24. *Some 2 : 2′-Derivatives of Diphenyl.*

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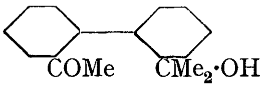
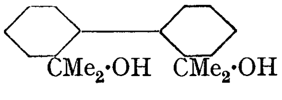
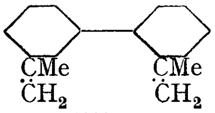
When diphenoyl chloride is allowed to react with excess of methylmagnesium iodide, two products are formed : *2-acetyl-2′-α-hydroxy*iso*propyldiphenyl* (I) and *2 : 2′-di-α-hydroxy*iso*propyldiphenyl* (II).



(I.)



(II.)



(III.)

Under similar conditions, methyl diphenate and 2 : 2′-diacetyldiphenyl react with the same Grignard reagent to give mainly the glycol (II) (cf. Schenk and Brauns, *Ber.*, 1915, **48**, 716; Tschitschibabin and Ssergejeff, *Ber.*, 1926, **59**, 654). The alcohol-ketone (I) reacts with excess of the Grignard reagent to give (II), but the yield is poor.

The glycol (II) undergoes dehydration with great readiness, and it was found that phosphorus tribromide, or this substance mixed with phosphorus pentabromide at temperatures up to 100°, or dry hydrogen chloride at 150°, gave no di-α-halogeno*iso*propyldiphenyl, but only 2 : 2'-*di-α-methylethenyldiphenyl* (III). 2 : 2'-Dihydroxybenzhydryldiphenyl (Tschitschibabin and Ssergejeff, *loc. cit.*) was found to be unaffected when heated in a current of dry hydrogen chloride at 200°.

2 : 2'-Diacetyldiphenyl would be expected to undergo smooth ωω'-dibromination. We find that carefully controlled interaction of the diketone with two molecular proportions of bromine in glacial acetic acid, in the absence or in the presence of anhydrous sodium acetate, gives only one substance, the constitution of which has not been investigated, but which appears to have the empirical formula $C_{24}H_{18}O_3Br_4$.

EXPERIMENTAL.

Action of Methylmagnesium Iodide on Diphenoyl Chloride.—The solid acid chloride (9 g.; 1 mol.) was gradually added to a decanted Grignard reagent prepared from 40 g. (8 mols.) of methyl iodide. When the initial vigorous reaction was over, the mixture was boiled for 3 hours, and then decomposed in the usual manner. The semi-crystalline residue (8 g.) obtained by removal of the ether was crystallised from light petroleum (b. p. 80—100°) and so separated into a more and a less soluble fraction. The former crystallised from light petroleum (b. p. 60—80°) in rectangular prisms (2 g.), m. p. 138—139°, and was 2 : 2'-*di-α-hydroxy*iso*propyldiphenyl* (Found: C, 80·0; H, 8·0. $C_{18}H_{22}O_2$ requires C, 79·95; H, 8·2%). The less soluble fraction crystallised from acetone–light petroleum (b. p. 60—80°) in needles (2 g.), m. p. 164—165°, and was 2-*acetyl-2'-α-hydroxy*iso*propyldiphenyl* (Found: C, 80·1; H, 6·9. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%). Addition of benzene to the original reaction mixture, with consequent increase in the boiling temperature, had the effect of slightly increasing the proportion of glycol formed.

Action of Methylmagnesium Iodide on 2 : 2'-Diacetyldiphenyl.—Diacetyldiphenyl (12 g.; 1 mol.) was gradually added to a decanted Grignard reagent prepared from 28 g. (4 mols.) of methyl iodide. The mixture was then boiled for 3 hours and decomposed in the usual manner. Evaporation of the dried ethereal extract gave 10 g. of almost pure 2 : 2'-di-α-hydroxy*iso*propyldiphenyl, and this, crystallised from light petroleum, became 8 g. of the pure glycol. 2 : 2'-Diacetyldiphenyl was conveniently prepared by the method of Zincke and Tropp (*Annalen*, 1908, **363**, 305); it melted at 94—95° and not at 84° as these authors state.

Action of Methylmagnesium Iodide on Methyl Diphenate.—The ester (9 g.; 1 mol.) was added rapidly to a Grignard reagent made from 50 g. (10 mols.) of methyl iodide, and the mixture boiled for 3 hours. After the usual subsequent procedure, 4 g. of pure glycol were obtained.

*Action of Methylmagnesium Iodide on 2-Acetyl-2'-α-hydroxy*iso*propyldiphenyl.*—The alcohol-ketone (1 mol.) was added to 4 mols. of Grignard reagent, and the mixture boiled for 6 hours. The yield of pure glycol was 10% of the theoretical.

Formation of 2 : 2'-Di-α-methylethenyldiphenyl.—(*a*) The glycol was added to 10 parts of phosphorus tribromide and the solution was heated at 90—100° for 15 minutes, cooled, and decomposed with ice. Extraction with ether, etc., led to a solid which, when crystallised from light petroleum (b. p. 40—60°), gave the 2 : 2'-*di-α-methylethenyldiphenyl* in prisms, m. p. 97—98° (yield, 85%) (Found: C, 92·15; H, 7·8. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Replacement of the phosphorus tribromide by a mixture of this with the pentabromide caused no change in the result of the reaction, and a mixture of the tribromide with chloroform was without action on the glycol.

(*b*) The glycol was heated at 150° in a current of dry hydrogen chloride for 6 hours. Almost pure hydrocarbon remained (Found: C, 92·15; H, 7·8%).

Bromination of 2 : 2'-Diacetyldiphenyl.—(*a*) A solution of bromine (4 atom.) in glacial acetic acid was added to one of diacetyldiphenyl (1 mol.) in the same solvent. On warming to 50—60°, decolorisation occurred, and after a further short warming the solution was cooled; crystals then separated. These were recrystallised from methyl alcohol and then from light petroleum (b. p. 80—100°), and gave hair-like needles, m. p. 134—135°, of a *substance* (Found: C, 42·8; H, 2·8; Br, 47·3. $C_{24}H_{18}O_3Br_4$ requires C, 42·8; H, 2·7; Br, 47·4%). (*b*) The process was repeated, only 90% of the proportion of bromine being used in presence of anhydrous sodium acetate. The same product was obtained.

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