656. *Polycyclic Systems. Part IX.*[1] *A New Synthesis of Indeno(2′,3′ : 1,2)phenanthrene.**

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A new synthesis of indeno(2′,3′:1,2)phenanthrene by the application of Robinson–Mannich base ring-extension procedure to methyl 3′-oxo-1,2-cyclopentenophenanthrene-4-carboxylate (III; R = H) is described. The latter is obtained from 2-1′-naphthylethyl bromide and ethyl β-oxoadipate by successive alkylation, Bougault cyclisation, aromatisation, and Dieckmann condensation. The method with appropriate variation affords a convenient route to analogues especially suited to synthesis of compounds obtained as minor products during the dehydrogenation of steroids.

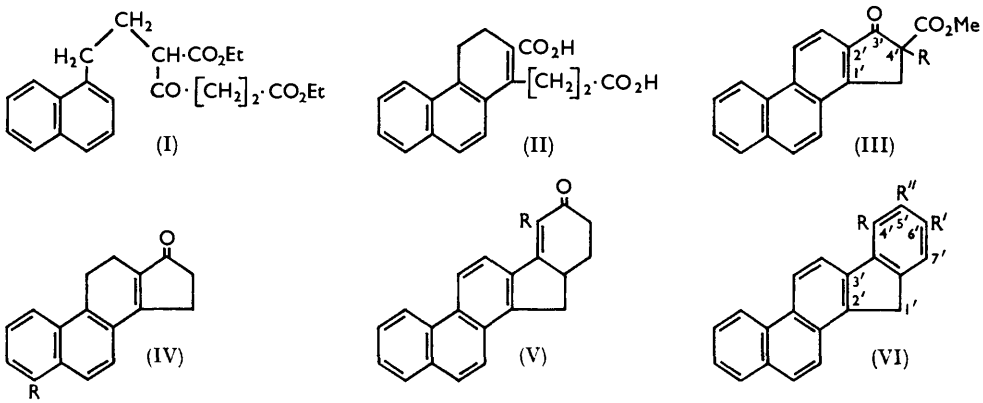
Several indeno(2′,3′:1,2)phenanthrene derivatives have been isolated as minor products on dehydrogenation of various steroidal compounds, *e.g.*, cholesterol,[2] ergosterol,[3] phytosterols,[4] and bile acids.[5] Recently, another hydrocarbon of uncertain identity but probably containing the same ring system has been reported in connection with helvolic acid.[6] There is, however, no satisfactory mechanism as yet, which can explain the formation of these hydrocarbons from steroids, the obvious cyclisation of the steroid side-chain with the original D-ring[7] having been disproved by the synthetic experiments of Cook *et al.*[8] In fact, except for the 4′-methyl derivative from cholic acid and the 6′-methyl derivative from strophanthidin,[9] the hydrocarbons are still not conclusively identified, although from the study of the absorption spectra and other physical and chemical properties, they are best to be represented as indeno(2′,3′:1,2)phenanthrenes.[8,10] An alternative mechanism proposed by Bergmann,[9] involving the opening of ring D and formation of a new five-membered ring in its place with the inclusion of the angular 13-methyl group, explains the formation of the 6′-methyl derivative from strophanthidin, but cannot be generally accepted in absence of further synthetic proof. The classical

* A preliminary account of this work appeared in *Science and Culture*, 1956, **22**, 232.

[1] Part VIII, Nasipuri, Roy, and Rakshit, *J. Indian Chem. Soc.*, 1960, **37**, 369.
[2] Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1.
[3] Diels and Karstens, *Annalen*, 1930, **478**, 129; Ruzicka, Goldberg, and Thomann, *Helv. Chim. Acta*, 1933, **16**, 812; Ruzicka and Goldberg, *ibid.*, 1935, **18**, 434; Diels and Stephan, *Annalen*, 1937, **527**, 279.
[4] Ruzicka and Goldberg, *Helv. Chim. Acta*, 1937, **20**, 1245.
[5] Ruzicka, Thomann, Brandenberger, Furter, and Goldberg, *Helv. Chim. Acta*, 1934, **17**, 200.
[6] Cram and Allinger, *J. Amer. Chem. Soc.*, 1956, **78**, 5278.
[7] Rosenheim and King, *Chem. and Ind.*, 1933, **52**, 299.
[8] Cook, Hewett, Mayneord, and Roe, *J.*, 1934, 1927.
[9] Bergmann, *J. Amer. Chem. Soc.*, 1938, **60**, 2306.
[10] Cook, Dansi, Hewett, Iball, Mayneord, and Roe, *J.*, 1935, 1319.

