317. *Polycyclic Systems. Part VI.* Synthesis of Hydrochrysene and Hydrophenanthrene Derivatives.*

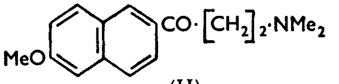
By D. NASIPURI and J. ROY.

Syntheses of octahydro-8-methoxy-1-oxo- and -1,11-dioxo-chrysene (IV; R = O) from 2-acetyl-6-methoxynaphthalene are reported. An extension of the general method has resulted in a new synthesis of phenanthrene derivatives.

MANNICH-BASE condensation of the methiodide of 2-dimethylaminoethyl β-naphthyl ketone with methyl β-oxoadipate (I) was shown earlier[1] to provide a simple route to valuable chrysene and hydrochrysene derivatives. In continuation of this work, 2-acetyl-6-methoxynaphthalene[2] was converted into its Mannich base (II), the methiodide of which on condensation with the potassium derivative of methyl β-oxoadipate gave methyl 2-(6-methoxy-2-naphthyl)-6-oxocyclohex-1-enylacetate (III) in 35—38% yield. The ester on catalytic hydrogenation in presence of palladium and subsequent hydrolysis afforded an acid, which was cyclised to the diketone (IV; R = O) with polyphosphoric acid in 30% yield. The diketone was further reduced by the use of platinum–palladium[3] to the octahydro-8-methoxy-1-oxochrysene (IV; R = H_2) obtained finally with m. p. 159—160°. By analogy with the demethoxy-series,[1] these compounds are assumed to have a *trans*-ring junction. The ketone (IV; R = H_2) was first synthesised by Bachmann

$MeO_2C\cdot CH_2\cdot CO\cdot[CH_2]_2\cdot CO_2Me$

(I)



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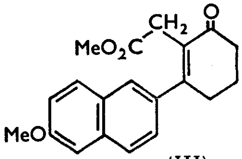

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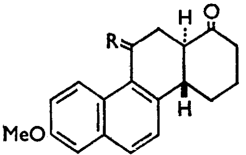

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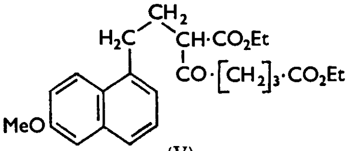

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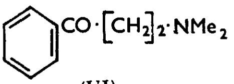

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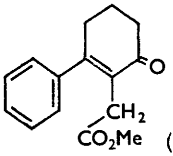

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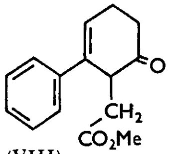

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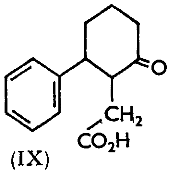

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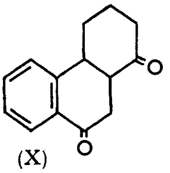
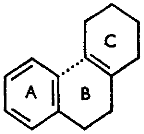


(X)



(XI)

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* Part V, *J. Indian Chem. Soc.*, 1959, **36**, 817.

[1] Nasipuri, Chaudhuri, and Roy, *J.*, 1958, 2734.

[2] Robinson and Rydon, *J.*, 1939, 1394.

[3] Zelinsky, *Ber.*, 1933, **66**, 872; Koebner and Robinson, *J.*, 1938, 1994.

et al.[4] who reported m. p. 139—140° for their compound. In view of very small amount of compound obtained by them, it is probable that their ketone was not stereochemically homogeneous. The corresponding phenol, however, had the same melting point (273—275°) as reported by Bachmann *et al.*[4] The present synthesis involves fewer steps and has the advantage of using easily accessible β-substituted naphthalene derivative as starting material.

An alternative synthesis of this ketone (IV; R = H_2) starting from the ester (V) and involving cyclodehydration, aromatisation, and Dieckmann cyclisation (cf. ref. 1) was also effected, and gave the same ketone.

