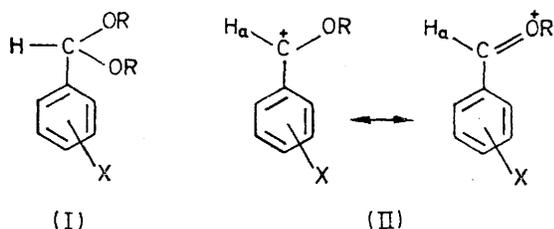


Observation of Stable Arylalkoxycarbenium Ions: a Nuclear Magnetic Resonance Study

By Daniel Bruck and Mordecai Rabinovitz,* Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Stable carbenium ions are formed by treatment of acetals of aromatic aldehydes with BF_3 or fluorosulphonic acid. The structure of these ions has been elucidated from their ^1H chemical shifts. Additional evidence is the presence of a common counter ion in the series. Very good correlations were observed between the ^1H chemical shifts and the respective Brown σ^+ substituent constants emphasizing the dependence of these quantities on the charge density of the ions. The value of σ^+ for the $\text{H}-\text{C}^+-\text{OCH}_3$ group is +1.074 in the *para*-position and +0.916 in the *meta*-position, reflecting the strong electron-withdrawing properties of this group.

KINETIC studies of the acid-catalysed hydrolysis of acetals have established that the rate-determining step in this reaction is the formation of a positively charged species.¹ The reaction has been shown to be specifically acid catalysed.^{2,3} Its mechanism involves a fast protonation of the acetal followed by a unimolecular rate-determining decomposition to the corresponding alcohol and a resonance stabilized carbenium ion. In the case of the acetals (I) derived from aromatic aldehydes, the carbenium ion (II) carries an aryl and an alkoxy-substituent. The stabilizing effect of the alkoxy-group is



demonstrated by the stability of the carbenium salts formed from orthoesters⁴ and dioxolans⁵ or by the facile alkylation of carbonyl compounds.⁶ Hart and Tomalia have studied 2-alkyl-1,3-dioxolenium cations in fluoro-

sulphonic acid.⁵ Boer and his co-workers have studied the reaction products of bromine with orthoesters and acetals.^{4c} Kabuss has shown that alkylation of benzaldehyde with dialkoxycarbenium salts afforded an arylalkoxycarbenium ion.⁶ We have studied carbenium ions of type (II) obtained from acetals of aromatic aldehydes in acidic media, applying n.m.r. spectroscopy.^{7,8} This study led to the observation of the stable arylalkoxy cations and provided an insight into the factors influencing these ions. Two acid systems have been studied: fluorosulphonic acid and boron trifluoride in deuteriochloroform.

EXPERIMENTAL

The acetals (13 methyl acetals and four ethyl acetals) were prepared from the parent benzaldehydes and methyl orthoformate and ethyl orthoformate respectively.⁹ The formation of the carbenium ions in the $\text{BF}_3\text{-CDCl}_3$ system was carried out by dissolving acetal (2 mmol) in CDCl_3 (2.5 ml) (containing 15% Me_4Si) in a 5 ml flask. The flask was then stoppered with a septum stopper and cooled to -76° . Through a hypodermic needle serving as a gas inlet, BF_3 gas was bubbled until the solution was saturated. A second hypodermic needle served as a gas outlet. The flask was then warmed to room temperature. A two-phase system is formed. Only the lower layer showed the presence of ions in the n.m.r. spectrum. In the upper layer only traces of the

¹ E. H. Cordes, *Progr. Phys. Org. Chem.*, 1966, **4**, 1.

² M. M. Kreevoy and R. W. Taft, *J. Amer. Chem. Soc.*, 1955, **77**, 3146.

³ H. K. Garner and H. J. Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5497.

⁴ (a) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Annalen*, 1960, **632**, 38; (b) H. Meerwein, V. Hederick, H. Morschel, and K. Wunderlich, *ibid.*, 1960, **635**, 1; (c) C. H. V. Dusséau, S. E. Schaafsma, H. Steinberg, and T. J. de Boer, *Tetrahedron Letters*, 1969, 467.

