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RAPID ALLYLIC REARRANGEMENTS IN 2-HALO-3-HYDROXY-2,4-DIMETHYLCYCLOBUTENONES

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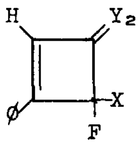
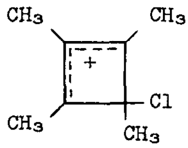
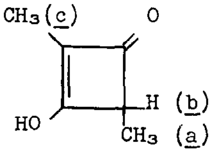
APPLICATION of the technique of Nuclear Magnetic Resonance spectroscopy (NMR) to a study of cyclobutene derivatives has led to several recent reports of unusual results. As representative of two types of such results may be cited the long range fluorine-hydrogen coupling constants observed by Roberts[2] in the NMR spectra of halogenated cyclobutenes of type I, and the demonstration of the structure of the 4-chlorotetramethyl cyclobutenyl cation II by Katz.[3] We report here some results of



I, X=halogen
Y=halogen or =o



II



III

our investigation of the properties of 3-hydroxy-2,4-dimethylcy-

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[1] Fellow of the Alfred P. Sloan Foundation

[2] C. M. Sharts and J. D. Roberts, *J. Amer. Chem. Soc.* 79, 1008 (1957).

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

clobut-2-enone (III) and its derivatives.

The NMR spectrum[4] of the ketone III[5] in aqueous potassium carbonate[6,7] exhibited a high field doublet at 8.90 τ (relative area 3.0, coupling constant 6 cps) which could be assigned to the methyl hydrogens (*a*) split by methine (*b*) with the appropriate coupling constant. The lower field peak at 8.58 τ (relative area 2.9) was split into a *doublet* with a coupling constant of 2.5 cps. This peak must correspond to methyl hydrogens (*c*) by virtue of its position and intensity, but evidences a long-range splitting of these hydrogens, presumably by methine (*b*) five bonds away. This interpretation is confirmed by the appearance of a multiplet (at least 10 peaks, relative area approximately 0.8) centered near 6.8 τ corresponding to the methine hydrogen (*b*) experiencing splitting by *both* sets of methyl hydrogens (*cf.* ref. 9).

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[4] NMR spectra were determined on a Varian A60 NMR spectrometer at 60 megacycles.

[5] R. B. Woodward and G. Small, Jr., *J. Amer. Chem. Soc.* **72**, 1297 (1950).

[6] The close similarity of the NMR spectra of hydroxyenone III in chloroform and in aqueous potassium carbonate (in which it must be completely ionized) establishes beyond doubt that the enol form III is the only important tautomer present in chloroform.

[7] Chemical shifts in aqueous mixtures are reported in τ values relative to tetramethylsilane. Determination of the values was accomplished by using tetramethylammonium tetrafluoroborate as an internal standard. The chemical shift in the tetramethylammonium ion was determined to be 6.87± .01 against acetonitrile and dioxane[8] as internal standards.

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

[9] M. Takahashi, D. R. Davis and J. D. Roberts, *J. Amer. Chem. Soc.* **84**, 2935 (1962).

The ketone III was readily converted to 5-bromo-3-hydroxy-2,4-dimethylcyclobut-2-enone (IV), m.p. 158-160°, by bromination in carbon tetrachloride as reported by Woodward and Small.[5] Bromoketone IV could be converted to a liquid methyl ether (V) with diazomethane in ether at 0°, or to the crystalline chloroketone VI, m.p. 185° (dec.), upon treatment with dry hydrogen chloride in methylene chloride at room temperature. The structures of the bromoketone IV and chloroketone VI were demonstrated by the near identity of their infrared spectra [$\lambda_{\max}^{\text{Nujol}}$ 3.0-4.3 (broad), 5.72, 6.5 μ (broad)], and the close similarity of these spectra to those of the ketone III [$\lambda_{\max}^{\text{Nujol}}$ 4.1-4.2 (broad), 5.75, 6.5 μ (broad)].

The NMR spectra of enol ether V and chloroketone VI in deutero-chloroform solution[10] are recorded in Table I. Assignment of the high field singlet to the vinyl methyl hydrogens (b) and the lower field singlet to the 4-methyl hydrogens (a) in the chloroketone VI was indicated by the expected change in chemical shift upon substitution of the chlorine in VI for the hydrogen of ketone III (observed 0.61 ppm.), expected[11] 0.62 ppm.) and a comparison of the NMR spectra of III, V and VI. Thus, according to the above assignments, the position of the resonance of the vinyl methyl hydrogens (b)

