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2,6-DI-t-BUTYLBIPHENYLS. THE ABSENCE OF APPRECIABLE BARRIERS TO ROTATION OF t-BUTYL GROUPS.

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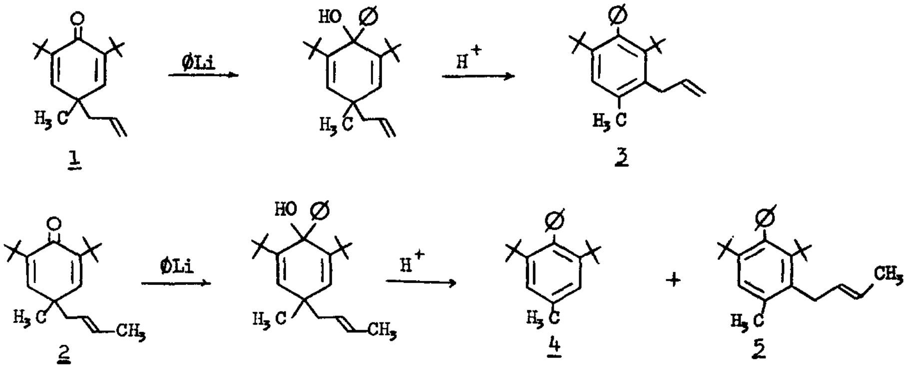
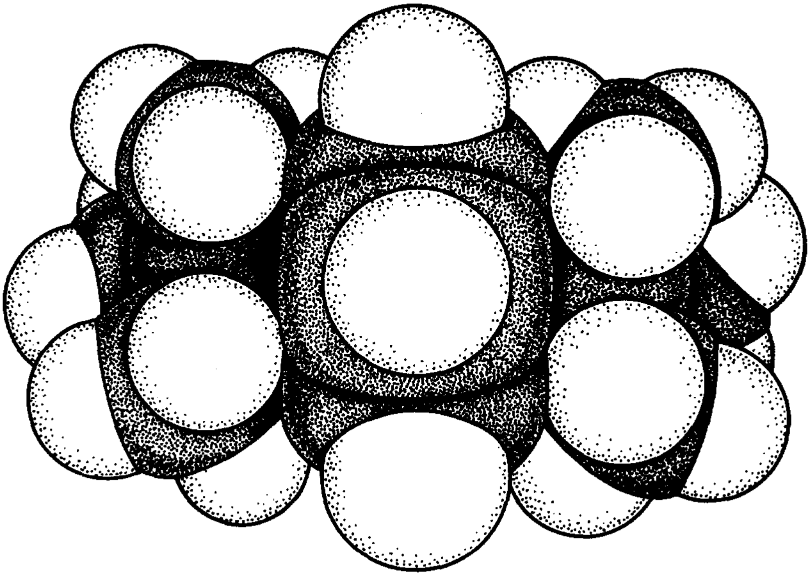
Nmr studies have shown that the normal rotational equivalence of the methyls in t-butyl groups can be altered by steric interference with adjacent groups.[1] The differences in chemical shifts for resonances of individual methyl groups within a t-butyl group is normally small, and the effect is usually observable only at low temperatures. In cases of severe hindrance, however, splitting of a t-butyl resonance has been observed at room temperature.[1c] Theoretically, it should be possible to observe separate resonances attributable to the individual hydrogens in a methyl group, provided that sufficient hindrance to rotation exists. This phenomenon, however, has never been observed.[2]

Possible inhibition of t-butyl rotations in the nmr spectra of 2,6-di-t-butylbiphenyls is of particular interest. Inspection of space filling molecular models (see illustration) suggests that rotation of the t-butyls around their axes is severely hindered by interactions with the unsubstituted phenyl ring. In these models, in fact, it is impossible to effect rotation of a t-butyl group without breaking a bond. In contrast, molecular models of most of the compounds which are known to exhibit hindered rotation of t-butyl groups [1] exhibit little apparent hindrance to rotation. The apparent hindrance to rotation in models of 2,6-di-t-butylbiphenyls, in fact, is so great as to suggest the possibility that separate resonances might be observed for individual protons within the methyl groups pressed against the phenyl ring. (Since the differences between the chemical shifts for those protons held in the shielding cone of the phenyl group and those held in the deshielding region of the polysubstituted aromatic ring should be large, phenomena due to hindered rotation of the t-butyl groups should be easy to observe).