In another series of experiments, the methiodide of β-dimethylaminopropiophenone [5] (VI) was likewise condensed with methyl β-oxoadipate and the product on hydrolysis and esterification afforded the keto-ester (VII), m. p. 82·5°, in about 50% yield. This is probably identical with a compound, m. p. 77—78°, obtained by Turner [6] by Stobbe condensation of ethyl γ-benzoylbutyrate and represented by the isomeric formulation (VIII) (see, however, Johnson, Christiansen, and Ireland [7]). The ultraviolet absorption and the dinitrophenylhydrazone of the present compound agree well with those reported by Turner. The ester (VII), on catalytic hydrogenation, gave a crystalline methyl ester in almost quantitative yield. An attempt to determine the configuration of the corresponding acid (IX) by conversion into the known *cis*- and *trans*-2-phenylcyclohexylacetic acid [8] by Huang-Minlon reduction [9] proved inconclusive, a mixture of easily separable *cis*- and *trans*-acid being obtained in almost equal amount: evidently, epimerisation took place during reduction in strongly alkaline medium. Clemmensen reduction of the keto-acid (IX) by Martin's procedure [10] was always incomplete but cyclisation by polyphosphoric acid was almost quantitative, and the resultant diketone (X) on reduction with lithium aluminium hydride followed by dehydrogenation with 30% palladium–charcoal [11] afforded phenanthrene in excellent yield. The present synthesis of phenanthrene differs from most of the current methods in the way the C-ring of the phenanthrene nucleus is built up: substituents in the phenyl group which may have adverse orienting effect in the phenanthrene ring-closure (as shown in XI) in classical methods, will favour cyclisation of compounds of the type (IX). The method is, therefore, expected to be useful.

EXPERIMENTAL

Methyl β-Oxoadipate (I).—Methyl β-oxoadipate was prepared by Bardhan's procedure [12] with a slight modification. The crude methyl α-acetyl-β-oxoadipate (70 g.), b. p. 140—142°/3 mm., prepared from β-methoxycarbonylpropionyl chloride (75·5 g.), methyl acetoacetate (58 g.), sodium (11·5 g.), and dry ether (800 ml.), and consisting mainly of *C*-acyl and only a little of *O*-acyl compound was dissolved in anhydrous ether (120 ml.), and dry ammonia passed in for 1 hr. Next day, after removal of most of the ether at the water-pump, the residue was shaken repeatedly with cold dilute hydrochloric acid. The acid washing was extracted with ether (3 × 100 ml.), the combined ethereal extracts were washed with water, dried (Na_2SO_4), and evaporated, and the residue was distilled *in vacuo*. After a few ml. of fore-run, methyl β-oxoadipate was collected as a colourless oil (35—36 g., 37—38%), b. p. 125—126°/3 mm., 100°/0·3 mm. (Found: C, 51·2; H, 6·5. Calc. for $C_8H_{12}O_5$: C, 51·1; H, 6·3%). The pyrazolone derivative obtained by heating the ester with phenylhydrazine, crystallised from ethyl acetate–light petroleum (b. p. 40—60°) in needles, m. p. 80° (Found: C, 63·2; H, 5·9. Calc. for

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[4] Bachmann, Gregg, and Pratt, *J. Amer. Chem. Soc.*, 1943, **65**, 2314.

[5] Vogel, " Practical Organic Chemistry," Longmans, Green & Co., Ltd., London, 3rd edn., p. 911.

[6] Turner, *J. Amer. Chem. Soc.*, 1951, **73**, 3017.

[7] Johnson, Christiansen, and Ireland, *J. Amer. Chem. Soc.*, 1957, **79**, 1995.

[8] (*a*) Cook, Hewett, and Lawrence, *J.*, 1936, 71; (*b*) Blumenfeld, *Ber.*, 1941, **74**, 524; (*c*) Linstead, Whetstone, and Levine, *J. Amer. Chem. Soc.*, 1942, **64**, 2014; (*d*) Gutsche and Johnson, *ibid.*, 1946, **68**, 2239; (*e*) Buchta and Ziener, *Annalen*, 1956, **601**, 155.

[9] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

[10] Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438.

[11] Linstead and Thomas, *J.*, 1940, 1127.

[12] Bardhan, *J.*, 1936, 1848.

$C_{13}H_{14}O_3N_2$: C, 63·4; H, 5·7%). This method proved superior in our hands to that described by Korman.[13]

Methyl 2-(6-*Methoxy*-2-*naphthyl*)-6-*oxocyclohex*-1-*enylacetate* (III).—2-Acetyl-6-methoxynaphthalene (20 g.), dimethylamine hydrochloride (8·3 g.), paraformaldehyde (4·5 g.), absolute ethanol (30 ml.), and concentrated hydrochloric acid (0·5 ml.) were refluxed for 5 hr. After removal of most of the alcohol at the water-pump, the crystalline hydrochloride was dissolved in the minimum quantity of water, any unused ketone removed by ether, and the cooled solution basified with 40% potassium hydroxide solution. The amino-ketone was extracted with ether, dried (K_2CO_3), and recovered; it (23·5 g.) melted at 72—74°.

