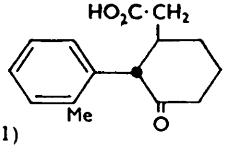
246. *Alicyclic Studies. Part VII.* An Alicyclic Approach to the Synthesis of Methylphenanthrenes and Benzo*[c]*phenanthrene.*

By YAIR KLIBANSKY and DAVID GINSBURG.

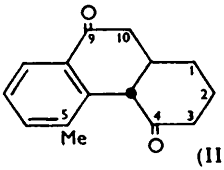
2-Aryl*cyclo*hex-2-enones are shown to be versatile intermediates for the synthesis of many substituted phenanthrenes.

THE efficacy of 2-aryl*cyclo*hex-2-enones as intermediates for construction of the phenanthrene system has been demonstrated through their use as acceptors in the Michael condensation.[1] Essentially the same approach was subsequently used to synthesise 2 : 9-dimethylphenanthrene by utilising the Grignard reaction of the carbonyl groups in the tricyclic diketone formed, as keys for introduction of methyl groups in their stead.[2] Further obvious uses of the carbonyl groups and differences in their reactivities for introduction of substituents in positions α to these key groups have been employed.[1]

In the present communication the same approach has been extended in that 2-*o*-tolyl*cyclo*hex-2-enone has been prepared from 1-*o*-tolyl*cyclo*hexene and has been shown to undergo Michael condensation with benzyl malonate to give an adduct which upon debenzylation with hydrogen bromide in glacial acetic acid[3] and decarboxylation finally gives *trans*-3-oxo-2-*o*-tolyl*cyclo*hexylacetic acid (I). This acid was quantitatively cyclised by anhydrous hydrogen fluoride to 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-octahydro-5-methyl-4 : 9-dioxophenanthrene (II). It has been shown that the 4-dioxolan can be formed selectively so that a methyl group can, for example, be introduced into the 10-position. This approach therefore affords a means for the synthesis of phenanthrenes substituted in any of the positions 1, 2, 3, 4 (aromatic numbering) (depending upon the aryl group in the αβ-ethylenic ketone used as an acceptor in the Michael condensation), in the 5 or 10 position (aromatic numbering) by Grignard addition to the carbonyl groups followed by dehydration and dehydrogenation and in the 6 or 9 position α to the carbonyl functions as exemplified in the present work. In principle, many combinations of polyalkylphenanthrenes may be prepared by this versatile route.



(I)



(II)

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* Part VI, preceding paper.

[1] Ginsburg and Pappo, *J.*, 1951, 938.

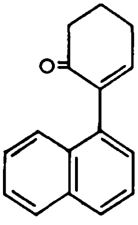
[2] Bergmann and Szmuszkovics, *J. Amer. Chem. Soc.*, 1953, **75**, 3226.

[3] Ben Ishai, *J. Org. Chem.*, 1954, **19**, 62.

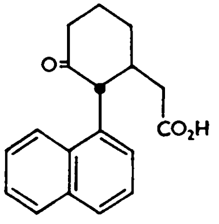
Analogously, derivatives of tetracyclic and higher polynuclear systems should be obtainable by a similar approach. For this reason the study of 2-α-naphthyl*cyclo*hex-2-enone as an acceptor in the Michael reaction was undertaken. As expected, this compound afforded a route to benzo[*c*]phenanthrene.

The oxime of 2-α-naphthyl*cyclo*hex-2-enone was prepared by dehydrochlorination of the nitrosochloride of 1-α-naphthyl*cyclo*hexene and afforded the αβ-ethylenic ketone (III) on acidic hydrolysis, whose structure was proved by dehydrogenation to the phenol and methylation to yield the known 2-α-naphthylanisole. Addition of benzyl sodiomalonate in boiling xylene to the unsaturated ketone, etc., led to *trans*-3-oxo-2-α-naphthyl*cyclo*hexylacetic acid (IV). Cyclisation of this acid with anhydrous hydrogen fluoride afforded the octahydrodioxobenzophenanthrene (V). Alternatively, if the cyclisation was carried out with polyphosphoric acid, a reagent often used for formation of cyclic seven-membered ketones, an isomeric ketone (VI) was obtained and characterised as its 2 : 4-dinitrophenylhydrazone. Huang-Minlon reduction of the keto-acid (IV) gave *trans*-2-α-naphthyl*cyclo*hexylacetic acid which on cyclisation with hydrogen fluoride yielded the octahydro-6-oxobenzophenanthrene. The diketone (V) was reduced to the hydrocarbon, 1 : 2 : 3 : 4 : 4*a* : 5 : 6 : 12*c*-octahydrobenzo[*c*]phenanthrene (numbering : Ring Index 2807) by treatment of its tetrabenzyl bisdithioacetal with Raney nickel. Dehydrogenation of the hydrocarbon with palladised carbon yielded the known benzo[*c*]phenanthrene.

