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ARYLALKOXYCARBONIUM IONS

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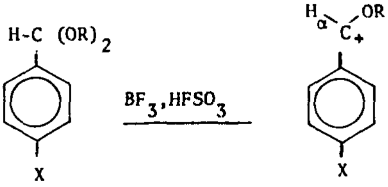
The rate determining step of the acid catalysed hydrolysis of acetals has been assumed to involve a carbonium ion intermediate.[1] Aliphatic alkoxycarbonium ions have been formed by the reaction of BF_3 or bromine with orthoesters and acetals.[2,3] Taft[4] obtained tertiary aromatic ions while a secondary phenylalkoxycarbonium ion has been reported only in the alkylation reaction of benzaldehyde.[3c] We wish to report the direct observation of stable arylalkoxycarbonium ions (II) by reaction of acetals of aromatic aldehydes (I) with boron trifluoride in $CDCl_3$ solution or with fluorosulfonic acid. When a solution of an aromatic acetal in deuterochloroform is treated with BF_3 at room temperature a stable[5] clear deep coloured solution is obtained. The ionic nature of the aryl carbonium ion (II) is deduced from the nmr data (Table); the substantial deshielding of the aromatic and benzylic protons observed indicate the presence of a positive charge and its delocalization over the molecule. The downfield shift of the order of 4.0 ppm of the benzylic proton H_α in the positively charged arylalkoxy ions is compared with the respective absorption in the covalent acetals. As charge delocalization in the carbonium ion increases, H_α will be expected to be less deshielded. Indeed, this hydrogen is least deshielded in the ion II ($X = OCH_3$, $R = CH_3$, $\delta H_\alpha = 9.17$ ppm) which suggests that charge delocalization makes an important contribution to the stabilisation of this ion. This carbonium ion shows a high rotational barrier about the $C_{aryl}-CHOCH_3^+$ bond; the coalescence temperature is +20°C. At lower temperatures an ACBB' spectrum is obtained while at +45°C the pattern is transformed to an AA'BB' spectrum. The spectrum of the parent acetal did not change significantly in the



I   II

$R = CH_3, C_2H_5$

$X = H, CH_3, OCH_3$

observed range +60 — -50°C. The above assumptions are strengthened by the deshielding of the protons of the ring substituent X. The two methoxy groups of the carbonium ions are not equivalent, for II (X = H, CH_3) each one corresponds to an equal number of protons, the δ = 3.55 ppm is assigned to $CH_3OBF_3^-$ while the absorption at δ = **4.98** ppm represents the methoxy group of the carbonium ion.

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TABLE. NMR Data of Arylalkoxy Carbonium Ions and their Parent Acetals*

	Substituent	Aromatic protons (cps)			Benzylic protons (cps)		Substituent protons (cps)	Methoxy protons (cps)	
		δA	δB	JAB	δH_α	Δ^a	δX	δ^b	δ^c
Carbonium Ions	X = H^d	818.0^e	761.0^e		956.0	418.0		356	498
	X = $CH_3{}^d$	751.2	817.3^d	8.3	947.1	420.3	254.0	352	498
	X = $OCH_3{}^f$	721.0	829.1^f	9.0	917.0	384.1	407.5	361	482
									δ
Acetals	X = H^d				538.1				329.5
	X = $CH_3{}^d$	714.0	731.6	7.8	533.7		232.0		328.6
	X = $OCH_3{}^f$	684.0	733.4	8.8	532.9		373.4		325.6

* 100 MHz in $CDCl_3$, TMS reference.
a) Chemical shift difference between H_α of the acetal and the carbonium ion. b) Chemical shift of $CH_3OBF_3^-$. c) Chemical shift of the carbonium ion methoxy group -$CHOR^+$. d) At probe temperature. e) Centre of multiplets. f) At +50°C.

References

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5. For I, R = CH_3, X = OCH_3, the nmr spectrum did not change even after one week at room temperature. Reaction of the acetals with FSO_3H gave similar results.