

INTRAMOLECULAR ALKYLATION OF *O*-*T*-BUTYL GROUPS IN
2,4,6-TRI-*T*-BUTYLBENZYL ALCOHOL AND METHYL ETHER

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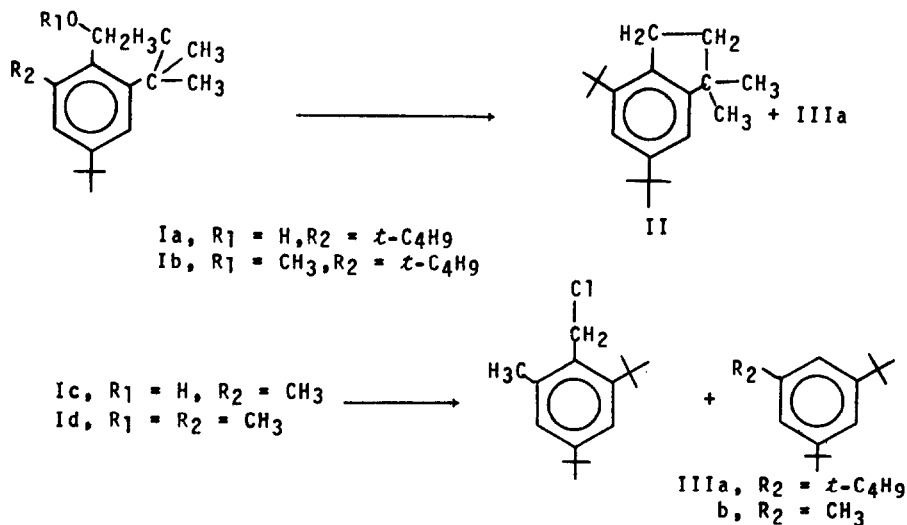
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Reference has been made to 2,4,6-tri-*t*-butylbenzyl alcohol (1) (Ia) and to physical properties of various substituted tri-*t*-butylbenzenes (2). In this communication we report the synthesis of Ia, its methyl ether (Ib) and a novel acid-catalyzed "insertion" reaction into the *ortho*-*t*-butyl groups of Ia and Ib. A comparative study is reported of the products from reactions of 2-methyl-4,6-di-*t*-butylbenzyl alcohol (Ic) and the methyl ether (Id) with several acids.

Treatment of tri-*t*-butylphenyllithium (3) with chloromethyl methyl ether yielded the ether (Ib) (25%); m.p. 79-80°, ν_{\max} (KBr) 1050 cm^{-1} due to the ether group; n.m.r. (CCl_4 -TMS) showed (singlets) one *t*-butyl group at 8.72 τ , the *o*-*t*-butyl groups at 8.56 τ , -O-CH₃ at 6.76 τ , benzylic -CH₂- at 5.38 τ , and the aromatic protons at 2.72 τ . The ether (Ib) was cleaved by treatment with boron chloride to yield the alcohol (Ia) in 87% yield; m.p. 178-179°, ν_{\max} (KBr) 3280 cm^{-1} (hydroxyl), n.m.r. spectrum showed (singlets) one *t*-butyl at 8.72 τ , the *o*-*t*-butyl groups at 8.54 τ , benzylic -CH₂- at 5.04 τ , hydroxyl at 4.26 τ , (with a trace of acid present) and aromatic protons at 2.72 τ .

Treatment of the methyl ether (Ib) with hydriodic acid in acetic acid yielded 15% of tri-*t*-butylbenzene (III) and 85% of a new hydrocarbon, m.p. 129-130°, which analyzed for C₁₉H₃₀ (mass spectral and elemental analyses). The n.m.r. spectrum of this hydrocarbon (II) showed one *t*-butyl group at 8.72 τ , another *t*-butyl (*ortho*) at 8.65 τ , a singlet at 8.78 τ integrating for two (gem) methyls, two triplets (8.15 and 7.00 τ) assigned to a -CH₂-CH₂-

group, and a AB quartet centred at 3.00 τ ($J_{AB} = 2$ c.p.s.) assigned to two non-equivalent *meta* protons. This evidence, together with the similarity of the n.m.r. spectrum of II with a model compound 1,1-dimethylindane, established II to be 1,1-dimethyl-4,6-di-*t*-butylindane.



Hydrocarbon II was also formed by treatment of 2,4,6-tri-*t*-butylbenzyl alcohol (Ia) with thionyl chloride, zinc chloride-hydrochloric acid (Lucas Reagent), or with antimony pentafluoride-fluorosulfonic acid in liquid SO₂ at -78°. Smaller amounts of tri-*t*-butylbenzene were also formed in these reactions. The results of this preliminary work are summarized in Table I.

