17. *The Catalytic Hydrogenation of Diphenyl Triketone. Part I.*

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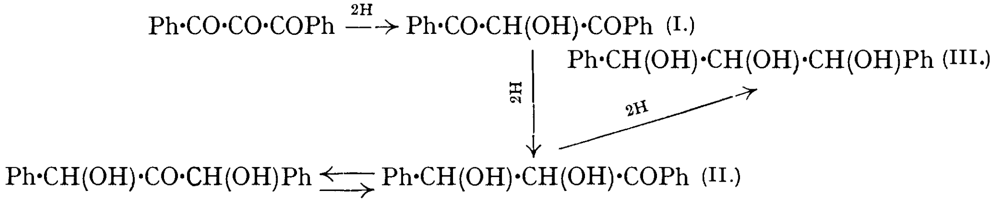
The catalytic hydrogenation of benzil and its derivatives has been shown to be a simple and effective method of obtaining the numerous reduction products of these 1 : 2-diketones (Buck and Jenkins, *J. Amer. Chem. Soc.*, 1929, **51**, 2163; Buck, Jenkins, and Bigelow, *ibid.*, 1930, **52**, 4495, 5198). It seemed, therefore, that the method might well be applied with success to the more complex case of a 1 : 2 : 3-triketone, and this paper describes the first steps in the catalytic reduction of the simplest possible aromatic triketone, $C_6H_5\cdot CO\cdot CO\cdot CO\cdot C_6H_5$. The theoretical possibilities are relatively numerous owing to isomerisation, but the first changes may be summarised in the following scheme :



$$\begin{tikzcd}
\mathrm{Ph\cdot CO\cdot CO\cdot COPh} \arrow[r, "2H"] & \mathrm{Ph\cdot CO\cdot CH(OH)\cdot COPh}\ \mathrm{(I.)} \arrow[d, "2H"'] & \\
& & \mathrm{Ph\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)Ph}\ \mathrm{(III.)} \\
\mathrm{Ph\cdot CH(OH)\cdot CO\cdot CH(OH)Ph} \arrow[r, shift left, leftarrow] \arrow[r, shift right] & \mathrm{Ph\cdot CH(OH)\cdot CH(OH)\cdot COPh}\ \mathrm{(II.)} \arrow[ur, "2H"] &
\end{tikzcd}$$

The reactions were carried out at room temperature in the well-known Adams apparatus as described by Buck and Jenkins (*loc. cit.*), the usual platinum–platinum oxide catalyst being used. Pure benzene was employed as solvent and the reduction occurred readily under a pressure of 2—5 atmospheres. The character and quantity of the catalyst, however, had a marked influence upon the speed of reaction and, by adjusting the amount used, the triketone could be made to take up 1, 2, or 3 moles of hydrogen at will.

When allowed to take up 1 mole of hydrogen, the triketone yielded *dibenzoylcarbinol* (I). On treatment with acetyl chloride the carbinol was converted into the acetyl derivative described by Neufville and Pechmann (*Ber.*, 1890, **23**, 3375).

Dibenzoylcarbinol readily underwent further hydrogenation. Rapid reduction led without any break in the time–pressure curve to the absorption of 2 moles of hydrogen, with formation of *αγ-diphenylglycerol* (III). On employing a smaller amount of catalyst, a break in the hydrogenation became evident after the absorption of 1 mole, at which point crystals of diphenylglycerol began to separate. A point of interest lies in the structural resemblance between this compound and trihydroxyglutaric acid, which exists in two *meso-* and two optically active forms. It is hoped to deal more fully with this problem in a later communication.

In the hydrogenation of either dibenzoylcarbinol or diphenyl triketone with a suitable amount of catalyst, a break in the time–pressure curve was noted at the stage corresponding to the formation of the intermediate *dihydroxy*-compound (II). When the absorption was interrupted at this point, an oil was obtained, purifiable with some loss to give colourless needles which exhibited small variations in melting point according to the rate of heating. This compound readily underwent further hydrogenation to form diphenylglycerol in good yield, but acetylation gave rise only to an uncrystallisable oil. The variable melting point and difficulty of isolating any definite acetyl derivative suggest that the dihydroxy-compound readily isomerises on heating or in solution.