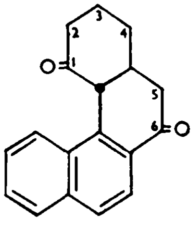
When the diketone (V) was treated with ethylene glycol in the presence of toluene-*p*-sulphonic acid the 1-oxo-group was selectively converted into the ketal, so that in this case also it is possible to introduce alkyl groups selectively into the skeleton. A by-product obtained during the reaction had the empirical formula $C_{36}H_{24}$ and showed no carbonyl or hydroxyl absorption in the infrared spectrum; presumably it is formed by self-condensation of the diketone with concomitant or subsequent cyclodehydration; its structure was not elucidated.



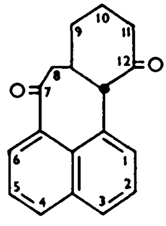
(III)



(IV)



(V)



(VI)

The infrared absorption of the tetracyclic diketone (V) is worthy of note. In contradistinction to 1 : 2 : 3 : 4 : 4*a* : 9 : 10 : 10*a*-octahydro-4 : 9-dioxophenanthrene which exhibits a saturated carbonyl band at 1710 cm.$^{-1}$ and an acetophenone-type carbonyl band at 1695 cm.$^{-1}$, diketone (V) has one broad absorption band at 1702 cm.$^{-1}$, intermediate between the two. The infrared data for the significant functional groups in the various products now obtained are reported in the Experimental section.

EXPERIMENTAL

1-o-*Tolyl*cyclo*hexene*.—*o*-Tolylmagnesium bromide was prepared from *o*-bromotoluene (172 g.) and magnesium (24 g.) in dry ether (1 l.). *cyclo*Hexanone (98 g.) in ether (100 ml.) was added to the Grignard solution at −10° to −5°. Then the mixture was refluxed for 3 hr., cooled, and decomposed with saturated ammonium chloride solution. After the usual working up, the solvent and unchanged starting materials were removed at the water-pump. The yellow-brown residual oil was boiled with anhydrous oxalic acid (20 g.) and toluene (400 ml.) until no more water was obtained in the azeotropic collector (90 min.). After the usual working up, the *cyclo*alkene was obtained as a colourless oil, b. p. 108—111°/1 mm. (110 g., 64%).

2-o-*Tolyl*cyclo*hex-2-enone*.—Cold *n*-pentyl nitrite (88 g., 0·75 mole) was added with stirring at 8° to a mixture of 1-*o*-tolyl*cyclo*hexene (100 g., 0·58 mole) and propionic acid (200 ml.). Concentrated hydrochloric acid (75 ml.) was then added dropwise at −15° to −12° with stirring, and the mixture was stirred for a further 3 hr. at −12°. The temperature was raised to 0° and the mixture was poured into a cold solution of ethanolic (2 l.) potassium hydroxide (560 g.) and the solution was refluxed for 30 min., then steam-distilled until 5 l. of distillate were obtained (colourless crystals appear in the condenser). The residue was cooled, diluted (stirring) with water and ice, and neutralised with cold hydrochloric acid. A brown flocculent precipitate of the oxime was obtained, filtered off, washed with water, and dried (70 g., 60%).

