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ALKOXY CARBONIUM IONS. NMR EXAMINATION OF 2-ALKYL-1,3-DIOXOLENIUM CATIONS

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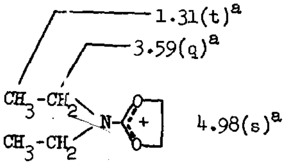
The direct observation of carbonium ions by nmr spectroscopy has received considerable attention recently.[1] Conspicuously absent from the literature is a systematic spectral examination of alkoxycarbonium ions.[2] We wish to report here the interaction of 2-alkyl substituents with 1,3-dioxolenium cation systems as well as several new methods for generating these cations.

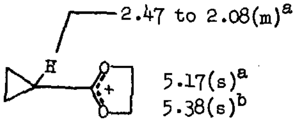
Using the method of Meerwein,[3] a number of these cations were prepared by reacting equimolar amounts of appropriate 2-bromoethyl esters with anhydrous silver tetrafluoroborate in methylene chloride. The tetrafluoroborates were obtained as stable salts in yields of 50-80%. Their nmr spectra were examined in SO_2 at -20° and in FSO_3H at room temperature (Table I). Characteristic spectra contain a sharp singlet for the equivalent ring methylene protons as well as appropriate downfield absorptions for the corresponding 2-alkyl groups.[4] Compared to 2-alkyl-1,3-dioxolanes, the ring protons in the corresponding cations were generally shifted downfield 1.5 to 1.7 ppm in FSO_3H. A downfield solvent shift of approximately 0.16 ppm was observed in going from FSO_3H to SO_2.

TABLE I

2-Alkyl-1,3-dioxolenium Cations in Order of Decreased Shielding of the Ring Proton



I



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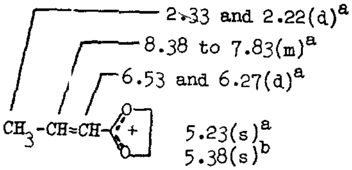

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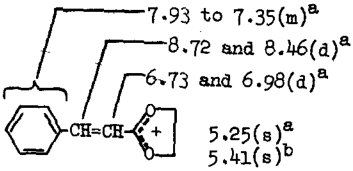

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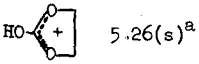

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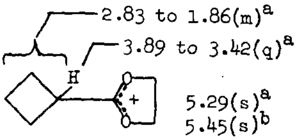

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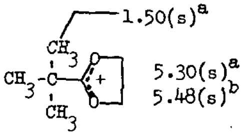
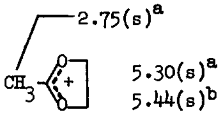
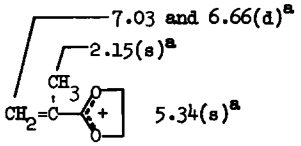


VII

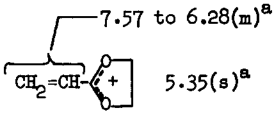
TABLE I (CONT.)



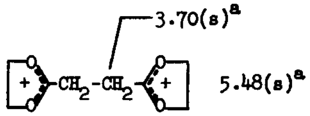
VIII



IX



X



XI

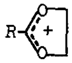
(a) In ppm downfield from TMS using $(Me)_4N^{\oplus}Br_4^{\ominus}$ as an internal standard in 100% FSO_3H. $(Me)_4N^+$ is reported to have an absorption peak at -3.10 ppm, relative to TMS in 100% H_2SO_4.[7]

(b) In ppm downfield from the internal standard TMS, using SO_2 as a solvent at -20°.

The chemical shifts of the heterocyclic ring protons should indicate the relative amount of delocalization or inductive neutralization of positive charge by the alkyl substituent. This criterion has been employed by Olah and Deno[5] on other carbonium ion systems and has been shown to be valid for the 2-aryl-1,3-dioxolenium ions.[6] These data indicate that the cyclopropyl group is the most effective alkyl substituent in this series for the delocalization of charge from the ring, whereas the positive charge is removed least effectively in the dication (XI).

