

77. *von Braun's "Diphenylcyclobutane Derivative": 6,6'-Dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobi-indane and a Related Compound.*

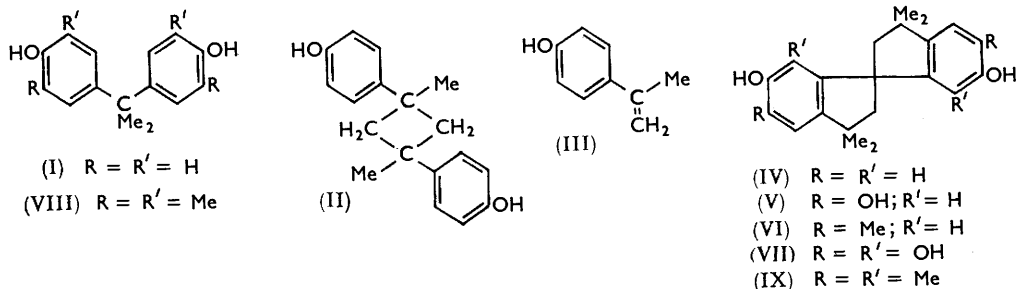
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Further investigation of the alleged cyclobutane derivative (II) has shown that it is the spirobi-indane (IV). A similar spirobi-indane derived from 2,6-dimethylphenol is described.

2,2-DI-*p*-HYDROXYPHENYLPROPANE (I) rearranges on vigorous treatment with acid to a compound, m. p. 181°, which was assigned the structure (II) by von Braun,¹ who observed that this production of compound (II) was accompanied by the liberation of phenol. It was suggested that cleavage of the propane (I) to *p*-isopropenylphenol (III) and phenol occurred and that this was followed by dimerisation of (III) to the cyclobutane (II).

¹ von Braun, *Annalen*, 1929, **472**, 65.

However, the similarity between this reaction and the well-established conversion of *p*-hydroxyphenylpropane derivatives into spirobi-indanes under similar conditions suggested that a spirobi-indane structure (IV) was more likely. Examination of the



supposed "cyclobutane" (II) has shown that it is a spirobi-indane derivative and this result has already been briefly reported.²

Treatment of 2,2-di-*p*-hydroxyphenylpropane (I) with hydrochloric acid at 100° as described by von Braun gave very low yields of the compound, m. p. 181°, but similar treatment with boiling hydrobromic acid gave good yields. The product was a hemihydrate, and crystallisation from benzene or sublimation in a high vacuum gave the anhydrous compound, $C_{21}H_{24}O_2$. The presence of water was confirmed by vapour-phase chromatography of a solution of the hemihydrate in anhydrous benzene. Rast determinations of molecular weight proved unreliable but determinations by a microebullioscopic method, especially on the dimethyl derivative, conformed the $C_{21}H_{24}O_2$ formula.

The formation of a compound $C_{21}H_{24}O_2$ and the simultaneous liberation of phenol in 65% of the yield expected in such a reaction are analogous to the reaction of the diphenylpropanes derived from catechol,^{3,4} *o*-cresol,^{5,6} and pyrogallol⁷ under similar conditions. These have been shown by Baker *et al.*⁸ to be converted into spirobi-indanes [(V), (VI), and (VII), respectively] with the simultaneous liberation of the corresponding phenol. Thus, the most reasonable structure for von Braun's compound with two phenolic hydroxyl groups is 6,6'-dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobi-indane (IV). The proton magnetic resonance spectra of this compound and of 5,6,5',6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobi-indane (V) at 40 Mc./sec. in dioxan showed identical curves in the region of the methyl and methylene resonances, and this confirmation of structure (IV) is independently supported by the high-resolution infrared spectra.⁹

2,2'-Di-(4-hydroxy-3,5-dimethylphenyl)propane (VIII) is also rearranged to a compound ($C_{25}H_{32}O_2$) which by analogy and from the similarity of the ultraviolet absorption spectra must be 6,6'-dihydroxy-3,3,5,7,3',3',5',7'-octamethyl-1,1'-spirobi-indane (IX). The same compound can be prepared directly from acetone and 2,6-dimethylphenol by vigorous reaction.

