532. *Studies in Polycyclic Systems. Part I. A New Synthesis of Picene.**

By D. NASIPURI.

Picene is prepared by a method starting with condensation of ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate with 2-1′-naphthylethyl bromide, the further rings being built on by Dieckmann condensation and reaction with the methiodide of 4-piperidinobutan-2-one. The method affords a convenient route also to methylpicenes and the preparation of 4-methyl- and 2 : 9-dimethyl-picene is reported.

A NUMBER of routes has been used for the synthesis of picene and its derivatives,[1] but most of them are lengthy and give a poor overall yield. In a more recent synthesis by Phillips,[2] the yield is comparatively high but the method involves separation of isomers in at least one stage. In view of the excellent results obtained by Wilds and his co-workers [3,4] in the preparation of chrysene derivatives by the application of the

---

* A preliminary account of this work appeared in *Chem. and Ind.*, 1956, 795, and in *Naturwiss.*, 1956, **43**, 469.

[1] Newman, *J. Org. Chem.*, 1944, **9**, 518, and references cited therein.

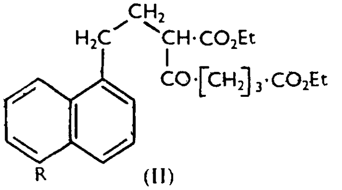
[2] (*a*) Phillips, *J. Amer. Chem. Soc.*, 1953, **75**, 3223; (*b*) Phillips and McWhorter, *ibid.*, 1955, **77**, 3856; (*c*) Phillips and Tuites, *ibid.*, 1956, **78**, 5438.

[3] Wilds and Shunk, *ibid.*, 1943, **65**, 469.

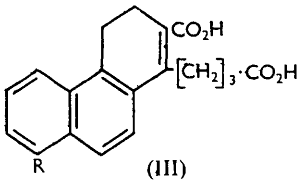
[4] Wilds and Werth, *J. Org. Chem.*, 1952, **17**, 1149.

Robinson–Mannich base synthesis [5] of unsaturated ketones, similar methods were investigated for the synthesis of alkylpicenes. Suitable starting materials would be 2-alkoxycarbonyl-1 : 2 : 3 : 4-tetrahydro-1-oxochrysenes (V). Ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate [6] (I) was therefore alkylated with 2-1′-naphthylethyl bromide; the product (II; R = H) on cyclodehydration with concentrated sulphuric acid and subsequent saponification gave γ-(2-carboxy-3 : 4-dihydro-1-phenanthryl)butyric acid (III; R = H) in an overall yield of 40%. The ester of the dihydro-acid was dehydrogenated with sulphur, and the dimethyl ester of the aromatic acid (IV; R = H) underwent Dieckmann cyclisation smoothly. The resultant sodio-derivative was treated *in situ* with a methanolic solution of 4-piperidinobutan-2-one methiodide [4] to afford the tetrahydrochrysene derivative (VI; R = H, R′ = Me) in about 60% yield. A preliminary attempt to cyclise this compound by two-stage aqueous alkaline procedure of Wilds and Close [7] proved unsatisfactory, presumably owing to the high melting point and low solubility. Cyclisation by acid, however, gave good results; the pentacyclic ketone (VII; R = H), obtained in about 70% yield, was reduced by lithium aluminium hydride, and the resultant alcohol was converted into picene by heating it with 30% palladium–charcoal.[8]

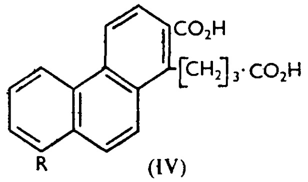
$EtO_2C\cdot[CH_2]_3\cdot CO\cdot CH(CO_2Et)\cdot CO\cdot CH_3$ (I)



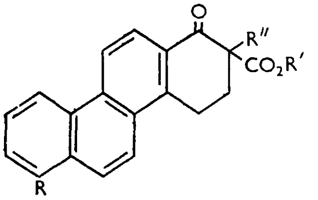
(II)



(III)

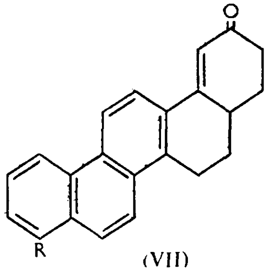


(IV)

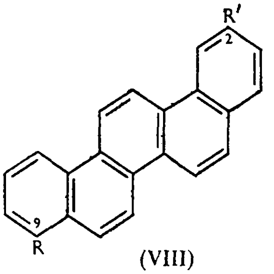


(V) : R″ = H

(VI) : R″ = $CH_2\cdot CH_2\cdot CO\cdot CH_3$



(VII)



(VIII)

