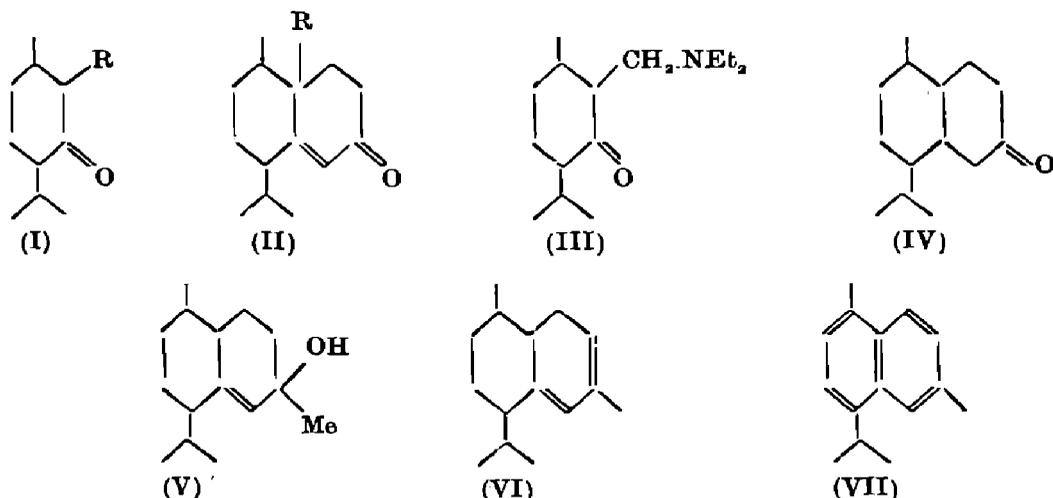


## Polycyclic Compounds. Part I. Synthesis of Sesquiterpene Compounds

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A synthesis of 1,6-dimethyl-4-isopropynaphthalene (VII) from the ketone (II) is described. 3-Methyl-6-isopropyl-2-hydroxymethylenecyclohexanone<sup>1</sup> (I: R=CHO) on alkylation with 4-diethylaminobutan-2-one methiodide according to the known procedure<sup>2</sup>, followed by treatment with dilute methanolic alkali, leads to 5-methyl-8-isopropyl-2-oxo-10-formyl-2,3,4,5,6,7,8,10-octahydronaphthalene (II: R=CHO).<sup>3</sup> The basic cleavage<sup>3</sup> of the hydroxymethylene group under such mild condition is not effected.

Gills and Lions<sup>4</sup> induced alkylation of ethyl acetoacetate with 3-methyl-6-isopropyl-2-morpholinomethylcyclohexanone. Failing to prepare 3-methyl-6-isopropyl-2-morpholinomethylcyclohexanone, the following method was adopted to obtain the ketone (II: R=H) in good quantity and in the pure state. A solution of 3-methyl-6-isopropyl-2-diethylaminomethylcyclohexanone (III) methiodide in ethanol was added to the sodio derivative of ethyl acetoacetate and the crude material so obtained was hydrolysed with ethanolic caustic potash by an improved method to effect both ring closure and decarboxylation.



It was planned to carry out the synthesis of the ketone (II: R=H) from 3-methyl-6-isopropyl-2-hydroxymethylenecyclohexanone (I: R=CHO) by alkylation with 4-diethylaminobutan-2-one methiodide according to the known procedure<sup>2</sup>. Reaction of the hydroxymethylene ketone (I: R=CHO) with 4-diethylaminobutan-2-one methiodide result-

1. Johnson *et al.*, *J. Amer. Chem. Soc.*, 1946, **67**, 1750.
2. Shunk and Wilds, *ibid.*, 1949, **71**, 3948; 1950, **72**, 2392; Woodward *et al.*, *ibid.*, 1952, **74**, 4223.
3. Wilds and Werth, *J. Org. Chem.*, 1962, **17**, 1149, 1154.
4. *J. Amer. Chem. Soc.*, 1950, **72**, 3468.

ed in introduction of  $\gamma$ -keto-butyl group in excellent yield. In the present instance, the product consisted of one in which the formyl group was retained. This was cyclised smoothly with dilute methanolic alkali at the room temperature to 5-methyl-8-isopropyl-2-oxo-10-formyl-2,3,4,5,6,7,8,10-octahydronaphthalene (II: R=CHO).

The pure ketone (II: R=H) on catalytic hydrogenation afforded the saturated ketone (IV) stereospecifically<sup>5</sup>. The alcohol derived from it by the action of methylmagnesium iodide resisted dehydrogenation. The ketone (II: R=H) on further reaction with methylmagnesium iodide, followed by dehydration, provided the diene (VI). The latter afforded cadalene on dehydrogenation<sup>6</sup> with sulphur. The homogeneity has been established by the m.p. and the mixed m.p. of the picrate<sup>7</sup>.

#### EXPERIMENTAL

*3-Methyl-6-isopropyl-2-diethylaminomethylcyclohexanone* (III).—A mixture of 1-menthone (30.5 g.), diethylamine hydrochloride (28 g.), paraformaldehyde (8 g.), HCl (conc., 2 ml), and ethanol (32 ml) was refluxed on a steam bath for 10 hr. Ethanol was removed, the residue was diluted with water (10 ml), and to it KOH (30 g.) in water (15 ml.) was added. The mixture was then saturated with excess of  $K_2CO_3$ , filtered, and washed with ether. The mother liquor was once extracted with ether and the solvent evaporated. The residue on distillation afforded a colorless oil (26.5 g.), b.p. 120-22°/8 mm. (Found: C, 75.26; H, 12.16.  $C_{13}H_{29}ON$  requires C, 75.3; H, 12.1%).