⁵ H. Hart and D. Tomalia, *Tetrahedron Letters*, 1966, 3383, 3389.

⁶ S. Kabuss, *Angew. Chem.*, 1966, **78**, 714.

⁷ M. Rabinovitz and D. Bruck, *Tetrahedron Letters*, 1971, 245.

⁸ M. Rabinovitz and D. Bruck, *Tetrahedron Letters*, 1972, 1831.

⁹ J. Klein and E. D. Bergmann, *J. Amer. Chem. Soc.*, 1957, **79**, 3452.

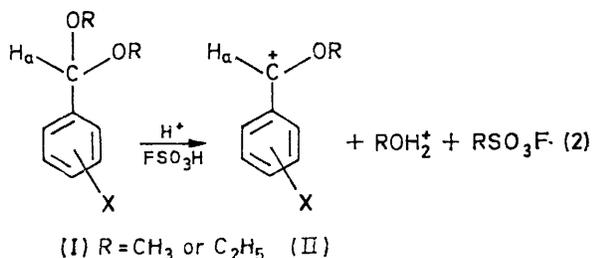
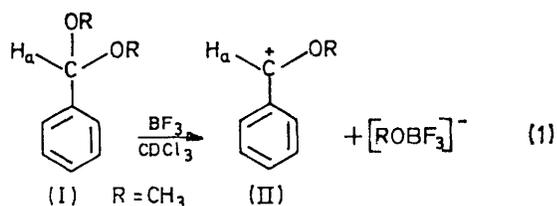
starting acetal could be detected. The formation of the ions in fluorosulphonic acid was obtained as follows. To acetal (0.3 mmol) in an n.m.r. tube cooled to -76° cooled fluorosulphonic acid (0.5 ml) was added. The tube was immediately stoppered and left to reach room temperature. In the formation of the doubly charged ions acetal (0.15 mmol) was added.

All spectra were recorded on a Varian HA-100D spectrometer, probe temperature 34.5° . When the measurements were carried out in CDCl_3 , internal Me_4Si served as standard. In fluorosulphonic acid external Me_4Si served as a standard.

The correlations were programmed with a Fortran IV program. The input of the program consists of the data matrix previously described.¹⁰ In the present study we have used this program to correlate between spectral parameters, *e.g.* chemical shifts and substituent constants such as σ , σ^+ , and σ^R .

RESULTS AND DISCUSSION

Two modes of formation of the cations were practised. In the first mode [equation (1)] the acetal, dissolved in deuteriochloroform, reacts with boron trifluoride which is passed through the solution. A two-phase system is formed and the ion is observed in the lower layer. In the second mode [equation (2)] the acetal is dissolved in fluorosulphonic acid and the acid acts both as an acid and as solvent, to yield the ion.



Although both the initial acetals and the final arylalkoxy ions are the same in both reaction modes, the different counter-ion species as well as the different solvent systems lead to different chemical shifts in the two systems. The advantage of $\text{BF}_3\text{-CDCl}_3$ lies in its being an organic non-viscous solvent system in the mild conditions employed. The advantage of the FSO_3H system lies in its being a stronger acid which stabilizes the

carbenium ion; under these conditions ions with a strong electron-withdrawing group, *e.g.* a nitro-substituent, may be obtained. The dimethyl acetal derived from *para*-nitrobenzaldehyde afforded the ion only in FSO_3H ; it did not ionize in $\text{BF}_3\text{-CDCl}_3$. Hence, the two systems are complementary. The chemical shifts of these two systems correlate well with each other (see later).

