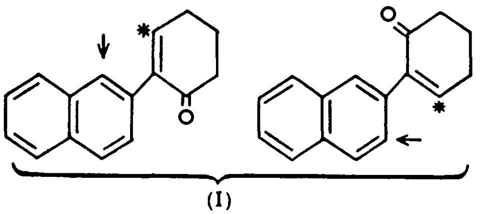
247. *Alicyclic Studies. Part VIII.* An Alicyclic Approach to the Synthesis of Chrysene.*

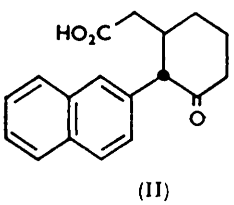
By Yair Klibansky and David Ginsburg.

2-β-Naphthyl*cyclo*hex-2-enone was prepared *via* the nitrosochloride of 1-β-naphthyl*cyclo*hexene. Michael condensation of this ketone with benzyl malonate affords an adduct which on debenzylation and decarboxylation affords *trans*-2-β-naphthyl-3-oxo*cyclo*hexylacetic acid. Hydrogen fluoride cyclises this keto-acid to 1 : 2 : 3 : 4 : 4*a* : 11 : 12 : 12*a*-octahydro-4 : 11-dioxochrysene. Reduction of the diketone by sodium borohydride, followed by dehydration and dehydrogenation, yields chrysene.

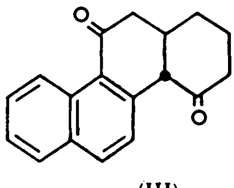
In the preceding paper it was shown that 2-α-naphthyl*cyclo*hex-2-enone acts as an acceptor in the Michael condensation, and its adduct with benzyl malonate is an intermediate in the synthesis of benzo[*c*]phenanthrene. In that case the result confirmed expectation but for the similar adduct of 2-β-naphthyl*cyclo*hex-2-enone (I) it is difficult to prophesy the direction of cyclisation of the keto-acid (II). From structures (I) it may be seen that an acetic acid side chain in the starred position can, in principle, be cyclised to either of the positions marked with an arrow. Perhaps a mixture of two products might be formed. It is known, for example, that γ-2-phenanthrylbutyric acid is cyclised in 23% yield to a benz[*a*]anthracene precursor by means of hydrogen fluoride [1] but cyclisation of the corresponding acid chloride with stannic chloride gives the isomeric hydrochrysene in excellent yield.[2] It is clear from the work of other authors who used 85% sulphuric acid as the cyclising agent that mixtures of both ketones must be formed.[3]



(I)



(II)



(III)

trans-2-β-Naphthyl-3-oxo*cyclo*hexylacetic acid (II) was prepared by debenzylation and decarboxylation of the adduct of the αβ-ethylenic ketone (I) with benzyl malonate. Cyclisation with hydrogen fluoride afforded 1 : 2 : 3 : 4 : 4*a* : 11 : 12 : 12*a*-octahydro-4 : 11-dioxochrysene (III). The crude ketone was reduced with sodium borohydride to the diol

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* Part VII, preceding paper.

[1] Fieser and Johnson, *J. Amer. Chem. Soc.*, 1939, **61**, 1647.

[2] Bachmann and Struve, *J. Org. Chem.*, 1939, **4**, 456.

[3] Haworth and Mavin, *J.*, 1933, 1012; Burger and Mosettig, *J. Amer. Chem. Soc.*, 1937, **59**, 1302.

which, without isolation, was dehydrated and dehydrogenated with palladised charcoal to yield chrysene. Since similar dehydrogenation of various hydrobenz[*a*]anthracenes yields the corresponding benz[*a*]anthracenes[2, 4] without rearrangement to the chrysene ring system and none of the easily isolable benz[*a*]anthracene was obtained in the present work, it is believed that in this case cyclisation gives exclusively the chrysene precursor.

Here, also, as in the case of 1 : 2 : 3 : 4 : 4*a* : 5 : 6 : 12*c*-octahydro-1 : 6-dioxobenzo[*c*]-phenanthrene,[5] the diketone (III) exhibited a broad carbonyl infrared absorption band at 1702 cm.$^{-1}$, intermediate between the value expected for the saturated carbonyl group and that for the one adjacent to the aromatic nucleus.

Analogous Michael condensations of 2-β-naphthyl*cyclo*pent-2-enone and 2-β-naphthyl-*cyclo*hept-2-enone[6] with the view of obtaining tetracyclic systems are in progress.

EXPERIMENTAL

1-β-*Naphthyl*cyclo*hexene*.—To a solution of β-naphthyl-lithium[7] prepared from β-bromonaphthalene (10 g.) was added at −10° with vigorous stirring, under nitrogen, a solution of *cyclo*hexanone (4·5 g.) in dry ether (8 ml.). A white precipitate was formed. The temperature was raised to 25° during 2·5 hr. and the mixture left overnight. After the usual working up the *cyclo*alkene was distilled (b. p. 150—156°/0·7 mm.; 7·5 g., 75%); it formed colourless needles, m. p. 59°, from methanol (lit.,[8] m. p. 61—62°) (Found: C, 92·7; H, 7·7. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%). The picrate formed red needles, m. p. 78° (lit.,[8] m. p. 78°).

