrate or perchlorate.

2,3-Dihydroxy-2,4-dimethylcyclobutenone (XV).—A solution of the bromide IX (0.35 g., 1.6 mmoles) in distilled water (5 ml.) was added to a solution of silver nitrate (0.5 g., 2.9 mmoles) in the same volume of distilled water contained in a small liquid–liquid extraction apparatus. A precipitate of silver bromide formed immediately, and after 5 min. the mixture was saturated with sodium chloride to remove excess silver ions. The mixture was extracted continuously with ether for 40 hr. after which time white needles had separated in the receiver. The ether was evaporated almost to dryness and the product filtered. Without further purification, the 2,3-dihydroxy-2,4-dimethylcyclobutenone (XV) (0.18 g., 72%) so obtained had m.p. 205–210° dec.; infrared: λ_{max} (Nujol) 2.96 (m), 5.72 (w), 6.9 (s), 7.6 (s), 11.25 (m) μ; ultraviolet: λ_{max} (H_2O) 248 mμ, ϵ 1.7 × 10^4; λ_{max} (Et_2O) 238 mμ, ϵ 1.4 × 10^4.

Anal. Calcd. for $C_6H_8O_3$: C, 56.25; H, 6.25. Found: C, 55.89; H, 6.31.

Reconversion of XV to the Bromide IX.—In a 50-ml. round-bottomed flask equipped with a gas inlet tube, thermometer, and magnetic stirrer bar was placed the alcohol XV (26 mg., 0.2 mmole) suspended in chloroform (10 ml.). The mixture was cooled, with stirring, to 10° and anhydrous hydrogen bromide bubbled through for 20 min. The temperature rose slowly while the suspended solid appeared to dissolve to give a yellow solution. On stirring for a further 20 min. a solid was again precipitated. This was collected (16 mg. 41%, m.p. 155–160°) and washed with a little benzene. It was shown to be identical with IX by its infrared spectrum.

2-Chloro-2,4-dimethyl-3-hydroxycyclobutenone (XVI).—In the same apparatus as in the previous experiment the alcohol XV (0.12 g., 0.94 mmole) in chloroform (20 ml.) was treated with anhydrous hydrogen chloride for 10 min. at 6°. The mixture was allowed to warm to room temperature while the gas was passed for a further 5 min. and the solid went into solution. After 1 hr. stirring at room temperature an oil had separated. The chloroform was removed by evaporation and the oily residue treated with benzene which caused it to solidify partially. The solid was filtered (77 mg., 56%) and crystallized from ethyl acetate. The chloride so obtained had m.p. 185° dec.; infrared: λ_{max} (Nujol) 4.3 (w), 5.72 (m), 6.8 (s), 7.7 (s), 12.95 (m), 14.05 (w) μ.

Anal. Calcd. for $C_6H_7O_2Cl$: C, 49.15; H, 4.81; Cl, 24.19. Found: C, 49.06; H, 4.88; Cl, 24.02.

2,4-Dimethyl-3-methoxycyclobutenone (XVII).—To 2,4-dimethyl-3-hydroxycyclobutenone (X, 0.5 g., 4.5 mmoles) suspended in dry ether (25 ml.) was added a slight excess of diazomethane in ethereal solution. On removal of the solvent the methyl ether was obtained as a yellow oil. It was purified by distillation (0.4 g., 72%) at atmospheric pressure, b.p. 209–210° (lit.[12] b.p. 209°); infrared: λ_{max} (neat) 5.72 (s), 6.15 (s), 6.9 (s), 7.2 (s), 7.4 (s), 7.65 (s), 10.4 (s) μ.

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[37] R. A. Y. Jones, A. R. Katritzky, J. N. Murrell, and N. Sheppard, *J. Chem. Soc.*, 2576 (1962).

[38] See ref. 12. In the description of this experiment in the original paper the amounts of fuming and concentrated acid have become transposed.

[39] J. F. Arens, *Rec. trav. chim.*, **74**, 275 (1955).

[40] Compare ref. 15.

[41] J. C. Sauer, *J. Am. Chem. Soc.*, **69**, 2444 (1947).

