56. *Reactions of αβ-Unsaturated Cyclic Aldehydes and Ketones. Part IV.* d-*Cryptone and* trans-d-*Cryptol.*

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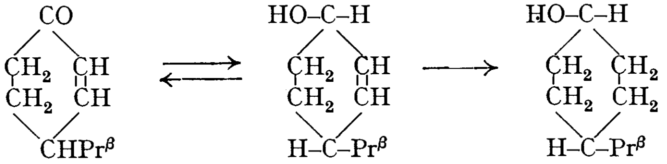
d-Cryptone, when reduced by aluminium *iso*propoxide, yields *d*-cryptol. The latter is obtained stereochemically pure by repeated crystallisation of the p-*nitrobenzoate*, which on hydrolysis gives *d*-cryptol having $[\alpha]_{\mathrm{D}}^{25^\circ}$ + 146·4°. The alcohol is further characterised by its α-*naphthylurethane*.

> *d*-Cryptol is the *trans*-epimer, since on catalytic hydrogenation it yields a dihydrocryptol characterised by an α-naphthylurethane, m. p. 159°, which is known to have the *trans*-configuration.
>
> On oxidation, pure *d*-cryptol gives *d*-cryptone having $[\alpha]_D + 102°$.

d-CRYPTONE (I) was isolated from water-fennel oil (compare Berry, Macbeth, and Swanson, J., 1937, 1448) and reduced by Ponndorf's method. The *d*-cryptol obtained had $[\alpha]_D + 66°$, but repeated crystallisation of the p-*nitrobenzoate* from methyl alcohol gave a specimen of the ester ($[\alpha]_D + 174°$, unchanged after further crystallisation) which on hydrolysis yielded pure *d*-cryptol having $[\alpha]_D^{25°} + 146{\cdot}4°$ in alcohol.

The epimeric forms of dihydrocryptol have been characterised by a series of crystalline derivatives (Gillespie, Macbeth, and Swanson, J., 1938, 1820) and it has since been established that the alcohol giving an α-naphthylurethane, m. p. 159·5°, has the *trans*-configuration (III), whereas the epimer yields an α-naphthylurethane, m. p. 113° (Cooke, Gillespie, and Macbeth, unpublished work). Since both *d*- and *l*-cryptol on hydrogenation give the dihydrocryptol characterised by the α-naphthylurethane of higher melting point, their configurations are established as the *trans*-forms (II).



(I.) (II.) (III.)

Samples of *d*-cryptone from water-fennel oil are partially racemised ($\alpha_D + 52{\cdot}16°$, $+ 75{\cdot}1°$), but a ketone of greater stereochemical purity ($[\alpha]_D + 102°$) has been obtained by oxidation of pure *d*-cryptol. It is not claimed that this material is stereochemically pure on account of the small amounts available for experimental purposes and in view of the higher value recorded by Galloway, Dewar, and Read (J., 1936, 1595) for *l*-cryptone ($[\alpha]_D - 119{\cdot}3°$).

EXPERIMENTAL.

d-*Cryptone from Water-fennel Oil.*—The sample of water-fennel oil was kindly distilled for us by Messrs. Stafford Allen and Sons, Ltd.; its physical constants, $d_{20°}^{20°}$ 0·8811, $n_D^{21°}$ 1·4788, $[\alpha]_D +$ 21·4° (homogeneous), were in good agreement with those previously recorded (see Berry, Macbeth, and Swanson, *loc. cit.*).

The ketone was extracted by treating the oil (300 g.) with its own volume of neutral sodium sulphite solution (50%), 10% sulphuric acid being added as required to neutralise the alkali liberated during the reaction. After separation of the aqueous extract, and its treatment with ether to remove traces of oil, the ketone was liberated by the addition of 40% sodium hydroxide solution and simultaneously extracted with ether. From the washed and dried ethereal solution, crude *d*-cryptone (10 g.), $\alpha_D + 75{\cdot}1°$ (homogeneous), was recovered. A better yield of ketone, of higher rotation, was obtained by such direct extraction than was isolated in the previous work after rigorous fractionation of the oil.

