272. *Synthesis of Polycyclic Compounds. Part IV.* Substituted 3-Alkylphenanthrenes.*

By J. C. BARDHAN, R. N. ADHYA, and K. C. BHATTACHARYYA.

The synthesis described in Part I * has been extended to the preparation of 3-methyl-, 1 : 3-, 2 : 3-, and 3 : 8-dimethyl-, 1 : 2 : 3-, 2 : 3 : 8-, and 1 : 3 : 8-trimethyl-, and 1 : 2 : 3 : 8-tetramethyl-phenanthrene.

IN Part I * a new synthesis of alkylphenanthrenes was described starting from ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate, $CO_2Et\cdot[CH_2]_3\cdot CO\cdot CH(CO_2Et)\cdot COMe$. In continuation of this work γ-ethoxycarbonyl-β-methylbutyryl chloride has been condensed with ethyl sodioacetoacetate giving ethyl 2-methyl-4 : 6-dioxoheptane-1 : 5-dicarboxylate (I), which reacted with phenethyl bromide in presence of sodium ethoxide to yield ethyl 2-methyl-4-oxo-7-phenylheptane-1 : 5-dicarboxylate (II; $R' = H$). This was cyclised with concentrated sulphuric acid at 0°, and the product on hydrolysis furnished γ-(2-carboxy-3 : 4-dihydro-1-naphthyl)-β-methylbutyric acid (III; $R' = H$). The ethyl ester of this acid was dehydrogenated with sulphur, to yield ethyl γ-(2-ethoxycarbonyl-1-naphthyl)-β-methylbutyrate (IV; $R = Et$, $R' = H$), which on condensation by means of sodium and then hydrolysis gave 1 : 2 : 3 : 4-tetrahydro-3-methyl-1-oxophenanthrene (V; $R' = R'' = H$). Similarly, the ester (IV; $R = Et$, $R' = H$) on treatment with sodium followed by methylation and hydrolysis afforded 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethyl-1-oxophenanthrene (V; $R' = H$, $R'' = Me$). The cyclic ketones (V; $R' = R'' = H$) and (V; $R' = H$, $R'' = Me$) on Clemmensen reduction and dehydrogenation, in the usual way, gave 3-methyl- [1] and 2 : 3-dimethyl-phenanthrene [2] respectively.

1 : 2 : 3 : 4-Tetrahydro-3-methyl-1-oxophenanthrene (V; $R' = R'' = H$) was condensed with methylmagnesium iodide in ethereal solution, the resultant alcohol dehydrated with 100% formic acid, and the unsaturated product dehydrogenated to 1 : 3-dimethylphenanthrene [3] by selenium. 1 : 2 : 3-Trimethylphenanthrene was prepared in a similar manner from 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethyl-1-oxophenanthrene (V; $R' = H$, $R'' = Me$). The constants for this hydrocarbon and its derivatives are, however, slightly lower than those previously recorded.[4]

In other experiments 2-*o*-tolylethyl bromide was condensed with the ester (I), yielding ethyl 2-methyl-4-oxo-7-*o*-tolylheptane-1 : 5-dicarboxylate (II; $R' = Me$). This was converted by way of ethyl γ-(2-ethoxycarbonyl-5-methyl-1-naphthyl)-β-methylbutyrate (IV; $R = Et$, $R' = Me$), 1 : 2 : 3 : 4-tetrahydro-3 : 8-dimethyl-1-oxophenanthrene (V; $R' = Me$, $R'' = H$), and 1 : 2 : 3 : 4-tetrahydro-2 : 3 : 8-trimethyl-1-oxophenanthrene (V; $R' = R'' = Me$), into 1 : 6-dimethyl- [2a] and 1 : 6 : 7-trimethyl-phenanthrene [5] by methods

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* Parts I, II, III, *J.*, 1956, 350, 355, and preceding paper.

[1] (*a*) Pschorr, *Ber.*, 1906, **39**, 3111; (*b*) Haworth, *J.*, 1932, 1132.

[2] (*a*) Haworth *et al.*, *J.*, 1934, 458; (*b*) Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1935, **57**, 1508.

[3] Bogert and Stamatoff, *Rec. Trav. chim.*, 1933, **52**, 584.

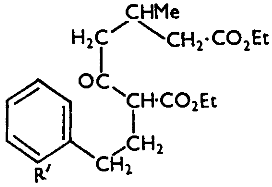
[4] Fieser and Daudt, *J. Amer. Chem. Soc.*, 1941, **63**, 782.

