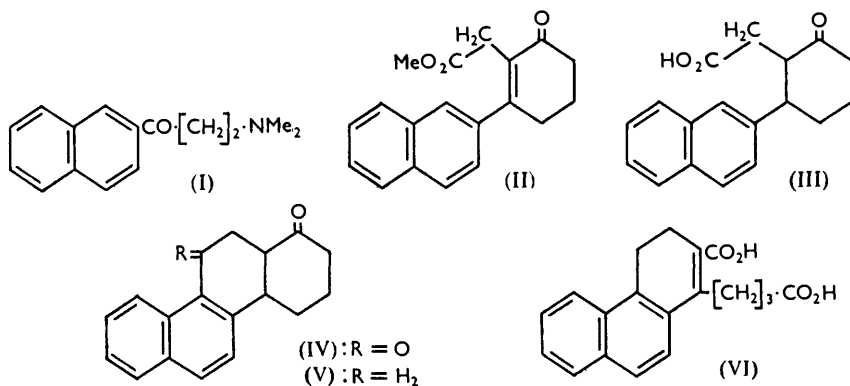


556 Polycyclic Systems. Part II.* Synthesis of Some Chrysene and Hydrochrysene Derivatives.

By D. NASIPURI, A. C. CHAUDHURI, and J. ROY.

The methiodide of 2-dimethylaminoethyl β -naphthyl ketone (I) on usual Mannich-base condensation with methyl β -oxoadipate gives methyl 2- β -naphthyl-6-oxocyclohex-1-enylacetate (II). The latter provides a simple route to chrysene and hydrochrysene derivatives and has been employed for the synthesis of octahydro-1-oxo- and -1:11-dioxo-chrysenes. A preliminary account of this work has already appeared.¹

2-DIMETHYLAMINOETHYL β -NAPHTHYL KETONE (I), prepared by Blicke and Maxwell's method,² gave a crystalline methiodide which reacted with the potassium derivative of methyl β -oxoadipate. The product, on hydrolysis and re-esterification, afforded methyl 2- β -naphthyl-6-oxocyclohex-1-enylacetate (II) in about 30% overall yield. The ester on



hydrogenation in presence of colloidal palladium and subsequent saponification gave the acid (III) which was isolated mainly in one stereoisomeric form. The latter was cyclised with polyphosphoric acid to 1 : 2 : 3 : 4 : 4a : 11 : 12 : 12a-octahydro-1 : 11-dioxochrysene (IV) in good yield, which was hydrogenated by the use of platinum-palladium³ to the

* Part I, Nasipuri, *J.*, 1958, 2618.

¹ Nasipuri, Chaudhuri, and Roy, *Chem. and Ind.*, 1957, 422.

² Blicke and Maxwell, *J. Amer. Chem. Soc.*, 1942, **64**, 428.

³ (a) Zelinsky, *Ber.*, 1933, **66**, 872; (b) Koebner and Robinson, *J.*, 1938, 1994.

octahydro-1-oxochrysenes (V). This stage was analogous to the synthesis of the corresponding hydrocyclopentenophenanthrene derivatives by Robinson and his co-workers;⁴ but while, in the latter case, the products were presumably the *cis*-isomers,⁵ these hydrochrysenes ketones were expected to be more stable in *trans*-configuration. In fact, the ketone (V) on treatment with mineral acid was recovered mostly unchanged. An authentic specimen of this ketone was prepared by an alternative route from γ -(2-carboxy-3:4-dihydro-1-phenanthryl)butyric acid (VI) (cf. Part I). The latter was reduced by sodium amalgam, and the derived diethyl ester on Dieckmann cyclisation and subsequent hydrolysis afforded the ketone (V).

The diketone (IV) was converted into chrysenes by reduction with lithium aluminium hydride, followed by aromatisation with 10% palladium-charcoal.⁶ The ketone (V) was converted into 1-methylchrysenes by the standard procedure.

