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HIGH BARRIER TO ROTATION ABOUT AN SP^2-SP^3 CARBON-CARBON BOND.

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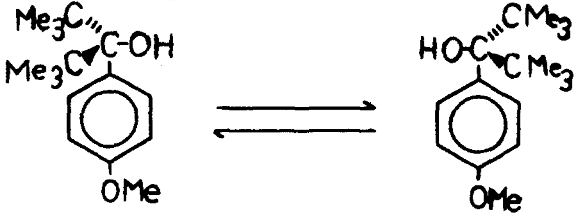
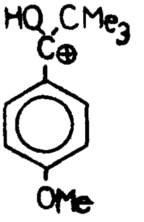
Treatment of p-methoxyphenyl t-butyl ketone with t-butyl lithium in dry ether at -40°C gave a 12% yield of a crystalline product , m.p. 110-111° , which analysed well for $C_{16}H_{26}O_2$. UV (in ethanol) : λ_{max} 225.5 mμ (ε 11300) , 275 mμ (ε 1470) . IR (chloroform) : 3650 cm^{-1} , 840 cm^{-1} . Mass spectrum: base peak m/e 193 and significant peaks at m/e 135 and 109. NMR (deuterochloroform , 40°C) : sharp singlet at 1.10 ppm (18 H) , singlet at 1.9 ppm (1 H) , sharp singlet at 3.80 ppm (3 H) and a complex unsymmetric multiplet at 7.7 - 6.7 ppm (4 H).

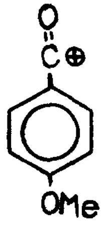


(a) (b)

(I)



(II)



(III)

In spite of the absence of the parent peak in the mass spectrum, we consider this material to be the expected di-t-butyl p-methoxyphenyl carbinol (I), as the fragment ion at m/e 193 corresponds to the stable carbonium ion (II). The peak at m/e 135 presumably corresponds to the loss of isobutane to give the ion (III) thus providing further evidence for the structure of the sidechain.

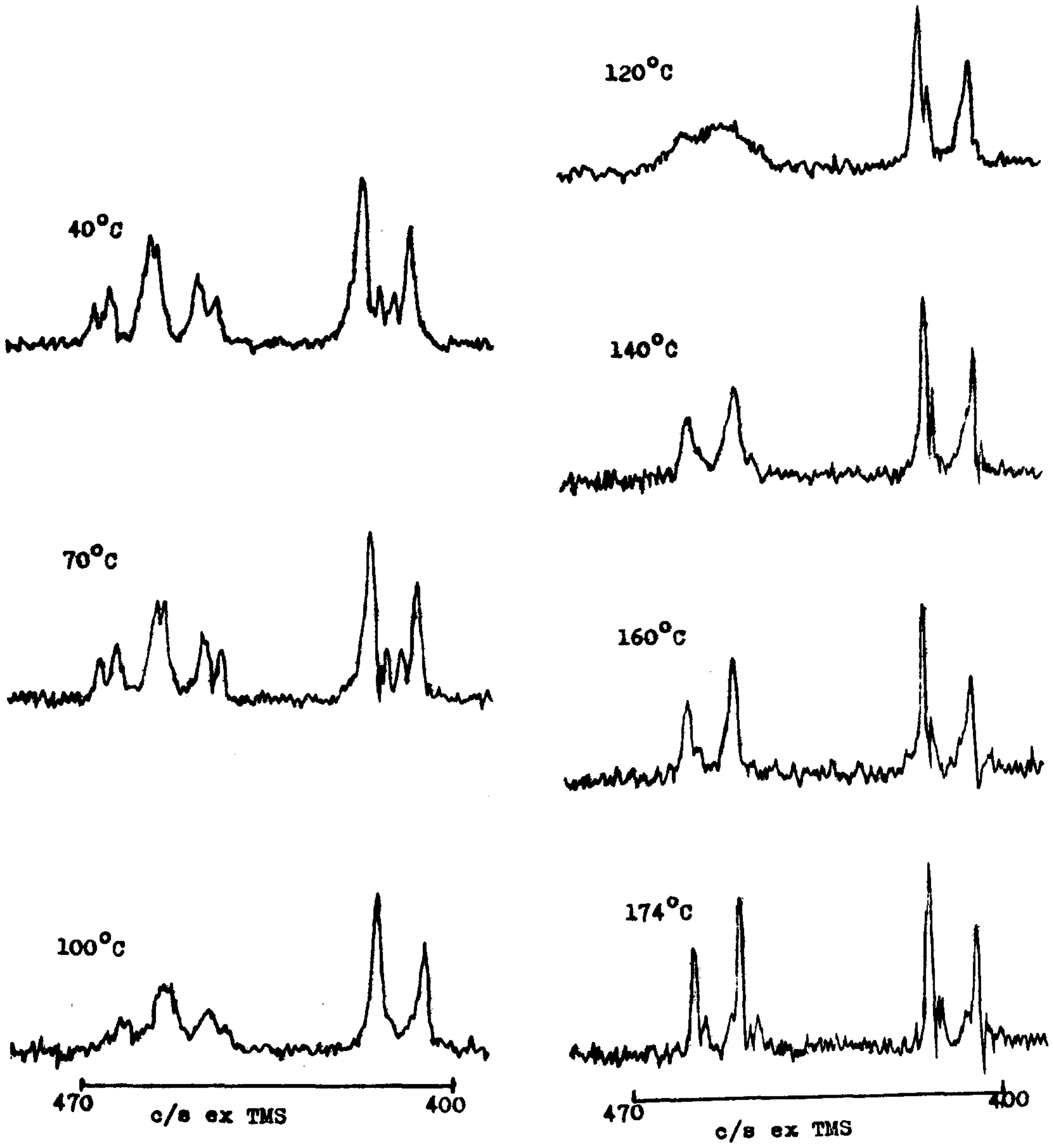
The appearance of the aromatic protons as a complex multiplet, rather than as a symmetric AA'BB' multiplet, possibly slightly distorted by long-range coupling[1], indicates that, on the NMR time scale, (I) is not symmetric about a plane passing through C-1 and C-4 at right angles to the aromatic ring. FIG 1 shows parts of 60 Mc/s NMR spectra of (I) in dimethyl sulphoxide d-5 taken over a range of temperatures. It can be seen that at higher temperatures the signals assigned to aromatic protons closely approach a symmetric AA'BB' multiplet. The temperature variability of the NMR spectra was reversible and was also exhibited in dioxan solution. In all cases the signals assigned to the methoxyl and t-butyl groups were sharp singlets.

On the basis of the above data and a consideration of molecular models, we conclude that (I) exists predominantly (if not entirely) in the conformations shown and that the time-dependent phenomenon responsible for the variation of the NMR spectra with temperature is the interconversion between Ia and Ib, which must be therefore associated with an appreciable energy of activation. We are engaged in the preparation of suitably substituted compounds which should enable us to determine the height of this energy barrier.

While several examples of restricted rotation of groups attached to aromatic rings by bonds with some double bond character

FIG. 1

Portions of 60 Mc/s NMR spectra
of (I) in dimethyl sulphoxide d-5.



are known[2] and at least one elegant indirect demonstration[3] of restricted rotation in a highly substituted benzene has been reported , the present example is , to our knowledge, the only direct evidence of restricted rotation about an sp^2-sp^3 carbon-carbon bond in a simple aromatic derivative[4] . It is interesting to note that the stable conformation postulated here for (I) is analogous to those proposed[5] for a number of allyl derivatives.

References

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