

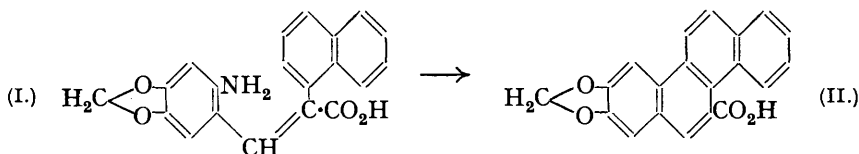
### 87. 4 : 5-Methylenedioxychrysene.

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4 : 5-Methylenedioxychrysene has been synthesised according to the method of Weitzenböck and Lieb.

OWING to the relation of chrysene to *cyclopentenophenanthrene*, the nucleus of which is present in many compounds of physiological importance, experiments have been commenced on the synthesis of its unsymmetrical derivatives, of which very few are known. The synthesis of 4 : 5-methylenedioxychrysene described below follows the well-known Pschorr pattern as applied by Weitzenböck and Lieb (*Monatsh.*, 1912, **33**, 556) to chrysene itself.

6-Nitropiperonal condenses with the potassium salt of  $\alpha$ -naphthylacetic acid in the



presence of acetic anhydride to form 2-nitro-4 : 5-methylenedioxy- $\alpha$ -1'-naphthylcinnamic acid. This is reduced by ammoniacal ferrous sulphate to the corresponding amine (I),

diazotisation of which, followed by treatment with copper powder and copper bronze in the presence of sodium hypophosphite (cf. Ruggli and Staub, *Helv. Chim. Acta*, 1937, 20, 37), affords 4 : 5-methylenedioxychrysene-1-carboxylic acid (II). This gives 4 : 5-methylenedioxychrysene on distillation at 0.04 mm. in the presence of copper bronze.

## EXPERIMENTAL.

*α-Naphthylacetoneitrile*.—To a solution of *α*-chloromethylnaphthalene (Anderson and Short, *J.*, 1933, 485; Coles and Dodds, *J. Amer. Chem. Soc.*, 1938, 60, 853) (101 g.) in hot alcohol (200 c.c.), potassium cyanide (37 g.) in alcohol (40 c.c.) and water (75 c.c.) was added, and the mixture refluxed for 7 hours. The alcohol was then distilled off, the residue extracted with ether, and the *α*-naphthylacetoneitrile obtained therefrom as a colourless liquid, b. p. 183—187°/13 mm., in 87% yield. On standing, it solidified to a white waxy solid, m. p. 32—33°. Wislicenus and Wren (*Ber.*, 1905, 38, 507) obtained a 40% yield by this method and Wislicenus and Elvert (*Ber.*, 1916, 49, 2820) record m. p. 5°. The nitrile was converted into the acid according to Mayer and Oppenheimer (*ibid.*, p. 2139).

*2-Nitro-4 : 5-methylenedioxy-α-1'-naphthylcinnamic Acid*.—6-Nitropiperonal (20 g.) and the potassium salt of *α*-naphthylacetic acid (23 g.) were heated at 100° in acetic anhydride (100 c.c.) for 25 hours, and the mixture poured into water (1500 c.c.) and kept for 24 hours. The aqueous layer was decanted, and the resinous mass extracted repeatedly with potassium carbonate solution. From the hot extracts, potassium 2-nitro-4 : 5-methylenedioxy-*α*-1'-naphthylcinnamate separated in yellow plates. The acid, liberated from a suspension of the potassium salt in water by hydrochloric acid and twice crystallised from dilute alcohol, formed yellow plates, m. p. 203.5—206.5° (yield, 54%) (Found : C, 66.2; H, 3.5.  $C_{20}H_{13}O_6N$  requires C, 66.1; H, 3.6%).

*2-Amino-4 : 5-methylenedioxy-α-1'-naphthylcinnamic Acid* (I).—The nitro-acid (20 g., 1 mol., in 25% aqueous ammonia, 420 c.c.) was reduced with ferrous hydroxide (hydrated ferrous sulphate, 108 g., 7 mols.; water, 320 c.c.; concentrated aqueous ammonia, 25 c.c.), a further 145 c.c. of concentrated aqueous ammonia being added during 1½ hours. After cooling, the sludge was separated and extracted three times with dilute aqueous ammonia, and the combined filtrate and washings acidified with acetic acid. The voluminous yellow precipitate, which rapidly became green, was filtered off, redissolved in boiling dilute aqueous ammonia (charcoal), cooled, and made acid to methyl-red with acetic acid. The green solid separating was filtered off; the filtrate, made more strongly acid with acetic acid, deposited a yellow solid in 43% yield. After two crystallisations from dilute alcohol *2-amino-4 : 5-methylenedioxy-α-1'-naphthylcinnamic acid* formed pale yellow needles, m. p. 161.5—163.5° (decomp.) (Found : C, 72.2; H, 4.5.  $C_{20}H_{15}O_4N$  requires C, 72.1; H, 4.5%).

*4 : 5-Methylenedioxychrysene*.—The amino-acid (7.2 g.), dissolved in a mixture of dioxan (190 c.c.) and alcohol (250 c.c.), was diazotised at 25—30° by the addition of concentrated sulphuric acid (1.65 c.c.), followed by amyl nitrite (4 c.c.) during 30 minutes, with mechanical stirring. The deep red solution was added with stirring to a suspension of copper powder (Gattermann) and copper bronze in a solution at 45° of sodium hypophosphite (22.6 g.) in water (23 c.c.), the temperature being gradually raised to the b. p. during the addition. The filtered solution was concentrated to half volume by distillation and poured into dilute sodium hydroxide solution (2000 c.c.), and the mixture boiled with charcoal and acidified with hydrochloric acid. The brown amorphous product (6.7 g.) was soluble in all the usual solvents except light petroleum and could not be crystallised. It (0.58 g.) was mixed with copper bronze (0.25 g.) and heated at 0.04 mm. in a small flask with a finger condenser placed *ca.* 1 cm. above the solid. Between *ca.* 200° (m. p.) and 240° a yellow crystalline solid slowly sublimed (0.17 g.). After two crystallisations from glacial acetic acid (charcoal) *4 : 5-methylenedioxychrysene* was obtained in colourless prisms, m. p. 222—223° (Found : C, 83.7; H, 4.5.  $C_{19}H_{12}O_2$  requires C, 83.8; H, 4.4%). The picrate, prepared in benzene solution and recrystallised from the same solvent, formed orange-red needles, m. p. 202—202.5°.

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