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THE REARRANGEMENT OF DI-t-BUTYLPHENYL CARBINOL

P. D. Bartlett, T. R. Steadman, T. T. Tidwell, and W. P. Weber
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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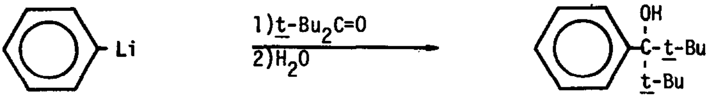
There have been reports of the syntheses of the ortho and para methoxy derivatives of di-t-butylphenyl carbinol[1,2] and more recently there has been a report of the preparation of the parent compound 1[3]. We report herein the preparation and characterization of 1, its rearrangement to the isomeric secondary carbinol, and the implications of the multiplicity of its hydroxyl stretching frequency for conformational isomerism in the compound.

Di-t-butylphenyl carbinol (1) bp. 140-143° (12 mm), was originally prepared some time ago[4] by the reaction of di-t-butyl ketone and phenyllithium as a precursor for a projected synthesis of 1,1,2,2-tetra-t-butyldiphenylethane. Treatment of 1 with potassium metal in boiling toluene followed by the addition of methyl iodide led to a 40% yield of what has now been identified as the methyl ether 2 of t-butyl-p-t-butylphenyl carbinol (3). This arrangement of the carbon skeleton could occur formally by the steps shown.



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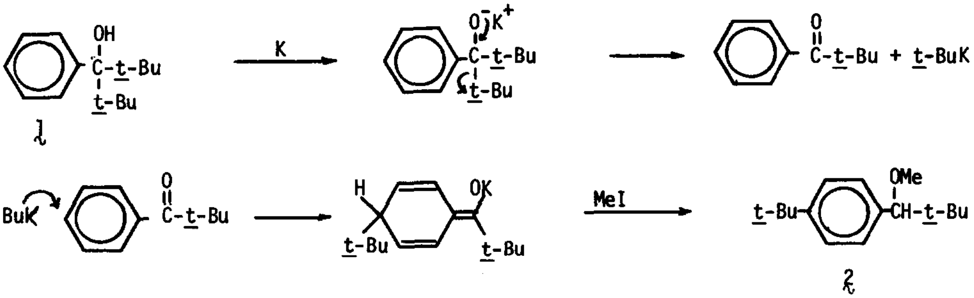

t-Butylpotassium would be expected to be extremely reactive toward toluene, and indeed it was found that when the reaction was conducted in n-octane as solvent the rearranged product was obtained in essentially quantitative yield. There is good analogy for the steps of the rearrangement in that alkali metal salts of tertiary aliphatic carbinols have been shown to dissociate to ketones on heating[5] and 1,6-conjugate additions of Grignard and lithium reagents to hindered aromatic ketones have demonstrated.[6] 1,6-Addition of t-butyllithium and t-butylpotassium to t-butyl phenyl ketone is reported in the papers of Fraenkel.[3] Further it has been reported that the Grignard adducts of crotylmagnesium bromide with hindered ketones are formed reversibly with the initial products of α-methylallyl addition reverting to crotyl addition products.[7]

The nmr spectrum* of 1 showed a singlet for the t-butyls at δ 1.10, the OH singlet at 1.78, and a complicated aromatic multiplet at 7.1 - 7.8. The nmr spectrum of 2 showed singlets at δ 0.88, 1.32, 3.14, and 3.68 corresponding to the carbinyl t-butyl, the ring t-butyl, the methoxyl group, and the carbinyl hydrogen, respectively. The aromatic protons gave a multiplet at 7.0 - 7.4. The ether (2), b.p. 122-129° (10 mm), was treated with hydriodic acid to give the corresponding carbinol (3), mp 90.0-90.6°, identical with material prepared from reduction of the corresponding ketone.[8] The nmr of 3 showed t-butyl singlets at δ 0.84 and 1.30, the OH and benzyl hydrogens at 1.97 and 4.17, respectively, and the aromatic multiplet at 6.8 - 7.5.

The infrared spectrum of 1 (recorded with a Perkin-Elmer 521 spectrophotometer) showed two concentration independent hydroxyl stretching frequencies, (in CCl_4), of approximately equal intensities, at 3636 and 3611 cm^{-1}. These positions correspond to free and pi-bonded hydroxyl groups[9] and some possible conformations for the present example are illustrated in which a primary consideration is to avoid steric interaction between the t-butyl groups and

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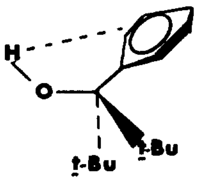
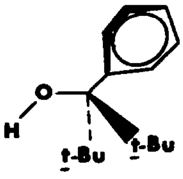
*nmr spectra were recorded from CCl_4 solutions at 60 MHz. All new compounds gave acceptable elemental analyses.

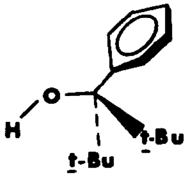
the ortho protons of the phenyl ring. In the p-methoxy analog a temperature variation of the



π-Bonded (1a)



Free (1b)



Free (1c)

ring protons was observed[2] which was ascribed to slow rotation around the C-C bond from the ring to the carbinyl carbon so that a static structure analogous to 1b predominated at lower temperatures with nonequivalent ortho and nonequivalent meta protons.[2] The present results support this idea of restricted rotation but suggest the presence of an additional structure analogous to 1a.

The possibility has been discussed that the bands sometimes assigned to free and π-bonded OH may actually arise from more than one free conformation[10], and saturated cases are known[10a] which have as large a frequency shift as that noted here. Two possible free conformations for 1 are depicted and others would be possible with the O-H bond gauche to the C-phenyl bond.

The apparent greater lability of the potassium salt of 1 relative to its lithium salt is in accord with the reported[11] relative rates of cleavage of alkali metal alkoxides in DMSO: ROK >>RONa>>ROLi.

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