627. *Hydrogen Transfer. Part XV.*[1] *The Synthesis and Cyclodehydrogenation of 2-Diphenylmethylstyrene.*

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A synthesis of 2-diphenylmethylstyrene from *o*-diphenylmethylbenzoic acid is described. The styrene is shown to undergo cyclodehydrogenation to 1,1-diphenylindene when treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. 1,2-Diphenylindene has also been prepared by dehydration of 3,3-diphenylindan-1-ol followed by dehydrogenation.

In Part XIV [1] the formation of lactones and ethers from acids and alcohols by cyclodehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was described. We next proceeded to determine whether the reaction could be extended to the formation of carbocyclic structures. Mechanistically such a reaction would resemble acid-catalysed cyclisation of alkadiene systems, of which there are numerous examples. These reactions proceed by electrophilic attack by a carbonium ion on a double bond, the carbonium ion being produced by protonation of one of the double bonds. In a quinone dehydrogenation the carbonium ion could be generated by hydride-ion abstraction. Cyclodehydrogenation

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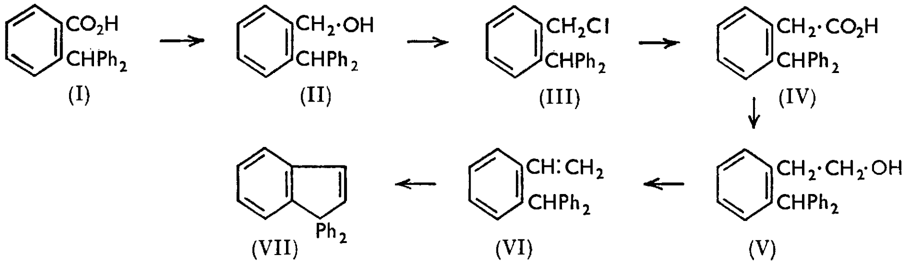
[1] Part XIV, Creighton and Jackman, preceding paper.

therefore requires a CH group suitably activated for hydride-ion abstraction and in proximity to an ethylenic double bond. These conditions are fulfilled by 2-diphenylmethylstyrene in which the triphenylmethane structure provides a suitably activated hydrogen atom.



2-Diphenylmethylstyrene (VI) was synthesised in seven stages from phthalic anhydride in an overall yield of $12\frac{1}{2}\%$. Phthalic anhydride was converted, *via* 3,3-diphenylphthalide, into 2-diphenylmethylbenzoic acid (I) by Brisson's method [2] which was converted into the chloride (III), all in good yield. The step, (III) ⟶ (IV), proved more troublesome. Attempted replacement of the halogen by cyanide gave only low yields of the amide which could be hydrolysed to the desired acid. However, carboxylation of the Grignard reagent gave the acid in 55% yield together with a mixture of neutral compounds (mainly *o*-methyltriphenylmethane). (Benzylic Grignard reagents usually give rearranged product with aldehydes and ketones but sometimes behave normally on carboxylation.[3]) Reduction of the acid (IV) with lithium aluminium hydride afforded 2-diphenylmethylphenethyl alcohol (V), which was dehydrated at 260° by solid potassium hydroxide to the styrene (VI) in 55% yield.

2-Diphenylmethylstyrene reacted slowly (3 days) with dichlorodicyanobenzoquinone in benzene at 80°. The hydrocarbon product was a mixture from which 1,1-diphenylindene [4] was separated by chromatography and crystallisation in 45% yield. A specimen for comparison was prepared by reduction of 3,3-diphenylindan-1-one with lithium aluminium hydride and acid-catalysed dehydration of the resulting indan-1-ol.

The reactivity of the styrene appears to be less than of the corresponding acid (I) studied in the preceding paper [1] and, since a carboxyl group is more strongly deactivating than a vinyl group, it must be concluded that here the vinyl group provides less driving force as a neighbouring group than does the carboxyl group. Models of the *o*-vinyltriphenylmethyl cation show that it is difficult to orientate the vinyl group such that its π-molecular orbital is correctly directed for effective overlap with the $2p\pi$-orbital. It is of course possible that the cyclisation only occurs under the polarising influence of a fully formed carbonium ion.

EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Laboratory (Miss J. Cuckney) of this Department.

3,3-*Diphenylphthalide*.—Recrystallised phthalic anhydride (74 g.) was added to a stirred ice-cold solution of phenylmagnesium bromide (165 g. of bromobenzene; 25·2 g. of magnesium) in ether (500 ml.). After 1 hr. benzene (500 ml.) was added and the mixture was refluxed for 3 hr. The solution was cooled and ice-cold concentrated hydrochloric acid (200 ml.) was added. The organic layer was washed with acid, alkali, and water, dried (Na_2SO_4), and evaporated. Hot methanol (300 ml.) was added. On cooling, the product (108 g.) separated and was collected. Concentration of the mother-liquors gave a further quantity (8 g.) of product. The combined crops were added to a solution of sodium hydroxide (120 g.) in water (1200 ml.)