The Acetals.—We have prepared a series of methyl and ethyl acetals of substituted benzaldehydes.* The n.m.r. data of the methyl acetals are given in Table 1. The data in the Table emphasize the significant high field shift of the acetal proton (H_α) compared with the formyl proton of the parent benzaldehyde.¹⁰ This effect is undoubtedly due to the absence of the anisotropy of the carbonyl group in the acetals. The substituents of the benzene ring in the *meta*- and *para*-positions show very little effect on the chemical shifts of H_α . In benzaldehyde dimethyl acetal and in eight ring-substituted derivatives this chemical shift differs by only 0.05 p.p.m. (excluding the *p*-nitro-substituted acetal). This fact illustrates the absence of conjugation between the aromatic ring and the dimethoxymethyl substituent. Obviously, there is no correlation between σ or σ^+ substituent constants and these chemical shifts.^{11,12} In the case of the *ortho*-substituted benzaldehyde acetals both the α -proton and the methoxy-protons of the acetal group are shifted to lower field. A similar effect is also reported in *ortho*-substituted benzaldehydes where the formyl proton is shifted to lower field compared with the respective *meta*- or *para*-substituted benzaldehydes.¹⁰ The *ortho*-ring protons of the acetals (excluding *p*-nitrobenzaldehyde acetal) do not show significant variations in their chemical shifts. However, protons at *meta*-positions (of *para*-substituted acetals) do show a diversity of chemical shifts.

The Ions.—The carbenium ions manifest a significant low-field shift of H_α and aromatic protons. The down-field shifts of H_α are of the order of 3–4 p.p.m. compared with H_α of the parent acetals. The ionic nature is deduced from the n.m.r. data of the ions derived from methyl acetals (II; $R = \text{CH}_3$) (Tables 2 and 3) and the n.m.r. data of the ions derived from ethyl acetals (II; $R = \text{C}_2\text{H}_5$) (Table 4). We found it more convenient to study the methyl acetals because of the simplicity of the spectra obtained from the respective ions. The arylmethoxy ions and arylethoxy-carbenium ions show similar chemical shifts of H_α . The deshielding effect of H_α indicates a positive charge next to it and its delocalization over the molecule. Figure 1 shows the n.m.r. spectra of *p*-bromobenzaldehyde dimethyl acetal and the carbenium ion obtained by treating it with $\text{BF}_3\text{-CDCl}_3$ (II; $X = p\text{-Br}$, $R = \text{CH}_3$). Figure 2 shows the n.m.r. spectra of anisaldehyde dimethyl acetal and the ion obtained from it in fluorosulphonic acid (II; $X = p\text{-OCH}_3$, $R = \text{CH}_3$).

New additional peaks appeared in the n.m.r. spectrum of the ionic species. The ionization is followed by one

* The ethyl acetals have a prochiral carbon atom and therefore show an even more complex spectrum for the methylene protons.

¹⁰ (a) M. Rabinovitz and A. Grinvald, *J. Amer. Chem. Soc.*, 1972, **94**, 2724; (b) A. Grinvald and M. Rabinovitz, *J.C.S. Perkin II*, 1974, 94.

¹¹ C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

¹² H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

TABLE 1

N.m.r. data * of substituted benzaldehyde dimethyl acetals

Substituent	H_{α} ^a	Methoxy protons	Substituent protons	Aromatic protons		
				<i>ortho</i> -protons ^b	<i>meta</i> -Protons ^b	Δ ^c
H	537.3	330.4				
4-CH ₃	534.3	329.0	232.6	731.5	714.5	17.0
4-OCH ₃	533.2	328.0	376.5	732.8	688.1	44.7
4-Cl	535.6	328.3		734.4	734.4	0.0
4-Br	533.4	328.2		730.7	746.7	-16.0
4-F	534.3	329.2				
4-NO ₂	546.6	332.6		736.3	820.2	-56.9
3-F	536.6	330.2				
2-CH ₃	544.2	329.8	235.0			
2-OCH ₃	566.6	357.8	380.8			
2-CH(OCH ₃) ₂	567.9	331.0				
3-CH(OCH ₃) ₂	538.9	330.4				
4-CH(OCH ₃) ₂	538.3	330.6		744.4	744.4	0.0

* In Hz from internal Me₄Si, recorded on a 100 MHz n.m.r. spectrometer, CDCl₃ solutions.^a Acetal group proton (α -proton). ^b Relative to the acetal group. ^c Chemical shift difference between *ortho*- and *meta*-protons.