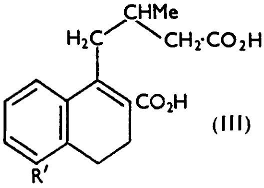
[5] Haworth and Bolam, *J.*, 1932, 2248.

developed in an analogous case. The properties and derivatives of these hydrocarbons agree with those recorded previously.

$CO_2Et{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Et){\cdot}COMe$ (I)

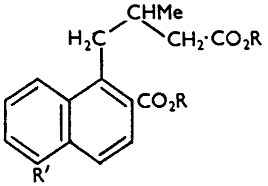
(II)

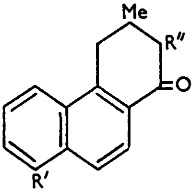




(III)

(IV)





(V)

The action of an excess of methylmagnesium iodide on an ethereal solution of 1 : 2 : 3 : 4-tetrahydro-3 : 8-dimethyl-1-oxophenanthrene (V; R′ = Me, R″ = H), followed by dehydration and dehydrogenation, gave 1 : 3 : 8-trimethylphenanthrene,[6] which has been prepared recently by an alternative route. In an analogous manner 1 : 2 : 3 : 4-tetrahydro-2 : 3 : 8-trimethyl-1-oxophenanthrene (V; R′ = R″ = Me) yielded 1 : 2 : 3 : 8-tetramethylphenanthrene, characterised as its picrate.

EXPERIMENTAL

γ-Ethoxycarbonyl-β-methylbutyric Acid.—Ethyl crotonate (34·2 g.) and ethyl malonate (48 g.) were refluxed with a solution of sodium (1·2 g.) in absolute ethanol (60 ml.) for 6 hr., yielding ethyl α-ethoxycarbonyl-β-methylglutarate[7] (73 g.), b. p. 136—138°/3 mm. This was converted into β-methylglutaric anhydride, b. p. 145—148°/3 mm., m. p. 41°, and γ-ethoxycarbonyl-β-methylbutyric acid, b. p. 141—143°/3 mm., in the usual way.[8]

Ethyl 2-Methyl-4 : 6-dioxoheptane-1 : 5-dicarboxylate (I).—To powdered sodium (10 g.) under ether (450 ml.), ethyl acetoacetate (56·4 ml.) in ether (125 ml.) was added slowly with cooling and occasional swirling. The suspension of the sodio-salt was cooled in a freezing mixture, and a solution of γ-ethoxycarbonyl-β-methylbutyryl chloride (from the acid, 75·3 g., and thionyl chloride, 33 ml.) in ether (150 ml.) was added dropwise with shaking. After remaining in the cold overnight the mixture was gently refluxed for 1 hr., and the product worked up in the usual manner. On repeated distillation the *diketo-ester* (86 g.) had b. p. 155—156°/3 mm. (Found : C, 58·5; H, 7·8. $C_{14}H_{22}O_6$ requires C, 58·7; H, 7·7%). It gives a crimson colour with ethanolic ferric chloride and probably contains a little of the isomeric *O*-acyl ester.

Ethyl 2-Methyl-4-oxo-7-phenylheptane-1 : 5-dicarboxylate (II; R′ = H).—The above diketo-ester (28·6 g.) was added with shaking to an ice-cold solution of sodium (2·3 g.) in absolute ethanol (40 ml.), and next morning the clear solution was mixed with phenethyl bromide (18·5 g.) and heated at 90° for 18 hr. On cooling, ice and dilute sulphuric acid were added, and the organic layer was collected in ether. The ethereal solution was washed, dried, and distilled. The substituted *keto-ester* (II; R′ = H) formed a pale yellow oil (14·7 g.), b. p. 191—193°/3 mm. (Found : C, 68·8; H, 8·1. $C_{20}H_{28}O_5$ requires C, 68·9; H, 8·0%). It gives a reddish-violet colour with ethanolic ferric chloride.

γ-(2-Carboxy-3 : 4-dihydro-1-naphthyl)-β-methylbutyric Acid (III; R′ = H).—The ester (II; R′ = H) (5 g.) was added dropwise with vigorous stirring during 5 min. to concentrated sulphuric

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[6] King and King, *J.*, 1953, 4158; 1954, 1373.

[7] Michael and Ross, *J. Amer. Chem. Soc.*, 1930, **52**, 4598; Hunsdiecker, *Ber.*, 1942, **75**, 1197; Auwers *et al.*, *Ber.*, 1891, **24**, 2887.

