244. *Alicyclic Studies. Part V.* The Preparation of 2-Naphthyl*cyclo*alk-2-enones.*

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2-α-Naphthyl- and 2-β-naphthyl-*cyclo*pent-2-enone and 2-β-naphthyl*cyclo*hept-2-enone have been prepared from the corresponding 1-naphthyl*cyclo*alkenes through the nitrosochlorides and oximes.

2-Aryl*cyclo*hex-2-enones,[1] 2-phenyl*cyclo*pent-2-enone,[2] and 2-phenyl*cyclo*hept-2-enone [3] have been prepared from the corresponding 1-aryl*cyclo*alkenes. This method of preparation has now been extended to 1-naphthyl*cyclo*alkenes. The use of 1-α- and 1-β-naphthyl*cyclo*hexene as starting materials for preparation of the corresponding αβ-ethylenic ketones as intermediates in the synthesis of 3 : 4-benzophenanthrene and chrysene, respectively, is being described elsewhere.[4, 5] In this communication, the analogous preparation of 2-α- and 2-β-naphthyl*cyclo*pent-2-enone and 2-β-naphthyl*cyclo*hept-2-enone as intermediates for the preparation of various tetracyclic systems is described.

Experimental

1-α-Naphthyl*cyclo*pentene was prepared by the method of Bachmann and Kloetzel [6] in 46% yield.

*2-α-Naphthyl*cyclo*pent-2-enone Oxime.*—(*a*) The nitrosochloride of the above *cyclo*alkene was prepared by dropwise addition of concentrated hydrochloric acid (5 ml.) to a vigorously stirred mixture of the hydrocarbon (5 g.), *n*-pentyl nitrite (7 ml.), and glacial acetic acid (10 ml.) at −10° to −7°.

(*b*) The crystalline nitrosochloride was removed and added without purification to pyridine

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* Part IV, preceding paper.

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

[2] Amiel, Loeffler, and Ginsburg, *J. Amer. Chem. Soc.*, 1954, **76**, 3625.

[3] Ginsburg and Pappo, *ibid.*, 1953, **75**, 1094.

[4] Klibansky and Ginsburg, *J.*, 1957, 1293.

[5] *Idem, ibid.*, p. 1299.

[6] Bachmann and Kloetzel, *J. Amer. Chem. Soc.*, 1938, **60**, 2204.

(40 ml.). The mixture was warmed on a steam-bath for 15 min. The solid dissolved and the brown solution was diluted with cold water (100 ml.). Crystallisation of the precipitated oil was induced by scratching. Filtration yielded the crude *oxime*. The analytical sample obtained by recrystallisation from benzene had m. p. 208—210° (1·9 g.) (Found : C, 80·6; H, 5·8; N, 6·25. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·9; N, 6·3%).

2-α-*Naphthyl*cyclo*pent-2-enone*.—The oxime (1 g.) was hydrolysed by refluxing it with concentrated hydrochloric acid (2 ml.) and water (30 ml.) for 4 hr. The *ketone*, recrystallised from *cyclo*hexane, had m. p. 110—112° (0·8 g.) (Found : C, 86·6; H, 5·7. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%). Infrared absorption (C=O) : 1700 cm.$^{-1}$. The orange-red 2 : 4-*dinitrophenylhydrazone* obtained in the usual way had m. p. 248—250° (from ethanol–ethyl acetate) (Found : C, 65·1; H, 4·0; N, 14·45. $C_{21}H_{16}O_4N_4$ requires C, 64·9; H, 4·15; N, 14·4%).

2-α-*Naphthyl*cyclo*pentanone*.—Hydrogenation of the αβ-ethylenic ketone (0·5 g.) in ethyl acetate with 10% palladised carbon (0·2 g.) during 1 hr. yielded the saturated ketone, m. p. 92—93° (methanol). The orange 2 : 4-dinitrophenylhydrazone had m. p. 213—214° (from acetonitrile). Klemm and Ziffer [7] report m. p. 91—93° and 212·5—213·5°, respectively, for these compounds.

1-β-*Naphthyl*cyclo*pentanol*.—*n*-Butyl-lithium was prepared in the usual way [8] from lithium wire (5·5 g.) and *n*-butyl bromide (43 g.) in dry ether (200 ml.). The solution was filtered under nitrogen and a solution of β-bromonaphthalene (50 g.) in dry ether (100 ml.) was added during 1 hr. under nitrogen at room temperature. The mixture was stirred for an additional 30 min., then cooled to $-10°$, and a solution of *cyclo*pentanone (20 g.) in dry ether (40 ml.) was added dropwise at $< -5°$. The temperature was permitted to rise slowly and the mixture kept overnight. It was decomposed with saturated ammonium chloride solution and the ether was removed. The *alcohol* solidified and, recrystallised from hexane, had m. p. 83—85° (25 g.), infrared absorption (OH) at 3590 cm.$^{-1}$ (Found : C, 84·95; H, 7·5. $C_{15}H_{16}O$ requires C, 84·9; H, 7·6%).