TABLE I

Compound Treated	Catalyst	Product Composition (%) [*]		
		Ia	II	IIIa
Ib	BCl ₃	87	10	3
Ib	HI-CH ₃ COOH	--	85	15
Ia	SOCl ₂	40	55	5
Ia	HCl-ZnCl ₂	--	64	36
Ia	SbF ₅ -FSO ₃ H	16	81	3

^{*}Determined by gas chromatography on 30% apiezon-Chromosorb W.

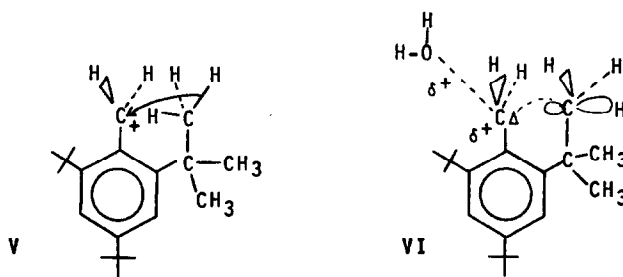
A comparative study was carried out on methyl 2-methyl-4,6-di-*t*-butylbenzyl ether (Id) and 2-methyl-4,6-di-*t*-butylbenzyl alcohol (Ic), which were synthesized from 3,5-di-*t*-butyltoluene by the method of Beets and co-workers (4). On treatment with hydriodic acid-acetic acid, the ether (Id) yielded 2-methyl-4,6-di-*t*-butylbenzyl acetate (90.5%) and 3,5-di-*t*-butyltoluene (9.5%). The acetate showed ν_{\max} (film) 1730 cm^{-1} for the carbonyl group. The n.m.r. spectrum showed (singlets) one (*para*) *t*-butyl at 8.72τ , the other *t*-butyl (*ortho*) at 8.60τ , the ring methyl at 7.71τ , the acetate methyl at 8.08τ , benzylic $-\text{CH}_2-$ at 4.72τ , and a quartet centred at 2.86τ ($J_{AB} = 2\text{ c.p.s}$) for the *meta*-coupled aromatic protons.

Cleavage of the ether (Id) with boron chloride yielded 92% of 2-methyl-4,6-di-*t*-butylbenzyl chloride (IV) (4).

Reaction of 2-methyl-4,6-di-*t*-butylbenzyl alcohol (Ic) with hydrochloric acid-zinc chloride yielded the chloride (IV) (35%) along with 3,5-di-*t*-butyltoluene (38%) and unreacted alcohol (27%). The chloride (IV) was produced in high yield (86%) by treatment of Ic with thionyl chloride. Treatment of the alcohol (Ic) with antimony pentafluoride-fluorosulfonic acid in liquid sulfur sulfur dioxide yielded some 3,5-di-*t*-butylbenzene (2.3%), starting material (8.5%) and a new compound proposed to be 2,2'-dimethyl-4,4',6,6'-tetra-*t*-butyldibenzyl ether (88%) (m.p. $122-124^\circ$), ν_{\max} (KBr) 1050 cm^{-1} for C-O-C, n.m.r. showed two *t*-butyls at 8.72τ and two *t*-butyls at 8.53τ , two ring methyls at 7.64τ , two benzylic groups at 5.24τ , and a quartet centred at 2.95τ ($J_{AB} = 2\text{ c.p.s.}$) for the two sets of *meta* coupled hydrogens.

Thus treatment of the benzylic alcohol and methyl ether with the functional group flanked by an *ortho* methyl and an *ortho-t*-butyl group yielded mainly the products of substitution (nucleophilic). Varying amounts of the hydrocarbon 3,5-di-*t*-butylbenzene were formed but there was no evidence of any products from insertion into the side chain such as were found from the treatment of Ia and Ib with various acids.

There is no close analogy to this side chain alkylation reaction in the literature. A comparison can be made with the "bond insertion by cationic nitrogen" into an *ortho* *t*-butyl group observed by Lansbury and co-workers (5). Our reaction apparently requires two *ortho* *t*-butyl groups, otherwise competing substitution reactions predominate, as in the case of Ic and Id. Various reaction mechanisms are being considered for this reaction. These include carbon-carbon side chain alkylation through a hindered benzylic cation (V). A possible concerted mechanism (VI) involves carbon-carbon bond formation through back lobe attack at the benzylic carbon by the nearby tail of the sp^3 orbital of a C-H bond.



The formation of trialkylbenzenes (IIIa and IIIb) as by-products of the reactions can be explained by reverse Friedel-Crafts types of alkylations. Relief of steric strain is undoubtedly a driving force in these reactions.

Satisfactory elemental analyses were obtained for all new compounds.

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References

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