[8] Darbishire and Thorpe, *J.*, 1905, **87**, 1716; Stallberg-Stenhagen, *Arkiv Kemi, Min., Geol.*, 1948, **25**, *A*, No. 10; Linstead *et al.*, *J.*, 1950, 3332.

acid (30 ml.) cooled in a freezing mixture. The brownish liquid was stirred in the cold for 3 hr. more and then poured on powdered ice, and the mixture repeatedly extracted with ether. The ethereal solution was washed, dried, and evaporated. The residual oil was hydrolysed with a solution of potassium hydroxide (3 g.) in water (3 ml.) and ethanol (30 ml.) and worked up in the usual way. The *acid* separated from aqueous acetic acid (charcoal) (2·5 g.) as prisms, m. p. 166° (Found : C, 70·3; H, 6·6. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·5%). The *ethyl ester* had b. p. 188—190°/3 mm. (Found : C, 72·5; H, 7·9. $C_{20}H_{26}O_4$ requires C, 72·7; H, 7·8%).

*γ-(2-Carboxy-*1-*naphthyl)-β-methylbutyric Acid* (IV; R = R′ = H).—The preceding ester (8 g.) was heated with sulphur (0·8 g.) at 240—260° for 2 hr., and the product on distillation gave an oil (7·8 g.), b. p. 200—205°/3 mm. This was hydrolysed with 10% ethanolic potassium hydroxide, and the crude acid (7·5 g.) purified by esterification. The *ethyl ester* (IV; R = Et, R′ = H), b. p. 202—203°/3 mm. (Found : C, 73·2; H, 7·4. $C_{20}H_{24}O_4$ requires C, 73·1; H, 7·3%), on hydrolysis gave the *acid*, prisms, m. p. 169° (from benzene; charcoal) (Found : C, 70·9; H, 6·1. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

1 : 2 : 3 : 4-*Tetrahydro*-3-*methyl*-1-*oxophenanthrene* (V; R′ = R″ = H).—The ester (IV; R = Et, R′ = H) (9·8 g.), benzene (25 ml.), and finely divided sodium (0·8 g.) were heated on the steam-bath until the sodium dissolved and the liquid was filled with the crystalline sodio-derivative of the condensation product (3 hr.). This was decomposed with ice and dilute hydrochloric acid, and the benzene layer isolated, washed with aqueous sodium carbonate, dried, and evaporated. The crude oil (10 g.) was hydrolysed with hot hydrochloric acid (20 ml.) and acetic acid (40 ml.) for 10 hr. The cyclic *ketone*, b. p. 182—183°/3 mm., solidified. From light petroleum (b. p. 60—80°) it formed prisms, m. p. 102—103° (Found : C, 85·9; H, 6·7. $C_{15}H_{14}O$ requires C, 85·7; H, 6·6%). The *semicarbazone* crystallises from ethanol in plates, m. p. 262° (Found : C, 71·5; H, 6·4. $C_{16}H_{17}ON_3$ requires C, 71·9; H, 6·3%).

1 : 2 : 3 : 4-*Tetrahydro*-2 : 3-*dimethyl*-1-*oxophenanthrene* (V; R′ = H, R″ = Me).—The solid sodio-salt produced by the Dieckmann condensation of the ester (IV; R = Et, R′ = H) (10 g.), finely divided sodium (0·9 g.), and benzene (25 ml.) was cooled in ice, methyl iodide (6 ml.) added, and the reaction allowed to proceed at room temperature. The mixture was then refluxed for 20 hr., and the product (11 g.), isolated in the usual way, was hydrolysed with hydrochloric acid (22 ml.) and acetic acid (44 ml.) as described above. The *oxo-compound* (V; R′ = H, R″ = Me) on distillation afforded an oil (3·8 g.), b. p. 182—187°/3 mm., which solidified and afforded colourless needles, m. p. 99°, from light petroleum (b. p. 40—60°) (Found : C, 85·6; H, 7·2. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). The *semicarbazone* separated from ethanol in prisms, m. p. 253° (decomp.) (Found : C, 72·1; H, 6·7. $C_{17}H_{19}ON_3$ requires C, 72·6; H, 6·7%).