EXPERIMENTAL.

The platinum catalyst was prepared by the method of Adams (" Organic Syntheses," 1928, **8**, 92), and the diphenyl triketone, m. p. 69—70°, by the method of Bigelow and Hauslick (*op. cit.*, 1933, **13**, 38). A preliminary calibration of the apparatus was carried out for the absorption of one and two molecular proportions of hydrogen, using 0·01 mole of pure benzoin and benzil respectively as standards. Complete hydrogenation to hydrobenzoin corresponded in the first case to a fall of 16 lb./sq. in. in pressure and in the second case to 32 lb./sq. in. All hydrogenations were carried out under pressures of 2—3 atmospheres, except in the direct reduction of the triketone to diphenylglycerol, where an initial pressure of 5 atmospheres was employed.

Dibenzoylcarbinol from Diphenyl Triketone.—A solution of 2·38 g. (0·01 mole) of diphenyl triketone in 50 c.c. of pure benzene containing 0·05 g. of the catalyst in suspension was hydrogenated at 15° until after 1 hour the pressure had fallen 16 lb., corresponding to the absorption of 0·01 mole of hydrogen. The catalyst was then removed, and the volume of the filtrate reduced to 20 c.c. by evaporation under diminished pressure at room temperature. Colourless needles separated (1·45 g.), m. p. 100—104°. Recrystallisation from 150 c.c. of ligroin (b. p. 80—100°) gave 1·15 g. of long needles, which melted at 110—111·5° to a yellow liquid, the m. p. being unaffected by further crystallisation from alcohol (Found : C, 75·0; H, 5·1; *M*, by the Menzies–Wright method, 238. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%; *M*, 240). The colourless solid turns yellow at 100°, and if maintained at 106—107° it melts, resolidifies, and again melts to a deep yellow liquid, the complete series of changes occupying about 15 minutes. The final equilibrium mixture (of isomerides ?) thus obtained solidifies on cooling and then melts at 96—98°.

Dibenzoylcarbinol dissolves readily in alcohol and ether, moderately readily in benzene, and more sparingly in ligroin, develops a light orange coloration when shaken in benzene solution with sulphuric acid (the triketone develops a blue colour), and gives no coloration with alcoholic ferric chloride.

The carbinol (1 g.), on treatment with 20 c.c. of acetyl chloride at 50° for ½ hour, gave the acetyl derivative (92% yield), separating from methyl alcohol in rhombic plates, m. p. 93° alone or admixed with an authentic specimen prepared by the method of Neufville and Pechmann (*loc. cit.*).

αγ-Diphenylglycerol from Dibenzoylcarbinol.—The carbinol (2·40 g., 0·01 mole) in 50 c.c. of benzene was reduced at room temperature by 0·10 g. of catalyst, until after 1 hour 2 mols. of hydrogen had been absorbed. No further hydrogenation could be effected by aeration of the catalyst or by addition of fresh catalyst. The syrup obtained by filtering the hot solution from the catalyst and evaporating the solvent crystallised when covered with light petroleum; m. p. 80—82° (yield, 97% of the theoretical). The crude product dissolved readily in hot benzene (45 c.c.) to a highly refracting solution, which deposited colourless needles or prisms. After being dried for several hours at 60°, or maintained in a vacuum over calcium chloride for several days, these gave the anhydrous compound, m. p. 84·5—85° [Found : C, 73·8; H, 6·5; *M*, in boiling benzene ($c = 0·4, 0·64$), 244, 246. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·5%; *M*, 244]. When the finely divided compound was kept over-night in a moist atmosphere, it was converted quantitatively into the *monohydrate*, m. p. 97—99°, also obtainable in rhombic plates by crystallising the anhydrous form from aqueous (1 : 1) alcohol (Found : C, 68·8; H, 6·9. $C_{15}H_{16}O_3,H_2O$ requires C, 68·7; H, 6·9%). *Diphenylglycerol* exhibits a very strong tendency to undergo hydration. If the anhydrous compound is crystallised from a small amount of dry benzene without filtration, the solution deposits the pure anhydrous product. When small quantities of such a solution are filtered through filter-paper which has not been specially dried, the deposited crystals are of the hydrated form. In a desiccator over calcium chloride, complete dehydration requires about a fortnight, the m. p. of the product passing through a minimum value of 80—81°.

