

PREPARATION OF 1,5-DIPHENYLNAPHTHALENE¹

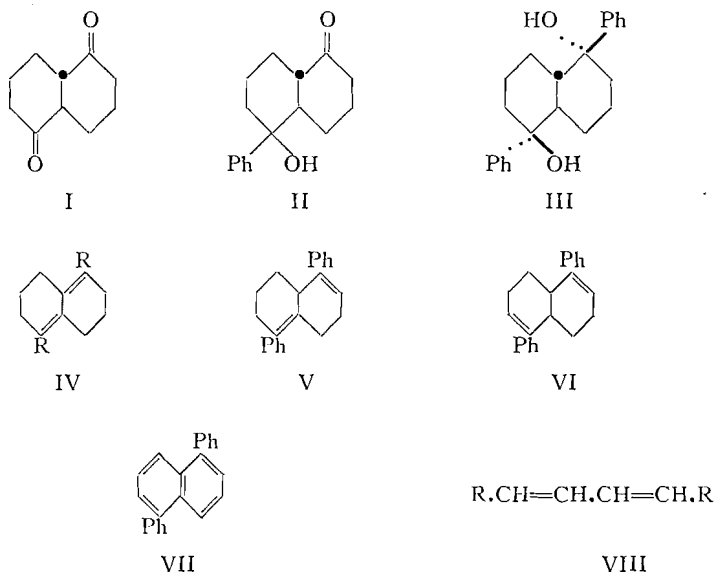
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ABSTRACT

The transformation of 1,5-dioxodecalin into 1,5-diphenylnaphthalene is described.

1-Phenylnaphthalene does not form solid complexes with the usual complexing agents (1) but has been found to form a complex with benzotrifuroxan (2). It was of interest, therefore, to prepare 1,5-diphenylnaphthalene and examine its complex-forming abilities. After this work was completed a synthesis of the hydrocarbon was reported in the literature (3).

It is stated (3) that treatment of 1,5-dioxodecalin (I, mixture of isomers) with phenylmagnesium bromide gives the glycol (III, m.p. 233–249°) in 33% yield. Under these conditions and using the pure *trans*-diketone (I) the only crystalline material isolated



was the monoadduct (II, yield 45%), none of the glycol being formed. However, treatment of the diketone (I) with lithium phenyl gave an excellent yield of 1,5-dihydroxy-1,5-diphenyldecahydronaphthalene (III, m.p. 275–277°). The material appeared to be homogeneous and it most probably has structure (III) with the two phenyl groups equatorial. This is the most stable isomer, having the larger groups equatorial, and its formation is likely to be favored by “steric approach control” (4).

Buchta and co-workers dehydrated the glycol (m.p. 233–249°) with potassium hydrogen sulphate, affording an olefin (m.p. 117–119°, 22% yield) to which structure (IV, R = Ph) was assigned without any supporting evidence (3). By dehydrating the pure glycol (III) with formic acid, an olefin (m.p. 179–182°) has now been obtained which may have structure (IV, R = Ph), (V), or (VI); the ultraviolet spectrum of the olefin

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showed λ_{\max} 235 m μ (ϵ 19,300); λ_{inflex} 284 m μ (ϵ 6020); the absorption then steadily decreased (at 310 m μ , ϵ = 2400). Styrene has two absorption bands (λ_{\max} 244 m μ , ϵ 12,000 and λ_{\max} 282 m μ , ϵ 450) and the ultraviolet spectrum of 1-phenylcyclohexene contains only a single band (λ_{\max} 247 m μ , ϵ 12,940) (5). Compounds having structures (V) or (VI) would be expected to show absorption of this type, the value of ϵ being smaller than 24,000 because of the non-coplanarity of the phenyl and reduced naphthalene rings (6). This evidence suggests that the olefin obtained in this work is the conjugated diene (IV, R = Ph). The ultraviolet spectrum of (IV, R = Ph) indicates that the benzene and hexahydronaphthalene rings in this compound must be non-coplanar, since 1,4-diphenylbutadiene (VIII, R = Ph) has λ_{\max} 328 m μ , ϵ 41,000 (5).

