CLXXXIII.—l-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one*.

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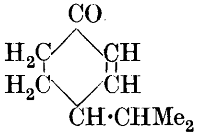
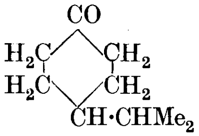
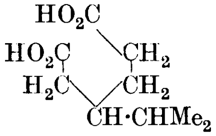
THE aldehyde, *l*-cryptal, has recently been shown to be 4-*iso*propyl-Δ^2-*cyclo*hexenal (J., 1930, 403) and since a more detailed study of its reactions appeared to us to be of interest, the isolation of a further quantity of this aldehyde from the oil of *Eucalyptus cneorifolia* was undertaken. Although in four distinct preparations an oil was obtained which had physical properties agreeing very closely with those observed previously for cryptal, a careful examination has shown it to be the unsaturated ketone, l-4-iso*propyl*-Δ^2-cyclo*hexen*-1-*one* (I). *dl*-4-*iso*Propyl-Δ^2-*cyclo*hexenone was prepared originally by Wallach (*Annalen*, 1905, **343**, 30) by the oxidation of β-phellandrene and later by the same author (*ibid.*, 1907, **356**, 235; 1908, **359**, 270) from sabinaketone and nopinone, but its occurrence in nature does not appear to have been observed previously. The constitution of the ketone was established by the preparation of the *semicarbazone*, m. p. 185°, by the formation of an additive compound with hydrogen sulphide, a property characteristic of ketones containing an ethylenic linkage in the αβ-position to the carbonyl group, and finally by its reduction, both catalytically and electrolytically, to the saturated ketone, 4-*iso*propyl*cyclo*hexanone (II). This ketone gave, on oxidation with chromic acid, β-*iso*propyladipic acid (III), its identity with the ketone described by Wallach (*ibid.*, 1905, **343**, 33; 1908, **359**, 280) thus being proved.


(I.)


(II.)


(III.)

In addition to the saturated ketone, a small quantity of the corresponding alcohol, 4-*iso*propyl*cyclo*hexanol, was obtained by the electrolytic reduction of *l*-4-*iso*propyl-Δ^2-*cyclo*hexenone. This alcohol, which was prepared by Wallach (*ibid.*, 1905, **343**, 32) by the reduction of the unsaturated ketone with sodium and alcohol, has now been characterised by the preparation of the *phenylurethane*, m. p. 75—77°, and the naphthylurethane, m. p. 115—116°.

In view of the above results, the question naturally arose as to whether *l*-cryptal actually occurs in nature or whether the previous conclusions were based on erroneous analytical data, since both cryptal and 4-*iso*propyl-Δ^2-*cyclo*hexenone would yield the same products on oxidation with potassium permanganate.

l-Cryptal was isolated originally from the oil derived from *E. hemiphloia* (Maiden and Smith, " A Research on the Eucalypts," 2nd Ed., p. 387; compare Penfold, J., 1922, **121**, 266) and later from the oils of *E. polybractea* and *E. cneorifolia.* Unfortunately no sample of the original aldehyde was available, but we had in our possession small specimens of the semicarbazones prepared from the aldehyde isolated from the first two oils and also a specimen of *l*-cryptal *p*-nitrophenylhydrazone. The semicarbazone from the oil of *E. hemiphloia*, m. p. 177—179°, crystallised from methyl alcohol in prismatic needles, which decomposed at 182—183° (Found: C, 63·3; H, 8·5. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·1%). There can be no doubt that this semicarbazone was derived from a carbonyl derivative containing ten carbon atoms. We found, however, the semicarbazone from the oil of *E. polybractea*, irregular prisms, decomp. 185—187°, to be that of *l*-4-*iso*propyl-Δ^2-*cyclo*hexenone (Found: C, 61·3; H, 8·7. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·7%). A mixture of the two semicarbazones decomposed at 182°. *l*-Cryptal *p*-nitrophenylhydrazone differed markedly in appearance from l-4-iso*propyl*-Δ^2-cyclo*hexenone*-p-*nitrophenylhydrazone.* The melting points of these derivatives lie very close together but on admixture there is a depression of 10°.

Although we have not, in our more recent experiments, succeeded in isolating *l*-cryptal, there would appear to be no doubt of its separate existence and it is possible that it is only present during certain seasons. There is no method available for the separation of cryptal from the unsaturated ketone, and the presence of the aldehyde has been definitely established only in the specimen of the oil from *E. hemiphloia* examined by Maiden and Smith (*loc. cit.*).

In our previous communication (*loc. cit.*, p. 404) attention was directed to the relationship of cryptal, phellandral, and cuminaldehyde to α-phellandrene. 4-*iso*Propyl-Δ^2-*cyclo*hexenone is derived most simply from the related hydrocarbon, β-phellandrene, yet it is not improbable that it is an oxidation product of the enolic form of cryptal, which would account for the apparently complete absence of this aldehyde in the oils examined recently.

So far as we are aware, this is the first cyclic ketone containing nine carbon atoms which has been found to occur in nature, the only other natural products in the terpene series containing this number of carbon atoms being santene and its derivatives.

EXPERIMENTAL.

