

78. Barnes's "Tetrahydroindenoindene" Derivatives: Two Spiroindanes.

By R. F. CURTIS and K. O. LEWIS.

The compound supposed to be the tetrahydroindenoindene (III) has been shown to be the spiroindane (VII) by conversion into the known dihydroxy-spiroindane (XII) in the series of steps (VII) \longrightarrow (X) \longrightarrow (XI) \longrightarrow (XII). The analogous compound believed to have structure (IV) has been correlated with compound (VII) and hence must be the spiroindane (VIII).

THE reaction of 4-methyl-4-phenylpentan-2-one (I) with zinc chloride was originally described by Hoffmann,¹ who assigned the formula $C_{24}H_{28}$ to the product. A similar reaction was described by Barnes and Beitchman² who treated the homologue, 4-methyl-4-*p*-tolylpentan-2-one (II) with boiling dilute sulphuric acid and isolated a hydrocarbon $C_{23}H_{28}$. It was realized that such a product could only arise from two molecules of the ketone (II) by loss of a three-carbon fragment as well as water and the molecular formula was therefore rigorously established by molecular-weight determinations and the formation of substituted derivatives. It was also found that the same hydrocarbon was produced by the action of zinc chloride and thus it was clear that the reaction was related to that described earlier by Hoffmann.¹ However, similar loss of a three-carbon fragment from two molecules of the ketone (I) would lead to a formula $C_{21}H_{24}$ for Hoffmann's compound and this was confirmed on re-investigation by Barnes *et al.*²

On the basis of the lack of reactivity and reactions involving the nuclear methyl groups Barnes *et al.* assigned indenoindene structure (III) to the compound $C_{23}H_{28}$ and, by analogy, structure (IV) to the hydrocarbon described by Hoffmann. These structures were supported by synthetic studies which are however ambiguous.

Our attention was directed to these compounds as the result of the observation³ during the study of the related compound (V)⁴ that attempted demethylation with hydrobromic

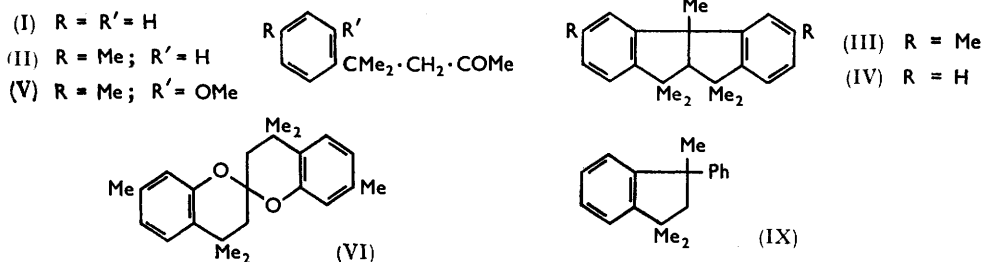
¹ Hoffmann, *J. Amer. Chem. Soc.*, 1929, **57**, 2542.

² Barnes and Beitchman, *J. Amer. Chem. Soc.*, 1954, **76**, 5430.

³ Baker, Curtis, and McOmie, *J.*, 1952, 1774.

⁴ Baker, Curtis, and McOmie, *J.*, 1951, 76.

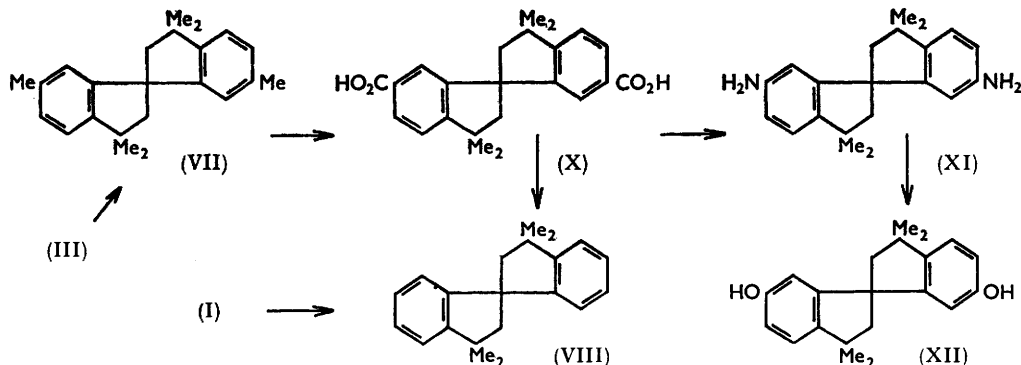
acid in acetic acid led to a product which was shown to be the spirochroman (VI). Generation of the $\text{Me}_2\text{C}\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH}_2\cdot\text{CMe}_2$ (phorone) residue in the course of this reaction suggested that a similar skeleton might have arisen during the acid treatment of the ketones (I) and (II). If so, then the hydrocarbons (III) and (IV) might be expected to