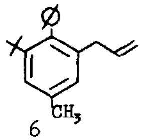
The problem of synthesis of 2,6-di-t-butylbiphenyls was solved by the novel path shown below. Reaction of cyclohexadienone 1[3] with phenyl lithium, followed by dehydration with 10% sulfuric acid in acetic acid, gave biphenyl 3 (m.p. 57-59°) in 95% yield, as estimated by vpc. A similar





2,6-Di-t-butyl-4-methylbiphenyl. View from End of Monosubstituted Ring.

sequence with cyclohexadienone 2[3] gave compounds 4 (m.p. 122-124°) and 5 (m.p. 77-79°) in the ratio 89:11. Use of other dehydrating agents (e.g., Florisil in refluxing benzene or phosphorus oxychloride in pyridine) gave the products reported above in varying yields, except that rearrangement of 1 in the presence of Florisil gave a 20% yield of hydrocarbon 6, in addition to 3 and traces of 4. Each product was isolated by preparative vpc.



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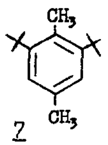

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The structures of compounds 3-6 were established by their elemental analyses, their mode of formation, and their ir, uv, and nmr spectra. The most significant information was obtained from their nmr spectra, whose salient features are summarized in the Table. The spectrum of 2,6-di-t-butyl-1,4-dimethylbenzene (7)[4] is included for comparison.

Several features of these spectra are noteworthy. A) The peaks for the t-butyl groups in compounds 3-6 are shifted upfield by more than 0.3 ppm from the positions of the t-butyl peaks in

Table

NMR Spectra (in CCl_4)

(Chemical shifts in units of τ)

Cmpd.	t-Bu (s)	Ar-CH_3 (s)	Ar-H	Ar-CH_2-CH=C
3	9.00 (9H)		s2.87 (1H)	
	8.95 (9H)	7.70	s2.79 (5H)	6.24 (J=5.0)[a]
4	8.97 (18H)	7.67	s2.76 (7H)	- - - -
5	9.00 (9H)		s2.81 (1H)	
	8.95 (9H)	7.73	s2.71 (5H)	m6.25
6	8.88 (9H)	7.69	m2.83 (7H)	7.24 (J=6.0)[a]
7	8.58 (18H)	7.77 (3H)		
		7.43 (3H)	s3.02 (2H)	- - - -

a - A broad doublet

most t-butylbenzenes.[5] (t-Butyl groups adjacent to alkyl substituents, such as those in 7, have resonances at still lower fields than those of other t-butylbenzenes).[4,6] This demonstrates that the t-butyl groups in 3-6 are located in the shielding cone of the phenyl substituent. B) The occurrence of a single t-butyl singlet in 4, in contrast to the presence of two readily distinguishable t-butyl peaks in both 3 and 5, strongly supports the postulated symmetrical structure for 4. C) The methyl groups at C-4 in all the reaction products are clearly not ortho to t-butyl groups, since aromatic methyls ortho to t-butyl groups absorb near τ 7.45, rather than τ 7.7.[4,7] D) The low field positions of the allylic methylene resonances in the spectra of 3 and 5 confirm that these groups are ortho to t-butyl groups, since in other allylbenzenes the allylic methylene peaks appear around τ 6.4.[4] E) The high field position of the allylic methylene doublet in the spectrum of 6 confirms its location in the shielding region of the phenyl substituent.

The structures of compounds 3-6 are thus uniquely determined by their nmr spectra.

The room temperature spectra of these molecules present no evidence for any barriers to rotation of t-butyl groups around their axes. Surprisingly, the spectra of 3 and 4 in methylene chloride show no evidence for inhibition of rotation at temperatures as low as -80°. The t-butyl peak in the spectrum of 3 broadens at low temperatures, but the broadening does not seem to be greater than that exhibited by the aromatic methyl groups, and is presumably due to increased viscosity of the solutions.

The contrast between the large barriers to free rotation observed in molecular models of these compounds and the very small barriers found in nmr studies is striking. A somewhat similar absence of hindrance to t-butyl group rotation is observed in 1,8-di-t-butylnaphthalene, and has been ascribed to out of plane bending of the t-butyl groups.[8] This suggestion is supported by the chemical shifts for the t-butyl resonances.[8] Inspection of models of compounds 3-5 suggests that, due to the planar structure of the phenyl substituent, a large deformation in out-of-plane bond angles would be necessary to allow relatively free rotation of the t-butyl groups. We suggest that rotation of the t-butyl groups in 3-5 would most easily occur by an in-plane bending of the t-butyl groups away from the phenyl substituent.

Although such bond distortion should be somewhat more difficult than out of plane bending,[9] models indicate that a smaller distortion of the normal bond angles would be necessary to allow rotation of the t-butyl group. The fact that in-plane bond distortions occur more easily with sp^2 than sp^3 bonds[9] may account for the relative ease of bond rotation in compounds 3-5 compared to other molecules in which t-butyl groups are bonded to tetrahedral carbon.[1]

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