The Dieckmann condensation products of the dialkyl esters of the acids (III and IV; R = H) on hydrolysis gave 1 : 2 : 3 : 4 : 11 : 12-hexahydro- and 1 : 2 : 3 : 4-tetrahydro-1-oxochrysene respectively which were previously prepared by other workers.[9, 10]

Lastly, the use of 2-(5-methyl-1-naphthyl)ethyl bromide [11] in the above series of reactions led to the substituted pentacyclic ketone (VII; R = Me) which was converted into (*a*) 4-methyl- and (*b*) 2 : 9-dimethyl-picene by (*a*) reduction with lithium aluminium hydride and (*b*) a Grignard reaction with methylmagnesium iodide, followed by dehydration and dehydrogenation with palladium–charcoal. The hydrocarbons were characterised by their ultraviolet absorption spectra and formation of 2 : 4 : 7-trinitrofluorenone complexes.[12]

---

[5] du Feu, McQuillin, and Robinson, *J.*, 1937, 53.

[6] Bardhan and Nasipuri, *J.*, 1956, 350.

[7] Wilds and Close, *J. Amer. Chem. Soc.*, 1946, **68**, 83.

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

[9] Robinson and Thompson, *J.*, 1939, 1739.

[10] (*a*) Bachmann and Struve, *J. Org. Chem.*, 1940, **5**, 416; (*b*) Cook and Schoental, *J.*, 1945, 288.

[11] Bardhan, Nasipuri, and Mukherjee, *J.*, 1957, 921.

[12] Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727.

EXPERIMENTAL

γ-(2-*Carboxy*-3 : 4-*dihydro*-1-*phenanthryl*)*butyric Acid* (III; R = H).—To a cold mixture of ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (27·2 g.) and ethanolic sodium ethoxide [from sodium (2·3 g.) and ethanol (60 ml.)] was added 2-1′-naphthylethyl bromide (23·5 g.), and the whole was heated under reflux in the water-bath at 90° for 15 hr. After removal of most of the ethanol at the water-pump, the residue was treated with cold 2N-sulphuric acid, and the heavy organic matter taken up in ether. The ethereal extract was washed with water, dried, and evaporated, first at the water-pump, then at the oil-pump to remove the lower-boiling fractions. The residue (28—30 g.) was cyclised by concentrated sulphuric acid (2 vols.) at $-10°$ during 15 min., in small lots (6 g.) at a time. The dark brown products from the combined lots were poured over crushed ice and extracted with ether. The residue after the evaporation of ether was hydrolysed by 5% ethanolic potassium hydroxide to give the crude *acid* (12 g., 40%) which crystallised from dilute acetic acid as prisms, m. p. 203° (Found: C, 73·7; H, 5·8. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%). The diethyl ester was obtained as a viscous oil, b. p. 220—225°/0·1 mm., by refluxing the acid with ethanol and concentrated sulphuric acid.

1 : 2 : 3 : 4 : 11 : 12-*Hexahydro*-1-*oxochrysene*.—A mixture of the foregoing ester (1 g.), finely divided sodium (70 mg.), and dry benzene (6 ml.) was heated under reflux until the formation of the solid sodio-derivative was complete (2 hr.). The product was decomposed with ice and dilute hydrochloric acid, and the organic layer was separated with some more benzene. The residue after the evaporation of benzene was hydrolysed by heating it with acetic acid (10 ml.) and concentrated hydrochloric acid (5 ml.) and worked up as usual, to give 1 : 2 : 3 : 4 : 11 : 12-hexahydro-1-oxochrysene, m. p. 159° (from benzene–light petroleum) (Found: C, 87·3; H, 6·7. Calc. for $C_{18}H_{16}O$: C, 87·1; H, 6·5%). Robinson and Thompson [9] give m. p. 154—156°.

γ-(2-*Carboxy*-1-*phenanthryl*)*butyric Acid* (IV; R = H).—The diethyl ester of the acid (III; R = H) (3·6 g.) was heated with powdered sulphur (0·32 g.) in a nitrate-bath at 245—250° for 2 hr. and the resultant brown product was taken up in ethanol and hydrolysed with potassium hydroxide in the usual way, to give the aromatic *acid* (3·2 g.) which crystallised from aqueous methanol in needles, m. p. 228° (Found: C, 74·1; H, 5·2. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). The *dimethyl ester* crystallised from methanol in needles, m. p. 72—73° (Found: C, 75·2; H, 6·1. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%).

1 : 2 : 3 : 4-*Tetrahydro*-1-*oxochrysene*.—The above dimethyl ester (1 g.) in a suspension of sodium (70 mg.) in dry benzene (7 ml.) was heated under reflux with the addition of one drop of methanol. Formation of sodio-derivative was completed in about 1 hr. The product was worked up and hydrolysed as described above, to give 1 : 2 : 3 : 4-tetrahydro-1-oxochrysene (0·40 g.) in light yellow plates (from benzene), m. p. 226—227° (Found: C, 87·6; H, 5·8. Calc. for $C_{18}H_{14}O$: C, 87·8; H, 5·7%). Bachmann *et al.*[10a] give m. p. 228—229° and Cook and Schoental [10b] 227—228°.