TABLE 2

N.m.r. data * of arylmethoxycarbenium ions in CDCl₃-BF₃

Substituent	H_{α} ^a	Methoxy-protons ^b	Methoxy-protons ^c	Substituent protons	Aromatic protons (<i>ortho</i>) ^d	Aromatic protons (<i>meta</i>) ^e
H	961.5	502.6	356.1			
4-CH ₃	950.4	494.8	354.0	253.3	819.9	751.6
4-OCH ₃	915.9	481.1	357.3	405.0	826.2	717.7
4-Cl	960.9	502.7	350.8		826.4	765.2
4-Br	963.0	502.7	351.0		814.3	783.6
4-F	958.4	503.6	355.8			
3-F	974.2	512.8	355.7			
2-CH ₃	962.2	498.6	353.7	267.9		
2-OCH ₃	956.0	487.7	357.8	404.1		

* In Hz from internal Me₄Si, recorded on a 100 MHz n.m.r. spectrometer.^a Benzylic proton (α -proton). ^b Remaining methoxy-group protons. ^c Leaving methoxy group protons. ^d *ortho* to the carbenium centre. ^e *meta* to the carbenium centre.

TABLE 3

N.m.r. data * of arylmethoxycarbenium ions in FSO₃H

Substituent	H_{α} ^a	ΔH_{α} ^b	Methoxy protons ^c	Methoxy protons ^d	Additional peak ^e	Substituent protons	Aromatic protons			
							<i>ortho</i> Protons ^f	Δ <i>ortho</i> ^g	<i>meta</i> Protons ^h	Δ <i>meta</i> ⁱ
H	912.6	375.3	477.7	390.7	399.3					
4-CH ₃	895.6	361.3	470.9	394.1	403.1	240.3	800.0	68.5	743.9	29.4
4-OCH ₃	857.0	323.8	451.1	392.2	400.8	389.5	793.6	60.8	702.3	14.2
4-Cl	912.3	376.7	479.0	393.9	402.7		808.5	74.1	755.6	21.2
4-Br	912.7	379.3	477.7	393.5	401.7		793.1	62.4	776.9	30.2
4-F	907.0	372.7	477.5	393.7	401.9					
4-NO ₂	954.8	408.2	501.3	390.4	400.0		836.4	73.1	836.4	16.2
3-F	924.8	388.2	488.0	395.1	403.6					
2-CH ₃	926.1	381.9	478.7	394.6	403.9	256.5				
2-OCH ₃	930.8	364.2	461.2	395.2	403.7	390.2				
2-CH(OCH ₃) ₂	984.7	416.8	515.6	392.3	401.1					
3-CH(OCH ₃) ₂	961.7	422.8	506.8	392.5	400.5					
4-CH(OCH ₃) ₂	971.0	432.7	511.9	391.0	399.2		844.5	100.1	844.5	100.0

* In Hz from external Me₄Si, recorded on a 100 MHz n.m.r. spectrometer.^a Benzylic proton (α -proton). ^b Chemical shift difference of H_{α} between acetal and ion. ^c Chemical shift of remaining methoxy-group protons. ^d Chemical shift of leaving methoxy-group protons. ^e Assigned to methylfluorosulphonic acid. ^f Chemical shift of protons *ortho* to the carbenium centre. ^g Chemical shift difference between the *ortho*-protons of the acetals and the ions. ^h Chemical shift of protons *meta* to the carbenium centre. ⁱ Chemical shift difference of *meta*-protons between the acetals and the ions.

