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NUCLEAR MAGNETIC RESONANCE SPECTRA OF PROTONATED 2,2'-DIMETHYLBENZOPHENONE

by

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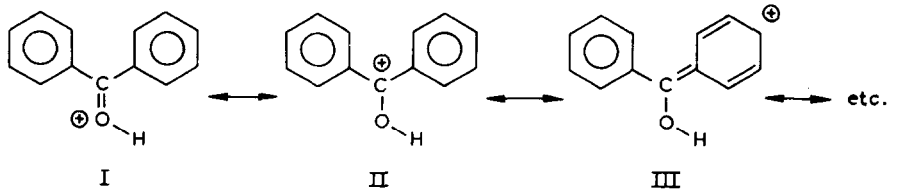
At 0°C the NMR spectrum (60 Mc) of protonated 2,2'-dimethylbenzophenone in HSO_3F/SbF_5 shows a sharp signal for the captured proton. This indicates that exchange with the medium is slow on the NMR time scale. At the same temperature only one signal for the two ortho-methyl groups is observed, but when the temperature is lowered, this signal broadens and at -40°C two sharp singlets are found. In the whole temperature range the captured proton is found as a sharp singlet. (Figure 1).

Mesomeric structures given in Figure 2 contribute to the ground state of protonated benzophenones.

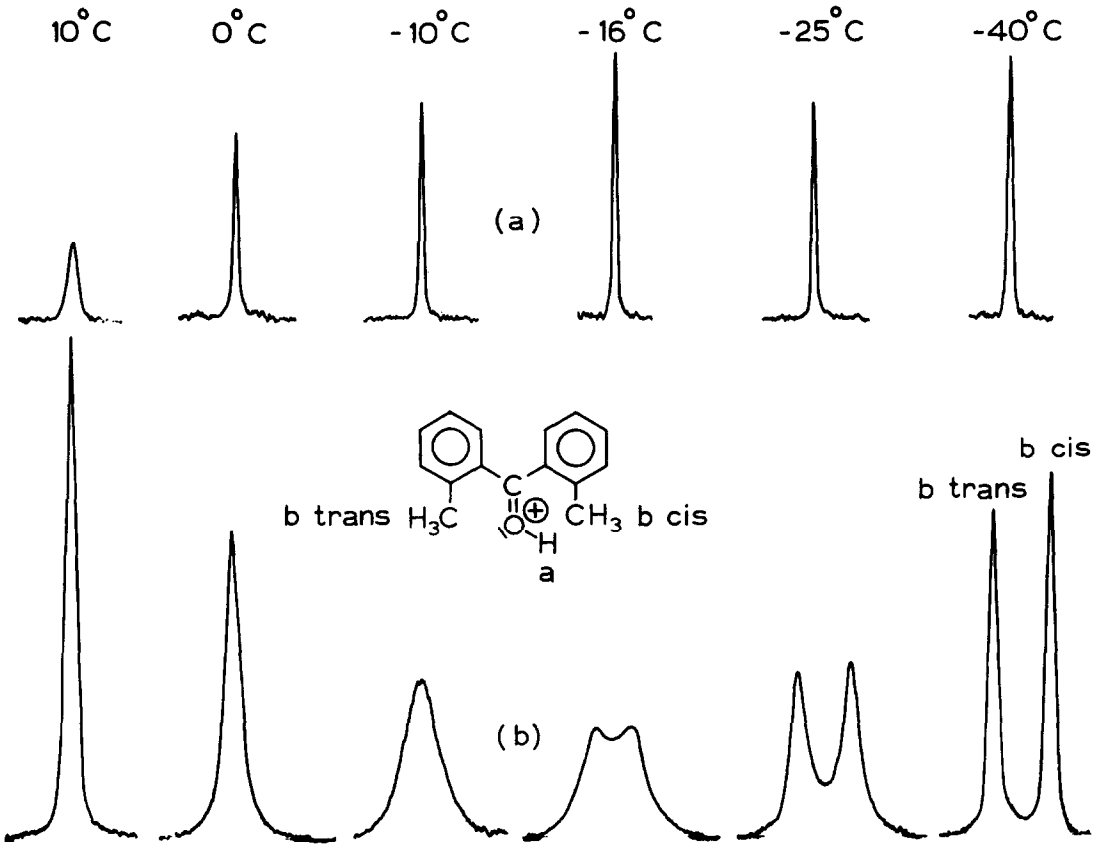
FIG. 2



I II III

FIG. 1

NMR signals of captured proton (a) and ortho-methyl groups (b) of protonated 2,2'-dimethylbenzophenone at different temperatures. Solvent: HSO_3F/SbF_5.



Due to contributions of structure II and structures of type III the double bond character of the carbon-oxygen bond is reduced. Apparently thermal energy at 0°C is already sufficient to effect rapid rotation round the carbon-oxygen bond, averaging the signals of the ortho-methyl groups in the spectrum of protonated 2,2'-dimethylbenzophenone. When the temperature is lowered, the rotation becomes slower and eventually two ortho-methyl signals can be observed. Thermodynamic data for the rotation have been determined by

the method of Rogers and Woodbrey (1, 2): $\Delta H^{\ddagger} = 9.3 \pm 0.3$ kcal mol^{-1}; $\Delta S^{\ddagger} = -14.5 \pm 1$ cal mol^{-1} K^{-1}; $\Delta G^{\ddagger}_{25°C} = 13.58 \pm 0.05$ kcal mol^{-1}.

2,2'-dimethylbenzophenonimine, which is isoelectronic with protonated 2,2'-dimethylbenzophenone, at low temperature (-60°C) also shows two separate ortho-methyl signals (2).

For alkoxycarbonium ions (3, 4) and protonated aliphatic aldehydes (5, 6) and ketones (6, 7) cis-trans isomerism has been reported recently.

In forthcoming publications cis-trans protonation of substituted benzophenones will be discussed.

Acknowledgment.

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