[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Synthesis of 1,3-Di-*t*-butylbenzene and 1,3-Di-*t*-butylcyclohexane[1]

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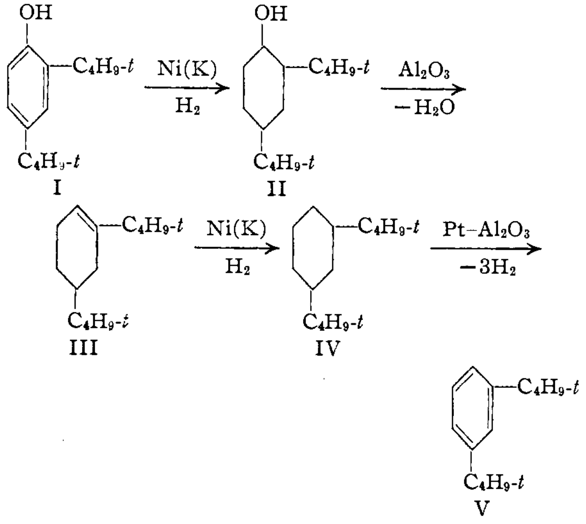
m-Di-*t*-butylbenzene has heretofore not been synthesized; this compound cannot be prepared by the alkylation of benzene with isobutylene. The present paper describes the synthesis of this hydrocarbon from 2,4-di-*t*-butylphenol. The following steps were involved in the synthesis of *m*-di-*t*-butylbenzene.



In order to be certain that rearrangement did not occur during the dehydration of 2,4-di-*t*-butylcyclohexanol (II) nor during the dehydrogenation of 1,3-di-*t*-butylcyclohexane (IV), compound V was hydrogenated and the infrared spectrum of the product was compared with the spectra of compound IV and of 1,3-di-*t*-butylcyclohexane (Graph I) prepared by the Wolff–Kishner reduction of 2,4-di-*t*-butylcyclohexanone. It was found that all the three spectra were identical with the exception of minor outside absorptions in the spectrum of the compound obtained from hydrogenation 1,3-di-*t*-butylcyclohexene. The infrared and ultraviolet spectra of *m*-di-*t*-butylbenzene are given in Graphs 2 and 3.

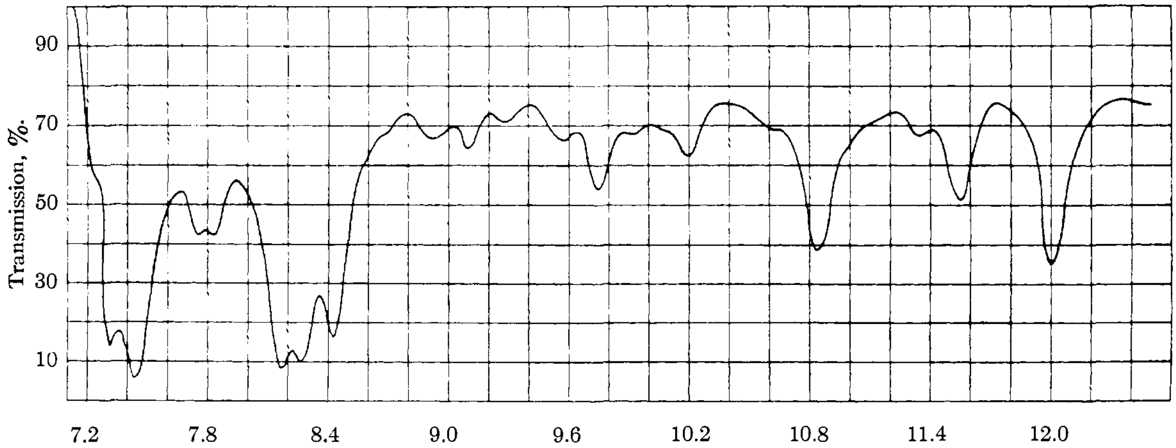


Fig. 1.—1,3-Di-*t*-butylcyclohexane; cell thickness, 0.1 mm.

Experimental Part

I. Synthesis of 1,3-Di-*t*-butylbenzene

2,4-Di-*t*-butylcyclohexanol (II).—One hundred grams of 2,4-di-*t*-butylphenol (I) (Dow Chemical Co.) was hydrogenated in a 450-cc. capacity autoclave at 115–125° in the presence of nickel–kieselguhr catalyst and under 100 atmospheres of hydrogen. Three moles of hydrogen was absorbed per one mole of compound charged. The product was in the form of white crystals; it distilled at 125° (14 mm.), m. p. 107–109°; yield 92%.

