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ANISYL CARBONIUM IONS

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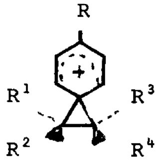
The nature of transition states and intermediates in the solvolysis of 2,4-, and 5-aryl substituted alkyl halides, etc. continues to be a source of controversy (1). Rate and product studies (1-3) have been interpreted as proceeding through intermediates or transition states such as I and II. Recently, for p-$CH_3OC_6H_4C(CH_3)_2C(CH_3)_2X$ (X = OH, Cl, DNB) and related compounds, Brown and Kim (1) have argued for rapidly equilibrating π bridged intermediates eq. (1) in reactions considered to proceed by a carbonium ion mechanism.



I(a) R=OCH_3
$R^1=R^2=R^3=R^4=H$
(b) R=H
$R^1=R^2=R^3=R^4=CH_3$

II

eq. (1)

III(a) R = OCH_3, $R^1=R^2=R^3=R^4=CH_3$; (b) R = H, $R^1=R^2=R^3=R^4=CH_3$

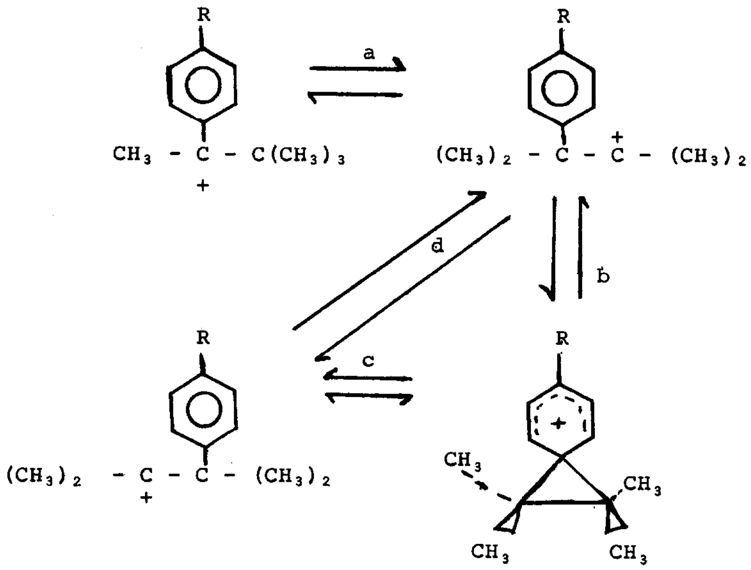
Observation of both stable para-anisonium ion (Ia) (4) and rapidly equilibrating ion III(b) eq. (1) (5) was suggested recently. Olah (6) now believes the latter to be I(b), not III(b), on the basis of drowning products and reaches a similar conclusion to that in this paper concerning the system III(a).

Under conditions (-70°, $SbF_5 \cdot SO_2$) where I(a) is formed from 2-p-anisylethylchloride or alcohol (4), we have examined ions produced from p-$CH_3OC_6H_4(CH_2)_4Cl$ and p-$CH_3OC_6H_4C(CH_3)_2C(CH_3)_2OH$. The 4-p-anisylbutylchloride gives not II, but the ion IV, which was also generated from the corresponding methyl ether, Fig. 1. Since rearrangement of II to IV requires opening a highly stabilized alkoxyalkenyl cation to at best a primary π complexed carbonium ion, we feel that had II been initially formed, it would have been observed by nmr spectroscopy.

Further, p-$CH_3OC_6H_4C(CH_3)_2C(CH_3)_2OH$ at -70° in $SbF_5 \cdot SO_2$ produces neither the corresponding anisonium ion nor the equilibrating π complexed ion III as postulated by Brown, but yields the benzylic ion V whose nmr spectrum is given in Fig. 2. The same spectrum is obtained from p-$CH_3OC_6H_4C(OH)(CH_3)(C(CH_3)_3)$.