methods for the synthesis of this ring system are few and require generally inaccessible starting materials. Besides, they involve, in one step or other, intramolecular cyclisation requiring prolonged treatment with anhydrous aluminium chloride, a process which might cause the migration of alkyl groups.[11] A more reliable method is, therefore, desirable. The present communication describes a new synthesis on lines similar to those followed in our laboratory for the synthesis of alkylpicenes.[12]

The method consists in condensation of the methiodide of a suitable Mannich base with the sodio-derivative of methyl-3′-oxo-1,2-cyclopentenophenanthrene-4′-carboxylate (III; R = H) and cyclisation of the resulting dioxo-ester to the unsaturated ketone (V) which is then easily converted into the aromatic system (VI). In order to prepare the desired β-oxo-ester (III; R = H), ethyl β-oxoadipate [13] was treated with 2-1′-naphthylethyl bromide and the crude product (I) was cyclodehydrated with concentrated sulphuric acid to give β-(2-carboxy-3,4-dihydro-1-phenanthryl)propionic acid (II). This was dehydrogenated to the corresponding aromatic acid, whose dimethyl ester was submitted to Dieckmann cyclisation. The sodio-derivative of the β-oxo-ester (III; R = H), thus obtained, was treated *in situ* with a cold methanolic solution of 4-piperidinobutan-2-one methiodide.[14] The ester (III; R = ·CH_2·CH_2·COMe) was isolated from the reaction mixture in about 70% yield and hydrolysed by a refluxing mixture of glacial acetic acid and hydrochloric acid to the pentacyclic ketone (V; R = H) in an excellent yield. The ketone was smoothly reduced with lithium aluminium hydride and subsequently dehydrated and dehydrogenated to indeno(2′,3′:1,2)phenanthrene (VI; R = R′ = R″ = H) by heating it with 30% palladium–charcoal,[15] the total over-all yield being 10—12%.



The ketone (IV; R = H) and its aromatic analogue were prepared by Dieckmann cyclisation of the dialkyl ester of appropriate acid (as II) and found to be identical with the ketones obtained by Bardhan [13a] and Bachmann *et al.*,[16] respectively. In a similar way, 2-(5-methyl-1-naphthyl)ethyl bromide [17] was converted into 3,4-dihydro-8-methyl-3′-oxo-1,2-cyclopentenophenanthrene (IV; R = Me) which had been prepared by Woodward *et al.*[18] by another method.

[11] Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publ. Co., New York, 1941, pp. 77—94; Price and Adams, "Organic Reactions," John Wiley & Sons, Inc., New York, 1947, Vol. III, pp. 9—10.
[12] Nasipuri, *J.*, 1958, 2618, 4192; Nasipuri and Roy, *J. Indian Chem. Soc.*, 1959, **36**, 817.
[13] (*a*) Bardhan, *J.*, 1936, 1848; (*b*) Guha, Rakshit, and Nasipuri, *J. Indian Chem. Soc.*, 1960, **37**, 267.
[14] Wilds and Werth, *J. Org. Chem.*, 1952, **17**, 1149.
[15] Linstead and Thomas, *J.*, 1940, 1127.
[16] Bachmann and Kloetzel, *J. Amer. Chem. Soc.*, 1937, **59**, 2207.
[17] Bardhan, Nasipuri, and Mukherjee, *J.*, 1957, 921.
[18] Woodward, Inhoffen, Larson, and Menzel, *Chem. Ber.*, 1953, **86**, 594.

Similarly, the sodio-derivative of the β-oxo-ester (III; R = H) with 1-chloropentan-3-one[19] led successively to the dioxo-ester (III; R = CH_2·CH_2·COEt), the pentacyclic ketone (V; R = Me), and 4′-methylindeno(2′,3′:1,2)phenanthrene (VI; R = Me, R′ = R″ = H), identical with that obtained from cholic acid.[5] The ketone (V; R = Me), on condensation with methylmagnesium iodide followed by dehydration and dehydrogenation, gave the 4′,5′-dimethyl derivative (VI; R = R″ = Me, R′ = H).