*5-Methyl-8-isopropyl-2-oxo-2,3,4,5,6,7,8,10-octahydronaphthalene* (II: R=H). — Ethyl acetoacetate (5.2 ml) was added to a solution of sodium (0.92 g.) in ethanol (16 ml). *3-Methyl-6-isopropyl-2-diethylaminomethylcyclohexanone* (III) methiodide, prepared from amino-ketone (9.4 g.) and methyl iodide (3 ml) in a little anhydrous ethanol, was added slowly to it. The mixture was allowed to stand overnight and then refluxed for 6 hr. The solvent was removed on a water bath; the residue was cooled, diluted with water, and extracted with ether. The solvent was removed and the residue distilled. The ester (3.5 g.) had b.p. 145-47°/4 mm.

The preceding ester (3.5 g.) was refluxed with a solution of KOH (6 g.) in water (10 ml) and spirit (30 ml) for 3 hr. The solvent was removed on a water bath, the residue cooled, diluted with water, and extracted with ether. The ether extract was once washed with water, dried, ( $CaCl_2$ ), and the solvent removed. The residue on distillation provided a pale yellow oil (1.7 g.), b.p. 133-35°/6 mm (bath temp. 185-90°). (Found: C, 81.42; H, 10.70. Calc. for  $C_{14}H_{22}O$ : C, 81.54; H, 10.63%). The 2,4-DNP formed brick-red plates (from methanol), m.p. 152-53° (lit<sup>4</sup>. m.p. 152-53°). (Found: C, 62.05; H, 6.70. Calc. for  $C_{20}H_{26}O_4N_4$ : C, 62.17; H, 6.73%).

*5-Methyl-8-isopropyl-2-oxo-10-formyl-2,3,4,5,6,7,8,9,10-octahydronaphthalene* (II: R=CHO).—The hydroxymethylene ketone (I: R=CHO) (9.1 g.) was added to a solution of sodium (1.15 g.) in anhydrous ethanol (20 ml) and to the solid sodio salt, cooled

5. Robinson *et al.*, *J. Chem. Soc.*, 1937, 53.

6. Ruzicka, *Helv. Chim. Acta*, 1922, 5, 345.

7. Ruzicka, *Helv. Chim. Acta*, 1922, 5, 369; Barnett *et al.*, *J. Chem. Soc.*, 1933, 22; Bardhan *et al.*, *ibid.*, 1935, 476; Chatterjee, *this Journal*, 1936, 13, 588; Gills and Lions, *ref. No. 4*.

in ice, 4-diethylaminobutan-2-one methiodide, prepared from amino-ketone (7.2 g.) and methyl iodide (4 ml) in a little anhydrous ethanol, was added all at once. After storage for 48 hr. at the room temperature, the product was warmed at 40° for 1 hr. It was then cooled and mixed with a solution of KOH (8 g.) in water (500 ml). After 12 hr., the clear solution was saturated with salt and extracted with ether. The product (4 g.) had b.p. 145-50°/10 mm. (Found: C, 76.83; H, 9.5.  $C_{13}H_{22}O_2$  requires C, 76.90; H, 9.40%). The *semicarbazone* formed prisms (from ethanol), m.p. 225°. (Found: C, 65.80; H, 8.60.  $C_{16}H_{25}O_2N_3$  requires C, 65.90; H, 8.59%).

5-*Methyl-8-isopropyl-2-oxo-1,2,3,4,5,6,7,8,9,10-decahydronaphthalene* (IV).— The preceding octalone (II: R=H) (5 g.) was hydrogenated with palladous chloride (0.2 g.) and gum arabic (0.2 g.) in a minimum quantity of water till the calculated quantity (550 ml) of hydrogen was consumed. The product (4 g.), isolated in the usual manner, had b.p. 130°/4 mm. (Found: C, 80.70; H, 11.60.  $C_{14}H_{24}O$  requires C, 80.76; H, 11.53%).

The *semicarbazone* formed prisms (from EtOH), m.p. 186-87°. (Found: C, 67.80; H, 10.20.  $C_{15}H_{22}ON_3$  requires C, 67.90; H, 10.18%). The *alcohol*, prepared by the action of methylmagnesium iodide on the preceding  $\beta$ -decalone, had b.p. 120-22°/4 mm.

2,5-*Dimethyl-8-isopropyl-4,5,6,7,8,10-hexahydronaphthalene* (VI).— A solution of the octalone (II: R=H) (15 g.) in dry ether was added with stirring to a Grignard reagent, prepared from magnesium (2.1 g.) and methyl iodide (12.4 g.) in ether. The carbinol (6 g.), worked up in the usual manner, was heated with pyridine (30 ml) and  $POCl_3$  (5 ml) in an oil bath (130-40°) for 4 hr. The product was worked up in the usual way and distilled over sodium, affording the pure hydrocarbon, b.p. 107°/4 mm. (Found: C, 88.15; H, 11.80.  $C_{15}H_{24}$  requires C, 88.23; H, 11.77%). The hydrocarbon became viscous on storage for sometime in contact with air.

1,6-*Dimethyl-4-isopropyl-naphthalene* (VII).—The preceding diene (VI) (1 g.) was heated with sulphur (0.5 g.) on a nitre bath (240°) for 4 hr. The product was isolated in the usual way and distilled over sodium to provide a pale yellow hydrocarbon (0.5 g.), b.p. 112-13°/4 mm. (Found: C, 90.80; H, 9.10. Calc. for  $C_{15}H_{18}$ : C, 90.91; H, 9.09%). The picrate formed orange plates (from EtOH), m.p. 114-15° (lit.<sup>7</sup> m.p. 114-16°). (Found: C, 59.00; H, 5.00. Calc. for  $C_{21}H_{21}O_7N_3$ : C, 59.01; H, 4.90%).

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