TABLE 4

N.m.r. data * of aryloxy-carbenium ions in FSO₃H

Substituent	H _α ^a		Methylene		Methyl		Methyl-ene ^d	Methyl ^d	Substituent protons		Aromatic protons, acetal		Aromatic protons, ion	
	Acetal	Ion	Acetal ^b	Ion ^c	Acetal ^b	Ion ^c			Acetal	Ion	<i>ortho</i> ^e	<i>meta</i> ^f	<i>ortho</i> ^g	<i>meta</i> ^h
	H	549.3	910.8	357.9	503.2	121.7	144.7	440.8	118.0					
4-CH ₃	546.4	889.5	355.2	490.4	120.8	138.0	438.6	115.5	232.4	226.2	732.7	715.6	784.5	732.2
4-OCH ₃	545.0	857.0	360.6	473.4	121.1	134.5	441.0	118.9	377.9	378.6	737.6	686.4	800.4	697.2
3,4,5-OCH ₃	540.1	864.0	353.6	481.9	124.0	138.6	440.8	119.2	385.6	394.1	671.5		740.8	
			356.6						382.2	387.5				

* In Hz from external Me₄Si recorded on a 100 MHz n.m.r. spectrometer.

^a Benzylic proton (α-proton). ^b Protons of the ethoxy-group. ^c Protons of the remaining ethoxy-group. ^d Protons of the leaving ethoxy-group. ^e *ortho* to the acetal group. ^f *meta* to the acetal group. ^g *ortho* to the carbenium centre. ^h *meta* to the carbenium centre.

alkoxy-group leaving the acetal. This alkoxy-group is in the form of a protonated or a complexed species; it

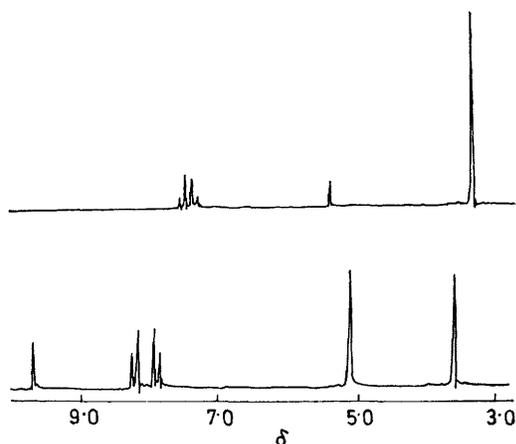


FIGURE 1 N.m.r. spectra (100 MHz; CDCl₃; Me₄Si internal reference) of *para*-bromobenzaldehyde dimethyl acetal (top) and the ion (II; X = *p*-Br, R = CH₃) (bottom) obtained in BF₃-CDCl₃.

appears in the spectrum as an additional peak of the leaving group. This leaving group can, however, undergo additional reactions to form other species in the system (see later). H_α is expected to be less deshielded as charge delocalization increases. Indeed, the least deshielded α-proton is found in the *p*-methoxy-substituted ion (II; X = *p*-OCH₃, R = CH₃) (Tables 2 and 3). This phenomenon contrasts with the behaviour of the parent acetal; it suggests that charge delocalization makes an important contribution to the stabilization of the carbenium ions. In other words, there is a strong interaction between the charged group (H-C-OCH₃)⁺ and the other substituent of the aromatic ring. This interaction can be demonstrated by the good correlation of the chemical shifts of H_α with Brown's σ⁺ constants¹² of seven ions in BF₃-CDCl₃ [equation (3)]. However, the

$$\delta^{\text{H}\alpha} = 48.75 \sigma^+ + 958.7 \text{ Hz} \quad (3)$$

[no. of points *n* 7; correlation coefficient *r* 0.972; standard deviation *s* 4.7 Hz for (II; R = CH₃, X = *p*-CH₃, *p*-OMe, H, *p*-Cl, *p*-Br, *p*-F, *m*-F)]

correlation with Hammett's σ constants¹¹ is poor (*r* 0.852). The good correlation (3) suggests that a significant charge is localized on the carbon atom. A similar result was obtained in the FSO₃H system [equation (4)].

$$\delta^{\text{H}\alpha} = 58.8\sigma^+ + 907.8 \text{ Hz} \quad (4)$$

[*n* 8; *r* 0.987; *s* 4.7 Hz for (II; R = CH₃, X = H, *p*-CH₃, *p*-OCH₃, *p*-Cl, *p*-Br, *p*-F, *p*-NO₂, *m*-F)]

