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

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The only quantitative correlation of carbonium ions by nmr chemical shifts in the literature was reported recently by Taft and McKeever,[1] who found that a linear relationship exists between the fluorine nmr chemical shifts and stabilization energies of *para* fluorine substituted triphenylmethyl cations. Although Olah[2] has suggested that a quantitative correlation of charge densities with proton-nmr chemical chemical shifts might be possible in the benzyl cation system, this relationship has not yet been demonstrated. We wish to report here a quantitative correlation of proton-nmr chemical shift with Hammett σ values for *meta* and *para*-substituted 2-aryl-1,3-dioxolenium cations (cyclic dialkoxy carbonium ions)[3] as well as the preparation of two new dications and a trication in this series.

The 2-aryl-1,3-dioxolenium cations were prepared according to the method of Meerwein[4] by reacting equimolar amounts of appropriate 2-bromoethyl esters with anhydrous silver tetrafluoroborate in methylene chloride. The tetrafluoroborates were obtained as stable, white salts in yields of 55-87%. Nmr spectra of the cations, obtained in SO_2 at -20° and in FSO_3H

at room temperature, contained a sharp singlet for the equivalent ring methylene protons as well as appropriate downfield absorptions for the corresponding aromatic nuclei.[6] As with the 2-alkyl-1,3-dioxolenium cations[7], the heterocyclic ring protons were shifted downfield 1.6-1.8 ppm compared to the corresponding 1,3-dioxolanes. A downfield solvent shift of approximately 0.16 ppm was observed in going from FSO_3H to SO_2 (see Table I).

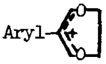
The chemical shifts of the ring protons were plotted against Hammett σ and σ^+ values.[8] A least squares treatment of the σ values (Figure 1) gave a reasonably good linear correlation in FSO_3H: standard error = 0.022, correlation coefficient = 0.966, $\sigma = 0$ ordinate intercept = 5.40, whereas σ^+ values gave a somewhat less satisfactory correlation: standard error = 0.038, correlation coefficient = 0.940, $\sigma^+ = 0$ ordinate intercept = 5.42. It seems that δ is directly related to the Hammett σ values; it should therefore also be proportional to log k/ko, and this conjecture will be tested by determining the reaction rates for a standard nucleophilic reaction on this series of cations.

Closer adherence to σ rather than σ^+ values suggests that resonance interactions between electron-supplying substituents (i.e. p-CH_3-O-) and the electron deficient 1,3-dioxolenium moiety are not strong. This may indicate that the most important contributor to the resonance hybrid is XIX rather than XX.[7]

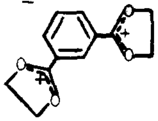
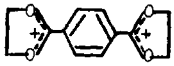
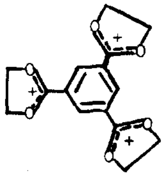
The dications (XVI and XVII) and the trication (XVIII) were obtained

TABLE I

H-NMR CHEMICAL SHIFTS FOR 2-ARYL-1,3-DIOXOLENIUM CATIONS



BF_4^-

	Aryl Substituent	Ring Protons		Aromatic Protons	Other Protons
		A	B	A	
I	p-Methoxy	5.33	5.48	8.31 and 7.26(d)	CH_3-O- 4.08(s)
II	3,4,5-Trimethoxy	5.37	5.53	7.72(s)	p-CH_3O- 4.28(s) m-CH_3O- 4.09(s)
III	p-Methyl	5.37	5.53	8.20 and 7.55(d)	CH_3- 2.55(s)
IV	m-Methyl	5.40	5.56	8.24 to 7.43(m)	CH_3- 2.47
V	Phenyl	5.42	5.57	8.47 to 7.55(m)	
VI	p-Fluoro	5.42	5.52	7.42(t) and 8.41(q)	
VII	p-Chloro	5.43	5.60	8.25 and 7.71(d)	
VIII	m-Chloro	5.44	5.65	8.32 to 7.52(m)	
IX	m-Bromo	5.47	5.63	8.34 to 7.52(m)	
X	m-Fluoro	5.47	5.62	8.27 to 7.63(m)	
XI	3,4-Dichloro	5.47	5.63	8.43 to 7.73(m)	
XII	m-Trifluoromethyl	5.52	5.68	8.64 to 7.68(m)	
XIII	p-Trifluoromethyl	5.52	5.68	8.47 and 8.01(d)	
XIV	m-Nitro	5.58	5.70	7.90 to 9.25(m)	
XV	p-Nitro	5.59	5.73	8.58(s)	
XVI		5.60	-	8.03 to 9.26(m)	
XVII		5.63	-	8.72(s)	
XVIII		5.77	-	9.58(s)	

(A) δ in ppm downfield from TMS using $(Me)_4^{\oplus}$ $BF_4^{\ominus}$ as an internal standard in 100% FSO_3H. $(Me)_4N^{\oplus}$ is reported to have an absorption peak at -3.10 ppm, related to TMS in 100% H_2SO_4.[5]