The crude oxime (24 g.) was refluxed with dilute sulphuric acid (50 ml. of concentrated acid + 300 ml. of water) for 3 hr. After cooling, extraction with ether–benzene, washing of the extract with saturated aqueous sodium hydrogen carbonate and with water, and drying (Na_2SO_4), the solvents were removed and the residue was distilled in a high vacuum. The αβ-ethylenic ketone was obtained as a light yellow oil, b. p. 152—154°/2 mm. (12 g., 54%). Ultraviolet absorption : $\lambda_{max.}$ 2550 Å (log ε 3·98 in EtOH). Infrared absorption (in $CHCl_3$) : 1675 cm.$^{-1}$ (C=C·C=O).

The ketone formed the 2 : 4-*dinitrophenylhydrazone* as orange-red plates, m. p. 128° (from ethanol–ethyl acetate) (Found : C, 62·3; H, 5·1; N, 15·7. $C_{19}H_{18}O_4N_4$ requires C, 62·3; H, 5·0; N, 15·3%). Ultraviolet absorption : $\lambda_{max.}$ 3810—3860 Å (log ε 4·48 in $CHCl_3$). The *oxime*, obtained by the pyridine method, formed elongated rhombs, m. p. 152·5—153° (from aqueous ethanol) (Found : C, 77·6; H, 7·8; N, 7·2. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5; N, 7·0%).

trans-3-*Oxo*-2-o-*tolyl*cyclo*hexylacetic Acid* (I).—A mixture of 2-*o*-tolyl*cyclo*hex-2-enone (18 g., 0·1 mole), freshly distilled benzyl malonate (36 g., 0·13 mole), and potassium *tert.*-butoxide [from 420 mg. of potassium and 6·6 ml. of *tert.*-butyl alcohol (0·013 mole)] was set aside for 15 hr. at 60°, then cooled, acidified with acetic acid, diluted with ether, and washed with water to remove precipitated potassium acetate. The ethereal solution was dried (Na_2SO_4) and the solvent was removed. To the residue was added a saturated glacial acetic solution of hydrogen bromide (100 g.; *ca.* 25% HBr). The mixture was kept overnight at room temperature, then refluxed for 4 hr., and the acetic acid and part of the benzyl bromide formed were removed at reduced pressure. This treatment was repeated with an additional portion (100 g.) of hydrogen bromide in acetic acid. After the acetic acid and benzyl bromide had again been removed the residue was diluted with ether and the malonic acid was extracted several times by saturated sodium carbonate solution and then once with 5% sodium hydroxide solution. The combined alkaline extracts were washed once with ether and then acidified, while cooling, with hydrochloric acid. Unchanged αβ-ethylenic ketone can be recovered from the organic phase. The oily malonic acid precipitated in the aqueous phase was taken up in ether and on removal of the ether the residual oil was heated at 200° until evolution of carbon dioxide was complete. The residual viscous monobasic *acid* crystallised (14 g.). It had b. p. 122°/0·4 mm., m. p. 101—103° (from heptane) (Found : C, 72·9; H, 7·0. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%). Infrared absorption (in $CHCl_3$) : 3300—2900 (OH of CO_2H), 3500 (OH), 1710 cm.$^{-1}$ (v.s.; includes carbonyl C=O and carboxyl C=O).

The *methyl ester*, prepared by diazomethane, slowly crystallised as plates, m. p. 77—78° (from ethanol) (Found : C, 73·7; H, 7·4. $C_{16}H_{20}O_3$ requires C, 73·9; H, 7·7%). Its 2 : 4-*dinitrophenylhydrazone* formed golden crystals, m. p. 153—154° (from ethanol–ethyl acetate) (Found: C, 60·0; H, 5·2; N, 12·4. $C_{22}H_{24}O_6N_4$ requires C, 60·0; H, 5·5; N, 12·7%).