The corresponding diketone (IV, R = CO.CH₃) (7) has an absorption band at 295 m μ whose intensity (ϵ = 9020) is only one third of that of the open-chain analogue (VIII, R = COCH₃) which has λ_{\max} 272 m μ (ϵ 31,000) and λ_{\max} 279 m μ (ϵ 32,000) (8).

Dehydrogenation of the hexahydro compound using palladium-charcoal gave 1,5-diphenylnaphthalene (VII) in 80% yield as compared with the 20% obtained using sulphur (3). The ultraviolet spectra of 1-phenylnaphthalene and 1,5-diphenylnaphthalene are very similar, indicating non-coplanarity of the benzene and naphthalene rings.

EXPERIMENTAL

Ultraviolet spectra were determined in ethanol solution; infrared spectra measured in Nujol mulls unless otherwise indicated. All melting points are uncorrected.

1-Hydroxy-5-oxo-1-phenyldecahydronaphthalene (II)

To a solution of phenylmagnesium bromide (magnesium 3 g, bromobenzene 20 cc) in ether (50 cc) was added *trans*-1,5-dioxodecalin (5 g, m.p. 160°) (9) in benzene (100 cc) and the mixture refluxed and stirred for 5 hours. Next day water and saturated ammonium chloride solution were added, the aqueous layer extracted with benzene, the combined organic layers dried (magnesium sulphate), and the solvents removed. The semisolid residue was triturated with petroleum ether (10 cc, b.p. 60–80°) and then crystallized from benzene (25 cc) giving a solid (3.3 g, 45%) of m.p. 150–155°. Crystallization from benzene and then from methanol gave 1-hydroxy-5-oxo-1-phenyldecahydronaphthalene, colorless plates, m.p. 163–164° (mixed m.p. with starting material, 130–145°). Found: C, 78.4; H, 8.1%. Calc. for C₁₆H₂₀O₂: C, 78.7; H, 8.2%. Ultraviolet spectrum: λ_{\max} 205 m μ (ϵ 9620); λ_{\max} 251 m μ (ϵ 205); λ_{\max} 257 m μ (ϵ 246); λ_{\max} 263 m μ (ϵ 204); λ_{\max} 266 m μ (ϵ 161). Infrared spectrum contained bands at 3390 cm⁻¹ (OH); 1686 cm⁻¹ (CO); 1600 cm⁻¹ (ar. CC). The *2,4-dinitrophenylhydrazone* formed orange-colored needles (from acetic acid), m.p. 207–209°. Found: C, 62.2; H, 5.6; N, 13.4%. Calc. for C₂₂H₂₄O₅N₄: C, 62.3; H, 5.7; N, 13.2%. The *semicarbazone* crystallized from 2-methoxyethanol as colorless prisms, m.p. 253–255°. Found: C, 67.2; H, 7.9; N, 13.3%. Calc. for C₁₇H₂₃N₃O₂: C, 67.7; H, 7.7; N, 13.9%. A solution of the carbinol (1 g) in formic acid (10 cc) was refluxed for 30 minutes, the solution cooled, diluted with water, and the mixture extracted with ether. The ethereal extracts were washed with sodium carbonate solution, dried (magnesium sulphate), and the solvent removed, giving an oil whose ultraviolet absorption λ_{\max} 240 m μ (ϵ 11,100) indicated that the double bond formed was conjugated with the benzene nucleus; but the infrared spectrum of the oil (natural film) contained two carbonyl bands (1710 and 1665 cm⁻¹) indicating the presence of some $\alpha\beta$ -unsaturated ketone. The benzene mother liquors from the Grignard reaction were evaporated giving an oil which did not crystallize and whose infrared spectrum contained bands at 3370

cm^{-1} , 1692 cm^{-1} , and 1595 cm^{-1} . A portion of this oil was dehydrated with formic acid, the product isolated in the usual way and distilled up to 259° (oil bath) at 0.01 mm . The infrared spectrum of the resulting glass contained intense carbonyl bands (1715 and 1645 cm^{-1}) indicating absence of the glycol (III) in the original preparation. Ultraviolet spectrum of the glass: $\lambda_{\text{max}}\ 237\text{ m}\mu$ ($\epsilon\ 11,100$).