Diphenylglycerol has a sweet taste and is appreciably soluble in water. It dissolves readily in alcohol and ether, is moderately soluble in benzene and sparingly in light petroleum. A benzene solution shaken with concentrated sulphuric acid gives a characteristic bright red coloration. The solid compound dissolves in sulphuric acid to a brilliant purple solution.

Diphenylglycerol (1 g.) was boiled for 30 minutes with 20 c.c. of acetic anhydride. When the cooled solution was poured into water, 1·4 g. (93% yield) of the *triacetate* were deposited, m. p. 84—85°. The pure derivative separated from alcohol in plates, m. p. 85—86° (Found : C, 68·1; H, 5·8; CH_3·CO, 34·0. $C_{21}H_{22}O_6$ requires C, 68·1; H, 6·0; CH_3·CO, 35·0%). On admixture with diphenylglycerol the product melted at 67—70°. The triacetate on hydrolysis regenerated diphenylglycerol.

When the above hydrogenation was repeated with a smaller amount of catalyst (0·075 g.), a deposition of crystalline diphenylglycerol began as soon as 1 mol. of hydrogen had been absorbed. This deposit appeared to envelop and deactivate the catalyst, with the result that the absorption of the final molecular proportion of hydrogen occupied 3 hours.

Diphenyl triketone (2·38 g.) in 50 c.c. of benzene was converted into diphenylglycerol in one operation by using 0·15 g. of the catalyst and an initial pressure of 5 atmospheres. The first molecular proportion of hydrogen was absorbed in 30 minutes, and the second in 40 minutes. The third stage occupied 4 hours, apparently owing to the crystalline deposit carrying down part of the catalyst. An almost theoretical yield was obtained.

All the hydrogenations described in this paper may be carried out in glacial acetic acid or 95% alcohol as solvent : in the majority of cases the reaction is completed more rapidly than in benzene. For example, diphenyl triketone in alcohol was converted into diphenylglycerol (87% yield) in 2 hours, as compared with 4 or 5 hours for a benzene solution. The latter solvent is, however, more suitable for the final purification.

αβ-Dihydroxy-γ-keto-αγ-diphenylpropane or an Isomeride thereof.—Dibenzoylcarbinol (2·40 g.) was reduced as above, 0·05 g. of catalyst being used, until after 2 hours 0·01 mole of hydrogen had been absorbed. After filtration the pale yellow solution was seeded with diphenylglycerol and kept over-night; 0·3 g. of diphenylglycerol (hydrated form) was then deposited and removed. Evaporation of the solvent left a white solid (1·9 g.), m. p. 67—70°, which on being twice recrystallised from ligroin (b. p. 100—120°) gave colourless well-formed needles (0·6 g.), m. p. 87—89°. As in the case of dibenzoylcarbinol, fusion is accompanied by a colour change to yellow (Found : C, 74·2; H, 5·9. $C_{16}H_{14}O_3$ requires C, 74·4; H, 5·8%). The same product, m. p. 86—88°, was obtained by reducing 2·38 g. of diphenyl triketone, using 0·1 g. of catalyst and 50 c.c. of benzene, until 2 mols. of hydrogen had been absorbed.

The *dihydroxy*-compound strongly depresses the melting points of dibenzoylcarbinol and of diphenylglycerol. It dissolves in sulphuric acid to a clear yellow solution, which gradually turns red and develops a green fluorescence. An alcoholic solution gives no coloration with ferric chloride. The solubility in organic solvents is intermediate between that of the related carbinol and glycerol.

Hydrogenation of the dihydroxy-compound (1·21 g.) in benzene (30 c.c.) with 0·05 g. of catalyst converted it in 40 minutes into diphenylglycerol (1·0 g.). The latter was deposited from benzene in rhombic plates of the hydrated form, m. p. 97—98°.

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