3-*Methylphenanthrene*.—The ketone (V; R′ = R″ = H) (1 g.) was reduced by boiling with amalgamated zinc (10 g.), concentrated hydrochloric acid (15 ml.), and water (3 ml.) for 24 hr. On distillation over sodium 1 : 2 : 3 : 4-*tetrahydro*-3-*methylphenanthrene* formed a pale yellow oil (0·5 g.), b. p. 160—163°/3 mm. (Found : C, 91·5; H, 8·2. $C_{15}H_{16}$ requires C, 91·8; H, 8·2%). The product was dehydrogenated with selenium (1 g.) at 310—320° for 24 hr. The hydrocarbon was isolated and distilled over sodium, and recrystallised from ethanol in needles, m. p. 60—61° (Found : C, 93·8; H, 6·2. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·3%). The picrate crystallises from ethanol in needles, m. p. 136—137° (Found : C, 59·5; H, 3·6. Calc. for $C_{15}H_{12},C_6H_3O_7N_3$: C, 59·8; H, 3·5%). Pschorr[1b] gives m. p.s 65° and 141°, and Haworth[1b] 62—63° and 137—138° respectively.

2 : 3-*Dimethylphenanthrene*.—The cyclic ketone (V; R′ = H, R″ = Me) was reduced by Clemmensen's method, and the product distilled over sodium. 1 : 2 : 3 : 4-*Tetrahydro*-2 : 3-*dimethylphenanthrene* had b. p. 165°/3 mm. (Found : C, 91·3; H, 8·7. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%). 2 : 3-Dimethylphenanthrene, obtained on dehydrogenation with selenium, crystallised from ethanol in prisms, m. p. 78—79° (Found : C, 93·4; H, 6·9. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). The picrate separated in orange needles (from ethanol), m. p. 145—146° (Found : C, 60·2; H, 4·0. Calc. for $C_{16}H_{14},C_6H_3O_7N_3$: C, 60·7; H, 3·9%). Fieser and Hershberg[2b] give m. p.s 78—78·5° and 146—147°, and Haworth *et al.*[2a] give 65—66° and 138—140° respectively.

1 : 3-*Dimethylphenanthrene*.—The ketone (V; R′ = R″ = H) (1·2 g.), in dry ether (30 ml.), was added slowly at room temperature to ethereal methylmagnesium iodide (from magnesium, 0·6 g., methyl iodide, 2 ml., and ether, 30 ml.). The mixture was gently boiled for 4 hr., and decomposed with ice and dilute sulphuric acid, the ethereal layer was separated and dried (K_2CO_3), and the solvent removed. The alcohol (1·2 g.) was heated with 100% formic acid (3 ml.) for 0·5 hr., and the product (1 g.) on dehydrogenation with selenium afforded 1 : 3-dimethylphenanthrene, which crystallised from ethanol in prisms, m. p. 75—76° (lit.,[3] 76—77°)

(Found : C, 93·0; H, 6·7%). The picrate crystallised from ethanol in orange needles, m. p. 154—155° (lit.,[3] 154—155°) (Found : C, 60·3; H, 4·0%).

1 : 2 : 3-*Trimethylphenanthrene*.—This was prepared by the action of methylmagnesium iodide on 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethyl-1-oxophenanthrene as described above. It had b. p. 180°/3 mm., but solidified ; it recrystallised from ethanol as plates, m. p. 58—59° (Found : C, 93·1; H, 7·3. Calc. for $C_{17}H_{16}$: C, 92·8; H, 7·2%). The picrate formed bright orange needles (from ethanol), m. p. 181° (Found : C, 61·2; H, 4·3. Calc. for $C_{17}H_{16},C_6H_3O_7N_3$: C, 61·5; H, 4·2%). The trinitrobenzene derivative formed yellow needles (from ethanol), m. p. 192°. Fieser and Daudt [4] record m. p.s 63·8—64·8°, 187—188°, and 200·7—201·5°, respectively.

Ethyl 2-Methyl-4-oxo-7-o-tolylheptane-1 : 5-dicarboxylate (II ; R′ = Me).—This was prepared as described above for an analogous case, from sodium (2·3 g.), absolute ethanol (40 ml.), the ester (I) (28·6 g.), and 2-*o*-tolylethyl bromide (19·9 g.). The *keto-ester* (II ; R′ = Me) (14 g.), b. p. 206—208°/3 mm. (Found : C, 69·4; H, 8·4. $C_{21}H_{30}O_5$ requires C, 69·6; H, 8·3%), gave a positive ferric reaction.

γ-(2-Carboxy-5-methyl-3 : 4-dihydro-1-naphthyl)-β-methylbutyric Acid (III ; R′ = Me).—The preceding keto-ester was cyclised with concentrated sulphuric acid as described above and the product hydrolysed in the usual way. The *acid* (III ; R′ = Me) was purified by repeated crystallisation from dilute acetic acid (charcoal), and formed colourless prisms, m. p. 212° (Found : C, 70·9; H, 6·8. $C_{17}H_{20}O_4$ requires C, 70·8; H, 6·9%). The *diethyl ester* distills at 200—203°/3 mm. (Found : C, 73·1; H, 8·2. $C_{21}H_{28}O_4$ requires C, 73·2; H, 8·1%).