To synthesise the 6′-methyl derivative (VI; R′ = Me, R = R″ = H), the methiodide of the Mannich base of butan-2-one[20] was condensed with the potassio-derivative of the β-oxo-ester (III; H), and the crude product directly hydrolysed to give a pentacyclic ketone, isolated in about 50% yield. This ketone, however, was identical with the foregoing one (V; R = Me), the identity being further established by its conversion into 4′-methyl- and 4′,5′-dimethyl-indeno(2′,3′:1,2)phenanthrene and their derivatives. This result is unexpected in view of the known[21] preponderance of 4-piperidino-3-methylbutan-2-one over the isomeric 1-piperidinopentan-3-one in the Mannich reaction product of ethyl methyl ketone. This point was not, however, pursued further at present.

Indeno(2′,3′:1,2)phenanthrene and its monomethyl and dimethyl derivatives have been characterised by their ultraviolet absorption spectra, by conversion into monoketones by chromic acid, and by formation of 2,4,7-trinitrofluorenone complexes.[22]

Experimental

M. p.s are corrected. The ultraviolet absorption spectra were recorded on a Beckman spectrophotometer.

Ethyl α-(2-1′-*Naphthylethyl*)-β-*oxoadipate* (I).—To a cold solution of potassium (4·0 g.) in t-butyl alcohol (80 ml.), ethyl β-oxoadipate (21·6 g.) was added with stirring. 2-1′-Naphthylethyl bromide (25 g.) was then added and the whole refluxed in nitrogen atmosphere for 20 hr. After removal of most of the alcohol at water-pump vacuum, the residue was acidified and extracted thoroughly with benzene. The benzene extract was washed once with water and dried (Na_2SO_4), and benzene was removed under reduced pressure. The product was distilled carefully up to 150°/0·2 mm. in order to eliminate the low-boiling impurities as far as possible and the residue (36—40 g.) used directly for the next operation.

β-(2-*Carboxy*-3,4-*dihydro*-1-*phenanthryl*)*propionic Acid* (II).—The above condensation product (40 g.) was cyclised, in 6 g. batches, by treatment with concentrated sulphuric acid (3 vols.) in a bath of carbon dioxide–acetone at −20° for 30 min., ether (1 vol.) being used as co-solvent. The brown mass was decomposed with ice and the organic matter taken up in ether. After removal of ether, the residue was hydrolysed to the acid (II) which was purified through the *diethyl ester* (12·4 g.), b. p. 210—220°/0·1 mm., the yield being 35% based on ethyl β-oxoadipate. The ester slowly solidified and crystallised from ethanol in needles, m. p. 64° (Found: C, 74·7; H, 7·0. $C_{22}H_{24}O_4$ requires C, 75·0; H, 6·8%). The corresponding acid crystallised from dilute methanol in stout prisms, m. p. 240° (Found: C, 72·6; H, 5·7. Calc. for $C_{18}H_{16}O_4$: C, 73·0; H, 5·4%). Bardhan [13a] reports m. p. 237—238°.

Methyl β-(2-*Methoxycarbonyl*-1-*phenanthryl*)*propionate*.—The preceding ester (6·5 g.) was heated with sulphur (0·7 g.) at 240—250° for 1 hr. and the product hydrolysed directly with 10% methanolic potassium hydroxide. The aromatic *acid*, thus obtained in about 90% yield and crystallised several times from aqueous methanol, formed thin needles, m. p. 245—247° (Found: C, 73·5; H, 5·1. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8%). The *dimethyl ester* was prepared by boiling the acid with 5% methanolic sulphuric acid and crystallised from benzene–light petroleum (b. p. 40—60°) or methanol in light yellow flakes, m. p. 125° (Found: C, 74·4; H, 5·6. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

3′-*Oxo*-1,2-*cyclopentenophenanthrene*.—The above ester (1 g.) was heated on the water-bath with a suspension of finely divided sodium (0·1 g.) in benzene (5 ml.) containing a drop of methanol, for 2 hr. The resultant β-oxo-ester (III; R = H) was worked up as usual and on

[19] McMahon, Roper, Utermohlen, Hasek, Harris, and Brant, *J. Amer. Chem. Soc.*, 1948, **70**, 2971.
[20] Mannich and Hof, *Arch. Pharm.*, 1927, **265**, 489.
[21] Downes, Gill, and Lions, *J. Amer. Chem. Soc.*, 1950, **72**, 3464.
[22] Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727.

hydrolysis with boiling acetic acid and hydrochloric acid afforded 3′-oxo-1,2-cyclopentenophenanthrene (0·4 g.), plates (from benzene), m. p. 200—201° (Found: C, 87·7; H, 5·2. Calc. for $C_{17}H_{12}O$: C, 87·9; H, 5·2%). Bachmann and Kloetzel [16] report m. p. 195—196°. The analogous dihydro-compound (IV; R = H) was obtained from the ethyl ester of the acid (II) by a similar cyclisation and had m. p. 211—212°. Bardhan [13a] reports m. p. 210°.