1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-*Octahydro*-5-*methyl*-4 : 9-*dioxophenanthrene* (II).—The above acid (I) (2·5 g.) was treated with anhydrous hydrogen fluoride (*ca.* 50 g.) and after 4 hr. the mixture was worked up in the usual way. The *diketone* (2 g.) gave light yellow crystals, m. p. 128—130°, from aqueous ethanol (Found : C, 78·8; H, 7·3. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·0%). Infrared absorption (in $CHCl_3$) : 1683 (C=O adjacent to aromatic nucleus), 1713 cm.$^{-1}$ (C=O in six-membered ring). Ultraviolet absorption : $\lambda_{max.}$ 2550, 3000 Å (log ε 4·04, 3·28 in EtOH). The *mono-oxime* formed colourless crystals, m. p. 245—247°, from ethanol [Found : C, 73·3; H, 7·0. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0. Calc. for $C_{15}H_{18}O_2N_2$ (dioxime) : C, 69·8; H, 7·0%]. The orange-red *mono*-2 : 4-*dinitrophenylhydrazone* had m. p. 219·5—221·5° (from ethanol–ethyl acetate) (Found : C, 61·3; H, 5·5; N, 13·9. $C_{21}H_{20}O_5N_4$ requires C, 61·8; H, 4·9; N, 13·7%). Ultraviolet absorption : $\lambda_{max.}$ 3850 Å (log ε 4·62 in $CHCl_3$). Infrared absorption (in $CHCl_3$) : 1718 cm.$^{-1}$. The 4-oxo-group is therefore free in these derivatives.

4-*Ethylenedioxy*-1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-*octahydro*-5-*methyl*-9-*oxophenanthrene*.—The diketone (4·5 g.) was heated with benzene (20 ml.), ethylene glycol (10 ml.), and toluene-*p*-sulphonic acid (150 mg.) for 3 hr. in a flask attached to an azeotropic collector. After cooling and neutralisation of the acid catalyst with a small quantity of sodium methoxide, water was added and the benzene layer dried (Na_2SO_4). The benzene was removed and the residual *dioxolan* (4·2 g., 77%) gave colourless crystals, m. p. 72—73°, from hexane (Found : C, 74·5; H, 7·4. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·4%). Infrared absorption (in $CHCl_3$) : 1688 cm.$^{-1}$ (C=O adjacent to aromatic ring), 1157, 1083 cm.$^{-1}$ (ketal).

1 : 2 : 3 : 4 : 4a : 9 : 10 : 10a-*Octahydro*-5 : 10-*dimethyl*-4 : 9-*dioxophenanthrene*.—A solution of the dioxolan (5·5 g., 0·02 mole) in dry ether–benzene (3 : 1; 20 ml.) was added dropwise with stirring to a boiling suspension of sodium hydride (0·6 g., 0·025 mole) in dry ether. After refluxing for 5 hr. (it may be necessary to clean the surface of the sodium hydride by the careful addition of a drop of ethanol) the mixture was cooled and methyl iodide (5·1 g., 0·035 mole) in dry benzene (5 ml.) was added. The mixture was kept overnight at room temperature and finally refluxed for 3 hr. After the usual working up, the ethylenedioxy-derivative of the dimethyl derivative was obtained as a yellow oil which afforded light yellow needles (5·1 g.). Infrared absorption of the crude dioxolan in $CHCl_3$ showed the presence of the free C=O group at 1683 cm.$^{-1}$ and the ketal at 1150, 1080 cm.$^{-1}$. A strong band was found at 1379 cm.$^{-1}$ (*C*-Me) in much higher concentration than in the starting material.

The crude ketal (1 g.) was warmed with ethanol (25 ml.), water (5 ml.), and concentrated hydrochloric acid (0·5 ml.) on the steam-bath for 2 hr. The usual working up gave the 5 : 10-*dimethyl derivative* (0·82 g.), m. p. 140—142° (from heptane) (Found : C, 79·3; H, 7·2. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%). Infrared absorption (in $CHCl_3$) : 1713 (*cyclo*hexanone C=O), 1683 cm.$^{-1}$ (acetophenone C=O). Ultraviolet absorption : $\lambda_{max.}$ 2550, 2970 Å (log ε 4·07, 3·34 in EtOH).

The dark red *mono*-2 : 4-*dinitrophenylhydrazone* had m. p. 223—225° (from ethanol–ethyl acetate) (Found : C, 61·9; H, 5·1; N, 13·6. $C_{22}H_{22}O_5N_4$ requires C, 62·6; H, 5·2; N, 13·2%). Infrared absorption (in $CHCl_3$) : 1719 cm.$^{-1}$ (free *cyclo*hexanone C=O). Ultraviolet absorption : $\lambda_{max.}$ 3850 Å (log ε 4·67 in $CHCl_3$). The *dioxime*, formed in hot pyridine by a large excess of hydroxylamine (4 hr.), was yellowish needles, m. p. 254—255° (decomp.) (from aqueous ethanol) (Found : C, 70·5; H, 7·3; N, 9·7. $C_{16}H_{20}O_2N_2$ requires C, 70·6; H, 7·4; N, 10·3%).