EXPERIMENTAL

Methyl 2- β -Naphthyl-6-oxocyclohex-1-enylacetate (II).—A mixture of methyl β -naphthyl ketone (17 g.), dimethylamine hydrochloride (8.3 g.), paraformaldehyde (4.5 g.), absolute ethanol (30 ml.) and concentrated hydrochloric acid (0.5 ml.) was refluxed on the steam-bath for 3 hr. Most of ethanol was removed at the water-pump, and the crystalline hydrochloride was dissolved in the minimum quantity of water and basified with an excess of 40% potassium hydroxide solution. The amino-ketone was extracted with ether, dried (K_2CO_3), and evaporated. The residue (21 g.) was taken up in dry benzene (75 ml.) and cooled in ice, methyl iodide (7 ml.) was added dropwise during 30 min. with stirring, and the whole was left overnight at 0°. Next day, to the cold mixture was added a solution of methyl β -oxoadipate (19 g.) in benzene (25 ml.), followed by ethanolic potassium ethoxide [from potassium (6 g.) in ethanol (100 ml.)]. Air in the flask was displaced by nitrogen and the mixture was stirred in the cold for 1 hr., then refluxed for 30 min. The cooled solution was decomposed with 2*N*-sulphuric acid, and the benzene layer was separated. The aqueous solution was extracted with ether, and the combined organic layers were washed with water and dried. On their evaporation a gum (36 g.) was left which was hydrolysed by potassium hydroxide (30 g.) in boiling water (900 ml.) for 6 hr. under nitrogen. The alkaline solution was once extracted with ether, then cautiously acidified. The precipitated acid (20 g.) was taken up in ether and esterified by refluxing methanolic 2.5% hydrochloric acid (150 ml.). The *methyl ester* boiled at 220–230°/0.1 mm. and on crystallisation from methanol afforded prisms (9.3 g., 31%), m. p. 131° (Found: C, 77.5; H, 6.2. $C_{19}H_{18}O_3$ requires C, 77.6; H, 6.1%), λ_{max} . 219, 265, and 287 m μ ($\log \epsilon$ 4.73, 4.33, and 4.04). The *acid* obtained on hydrolysis crystallised from aqueous acetone in needles, m. p. 156° (Found: C, 77.1; H, 5.8. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.7%) and gave a *semicarbazone*, m. p. 218° (Found: C, 67.3; H, 5.7; N, 12.9. $C_{19}H_{19}O_3N_3$ requires C, 67.7; H, 5.7; N, 12.5%).

2- β -Naphthyl-6-oxocyclohexylacetic Acid (III).—The foregoing ester (II) (10.5 g.) was shaken in ethanol (200 ml.) with hydrogen, palladium chloride (0.2 g.), and gum arabic (0.2 g.) at 40°. Absorption of hydrogen (1050 ml., 1 mol.) was complete in 4 hr. The solution was filtered and hydrolysed by refluxing aqueous 10% potassium hydroxide (40 ml.). The *acid*, on crystallisation from acetic acid, melted at 143–148°. After several crystallisations from aqueous acetone, the m. p. rose to 170–172° (Found: C, 76.5; H, 6.4. $C_{18}H_{16}O_3$ requires C, 76.6; H, 6.4%). The *semicarbazone* formed prisms (from ethanol), m. p. 228° (Found: C, 67.1; H, 6.3; N, 12.6. $C_{19}H_{21}O_3N_3$ requires C, 67.3; H, 6.2; N, 12.4%).

1:2:3:4:4a:11:12:12a-Octahydro-1:11-dioxochrysenes (IV).—The acid (III) (3 g.) was kept in with polyphosphoric acid [from phosphoric oxide (10 g.) and 89% phosphoric acid (8 ml.)] at 70–75° for 2 hr., then decomposed with ice and extracted with benzene. The extract was washed with dilute sodium hydroxide solution, then with water. The *diketone* obtained on evaporation crystallised from methanol in needles (2.4 g., 80%), m. p. 158–160°, increased by several crystallisations to 175° (Found: C, 82.0; H, 6.2. $C_{18}H_{16}O_2$ requires C, 81.8; H, 6.1%). It had λ_{max} . 214, 247, and 318 m μ ($\log \epsilon$ 4.91, 4.70, and 4.25). The *semicarbazone* formed a powder (from acetic acid), m. p. 264–266° (decomp.) (Found: C, 70.8; H,

⁴ Robinson, *J.*, 1938, 1390; also ref. 3b.

