376. *Synthesis of Phenanthrene Derivatives.*

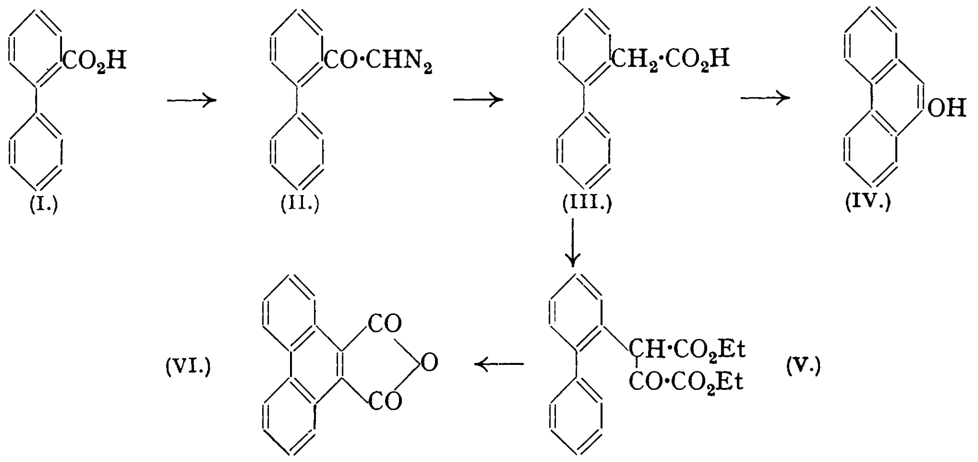
By Alexander Schönberg and Frank L. Warren.

Diphenyl-2-carboxylic acid (I) is converted into the acid chloride and treated with diazomethane to give *ω-diazo-*o*-phenylacetophenone* (II), which in the presence of aqueous colloidal silver yields diphenyl-2-acetic acid (III). The acid (III) is cyclised with acetic anhydride to give 9-phenanthryl acetate, which readily yields 9-phenanthrol (IV) and other derivatives, *e.g.*, 9-phenanthrylamine and phenanthraquinone. The ethyl ester of (III) is condensed with ethyl oxalate to give ethyl α-keto-β-2-diphenylyl-succinate (V), which on treatment with sulphuric acid yields phenanthrene-9 : 10-dicarboxylic anhydride (VI).

Since the acid (I) is really obtainable from fluorene *via* fluorenone, the method permits the easy passage from the fluorene to the phenanthrene series.

Braun and Manz (*Annalen*, 1928, **468**, 276) synthesised diphenyl-2-acetic acid, but reported no experiments on its conversion into phenanthrene. Chatterjee (*J. Indian Chem. Soc.*, 1935, **12**, 591), however, treated this acid with sulphuric acid to obtain 9-phenanthrol, but recorded no yields. [For similar cyclisations compare Cook, Hewett, and Lawrence (J., 1936, 71), Sherwood, Short, and Woodcock (*ibid.*, p. 322), Hewett (*ibid.*, p. 596), and Newman (*J. Amer. Chem. Soc.*, 1938, **60**, 2947).]

Diphenyl-2-acetic acid, hitherto obtainable only with difficulty, has now been readily synthesised as follows: The acid chloride of diphenyl-2-carboxylic acid (I) was treated with excess of diazomethane to give ω-*diazo*-o-*phenylacetophenone* (II) (compare Bradley and Robinson, J., 1928, 1310), which was converted by the action of aqueous colloidal silver (compare Arndt and Eistert, *Ber.*, 1935, **68**, 204) into diphenyl-2-acetic acid (III).



This acid (III) was cyclised by acetic anhydride by the procedure of Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1937, **59**, 1208) to give 9-phenanthryl acetate, which yielded 9-phenanthrol (IV). This method proved more satisfactory than the direct ring closure with sulphuric acid as adopted by Chatterjee (*loc. cit.*).

Ring closure was also accomplished very readily by applying the method used by Bougault for the synthesis of indene derivatives (*Compt. rend.*, 1914, **159**, 745; see also Auwers and Moller, *J. pr. Chem.*, 1925, **109**, 124; Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1935, **57**, 1851). Ethyl diphenyl-2-acetate was condensed with ethyl oxalate in the presence of potassium ethoxide to give ethyl α-keto-β-2-diphenylylsuccinate (V), which was cyclised with 80% sulphuric acid to phenanthrene-9 : 10-dicarboxylic anhydride (VI).