1-α-*Naphthyl*cyclo*hexene*.—In the preparation of the Grignard reagent on a molar scale the method described in *Org. Synth.* was followed.[4] *cyclo*Hexanone (100 g.) in dry ether (400 ml.) was added during 30 min. with vigorous stirring at −15°. Stirring was continued for 15 min. at this temperature and the mixture was then refluxed with stirring for 3 hr. After the usual working up and removal of unchanged starting materials a crude alcohol was obtained (255 g.). This was dehydrated in the usual way [5] with oxalic acid in boiling toluene. Water (16 ml.) was obtained during 1 hr. The *cyclo*alkene distilled at 136—140°/0·5 mm. (160 g., 70%), crystallised, and formed colourless needles (from methanol), m. p. 47—48° (Cook *et al.*[6] give m. p. 46°). The *picrate*, prepared in ethanol, gave yellow-orange crystals, m. p. 124—125° (Cook *et al.* give m. p. 124·5—125·5°).

2-α-*Naphthyl*cyclo*hex*-2-*enone* (III).—The preparation was analogous to that described for 2-*o*-tolyl*cyclo*hex-2-enone (above). From the *cyclo*alkene (60 g.), the analogous mixture containing the nitrosochloride was poured into ethanolic (1·5 l.) potassium hydroxide (300 g.) and refluxed for 30 min. Steam-distillation was then carried out until 2·9 l. of distillate had been obtained. After treatment analogous to that described above, brown crystalline oxime (66 g., 95%) was obtained.

The oxime (55 g.) was hydrolysed by heating it in dioxan (300 ml.) with 40% aqueous formaldehyde (300 ml.) and concentrated hydrochloric acid (60 ml.) on the steam-bath for 15 min. The mixture was cooled and diluted with water. A brown flaky precipitate was obtained. The mixture was extracted several times with ether–benzene, and the organic phase was filtered to remove insoluble material (4·5 g., 8%) whose infrared spectrum indicated that it may be a lactam (formed by Beckmann rearrangement of the oxime); it was not investigated further. The organic phase was then dried (Na_2SO_4) and the solvents were removed. The viscous oily residue was distilled and the αβ-ethylenic *ketone* was obtained as a yellow oil, b. p. 135—150°/0·5 mm. (37 g., 75%), colourless needles, m. p. 101·5—103° (from heptane) (Found : C, 86·7; H, 6·4. $C_{16}H_{14}O$ requires C, 86·5; H, 6·4%). Infrared absorption (in $CHCl_3$) : 1670 cm.$^{-1}$ (C=C–C=O). Ultraviolet absorption : $\lambda_{max.}$ 3850 Å (log ε 4·39 in $CHCl_3$). The

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[4] *Org. Synth.*, Wiley, New York, 1943, Coll. Vol. II, p. 425.

[5] Ginsburg and Pappo, *J.*, 1951, 516.

[6] Cook, Hewett, and Lawrence, *J.*, 1936, 71.

2 : 4-*dinitrophenylhydrazone* formed red needles, m. p. 168—169° (from ethanol–ethyl acetate) (Found : C, 65·2; H, 4·9; N, 13·5. $C_{22}H_{18}O_4N_4$ requires C, 65·7; H, 4·5; N, 13·9%). Ultraviolet absorption : $\lambda_{max.}$ 3860 Å (log ε 4·40 in $CHCl_3$). The *oxime*, formed by the pyridine method, gave nearly colourless needles with a greyish cast, m. p. 211—212° (from ethanol) (Found : C, 81·1; H, 6·8. $C_{16}H_{15}ON$ requires C, 81·0; H, 6·4%).