1 : 2 : 3 : 4-*Tetrahydro*-2-*methoxycarbonyl*-1-*oxo*-2-3′-*oxobutylchrysene* (VI; R = H, R′ = Me).—To the sodio-derivative of the oxo-ester (V; R = H, R′ = Me) prepared from the dimethyl ester of the acid (IV; R = H) (2·7 g.), sodium (200 mg.), and benzene (30 ml.) as described above, was added with cooling a solution of the methiodide of 4-piperidinobutan-2-one (2·5 g., 2 mol.) in anhydrous methanol (15 ml.). The solid disappeared after a few minutes' shaking and the solution was left at the room temperature overnight. Next day, the reaction was completed by refluxing the mixture in the steam-bath for 1 hr. After cooling, the solution was diluted with water, the precipitated solid was extracted thoroughly with hot benzene, and the benzene extract washed successively with water, dilute alkali, and dilute acid. After evaporation of the solvent, the residual solid crystallised from ethyl acetate, to give 1 : 2 : 3 : 4-*tetrahydro*-2-*methoxycarbonyl*-1-*oxo*-2-3′-*oxobutylchrysene* (1·9 g., 60%), m. p. 192—195°. Further crystallisations from ethyl acetate (charcoal) afforded plates, m. p. 209° (Found: C, 77·2; H, 5·9. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%). The corresponding 2-*ethoxycarbonyl derivative* was also prepared from the diethyl ester of the acid (IV; R = H) in nearly the same yield and crystallised from ethyl acetate in cluster of plates, m. p. 195° (Found: C, 77·6; H, 6·3. $C_{25}H_{24}O_4$ requires C, 77·3; H, 6·2%).

2 : 3 : 4 : 4a : 5 : 6-*Hexahydro*-2-*oxopicene* (VII; R = H).—The above dioxo-ester (VI; R = H, R′ = Me) (2 g.) was refluxed in acetic acid (50 ml.), concentrated hydrochloric acid

(25 ml.), and water (5 ml.) for 15 hr. under nitrogen. After cooling, the mixture was diluted with water, and the precipitated solid was filtered off, to give the unsaturated *ketone* (VII; R = H) (1·1 g., 70%), m. p. 270—275°. Further crystallisations from benzene gave colourless crystals, m. p. 295° (Found: C, 88·7; H, 6·1. $C_{22}H_{18}O$ requires C, 88·6; H, 6·0%). The analogous 2-ethoxycarbonyl derivative (VI; R = H, R′ = Et) was similarly cyclised to the same ketone.

Picene.—A solution of the foregoing ketone (0·3 g.) in tetrahydrofuran (15 ml.) was added to lithium aluminium hydride (0·3 g.), suspended in ether (10 ml.), the mixture was heated under reflux for 1 hr., then decomposed with ethanol and dilute acid, and the organic matter was taken up into benzene and washed with water. The residue (0·3 g.) on evaporation of the solvent was heated with 30% palladium–charcoal (70 mg.) at 340° for 1 hr. The melt was extracted with hot benzene and, after evaporation, the product was sublimed in a high vacuum, to give picene (0·1 g.) which crystallised from xylene in fluorescent plates, m. p. 365—366° (Found: C, 94·8; H, 5·1. Calc. for $C_{22}H_{14}$: C, 95·0; H, 5·0%). The identity was confirmed by a mixed m. p. determination and ultraviolet absorption spectroscopy.[13] The 2 : 4 : 7-trinitrofluorenone derivative separated from benzene in red needles, m. p. 256—257° (Found: C, 70·5; H, 3·1; N, 7·3. Calc. for $C_{22}H_{14},C_{13}H_5O_7N_3$: C, 70·8; H, 3·2; N, 7·1%) (Orchin and Woolfolk[12] record m. p. 257—257·8°).

γ-(*2-Carboxy-3 : 4-dihydro-8-methyl-1-phenanthryl*)*butyric Acid* (III; R = Me).—2-(5-Methyl-1-naphthyl)ethyl bromide (25 g.) was added to a cold mixture of ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (27·2 g.) and ethanolic sodium ethoxide [from sodium (2·3 g.) and absolute ethanol (60 ml.)] and heated under reflux for 15 hr. The product was worked up in the usual way. The crude oxo-ester (II; R = Me) (38 g.), on cyclisation with sulphuric acid as described above, gave the *acid* (III; R = Me) (12 g.), m. p. 225° (from aqueous methanol) (Found: C, 73·8; H, 6·3. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%). The dimethyl ester boiled at 230—235°/0·1 mm.