Additional evidence for the existence of the ions is obtained from the presence of the leaving group. In the acetals (I; R = CH₃) both methoxy-groups appear in the n.m.r. spectrum as a single line. Their chemical shift [excluding (I; X = OCH₃)] is δ 3.30 ± 0.03 (Table 1). When the ionic species are formed, two resonances are expected for the methoxy-groups. One resonance corresponds to the remaining methoxy-group, *i.e.* linked to

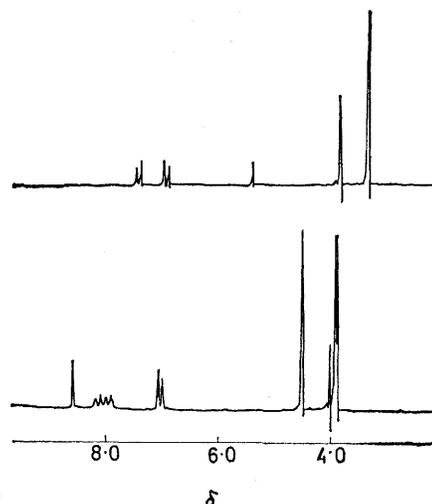


FIGURE 2 N.m.r. spectra (100 MHz) of anisaldehyde dimethyl acetal (CDCl₃; Me₄Si internal reference) (top) and *p*-methoxyphenylmethoxycarbenium ion (II; X = *p*-OCH₃, R = CH₃) (bottom) obtained in fluorosulphonic acid (Me₄Si external reference)

C_α of ion (II) and the other absorption corresponds to the leaving methoxy-group in the form of a protonated or a

complexed species. The methoxy-resonance of the leaving group in each solvent system should have the same chemical shift for each member of the series. On the other hand, the chemical shift of the remaining methoxy-group is influenced by the charge distribution of the various carbenium ions. This is indeed what is observed. In the two solvent systems the leaving methoxy-group resonates at δ 3.54 \pm 0.03 (BF₃-CDCl₃) and at 3.93 \pm 0.02 (FSO₃H), thus showing a common counter ion in each series.

In addition to protonated methanol another peak appears in fluorosulphonic acid. It is assigned to methyl-fluorosulphonic acid. Addition of methanol to the sample caused an enhancement of the peaks derived from the leaving methoxy-group, particularly the one which belongs to protonated methanol. In BF₃-CDCl₃ only one peak of the leaving methoxy-group appears; it is

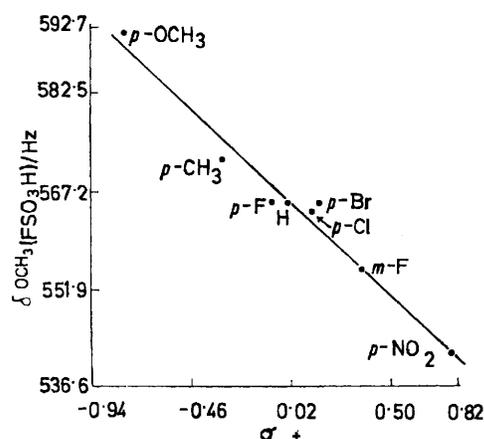


FIGURE 3 A computed best-fit line of the correlation of the chemical shift of the remaining methoxy-group of the ions (II; R = CH₃) (relative to FSO₃H δ 10.42) with Brown σ^+ substituent constants (n 8; r 0.985; s 2.6 Hz; slope -30.47)

assigned to the (CH₃OBF₃)⁻ counter ions.^{4,13} The remaining methoxy-group of cations (II) are expected to be influenced by the other parts of the molecule and hence their chemical shifts should correlate well with the chemical shifts of the other protons in the ions. Such a correlation should also hold with the substituent constants of the ions. In the BF₃-CDCl₃ acid-solvent system, the remaining methoxy-group correlates well with Brown's σ^+ substituent constants (r 0.971) but not with Hammett's σ constants. This result emphasizes the nature of the ionic species, having a delocalized charge of the carbenium-oxonium type ion (II). Figure 3 gives a computed best-fit line of the correlation of the chemical shift of the remaining methoxy-group with σ^+ (in FSO₃H). The chemical shifts of the remaining methoxy groups also correlate well with the chemical shifts of the H _{α} in the various ions in BF₃-CDCl₃ [equation (5)]. The high

$$\delta^{\text{H}_\alpha} = 1.847 \delta^{\text{OCH}_3} + 31.4 \text{ Hz} \quad (5)$$

