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# ON ORTHO-TERTIARYBUTYLBENZENES

## 1,2,4,5-TETRA-TERTIARYBUTYLBENZENE

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THE problem of the possible existence of a benzene with two t-butyl groups in the *o*-position has long been of interest. After studying reactions with homomorphs of di-*o*-t-butylbenzene Brown *et al.*[1] came to the conclusion that the synthesis of di-*o*-t-butylbenzene will probably require reactors of unusually high driving force and the avoidance of conditions conducive to molecular rearrangement and isomerization. The unsuccessful attempts[2] recently made in this field again show the difficulty of the problem. Some time ago we accomplished the synthesis of 1,2,4-tri-t-butylbenzene by treating the complex $Co_2(CO)_4(C_6H_{10})_3$, made from t-butylacetylene ($C_6H_{10}$) and $Co_2(CO)_8$, with bromine.[3] From spectroscopic data Dale[4] pointed out that the benzene ring in 1,2,4-tri-t-butylbenzene is distorted, so compensating the steric requirements for the bulky t-butyl groups. Starting from *o*-phenylene-di-isobutyric acid[5] Barclay *et al.*[6] prepared β,β'-di-hydroxy-*o*-di-t-butyl-

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[1] H.C. Brown, D. Gintis and L. Domash, *J.Amer.Chem.Soc.* **78**, 5387 (1956).

[2] For literature see ref. 3.

[3] U. Krüerke, C. Hoogzand and W. Hübel, *Chem.Ber.* In press.

[4] J. Dale, *Chem.Ber.* In press (1961).

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

[6] L.R.C. Barclay, N.H. Hall and J.W. Maclean, *Tetrahedron Letters* No. 7, 243 (1961).

benzene which has a similar U.V. spectrum to 1,2,4-tri-t-butylbenzene. However they concluded that there should be no serious strain or distortion of the benzene ring. Dale's conclusion raised the question whether one could introduce more than three t-butyl groups in a benzene ring. For, if the steric requirements of the t-butyl groups really force the ring out of a planar configuration, further substitution of t-butyl groups might effect an additional distortion of the ring and so make more space for the bulky substituents.

We now wish to report two syntheses of 1,2,4,5-tetra-t-butylbenzene, the one achieved by means of a cobaltcarbonyl-complex, the other by a purely organic route.

The complex $Co_2(CO)_6C_{10}H_{18}$ was prepared by the known method[7] from $Co_2(CO)_8$ and di-t-butylacetylene $(C_{10}H_{18})$[8] in ligroin at room temperature: yield 90%, dec. 115-120°. 21.2 g (0.05 mole) of this complex were refluxed in ligroin (b.p. 100-120°) with 24.6 g (0.3 mole) of t-butylacetylene[9] by adding the latter in six portions over a period of 60 hr. Repeated chromatography on neutral alumina gave with

(a) ligroin: 12.7 g of a mixture of unreacted $Co_2(CO)_6C_{10}H_{18}$, 1,2,4-tri-t-butylbenzene and 1,2,4,5-tetra-t-butylbenzene (I).

(b) ligroin/benzene: 3.2 g (13%) of violet $Co_2(CO)_4(C_6H_{10})_3$,[3] coming from $Co_2(CO)_6C_6H_{10}$ which is formed by alkyne exchange of $Co_2(CO)_6C_{10}H_{18}$.

(c) benzene and methylenechloride: 1.5 g of the unknown orange 2,3,5-tri-t-butylcyclopentadienone (II), m.p. 55-55.5° from methanol. (Found: C, 81.63; H, 11.45; O, 6.92. Calc. for $C_{17}H_{28}O$: C, 82.20; H, 11.36;

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[7] H. Greenfield, H.W. Sternberg, R.A. Friedel, J.H. Wotiz, R. Markby and I. Wender, J.Amer.Chem.Soc. **78**, 120 (1956).

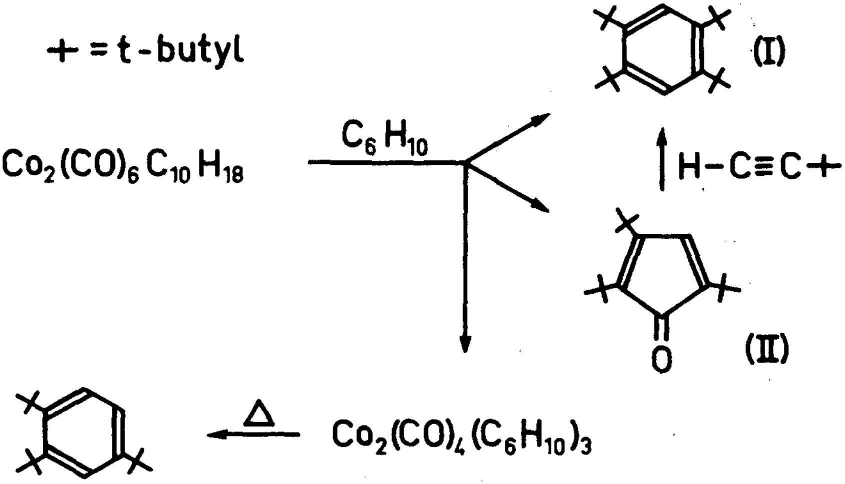
[8] G.F. Hennion and T.F. Banigan, Jr., J.Amer.Chem.Soc. **68**, 1202 (1946).