To a chilled solution of this Mannich-base (21·3 g.) in dry thiophen-free benzene (100 ml.) methyl iodide (6·5 ml.) was added during 1 hr. Stirring was continued for 4 hr. more and the mixture left overnight at 0°. Next day, to the methiodide so formed, a solution of methyl β-oxoadipate (20 g.) in dry benzene (100 ml.) was added, followed by cold ethanolic potassium ethoxide, prepared from potassium (6 g.) and ethanol (100 ml.). Stirring was continued for 6 hr. and reaction completed by refluxing the mixture on the water-bath for 1 hr. The solution was cooled, then decomposed with 2N-sulphuric acid, and the product extracted with benzene. The gummy residue (35 g.) obtained on removal of the benzene was hydrolysed by a boiling solution of potassium hydroxide (30 g.) in water (900 ml.) in 10 hr. The alkaline solution was once extracted with ether, then acidified, and the crude acid (23 g.) was esterified with 3% methanolic hydrochloric acid (150 ml.). The *ester* (III) (11—12 g.) had b. p. 220—230°/0·2 mm. and formed colourless plates, m. p. 96°, from methanol (Found: C, 73·9; H, 6·1. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

2-(6-*Methoxy*-2-*naphthyl*)-6-*oxocyclohexylacetic Acid*.—The ester (III) (11 g.) in ethanol (200 ml.) was hydrogenated at 40° in presence of palladium chloride (0·2 g.) and gum arabic (0·2 g.) (1 H_2 absorbed in 4 hr.). The solution was filtered and hydrolysed by refluxing alcoholic 10% potassium hydroxide. The crude *acid* (10 g.), crystallised several times from aqueous acetic acid, formed needles, m. p. 168—170° (Found: C, 73·3; H, 6·3. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%).

1,2,3,4,4*a*,11,12,12*a*-*Octahydro*-8-*methoxy*-1,11-*dioxochrysene* (IV; R = O).—The above acid (9 g.) was kept in polyphosphoric acid [from phosphoric oxide (33 g.) and 89% phosphoric acid (29 ml.)] at 70° for 3 hr. The dark brown solution was decomposed with ice and worked up in the usual way, to give the *diketone* (2·6 g.), m. p. 170—175°, which, crystallised several times from methanol, gave needles, m. p. 196—197° (Found: C, 77·3; H, 6·0. $C_{19}H_{18}O_3$ requires C, 77·6; H, 6·1%). The *dinitrophenylhydrazone* had m. p. 267° (Found: N, 11·7. $C_{25}H_{22}O_6N_4$ requires N, 11·9%). The *semicarbazone*, crystallised from ethanol, had m. p. 260° (Found: C, 68·0; H, 6·2; N, 11·9. $C_{20}H_{21}O_3N_3$ requires C, 68·4; H, 6·0; N, 12·0%).

1,2,3,4,4*a*,11,12,12*a*-*Octahydro*-8-*methoxy*-1-*oxochrysene* (IV; R = H_2).—The foregoing diketone (2 g.), m. p. 170—175°, in ethanol (70 ml.) was reduced by hydrogen in presence of palladium–platinum–charcoal.[3] The monoketone was worked up in the usual way and crystallised from benzene–light petroleum in nodules, m. p. 140—142°. After a few more crystallisations from the same solvent, the ketone was obtained in fine needles having a constant m. p. 159—160° (Found: C, 81·2; H, 6·9. Calc. for $C_{19}H_{20}O_2$: C, 81·4; H, 7·1%). Bachmann, Gregg, and Pratt[4] give m. p. 139—140°. The *dinitrophenylhydrazone* formed a yellow powder, m. p. 245—246° (Found: C, 65·5; H, 5·0; N, 12·1. $C_{25}H_{24}O_5N_4$ requires C, 65·2; H, 5·2; N, 12·2%).

Ethyl α-2-(6-*Methoxy*-1-*naphthyl*)*ethyl*-β-*oxopimelate* (V).—β-(6-Methoxy-1-naphthyl)ethyl bromide was prepared from 6-methoxy-1-tetralone[14] *via* ethyl 3,4-dihydro-6-methoxy-1-naphthylacetate.[15] The latter (50 g.) was heated with powdered sulphur (6·5 g.) at 240—250° for 2 hr. and the product on hydrolysis afforded 6-*methoxy*-1-*naphthylacetic acid*, m. p. 150° (Found: C, 72·1; H, 5·7. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%). The derived ethyl ester, b. p. 175°/0·5 mm. (46 g.), was reduced by lithium aluminium hydride (10 g.) in ether (200 ml.) to 2-(6-methoxy-1-naphthyl)ethyl alcohol (35·6 g.), b. p. 162—165°/2 mm., which was converted into the bromide with phosphorus tribromide in carbon tetrachloride.