EXPERIMENTAL

Ultraviolet absorption spectra were measured in ethanol with an Optica CF4 recording spectrophotometer. Nuclear magnetic resonance spectra were measured with a Varian Associates spectrometer at 40 Mc./sec. in dioxan at room temperature. Dioxan was used as internal reference and was assigned $\tau = +8.3$ relative to $H_2O = 0$. Molecular weights were determined by a semimicro-thermistor ebullioscopic technique in dichloromethane.

² Curtis, *Chem. and Ind.*, 1960, 928.

³ Baker, *J.*, 1934, 1678.

⁴ Baker and McGowan, *J.*, 1938, 347.

⁵ Fisher, Furlong, and Grant, *J. Amer. Chem. Soc.*, 1936, 58, 820.

⁶ Baker and Besly, *J.*, 1939, 1421.

⁷ Baker and Besly, *J.*, 1939, 195.

⁸ Baker and Williams, *J.*, 1959, 1295.

⁹ Private communication, Dr. W. L. Howard, Dow Chemical Co., Freeport, Texas.

2,2-Di-*p*-hydroxyphenylpropane (I).—Phenol (94 g.) and acetone (58 g.) were saturated with dry hydrogen chloride and set aside at room temperature for 2 days. The black mass was washed by stirring and decantation with water (4 × 1000 ml.) and aqueous sodium hydroxide (1% w/v; 6 × 1000 ml.), stirred with benzene (100 ml.), and filtered, and the solid washed with more benzene (50 ml.). Crystallisation from xylene (charcoal) and then water gave 2,2-di-*p*-hydroxyphenylpropane as stout prisms (46 g.), m. p. 155°. Dianin¹⁰ gives m. p. 155°.

6,6'-Dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobi-indane (IV).—The diphenylpropane (21 g.) in hydrobromic acid (*d* 1.48; 100 ml.) was heated under reflux for 7 hr., and then set aside overnight. The acid layer was then decanted and the residue was washed with water by decantation and dried in *vacuo*. Trituration with benzene (25 ml.) gave a colourless product (6.35 g.), m. p. 175—176°, which was recrystallised from aqueous methanol to give 6,6'-dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobi-indane hemihydrate (IV) as thin needles, m. p. 180—181°. von Braun¹ gives m. p. 181° for the "cyclobutane" (II) (Found: C, 78.8; H, 7.7; O, 13.1. C₂₁H₂₄O₂·½H₂O requires C, 79.4; H, 7.9; O, 12.6%).

In another experiment the diphenylpropane (I) (32 g.) was treated in the same way and the acid and aqueous residue steam distilled. The steam distillate was shaken with ether (2 × 100 ml.), and the extract shaken with saturated sodium hydrogen carbonate solution, dried, and distilled to give phenol (8.1 g., 65%), b. p. 180—181°.

Crystallisation of the spirobi-indane hydrate from benzene or sublimation at 205°/1 mm. gave the spirobi-indane (IV) as prisms, m. p. 213—214° [Found: C, 82.0; H, 7.9; O, 10.4%; *M*(Rast) 293, *M*(ebullioscopic), 311; λ_{max}, 286 (ε 3.91); N.M.R. resonances at +2.40 p.p.m. (methyl groups) and +1.50 p.p.m. (methylene groups) relative to dioxan. C₂₁H₂₄O₂ requires C, 81.8; H, 7.8; O, 10.4%; *M*, 308. C₁₈H₂₀O₂ requires C, 80.6; H, 7.5; O, 11.9%; *M*, 268]. Recrystallisation of the anhydrous compound from benzene saturated with water or aqueous methanol regenerated the hemihydrate, m. p. 181°. The spirobi-indane (VI) from catechol showed methyl and methylene proton resonances at the same positions with the same ratio of intensities.

Dimethyl ether. Methylation with dimethyl sulphate in aqueous alkaline acetone gave the *dimethyl ether* from aqueous methanol as thin needles, m. p. 118° (von Braun gives m. p. 115°) [Found: C, 81.8; H, 8.35; O, 10.2; OMe, 18.6%; *M*(Rast), 299, *M*(ebullioscopic), 337, 332, 335. C₂₃H₂₈O₂ requires C, 82.1; H, 8.4; O, 9.5; 2OMe, 18.5%; *M*, 336].