⁵ Birch, Jaeger, and Robinson, *J.*, 1945, 582.

⁶ Linstead and Thomas, *J.*, 1940, 1127.

6.1; N, 13.3. $C_{19}H_{19}O_2N_3$ requires C, 71.0; H, 5.9; N, 13.1%). The red dinitrophenylhydrazone had m. p. 274—275° (decomp.).

Chrysene.—The above diketone (0.5 g.) was reduced by lithium aluminium hydride (0.5 g.), and the crude diol (0.52 g.) was heated with 10% palladium-charcoal (0.1 g.) at 280° for 2 hr. The melt was taken up in hot benzene and filtered. The filtrate, on cooling, afforded chrysene in plates (0.36 g., 80%), m. p. 243—246°. On further crystallisation from toluene, it melted at 250° alone or mixed with an authentic sample (Found: C, 94.5; H, 5.3. Calc. for $C_{18}H_{12}$: C, 94.7; H, 5.3%). The trinitrofluorenone complex formed yellow needles (from ethanol), m. p. and mixed m. p. 248—249° (Found: N, 7.9. Calc. for $C_{18}H_{12}, C_{13}H_5O_7N_3$: N, 7.7%); Orchin and Woolfolk⁷ given m. p. 247.8—249°.

1 : 2 : 3 : 4 : 4a : 11 : 12 : 12a-Octahydro-1-oxochrysene (V).—(a) The diketone (IV) (1 g.) was reduced in ethanol (30 ml.) by hydrogen in presence of palladium-platinum-charcoal as described by Koebner and Robinson.^{3b} The ketone (V) crystallised from benzene-light petroleum (b. p. 40—60°) in prisms, m. p. 161—162° (Found: C, 86.4; H, 7.4. $C_{18}H_{18}O$ requires C, 86.4; H, 7.2%). The dinitrophenylhydrazone formed a yellow powder, m. p. 265—266° (decomp.) (Found: N, 13.1. $C_{24}H_{22}O_4N_4$ requires N, 13.0%).

(b) γ -(2-Carboxy-3 : 4-dihydro-1-phenanthryl)butyric acid (5 g.) was reduced in 2% aqueous potassium hydroxide (100 ml.) by gradual addition of 2.5% sodium amalgam (200 g.). The solution was filtered and acidified. The gummy acid was worked up in the usual way and with ethanolic sulphuric acid gave an ester, b. p. 220—230°/0.1 mm. The ester (3 g.) was heated with finely powdered sodium (0.21 g.) and dry benzene (12 ml.) on the steam-bath for 2 hr. The resultant β -oxo-ester was hydrolysed by refluxing hydrochloric acid (10 ml.) and acetic acid (20 ml.) for 5 hr. The ketone (V) was worked up in the usual way and crystallised from benzene-light petroleum in prisms, m. p. and mixed m. p. 163—164° (Found: C, 86.4; H, 7.4%). The dinitrophenylhydrazone formed a yellow powder (from acetic acid), m. p. 266—268° (decomp.). The ketone gave readily a *furfurylidene derivative* which crystallised from ethyl acetate in light yellow needles, m. p. 178—179° (Found: C, 84.0; H, 6.2. $C_{23}H_{20}O_2$ requires C, 84.1; H, 6.1%).

1-Methylchrysene.—A solution of the foregoing ketone (V) (0.2 g.) in benzene (15 ml.) was treated with excess of methylmagnesium iodide, and the product (0.2 g.) was heated with 10% palladium-charcoal at 280° for 2 hr. The melt was extracted with benzene, and 1-methylchrysene obtained from the extract crystallised from toluene, forming leaflets, m. p. 249° (Found: C, 94.1; H, 5.7. Calc. for $C_{19}H_{14}$: C, 94.2; H, 5.8%). Bachmann and Struve⁸ give m. p. 249.5—250°.

The authors thank Mrs. Chhabi Dutta, of University College of Science, Calcutta, for microanalyses.

UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA, INDIA.

[Received, March 17th, 1958.]

⁷ Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727.

⁸ Bachmann and Struve, *J. Org. Chem.*, 1940, **5**, 416.