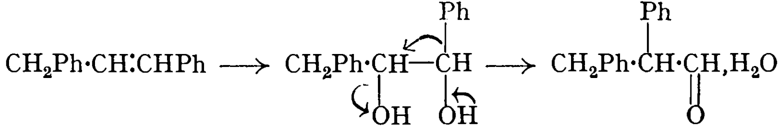
121. *αβ-Diphenylpropaldehyde.*

By Harold Burton and C. W. Shoppee.

αβ-Diphenylpropaldehyde has been described by Stoermer, Thier, and Laage (*Ber.*, 1925, **58**, 2607) as the monohydrate, a crystalline solid, m. p. 116°, possessing reducing properties, and characterised by a semicarbazone, m. p. 189° (decomp.). They obtained the substance by oxidation of αγ-diphenylpropene (I) with potassium permanganate in acetone solution in the presence of 2*N*-sulphuric acid, an observation which was interpreted by the suggestion that the intermediate glycol (II) underwent a pinacolic change to give the aldehyde hydrate (III) :



$$\underset{\text{(I.)}}{CH_2Ph\cdot CH{:}CHPh} \longrightarrow \underset{\text{(II.)}}{CH_2Ph\cdot \underset{OH}{CH}-\overset{Ph}{\underset{OH}{CH}}} \longrightarrow \underset{\text{(III.)}}{CH_2Ph\cdot\overset{Ph}{CH}\cdot\underset{O}{\overset{\|}{CH}},H_2O}$$

(I.) (II.) (III.)

It is recorded, however, that the substance by oxidation with ammoniacal silver nitrate, in spite of the ready production of silver, failed to yield the expected αβ-diphenylpropionic acid, m. p. 96°.

After several unsuccessful attempts, using various methods, we eventually obtained the aldehyde from αβ-*diphenylpropanilide* (IV) by reduction of the corresponding iminochloride (V) with stannous chloride and hydrolysis of the resulting aldimine (Sonn and Müller, *Ber.*, 1919, **52**, 1927). αβ-*Diphenylpropaldehyde* (VI) is a faintly yellow oil, b. p. 170°/11 mm., which crystallises after some weeks, and on recrystallisation forms colourless plates, m. p. 54°. It is oxidised by silver oxide to αβ-diphenylpropionic acid, and is characterised by a *semicarbazone*, m. p. 125°. It gives two (presumably stereoisomeric) 2 : 4-*dinitrophenylhydrazones*, m. p. 148—152° and 199°; the lower-melting form is obtained from the freshly distilled liquid aldehyde, and, since the m. p. is not sharp and tends to rise

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* A question of terminology arises here. From considerations based upon the transition-state method some authors have concluded that the "collision" factor is greater in solution than in the gas. By collision factor they have meant the temperature-independent factor of the Arrhenius equation, *i.e.*, our *PZ*, so their statement might refer either to *Z* or to *P*.

by repeated crystallisation, may contain some of the higher-melting form, which is obtained from the crystalline aldehyde. The aldehyde condenses readily with malonic acid in pyridine–piperidine to furnish a good yield of *γδ-diphenyl-Δ^α-pentenoic acid*, m. p. 89°.

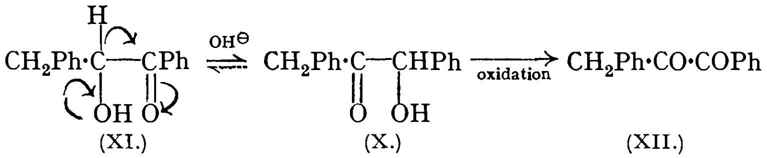
$$\underset{\text{(IV.)}}{CH_2Ph{\cdot}CHPh{\cdot}CO{\cdot}NHPh} \xrightarrow{PCl_5} \underset{\text{(V.)}}{CH_2Ph{\cdot}CHPh{\cdot}CCl{:}NPh} \xrightarrow[\text{hydrolysis}]{SnCl_2 \text{ and}} \underset{\text{(VI.)}}{CH_2Ph{\cdot}CHPh{\cdot}CHO}$$