[9] M.P. Ivitsky, Bull.Soc.Chim. [4] **35**, 357 (1924); W.H. Puterbaugh and M.S. Newman, J.Amer.Chem.Soc. **81**, 1611 (1959).

0, 6.44). The I.R. spectrum (KBr) shows a band at 5.83 $\mu$, due to the ketonic group.

As fraction (a) was very difficult to separate the complex was decomposed in boiling ligroin (b.p. 80-100°C) in a stream of air. The residual oil (6.2 g) was recrystallized from methanol and yielded 1.6 g (11%) I; from the mother liquor a further 3.4 g of 1,2,4-tri-t-butylbenzene, m.p. 49-50°,[3] were isolated. I was recrystallized from benzene/methanol; m.p. 156.5 - 158.5°, corr. (Found: C, 87.48; H, 12.40; mol. wt. (Rast): 286 and 311. Calc. for $C_{22}H_{38}$: C, 87.34; H, 12.66; mol. wt.: 302.5).

Since 1,2,4-tri-t-butylbenzene can be prepared by thermal decomposition of $Co_2(CO)_4(C_6H_{10})_3$,[3] it is likely that I is also formed from the probably less stable $Co_2(CO)_4[(C_6H_{10})_2;\ C_{10}H_{18}]$ which decomposes during the reaction.



A similar reaction of $Co_2(CO)_6C_6H_{10}$[10] with $C_{10}H_{18}$[8] in boiling ligroin (b.p. 80-100°) gave only II in about 10% yield.

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[10] M.R. Tirpak, C.A. Hollingworth and J.H. Wotiz, J. Org.Chem. 25, 687 (1960).

A second synthesis of I was found in the Diels-Alder reaction of II with t-butylacetylene. Heating both compounds in benzene in a sealed tube at 250° for 3 hr gave I in 70% yield. M.p. and I.R. spectrum were identical with those of I prepared by the first synthesis. Also the m.p. of the mixture showed no depression. This reactions proves the structure of II to be 2,3,5-tri-t-butylcyclopentadienone. It also represents the first preparation by a purely organic route of a benzene derivative with t-butyl groups in the ortho-position and is of general application. Thus when II and dicarbomethoxyacetylene were heated at 200° for a period of 10 min, 1,2,4-tri-t-butyl-5,6-dicarbomethoxybenzene was obtained in a 70% yield, m.p. 122-123° (from ethanol). (Found: C, 72.88; H, 9.12; O, 18.10. Calc. for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45; O, 17.66.)

The structural proof for I is derived from NMR measurements. The spectrum at 60 Mc/s in $CS_2$ shows only two narrow bands of half-peak width about 1.5 cps without any fine structure: one band for aromatic protons at $\tau = 2.46$ and the other for aliphatic protons at $\tau = 8.52$,[10a] relative to tetra-methylsilane as internal standard $\tau = 10$. Moreover the ratio of the peak areas (aromatic/aliphatic) is 2:34.5, which corresponds very well with the expected value 2 : 36. Also the high m.p. of I is in agreement with this structure; *cf.* the m.p. 119-119.4° of 1,2,4,5-tetra-isopropylbenzene[11].

The U.V. spectrum of I in n-hexane (Fig. 1) has the same pattern as that of 1,2,4-tri-t-butylbenzene:[4] $\lambda_{max}$ in m$\mu$ ($\epsilon$): 274 (359), 225 (sh., 12,500), 203.5 (56,500). 1,2,4,5-tetra-isopropylbenzene: $\lambda_{max}$ in m$\mu$ ($\epsilon$): 278 (662), 269 (587), 262 (sh., 328), 219 (infl., 13,500), 202 (65,000).

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[10a] For 1,2,3,4 aud 1,2,3,5 substitution two (intensity 1:1) or three (intensity 1:1:2) peaks respectively have to be observed for the t-butyl-groups.

[11] V.N. Ipatieff, B.B. Corson and H. Pines, J.Amer.Chem.Soc. **58**, 919 (1936).