Dehydrogenation of 2-α-*Naphthyl*cyclo*hex*-2-*enone* : 2-α-*Naphthylanisole*.—A mixture of the ketone (1·5 g.), 30% palladised charcoal (0·75 g.), and *p*-cymene (20 ml.) was refluxed for 5 hr. under nitrogen. After cooling and dilution with ether the catalyst was removed and washed with ether. The filtrate was extracted several times with Claisen's alkali. The alkaline extract was slowly acidified in the cold with concentrated hydrochloric acid, and the phenol was taken up in ether. After drying (Na_2SO_4) the ether was removed on the steam-bath and traces of *p*-cymene were removed under reduced pressure. The residue was dissolved in a small excess of 10% aqueous sodium hydroxide and approximately the equivalent quantity of dimethyl sulphate was added. The mixture was heated on the steam-bath for 15 min. and after the usual working up, light tan crystals of 2-α-naphthylanisole were obtained, having m. p. 90—91·5° (from light petroleum). Orchin [7] reports m. p. 91·2—92·6° (Found : C, 87·4; H, 6·2. Calc. for $C_{17}H_{14}O$: C, 87·2; H, 6·0%). Infrared absorption (in $CHCl_3$) : 1070—1000, 1300—1170 $cm.^{-1}$ (OMe).

trans-2-α-*Naphthyl*-3-*oxo*cyclo*hexylacetic Acid* (IV).—To a well-stirred mixture, under nitrogen, of sodium hydride (5·76 g., 0·24 mole) and dry xylene (85 ml.) was added in portions a solution of benzyl malonate (72 g., 0·25 mole) in dry xylene (210 ml.). The mixture was refluxed until the sodium hydride had reacted (2—3 hr.), then cooled to room temperature. A solution of 2-α-naphthyl*cyclo*hex-2-enone (35 g., 0·16 mole) in a minimum of dry xylene was added in one portion and the mixture was refluxed for 5 hr. After cooling and acidification with acetic acid the working up was analogous to that described for the preparation of 3-oxo-2-*o*-tolyl*cyclo*hexylacetic acid (see above). As described above, unchanged ketone can be recovered.

Decarboxylation of the crude malonic acid was effected at 200°. The oily residue was distilled and the *keto-acid* had b. p. 134°/3 mm. (15 g., 33%), m. p. 119—120° (needles from heptane) (Found : C, 76·5; H, 6·6. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). Infrared absorption (in $CHCl_3$) : very broad strong band at 1715 $cm.^{-1}$ (C=O of ketone and of carboxyl). The methyl ester (diazomethane) had b. p. 83°/0·5 mm., n_{D}^{25} 1·50184; it gave a very strong infrared band at 1729 $cm.^{-1}$, intermediate between the values to be expected for a saturated ketonic group and a saturated ester group.

trans-2-α-*Naphthyl*cyclo*hexylacetic Acid*.—The keto-acid (3·5 g.) was reduced by the Huang-Minlon procedure employing potassium hydroxide (2·4 g.), hydrazine hydrate (1·5 ml.), and diethylene glycol (18 ml.). Heating for 4 hr. at 200° was insufficient for complete reduction. The reduced *acid* (0·6 g.) was obtained by distillation (b. p. 165—180°/1·4 mm.) as a viscous yellow oil which slowly crystallised and formed colourless needles, m. p. 84—86°, from heptane (Found : C, 79·9; H, 6·9. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%).

1 : 2 : 3 : 4 : 4a : 5 : 6 : 12c-*Octahydro*-1 : 6-*dioxobenzo*[c]*phenanthrene* (V).—The keto-acid (2·3 g.) was treated with anhydrous hydrogen fluoride (*ca.* 50 g.). After the usual working up the crude diketone was obtained as a brownish oil (2·1 g., 95%) with a characteristic odour. A benzene solution of the oil was filtered through a column of neutral alumina. Evaporation of the eluate afforded a light yellow oil which soon crystallised to needles of the *diketone*. It formed yellowish needles, m. p. 40—41° (from heptane), and occasionally crystallised as glistening yellowish plates of the same m. p. which did not depress the m. p. of the needles (Found: C, 81·5; H, 6·2. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·0%). The infrared spectrum showed a very strong band at 1702 $cm.^{-1}$ intermediate between a *cyclo*hexanone- and an acetophenone-type ketone, and bands at 1278 (acetophenone) and 1176 $cm.^{-1}$ (*cyclo*hexanone). The *bis*-2 : 4-*dinitrophenylhydrazone* formed orange needles, m. p. 258—260° (decomp.), from methanol–ethyl acetate (Found : C, 57·7; H, 3·9; N, 17·7. $C_{30}H_{24}O_8N_8$ requires C, 57·7; H, 3·8; N, 17·9%). Ultraviolet absorption : $\lambda_{max.}$ 3920 Å (log ε 4·77 in $CHCl_3$). The *dioxime*, prepared in pyridine, formed needles, m. p. 117—119°, from aqueous methanol (Found : C, 73·4; H, 5·7; N, 9·1. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·2; N, 9·5%).