have the spiroindane structures (VII) and (VIII), especially in view of the established relation between spirochromans and spiroindanes. Interest increased when it was shown⁵ that the saturated dimer of α -methylstyrene, 1,1,3-trimethyl-3-phenylindane⁶ (IX), on treatment with aluminium chloride also produced a hydrocarbon $\text{C}_{21}\text{H}_{24}$. This was shown to be identical with the hydrocarbon prepared by the action of sulphuric acid on the ketone (I) as described by Barnes *et al.*, and the structure proposed by the latter authors was accepted.

A proton magnetic resonance spectrum of the hydrocarbon $\text{C}_{21}\text{H}_{24}$ measured at 40 Mc./sec. showed (a) a doublet at $\delta - 0.02$ p.p.m. (CH_3 groups) and (b) a single peak at $\delta - 0.88$ p.p.m. (CH_2 groups) relative to cyclohexane. The ratio of the integrated intensity of peak (a) to peak (b) was $3.40 \pm 0.5 : 1$. Structure (III) with no methylene groups could not be correct; of the four 1,1'-spirobi-indanes and two 2,2'-spirobi-indanes which were consistent with this spectrum and with the chemical evidence advanced by Barnes *et al.*, the 1,1'-derivative (VIII) appeared most reasonable. The structure (VIII) has been confirmed by the conversions shown in the annexed scheme.

4-Methyl-4-*p*-tolylpentan-2-one (II) was converted into the hydrocarbon $\text{C}_{23}\text{H}_{28}$ as described by Barnes *et al.*² Oxidation of the nuclear methyl groups with chromic acid



gave the dicarboxylic acid (X) which was converted by the Schmidt reaction into the diamine (XI) in high yield. A bisdiazonium reaction gave the corresponding dihydroxy-compound which was identical with the known dihydroxy-1,1'-spirobi-indane (XII).⁷

⁵ Adams, Lee, and Wadsworth, *J. Org. Chem.*, 1959, **24**, 1186.

⁶ Bergmann, Taubadel, and Weiss, *Ber.*, 1931, **64**, 1495.

⁷ Curtis, preceding paper.

Thus the compound $C_{23}H_{28}$ described as (III) must be 3,3,3',3',6,6'-hexamethyl-1,1'-spirobi-indane (VII).

Decarboxylation of the acid (X) with copper chromite in quinoline gave a hydrocarbon $C_{21}H_{24}$, identical with Hoffmann's hydrocarbon prepared from the ketone (I) by treatment with acid and with a sample, kindly provided by Dr. Adams, produced from the dimer of α -methylstyrene. This compound must be 3,3,3',3'-tetramethyl-1,1'-spirobi-indane (VIII) and is the parent hydrocarbon of a series of these substituted spirobi-indanes described by Baker and his co-workers.⁸

EXPERIMENTAL

M. p.s were taken on a Kofler block. Ultraviolet absorption spectra are for EtOH solutions and were measured on an Optica CF4 recording spectrophotometer. Proton magnetic resonance spectra were taken for $CHCl_3$ solutions at room temperature by using a Varian Associates spectrometer type V-4300B at 40 Mc./sec. calibrated by an audio-frequency side-band method. Cyclohexane was used as internal reference and was assigned $\delta = +3.43$ p.p.m., relative to $H_2O = 0$. Infrared spectra were determined for KBr discs on a Grubb-Parsons GS2 spectrometer.