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[2] Brisson, *Ann. Chim.* (*France*), 1952, **7**, 311.

[3] Kharasch and Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, 1954, p. 1144.

[4] Gagnon, *Ann. Chim.* (*France*), 1929, **12**, 296.

and ethanol (240 ml.). The mixture was distilled until the temperature of the solution reached 99°: part of the material dissolved, leaving an oil which solidified as ethanol was removed. The insoluble component was removed and crystallised from benzene, to yield *o*-dibenzoylbenzene as prisms (27·9 g., 19·5%), m. p. 147—148° (lit.,[2] m. p. 148°). The alkaline solution could be used directly for reduction to 2-diphenylmethylbenzoic acid. The phthalide (86 g., 61%) was recovered from the solution when it was acidified to Congo Red. The crude material had m. p. 115—117° (lit.,[2] m. p. 116—117°). Several recrystallisations raised the m. p. to 121—122°.

2-*Diphenylmethylbenzoic Acid*.—The alkaline solution prepared from the phthalide was refluxed with zinc dust (1 g. per g.) for 3—4 hr. The solution was filtered and acidified. The precipitated acid was removed, washed and dried. The crude product (92·5%), m. p. 163—165°, crystallised from carbon tetrachloride to give the pure acid, m. p. 166—166·5° (lit.,[2] m. p. 160—161°).

2-*Diphenylmethylbenzyl Alcohol* (II).—A solution of 2-diphenylmethylbenzoic acid (11·5 g.) in dry ether (250 ml.) was slowly added to a stirred solution of lithium aluminium hydride (1·5 g.) in ether (100 ml.). The mixture was refluxed for 1 hr., cooled, and decomposed with saturated sodium chloride solution (20 ml.).[5] The mixture was filtered and the residue washed with ether. The combined filtrate and washings were evaporated. The residue recrystallised from light petroleum (b. p. 80—100°) (yield, 10·1 g., 92%), to yield the *alcohol* as needles, m. p. 112—113° (Found: C, 87·9; H, 6·9. $C_{20}H_{18}O$ requires C, 87·55; H, 6·6%).

2-*Diphenylmethylbenzyl Chloride* (III).—A solution of the alcohol (21·9 g.) in carbon tetrachloride (125 ml.) containing pyridine (0·1 ml.) was slowly added to a refluxing solution of thionyl chloride (14·8 g.) in carbon tetrachloride (25 ml.), then the solution was refluxed for 2 hr., cooled, washed with ice-water, 2N-sodium carbonate, and water, dried ($CaCl_2$), and evaporated. The residue recrystallised from methanol (100 ml.) to give 2-*diphenylmethylbenzyl chloride* (22·3 g.), prisms, m. p. 115—116° (Found: C, 82·1; H, 6·05; Cl, 12·1. $C_{20}H_{17}Cl$ requires C, 82·0; H, 5·85; Cl, 12·1%). The chloride could be hydrolysed by N-aqueous-ethanolic (1 : 1) sodium hydroxide to the corresponding alcohol.

2-*Diphenylmethylphenylacetamide*.—The above chloride (2·9 g.), sodium cyanide (4·9 g.), and sodium iodide (1·0 g.) were dissolved in aqueous ethanol (1 : 3; 80 ml.), and the solution was refluxed for 46 hr. Most of the ethanol was removed on a steam-bath and the mixture was extracted with ether. The ethereal layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was recrystallised from light petroleum (yield, 0·7 g., 25%) and then from methanol, giving pure 2-*diphenylmethylacetamide*, m. p. 157—158° (Found: C, 83·7; H, 6·3; N, 4·6. $C_{21}H_{19}NO$ requires C, 83·2; H, 6·5; N, 4·5%).

2-*Diphenylmethylphenylacetic Acid* (IV).—(*a*) A solution of 2-diphenylmethylbenzyl chloride (73·1 g.) and methyl iodide (1 ml.) in ether (1·5 l.) was slowly (2 hr.) added with stirring to magnesium turnings (9·0 g.) under nitrogen. Reaction commenced immediately and the solution was kept at the b. p. during the addition and for a further 1 hr. The solution was cooled to 0° and poured on carbon dioxide (500 g.). After evaporation the mixture was washed with concentrated hydrochloric acid (3 × 100 ml.), water (100 ml.), 2N-sodium hydroxide (8 × 50 ml.), and again water (100 ml.). The alkaline extracts were combined and acidified to Congo Red. The precipitate was collected, washed with water, dried, and crystallised from benzene (yield, 141·6 g.; 57%) and then from ethanol, affording 2-*diphenylmethylphenylacetic acid*, m. p. 210—211° (Found: C, 83·35; H, 6·3. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%).