[42] J. Nieuwenhuis and J. F. Arens, *Rec. trav. chim.*, **77**, 766 (1958).

2-Bromo-2,4-dimethyl-3-methoxycyclobutenone (XIV).—The bromo compound IX (0.2 g., 1 mmole) suspended in dry ether (15 ml.) was treated with a slight excess of diazomethane in ethereal solution. Evaporation of the solvent left a yellow oil which was purified by distillation on a "molecular still" at 47–50° (0.05 mm.). On exposure of the oil to the atmosphere for a short while, crystals of IX were deposited. Erratic analytical results were obtained for this compound, evidently as a result of its facile hydrolysis; infrared: λ_{max} (neat) 5.63 (s), 6.15 (s), 7.2 (s), 7.4 (s), 8.0 (s), 10.3 (s), 13.1 (m), 14.65 (m) μ.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRANDEIS UNIVERSITY, WALTHAM, MASS., AND CHEMISTRY DEPARTMENT, ITEK CORP., LEXINGTON, MASS.]

Small Ring Bicyclic Azo Compounds and Bicyclic Hydrocarbons. Isomerization of Bicyclo[2.1.0]pentane and Bicyclo[2.2.0]hexane

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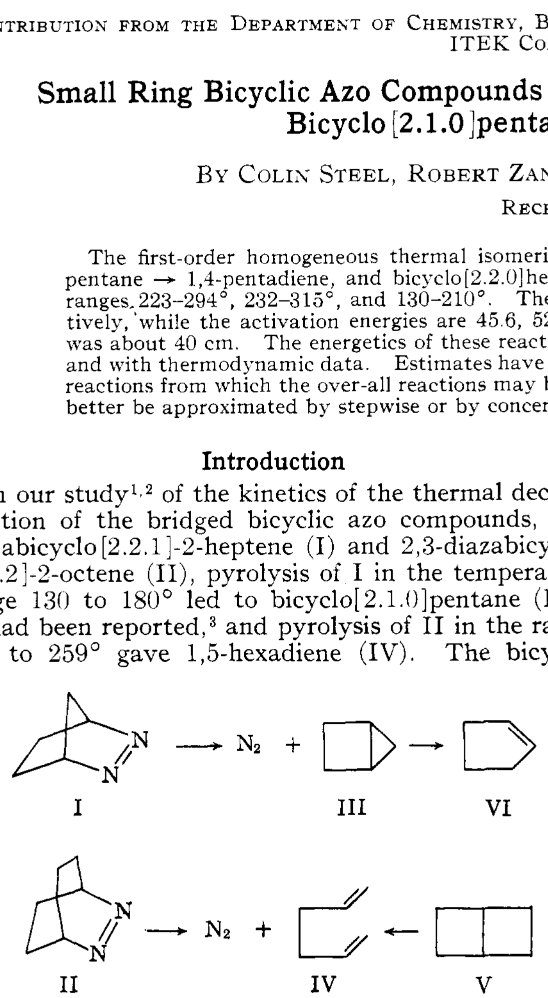
The first-order homogeneous thermal isomerizations bicyclo[2.1.0]pentane → cyclopentene, bicyclo[2.1.0]pentane → 1,4-pentadiene, and bicyclo[2.2.0]hexane → 1,5-pentadiene have been studied in the temperature ranges 223–294°, 232–315°, and 130–210°. The frequency factors are $10^{14.1}$, $10^{14.4}$, and $10^{13.4}$ sec.$^{-1}$, respectively, while the activation energies are 45.6, 52.3, and 36.0 kcal. mole^{-1}. In all cases the reaction pressure was about 40 cm. The energetics of these reactions are compared with those of other small-ring hydrocarbons and with thermodynamic data. Estimates have been made of the activation energies for the various elementary reactions from which the over-all reactions may be regarded as compounded to see whether the mechanisms can better be approximated by stepwise or by concerted processes.