1-β-*Naphthyl*cyclo*pentene*.—The above alcohol (25 g.) was boiled with anhydrous oxalic acid (6 g.) in toluene (150 ml.), until the theoretical quantity of water was removed azeotropically. After the usual working up [1] the *cyclo*alkene was obtained by distillation. It had b. p. 141°/0·6 mm., m. p. 84—85° (ethanol) (20 g.). Bachmann and Kloetzel [6] report m. p. 84—85°. Admixture with the alcohol gave a large m. p. depression.

2-β-*Naphthyl*cyclo*pent-2-enone Oxime*.—(*a*) The nitrosochloride could not be prepared from the *cyclo*alkene owing to sparing solubility of the latter in acetic acid. It was therefore prepared directly from the alcohol. Concentrated hydrochloric acid (6 ml.) was added dropwise at $-5°$ to 0° to a vigorously stirred mixture of the alcohol (5 g.), *n*-pentyl nitrite (7 ml.), and glacial acetic acid (20 ml.). The mixture was stirred for an additional 2 hr. and the nitrosochloride was filtered off and washed with cold methanol. (*b*) The crude nitrosochloride was treated as described above for its isomer. The *oxime*, recrystallised from benzene, had m. p. 181—182° (1·9 g.) (Found : C, 80·7; H, 6·0; N, 6·1%).

2-β-*Naphthyl*cyclo*pent-2-enone*.—Hydrolysis of the oxime (0·5 g.) was carried out as described above for its isomer. The crude ketone was extracted with ether, the solvent removed, and the residue was distilled, giving the *ketone* b. p. 157—158°/0·02 mm., m. p. 103—104° (from hexane) (0·4 g.) (Found : C, 86·0; H, 5·7%). Infrared absorption (C=O) : 1700 cm.$^{-1}$. The red 2 : 4-*dinitrophenylhydrazone* had m. p. 254—255° (from nitromethane) (Found : C, 64·8; H, 4·0; N, 14·6%). The colourless *semicarbazone* had m. p. 220—222° (from ethanol) (Found : C, 72·0; H, 5·75; N, 15·4. $C_{16}H_{15}ON_3$ requires C, 72·4; H, 5·7; N, 15·8%).

2-β-Naphthyl*cyclo*pentanone, obtained by reduction as described above for its isomer, had m. p. 80—81°. Its orange 2 : 4-dinitrophenylhydrazone had m. p. 163—164°. Klemm and Ziffer [7] report m. p.s 80—83° and 162—163°, respectively.

1-β-*Naphthyl*cyclo*heptene*.—This was prepared on the same scale as described for 1-β-naphthyl*cyclo*pentene from *n*-butyl-lithium and *cyclo*heptanone (27 g.). Dehydration of the crude mixture of alcohol (partially dehydrated even by ammonium chloride) and *cyclo*alkene was completed by refluxing with oxalic acid in toluene. The *cyclo*alkene distilled at 147°/0·35 mm. and appeared to have m. p. *ca.* 20° (27 g.).

2-β-*Naphthyl*cyclo*hept-2-enone Oxime*.—This was prepared as above. It did not crystallise and was therefore taken up in ether and extracted with Claisen's alkali. After acidification of

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[7] Klemm and Ziffer, *J. Org. Chem.*, 1956, **21**, 274.

[8] Gilman, Beel, Brannen, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499.

the latter extract the oxime was taken up in chloroform, and the solvent was removed. Attempted vacuum-distillation of the oxime was unsuccessful as the crude oxime largely decomposed to give polymeric material. A small amount of material (0·3 g.) was obtained having b. p. 200—206°/0·1 mm., m. p. 185° (from pentane).

2-β-*Naphthyl*cyclo*hept*-2-*enone*.—This ketone was obtained by hydrolysis of the crude undistilled oxime (5 g.) with boiling 10% hydrochloric acid for 15 hr. Chloroform-extraction yielded the crude oily ketone (3 g.) [infrared absorption (C=O) : 1685 cm.$^{-1}$], characterised as the orange-red 2 : 4-*dinitrophenylhydrazone*, m. p. 125° (from nitromethane) (Found : C, 66·35; H, 4·8; N, 13·5. $C_{23}H_{20}O_4N_4$ requires C, 66·3; H, 4·8; N, 13·5%).

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