1 : 2 : 3 : 4 : 4a : 5 : 6 : 12c-*Octahydro*-6-*oxobenzo*[c]*phenanthrene*.—2-α-Naphthyl*cyclo*hexylacetic acid (1·0 g.) was treated with anhydrous hydrogen fluoride (*ca.* 30 g.). The crude ketone

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[7] Orchin, *J. Amer. Chem. Soc.*, 1948, **70**, 495.

(0·9 g., 92%) was purified by filtration of its benzene solution through neutral alumina, and the eluate upon evaporation gave the ketone as a yellow oil (0·83 g.) which partially crystallised in the refrigerator. Infrared absorption (in $CHCl_3$) : 1709 cm.$^{-1}$, possibly indicating diminished coplanarity with the aromatic ring. It was characterised as the 2 : 4-*dinitrophenylhydrazone* which formed dark red plates, m. p. 186—188° (from ethanol) (Found : C, 66·5; H, 5·4; N, 13·5. $C_{24}H_{22}O_4N_4$ requires C, 67·0; H, 5·1; N, 13·0%) [ultraviolet absorption $\lambda_{max.}$ 3930 Å (log ε 4·55 in $CHCl_3$)], and as *oxime*, prepared in pyridine, needles, m. p. 118—123° (from aqueous ethanol) (Found : N, 5·7. $C_{18}H_{19}ON$ requires N, 5·3%).

Reductions of the Diketone Bisdithioacetals with Raney Nickel.—(*a*) The diketone (V) (1 g.) was treated in dioxan (5 ml.) with ethanethiol (2 g., 8 equivs.) and boron trifluoride–ether complex (1·5 ml.). A strong exothermic reaction occurred and crystals appeared in the solution. After 36 hr. at room temperature aqueous sodium hydrogen carbonate was added, whereupon the crystals dissolved. The organic phase was separated, the aqueous layer was extracted with ether, the organic phases were combined, washed with water, and dried (Na_2SO_4), and the ether and excess of thiol were removed on the steam-bath. The residue was refluxed in ethanol (100 ml.) with Raney nickel (15 g.) for 6 hr. After removal of the nickel and ethanol a brown oil, presumably the 1-ketone was characterised as the orange 2 : 4-*dinitrophenylhydrazone*, m. p. 214—216° (from ethanol) (Found : C, 66·6; H, 5·3. $C_{24}H_{22}O_4N_4$ requires C, 67·0; H, 5·1%).

(*b*) The 1 : 6-diketone (1 g.) was treated in dry dioxan (5 ml.) with toluene-ω-thiol (2 g., 4 equivs.) and boron trifluoride–ether complex (1 ml.). A strong exothermic reaction set in and a heavy crystalline deposit was formed. Working up was similar to that described in (*a*) but the residue was refluxed in dry dioxan (130 ml.) with active Raney nickel [8] (10 g.) for 5 hr. After removal of the catalyst and solvent, the viscous residue was distilled (b. p. 126—128°/0·2 mm.) and crystallised slowly at room temperature, affording colourless prisms and platelets. These were removed and the small amount of adhering oil was washed away with cold methanol. The crystals, m. p. 48—50°, appeared to be the tri- or tetra-benzyl bisdithioacetal (Found : C, 77·4; H, 6·5; S, 16·0. Calc. for $C_{19}H_{38}OS_3$: C, 75·7; H, 6·1; S, 15·5. Calc. for $C_{46}H_{44}S_4$: C, 76·2; H, 6·1; S, 17·7%).

