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# THE TERTIARYBUTYLBENZENES
# INTERMEDIATES IN THE PREPARATION OF
# ORTHO-DI-TERTIARYBUTYLBENZENE

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SINCE the publications of Brown and co-workers[1], there has been considerable interest devoted to attempted syntheses of the unknown hydrocarbon o-di-t-butylbenzene.[2] The interest has been increased since the preparation by Hübel and Hoogzand[3] of 1,2,4-tri-t-butylbenzene. Bruson and co-workers[4] have already reported the preparation of o-phenylene-di-isobutyric acid (III) which presents an obvious route for the synthesis of o-di-t-butylbenzene. Recently we converted III into a derivative β,β'-di-hydroxy-o-di-t-butylbenzene (V). We now wish to report on some of the properties of this derivative of o-di-t-butylbenzene.

1,1,4,4-Tetramethyltetralone (I) was prepared according to Bruson and co-workers. The structure assigned to this compound was confirmed by its

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[1] H.C. Brown and K. LeRoi Nelson, J.Amer. Chem. Soc. 75, 24 (1953) ; H.C. Brown, D. Gintis and L. Domash, Ibid. 78, 5387 (1956).

[2] E. M. Arnett, J. Org. Chem. 25, 324 (1960) and references reported therein.

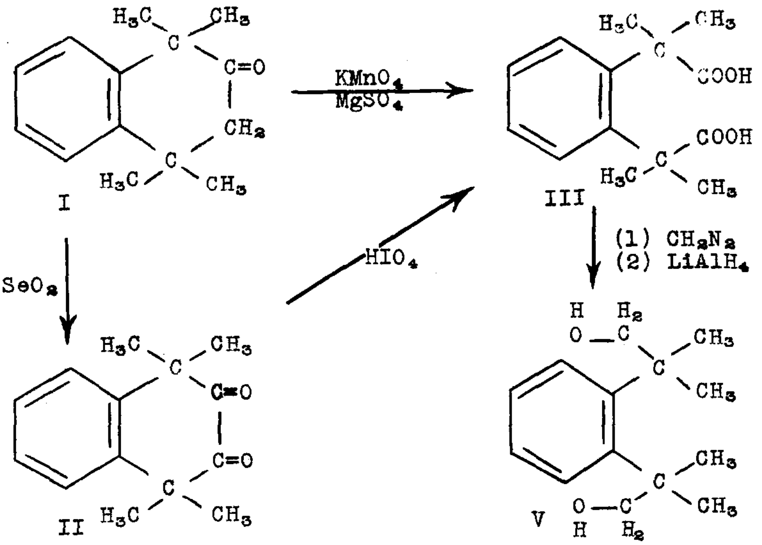
[3] W. Hübel and C. Hoogzand, Chem. Ber. 93, 103 (1960).

[4] H. A. Bruson, F.W. Grant and E. Bobko, J. Amer. Chem. Soc. 80, 3633 (1958).

NMR spectrum. This spectrum clearly showed the four C-methyl groupings. A peak at 8.69 (p.p.m. relative to tetramethylsilane = 10) is attributed to the methyl groups on carbon 4, while the peak at 8.56 is attributed to the methyl groups on carbon 1. The shift is due to the adjacent carbonyl function in the latter case. The two methylene hydrogens appear at 7.36 and the four aromatic hydrogens at 2.74. This compound showed a strong band in the infra-red at 749 $cm^{-1}$ ($CS_2$) attributed to ortho-di-substitution and carbonyl absorption at 1700 $cm^{-1}$. The ultra-violet spectrum (Fig. 1) showed two peaks at $\lambda_{max}$ 264 mμ, ε 281 and $\lambda_{max}$ 271 mμ, ε 242 (cyclohexane).

