

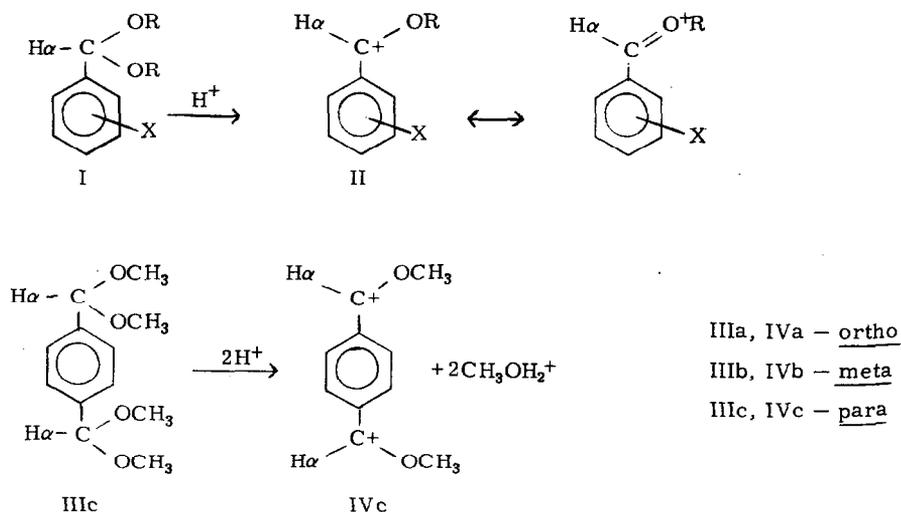
ARYLALKOXY DICARBONIUM IONS

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We have recently been able to observe directly the existence of stable arylalkoxy carbonium ions (II),¹ formed by treatment of acetals of aromatic aldehydes (I) with BF₃ in CDCl₃ or with fluorosulfonic acid. We wish to report the formation of dicarbonium ions obtained from the bisacetals of phthalaldehyde (IIIa), isophthalaldehyde (IIIb) and terephthalaldehyde (IIIc).^{2,3,4} Adding fluorosulfonic acid to (III) gave stable colored solutions of the dicarbonium ions (IV) as deduced from their nmr spectra⁵ (Table). The benzylic (H α) and the aromatic protons of (IV) are deshielded relative to the respective protons of the acetals (III). In all cases studied the leaving OCH₃ group appears as CH₃OH₂⁺ at ca. 3.93 ppm with an absorption area equal to that of the remaining OCH₃ group. An analogous absorption at ca. 3.93 ppm was observed in all arylmethoxy carbonium ions studied.⁶ The Figure shows the nmr spectrum of the bis-dimethylacetal (IIIc), and the dicarbonium ion (IVc) derived from the acetal of



terephthalaldehyde. The bisacetal (IIIc) shows three singlets at 3.30 (12H), 5.38 (2H) and 7.44 ppm (4H) assigned to the methyl, benzyl ($H\alpha$) and aromatic protons, respectively. In the dicarbonium ion (IVc) four signals are seen, at 3.91 (6H), 5.12 (6H), 8.44 (4H) and 9.71 ppm (2H). The signal at 3.91 ppm is assigned to the leaving methoxy group⁷ and that at 5.12 ppm to the methyl group remaining in the carbonium ion. The signals at 8.44 and 9.71 ppm belong undoubtedly to the aromatic and benzylic ($H\alpha$) protons, respectively.

Thus a conspicuous downfield shift of approx. 4.3 ppm of the benzylic ($H\alpha$) protons in the ionic species (IV) relative to (III) is observed (Table). The respective shift in the para-methoxy substituted arylmethoxy carbonium ion (I, $X=OCH_3$) is only ca. 3.2 ppm. The difference is due to the second carbonium ion bound to the aromatic ring which behaves as an extremely strong electron-withdrawing group. The Table includes the data of two monosubstituted arylmethoxy carbonium ions viz. II ($X=\textit{para-NO}_2^6$ and para- OCH_3). These cases emphasize the effect of the substituent on the chemical shift of the benzylic ($H\alpha$) proton. In the para-nitro derivative $H\alpha$ is shifted to lower field relative to the para-methoxy derivative. This shift which is attributed to the electron-withdrawing properties of the nitro group is even more pronounced in the dicarbonium ions. An analysis of the data obtained for the monosubstituted carbonium ions^{1,6} showed