4-Methyl-4-p-tolylpentan-2-one (II).—This ketone, prepared as described,⁹ had b. p. 134—140°/12 mm., n_D^{20} 1.5114 (Barnes *et al.* give n_D^{20} 1.5059). Distillation of the higher-boiling fractions as described by Barnes *et al.*² gave none of the hydrocarbon (VII).

3,3,3',3',6,6'-Hexamethyl-1,1'-spirobi-indane (VII).—The foregoing ketone (51.4 g.) in sulphuric acid (d 1.84; 300 ml.) and water (300 ml.) was heated under reflux for 8 hr. The mixture was extracted with ether (3×200 ml.) which was washed with saturated sodium hydrogen carbonate solution and dried ($MgSO_4$). Distillation gave unchanged ketone, b. p. 60—80°/1.2 mm. (16.5 g.), and a product, b. p. 130—180°/1.2 mm. (10 g.), which solidified. Recrystallisation from ethanol gave 3,3,3',3',6,6'-hexamethyl-1,1'-spirobi-indane (VII) as prisms (7.85 g.), m. p. 137—138°, λ_{max} 273,279 (ϵ 3.50, 3.51) (Found: C, 90.6; H, 9.25. $C_{28}H_{38}$ requires C, 90.7; H, 9.3%).

3,3,3',3'-Tetramethyl-1,1'-spirobi-indane-6,6'-dicarboxylic Acid (X).—Chromium trioxide (2.8 g.) was added in one portion to the preceding hydrocarbon (4.4 g.) in acetic acid (220 ml.), water (120 ml.) and sulphuric acid (d 1.84, 20 ml.), and heated under reflux for 7 hr.; a powder separated. The whole was poured into water (2 l.) and left at 0° overnight; the solid was collected and washed with water and then 10% sodium hydroxide solution (100 ml.). The alkaline filtrate was acidified with concentrated hydrochloric acid, and the resultant gel set aside overnight. The precipitated solid was dried (2.54 g.) and recrystallised from aqueous acetone to give the spirandicarboxylic acid (X) as prisms, m. p. 338—340°, subliming rapidly from 320°, m. p. (sealed tube) 350—352° (decomp.) (Barnes *et al.* give m. p. 340—346°), λ_{max} 278, 286 $m\mu$ ($\log \epsilon$ 3.40, 3.29), ν_{max} 1692 cm^{-1} (aromatic CO_2H). For analysis a sample was sublimed at 240°/0.1 mm. (Found: C, 76.3; H, 6.9. $C_{23}H_{24}O_4$ requires C, 75.8; H, 6.6%).

6,6'-Diamino-3,3,3',3'-tetramethyl-1,1'-spirobi-indane (XI).—The acid (X) (2.39 g.) in sulphuric acid (d 1.84; 100 ml.) was treated with sodium azide (3.3 g., 3.5 mol.) in small portions during 45 min. at 40—45° with stirring. Foaming occurred and stirring was continued at 50—55° for 2 hr., after which the solution was left overnight. The mixture was poured over ice (1 kg.) and then made alkaline with 40% aqueous sodium hydroxide and ice. Precipitated solid (1.90 g.), m. p. 200—205°, was recrystallised from benzene-light petroleum, to give 6,6'-diamino-3,3,3',3'-tetramethyl-1,1'-spirobi-indane (XI) as very pale brown prisms, (1.48 g.), m. p. 205—210°. For analysis a sample was sublimed at 200°/0.1 mm., forming triangular plates, m. p. 212°, λ_{max} 297 $m\mu$ (ϵ 3.80), ν_{max} 3436, 3350 cm^{-1} (aromatic NH stretch) (Found: C, 82.4; H, 8.3; N, 9.4. $C_{21}H_{26}N_2$ requires C, 82.3; H, 8.55; N, 9.1%).

3,3,3',3'-Tetramethyl-1,1'-spirobi-indane-6,6'-diol (XII).—The diamine (XI) (965 mg.) was suspended in concentrated hydrochloric acid (45 ml.) and water (25 ml.) and stirred with cooling in ice. Sodium nitrite (655 mg., 1.5 mol.) in water (2 ml.) was added during 10 min. at 3°, then stirring was continued at 5° for 1 hr. The diazonium solution was poured rapidly into 20% sulphuric acid (500 ml.) at 60° and heated with stirring at 60° for 20 min. Pale brown solid separated and, after cooling, was collected and dried (962 mg.; m. p. 170—175°).