γ-(2-Carboxy-5-methyl-1-naphthyl)-β-methylbutyric Acid (IV ; R = H, R′ = Me).—The above diethyl ester was heated with sulphur in the usual way and the product on hydrolysis gave the *acid* (IV ; R = H, R′ = Me), which recrystallised from acetic acid as needles, m. p. 202° (Found : C, 71·3; H, 6·2. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%). The corresponding *diethyl ester* (IV ; R = Et, R′ = Me) had b. p. 210—212°/3 mm. (Found : C, 73·6; H, 7·6. $C_{21}H_{26}O_4$ requires C, 73·7; H, 7·6%).

1 : 2 : 3 : 4-*Tetrahydro-3 : 8-dimethyl-1-oxophenanthrene* (V ; R′ = Me, R = H).—This was prepared according to Dieckmann's procedure followed by hydrolysis of the product with hydrochloric–acetic acid. The *ketone* (b. p. 187—189°/3 mm.) readily solidified and from benzene–light petroleum (b. p. 60—80°) formed prisms, m. p. 130° (Found : C, 85·9; H, 7·2. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). The *semicarbazone* separated from aqueous ethanol in prisms, m. p. 275—276° (Found : C, 72·2; H, 6·8. $C_{17}H_{19}ON_3$ requires C, 72·6; H, 6·7%).

1 : 2 : 3 : 4-*Tetrahydro-2 : 3 : 8-trimethyl-1-oxophenanthrene* (V ; R′ = R″ = Me).—The product of the sodium condensation described above was methylated and hydrolysed in the usual way. The *ketone* (V ; R′ = R″ = Me) (b. p. 192—194°/3 mm.) solidified and crystallised from light petroleum (b. p. 60—80°) as needles, m. p. 133° (Found : C, 85·9; H, 7·6. $C_{17}H_{18}O$ requires C, 85·7; H, 7·5%). The *semicarbazone* separated from ethanol in prisms, m. p. 225° (Found : C, 73·0; H, 7·1. $C_{18}H_{21}ON_3$ requires C, 73·2; H, 7·1%).

1 : 6-*Dimethylphenanthrene*.—The cyclic ketone (V ; R′ = Me, R″ = H) was reduced by Clemmensen's method, and the product dehydrogenated with selenium. 1 : 6-Dimethylphenanthrene crystallised from methanol in plates, m. p. 87—88° (lit.,[2a] 87—88°) (Found : C, 93·4; H, 6·9%), and the picrate in orange needles, m. p. 139—140° (lit.,[2a] 134°) (Found : C, 60·3; H, 4·0%).

1 : 6 : 7-*Trimethylphenanthrene*.—This was prepared in an analogous manner from the ketone (V ; R′ = R″ = Me). It crystallised from absolute ethanol in plates, m. p. 124° (lit.,[5] 123—124°) (Found : C, 92·9; H, 7·3%). The picrate, orange needles from ethanol, had m. p. 165—166° (lit.,[5] 165—166°) (Found : C, 61·1; H, 4·3%).

1 : 3 : 8-*Trimethylphenanthrene*.—The ketone (V ; R′ = Me, R″ = H) (1·5 g.) was treated with methylmagnesium iodide from magnesium (0·7 g.), methyl iodide (2·5 ml.), and ether (40 ml.), and the mixture boiled for 4 hr. The alcohol was isolated, dehydrated, and dehydrogenated as described above. The pure hydrocarbon separated from absolute ethanol (charcoal) in needles, m. p. 116° (lit.,[6] 116°) (Found : C, 92·9; H, 7·3%). The picrate crystallised from ethanol in orange needles, m. p. 174° (lit.,[6] 174—175°) (Found : C, 61·2; H, 4·2%), and the trinitrobenzene derivative in bright yellow needles, m. p. 188° (lit.,[6] 188°).

1 : 2 : 3 : 8-*Tetramethylphenanthrene*, prepared similarly from the ketone (V ; R′ = R″ = Me), crystallised from absolute ethanol in needles, m. p. 96—97° (Found : C, 92·6; H, 7·7. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%) and the *picrate* from ethanol in orange-red needles, m. p. 193° (Found : C, 62·0; H, 4·5. $C_{18}H_{18},C_6H_3O_7N_3$ requires C, 62·2; H, 4·5%).

UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY, CALCUTTA. [*Received, October* 31*st*, 1955.]