The tetralone I (m.p. 74-75°) was oxidized by potassium permanganate according to the procedure of Bruson[4] to produce a di-carboxylic acid which, after repeated recrystallizations, had a m.p. 218-219°. (Found: C, 67.03, 67.15; H, 7.32, 7.32. Calc. for $C_{14}H_{18}O_4$: C, 67.16; H, 7.25.) On the other hand, Bruson reported a melting point of 181-183° for this acid. In order to establish the identity of our acid, an alternate synthesis was carried out. In this synthesis the tetralone I was oxidized with selenium dioxide to produce a yellow di-ketone (II) in 80% yield of m.p. 64-65°. (Found: Calc. for C, 77.85, 77.85; H, 7.57, 7.62; O, 14.89, 14.80. $C_{14}H_{16}O_2$: C, 77.74; H, 7.46; O, 14.80%) This compound showed carbonyl absorption in the infra-red at 1690 $cm^{-1}$ and also a strong band at 748 $cm^{-1}$. The ultra-violet spectrum showed bands at $\lambda_{max}$ 264 mμ, and 271.5 mμ. This di-ketone was oxidized by periodic acid to produce the acid III which proved identical by mixed melting points and spectra to the acid obtained by direct oxidation of I with permanganate. The periodate oxidation of the diketone produced a high yield of the pure acid (III) whereas permanganate oxidation of I yielded an impure product melting as low as 185° before repeated recrystallizations. This probably explains the discrepancy between the melting point of III reported in the literature[4] and that of the pure acid. The acid (III) was converted to an anhydride in 87% yield by refluxing in excess acetic anhydride. The anhydride, o-phenylene-di-isobutyric anhydride, showed carbonyl absorption at 1770 and 1725 $cm^{-1}$ and a band at 756 $cm^{-1}$ indicated ortho-di-substitution. The acid was converted into its corresponding ester di-methyl-o-phenylene-di-isobutyrate (IV) in 92% yield with diazomethane. The purified ester had m.p. 102-103°. (Found: C, 69.33; H, 8.01; O, 23.39. Calc. for $C_{16}H_{22}O_4$: C, 69.03; H, 7.97; O, 23.00%) The ultra-violet spectrum showed a single broad band at 264 mμ, ε 252 and the infra-red spectra showed carbonyl absorption at 1720 $cm^{-1}$. The NMR spectrum showed the four C-methyl groups at 8.40 and the two O-methyls at 6.39, while the four aromatic hydrogens appeared at 2.73.

The di-ester (IV) was reduced with lithium aluminium hydride to give a 95% yield of the corresponding diol β,β'-di-hydroxy-o-di-t-butylbenzene (V) m.p. 115-116°. (Found: C, 75.34; H, 9.98; O, 15.12. Calc. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98; O, 14.39%). The infra-red spectrum of this compound lacked carbonyl absorption. In a KBR pellet the compound showed



broad hydroxyl absorption at 3350 $cm^{-1}$. A strong band at 1037 was attributed to the $-CH_2OH$ groups and a strong band at 750 $cm^{-1}$ to _ortho_-disubstitution. In chloroform solution, the compound showed hydroxyl bands at 3400 and 3570 $cm^{-1}$. The ultra-violet spectrum (Fig. 1) showed a single band at $\lambda_{max}$ 265 mμ , ε 225 and the fine structure exhibited by the tetralone (I) is absent in the diol. The relationships between these compounds are illustrated on p. 245.

The _ortho_-tertiarybutyl groups in the diol (V) apparently have not resulted in serious strain or distortion of the benzenoid ring, since such strain is known to cause a bathochromic shift in the ultra-violet spectra with increased intensity,[5,6] while the opposite has been observed for compound (V). A further clue to the unusual effects of the _ortho_-groupings in V is obtained from its NMR spectrum (Fig. 2). This spectrum shows a peak at 8.51 for C-methyls of intensity corresponding to the four groups. A peak at 8.21 corresponds to two hydroxyl hydrogens and the peak at 6.22 to the four methylene hydrogens. The absorption in the region for aromatic protons is now split into two groups of bands of approximately equal weights and corresponding to the total of four hydrogens. A detailed interpretation of this NMR spectrum is not offered at this time but an expedient suggestion would be that the peaks due to the hydrogens _ortho_ to the bulky groupings have been shifted and are represented by the bands near 2.55, whereas the bands near 2.78 represent the other (_meta_) hydrogens. It is to be noted that the aromatic hydrogens in compounds (I) and (IV) absorb near this region of 2.78. It may well be that the two _ortho_ hydrogens interact strongly through association with hydroxyl oxygens (see structure V) to account for the observed splittings. Such an interaction

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[5] M.P. Cava, A.A. Deana and K. Muth, _J. Amer. Chem. Soc_. **82**, 2524 (1960).

