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THE CIS-CYCLOHEXENE ACETOXONIUM ION.
2-METHYL-CIS-4,5-TETRAMETHYLENE-1,3-DIOXOLENIUM TETRAFLUOROBORATE.[1,2]

C. B. Anderson,[1] Edwin C. Friedrich[2] and S. Winstein

Department of Chemistry, University of California, Los Angeles, Calif.

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In these Laboratories we have long been interested in neighboring acetoxy group participation[3] and the intermediate olefin acetoxonium ion intermediates[3] which are responsible for the variation in structure and stereochemistry of the products of substitution reactions under various conditions. Because of the interesting behavior of the intermediate acetoxonium ions and the frequent occurrence of neighboring acyloxy groups in organic substrates, such groups are of considerable importance in many

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[3] (a) S. Winstein and R. E. Buckles, J. Amer. Chem. Soc. **64**, 2780 (1942); (b) R. M. Roberts, J. Corse, R. Boschan, D. Seymour and S. Winstein, J. Amer. Chem. Soc. **80**, 1247 (1958), and intervening papers in the series; (c) C. B. Anderson and S. Winstein, J. Org. Chem. **28**, 605 (1963).

areas of organic chemistry,[4] not only in substitution reactions, but others as well, e.g., "dry" and "wet" Prevost reactions[5,6] and other olefin oxidations.[3c]

A few years ago Meerwein[7] prepared and isolated the ethylene acetoxonium ion I as a stable salt, 2-methyl-1,3-dioxolenium tetrafluoroborate, and we have now prepared the analogous cis-cyclohexene acetoxonium salt, 2-methyl-cis-4,5-tetramethylene-1,3-dioxolenium tetrafluoroborate (II-BF_4). With this compound we have been able to obtain direct confirmation of the varied behavior previously ascribed to the cyclohexene acetoxonium ion intermediate[3] and to gain further insight into its nature and chemical behavior.

The cyclohexene acetoxonium tetrafluoroborate salt, m.p. 103-104° (dec.), was prepared in three ways, from trans-2-acetoxycyclohexyl bromide (VI-Br) and silver tetrafluoroborate in nitromethane,[7b] from 2-methyl-cis-4,5-tetramethylene-1,3-dioxolane (III) and trityl fluoroborate,[7d] and also from 2-ethoxy-2-methyl-cis-4,5-tetramethylene-1,3-dioxolane (X) and boron trifluoride etherate.[7c] The third method was the most satisfactory, the yield of II-BF_4