The conversion of 9-phenanthrol (IV) into phenanthrene effected by Chatterjee (*J. Indian Chem. Soc.*, 1936, **13**, 659) by heating with selenium and by us in moderate yield by zinc dust distillation in the presence of hydrogen, requires drastic conditions which might cause migration or elimination of groups with substituted derivatives. The almost quantitative conversion of 9-phenanthrol into 9-phenanthrylamine (Fieser, Jacobsen, and Price, *J. Amer. Chem. Soc.*, 1936, **58**, 2164) led us to investigate the elimination of the amino-group of the latter compound by the various methods involving diazotisation; but in no case could more than a trace of phenanthrene be obtained. On the other hand phenanthrene-9-carboxylic acid can be readily decarboxylated by the known methods (compare Pschorr, *Ber.*, 1896, **29**, 496), and the synthesis of this acid from compound (V) will be published later.

The method outlined above for the synthesis of phenanthrene derivatives involves few steps and the yields are high: calculated on the diphenyl-2-carboxylic acid, the yields of 9-phenanthrol, 9-phenanthrylamine and phenanthrene-9 : 10-dicarboxylic anhydride are 37, 37, and 42% of the theoretical respectively. Since diphenyl-2-carboxylic acid is readily obtained *inter alia* from fluorene *via* fluorenone, the method permits the easy passage from the fluorene to the phenanthrene series.

The acid chloride of diphenyl-2-carboxylic acid has never been prepared pure on account of its ready conversion into fluorenone. Graebe (*Annalen*, 1894, **279**, 260) obtained the acid chloride by grinding equimolecular quantities of the acid and phosphorus pentachloride, and reported that no fluorenone was formed below 50°. This method would not give a product sufficiently pure for our requirements, and quantitative experiments were carried out by treating the acid below 50° with different reagents to form the acid chloride and then regenerating the acid. Fluorenone was not produced, but varying amounts of a neutral oily white solid were isolated. After treatment with thionyl chloride at 45° and 40° the weight of regenerated acid was 33 and 60% respectively, and oxalyl chloride at 30° gave 70% of the weight of the original acid. The higher temperature was required by the former reagent to effect the formation of the acid chloride, which, however, was never complete below 50° and the reagent was not desirable (compare Fieser and Desreux, *J. Amer. Chem. Soc.*, 1938, **60**, 2255).

Original experiments with the acid chloride, prepared by means of thionyl chloride, and diazomethane gave only an oily product which was undoubtedly a mixture of the diazo-compound and methyl diphenyl-2-carboxylate, owing to the incomplete formation of the acid chloride. The action of colloidal silver on the oil gave a mixture of the two homologous acids, which were difficult to separate. The diazo-compound, however, crystallised almost completely on inoculation of the oil with a crystal of the substance; and the oily residue gave the original acid on hydrolysis. By adopting this method it was possible to get equally good yields of the diazo-compound, calculated on the acid used, with both reagents.

EXPERIMENTAL.

ω-Diazo-o-phenylacetophenone (II).—Diphenyl-2-carboxylic acid (10 g.; 1 mol.), dissolved in dry benzene (20 c.c.), was treated with oxalyl chloride (10 g.; 1·6 mols.) and kept at 30° until there was no further evolution of gas (about 1 hour). The solvent and the excess of reagent were removed in a vacuum at 35°. Dry ether (10 c.c.) was then added, and evaporated in a vacuum; the process was repeated to ensure the complete removal of the reagent and hydrogen chloride. The acid chloride thus formed was dissolved in ether (30 c.c.) and added drop by drop with shaking to a dry ethereal solution of diazomethane prepared from nitrosomethylurea (30 g.) by Arndt and Amende's method (*Z. angew. Chem.*, 1930, **43**, 444) and cooled in a freezing mixture. The whole was kept overnight at room temperature, and the ether removed in a vacuum. The yellow crystals, which were separated from the oil by filtration and washed with a little ether, were almost pure and were used for the next process. Yield, 7·1 g., *i.e.*, 61% of the theoretical. Crystallisation of a portion from alcohol gave *ω-diazo-o-phenylacetophenone* in stout yellow rods, m. p. 106° (Found: C, 75·8; H, 4·6; N, 12·4. $C_{14}H_{10}ON_2$ requires C, 75·6; H, 4·5; N, 12·6%). The crystals changed from yellow to red without losing their crystalline form after a few weeks. When smaller quantities of the acid (3 g.) were used, a 78% yield of the compound was obtained.