Jarrousse (*Compt. rend.*, 1935, **201**, 676) records the production, from α-hydroxy-γ-keto-β-phenyl-α-benzylglutaric acid (VII) by oxidation with permanganate, of αγ-diketo-βδ-diphenylvaleric acid (VIII), which easily loses carbon dioxide to give a substance, m. p. 114°. This was considered to be β-keto-αγ-diphenylbutaldehyde (IX), but is actually identical with the product, m. p. 116°, of Stoermer, Thier, and Laage. It has been shown

(VII.) $CH_2Ph{\cdot}C(OH)(CO_2H){\cdot}CHPh{\cdot}CO{\cdot}CO_2H$ $CH_2Ph{\cdot}CO{\cdot}CHPh{\cdot}CO{\cdot}CO_2H$ (VIII.)

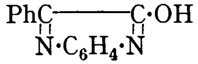
$CH_2Ph{\cdot}CO{\cdot}CHPh{\cdot}CHO$ (IX.)

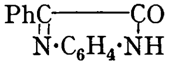
(Jarrousse, *Compt. rend.*, 1936, **203**, 259) to be phenylacetylphenylcarbinol (X) (previously prepared by Kohler and Timball, *J. Amer. Chem. Soc.*, 1934, **56**, 729), since it can be obtained from the isomeric benzoylbenzylcarbinol (XI) (McKenzie, Martin, and Rule, J., 1914, **105**, 1589) by pinacolic change in the presence of alkali (compare Shoppee, J., 1928, 1662), and by oxidation with Nessler's reagent it gives phenyl benzyl diketone (XII).


(XI.) (X.) (XII.)

We also have shown that the supposed aldehyde hydrate, m. p. 116°, is phenylacetylphenylcarbinol (X) by analysis of it and its derivatives, and have confirmed the production of phenyl benzyl diketone (XII) by oxidation with Nessler's reagent in dioxan, and by preparation of the quinoxaline (Widman, *Ber.*, 1916, **49**, 484) of (XII). Oxidation of (X) with Fehling's solution or phenylhydrazine acetate at 100° was unsatisfactory, and an earlier attempt with Nessler's reagent in acetone furnished a compound, $C_{18}H_{16}O_2$, which we consider to be the iso*propylidene* derivative, $CPh({:}CMe_2){\cdot}CO{\cdot}COPh$, since ozonolysis gave acetone, phenylglyoxylic acid, and benzoic acid.

Phenylglyoxylic acid condenses extremely easily with alcoholic *o*-phenylenediamine to give the *compound* (XIII or XIV); owing to its insolubility and sharp m. p. (247°), this substance should be valuable for the microchemical detection of phenylglyoxylic acid.

(XIII.)

$$\begin{array}{ccc} PhC & \text{---} & C{\cdot}OH \\ \| & & \| \\ N & {\cdot}C_6H_4{\cdot} & N \end{array}$$


$$\begin{array}{ccc} PhC & \text{---} & CO \\ \| & & | \\ N & {\cdot}C_6H_4{\cdot} & NH \end{array}$$
(XIV.)

EXPERIMENTAL.