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

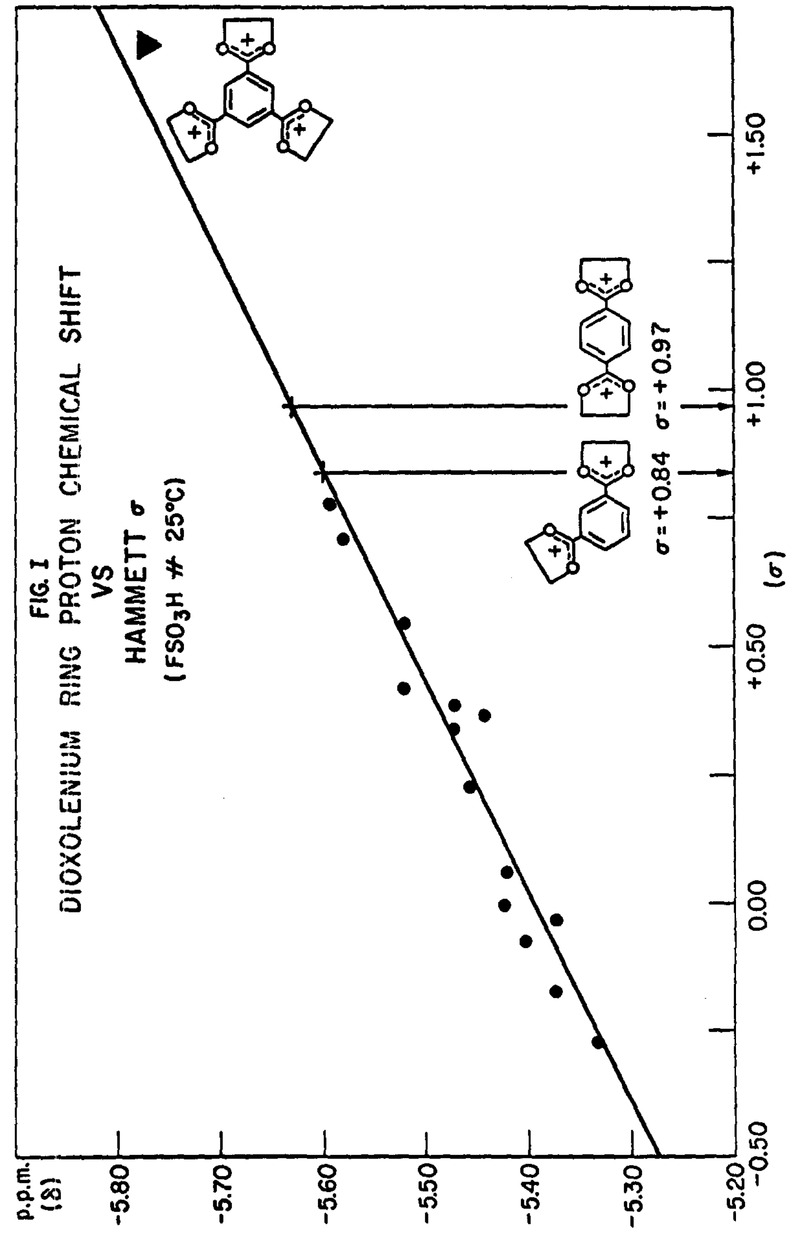
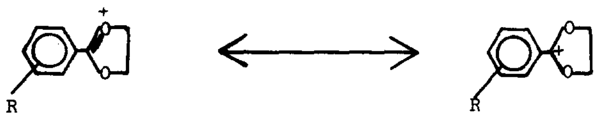


FIG. I
DIOXOLENIUM RING PROTON CHEMICAL SHIFT
VS
HAMMETT σ
(FSO_3H # 25°C)



XIX XX

as tetrafluoroborate salts by reacting the appropriate 2-bromoethyl phthalate or 2-bromoethyl trimesate with an equivalent amount of anhydrous silver tetrafluoroborate in methylene chloride. The polycations were insoluble in CH_2Cl_2, SO_2 and $SOCl_2$. However, satisfactory nmr spectra were obtained by extracting the AgBr plus polycation precipitates with FSO_3H and scanning. The relative deshielding of the dioxolenium ring protons was in the predicted order: XVI $<$ XVII $<$ XVIII (see Table I).

Using the Hammett plot (Figure 1) for the fourteen meta and para substituted monocations, σ values were obtained for the meta and para 1,3-dioxolenium cation moieties from the chemical shifts of the dioxolenium ring protons in the corresponding dications. The meta-1,3-dioxolenium cation has a σ value of +0.84, whereas the para-1,3-dioxolenium cation has a σ value of +0.97. The latter is the largest positive para σ value thus far reported. Assuming the additivity principle for multiple meta or para substituted benzenes[9] it was predicted from the meta σ value (2 x 0.84) that the trication dioxolenium ring protons should have a δ of 5.80 ppm. The observed δ was 5.77 ppm, designated by ▼ on the plot. The electron deficiency of the trication is dramatically reflected not only by the highly deshielded protons in the dioxolenium ring, but also by the low field position of the aromatic protons (Table I).

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6. Peak integrations were consistent with the respective structures in all of the spectra.
7. See H. Hart and D. A. Tomalia, *Tetrahedron Letters*, preceding paper.
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