Diphenyl-2-acetic Acid (III).—Silver oxide (2·4 g.; 0·6 mol.), freshly precipitated from silver nitrate (3·5 g.) and 2N-sodium hydroxide, was dissolved in a solution of sodium thiosulphate (7 g.; 0·84 mol.) in water (200 c.c.), and a warm solution of ω-diazo-*o*-phenylacetophenone (7·5 g.; 1 mol.) in dioxan (50 c.c.) added. The mixture was stirred for 3 hours at room temperature while a further quantity of freshly precipitated silver oxide (2·4 g.) was added in portions at intervals, and then the temperature was kept at 50° for 1 hour. The solution was cooled and filtered, and the residue (A) washed with 1% sodium hydroxide solution. The united filtrate and washings were acidified with 2N-nitric acid to give a turbid solution which slowly deposited a flocculent precipitate (5·1 g.). The residue (A) was retreated with silver oxide (1·4 g.), sodium thiosulphate (2 g.), water (50 c.c.), and dioxan (25 c.c.) and worked up as above, a further quantity of the acid (1·05 g.) being obtained. Total yield, 6·15 g. (86%). Diphenyl-2-acetic acid crystallised from benzene in microscopic, lath-shaped crystals and from alcohol in needles, m. p. 116° (Found: C, 79·5; H, 5·5. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·7%). Braun and Manz (*Annalen*, 1928, **468**, 276) give m. p. 114°. The ethyl ester was a colourless mobile liquid, b. p. 156°/4 mm. Chatterjee (*J. Indian Chem. Soc.*, 1935, **12**, 591) gives b. p. 165—175°/8 mm.

9-Phenanthryl Acetate.—Diphenyl-2-acetic acid (1·5 g.), acetic acid (5 c.c.), acetic anhydride (5 c.c.), and anhydrous zinc chloride (0·2 g.) were heated under reflux for 3 hours and then poured into water. The oil thus precipitated slowly solidified. The product was lixiviated with petroleum (b. p. 40—50°) and twice crystallised from the same solvent to give 9-phenanthryl acetate in colourless needles, m. p. 76—77·5°, undepressed on admixture with authentic specimen (Found: C, 81·4; H, 5·0. Calc. for $C_{16}H_{12}O_2$: C, 81·3; H, 5·1%). Yield, 0·92 g. (55%).

9-Phenanthrol.—9-Phenanthryl acetate (0·88 g.) was refluxed with 10% alcoholic potassium hydroxide (7 c.c.) for 15 minutes. Acidification with dilute hydrochloric acid gave very pure 9-phenanthrol. Yield, 0·71 g. (98%).

Phenanthrene.—9-Phenanthrol (0·55 g.), intimately mixed with zinc dust (6 g.), was gently heated in a current of hydrogen. The product was extracted with ether, and the ethereal solution washed with sodium hydroxide and water. The solid obtained by removal of the ether was distilled in a vacuum. Yield of phenanthrene, 0·36 g. (72%), m. p. 99—100°.

Ethyl α-Keto-β-2-diphenylylsuccinate (V).—Potassium (0·98 g.; 1 atom.) in dry ether (60 c.c.) was treated with ethyl alcohol (1·84 g.; 1·6 mols.) and, when all the potassium had dissolved, ethyl oxalate (5·48 g.; 1·5 mols.) and then ethyl diphenyl-2-acetate (6 g.; 1 mol.) were added. After standing overnight, the whole was refluxed for 6 hours and poured on dilute sulphuric acid and ice. The ethereal layer was washed with water, dried over sodium sulphate, and divided into two equal parts, and the solvent removed in a vacuum to give ethyl α-keto-β-2-diphenylylsuccinate as a yellow liquid, which was used without further purification.

Phenanthrene-9 : 10-dicarboxylic Anhydride.—Half of the keto-derivative (V) was stirred vigorously with a solution of 95% sulphuric acid (28 c.c.; *d* 1·84) and water (10 c.c.) in a water-bath at 100° for 3 hours, the oil slowly changing to a solid. The product was poured on ice and the brown solid was collected and extracted several times with hot dilute potassium hydroxide solution. The extract on acidification gave a white precipitate which rapidly changed to yellow. Crystallisation from acetic anhydride gave phenanthrene-9 : 10-dicarboxylic anhydride in yellow needles, m. p. 321—324° (Found : C, 77·7; H, 3·3. Calc. for $C_{16}H_8O_3$: C, 77·4; H, 3·3%). Jeanes and Adams (*J. Amer. Chem. Soc.*, 1937, **59**, 2608) give m. p. 322°. Yield, 1·9 g., *i.e.*, 63% of the theoretical calculated on the diphenyl-2-acetic ester (3 g.). The anhydride was practically insoluble in hot benzene, to which it imparted a blue-green fluorescence.

FUAD I UNIVERSITY, ABBASSIA, CAIRO.

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