1,5-Dihydroxy-1,5-diphenyldecahydronaphthalene (III)

Trans-1,5-dioxodecalin (5 g) in warm benzene (70 cc) was added dropwise to a solution of lithium phenyl prepared from lithium (1.7 g), bromobenzene (19 g), and ether (50 cc). The mixture was then stirred and boiled under nitrogen for 10 hours. Next day water and ammonium chloride solution were added, the suspension stirred for 2 hours, the solid collected, washed well with water, and dried (8.4 g, 87%), m.p. $250\text{--}255^\circ$. The glycol crystallized from 2-ethoxyethanol as colorless, hexagonal plates, m.p. $275\text{--}277^\circ$. Found: C, 81.7; H, 7.8%. Calc. for $\text{C}_{22}\text{H}_{26}\text{O}_2$: C, 82.0; H, 8.1%. Ultraviolet spectrum: $\lambda_{\text{max}}\ 207\text{ m}\mu$ ($\epsilon\ 21,080$), $\lambda_{\text{max}}\ 252\text{ m}\mu$ ($\epsilon\ 417$), $\lambda_{\text{max}}\ 257\text{ m}\mu$ ($\epsilon\ 487$), $\lambda_{\text{max}}\ 260\text{ m}\mu$ ($\epsilon\ 417$), $\lambda_{\text{max}}\ 263\text{ m}\mu$ ($\epsilon\ 368$), $\lambda_{\text{max}}\ 266\text{ m}\mu$ ($\epsilon\ 278$). The infrared spectrum contained bands at 3472 cm^{-1} (OH) and 1605 cm^{-1} (ar. CC).

1,5-Diphenylnaphthalene (VII)

The finely powdered glycol (2 g) was added to formic acid (25 cc) and the suspension heated under reflux (oil bath, 140°) for 30 minutes. Hot dimethylformamide (25 cc) was added, the solution boiled for 5 minutes, allowed to cool, the solid which separated collected, and washed with a little ethanol (1.3 g, 73%). After crystallization from acetic acid the product had m.p. $167\text{--}172^\circ$; crystallization from benzene gave a specimen of m.p. $179\text{--}182^\circ$. Found: C, 92.2; H, 7.3. Calc. for $\text{C}_{22}\text{H}_{22}$: C, 92.3; H, 7.7%. Ultraviolet spectrum: $\lambda_{\text{max}}\ 235\text{ m}\mu$ ($\epsilon\ 19,300$), $\lambda_{\text{inflex}}\ 284\text{ m}\mu$ ($\epsilon\ 6020$). Infrared spectrum 1597 cm^{-1} (ar. CC). The 1,5-diphenylhexahydronaphthalene (1.2 g) was mixed with 30% palladium-charcoal (0.2 g) (10) and heated (metal bath) at 240° for 30 minutes, the temperature of the bath was then raised to 300° (30 minutes), and finally to 330° (30 minutes), a slow stream of hydrogen being passed through the apparatus. The cold solid was extracted exhaustively with chloroform, the extracts evaporated, and the residue crystallized from benzene (0.94 g, 80%, m.p. $220\text{--}223^\circ$). 1,5-Diphenylnaphthalene formed colorless needles (from benzene) m.p. $223\text{--}224^\circ$, reported (3) m.p. $220\text{--}222^\circ$. Found: C, 94.2; H, 5.55. Calc. for $\text{C}_{22}\text{H}_{16}$: C, 94.3; H, 5.7%. Ultraviolet spectrum: $\lambda_{\text{max}}\ 228\text{ m}\mu$ ($\epsilon\ 48,200$), $\lambda_{\text{max}}\ 297\text{ m}\mu$ ($\epsilon\ 14,200$). The hydrocarbon did not give a solid complex with either 2,4,7-trinitrofluorenone or with benzotrifuroxan.

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