Introduction

In our study[1,2] of the kinetics of the thermal decomposition of the bridged bicyclic azo compounds, 2,3-diazabicyclo[2.2.1]-2-heptene (I) and 2,3-diazabicyclo-[2.2.2]-2-octene (II), pyrolysis of I in the temperature range 130 to 180° led to bicyclo[2.1.0]pentane (III), as had been reported,[3] and pyrolysis of II in the range 199 to 259° gave 1,5-hexadiene (IV). The bicyclic hydrocarbon III has been reported to be stable at 230° and to isomerize at 330° to cyclopentene (VI),[3] whereas V, which was obtained in low yield from the photolysis of bicyclo[3.2.0]heptanone-2, has been reported to isomerize to IV at 230°.[4] The absence of V as a product in the pyrolysis of II under the above experimental conditions is consistent with this latter isomerization. It seemed, therefore, of interest to examine the kinetics of the isomerization of III to cyclopentene, and to attempt the preparation of V and to examine its isomerization. While this work was in progress a study of the isomerization of III to cyclopentene was reported.[5] Our experiments were carried out over a wider temperature range, 223–294° as compared with 288–310°, and using a different technique. Although our results agree with and amplify those reported, our interpretations differ.



Experimental

Bicyclo[2.1.0]pentane (III).—The preparation of III was effected by pyrolysis of I for 15 hr. at 170°. From our earlier work[1] we know that this corresponds to 22 half-lives for the first-order decomposition of I. The infrared spectrum of III agreed exactly with that given by Criegee and Rimmelin,[3] while gas chromatographic analysis showed that this procedure gave less than 0.3% of VI as an impurity. The most satisfactory gas chromatographic column consisted of a series of two packings, 1 ft. of 20% (by weight) silicone oil Dow 710 on Chromosorb W followed by 3 ft. of 30% silver nitrate–ethylene glycol on Chromosorb W.[6] The nuclear magnetic resonance spectrum of III agreed exactly with that reported by Chesick.[7]

Bicyclo[2.2.0]hexane (V).—Small amounts of V (*ca.* 3 mg.) were prepared by the photolysis of carefully degassed samples of II (*ca.* 0.1 g.) using light from an Osram 100-w. high-pressure mercury arc which had been passed through a Corning 7-54 filter. Prolonged exposure (*ca.* 5 days) was necessary because of the strong fluorescence of II. The photolysis yielded a high boiling tarry product and a volatile liquid fraction. This liquid was analyzed by gas chromatography using the above-mentioned column and one consisting simply of 30% silver nitrate–ethylene glycol on Chromosorb W. In both cases three fractions in the ratio 0.16:0.11:0.73 were obtained. The short gas chromatographic retention time (r.t.) of the first fraction on the latter column indicated the absence of unsaturation. This was confirmed by the infrared spectrum, taken in the region 2–13 μ, which showed no absorption at 6.1 μ. Peaks were obtained at 3.44 (s), 3.53 (shoulder), 6.96 (w), 8.06 (w), and 10.96 (w) μ. With the exception of the weak absorption at 8.06 μ this agrees well with the spectrum for bicyclo[2.2.0]hexane reported by Cremer and Srinivasan[4]; *viz.*, 3.46 (s), 3.52 (shoulder), 6.98, (w) and 11.0 (w) μ. It does not agree with the spectrum reported for bicyclo-[2.1.1]hexane.[8] Mass spectrometry (Bendix, ionizing voltage 70 e.v., trap current 0.2 μa.) showed that the mol. wt. was 82. The major peaks occurred at masses 27, 39, 41, 54, and 67, with relative intensities 55.5, 75.9, 92.6, 83.3, and 100. These data, together with the fact that the material isomerized readily to 1,5-hexadiene at temperatures above 130°, confirm that the product is indeed bicyclo[2.2.0]hexane. The major component of the liquid fraction from the photolysis (73%) was biallyl. It was characterized by its r.t. and infrared spectrum. The minor product had the same r.t. as cyclohexene.

Isomerization of Bicyclo[2.1.0]pentane (III) to Cyclopentene (VI).—The isomerization was carried out in two ways. (a) A sample of III (*ca.* 1 μl.) which had been purified by gas chromatography was transferred from the gas chromatographic fraction collector into a small thin-walled ampoule (0.25 cc.). The ampoule was then sealed under a vacuum of 10^{-5} mm. and placed in a rapidly stirred salt bath, the temperature of which was kept constant to ±0.05°. The temperature was read on an N.B.S.

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