To a solution of potassium (4·4 g.) in t-butyl alcohol (90 ml.), was added diethyl 2-oxopentane-1,5-dicarboxylate[16] (25 g.). Then the above bromide (30 g.) was rapidly added and

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[13] Korman, *J. Org. Chem.*, 1957, **22**, 848.

[14] Stork, *J. Amer. Chem. Soc.*, 1947, **69**, 576.

[15] Burnop, Elliot, and Linstead, *J.*, 1940, 730.

[16] Nasipuri and Guha, unpublished work: Hunter and Hogg, *J. Amer. Chem. Soc.*, 1949 **71**, 1922.

the whole heated under reflux in an atmosphere of nitrogen for 20 hr. After removal of most of the t-butyl alcohol at the water-pump, the residue was diluted with water, and the heavy organic layer was taken up in ether. The ethereal solution was washed with water, dried, and evaporated. The product was distilled carefully in an oil-bath up to 150°/0·2 mm. in order to eliminate low-boiling impurities as far as possible and the residual β-oxo-ester (V) (36 g.) was used in the next operation.

γ-(2-Carboxy-3,4-dihydro-7-methoxy-1-phenanthryl)butyric Acid.—The crude ester (6 g.) from the foregoing experiment was cyclised by concentrated sulphuric acid (15 ml.) at −10° during 30 min. The dark brown mass was decomposed with ice and worked up in the usual way. The product on hydrolysis with alcoholic potassium hydroxide gave the *acid* (2·6 g.) which crystallised from acetic acid in plates, m. p. 220° (Found: C, 70·3; H, 5·7. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

Synthesis of the Ketone (IV; R = H_2).—The foregoing acid (5 g.) was dissolved in 2% aqueous potassium hydroxide (100 ml.) and reduced by gradual addition of 2·5% sodium amalgam (200 g.). The product was worked up in the usual way, to give a gummy acid (5 g.), evidently a mixture of *cis*- and *trans*-isomerides, which was converted directly into dimethyl ester (4·8 g.), b. p. 200—210°/0·15 mm., with methanolic sulphuric acid. A mixture of the ester (4·8 g.), pulverised sodium (0·32 g.), benzene (20 ml.), and anhydrous methanol (0·2 ml.) was heated under reflux for 4 hr. on the water-bath. The resultant β-oxo-ester was then heated with potassium hydroxide (5 g.) in 90% methanol (100 ml.) for 2 hr. The alkaline solution was next acidified with concentrated hydrochloric acid (15 ml.), heated (reflux) for 6 hr., and diluted with water. Methanol was removed by distillation, and the organic matter taken up in benzene, and washed with water, N-sodium hydroxide, and again water. After evaporation of solvent, the ketone (IV; R = H_2) crystallised from benzene–light petroleum in needles (1·8 g.), m. p. 159—160° (Found: C, 80·9; H, 7·2%) dinitrophenylhydrazone, m. p. 245—247° (Found: N, 12·0%). The *furfurylidene derivative,* prepared by allowing the ketone (1 g.) in methanol (25 ml.) to react with freshly distilled furfuraldehyde (5 ml.) in presence of 33% sodium hydroxide solution (90 ml.), crystallised from ethyl acetate in light yellow needles, m. p. 158—160° (Found: C, 80·1; H, 5·9. $C_{24}H_{22}O_3$ requires C, 80·4; H, 6·1%).

Methyl 6-Oxo-2-phenylcyclohex-1-enylacetate (VII).—β-Dimethylaminopropiophenone (VI) (18 g.) in dry benzene (50 ml.) was converted into its methiodide as described before. To a cooled suspension of the methiodide in benzene, was added a methanolic solution of potassio-derivative of methyl β-oxoadipate (I), prepared from potassium (4 g.), methyl β-oxoadipate (22·5 g.), and methanol (100 ml.), and stirring was continued for 8 hr. at room temperature, the solid methiodide being gradually replaced by a fine suspension of potassium iodide. The reaction was completed by refluxing the mixture for 30 min. The product was worked up in the usual way, and on hydrolysis and esterification (see below) afforded methyl 6-oxo-2-phenylcyclohex-1-enylacetate (VII) (12·3 g., 50%), b. p. 160—162°/0·4 mm., prisms, m. p. 82·5° [from benzene–light petroleum (b. p. 40—60°)] (Found: C, 73·6; H, 6·5. Calc. for $C_{15}H_{16}O_3$: C, 73·8; H, 6·6%). The ultraviolet absorption spectra showed a broad band with its centre at 258 mμ (log ε 4·13) in ethanol The dinitrophenylhydrazone crystallised from ethyl acetate–ethanol in orange needles, m. p. 174° (Found: C, 59·4; H, 4·9; N, 13·1. Calc. for $C_{21}H_{20}O_6N_4$: C, 59·4; H, 4·7; N, 13·2%). Turner[6] reports m. p. 77—78° and 174° for the ester and its dinitrophenylhydrazone respectively. The corresponding unsaturated acid was not obtained crystalline but gave a dinitrophenylhydrazone which crystallised from ethyl acetate in red needles, m. p. 240° (Found: N, 13·5. Calc. for $C_{20}H_{18}O_6N_4$: N, 13·7%) (Turner reports m. p. 239°).

