Tetrahedron Letters No.15, pp. 1347-1351, 1967. Pergamon Press Ltd. Printed in Great Britain.

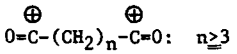
ALKOXYCARBONIUM IONS. III. NMR EXAMINATION OF BIS-2,2'-ALKYLENE-1,3-DIOXOLENIUM DICATIONS

Harold Hart and Donald A. Tomalia

Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

(Received 3 January 1967)

Careful investigation by Olah and Comisarow[1] of the reaction between dicarboxylic acid fluorides and antimony pentafluoride showed that alkylene dioxodicarbonium ions (acyl dications) were not formed unless the acyl groups were insulated by at least three methylene groups. It was considered of interest to investigate the synthesis of a series of bis-2,2'-alkylene-1,3-



$$O{=}\overset{\oplus}{C}-(CH_2)_n-\overset{\oplus}{C}{=}O:\quad n\geq 3$$

dioxolenium dications, to determine whether the charges might be brought closer together. Previous work[2,3] had shown that the nmr chemical shifts of ring protons in this type of cation

provide an excellent probe for measuring charge distribution in these systems.

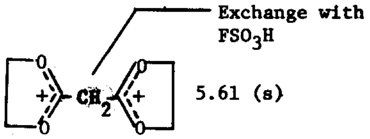
The bis-2,2'-alkyiene-1,3-dioxolenium dications, n = 1-5, were prepared according to the method of Meerwein[4] by reacting the appropriate bis(2-bromoethyl) esters with two equivalents of anhydrous silver tetrafluoroborate in methylene chloride. These reactions proceed in high yield to a mixture of the dication salt and silver bromide. Formation of the dications was complete in two hours at 25-30° when n = 3-5. When n = 1 or 2, substantially longer reaction times were required (i.e. 8-12 hours).

As previously observed for the analogous aryl dications,[3] common polar solvents such as SO_2 and nitromethane are inadequate as solvents for separating the dications from the silver halide. Suitable nmr spectra were obtained, however, by extracting the dication salt - AgBr mixtures with FSO_3H. Solutions of the dications in FSO_3H gave characteristic spectra containing a sharp singlet for the equivalent ring methylene protons as well as appropriate absorptions for the corresponding 2-alkylene groups.[5]

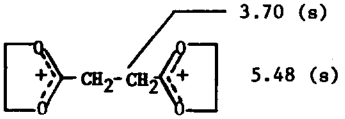
The nmr spectra of the dications are summarized in Table I.

Table I[6]

BIS-2,2'-ALKYLENE-1,3-DIOXOLENIUM CATIONS IN ORDER OF INCREASED SHIELDING OF THE RING PROTONS



I



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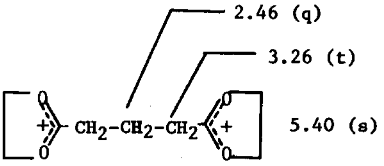

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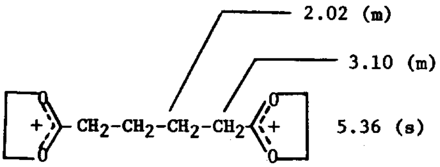

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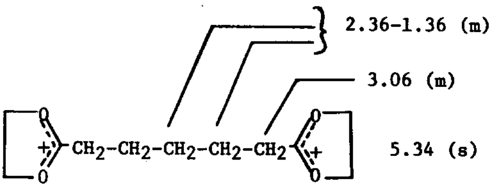


V

A plot of the chemical shifts of the ring protons vs the number of methylene groups between the cationic centers is given in Figure 1. The data are fit rather well by equation (1) where 5.30, the limiting value of δ when $n = \infty$, is identical with the chemical shift of the

$$\delta = 5.30 + \frac{1.60}{(n+1)^2} \qquad (1)$$

ring protons in the 2-methyl-1,3-dioxolenium monocation.[2] When n is large, the molecule behaves as if there were no interaction between the cationic centers. All points fit the equation precisely except for $n = 1$, and the reason for this discrepancy is discussed below.

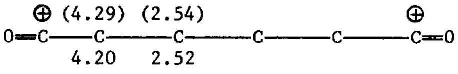
The chemical shifts of the methylene protons between the cationic centers provide an even more sensitive probe of charge distribution in these dications. Figure 2 shows a plot of the α-methylene proton chemical shifts as a function of n; the data are fit almost precisely by the equation.

$$\delta = 2.94\left(1 + \frac{1}{n^2}\right) \qquad (2)$$

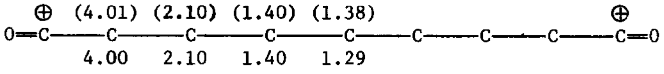
In Figures 1 and 2, the solid curves are drawn according to the equations, whereas the points are experimental.

Equation (2) suggests that the chemical shift of the α-methylene protons can be described as the sum of two terms, one of which is constant (i.e., the methylene is always adjacent to and a constant distance from one dioxolenium ring) and one of which varies inversely as the square of n, which may be proportional to the distance from the second cationic center.