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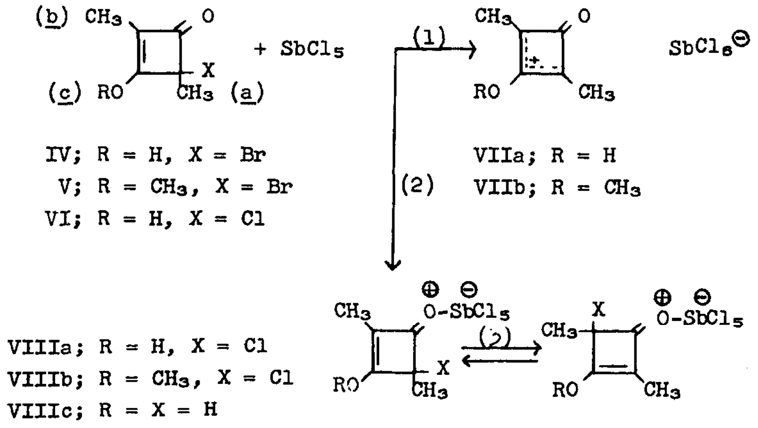
[10] The small chloroform peak was taken as internal reference, independently referenced to tetramethylsilane. It was demonstrated that the separation of the chloroform and tetramethylsilane peaks was not affected by added antimony pentachloride.

[11] L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, p. 53, Pergamon Press, New York (1959).

remains closely the same for the three ketones III, V and VI, as expected. The NMR spectrum of enol ether V with resonance at 5.78 ($OCH_{3}\underline{c}$), 8.11 ($4\text{-}CH_{3}\underline{a}$) and 8.29 τ ($2\text{-vinyl } CH_{3}\underline{b}$) was unexceptional. Its infrared spectrum ($\lambda_{\max}^{\text{Neat}}$ 5.64, 6.15 μ) was compatible with the assigned structure.[12]

Addition of antimony pentachloride to cold chloroform solutions of V and VI brought about striking changes in their NMR spectra as shown in Table I. The appearance of a sharp single peak at lower field for the methyl hydrogens in each case can be accommodated by one of the following hypotheses: (1) Conversion of the haloketones to a carbonium ion VII, (2) conversion to a complex such as VIII with fortuitous superposition of chemical shifts, (3) conversion to complex VIII with very rapid equilibration by allylic chloride migration. (*cf.* ref. 13).



IV; R = H, X = Br
V; R = CH_3, X = Br
VI; R = H, X = Cl

VIIa; R = H
VIIb; R = CH_3

VIIIa; R = H, X = Cl
VIIIb; R = CH_3, X = Cl
VIIIc; R = X = H

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[12] H. H. Wasserman and E. V. Dehmlow, J. Amer. Chem. Soc. 84, 3786 (1962).

[13] M. C. Caserio, H. E. Simmons, Jr., A. E. Johnson and J. D. Roberts, J. Amer. Chem. Soc. 82, 3102 (1960).

Table I

NMR Peaks of Some Cyclobutenones in Chloroform and Antimony Pentachloride

Solvent	Ketone III	Chloroketone VI	Enol ether V
$CHCl_3$	8.46, 8.79 (J=7)	8.18, 8.36	5.78,8.11,8.29
$SbCl_5$-$CHCl_3$	8.13(J=2), 8.46(J=7)	7.92	5.23, 7.78

Case (I), though attractive in the light of recent activities concerning derivatives of the closely related cyclobutadiene dication,[3,14] must be rejected as being incompatible with the chemical shift values observed. On the basis of Katz's study[3] of carbonium ion II, a downfield shift of considerably greater than 1 ppm. in the methyl resonances is expected for conversion of the covalent halides to carbonium ion VII. In fact, the downfield shift ranges from only 0.26 to 0.51 ppm. Case (2) seems unlikely in view of the similar behavior of chloroketone VI and enol ether V, and of the uniform downfield shift of 0.33 ppm. observed for both methyl groups in the conversion of ketone III to its antimony pentachloride complex VIIIc (see table I).[15] This latter observation is in good accord with case (3). In particular the average deshielding of the methyls in the conversion of chloroketone VI to complex VIIIa (0.35 ppm.), is close to that observed (0.33 ppm.) for the similar conversion

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[14] H. H. Freedman and A. M. Frantz, Jr., Abstracts, 141st National meeting of the American Chemical Society, Washington, D.C. March, 1962, p.26-O. J. Amer. Chem. Soc. 84, 4165 (1962). We thank Dr. Freedman for a prepublication account of his results.

[15] The assignment of the chemical shifts in complex VIIIc is unequivocal by virtue of the near constancy of the coupling constants of each methyl to the methine hydrogen.

of III to VIIIc. If the separation of methyl resonances in the complex VIIIa is assumed to be the same as that in the chloroketone VI (10.8 cps.), then the equilibration of the two complexes must be taking place with a frequency greater than 65 times per second at room temperature.[16] The possibility that this equilibration is taking place through rapid, reversible formation of small amounts of carbonium ion VII is not ruled out.

The authors are indebted to the National Science Foundation for partial support of this work under Research Grant NSF-G-14454, to G. H. Carroll for the determination of the NMR spectra, and to Professor C. F. Wilcox for many stimulating discussions.

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[16] J. A. Pople, W. G. Schneider and H. J. Bertstein, High Resolution Nuclear Magnetic Resonance., p. 223, McGraw-Hill, New York (1959).