6-Oxo-2-phenylcyclohexylacetic Acid (IX).—The unsaturated ester (VII) (5 g.) was hydrogenated in presence of colloidal palladium as before; the reduced *ester,* b. p. 155—160°/0·3 mm., crystallised from ethyl acetate–light petroleum (b. p. 40—60°) in needles, m. p. 77° (Found: C, 73·4; H, 7·3. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%). The *dinitrophenylhydrazone* crystallised from ethyl acetate–ethanol in yellow needles, m. p. 213—214° (Found: N, 12·9. $C_{21}H_{22}O_6N_4$ requires N, 13·1%). The *acid,* obtained by hydrolysing the ester with 5% alcoholic sodium hydroxide, crystallised from ethyl acetate–light petroleum (b. p. 40—60°), m. p. 140—141° (Found: C, 72·2; H, 6·6. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%), and gave a *semicarbazone,* plates (from ethanol), m. p. 209—210° (Found: C, 62·0; H, 6·4; N, 14·3. $C_{15}H_{19}O_3N_3$ requires C, 62·3; H, 6·6; N, 14·5%), and a *dinitrophenylhydrazone,* yellow needles (from ethyl acetate–methanol), m. p. 245° (Found: N, 13·4. $C_{20}H_{20}O_6N_4$ requires N, 13·6%).

1,2,3,4,4a,9,10,10a-Octahydro-1,9-dioxophenanthrene (X).—The acid (IX) (1·7 g.) was treated at 75° for 3 hr. with polyphosphoric acid, prepared from phosphoric oxide (8·4 g.) and 89% phosphoric acid (7·5 ml.). The product was decomposed with ice and extracted with ether, and the ethereal layer washed with 5% sodium hydroxide solution and then with water. The *diketone* (1·6 g.) obtained on evaporation of the ether crystallised from ethyl acetate–light petroleum (charcoal) in colourless plates, m. p. 150—152° (Found: C, 78·2; H, 6·7. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%). The *dinitrophenylhydrazone* crystallised from benzene–cyclohexane as an orange powder, m. p. 263—264° (Found: N, 14·4. $C_{20}H_{18}O_5N_4$ requires N, 14·2%).

Phenanthrene.—The above diketone (0·5 g.) was reduced by lithium aluminium hydride (0·5 g.) in ether. The crude diol (0·5 g.) was distilled over anhydrous potassium hydrogen sulphate and finally dehydrogenated by 30% palladium–charcoal (0·1 g.) at 300° for 1 hr. The resultant phenanthrene was worked up in the usual way and on crystallisation from ethanol formed plates (0·2 g.), m. p. and mixed m. p. 99°. The picrate had m. p. and mixed m. p. 142—143°.

Huang-Minlon Reduction of the Keto-acid (IX).—The keto-acid (1 g.), potassium hydroxide (1 g.), 85% hydrazine hydrate (1·5 ml.), and diethylene glycol (7 ml.) were heated under reflux for 2 hr. Water was then removed by distillation until the internal temperature reached 195°. The residue was refluxed for 8 hr. more. The cooled solution was diluted with water, then acidified, and the product taken up in ether. The residue (0·8 g.) obtained by evaporation of ether was dissolved in a few drops of ethyl acetate, and then light petroleum (b. p. 40—60°) was added until turbidity appeared. The *cis*-acid crystallised first and on recrystallisation melted at 168—170° (Found: C, 76·9; H, 8·2. Calc. for $C_{14}H_{18}O_2$: C, 77·1; H, 8·3%). The mother-liquor on further dilution with light petroleum (b. p. 40—60°) afforded the *trans*-acid, m. p. 112—114° (Found: C, 76·8: H, 8·4%).

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