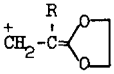
In order to rationalize the relative order of the other cations (III-X) in this series one must consider their dual oxonium-carbonium character (see structures XII-XIV). In carbonium ion systems one would expect the positive charge in the 2-vinyl and 2-isopropenyl cations to be

XII XIII



XIV

more delocalized by means of allylic resonance such as in XV. The



XV

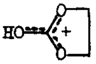
anomalous order of these two cations may reflect the high order of their oxonium ion character (XIII); such structures are stabilized by conjugation with the carbon-carbon double bond. The higher electronegativity of the sp^2 hybridized carbon substituent and the predominate oxonium ion character of IX and X may account for the fact that the ring protons in these cations are more deshielded than in the methyl and t-butyl cations VII and VIII.

In the case of the crotonyl (III) and styryl (IV) cations more interaction of the double bond with the positive charge occurs since the cation (XVI) resulting from allylic type resonance can be stabilized by the methyl or phenyl group.

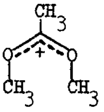
; $R=CH_3, C_6H_5$

XVI

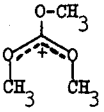
Protonated ketones can be considered as hydroxycarbonium ions $R-\overset{+}{C}(OH)R$.[1] Protonation of ethylene carbonate in FSO_3H was expected to give the 2-hydroxy-1,3-dioxolenium cation, V. It was surprising to find that the ring protons in this cation were deshielded more than in cations II-IV, even though considerable charge delocalization could be realized through the resonance structure shown below. A similar observation was reported by Taft and Ramsey[1b] for the analogous acylic series, in which case



it was found that the methoxy protons were more deshielded in the trimethoxy cation than in the dimethoxymethyl cation. A good explanation for these observations is not immediately obvious.[8]

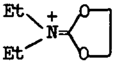


5.0 ppm

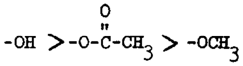


5.1 ppm

The 2-diethylamino-1,3-dioxolenium cation, I, was the most shielded species in this series; a structure with charge on nitrogen very likely predominates and accounts for the delocalization of charge from the ring.

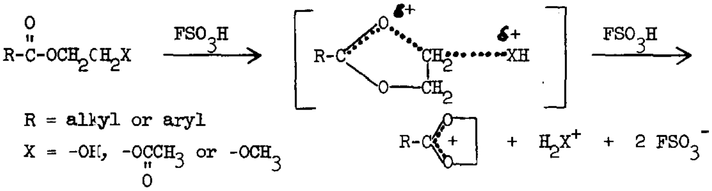


During the course of our investigation with FSO_3H as a solvent, three new routes to the 1,3-dioxolenium cation system were discovered. Adding 2-hydroxy, 2-acetoxy or 2-methoxyethyl esters to FSO_3H at room temperature led to the corresponding 2-alkyl or aryl-1,3-dioxolenium cations as determined by nmr. The spectra were identical to those obtained for authentic cation tetrafluoroborate salts in FSO_3H. The rate of formation of these cations was found to be in the order.



$$-OH > -O-\overset{\overset{O}{\|}}{C}-CH_3 > -OCH_3$$

It is likely that the incipient primary carbonium ion is stabilized by the neighboring carbonyl as shown:



R = alkyl or aryl

X = $-OH$, $-OCCH_3$ (with =O on the C) or $-OCH_3$

Whether the 1,3-dioxolenium cations are produced in a stepwise or concerted fashion cannot be stated at present.

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2. The nmr spectrum of 2-methyl-1,3-dioxolenium tetrafluoroborate was reported as two singlets at -5.31 ppm and 2.67 ppm from TMS in acetonitrile. C. B. Anderson, E. C. Friedrich and S. Winstein, Tetrahedron Letters, 2037 (1963).
3. H. Meerwein, V. Hederich and K. Wunderlich, Arch Pharm., 291, 541 (1958).
4. Peak integrations were consistent with the respective structures in all of the spectra.
5. See G. A. Olah, J. Am. Chem. Soc., 86, 932 (1964); N. C. Deno, et al., ibid., 87, 2991, 2995, 2998 (1963) and other papers from their laboratories.
6. See the subsequent paper.
7. N. C. Deno, H. C. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., ibid., 85, 2991 (1963).
8. It is possible that ethylene carbonate is protonated on the ether oxygen.