γ-(*2-Carboxy-8-methyl-1-phenanthryl*)*butyric Acid* (IV; R = Me).—The preceding dihydro-ester was dehydrogenated with sulphur in the usual way and on hydrolysis afforded the *acid* (IV; R = Me) which crystallised from methanol in prisms, m. p. 238° (Found: C, 74·6; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·5%). The *dimethyl ester* formed needles (from methanol), m. p. 113° (Found: C, 75·5; H, 6·3. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·3%).

1 : 2 : 3 : 4-*Tetrahydro-2-methoxycarbonyl-7-methyl-1-oxo-2-3′-oxobutylchrysene* (VI; R = R′ = Me).—The preceding ester (5 g.) was added to a suspension of sodium methoxide [from sodium (0·4 g.) and methanol (0·5 g.) in dry benzene (20 ml.)] and the mixture was refluxed for 2 hr. under nitrogen. To the sodio-derivative thus formed was gradually added, with cooling, a solution of the methiodide prepared from 4-piperidinobutan-2-one (5 g.) and the whole left overnight. The reaction was completed next day by 1 hour's heating on the steam-bath and the product was worked up as in the analogous case, to afford the *dioxo-ester* (VI; R = R′ = Me) (3·3 g., 65%), m. p. 233° (from ethyl acetate) (Found: C, 76·9; H, 6·3. $C_{25}H_{24}O_4$ requires C, 77·3; H, 6·2%).

2 : 3 : 4 : 4a : 5 : 6-*Hexahydro-9-methyl-2-oxopicene* (VII; R = Me).—The dioxo-ester (VI; R = R′ = Me) (1 g.) was heated with acetic acid (40 ml.), concentrated hydrochloric acid (20 ml.), and water (5 ml.) for 20 hr. under nitrogen. The solution was diluted with water, and the precipitate was collected and crystallised from benzene, to give the *ketone* (VII; R = Me) (0·5 g.), m. p. 313—314° (from benzene) (Found: C, 88·7; H, 6·3. $C_{23}H_{20}O$ requires C, 88·5; H, 6·4%).

4-*Methylpicene* (VIII; R = Me, R′ = H). The preceding ketone (200 mg.) was reduced by lithium aluminium hydride (100 mg.) in tetrahydrofuran (20 ml.), and the resultant alcohol was heated with 30% palladium–charcoal (40 mg.) at 340° for 1 hr., then sublimed in a high vacuum, to yield 4-methylpicene (80 mg.) which crystallised from chloroform in almost colourless leaflets, m. p. 370—372° (sealed tube) (Found: C, 94·3; H, 5·5. Calc. for $C_{23}H_{16}$: C, 94·5; H, 5·5%). Its 2 : 4 : 7-trinitrofluorenone complex formed a red powder (from acetic acid), m. p. 270° (Found: C, 71·05; H, 3·6; N, 7·0. Calc. for $C_{23}H_{16},C_{13}H_5O_7N_3$: C, 71·2; H, 3·5; N, 6·9%). Phillips and McWhorter[2b] give 372—374° and 267—268° as the respective m. p.s. The ultraviolet absorption spectrum is identical with that described by Phillips *et al.*

2 : 9-*Dimethylpicene* (VIII; R = R′ = Me).—A solution of the ketone (VII; R = Me) (300 mg.) in dry benzene (30 ml.) was treated with an excess of methylmagnesium iodide in

---

[13] Clar and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235.

ether, and the resultant alcohol was dehydrated and dehydrogenated by 30% palladium–charcoal (80 mg.) at 340° for 1 hr. The product was taken up in hot benzene, chromatographed on alumina, and crystallised from benzene, to yield 2 : 9-dimethylpicene (140 mg.), m. p. 303—304° (Found: C, 93·8; H, 5·9. Calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9%). It caused no m. p. depression when mixed with an authentic specimen and the ultraviolet absorption spectrum is very similar to that of picene. Ruzicka and Hofmann [14] give m. p. 305—306°, and Newman and Cline [15] 304·2—304·8°. The 2 : 4 : 7-trinitrofluorenone complex crystallised from benzene in red needles, m. p. 257° (Found: C, 71·4; H, 3·6; N, 6·9. Calc. for $C_{24}H_{18},C_{13}H_5O_7N_3$: C, 71·5; H, 3·7; N, 6·8%). Newman *et al.* give m. p. 257·8—258·6°.

The author thanks Professor J. C. Bardhan for his kind encouragement and Mrs. Chhabi Dutta for microanalyses. He is indebted to Professor M. S. Newman for gifts of picene and 2 : 9-dimethylpicene.

UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA, INDIA. [*Received, February 27th,* 1958.]

[14] Ruzicka and Hofmann, *Helv. Chim. Acta,* 1937, **20**, 1155.
[15] Newman and Cline, *J. Org. Chem.*, 1951, **16**, 934.