αβ-Diphenylpropaldehyde could not be obtained by reduction (Adams's catalyst, various solvents, and pressures up to 100 atms.) of α-phenylcinnamaldehyde, m. p. 97—98° [2 : 4-*dinitrophenylhydrazone*, m. p. 240—241° (Found : C, 65·0; H, 4·0. $C_{21}H_{16}O_4N_4$ requires C, 64·9; H, 4·1%)]. αβ-Diphenylpropionitrile, prepared from benzyl chloride and sodiophenylacetonitrile in liquid ammonia or by the method of Janssen (*Annalen*, 1889, **250**, 129), b. p. 208—210°/23 mm., m. p. 58° after crystallisation from carbon tetrachloride–ligroin, could not be reduced by Stephen's method (J., 1925, **127**, 1874); it was smoothly and completely hydrolysed by 50% sulphuric acid (20 parts) and glacial acetic acid (15 parts) in 24 hours to αβ-diphenylpropionic acid, m. p. 96° after crystallisation from ligroin (b. p. 60—80°). The acid was converted by treatment with thionyl chloride (von Auwers and Auffenberg, *Ber.*, 1919, **52**, 108) into αβ-diphenylpropionyl chloride, which condensed with aniline (2 mols.) to give αβ-*diphenylpropanilide*, m. p. 166°, colourless needles from alcohol (Found : C, 83·8; H, 6·4. $C_{21}H_{19}ON$ requires C, 83·7; H, 6·3%); it is not necessary to distil the acid chloride, as the crude product remaining after removal of the excess of thionyl chloride may be used to form the anilide without disadvantage (compare Rupe and Kerkovius, *Ber.*, 1912, **45**, 1399). The anilide (25 g.) and phosphorus pentachloride (18 g.) were heated in tetrachloroethane for 1 hour at 140°; after removal of phosphorus oxychloride in a vacuum, the iminochloride, redissolved in tetrachloroethane, was added to 70 g. of anhydrous stannous chloride dissolved in ether (350 c.c.) saturated with hydrogen chloride at 0°. After standing overnight, the yellow crystalline stannichloride was filtered off, washed with ether, and hydrolysed with hot 2*N*-hydrochloric acid (500 c.c.); extraction with ether and subsequent drying (calcium chloride), evaporation, and distillation gave αβ-diphenylpropaldehyde as a pale yellow oil (9 g.), b. p. 170°/11 mm. (Found: C, 85·6; H, 6·8%). The aldehyde solidified after some weeks, and two recrystallisations from ligroin (b. p. 40—60°) gave colourless plates, m. p. 54° [Found: C, 85·6; H, 6·3; *M* (Rast), 199. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%; *M*, 210]. It was not readily volatile in steam and did not give a crystalline bisulphite compound. The *semicarbazone* formed colourless felted needles from dilute alcohol, m. p. 124—125° (Found: C, 72·0; H, 6·5; N, 15·5. $C_{16}H_{17}ON_3$ requires C, 71·9; H, 6·4; N, 15·7%); the same semicarbazone was produced both from the freshly distilled liquid aldehyde and from a crystalline specimen. The aldehyde appears to afford two orange-yellow 2 : 4-*dinitrophenylhydrazones*; by the procedure of Brady (J., 1931, 756) the freshly distilled liquid aldehyde gave one form, which separated from ethyl acetate–ethyl alcohol in yellow plates, m. p. 148—152° (Found: C, 64·6; H, 4·8; N, 13·6. $C_{21}H_{18}O_4N_4$ requires C, 64·6; H, 4·65; N, 14·4%); the m. p., however, rose on further crystallisation, *e.g.*, a specimen, m. p. 164°, gave C, 64·4; H, 5·0; N, 13·7%. The crystalline aldehyde gave another form, which crystallised from ethyl acetate–ethyl alcohol in orange-yellow plates, m. p. 199° (Found: C, 63·8; H, 4·5; N, 15·1%).

γδ-Diphenyl-Δ^{α}-pentenoic Acid.—αβ-Diphenylpropaldehyde (9·0 g.) was condensed with a 10% excess of malonic acid (4·5 g.) in 40 c.c. of pyridine containing 4 drops of piperidine, by standing overnight at 15°, followed by heating on the steam-bath for 3 hours. The mixture having been poured into ice–hydrochloric acid, extraction with ether, re-extraction with sodium carbonate solution, acidification of the alkaline extract, and ether extraction of the last-named gave a solution the oil obtained from which by drying (calcium chloride) and evaporation was kept in a vacuum over potash. By removal of traces of acetic acid, solidification of the product readily occurred; after crystallisation from ligroin containing a trace of ether, and subsequently from ligroin (b. p. 60—80°), *γδ-diphenyl-Δ^{α}-pentenoic acid* (8 g.) formed colourless prisms, m. p. 89°, which decolorised alkaline permanganate instantly [Found: C, 81·0; H, 6·4; *M* (Rast), 223, 224. $C_{17}H_{16}O_2$ requires C, 81·0; H, 6·4%; *M*, 252].