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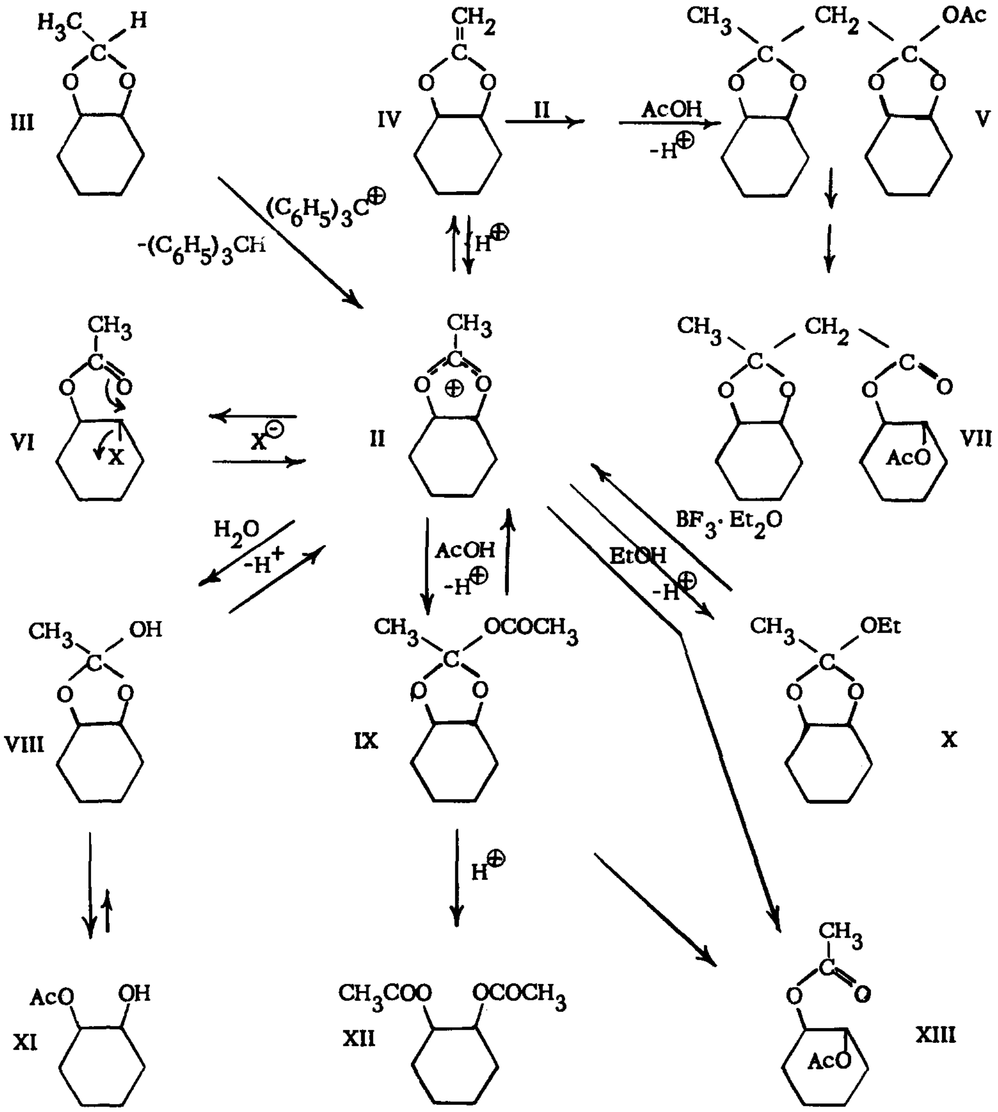
[4] E.g., the carbohydrate field: (a) Pacsu, Advances in Carbohydrate Chem. 1, 77 (1945); (b) R. U. Lemieux, ibid. 9, 1 (1954); (c) H. J. Haynes and F. H. Newth, ibid. 10, 207 (1955).

[5] (a) C. Prevost, Compt. rend. 196, 1129 (1933); (b) C. Prevost and J. Wiemann, Compt. rend. 204, 700 (1937).

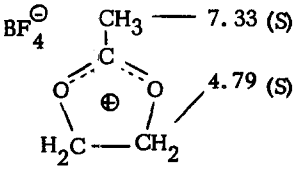
[6] R. B. Woodward and F. V. Brutcher, Jr., J. Amer. Chem. Soc. 80, 209 (1958).

[7] (a) H. Meerwein, Angew. Chem. 67, 374 (1955); (b) H. Meerwein, V. Hederick and K. Wunderlich, Arch. Pharm. 291, 541 (1958); (c) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert and K. Wunderlich, Ann. 632, 38 (1960); (d) H. Meerwein, V. Hederick, H. Morschel and K. Wunderlich, ibid. 635, 1 (1960).

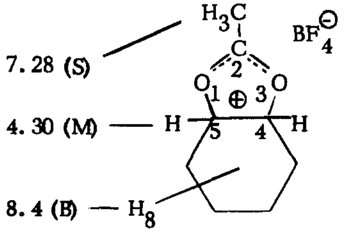

III
IV
V
VI
II
VII
VIII
IX
X
XI
XII
XIII
$(C_6H_5)_3C^{\oplus}$
$-(C_6H_5)_3CH$
II
AcOH
$-H^{\oplus}$
$H^{\oplus}$
$X^{\ominus}$
H_2O
$-H^+$
AcOH
$-H^{\oplus}$
$BF_3 \cdot Et_2O$
EtOH
$-H^{\oplus}$
$H^{\oplus}$