[6] M. Ballester and J. Castaner, _J. Amer. Chem. Soc_. **82**, 4259 (1960).

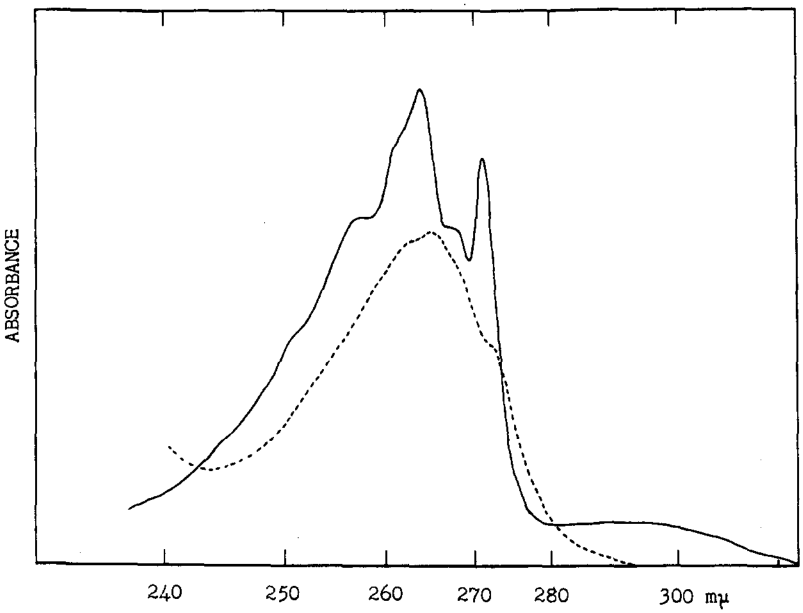

FIG. 1. Ultra-violet spectra.
——— 1,1,4,4-tetramethyltetralone (I);
- - - - β,β-di-hydroxy-*o*-di-t-butylbenzene (V).

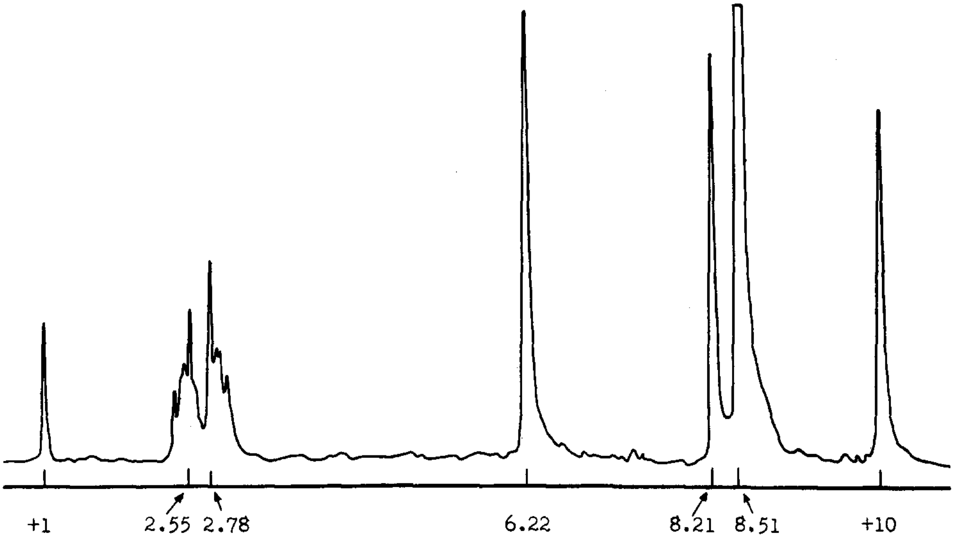

FIG. 2. NMR spectrum (V).

might also account for the ultra-violet spectrum of this compound.

A Stuart-Briegleb model was constructed of V and it was noted in this model that the $CH_2OH$ groupings would probably swing away from each other to permit the two t-butyl groupings to be ortho on the ring; and, if such is the case, the two oxygen atoms would interact very strongly with the ortho-situated hydrogens. It is conceivable that this association is sufficiently strong to relieve some of the strain expected in this system. Further experiments are continuing on these compounds and will be reported on at a later date.

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