An alternative, very simple way of correlating these data is also possible. Each methylene in ion II may be considered to be α to one dioxolenium ring and β to the other. The chemical shift can be expressed as the sum of two parameters, $\delta_\alpha + \delta_\beta$. Values of these empirical constants which fit the data are: $\delta_\alpha = 2.47$, $\delta_\beta = 1.23$, $\delta_\gamma = 0.79$, $\delta_\delta = 0.63$, $\delta_\varepsilon = 0.59$. The data of Table I provide only one independent check on the method, which happens to give a calculated δ that agrees exactly with the observed. However, we have also applied this method to the data in Table II of ref. 1. The best parameters are $\delta_\alpha = 3.60$, $\delta_\beta = 1.67$, $\delta_\gamma = 0.87$, $\delta_\delta = 0.69$, $\delta_\varepsilon = 0.53$, $\delta_\zeta = 0.43$, $\delta_\eta = 0.41$. Two examples of the closeness of fit are



$$O{=}\overset{\oplus}{C}-\underset{4.20}{\overset{(4.29)}{C}}-\underset{2.52}{\overset{(2.54)}{C}}-C-C-\overset{\oplus}{C}{=}O$$



$$O{=}\overset{\oplus}{C}-\underset{4.00}{\overset{(4.01)}{C}}-\underset{2.10}{\overset{(2.10)}{C}}-\underset{1.40}{\overset{(1.40)}{C}}-\underset{1.29}{\overset{(1.38)}{C}}-C-C-C-\overset{\oplus}{C}{=}O$$

where values in parentheses are calculated, and those below the formulas were observed by Olah and Comisarow. The parameters for bis-acylium ions are larger than those for bis-dioxolenium ions, due to less charge delocalization in the former.

Two cases deserve special mention. The central methylene protons of I could not be observed, presumably due to exchange with the solvent. Thus two carbonium ion centers attached to a single methylene cause the compound to become a rather strong acid. Exchange probably occurs via the monocation

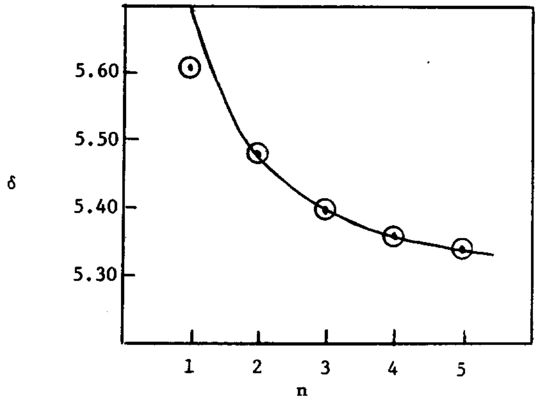


Figure 1. Dioxolenium Ring Proton Chemical Shift vs. **Number** of Methylene Groups

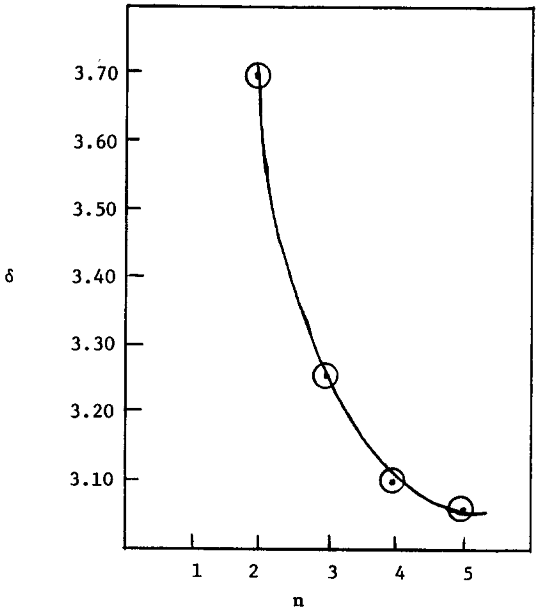
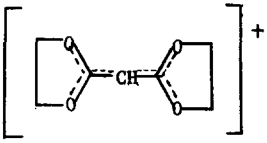


Figure 2. 2-Methylene Proton Chemical Shift vs. Number of Methylene Groups



and the reason why the observed chemical shift for the ring methylene falls below the curve in Figure 1 is that one is probably seeing an intermediate chemical shift between that expected for the mono and dication, due to rapid exchange.

Attempts to synthesize the bis-dioxolenium dication where n = 0 have thus far been unsuccessful. Treatment of bis(2-bromoethyl) oxalate[7] with $AgBF_4$ or $AgSbF_6$ gave a silver halide precipitate after several hours. The nmr spectrum of a FSO_3H extract, however, revealed a sharp singlet at δ 5.70 and a multiplet at δ 5.03 to 4.67 with nearly equal areas. This suggests that only one dioxolenium ring was formed.

Acknowledgement: We wish to thank the Dow Chemical Company for providing facilities and supporting this research. We are also grateful to the National Science Foundation for support.

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1. G. A. Olah and M. B. Comisarow, J. Am. Chem. Soc., **88**, 3313 (1966).
2. H. Hart and D. A. Tomalia, Tetrahedron Letters, 3383 (1966).
3. D. A. Tomalia and H. Hart, ibid., 3389 (1966).
4. H. Meerwein, V. Hederich and K. Wanderlich, Arch. Pharm., **291**, 541 (1958).
5. Peak integrations were consistent with the respective structures in all of the spectra.
6. The chemical shifts are in p.p.m. downfield from TMS using $(Me)_4N^+BF_4^-$ (-3.10 ppm) as an internal standard in 100% FSO_3H.
7. The oxalate ester gave an A_2X_2 pattern at -4.87 and -3.64 p.p.m. in FSO_3H.