being 90%. The C, H-analysis of the salt was satisfactory and its structure is confirmed by its n. m. r. spectrum in acetonitrile and nitromethane solvents. Thus, in acetonitrile solvent, proton signals occur at τ values of 7.28 (singlet, relative area 3) and 4.30 (multiplet, relative area 2) and ca. 8.4 (broad) for the 2-methyl, 4- and 5-α-protons and other ring hydrogens, respectively. The n. m. r. spectrum of the dioxolenium portion of salt II-BF_4 is similar to that of Meerwein's simpler dioxolenium salt I-BF_4 which we measured for comparison.

τ-Values (CH_3CN)



I-BF_4



II-BF_4

The qualitative behavior of the dioxolenium salt II-BF_4 under various conditions was in general agreement with our previous ideas.[3] Thus, in acetic acid containing excess water, cis-2-acetoxycyclohexanol (XI) is formed quantitatively. Acetylation of the product and v. p. c. examination of the diacetate XII showed it to be >99.5% cis, no trans being detected. This quantitative and stereospecific conversion of ion II to cis-exter XI presumably involves the orthomonoacetate VIII which is tautomerized to XI. When the salt II-BF_4 is treated with anhydrous acetic acid containing potassium acetate, potassium fluoroborate is precipitated quantitatively. Keeping the solution at 75° for a time produced ca. 50% yields of glycol diacetate 94% trans (XIII) and 6% cis (XII).

In anhydrous acetic acid at 75° the salt II-BF_4 gave rise quantitatively to mixed glycol diacetates XII and XIII. This product varied from predominantly trans to predominantly cis as the concentration of dioxolenium salt was varied from 0.015 M to 0.23 M. The present results are in line with the presence of an acid-catalyzed route[3] through orthodiester IX to cis-diacetate XII, the importance of this route varying with the prevailing concentration of strong acid in the run. The latter depends upon the initial concentration of salt employed.

In anhydrous acetic acid in the presence of added toluenesulfonic acid, up to 65% of dioxolenium salt was diverted to trans-2-acetoxycyclohexyl p-toluenesulfonate[3] (VI-OTs). This substance was isolated and shown to be identical with an authentic specimen. Similar diversion[3] of II to VI-Cl and VI-Br to the extent of 80-90% was observed with added lithium chloride or tetrabutylammonium bromide.

The remainder of the product (ca. 50%) from treatment of II-BF_4 with potassium acetate in anhydrous acetic acid turned out to be a dimeric material, the cis-1,2-cyclohexanediol ketal of trans-2-acetoacetoxycyclohexyl acetate (VII). The same material is also one of the products from treatment of the orthoester X with acetic acid-acetic anhydride. The structure of VII was clear from its C,H-analysis, I.R. and n.m.r. spectra, and its behavior in basic saponification and acid hydrolysis. Formation of VII from dioxolenium salt II-BF_4 may be visualized by way of addition of ion II to ketene acetal IV, the latter resulting from some proton loss from ion II (see later).

The n. m. r. spectra of solutions of II-BF_4 during its reactions in acetic acid solvent are most illuminating. At room temperature, solutions of II-BF_4 in anhydrous acetic acid show proton signals at τ equal to 7.23 and 4.23, corresponding to the dioxolenium ion, and no signals corresponding to a dioxolane derivative (e. g., IX) or diacetate product. Thus, under these conditions, the dioxolenium salt II-BF_4 can be only slightly acetolyzed to the orthodiacetate IX. It is interesting that the dioxolenium spectrum (and that of ethyl acetate) may also be obtained from orthoester X in acetic acid-acetic anhydride containing perchloric acid. Contrasting with the relative stability of II-BF_4 in anhydrous acetic acid is its behavior when water or potassium acetate is added. Addition of water caused immediate disappearance of the dioxolenium proton signals and appearance of cis-2-acetoxycyclohexanol signals at $\tau = 5.0$ (α-H to OAc) and 6.1 (α-H to OH). Addition of potassium acetate solution to II-BF_4 in an n. m. r. tube caused immediate acetolysis of the dioxolenium ion. The dioxolenium proton signals disappeared and a broad dioxolane signal at $\tau = 5.8$ appeared, corresponding to orthodiacetate IX, dimeric orthodiacetate V and dimeric product VII. A signal at $\tau = 5.2$ for protons alpha to acetoxy also appeared, corresponding to diacetate XIII and dimer product VII.