d-*Cryptol.*—The above sample of *d*-cryptone (10 g.) was reduced with aluminium (0·8 g.) dissolved in dry *iso*propyl alcohol (40 c.c.), the slow constant-volume distillation being continued for some 5 hours. The *iso*propyl alcohol was collected as a first fraction in the steam-distillation of the reaction mixture. The crude *d*-cryptol [7 g.; $\alpha_D + 66°$ (homogeneous, 1 dm.)] recovered from the subsequent distillate was, without further purification, converted into the *p*-nitrobenzoate by the action of *p*-nitrobenzoyl chloride (9·5 g.) and pyridine. After three crystallisations from methyl alcohol pure d-*cryptol* p-*nitrobenzoate* (5 g.) was isolated in pale yellow flakes, m. p. 84°, $[\alpha]_D^{25°} + 174°$ (*c* 2, chloroform). These values were unchanged after further crystallisation (Found: N, 4·9. $C_{16}H_{19}O_4N$ requires N, 4·84%).

Pure *d*-cryptol was obtained by refluxing the above pure ester for 30 minutes with 5% methyl-alcoholic potassium hydroxide (25 c.c.), followed by steam-distillation and extraction with ether. It had b. p. 72°/2 mm., $n_D^{20°}$ 1·4796, and $[\alpha]_D^{25°} + 146{\cdot}4°$ (*c* 2, alcohol).

A mixture of α-naphthyl *iso*cyanate (0·9 g.) and pure *d*-cryptol (0·6 g.) solidified after 2 hours; the α-naphthylurethane (0·65 g.) separated from light petroleum (b. p. 60—90°) in the same crystalline form as the *l*-cryptol derivative. Recrystallisation from the same solvent gave d-*cryptol-α-naphthylurethane*, m. p. 118°, $[\alpha]_D^{20°}$ + 135·3° (*c* 2·03, alcohol). After precipitation from alcoholic solution by water and further recrystallisation from light petroleum this separated in clusters of needles, m. p. 118·5°, $[\alpha]_D^{21°}$ + 136·2° (*c* 1·47, alcohol) (Found: N, 4·6. $C_{20}H_{23}O_2N$ requires N, 4·5%).

trans-*Dihydrocryptol.*—A solution of *d*-cryptol (0·5 g.) in alcohol (20 c.c.) containing palladised charcoal (0·4 g.) rapidly absorbed somewhat more than the theoretical amount of hydrogen. After filtration and removal of the solvent, the dihydrocryptol (0·4 g.) was converted into the α-naphthylurethane by the addition of α-naphthyl *iso*cyanate (0·6 g.). On crystallisation (twice) from light petroleum, fluffy felted needles (0·5 g.) were obtained, m. p. 158°, not depressed by authentic *trans*-dihydrocryptol-α-naphthylurethane.

Oxidation of d-*Cryptol to* d-*Cryptone.*—On addition of a warm (40°) solution of potassium dichromate (2·4 g.) in water (12 g.) containing concentrated sulphuric acid (2 g.) to pure *d*-cryptol (0·7 g.) the characteristic dark additive compound was immediately formed, and on shaking. oxidation took place with rise of temperature to 58—60° and liberation of the ketone. An ethereal extract of the product, washed till colourless and dried with anhydrous magnesium sulphate, gave, on removal of the solvent and distillation, *d*-cryptone (0·4 g.), b. p. 78°/3 mm., $n_D^{24°}$ 1·4811, $[\alpha]_D^{25°}$ + 102° (*c* 2·73, alcohol). The ketone was characterised by the *semicarbazone*, which after three crystallisations from dilute methyl alcohol had m. p. 187—188° and $[\alpha]_D^{20°}$ + 33° (*c* 1·0, chloroform) (Found: N, 21·5. $C_{10}H_{17}ON_3$ requires N, 21·5%), and the 2:4-dinitrophenylhydrazone, which after three crystallisations from methyl alcohol was obtained in red needles, m. p. 135—136° (Found: N, 17·5. Calc.: N, 17·6%).

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