The ethereal solution was dried (Na_2SO_4) and the solvent removed. The residue recrystallised from ethanol and from light petroleum (b. p. 60—80°), yielding, in addition to some unchanged chloride and the corresponding alcohol, *o*-methyltriphenylmethane (20 g.), m. p. 80—82° (lit.,[6] m. p. 82—83°). In another experiment there was isolated a small quantity of a substance, m. p. 168—170°.

(*b*) A solution of 2-diphenylmethylphenylacetamide (0·2 g.) and sodium hydroxide (1·0 g.) in ethylene glycol was heated for 3 hr. The mixture was cooled, acidified, and filtered. The dried residue had m. p. 206—212° and m. p. 208—210° with the acid from the Grignard reaction.

2-*Diphenylmethylphenethyl Alcohol* (V).—A solution of 2-diphenylmethylphenylacetic acid (45·3 g.) in tetrahydrofuran (300 ml.) was added in 1 hr. to a stirred solution of lithium aluminium hydride (7·0 g.) in tetrahydrofuran (200 ml.). The mixture was refluxed for an

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[5] Brown and van Gulick, *J. Amer. Chem. Soc.*, 1955, **77**, 1083.

[6] Bistrzycki and Gyr, *Ber.*, 1904, **37**, 1245.

additional 30 min., cooled, and decomposed with saturated sodium chloride solution (*ca.* 100 ml.). The mixture was filtered, the solvent removed, and the residue crystallised from light petroleum to give 2-*diphenylmethylphenethyl alcohol* as cubes (37·1 g., 86%), m. p. 77—78° (Found: C, 87·2; H, 7·4. $C_{21}H_{20}O$ requires C, 87·5; H, 7·0%).

2-*Diphenylmethylstyrene* (VI).—The alcohol (V) (10·9 g.) and solid sodium hydroxide (25 g.) were heated at 260° under a vacuum for ½ hr. After cooling, the mixture was extracted with hot benzene. Removal of the benzene afforded an oil which crystallised from methanol to yield 2-*diphenylmethylstyrene* as needles (6·0 g., 55%), m. p. 76—77° (Found: C, 93·05; H, 6·9. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%). This gave a *dibromide*, needles (from ethanol), m. p. 154—155° [Found: C, 58·7; H, 4·5; Br, 36·8%; *M* (Rast), 426. $C_{21}H_{18}Br_2$ requires C, 58·6; H, 4·2; Br, 37·2%; *M*, 430].

3,3-*Diphenylindan*-1-*ol*.—A solution of 3,3-diphenylindan-1-one (2·0 g.) in dry ether (70 ml.) was added to one of lithium aluminium hydride (1·3 g.) in ether (10 ml.). The mixture was refluxed for 3 hr. and decomposed with water (1 ml.). The ethereal solution was decanted and the residue washed with ether (20 ml.). The solution and washings were combined and evaporated to dryness. Crystallisation of the residue from benzene (10 ml.)–light petroleum (18 ml.; b. p. 60—80°) yielded 3,3-*diphenylindan*-1-*ol* as needles (1·82 g., 90%), m. p. 131—132° (Found: C, 88·0; H, 6·0. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%).

1,1-*Diphenylindene* (VII).—A solution of 3,3-diphenylindan-1-ol (500 mg.) and toluene-*p*-sulphonic acid (48 mg.) in acetic acid (5 ml.) was refluxed for ½ hr. and then poured into water (200 ml.). The precipitate was collected, dried, and crystallised from ethanol (3 ml.), to give 3,3-diphenylindene (325 mg.), m. p. 91—92° (lit.,[4] m. p. 91—92°).

Cyclodehydrogenation of 2-*Diphenylmethylstyrene*.—2-Diphenylmethylstyrene (2·70 g.), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2·27 g.), and benzene (40 ml.) were heated at 78° for 65 hr. The mixture was cooled and the quinol (1·6 g.) was removed. The filtrate was concentrated and then diluted with light petroleum (b. p. 40—60°). The gummy solid precipitate (1·7 g.) was separated. The filtrate was chromatographed over alumina and eluted with light petroleum (b. p. 60—80°). The evaporated eluate crystallised from methanol, to yield 1,1-*diphenylindene* (1·2 g., 45%), m. p. and mixed m. p. 91—92° (Found: C, 93·85; H, 6·2. Calc. for $C_{21}H_{16}$: C, 94·0; H, 6·0%).

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