3,4-Dihydro-8-methyl-3′-oxo-1,2-cyclopentenophenanthrene (IV; R = Me).—2-(5-Methyl-1-naphthyl)ethyl bromide was condensed with ethyl β-oxoadipate in the same way as described before, and the product (6 g.) cyclised by concentrated sulphuric acid at −20° for 20 min. to give β-(*2-carboxy-3,4-dihydro-8-methyl-1-phenanthryl*)*propionic acid* (2 g.), m. p. 254—256° (Found: C, 73·2; H, 5·7. $C_{19}H_{18}O_4$ requires C, 73·55; H, 5·8%). The dimethyl ester (1·7 g.), b. p. 215—220°/0·01 mm., on Dieckmann cyclisation followed by hydrolysis, as described above, afforded the ketone (0·5 g.) (IV; R = Me), thick prisms (from benzene), m. p. 250° (Found: C, 87·25; H, 6·4. Calc. for $C_{18}H_{16}O$: C, 87·1; H, 6·45%). Woodward *et al.*[18] report m. p. 237·5—241·5°.

Methyl 3′-Oxo-4′-3″-oxobutyl-1,2-cyclopentenophenanthrene-4′-carboxylate (III; R = CH_2·CH_2·COMe).—Methyl β-(2-methoxycarbonyl-1-phenanthryl)propionate, m. p. 125° (4 g.), was heated under reflux with finely divided sodium (0·33 g.) in dry thiophen-free benzene (30 ml.) and two drops of methanol until the formation of the sodio-salt of the β-oxo-ester (III; R = Na) was complete (4—5 hr.). The flask was then cooled in a freezing mixture and a solution of the methiodide of 4-piperidinobutan-2-one, prepared from the Mannich base (6 g.) and methyl iodide (6 g.), in absolute methanol (40 ml.) was gradually added with shaking. After 48 hr. at room temperature, the mixture was refluxed on the water-bath for 1 hr., cooled, and then decomposed with dilute sulphuric acid. The organic matter was taken up in benzene, the benzene layer washed successively with water, dilute alkali, and water, and the solvent evaporated. The residual *dioxo-ester* (III; R = CH_2·CH_2·COMe) crystallised from ethyl acetate (charcoal) in white plates (3·2 g., 70%), m. p. 170° (Found: C, 76·6; H, 5·65. $C_{23}H_{20}O_4$ requires C, 76·7; H, 5·6%).

5′,6′,7′,7′a-Tetrahydro-5′-oxoindeno(*2′,3′:1,2*)*phenanthrene* (V; R = H).—The preceding dioxo-ester (1·8 g.) was refluxed with acetic acid (50 ml.), concentrated hydrochloric acid (25 ml.), and water (2 ml.) for 20 hr. under carbon dioxide. On being cooled, the unsaturated *ketone* (V; R = H) was precipitated. It was filtered off and dried to give a product (1·2 g., 84%), m. p. 210—220°. This was twice crystallised from benzene, forming plates, m. p. 260—262° (Found: C, 88·8; H, 5·9. $C_{21}H_{16}O$ requires C, 88·7; H, 5·6%); $\lambda_{max.}$ (in ethanol) 219, 248, 274, 285, 299, and 329 mμ (log ε 4·38, 4·01, 4·61, 4·59, 4·62, and 4·54 respectively), $\lambda_{min.}$ 238, 250, 278, 295, and 310 mμ (log ε 3·94, 4·00, 4·52, 4·51, and 4·36 respectively).