The nmr of V is particularly interesting in its temperature dependence. At -70° the chemical shifts (-δ) for V are $(\underline{H_3}C)_3C$ 1.6; $\underline{CH_3}$-C^+ 3.1; $O\underline{CH_3}$ 4.3; ring $\underline{H}$ 7.4 and 8.9 ppm. As the temperature is raised the CH_3 protons signals broaden and collapse to give at 0° a single broad CH_3 peak of 12 protons at 1.95 ppm. (Fig. 2). The process is reversible, although there is minor decomposition at 0° characterized by the irreversible appearance of new peaks at 1.0 - 1.6 and 9.9 ppm. The important point is that even at 0° where all CH_3 are equivalent, the ring proton chemical shifts are still characteristic (4) of the benzyl ion, with a chemical shift difference of 1.5 ppm. between them, and at no point in the temperature progression is there substantial line broadening of the ring protons. These may be compared with the ring proton shifts of the anisonium ion of -7.3 ppm. and -7.9 ppm., a difference of only 0.6 ppm. It seems clear that the nmr spectrum (Fig. 2) at 0° does not represent a rapidly equilibrating system such as eq. (1), but instead equivalence of methyl groups is obtained by a mechanism of eq. 2(a), R = OCH_3. In view of results for V, the nmr spectrum assigned (6) to I(b), may instead be that of equilibrating benzyl and butyl ions (eq. 2a) of nearly equal stability. The gas phase 19-21 kcal/mole stabilization by p-CH_3O of the benzyl ion is close enough to the activation energy of eq. 2(a) (R = OCH_3) to strongly suggest this possibility. The importance of 2b, 2c and 2d was not evaluated quantitatively, but 2a seems to account for the major aspects of temperature dependence of the spectrum of V.

If one accepts recent arguments (1) for equilibrium eq (1) in solvolysis reactions, etc., of β-arylethyl derivatives, it is necessary to explain why p-$CH_3OC_6H_4C(CH_3)_2C(CH_3)_2OH$ behaves so differently in $SbF_5 \cdot SO_2$. Similarly one must account for respectable yields (7) of products derived from II in solvolysis reactions of 4-anisylbutyl derivatives but the total absence of formation of II eq. (2)



in SbF_5SO_2. It is possible to rationalize these differences in terms of different relative stabilities of ground states and transition states within a set of free carbonium ions in $SbF_5 \cdot SO_2$ and within the corresponding set of intimate ion pairs,

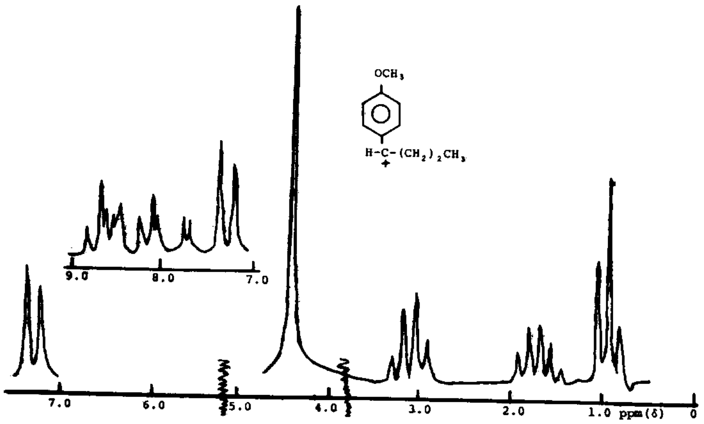


FIG. 1

The proton nmr spectrum of the 1-anisylbutyl cation IV at -70° in $SbF_5 \cdot SO_2$; scale ppm. downfield from TMSi(δ); nonlinear between 3-4 and 5-6.

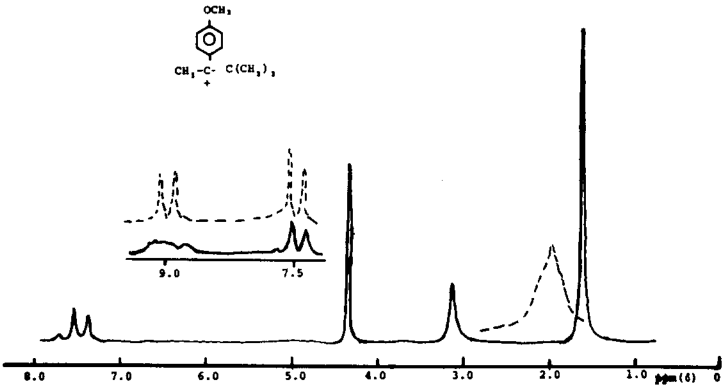


FIG. 2

The proton nmr spectra of the 2-anisyl-3,3-dimethylbutyl cation V in $SbF_5 \cdot SO_2$ at (——) -70°; (---) 0°. (offset 150 cps).

or in terms of relative intermediate lifetimes which depend on different solvent nucleophilicity. Further discussion, however, must be deferred to a full paper.

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