At 50.0°, solutions of dioxolenium salt II-BF_4 in anhydrous acetic acid show a steady decrease in the dioxolenium proton signals and a corresponding growth of diacetate proton signal at $\tau = 5.0$. No dioxolane proton signal corresponding to orthodiacetate IX was observed. From the change in n. m. r. spectrum of a 0.13 M solution of II-BF_4 a rate constant of $(1.1 \pm 0.2) \times 10^{-4}$

$sec.^{-1}$ was obtained. The same rate constant, $(1.1 \pm 0.1) \times 10^{-4}$ $sec.^{-1}$, was obtained from a procedure which involved quenching of II-BF_4 with wet acetic acid, acetylation and v.p.c. analysis of reaction products.

At 50.0° the solutions of orthodiacetate IX and dimeric orthodiacetate V obtained from treatment of II-BF_4 with potassium acetate showed a steady decay of the dioxolane proton signal at $\tau = 5.8$, with a corresponding growth of the $\tau = 5.2$ signal for proton alpha to acetoxy. A rough rate constant of 6×10^{-4} $sec.^{-1}$ was obtained for a solution of 0.2 M II-BF_4 in originally 0.5 M potassium acetate. A similar rate constant was obtained by a v.p.c. method which measured the disappearance of monomeric orthodiacetate IX.

The present work has shown that the dioxolenium ion and orthodiacetate species II and IX disappear with rate constants some 10^2-10^3 times as great as the one observed in acetolysis of trans-2-acetoxycyclohexyl p-toluenesulfonate (VI-OTs). However, detailed kinetic studies which would clarify the respective roles of dioxolenium ion and orthodiacetate intermediates in product determination have not yet been carried out.

When the dioxolenium salt II-BF_4 was dissolved in deuterio-acetic acid, the dioxolenium 2-methyl protons were exchanged for deuteriums. The signal for the methyl protons had decreased to a relative area of two (from three) during the time necessary to dissolve the compound (45 minutes). This exchange corresponds to a minimum first order rate constant of ca. 10^{-3} $sec.^{-1}$ at 25°. Longer reaction exchanges all three protons of the methyl group. The observed deuterium exchange presumably proceeds by way of the ketene acetal[8] IV, the equilibrium between ketene acetal and dioxolenium ion under these conditions being rapidly established and lying quite far on the side of the dioxolenium salt.

The relatively rapid proton loss from dioxolenium ion II to yield ketene acetal accounts for the tendency toward formation of dimeric product VII from dioxolenium ion II under certain conditions. Such easy proton loss from dioxolenium ions akin to II make intervention of ketene acetals in reactions of substrates with neighboring acyloxy groups quite common. The probable intervention of a ketene acetal to account for the chlorination of penta-O-acetyl-β-D-glucose by phosphorus pentachloride to give 3, 4, 6-tri-O-trichloroacetyl-β-D-glucosyl chloride[4b, 9] was discerned very early by Freudenberg.[10]

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[8] Balaban and Nenitzescu have reported a similar exchange in the methyl groups of 2, 4, 6-trimethylpyrylium perchlorate with deuterium oxide; A. T. Balaban and C. D. Nenitzescu, Rev. chim. Ac. rép. populaire Roumaine, 6, 291 (1961).

[9] (a) P. Brigl, Z. physiol. Chem. 116, 1 (1921); (b) W. Marcy and A. Scattergood, P. 46-L of Abstracts, of 115th Meeting of American Chemical Society, San Francisco, California, March 27-April 1, (1949).

[10] K. Freudenberg and H. Scholz, Ber. 63, 1969 (1930).