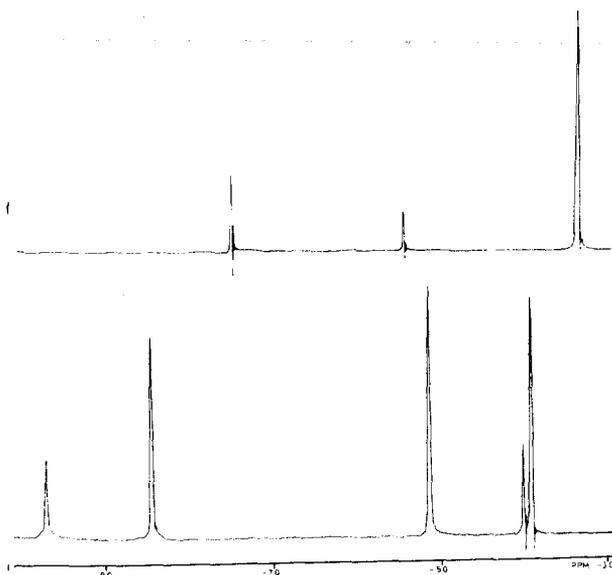


FIGURE: Nmr spectrum of the bisacetal IIIc (top) and the dicarbonium ion IVc (bottom).

a very good correlation between the chemical shift of the benzylic ($H\alpha$) protons and Hammett σ^+ constants^{8,9} as follows:

$$\delta^{H\alpha} = -58.8\sigma^+ + 135.2 \text{ Hz} \quad (1)$$

$$N = 8; \text{ CC} = 0.987; \text{ STD} = 4.7 \text{ Hz}$$

Substituting the $H\alpha$ chemical shift of the dicarbonium ions IVb and IVc in the correlation equation (1) leads to σ^+ values of +1.074 for the $H-C^+-OCH_3$ group in the para position and +0.916 in the meta position. As expected, this reflects the extremely strong electron withdrawing properties of the $H-C^+-OCH_3$ group.

TABLE: Nmr Data of Arylmethoxy Dicarbonium Ions and the Parent Acetals*

Compound	Aromatic Protons δ ppm	Benzylic Protons		Methoxy Protons	
		δ ($H\alpha$) ppm	$\Delta\delta^a$	δ^b ppm	δ^c ppm
<u>Carbonium Ions</u>					
IVa (<u>ortho</u>)	8.10 ^d	9.85	4.17	5.16	3.92
IVb (<u>meta</u>)	8.79 ^d	9.62	4.33	5.07	3.92
IVc (<u>para</u>)	8.44 ^e	9.71	4.33	5.12	3.91
II (X = <u>para</u> -NO ₂) ⁶	8.36 ^e	9.55	4.08	5.01	3.90
II (X = <u>para</u> -OCH ₃) ¹	7.96 ^f , 7.02 ^g	8.57	3.24	4.51	3.92
<u>Acetals</u>					
IIIa (<u>ortho</u>)	7.46 ^d	5.16		3.31	
IIIb (<u>meta</u>)	7.45 ^d	5.07		3.30	
IIIc (<u>para</u>)	7.44 ^e	5.12		3.31	

* 100 MHz, fluorosulfonic acid, TMS—external standard.

(a) Chemical shift difference of $H\alpha$ between acetal and ion.

(b) Chemical shift of the methoxy group of the ion, or of the parent acetal.

(c) Chemical shift of the leaving methoxy group.

(d) Center of aromatic multiplets.

(e) Aromatic singlet.

(f) δA (ortho-to acetal group), JAB = 91.3 Hz.

(g) δB (meta-to acetal group), JAB = 91.3 Hz.

References

1. M. Rabinovitz and D. Bruck, Tetrahedron Letters, 245 (1971).
2. Some examples of dicarbonium ions have been described in the literature, e.g., triaryl-methyl type ions in which the two sites of ionization were attached to a single benzene ring have previously been reported by Hart.^{3,4}
3. H. Hart, C. Y. Wu, R. H. Schwendeman, and R. H. Young, Tetrahedron Letters, 1343 (1967); H. Hart, T. Sulzberg, R. H. Schwendeman, and R. H. Young, Tetrahedron Letters, 1337 (1967).
4. R. J. Gillespie and E. A. Robinson, in "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Editors, Interscience Publishers, 1968, Vol. I, pp. 127.
5. The spectra were recorded on a Varian HA-100D spectrometer at 100 MHz, external TMS serving as standard. In all the cases studied the fluorosulfonic acid was B and A technical grade and the molar concentration 0.3 molar. Spectra were run at +31.5°C.
6. Unpublished data from our laboratory.
7. (a) An additional small signal is found close to the signal of the leaving methoxy group (8Hz apart to lower field). This signal is assigned to either a protonated dimethyl ether or to a product resulting from it.^{7b} Upon addition of dimethyl ether to the solution, this signal increases significantly. Upon addition of methanol the signal at 3.93 ppm becomes stronger.
(b) G. A. Olah, A. M. White, and D. H. O'Brien, Chem. Rev., 70, 561 (1970).
8. H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958).
9. As expected for positively charged substituted molecules the σ -constant did not correlate well with the chemical shift.