[n 7; r 0.979; s 4.2 Hz for (I; R = CH₃, X = H, *p*-CH₃, *p*-OCH₃, *p*-Cl, *p*-Br, *p*-F, *m*-F)]

charge density of the α -carbon is evident. However, in fluorosulphonic acid the above mentioned correlation is even better [equation (6), Table 3].

$$\delta^{\text{H}_\alpha} = 1.86 \delta^{\text{OCH}_3} + 19 \text{ Hz} \quad (6)$$

(n 10; r 0.997; s 2.6 Hz)

The chemical shifts of the remaining methoxy-groups of the ionic species (in FSO₃H) also correlate well with Brown's σ^+ constants [equation (7), Table 3]. Here

$$\delta^{\text{OCH}_3} = 30.47 \sigma^+ + 477 \text{ Hz} \quad (7)$$

(n 8; r 0.985; s 2.6 Hz)

again the correlation with σ constants is poor (r 0.925). In order to study the medium effect on the chemical shifts, we have correlated between the chemical shifts of H _{α} of the ions in the two media (BF₃-CDCl₃ and FSO₃H).

$$\delta^{\text{H}_\alpha(\text{BF}_3)} = 0.838 \delta^{\text{H}_\alpha(\text{FSO}_3\text{H})} + 198 \text{ Hz} \quad (8)$$

(n 7; r 0.998; s 1.4 Hz)

This correlation is very good indeed and it shows that the same factors are operating in both acid-solvent systems (this correlation includes only *para*- and *meta*-substituted ions).

The reaction of acetals of aromatic aldehydes with an acid was also carried out to obtain doubly charged ions.^{8,14} These dicarbenium ions (Table 3) are formed in the reaction of dimethyl acetals of phthalaldehyde [I; X = *o*-CH(OCH₃)₂], isophthalaldehyde [I; X = *m*-CH(OCH₃)₂], and terephthalaldehyde [I; X = *p*-CH(OCH₃)₂] with fluorosulphonic acid. The ionic structure was deduced from their n.m.r. spectra. The effect of deshielding of H _{α} observed in the singly charged ions is even more conspicuous in the doubly charged ions. The dications are stable in acid medium and they are deeply coloured. The leaving methoxy-group appears at δ 3.92, 3.93, and 3.91 for the *ortho*-, *meta*-, and *para*-substituted derivatives, respectively. This absorption is within the narrow range of the absorption of the previously mentioned leaving methoxy-group. However, in the spectra of the doubly charged carbenium ions, the area of the peaks was of the ratio of 2:3:3:1 for the aromatic, leaving methoxy, remaining methoxy, and H _{α} protons, respectively. Figure 4 shows the spectrum of the acetal of terephthalaldehyde and the doubly-charged carbenium ion derived from it (II; X = *p*-H-C⁺-OCH₃). Four main peaks can be observed in the spectrum. At δ 9.71 there is a signal assigned to H _{α} (2-H, s), at 8.44 an absorption assigned to the aromatic protons (4H, s), at 5.12 a peak for the remaining methoxy-groups (6H, s), and at 3.91 an absorption for the leaving methoxy-groups (6H, s). In the neighbourhood of the peak assigned to the leaving methoxy-group (protonated methanol) an additional peak appears and it is attributed to methylfluorosulphonic acid. The relative peak areas as well as the

¹³ H. Meerwein, *Angew. Chem.*, 1955, **67**, 374.

