CCCXXXIX.—*Some Acids derived from Diphenyl-4-aldehyde.*

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THIS communication deals with the preparation of diphenyl-4-aldehyde and its conversion into diphenyl-4-carboxylic acid, *diphenyl-4-acrylic* (by two methods) and *-4-propiolic acids*, and p-*phenylbenzylidenemalonic acid.*

From 4-methyldiphenyl, by side-chain chlorination and subsequent hydrolysis, Knowles (*J. Amer. Chem. Soc.*, 1921, **43**, 896) obtained a viscous oil, b. p. 121°, which he described as diphenyl-4-aldehyde, although this aldehyde had already been prepared as a solid, m. p. 57°, b. p. 184°/11 mm., by Rousset (*Bull. Soc. chim.*, 1897, **17**, 809) by hydrolysis of *p*-phenylbenzoylformanilide, and Gattermann (*Annalen*, 1906, **347**, 381) also had obtained it, m. p. 60—61°, from diphenyl by his method for the synthesis of aldehydes. The present work confirms Gattermann's results.

Oxidation of the aldehyde with alkaline potassium permanganate gave diphenyl-4-carboxylic acid. By heating the aldehyde with sodium acetate and acetic anhydride, diphenyl-4-acrylic acid was obtained together with p-*phenylbenzylidene diacetate.* The latter compound was also readily obtained by warming the aldehyde with acetic anhydride and a drop of sulphuric acid (compare Blanksma, *Chem. Weekblad*, 1909, **6**, 717). Addition of bromine to diphenyl-4-acrylic acid in acetic acid solution gave αβ-*dibromo*-β-4-*diphenylyl-propionic acid*, from which, by prolonged boiling with alcoholic potassium hydroxide, diphenyl-4-propiolic acid was obtained. Further, by the condensation of diphenyl-4-aldehyde with malonic acid, *p*-phenylbenzylidenemalonic acid was obtained, which when heated readily gave diphenyl-4-acrylic acid with the elimination of carbon dioxide.

Knowles obtained his methyldiphenyl by the action of solid benzenediazonium chloride on toluene in the presence of aluminium chloride, which is known to give rise to a mixture of 2- and 4-methyldiphenyls (Mohlau and Berger, *Ber.*, 1893, **26**, 1997; Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926 **48**, 1377); further, his " pure " 4-methyldiphenyl is described as an oily liquid, b. p. 264°, whereas it has been described elsewhere as a solid, m. p. 49—50° (*e.g.*, Kliegl and Huber, *Ber.*, 1920, **53**, 1655). Also, Bamberger (*Ber.*, 1895, **28**, 403), by coupling *p*-nitro*iso*diazobenzene hydroxide with toluene, and Kuhling (*Ber.*, 1895, **28**, 41; 1896, **29**, 165), by a somewhat similar reaction, obtained a 4-nitromethyldiphenyl, which, though first thought to be 4-nitro-4′-methyldiphenyl, was

later proved to be 4-nitro-2′-methyldiphenyl (Kliegl and Huber, *loc. cit.*, p. 1646), thus indicating that in these reactions union of the two benzene nuclei is effected mainly at the position ortho with respect to the methyl group. Consideration of these results therefore suggests that the products described by Knowles are probably mixtures of the 2- and 4-substituted compounds, or, if they are pure substances, the corresponding 2-substituted compounds, although both of these suggestions appear to be at variance with the low boiling point recorded by him for the aldehyde.

EXPERIMENTAL.

Diphenyl-4-aldehyde.—By the following modifications of Gattermann's method (*loc. cit.*) the yield of the aldehyde was increased to more than 70% of the yield calculated from the weight of diphenyl taken.

A stream of dry carbon monoxide and hydrogen chloride was passed for 8 hours into a well-stirred solution of 60 g. of diphenyl in 240 c.c. of dry benzene containing 90 g. of aluminium chloride and 12 g. of cuprous chloride at 35—40°. After standing overnight, the dark-coloured semi-solid product was poured on ice; a yellow oil then separated. The mixture was distilled with steam to remove the benzene and any unchanged diphenyl. The residue was extracted with ether, the extract washed with dilute hydrochloric acid and with water, and the ether evaporated. The semi-solid residue thus obtained was shaken with an excess of a saturated aqueous solution of sodium bisulphite, and after 12 hours the brown bisulphite compound was filtered off, washed with alcohol and with ether, and warmed with aqueous sodium carbonate. A brown oil separated which solidified on cooling; it was then dried on a porous plate and twice crystallised from light petroleum (b. p. 80—100°), diphenyl-4-aldehyde (52 g.) being obtained in very pale yellow plates, m. p. 60°. The 2 : 4-*dinitrophenylhydrazone* separated immediately when an alcoholic solution of 1 g. of the aldehyde was added to a solution of 1 g. of 2 : 4-dinitrophenylhydrazine in 2 c.c. of concentrated sulphuric acid and 15 c.c. of alcohol (compare Brady, this vol., p. 756); recrystallised from xylene, it formed brilliant scarlet plates, m. p. 239° (Found : N, 15·2. $C_{19}H_{14}O_4N_4$ requires N, 15·5%).

Diphenyl-4-carboxylic Acid.—Diphenyl-4-aldehyde (7 g.) was gently boiled for 3 hours with aqueous sodium carbonate with the gradual addition of an aqueous solution of potassium permanganate (8 g. in 150 c.c.). The liquid was saturated with sulphur dioxide, and the precipitated acid (6·5 g.) filtered off and recrystallised from alcohol (m. p. 224—225°).