Phenylacetylphenylcarbinol (X).—Diphenylpropene, readily obtained in good yield from phenylacetaldehyde by the method of Stoermer, Thier, and Laage (*loc. cit.*), was oxidised with potassium permanganate in acetone in the presence of 2*N*-sulphuric acid at 5—10° according to the directions of these authors. Filtration, and evaporation of the acetone filtrate gave an oil which crystallised overnight; after being pressed on porous porcelain and crystallised from alcohol, the α-ketol formed colourless plates, m. p. 116° [Found: C, 79·8; H, 6·0; *M* (Rast), 206. Calc. for $C_{15}H_{14}O_2$: C, 79·7; H, 6·2%; *M*, 226]. It formed a *semicarbazone* (described incorrectly by Stoermer, Thier, and Laage), which separated from alcohol in plates, m. p. 191—192° (decomp.) (Found: C, 68·0; H, 6·15. $C_{16}H_{17}O_2N_3$ requires C, 67·8; H, 6·05%), and a 2 : 4-*dinitrophenylhydrazone*, which formed orange plates from ethyl acetate–alcohol, m. p. 164—164·5° (Found: C, 62·7; H, 4·8; N, 13·6. $C_{21}H_{18}O_5N_4$ requires C, 62·1; H, 4·5; N, 13·8%); the 3 : 5-dinitrobenzoate could not be obtained. The ketol readily reduced ammoniacal silver nitrate to silver, and mercuric salts to mercury.

Phenyl Benzyl Diketone (XII).—Phenylacetylphenylcarbinol (1·0 g.), dissolved in dioxan (25 c.c.), was shaken with Nessler's reagent (100 c.c.) at 15° for 1 hour. The resulting solution was repeatedly extracted with ether, and the extract washed with water, dried (sodium sulphate), and evaporated. The yellow oil was treated with *o*-phenylenediamine in hot alcohol, whence, by cooling, 2-phenyl-3-benzylquinoxaline separated in yellow needles, m. p. 97°, unchanged by crystallisation (Found: C, 84·7; H, 5·6; N, 9·9. Calc. for $C_{21}H_{16}N_2$: C, 85·1; H, 5·4; N, 9·5%). The diketone appears to exist as the diketo-form even in the presence of potassium hydroxide, since acidification of the aqueous liquor and further ether extraction afforded only a trace of oil giving a brown-purple colour with aqueous-alcoholic ferric chloride.

When the above oxidation was performed with acetone in place of dioxan, the neutral product obtained consisted of an oil which solidified on scratching with evolution of heat. The substance was re-dissolved in ether, the solution decanted from a trace of tarry matter and evaporated, and the solid residue crystallised from carbon tetrachloride–ligroin (b. p. 80—100°); the *δε-diketo-γε-diphenyl-β-methyl-Δ^{β}-pentene* formed pale yellow prisms, m. p. 123° [Found: C, 82·05; H, 6·12; *M* (Rast), 241. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%; *M*, 264]. A quinoxaline could not be obtained. Ozonolysis in chloroform solution, and decomposition of the ozonide with hot water, gave, amongst the more volatile products, acetone (identified as iodoform with iodine and ammonia in the cold), phenylglyoxylic acid (characterised by the condensation product, m. p. 247°, with *o*-phenylenediamine described below), and benzoic acid.

3-*Hydroxy*-2-*phenylquinoxaline* (3-*Keto*-2-*phenyl*-3 : 4-*dihydroquinoxaline*) (XIII or XIV).—Phenylglyoxylic acid, obtained by oxidation of acetophenone with alkaline permanganate at 5—10° (Glücksman, *Sitzungsber. Akad. Wiss. Wien*, 1890, **99**, 273), readily condensed with *o*-phenylenediamine in alcohol to give the *hydroxyphenylquinoxaline*, which formed pale yellow needles from alcohol, m. p. 247° (Found : C, 75·4 ; H, 4·6. $C_{14}H_{10}ON_2$ requires C, 75·7 ; H, 4·55%).

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