Tetrahedron Letters No.21, pp. 1625-1626, 1965. Pergamon Press Ltd.
Printed in Great Britain.

SYNTHESIS AND SPECTRAL PROPERTIES OF 2,6-DIMETHYL-<u>t</u>-BUTYLBENZENE

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(Received 22 March 1965)

One of the sterically hindered aromatic hydrocarbons proposed for study some years ago (1,2) is 2,6-dimethyl-t-butylbenzene (I). Although previous attempts to synthesize I have not been successful (2), a minimum strain energy of 17 kcal./mole (2) and later 24 kcal./mole (3) was estimated for I and its homomorphs by indirect methods.

Efforts to prepare I by a route analogous to one used in the synthesis of o-di-t-butylbenzene (4) were unsuccessful. However, reaction of 2,6-dimethylphenylmagnesium bromide (2) with t-butyl chloride (5) in refluxing tetrahydrofuran slowly afforded I in low yield. After removal of unchanged 2,6-dimethylbromobenzene by repeated hydrogenolysis (Pd-C in ethanol), the hydrocarbon I was isolated in 2.5% yield by fractional distillation: b.p. 114-116° (16 mm.); $n^{25}D$ 1.5150; $\lambda_{max}^{CS_2}$ 7.2, 7.3, 7.4, 8.1, 8.4, 9.4, 9.7, 13.05, and 13.45 μ. The n.m.r. spectrum (CCl_4) had singlets at 8.45 (t-butyl group) and 7.45 τ (2 methyl groups), and a slightly broadened peak at 3.01 τ (3 aromatic protons). Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found (Weiler and Strauss): C, 88.53; H, 11.28.

The same procedure with the Grignard derivative of bromomesitylene gave, in 5% yield, 2,4,6-trimethyl-t-butylbenzene (II), b.p. 124-126° (16 mm.); $n^{25}D$ 1.5141; $\lambda_{max}^{CS_2}$ 7.2, 7.3, 7.4, 8.1, 8.4, 9.3, 9.7, 9.8, 11.8, and 13.5 μ. The n.m.r. spectrum (CCl_4) had singlets at 8.49 (t-butyl group), 7.82 (1 methyl group), 7.51 (2 methyl groups), and 3.30 τ (2 aromatic protons). Anal. Calcd. for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.70; H, 11.29.

The ultraviolet spectra of I and II are recorded in Fig. I and may be compared, respectively, with the spectra of 1,2,3-trimethylbenzene (III) (6) and 1,2,3,5-tetramethylbenzene (IV) (7). The loss of fine structure and decrease in absorption in the spectra of I and II are also analogous to the behavior of o-di-t-butylbenzene (4) and suggest the presence of a similar type of strain (8).

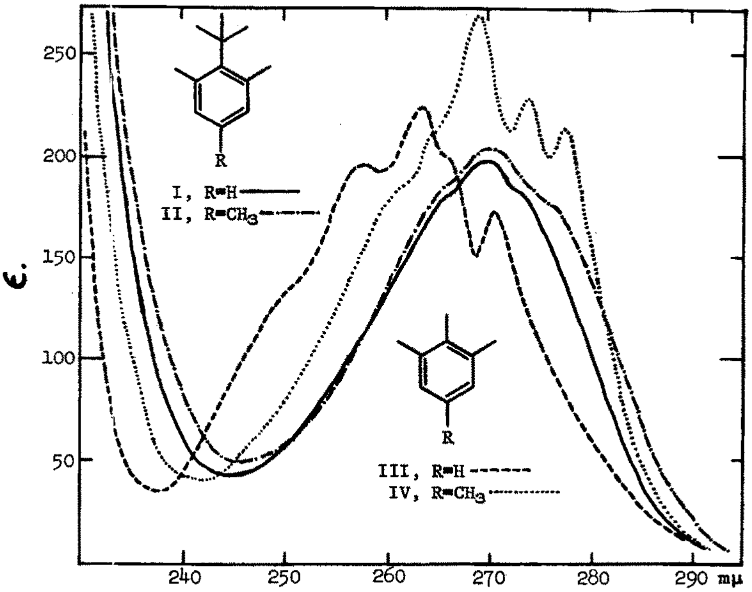

Fig. I: Ultraviolet Absorption Spectra in Iso-octane.

Acknowledgments.--We are indebted to Professor H. C. Brown for his suggestions concerning this work. Financial support from the National Science Foundation (G-19936), the Alfred P. Sloan Foundation, and the University of Kansas Center for Research in Engineering Sciences (CRES-40B) is gratefully acknowledged.

REFERENCES

1. H. C. Brown, et al., J. Am. Chem. Soc., 75, 1 (1953).
2. H. C. Brown and M. Grayson, ibid., 75, 20 (1953).
3. H. C. Brown, D. Gintis, and L. Domash, ibid., 78, 5387 (1956).
4. A. W. Burgstahler and M. O. Abdel-Rahman, ibid., 85, 173 (1963).
5. Cf. K. T. Serijan, H. F. Hipsher, and L. C. Gibbons, ibid., 71, 873 (1949).
6. A.P.I. Research Project 44, "Ultraviolet Spectral Data," Serial No. 140.
7. Ibid., Serial No. 426.
8. J. Dale, Chem. Ber., 94, 2821 (1961); cf. A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rahman, J. Am. Chem. Soc., 86, 5281 (1964).