The residue from the distillation was purified by filtering its solution in benzene–light petroleum through neutral alumina, followed by elution with light petroleum. The hydrocarbon was obtained as needles, m. p. 47°. Its infrared spectrum showed no oxygen functions but only the bands at 1604 and 1492 (aromatic C=C), 2910 and 1454 (CH_2), and 3040 cm.$^{-1}$ (aromatic CH).

Benzo[c]*phenanthrene*.—The hydrocarbon just described (100 mg.) was heated with 30% palladised carbon (15 mg.) at 310—320° under nitrogen for 1 hr. After cooling and extraction with hot benzene, the catalyst was removed. Concentration of the benzene solution afforded colourless needles of benzo[*c*]phenanthrene, m. p. and mixed m. p. 69° (from ethanol) (lit., m. p. 68°,[9] 67·5—68·3° [10]) (Found : C, 94·7; H, 5·3. Calc. for $C_{18}H_{12}$: C, 94·7; H, 5·3%). The picrate was prepared in ethanol on the steam-bath, and crystallised as red needles, m. p. 125—126° (lit., m. p. 126—127°,[9] 128—128·5° [10]).

1-*Ethylenedioxy*-1 : 2 : 3 : 4 : 4a : 5 : 6 : 12c-*octahydro*-6-*oxobenzo*[c]*phenanthrene*.—The diketone (V) (1·5 g.), toluene (10 ml.), ethylene glycol (3 ml.), and toluene-*p*-sulphonic acid (45 mg.) were refluxed for 8 hr. under an azeotropic separator, giving the *dioxalan* as yellowish needles, m. p. 136—138° (from toluene) (Found : C, 77·9; H, 6·0. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·5%). Infrared absorption (in $CHCl_3$) : 1678 (acetophenone C=O), 1183, 1156, 1096 cm.$^{-1}$ (ketal).

A *by-product* was obtained in the reaction flask during the boiling period. It formed glistening yellow plates, m. p. *ca.* 340° with some pre-sintering (Found : C, 94·7; H, 5·2. $C_{36}H_{24}$ requires C, 94·7; H, 5·3%). It was not investigated further.

Cyclisation of 2-α-*Naphthyl*-3-*oxo*cyclo*hexylacetic Acid by Polyphosphoric Acid*.—The acid (2 g.) was warmed on the steam-bath with polyphosphoric acid (60 g.) for 4 hr. with occasional shaking. After cooling and dilution with water, the turbid solution was extracted several times with ether. The ether extract was washed with aqueous sodium carbonate and with water and dried (Na_2SO_4). After removal of the ether an oily residue (1·2 g.) was obtained. The starting

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[8] *Org. Synth.*, Wiley, New York, 1955, Coll. Vol. III, p. 181.

[9] Cook, *J.*, 1931, 2524.

[10] Bachmann and Edgerton, *J. Amer. Chem. Soc.*, 1940, **62**, 2970.

material (0·3 g.) was recovered by acidification of the sodium carbonate extract. The infrared spectrum showed strong bands at 1712 and 1678 cm.$^{-1}$. No hydroxyl absorption was observed. Benzosuberone has a band at 1678 cm.$^{-1}$ (C=O).

The crude product was treated with 2 : 4-dinitrophenylhydrazine solution and the mixture of hydrazones thus obtained was dissolved in benzene and chromatographed on neutral alumina. The major fraction formed red rods and rhombs, m. p. 283° (decomp.) (from ethanol–ethyl acetate) (Found : C, 57·4; H, 3·8; N, 17·5. $C_{30}H_{24}O_8N_8$ requires C, 57·7; H, 3·8; N, 17·9%). This is formulated as the 2 : 4-*dinitrophenylhydrazone* of 7 : 8 : 8*a* : 9 : 10 : 11 : 12 : 12*a*-octahydro-7 : 12-dioxobenzo[4 : 5]*cyclo*hepta[1 : 2 : 3-*de*]naphthalene (VI). Ultraviolet absorption : $\lambda_{max.}$ 3910 Å (flat) (log ε 4·74 in $CHCl_3$). Two other bands were observed on the column but elution gave negligible material. The corresponding derivative of (V) was not obtained.

DANIEL SIEFF RESEARCH INSTITUTE, REHOVOT.
ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL.

[*Received, September 24th,* 1956.]