Indeno(*2′,3′:1,2*)*phenanthrene*.—A solution of the foregoing ketone (200 mg.) in tetrahydrofuran (50 ml.) was heated under reflux with lithium aluminium hydride (200 mg.) for 2 hr. and then decomposed with cold dilute sulphuric acid. The crude alcohol (200 mg.) was heated with 30% palladium–charcoal (100 mg.) at 300—320° for 1 hr. The product was repeatedly extracted with hot benzene, and the extract filtered and reduced to small volume to afford light yellow flakes (130 mg.), m. p. 315—320°. These sublimed at 280°/0·01 mm. and finally crystallised from pyridine in colourless plates (50 mg.), m. p. 331—332° (Found: C, 94·6; H, 5·4. Calc. for $C_{21}H_{14}$: C, 94·7; H, 5·3%). The ultraviolet absorption spectrum was found identical with that recorded by Cook *et al.*[8] On oxidation with sodium dichromate in acetic acid, the hydrocarbon afforded an orange-red ketone, m. p. 208° (Found: C, 89·6; H, 4·1. Calc. for $C_{21}H_{12}O$: C, 90·0; H, 4·3%). Reported [8] m. p.s are 327—328° and 207—208°, respectively. The *2,4,7-trinitrofluorenone complex* was prepared in benzene–ethanol and obtained from benzene as a red amorphous powder, m. p. 216—217° (Found: C, 70·0; H, 3·0; N, 6·9. $C_{21}H_{14},C_{13}H_5N_3O_7$ requires C, 70·2; H, 3·3; N, 7·2%).

Methyl 3′-Oxo-4′-3″-oxopentyl-1,2-cyclopentenophenanthrene-4′-carboxylate (III; R = CH_2·CH_2·COEt).—To a cold suspension of the sodio-salt of the β-oxo-ester (III; R = H) prepared from methyl β-(2-methoxycarbonyl-1-phenanthryl)propionate (3·3 g.), sodium (0·3 g.), and dry benzene (25 ml.), was added with stirring a solution of 1-chloropentan-3-one, b. p. 55—57°/18 mm. (3 g.), in benzene (10 ml.). Next day, the almost clear solution was heated under reflux for 1 hr., cooled, and decomposed with cold dilute sulphuric acid, and the product was extracted with benzene. After removal of the solvent, the residual solid crystallised from ethyl acetate to furnish the *dioxo-ester* (2·4 g.), m. p. 157° (Found: C, 77·3; H, 5·9. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%).

5',6',7',7'a-Tetrahydro-4'-methyl-5'-oxoindeno(2',3':1,2)phenanthrene (V; R = Me).—The preceding dioxo-ester (2·4 g.) was refluxed with glacial acetic acid (70 ml.), concentrated hydrochloric acid (35 ml.), and water (5 ml.) for 20 hr. under carbon dioxide. On cooling, the solution deposited the *ketone* (V; R = Me) (2·0 g.), m. p. 220—225° which was collected and crystallised from benzene in colourless plates, m. p. 252° (Found: C, 88·3; H, 6·2. $C_{22}H_{18}O$ requires C, 88·6; H, 6·0%), $\lambda_{max.}$ (in ethanol), 220, 249, 275, 286, 300, and 330 mμ (log ε 4·43, 4·08, 4·58, 4·59, 4·65, and 4·57, respectively), $\lambda_{min.}$ 238, 255, 280, 295, and 310 mμ (log ε 3·99, 4·05, 4·54, 4·54, and 4·36, respectively).

4'-Methylindeno(2',3':1,2)phenanthrene (VI; R = Me, R' = R'' = H).—The ketone (V; R = Me) (300 mg.) was reduced, as above, with lithium aluminium hydride in tetrahydrofuran and the crude alcohol, m. p. 110—115°, was heated with 30% palladium–charcoal (150 mg.) at 300—320° for 1 hr. The melt was extracted repeatedly with hot benzene, and the extract filtered and evaporated. The residue sublimed at 280—290°/0·01 mm. and was finally crystallised several times from pyridine, to afford the 4'-methyl hydrocarbon (120 mg.), m. p. 274—275° (Found: C, 94·1; H, 5·8. Calc. for $C_{22}H_{16}$: C, 94·3; H, 5·7%), $\lambda_{max.}$ (in ethanol) 220, 272, 282, 298, 320, 348, 357, and 365 mμ (log ε 4·46, 4·77, 4·88, 4·56, 4·37, 3·11, 2·71, and 3·12 respectively), $\lambda_{min.}$ 246, 276, 294, 314, 344, 354, and 360 mμ (log ε 4·02, 4·76, 4·51, 4·23, 2·75, 2·65, and 2·49 respectively). The ketone derivative, obtained by oxidation of the hydrocarbon by sodium dichromate in acetic acid and purified by chromatography, afforded orange needles, m. p. 208° (Found: C, 88·65; H, 4·8. Calc. for $C_{22}H_{14}O$: C, 89·8; H, 4·8%), from ethyl acetate. Bachmann *et al.*[23] report m. p.s 275—276° and 209—210°. The *trinitrofluorenone complex* crystallised from benzene–ethanol in needles, m. p. 232° (Found: C, 70·4; H, 3·6; N, 7·35. $C_{22}H_{16},C_{13}H_5N_3O_7$ requires C, 70·6; H, 3·5; N, 7·1%).