Anal. Calcd. for $C_{14}H_{28}O$: C, 79.25; H, 13.20. Found: C, 78.86; H, 13.53.

1,3-Di-*t*-butyl-x-cyclohexene (III).—Compound II (48 g.) was dissolved in 50 cc. of *t*-butyl alcohol and dehydrated by passing it over activated alumina pills at 410–420°. The olefin formed was separated, dried and distilled; b. p. 114–115° at 25 mm.; $n^{20}D$ 1.4640; d^{20}_4 0.8338; yield 66%.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.65; H, 13.30.

1,3-Di-*t*-butylcyclohexane (IV).—Compound III (29.0 g.) was hydrogenated at 50° in a 125-cc., rotating autoclave in the presence of 4 g. of nickel–kieselguhr catalyst and under an initial hydrogen pressure of 100 atmospheres. Twenty-six grams of compound IV was obtained; yield 90%. The pure compound had the following properties: boiling points, 70° at 2.4 mm., 86.4° at 6.0 mm., 93.8° at 9.4 mm., 102° at 13.5 mm., 122° at 31.5 mm.; d^{20}_4 0.8312, d^{25}_4 0.8273; $n^{20}D$ 1.45727, $n^{25}D$ 1.45527; specific dispersion, $(\delta H\beta\text{-}H\alpha) = 85.2$ at 20°, 84.4 at 25°

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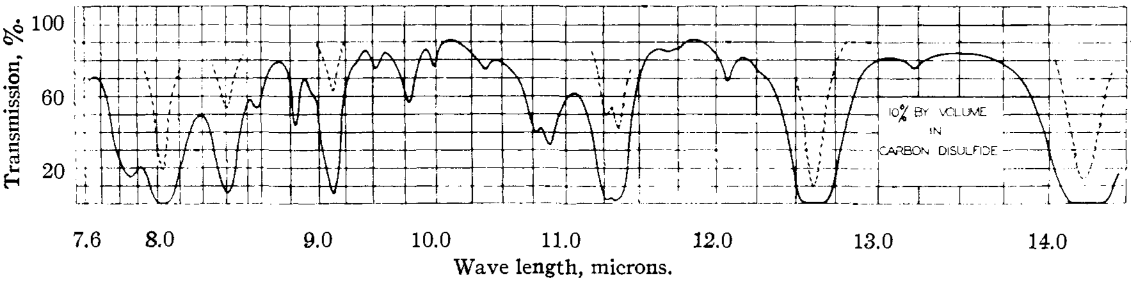

Fig. 2.—*m*-Di-*t*-butylbenzene; cell thickness, 0.1 mm.

Anal. Calcd. for $C_{14}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.78; H, 14.32.

m-**Di-*t*-butylbenzene** (V).—Sixteen grams of (IV) was dehydrogenated by passing it three times over platinum-aluminum oxide catalyst at 275° according to the procedure described previously.[2] The aromatic hydrocarbon formed was purified chromatographically by dissolving it in four parts of pentane and passing the solution over a five-foot column of through-200 mesh silica gel.[3] This method enabled the separation of any unreacted 1,3-di-*t*-butylcyclohexane which might have remained. *m*-Di-*t*-butylbenzene thus purified had the following properties: boiling points, 73° at 2.5 mm.; 89.5 at 6.6 mm., 101° at 11.2 mm.; d^{20}_4 0.8589, d^{25}_4 0.8547; n^{20}_D 1.4879, n^{25}_D 1.4874; specific dispersion ($\delta H\beta$-$H\alpha$) = 126.6 at 20°, 126.7 at 25°.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.42; H, 11.58. Found: C, 88.34; H, 11.73.

Compound V (2.2 g.) was acetylated according to the procedure described previously[4]; the 2,4-dinitrophenylhydrazone of the ketone melted at 208–210°. *Anal.* Calcd. for $C_{22}H_{28}N_4O_4$: C, 64.05; H, 6.84; N, 13.59. Found: C, 64.17; H, 6.82; N, 13.73.