Diacetyl derivative. The *diacetyl* derivative (acetic anhydride-sodium acetate) recrystallised from aqueous methanol as thin needles, m. p. 149—150°, resolidifying to rectangular plates, m. p. 165° (Found: C, 76.8; H, 7.3; O, 15.7. C₂₅H₂₈O₂ requires C, 76.5; H, 7.2; O, 16.3%). Hydrolysis with alkaline aqueous methanol gave the spirobi-indane hydrate (IV), m. p. and mixed m. p. with original material, 181°.

2,2'-Di-(4-hydroxy-3,5-dimethylphenyl)propane (VIII).—2,6-Dimethylphenol (61 g.) and acetone (29 g.) were saturated with dry hydrogen chloride and set aside for 48 hr. The crystalline solid was then broken, washed with water, and dried. Recrystallisation from aqueous methanol and then benzene gave 2,2'-di-(4-hydroxy-3,5-dimethylphenyl)propane (VIII) as needles (60.0 g.), m. p. 164—165° (Found: C, 80.7; H, 8.5. C₁₉H₂₄O₂ requires C, 80.2; H, 8.5%).

Diacetyl derivative. The *diacetyl* derivative (acetic anhydride-sodium acetate) was crystallised from aqueous methanol, forming plates, m. p. 138° (Found: C, 75.1; H, 7.6. C₂₃H₂₈O₄ requires C, 75.0; H, 7.7%).

6,6'-Dihydroxy-3,3,5,7,3',3',5',7'-octamethylbis-1,1'-spirobi-indane (IX).—(a) 2,6-Dimethylphenol (55 g.) with acetic acid (175 ml.), acetone (37.5 ml.), and concentrated hydrochloric acid (95 ml.) was heated under reflux for 68 hr. The product was poured into water, the mixture extracted with ether, and the ethereal layer washed with saturated sodium hydrogen carbonate solution, dried, and distilled, giving fraction 1, b. p. 80—90°/2 mm. (5.9 g.) (recovered 2,6-dimethylphenol), and fraction 2, b. p. 230—240°/1.3 mm. (33.1 g.), cooling to a pale yellow glass.

A portion of the latter (9.7 g.) was heated under reflux with acetic anhydride (50 ml.) and sodium acetate (1 gm.) for 4 hr., poured into water, and recrystallised from ethanol, to give the *diacetyl derivative* of 6,6'-dihydroxy-3,3,5,7,3',3',5',7'-octamethylbis-1,1'-spirobi-indane (IX), prisms (2.59 g.), m. p. 236—238° (Found: C, 77.9; H, 8.1. C₂₉H₃₆O₄ requires C, 77.6; H, 8.1%).

Hydrolysis of this *diacetyl* derivative with boiling aqueous ethanolic potassium hydroxide

¹⁰ Dianin, *J. Russ. Phys. Chem. Soc.*, 1891, **23**, 492.

gave 6,6'-*dihydroxy-3,3,5,7,3',3',5',7'-octamethylbis-1,1'-spirobi-indane* (IX), as stout needles from benzene-light petroleum (b. p. 60—80°), m. p. 196° (λ_{max} 283, ϵ 3.73) (Found: C, 82.4; H, 8.9. $\text{C}_{25}\text{H}_{32}\text{O}_2$ requires C, 82.4; H, 8.8%).

(b) 2,2'-Di-4-hydroxy-(3,5-dimethylphenyl)propane (VIII) (15 g.) in hydrobromic acid (*d* 1.48; 75 ml.) was heated under reflux overnight. The product was poured into water, the mixture extracted with ether, and the ethereal extract washed with sodium hydrogen carbonate solution, and dried. Distillation gave fraction 1 (2,6-dimethylphenol), b. p. 80—90°/2 mm., and fraction 2, b. p. 190—220°/1.5 mm. (10.39 g.). The second fraction was acetylated with acetic anhydride-sodium acetate giving the diacetyl derivative of (IX) (8.29 g., 52%), m. p. 230—236° undepressed when mixed with authentic material.

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