¹⁴ Several doubly charged ions have been prepared previously, e.g. see (a) H. Hart, C. Y. Wu, R. H. Schwendeman, and R. H. Young, *Tetrahedron Letters*, 1967, 1343; (b) H. Hart, T. Sulzberg, R. H. Schwendeman, and R. H. Young, *ibid.*, p. 1337.

chemical shifts prove the existence of a doubly charged molecule. This doubly charged molecule represents an aromatic ring bearing two strong electron-withdrawing groups and its n.m.r. spectrum should be similar to that of the *para*-nitro-substituted ion in the singly charged series (II; X = *p*-NO₂, R = CH₃) (Table 3). The doubly charged molecules show, however, a more pronounced downfield shift of H_α and the aromatic protons relative to the parent acetals, than any of the singly charged molecules. These low-field shifts emphasize the stronger electron-withdrawing properties of the H-C⁺-OCH₃

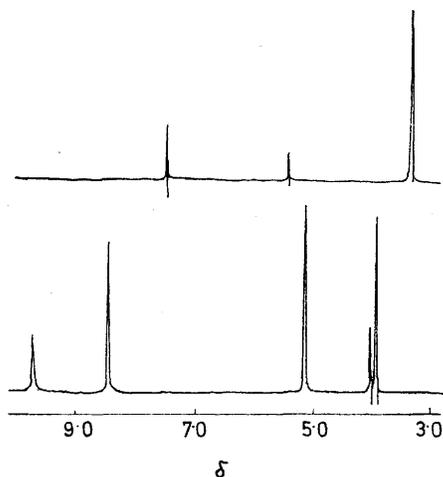


FIGURE 4 N.m.r. spectra (100 MHz) of terephthalaldehyde dimethyl acetal (top) in CDCl₃ (Me₄Si internal reference) and the doubly charged ion (bottom) obtained in fluorosulphonic acid (Me₄Si external reference)

group compared with the nitro-substituent. Substituting the H_α chemical shifts of the dicarbenium ions (II; X = *m* and *p*-H-C⁺-OCH₃) in the correlation equation (4)

leads to σ^+ values of +1.074 and +0.916 for the *para*- and *meta*-positions respectively (Figure 5). As expected,

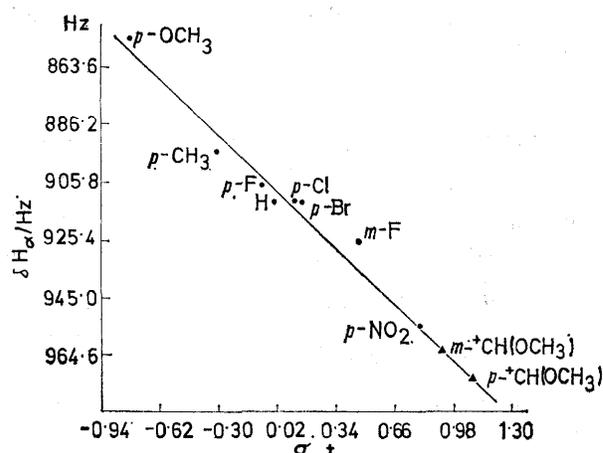


FIGURE 5 A computed best-fit line of the correlation of the chemical shifts of H_α of singly charged ions bearing *meta*- and *para*-substituents (obtained in fluorosulphonic acid) with Brown σ^+ substituent constants (●; *n* 8; *r* 0.987; *s* 4.7; slope 58.8; equation (4)). The chemical shifts of H_α of the doubly charged ions were substituted into equation (4) (▲; *n* 2)

these values reflect the extremely strong electron-withdrawing properties of the charged substituent.

The good correlation of the chemical shifts of the remaining methoxy group with H_α [equations (5) and (6)] as well as the good correlation between the remaining methoxy-groups and σ^+ constants indicate that the H-C⁺-OCH₃ group has also some oxonium contribution to its structure, and it should be referred to as a carbenium-oxonium ion. This ion is undoubtedly stabilized by the remaining methoxy-group

[5/748 Received, 21st April, 1975]