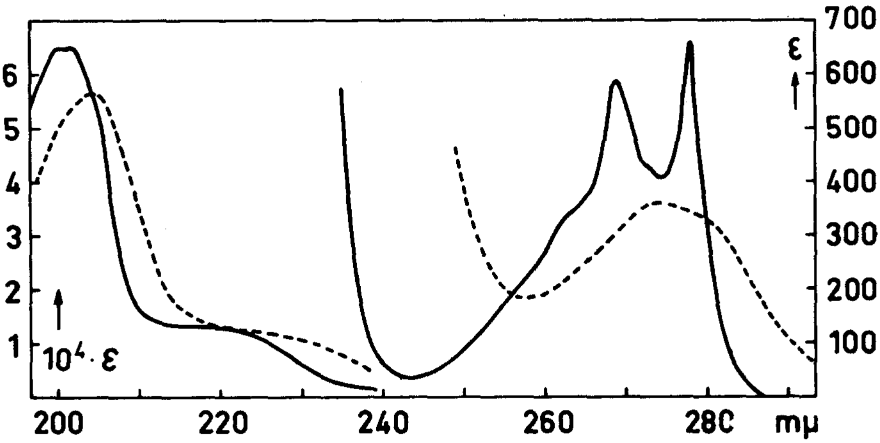

FIG. 1. U.V. spectrum in n-hexane.
---- 1,2,4,5-tetra-t-butylbenzene.
——1,2,4,5-tetra-iso-propylbenzene.

Comparing the spectrum of I with that of 1,2,4,5-tetra-isopropylbenzene,[12] which shows fine structure and higher values of ε in the 270μ region, we again conclude that the benzene ring is distorted.

Furthermore, the I.R. spectrum (Fig. 2) is in agreement with the assigned structure: the band at 11.21μ (KBr) must be attributed to the aromatic C-H out of plane vibration, which has practically the same position as in 1,2,4,5-tetra-isopropylbenzene (11.19μ). In $CHCl_3$ solution I has a weak band at 6.31μ, which may be attributed to a ring stretching frequency, normally only observable in the Raman spectrum of 1,2,4,5-tetra-alkyl substituted benzenes.

The activity of this vibration indicates the loss of the centre of symmetry of I and would exclude a chair type form for the benzene ring. This leads to the conclusion that the benzene ring has been twisted into

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[12] prepared following ref. 11.

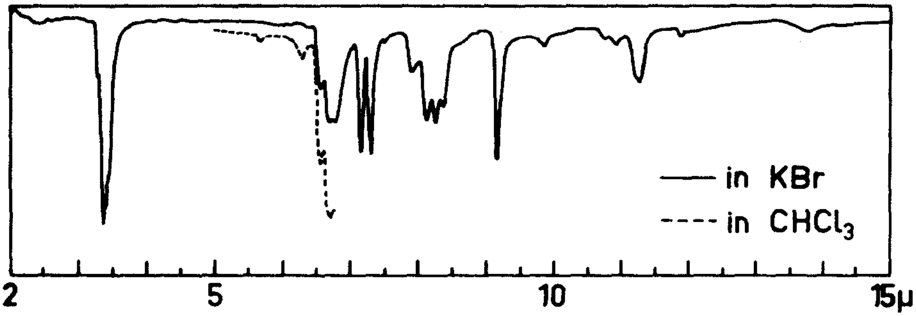

FIG. 2. I.R.-spectrum of 1,2,4,5-tetra-t-butylbenzene.

the "boat" form, comparable with one of the possible conformations for a cyclohexane ring. From a (too rigid) Stuart-Briegleb model it is indeed evident that a "boat" form is rather easy to realize and makes more space available for the bulky groups. Moreover the model suggests a structure in which the substituents on the ring carbon atoms 1,2,4 and 5 are alternating slightly upwards and downwards from the plane through these carbon atoms.

The heat of combustion of the solid I has been determined as 3295.9 ± 2.3 kcal/mole,[13] without taking into account the heat of sublimation. For a hypothetical undistorted tetra-t-butylbenzene a heat of combustion of 3264.9 ± 1.4 kcal/mole was calculated.[14] The difference between these values (31.0 ± 3.7 kcal/mole) still contains the difference in the heats of sublimation of I and 1,3,5-tri-t-butylbenzene as an unknown factor, being of the order of a few kcal/mole. Nevertheless it is evident that the resonance energy of I is considerably decreased.

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[13] For these measurements we are indebted to Dr. A. Reckziegel and Prof. E.O. Fischer, University of Munich.

[14] From the heats of combustion of 1,3,5-tri-t-butylbenzene,[3] t-butylbenzene: (2640.7 + 1413.3 - 789.1) ± 1.4 kcal/mole.

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