

THE SYNTHESIS, NUCLEAR MAGNETIC RESONANCE AND ULTRAVIOLET
SPECTRUM OF 2,4,6-TRI-T-BUTYLTOLUENE

W. A. Gibbons* and H. Fischer**

Department of Chemistry, University of Sheffield,

Sheffield, 10, England.

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1,2-di-t-butylbenzene⁽¹⁾ and 1,2,4,5-tetra-t-butylbenzene⁽²⁾ have recently been synthesized from substituted acetylenes. The conditions used were quite vigorous. As a preliminary to the synthesis of 1,2,3,5-tetra-t-butylbenzene, 2,4,6-tri-t-butyltoluene has been prepared by the addition of excess methyl iodide to a solution of 2,4,6-tri-t-butylphenyl-lithium⁽³⁾ in anhydrous ether at 14°C. After four hours the solution was worked up giving a white crystalline solid, m.p. = 149°C, in 85% yield. The mass spectrum showed the molecular weight to be 260 and that no impurities were present. Confirmation of purity was obtained by thin layer chromatography on silica gel.

The chemical shifts and integrated intensities (brackets) of the four bands in the nuclear magnetic resonance spectrum (Fig. 1) confirm the synthesis of 2,4,6-tri-t-butyltoluene.

** Present address Max Planck Institut fur Chemie, Heidelberg.

* On leave of absence from Notre Dame University, Nelson, British Columbia.

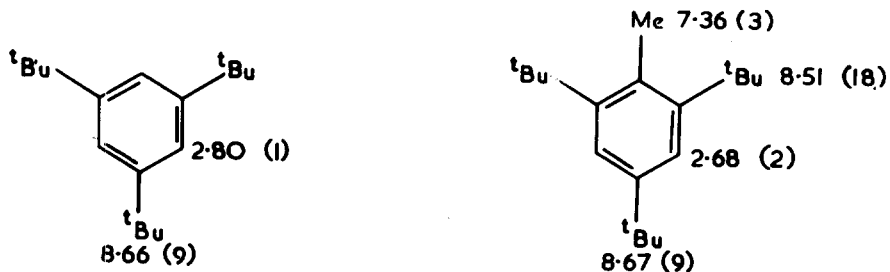


Fig 1. Nuclear Magnetic Resonance Data. All solutions 0.1M in CCl_4 Chemical shift relative to TMS as internal standard.

With benzene, the introduction of one or more alkyl groups usually results in the shift of the *ortho*, *meta* and *para* proton resonances to higher applied field⁽⁴⁾. Methyl substitution in 1,3,5-tri-*t*-butylbenzene seems to be quite unusual. The ring protons and the *ortho* *t*-butyl protons shift to low field whilst the *para* *t*-butyl protons are not shifted. Hence, substitution of an electron-donating group in 1,3,5-tri-*t*-butylbenzene has qualitatively the same effect as substitution of an electron-withdrawing substituent in benzene. A complete study of the effect of monosubstitution in 1,3,5-tri-*t*-butylbenzene, by nuclear magnetic resonance, has been carried out and will be published shortly.

The ultraviolet spectrum of 2,4,6-tri-*t*-butyltoluene shows (Table 1) the secondary band at 259 μ , characteristic of alkyl-substituted benzenes. Methyl substitution in benzene and mesitylene shifts this band to longer wavelengths with a concomitant increase in ϵ_{max} .

TABLE I

Compound	λ_{\max}	ϵ_{\max}	Compound	λ_{\max}	ϵ_{\max}	Compound	λ_{\max}	ϵ_{\max}
benzene ^a	254	230	1,3,5-trimethylbenzene ^a	261	210	1,3,5-tri- <i>t</i> -butylbenzene ^a	262	182
toluene ^a	262	270	1,2,3,5-tetramethylbenzene ^a	268	264	2,4,6-tri- <i>t</i> -butyltoluene ^b	259	220

a API catalogue of Ultraviolet Spectra

b This work - methyl cyclohexane as solvent

The hypsochromic shift on methyl substitution in 1,3,5-tri-*t*-butylbenzene would thus appear anomalous. Similar effects are observed when ortho alkyl substituents prevent coplanarity of the two chromophones in molecules such as biphenyl, benzaldehyde and acetophenone⁽⁵⁾. Since the methyl group cannot rotate out of the plane of the benzene ring, some other effect must be present to relieve steric strain. In addition to the above effects, there is a loss of structure in the 259 m μ band of 2,4,6-tri-*t*-butyltoluene. This phenomenon has been taken by other workers⁽⁶⁾ as indication of ring puckering.

The present results therefore indicate that in spite of the ease and specificity of synthesis, the nuclear magnetic resonance and ultraviolet spectra exhibit anomalies, indicative of a high degree of strain in 2,4,6-tri-*t*-butyltoluene, and possibly of ring puckering.

The usefulness of aryl-lithium compounds has been further demonstrated by synthesis of the corresponding triphenyl and tri-*t*-butylbenzaldehyde and triphenyl and tri-*t*-butylbenzyl alcohol for the first time. Details of these syntheses will be published in due course.

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REFERENCES

1. Hoogzand, C., and Hubel, W., Angew. Chem., 73, 680, (1961).
2. Arnett, E.M., Strem, M.E., and Friedel, R.A., Tetrahedron Letters 19, 658, (1961).
Hoogzand, C., and Hubel, W., Ibid., 18, 637, (1961).
3. Betts, E.E., and Barclay, L.R.C., Can. J. Chem., 33, 1768, (1955).
4. Pople, J. A., Schneider, W.G., and Bernstein, H.J., "High Resolution Nuclear Magnetic Resonance" Chapter II, McGraw-Hill, New York, (1959).
5. Jaffe, H.H., and Orchin, M., "Theory and Applications of Ultraviolet Spectroscopy", Chapters 12, 15, Wiley, New York, (1962).
6. Cram, D.J., and co-workers, J. Amer. Chem. Soc., 81, 5963, 5971 and 5977, (1957).