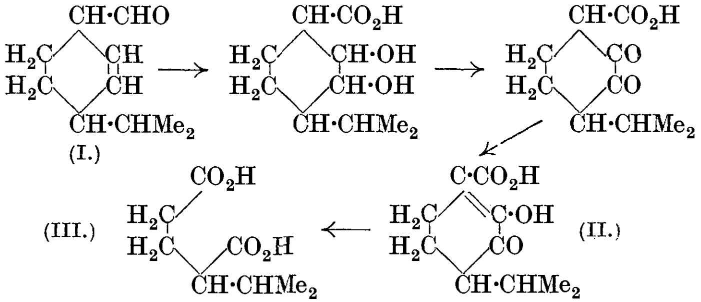
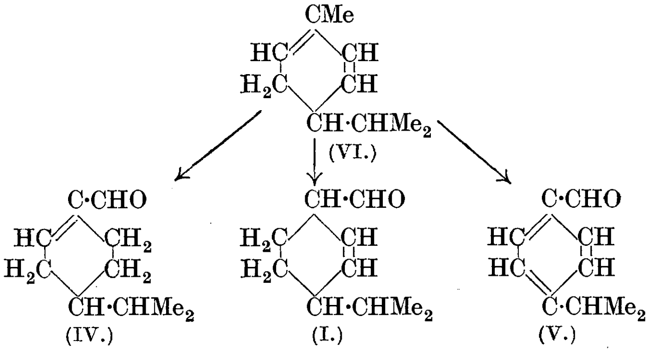
LV.—*The Constitution of Cryptal.*

By Arthur Ramon Penfold and John Lionel Simonsen.

It was shown some years ago (Penfold, J., 1922, **121**, 266) that the aldehyde " aromadendral " described by Smith (*J. Roy. Soc. New South Wales*, 1900, **34**, 286; *Pharm. J.*, 1905, **75**, 356, 382; *Trans. Roy. Soc. South Australia*, 1916, **40**, 485) was a mixture of cuminaldehyde, phellandral, and a new aldehyde, *l*-cryptal, isomeric with phellandral. This aldehyde has now been found to be 4-iso*propyl*-Δ^2-cyclo*hexenal* (I), since on oxidation with potassium permanganate in acetone solution it gives *d*-α-*iso*propylglutaric acid (III) in almost quantitative yield, oxidation evidently proceeding in accordance with the following scheme, diosphenolcarboxylic acid (II) being formed as an intermediate product :



A number of experiments were made with the object of oxidising *l*-cryptal to the corresponding *cyclo*hexenecarboxylic acid, but these were uniformly unsuccessful. The reaction with silver oxide proceeds smoothly, but, under all the conditions employed, the acid was a gum which showed no tendency to crystallise. This was possibly due to its being a mixture of αβ- and βγ-isomerides, but the quantity of material available was insufficient for a separation to be attempted. In another series of experiments, l-*cryptaloxime* was treated with acetic anhydride with the object of converting it into the nitrile: the reaction, however, proceeded abnormally and, although a little impure nitrile was obtained, the main product was a crystalline *substance*, m. p. 102—103°, which from its analysis appeared to have the formula $C_{22}H_{30}O_2N_2$ or $C_{22}H_{32}O_2N_2$. It had the properties of a weak base, but its constitution was not determined.



The constitution which is now shown to be that of *l*-cryptal was assigned originally by Wallach (*Annalen*, 1905, **340**, 15; **343**, 34) to the tetrahydrocuminaldehyde formed by the action of dilute sulphuric acid on β-phellandreneglycol. This aldehyde was shown subsequently to be identical with phellandral (4-*iso*propyl-Δ^1-*cyclo*-

hexenal) (IV) (compare Schimmel's Report, 1909, October, p. 88). The occurrence in admixture with each other of the three aldehydes cuminaldehyde (V), phellandral (IV), and cryptal (I), is not without biogenetic interest, since they can all three arise very simply from α-phellandrene (VI), the chief hydrocarbon constituent of the oils in which they occur.

EXPERIMENTAL.

The *l*-cryptal used in these experiments was the original specimen prepared by Penfold in 1922.

l-*Cryptaloxime* was readily obtained by the interaction of an alcoholic solution of cryptal with hydroxylamine hydrochloride in the presence of sodium acetate. After distillation in steam the oxime was obtained as a thick oil, b. p. 150°/17 mm., $n_D^{19\cdot5^\circ}$ 1·5139; it did not crystallise even when cooled to a low temperature (Found: C, 71·7; H, 9·8. $C_{10}H_{17}ON$ requires C, 71·8; H, 10·2%).

When the oxime was mixed with an excess of acetic anhydride in the presence of sodium acetate, heat was generated and the solution became yellow. After 30 minutes' boiling, a very vigorous reaction occurred and the solution became deep brown. When the cooled solution was poured into water, a viscid brown oil separated: this was dissolved in ether, the extract washed with sodium carbonate solution, dried, and evaporated, and the residual oil distilled under diminished pressure; the greater part boiled at 200—210°/23 mm., leaving a considerable residue. The distillate, which smelt strongly of a nitrile, crystallised almost completely on keeping. The solid, after being drained on porous porcelain, crystallised from light petroleum (b. p. 60—80°) in fine long needles, m. p. 102—103° (Found: C, 74·1, 74·3; H, 8·8, 8·6; N, 8·4. $C_{22}H_{30}O_2N_2$ requires C, 74·6; H, 8·5; N, 7·9. $C_{22}H_{32}O_2N_2$ requires C, 74·1; H, 9·0; N, 7·9%). This *substance*, which was optically inactive, was not attacked by alkali even on prolonged boiling; it was soluble in concentrated mineral acids and precipitated on dilution with water.

l-Cryptalphenylhydrazone is an oil, but the p-*nitrophenylhydrazone* crystallised from alcohol in terra-cotta, highly iridescent, soft needles, m. p. 167° (Found: N, 14·9. $C_{16}H_{21}O_2N_3$ requires N, 14·6%).

Oxidation of l-*Cryptal.*—To the aldehyde (10 g.), dissolved in acetone (200 c.c.) and cooled to 0°, potassium permanganate (25 g.) was gradually added. The oxidation proceeded rapidly at first but later became very slow. Water (50 c.c.) was then added and the oxidation completed by the addition of potassium permanganate (20 g.). The manganese dioxide sludge was separated and well washed with boiling water and the filtrate was evaporated to a small bulk in a current of carbon dioxide. After acidification the oxidation product was extracted with ether (10 times), the extract dried, and the solvent evaporated. The residual oil (11 g.) crystallised on keeping and after draining on porous porcelain had m. p. 90°. It was recrystallised from hydrochloric acid, yielding small glistening plates, m. p. 93—94°, of *d*-α-*iso*propylglutaric acid (Found : C, 55·2; H, 7·9; *M*, 175. Calc. : C, 55·1; H, 8·0%; *M*, 174). In aqueous solution ($c = 0{\cdot}766$), $[\alpha]_{5461} + 14{\cdot}2°$ was observed. The anhydride crystallised from light petroleum in the curious soft needles, resembling cotton-wool, described by Perkin (J., 1896, **69**, 1495); the anilic acid had m. p. 154—155°.

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