A higher-boiling fraction (1 g.) obtained in the distillation (b. p. >175°/0·7 mm.) gave a grey solid which formed yellowish plates, m. p. 187—188°, from benzene. This was ββ′-dinaphthyl (Found: C, 94·6; H, 5·7. Calc. for $C_{20}H_{14}$: C, 94·5; H, 5·5%).

2-β-*Naphthyl*cyclo*hex-2-enone*.—This preparation was carried out as was that of its α-naphthyl isomer.[5] From 10 g. of the *cyclo*hexene, 10·5 g. of crude oxime (91%) were obtained. The αβ-ethylenic *ketone* was obtained from the oxime in 65% yield. It had b. p. 160—175°/0·5 mm. and was purified by filtering its benzene solution through neutral alumina. The residual oil after evaporation of the benzene formed colourless needles, m. p. 96° (from heptane) (Found: C, 86·1; H, 6·0. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). Infrared absorption (in $CHCl_3$): 1674 cm.$^{-1}$ (C=C–C=O). The 2 : 4-*dinitrophenylhydrazone* was obtained as short orange needles or leaves, m. p. 209·5—211° (from ethanol–ethyl acetate) (Found: C, 65·3; H, 4·5; N, 13·5. $C_{22}H_{18}O_4N_4$ requires C, 65·7; H, 4·5; N, 13·9%). Ultraviolet absorption: $\lambda_{max.}$ 3870 Å (log ε 4·37 in $CHCl_3$). The *oxime* formed colourless needles, m. p. 205°, from aqueous ethanol (Found: C, 80·8; H, 6·0; N, 5·5. $C_{16}H_{15}ON$ requires C, 81·0; H, 6·3; N, 5·9%).

trans-2-β-*Naphthyl-3-oxo*cyclo*hexylacetic Acid*.—This *acid*, prepared in 33% yield as was its α-naphthyl isomer,[5] crystallised as needles, m. p. 181—182°, from heptane (Found: C, 76·1; H, 6·1. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). The infrared spectrum showed a very strong broad band at 1710 cm.$^{-1}$, both carbonyl functions overlapping. Most (55%) of the original ketone can be recovered after debenzylation and alkali-extraction.

1 : 2 : 3 : 4 : 4a : 11 : 12 : 12a-*Octahydro-4 : 11-dioxochrysene*.—The keto-acid (4 g.) yielded the diketone (3·2 g., 86%) by cyclisation with hydrogen fluoride. The procedure paralleled that for the cyclisation of the α-naphthyl isomer.[5] The *diketone* formed yellowish needles, m. p. 35—40°, from pentane. The infrared spectrum showed a very broad band at 1702 cm.$^{-1}$ and bands at 1278 (acetophenone C=O) and 1176 cm.$^{-1}$ (*cyclo*hexanone C=O). The *bis-2 : 4-dinitrophenylhydrazone* formed orange needles, m. p. 261—262·5° (decomp.), from ethanol–ethyl acetate. It sometimes crystallised as orange-red needles of the same m. p. and ultraviolet absorption (Found: C, 57·7; H, 3·75; N, 17·8. $C_{30}H_{24}O_8N_8$ requires C, 57·7; H, 3·8; N, 17·9%). Ultraviolet absorption: $\lambda_{max.}$ 3140, 3910 Å (log ε 4·13, 4·87 in $CHCl_3$). The *dioxime*, prepared in pyridine, formed colourless needles, m. p. 145—145·5°, from water (Found: C, 73·4; H, 6·0. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·1%).

Chrysene.—(*a*) The diketone (1·5 g.) was dissolved in methanol (50 ml.) and sodium borohydride (1·8 g.) was added in small portions with shaking. The solution began nearly to boil.

[4] Bachmann and Chemerda, *J. Org. Chem.*, 1941, **6**, 36, 50.

[5] Klibansky and Ginsburg, preceding paper.

[6] Bar-Shai and Ginsburg, *J.*, 1957, 1289.

[7] Gilman and Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 1843.

[8] Bergmann and Bergmann, *ibid.*, 1940, **62**, 1699.

After several hours at room temperature, methanol (25 ml.) and sodium borohydride (1·5 g.) were added. After being kept overnight the mixture was worked up in the usual way and the product was obtained as a brown oil (1·25 g.). It gave no precipitate with 2 : 4-dinitrophenylhydrazine and its infrared spectrum exhibited no carbonyl absorption but showed a strong band at 3385 cm.$^{-1}$ (OH). (*b*) The oil was boiled with oxalic acid (0·5 g.) in toluene (50 ml.). A small amount of water was collected in the azeotropic adapter. After the usual working up an oil (1·2 g.) was obtained whose infrared spectrum showed no oxygen-containing functional groups. (*c*) The oil was heated under nitrogen with 30% palladised charcoal (200 mg.) at 310—320° for 1 hr. After cooling and extraction with hot benzene the catalyst was removed and the benzene solution was filtered through neutral alumina. Evaporation of the eluate gave chrysene, m. p. 252—255° (from toluene) (lit.,[9] m. p. 263—267°). It did not depress the m. p. of authentic chrysene, which in our hands had m. p. 253—255°.

No benz[*a*]anthracene was isolated from the dehydrogenations.

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