⁸ See Baker and Williams, *J.*, 1959, 1295, for collected references.

⁹ Barnes and Buckwalter, *J. Amer. Chem. Soc.*, 1951, **73**, 3858.

Chromatography on deactivated alumina in benzene and elution with benzene-chloroform-methanol (25 : 75 : 5) gave a crude product (565 mg.) which with acetic anhydride (5 ml.) and potassium acetate (500 mg.) gave the diacetyl derivative, m. p. 155—160°. This was crystallised once from ethanol, hydrolysed by boiling aqueous-methanolic 2*N*-sodium hydroxide (20 ml.), and poured into dilute hydrochloric acid. Precipitated solid was collected, passed on to an alumina column in benzene, and eluted with chloroform-benzene-methanol (75 : 25 : 5). Crystallisation from benzene-light petroleum (b. p. 60—80°) gave 3,3,3',3'-tetramethyl-1,1'-spirobi-indane-6,6'-diol (XII) as needles (251 mg.), m. p. and mixed m. p. 214°. Samples were sublimed at 200°/0.1 mm. for comparison of infrared spectra which were identical.

4-Methyl-4-phenylpentan-2-one (I).—This ketone was prepared essentially as described by Barnes *et al.*² although isolation of the hydrocarbon C₂₁H₂₄ from the distillation residue could not be achieved.

3,3,3',3'-Tetramethyl-1,1'-spirobi-indane (VIII).—(a) *By acid rearrangement of ketone (I)*. The ketone (I) (30 g.) was heated under reflux with concentrated sulphuric acid (180 ml.) and water (180 ml.) for 8 hr. The product was extracted into benzene, washed with water and saturated sodium hydrogen carbonate solution, and dried (MgSO₄). Distillation gave a fraction (b. p. 130—150°/0.4 mm.) which solidified (3.0 g.; m. p. 124°). Three crystallisations from ethanol gave 3,3,3',3'-tetramethyl-1,1'-spirobi-indane (VIII) as needles (1.9 g., 6%), m. p. 133—134° (Found: C, 91.6; H, 8.3. C₂₁H₂₄ requires C, 91.3; H, 8.7%) (Barnes *et al.* give m. p. 133—134°, λ_{max} 267—274 mμ (ε 3.30, 3.24), δ — 0.02 p.p.m., double peak (CH₃ groups), — 0.88 p.p.m. (CH₂ groups).

(b) *By decarboxylation*. The dicarboxylic acid (X) (500 mg.) and copper chromite¹⁰ (500 mg.) in quinoline (12 ml.; redistilled from copper chromite) were heated under reflux for 90 min. The cooled product was extracted with ether (3 × 20 ml.) which was filtered, washed several times with 50% hydrochloric acid (v/v) and then aqueous sodium hydrogen carbonate, and dried (MgSO₄). Evaporation gave crystals that, recrystallised three times from ethanol, afforded 3,3,3',3'-tetramethyl-1,1'-spirobi-indane (VIII) (125 mg.), needles, m. p. 133° alone or mixed with a sample prepared as under (a) and showing an identical infrared spectrum. Comparison of the foregoing samples with the supposed "tetrahydroindenoindene" (IV), m. p. 133—134°, prepared from α-methylstyrene and supplied by Dr. Adams also showed no depression of m. p. and identical infrared spectra.

We are grateful to Dr. Adams for samples, to Dr. H. E. Hallam and Mr. D. Jones for infrared spectra, and Mr. J. H. Beynon and Dr. J. K. Beconsall, Imperial Chemical Industries Limited (Dyestuffs Division), for the nuclear magnetic resonance spectra.

DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE OF SWANSEA,
SINGLETON PARK, SWANSEA.

[Received, June 20th, 1961.]

¹⁰ Adkins and Connor, *J. Amer. Chem. Soc.*, 1931, **53**, 1091.