4',5'-Dimethylindeno(2',3':1,2)phenanthrene (VI; R = R'' = Me, R' = H).—The ketone (V; R = Me) (600 mg.) in dry benzene (50 ml.) was added to an excess of methylmagnesium iodide (10 mol.) in ether, and the whole was refluxed for 4 hr. and then decomposed with cold dilute sulphuric acid. The crude alcohol (700 mg.) was heated with 30% palladium–charcoal (350 mg.) at 300—320° for 1 hr. The resultant hydrocarbon was worked up in the usual way and sublimed at 290—300°/0·01 mm., to give *4',5'-dimethylindeno(2',3':1,2)phenanthrene* (420 mg.), m. p. 270—275°. Two crystallisations from benzene afforded white needles, m. p. 281—282° (Found: C, 93·7; H, 6·2. $C_{23}H_{18}$ requires C, 93·9; H, 6·1%), $\lambda_{max.}$ (in ethanol) 220, 240, 273, 283, 299, 321, 350, 357, and 366 mμ (log ε 4·32, 4·06, 4·43, 4·54, 4·22, 4·07, 3·29, 2·75, and 3·01 respectively), $\lambda_{min.}$ 238, 249, 276, 294, 316, 344, 354, and 362 mμ (log ε 3·87, 3·91, 4·43, 4·19, 3·96, 2·77, 2·74, and 2·65 respectively).

The hydrocarbon (78 mg.) was oxidised by sodium dichromate (250 mg.) in hot acetic acid (5 ml.) for 5 min., affording *4',5'-dimethyl-1'-oxoindeno(2',3':1,2)phenanthrene* which was collected and separated from the associated triketone by chromatography over alumina. The ketone was crystallised several times from ethyl acetate and finally obtained in orange-red needles, m. p. 255° (Found: C, 89·6; H, 5·2. $C_{23}H_{16}O$ requires C, 89·6; H, 5·2%).

The *trinitrofluorenone complex* of the hydrocarbon crystallised from benzene in red needles, m. p. 248—250° (Found: C, 71·2; H, 3·75; N, 7·0. $C_{23}H_{18},C_{13}H_5N_3O_7$ requires C, 70·9; H, 3·8; N, 6·9%).

4-Piperidino-3-methylbutan-2-one.—This was prepared by the method of Mannich and Hof [20] by refluxing a mixture of piperidine hydrochloride (15 g.), paraformaldehyde (5 g.), ethyl methyl ketone (70 ml.), methanol (7·5 ml.), and concentrated hydrochloric acid (0·5 ml.) for 6 hr. The product was worked up as usual and a middle fraction (8·5 g.), b. p. 113—114°/15 mm., was used for the subsequent reaction.

Condensation of the Methiodide of the above Mannich Base with the β-Oxo-ester (III; R = H).—The ester (2·8 g.), finely divided potassium (0·4 g.), and dry thiophen-free benzene (25 ml.) were heated under reflux for 4 hr. To the potassio-derivative of the β-oxo-ester (III; R = H) thus obtained was added, with cooling, a solution of the methiodide of 4-piperidino-3-methylbutan-2-one (8·5 g.) in methanol (15 ml.). The mixture was left at room temperature for 48 hr. and then refluxed on the water-bath for 1 hr. and worked up as in the previous cases to give a highly viscous oil (3·7 g.). Without purification, this was boiled with acetic acid (100 ml.), concentrated hydrochloric acid (50 ml.), and water (2 ml.) under carbon dioxide for 20 hr. The solution was cooled to the room temperature and filtered, to afford crystals (2 g.), m. p. 220—225°. This material was purified by chromatography over alumina and

[23] Bachmann, Cook, Hewett, and Iball, *J.*, 1936, 54.

crystallised from benzene in pale yellow flakes (1·3 g.), m. p. 250—251° (Found: C, 88·4; H, 6·1. Calc. for $C_{22}H_{18}O$: C, 88·6; H, 6·0%). The m. p. did not depress that of the ketone (V; R = Me).

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