Diphenyl-4-acrylic Acid.—Diphenyl-4-aldehyde (5 g.) was boiled under reflux for 8 hours with 3 g. of fused sodium acetate and 25 c.c. of acetic anhydride. [After a shorter period of heating (2 hours) the greater part of the aldehyde was recovered unchanged.] The mixture was poured into water and warmed with an excess of sodium carbonate. The brown insoluble material was filtered off and crystallised twice from toluene, *diphenyl-4-acrylic acid* being obtained in mats of very pale buff needles, m. p. 223—224° to a cloudy liquid, which finally became clear at 240° (Knowles, *loc. cit.*, gives m. p. 184°) (Found : C, 80·6, 80·4; H, 5·5, 5·6. $C_{15}H_{12}O_2$ requires C, 80·4; H, 5·4%). The acid was almost insoluble in sodium carbonate and sodium hydroxide solutions.

The toluene mother-liquors on evaporation deposited a second substance, which on recrystallisation from absolute alcohol gave p-*phenylbenzylidene diacetate* in pale buff plates, m. p. 131° (Found : C, 71·7; H, 5·8. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%). The diacetate was hydrolysed to diphenyl-4-aldehyde and acetic acid by warming with moderately concentrated sulphuric acid. *Ethyl diphenyl-4-acrylate*, obtained by refluxing 2 g. of the acid for 6 hours with absolute alcohol saturated with dry hydrogen chloride and then evaporating the alcohol, crystallised (twice) from light petroleum (b. p. 80—100°) in very pale yellow prisms, m. p. 87° (Found : C, 80·85; H, 6·2. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·35%).

Action of Bromine on Diphenyl-4-acrylic Acid.—4 G. of the acid were dissolved in approximately 250 c.c. of glacial acetic acid, and a solution of 2·9 g. of bromine in 20 c.c. of the same solvent added. After 48 hours, the solution was diluted with water until, after further standing, a white solid gradually settled, which was filtered off and dried. Recrystallisation from light petroleum (b. p. 80—100°), to which a small quantity of absolute alcohol had been added, gave small white plates of αβ-*dibromo*-β-4-*diphenylylpropionic acid* (5 g.), m. p. 196—197° (decomp.) (Found : Br, 41·9. $C_{15}H_{12}O_2Br_2$ requires Br, 41·7%). The acid, esterified as described above, gave the *ethyl* ester, which crystallised from absolute alcohol in small white needles, m. p. 123° (Found : Br, 39·2. $C_{17}H_{16}O_2Br_2$ requires Br, 38·8%).

Action of Alcoholic Potassium Hydroxide on αβ-Dibromo-β-4-diphenylylpropionic Acid.—Solutions of 2·5 g. of the dibromo-acid and of 2 g. of potassium hydroxide in alcohol were mixed (immediate white precipitate), boiled under reflux for 6 hours, and poured into water. After evaporation of most of the alcohol, the clear alkaline solution was acidified; a white flocculent precipitate then separated, which was dried and crystallised from light petroleum (b. p. 40—60°)–chloroform, pale yellow, microscopic crystals, m. p. 158—

165°, being obtained which still contained bromine. This product, which appeared to consist mainly of α-bromodiphenyl-4-acrylic acid (Found : C, 63·6; H, 4·5. Calc. for $C_{15}H_{11}O_2Br$: C, 59·4; H, 3·6%), was refluxed for 5 hours with alcoholic potassium hydroxide and subsequently treated as before. Recrystallisation of the product twice from light petroleum (b. p. 40—60°)–chloroform gave *diphenyl-4-propiolic acid* in small, pale yellow prisms, m. p. 175—176° (Knowles, *loc cit.*, gives m. p. 147°) (Found : C, 81·0; H, 4·8. $C_{15}H_{10}O_2$ requires C, 81·1; H, 4·5%). The bromine was not completely removed even by this prolonged treatment with alcoholic potassium hydroxide, for the first small batch of crystals obtained gave low results for carbon (Found : C, 79·2; H, 4·3%). Unlike diphenyl-4-acrylic acid, diphenyl-4-propiolic acid is readily soluble in aqueous alkali.

p-*Phenylbenzylidenemalonic Acid.*—3 G. of diphenyl-4-aldehyde, 1·8 g. of malonic acid, and 2 c.c. of glacial acetic acid were heated on the water-bath for 1½ hours. On cooling, the product, which solidified, was filtered off and washed with chloroform. Recrystallisation from either aqueous alcohol or aqueous acetic acid gave p-*phenylbenzylidenemalonic acid* in very pale yellow prisms, m. p. 215° (decomp.) (Found : C, 71·5; H, 4·7. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). The acid was readily soluble in alkalis, alcohol and acetic acid, but only sparingly soluble in light petroleum, toluene and chloroform. If the period of heating in the above condensation was extended to 12 hours on the steam-bath, and the product digested with hot toluene and filtered, a large proportion of diphenyl-4-acrylic acid separated. When *p*-phenylbenzylidenemalonic acid was heated at 215—220° for a short time, rapid evolution of carbon dioxide took place : the product, which solidified on cooling, was recrystallised from toluene, and diphenyl-4-acrylic acid obtained (m. p. and mixed m. p. 223—224°), identical with that synthesised by the Perkin reaction.

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