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NUCLEAR MAGNETIC RESONANCE SPECTRA OF ASYMMETRICALLY SUBSTITUTED BENZOPHENONES IN STRONGLY ACIDIC MEDIA

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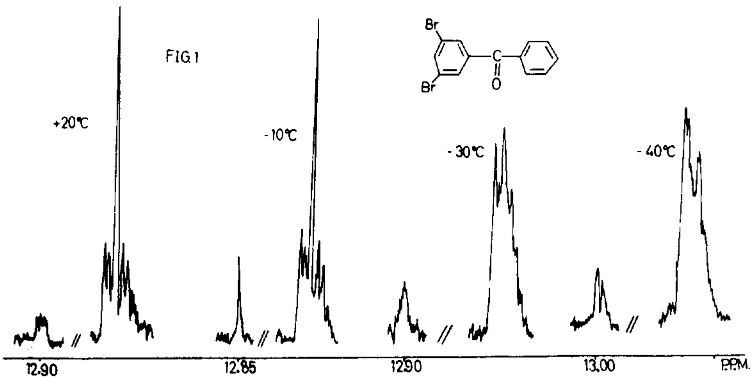
It is well known that aromatic aldehydes and ketones are protonated in strongly acidic media (1,2,3,4). NMR data of protonated acetophenones have been published (4). We now wish to report NMR data on protonated benzophenones in HSO_3F - SbF_5.

The spectra of p-substituted benzaldehydes show two low field doublets due to the $=\overset{+}{O}H$ proton and the aldehydic hydrogen (J=8 cps). The captured proton in acetophenones and symmetrically substituted benzophenones causes a sharp singlet between 12.50 and 14.00 ppm from TMS, even at temperatures as low as -80°C.

However, in the spectra of the ions derived from asymmetrically substituted benzophenones and recorded at sufficiently low temperatures, the $=\overset{+}{O}H$ signal shows as a doublet. The spectrum of 3,5-dibromobenzophenone *e.g.*, recorded at +20°C , shows an exchange broadened singlet and at -10°C a sharp singlet; at -30°C this signal is broadened and at -40°C a doublet is observed. (Fig. 1) . On raising the temperature the two lines merge into a singlet again.

As an explanation for this phenomenon we suggest the presence of an equilibrium between two conformations. In benzophenone the two phenyl groups cannot be coplanar with the carbonyl group simultaneously (5). In the asymmetrically substituted compounds there is competition for coplanarity between the two different aryl systems. In these molecules an equilibrium may occur between two conformations with different NMR spectra. For when the carbonyl group is alternately coplanar with two different aryl systems, two absorptions for the captured proton will be found. The difference in chemical shift



between these absorptions depends on the differences between the aryl systems. The differences in intensity of both $=\overset{+}{O}H$ signals is a measure for the position of the conformational equilibrium and presumably depends on the degree of conjugation.

Concurring with the $=\overset{+}{O}H$ signal, the signals of the phenyl protons broaden. At sufficiently low temperatures the $=\overset{+}{O}H$ proton shows as a doublet, whereas at raising the temperature this doublet broadens to a singlet and at considerably higher temperatures becomes a sharp singlet. When the $=\overset{+}{O}H$ doublet is observed the spectrum of the phenyl proton differs, in most cases, from that at higher temperatures. The protonated carbonyl group will exert a different influence on the hydrogen atoms at the ortho positions especially.

Support for our proposed explanation is also found in the fact that 4-bromobenzophenone shows a broadened $=\overset{+}{O}H$ singlet (only under favourable conditions a doublet) and 3,5-dibromobenzophenone a sharp doublet, whereas the compounds 2,6-dibromobenzophenone and 2,4,6-tribromobenzophenone show sharp singlets. In the latter two compounds the bulky ortho substituents inhibit resonance interaction between the substituted ring and the (protonated) carbonyl group.

We have tried to obtain further support for our explanation by investigating the NMR spectra of asymmetrically substituted fluorenones, where the rigid structure of the system prevents competition in coplanarity. We did not succeed in preparing the corresponding ions, however, because of decomposition of the samples.

TABLE

Chemical Shift of the Captured Proton in Protonated Benzophenones

Starting compound	$\delta = \overset{+}{O}H$ *)	Signals
4-Bromobenzophenone	12.60	broadened singlet
4,4'-Dibromobenzophenone	12.47	singlet
3,5-Dibromobenzophenone	13.03;12.83	doublet
2,6-Dibromobenzophenone	13.67	sharp singlet
2,4,6-Tribromobenzophenone	13.70	sharp singlet
4-Bromo-4'-nitrobenzophenone	13.87;13.57	doublet
4-Bromo-4'-ethoxybenzophenone**)	13.15;13.00	doublet
4-Chlorobenzophenone	12.50	broadened singlet
4-Chloro-4'-methoxybenzophenone	13.05;12.95	doublet
4-Nitrobenzophenone	13.87;13.50	doublet
2,4,6-Trimethylbenzophenone	13.70	sharp singlet
4-Ethoxybenzophenone**)	12.90;12.54	doublet

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*) Spectra were recorded at 60 Mc at temperatures between +35° and -85°C.

$\delta = \overset{+}{O}H$ in ppm down field from TMS. The $(CH_3)_4N^+$ ion was used as an internal reference. The difference in chemical shift between the reference and TMS (external) was taken as -3.20 ppm.

The shift of the $=\overset{+}{O}H$ proton depends on both the temperature and the acidity of the solvent, therefore no temperatures are given.

The compounds were dissolved in mixtures of HSO_3F and SbF_5, containing less than 20% SbF_5 (b.w.)

**) In HSO_3F-SO_2

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