II. Synthesis of 1,3-Di-*t*-butylcyclohexane from the Corresponding Ketone

1. **2,4-Di-*t*-butylcyclohexanone** (VI) was prepared in 51% yield from 50 g. of 2,4-di-*t*-butylcyclohexanol (II) dissolved in 200 ml. of acetone by means of oxidation as described previously.[5] The ketone distilled at 143° at 28 mm., n^{20}_D 1.4645, d^{20}_4 0.8946, MR_D calculated 64.7, observed 65.1. *Anal.* Calcd. for $C_{14}H_{26}O$: C, 80.00; H, 12.34. Found: C, 79.76; H, 12.77.

The 2,4-dinitrophenylhydrazone of VI melted at 174–176°. *Anal.* Calcd. for $C_{20}H_{29}N_4O_4$: N, 14.39. Found: N, 14.37.

2. **The ketone** (VI) was reduced to the hydrocarbon by means of the modified Wolff–Kishner method[6]; 17.5 g. of 2,4-di-*t*-butylcyclohexanone, 8.5 ml. of hydrazine hydrate (85%), 85 ml. of 1,4-dioxane and 11.2 g. of potassium hydroxide were used. A 79% yield of hydrocarbon was obtained, n^{20}_D 1.4585, whose infrared spectrum was essentially the same as that of compound (IV).

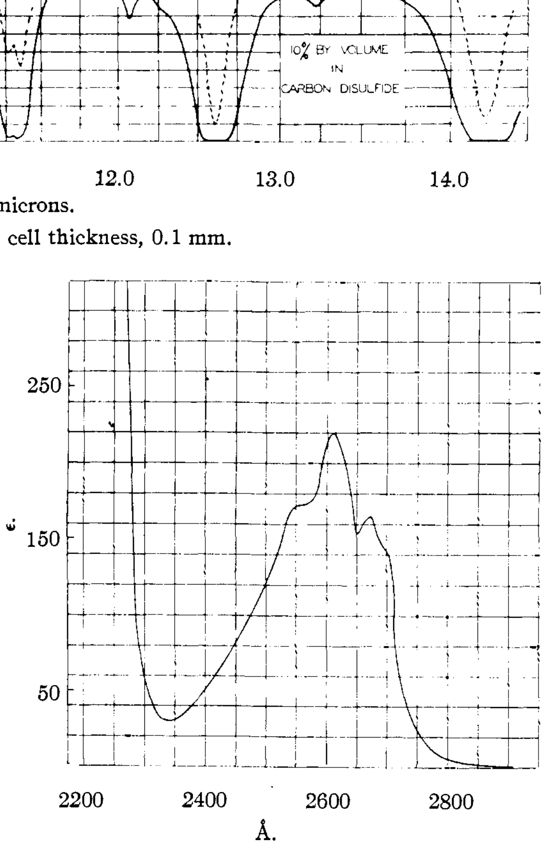

Fig. 3.—Ultraviolet absorption spectrum of 1,3-di-*t*-butylbenzene.

3. **Hydrogenation of *m*-Di-*t*-butylbenzene.**—Compound (V), 3.7 g., was hydrogenated in a 125-cc. autoclave at a temperature of 150° in the presence of a nickel-kieselguhr catalyst and 100 atmospheres of hydrogen pressure. The product gave a negative test for aromatics and its infrared spectrum showed it to be the same as that of compound (IV).

The test for aromatics was made by treating a few drops of the hydrocarbon with 1 ml. of 96% sulfuric acid solution containing 5% by weight of paraformaldehyde. The presence of traces of aromatics after two to three minutes causes a brown coloration of the sulfuric acid layer.

Summary

m-Di-*t*-butylbenzene was prepared by the dehydrogenation of 1,3-di-*t*-butylcyclohexane; the latter was obtained from 2,4-di-*t*-butylcyclohexanol by means of dehydration followed by hydrogenation.

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[2] H. Pines, R. C. Olberg and V. N. Ipatieff, This Journal, **70**, 533 (1948).

[3] B. J. Mair and A. F. Forziati, *J. Research Natl. Bureau Stand.*, **32**, 151, 165 (1944).

[4] H. Pines, A. Weizmann and V. N. Ipatieff, This Journal, **70**, 3859 (1948).

[5] H. Pines, A. Edeleanu and V. N. Ipatieff, *ibid.*, **67**, 2193 (1945).

[6] Huang-Minlon, *ibid.*, **68**, 2487 (1946).