1-4-iso*Propyl*-Δ^2-cyclo*hexenone*.—For the experiments to be described in the sequel, four different samples of the unsaturated ketone were available, which had been separated from the oil of *E. cneorifolia* by the method described for the isolation of cryptal (Penfold, *loc. cit.*). These had the following constants :—

(A)	b. p. 98—100°/10 mm.,	$d_{15^\circ}^{15^\circ}$ 0·9481,	$n_D^{20^\circ}$ 1·4836,	α_D – 66·4°
(B)	,, ,,	0·9472	1·4820	– 65·0
(C)	,, ,,	0·9476	1·484	– 59·3
(D)	,, ,,	0·9483	1·4848	– 66·1

Sample (B) was analysed (Found : C, 77·9; H, 10·2. $C_9H_{14}O$ requires C, 78·2; H, 10·1%) and gave a *semicarbazone*, which crystallised from methyl alcohol in irregular prisms, decomp. 185° (Found : C, 61·3; H, 8·8. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·7%). The p-*nitrophenylhydrazone* separated from alcohol in pale brown needles, m. p. 168—169° (Found : C, 65·8; H, 7·0. $C_{15}H_{19}O_2N_3$ requires C, 65·9; H, 7·0%). On admixture with *l*-cryptal *p*-nitrophenylhydrazone, m. p. 167°, the melting point was depressed to 157°. These derivatives were prepared also from sample (A). By treatment of the ketone with hydrogen sulphide under the conditions used by Wallach (*Annalen*, 1899, **305**, 224; 1905, **343**, 32) the hydrogen sulphide derivative was obtained as an amorphous solid, which was purified by precipitation from its chloroform solution with alcohol. It then decomposed at 82°.

Reduction of 1-4-iso*Propyl*-Δ^2-cyclo*hexenone*.—(i) *Electrolytic*. Samples (A), (B), and (C) were reduced electrolytically, the anode being a platinum spiral and the cathode freshly etched nickel (2 sq. dcm.). The liquid in the outer (cathodic) cell consisted of a mixture of the unsaturated ketone (125 c.c.), alcohol (95%, 250 c.c.), sulphuric acid (10%, 50 c.c.), and nickel sulphate (1·5 g.), and the inner (anodic) cell contained sulphuric acid (10%). During the reduction, which lasted 6·75 hours, a further quantity of acid (90 c.c.) was added, the bath being maintained at 26°; *C.D.* 3—4 amps., *E.M.F.* 13—14 volts. After reduction was complete, the contents of the cathodic cell were poured into a large volume of water, and the oil was separated and purified by distillation in steam. The distillate was extracted with ether, and the ethereal solution shaken with sodium sulphite solution to remove unchanged unsaturated ketone and with sodium bisulphite solution; a crystalline compound

(E) was then obtained. This was separated, and the ethereal solution dried and evaporated. The residual oil, m. p. 8—10°, b. p. 143°/100 mm., $d_{15^\circ}^{15^\circ}$ 0·9232, $n_D^{20^\circ}$ 1·4661, had a pleasant smell of hyacinths and was identified by analysis as 4-*iso*propyl*cyclo*hexanol (Found : C, 76·0; H, 12·7. Calc. : C, 76·0; H, 12·7%). It is possible that the alcohol was not quite pure, since it was slightly optically active ($\alpha_D + 2^\circ$). The *phenylurethane* crystallised from light petroleum in large cubes, m. p. 75—77° (Found : C, 73·7; H, 8·9. $C_{16}H_{23}O_2N$ requires C, 73·6; H, 8·8%).

From the sodium bisulphite compound (E) a ketone was regenerated by alkali; this was further purified by conversion into the *semicarbazone*, which crystallised from alcohol in leaflets, m. p. 188—189° (Found : C, 60·8; H, 9·3. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·6%). 4-*iso*Propyl*cyclo*hexanone, obtained from the semicarbazone by hydrolysis with sulphuric acid (10%), had b. p. 139—140°/100 mm., $d_{25^\circ}^{25^\circ}$ 0·9185, $n_D^{25^\circ}$ 1·4552 (Found : C, 76·7; H, 11·2. Calc. : C, 77·1; H, 11·4%). The p-*nitrophenylhydrazone* crystallised from alcohol in pale yellow needles, m. p. 123—124° (Found : C, 65·6; H, 7·6. $C_{15}H_{21}O_2N_3$ requires C, 65·4; H, 7·6%).

(ii) *Catalytic.* Samples (A) and (B) were reduced catalytically with identical results. A mixture of the unsaturated ketone (sample A) (7 g.), alcohol (70 c.c.), and palladinised charcoal (1 g.) was shaken in hydrogen, absorption of the gas (1050 c.c.; calc., 1136 c.c.) being complete in 15 minutes. The saturated ketone so obtained was identified by conversion into the semicarbazone, m. p. 188—189°, and the *p*-nitrophenylhydrazone, m. p. 123—124°.

Oxidation of 4-iso*Propyl*cyclo*hexanone.*—A mixture of the ketone (5 c.c.) and dilute sulphuric acid (50 c.c.; H_2SO_4,5 c.c.) was warmed on the water-bath, and chromic acid solution (CrO_3, 6·5 g.; H_2O, 10 c.c.) added gradually. When the oxidation was complete, the solution was extracted with ether, the ethereal extract washed with sodium carbonate solution, and the latter warmed to precipitate chromium salts, filtered, acidified, and extracted with ether. On evaporation of the solvent a solid remained which, after crystallisation from water, had m. p. 80°. It was identified as β-*iso*propyladipic acid, which is stated to melt at 83—84° (Crossley, J., 1915, **107**, 175) (Found : C, 57·5; H, 8·6; *M*, 188·2. Calc. : C, 57·4; H, 8·5%; *M*, 188).

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