526. *The Structure of Cyperone. Part V.* The Steric Course of Reduction of the Cyperones.*

By R. Howe and F. J. McQuillin.

The products of reduction of (+)-α-cyperone, (+)-β-cyperone, and (+)-*epi*-α-cyperone by various methods have been characterised, and configurations assigned. A novel inversion has been encountered during hydrogenation of members of the *epi*-series and its mechanism is discussed.

Hydrogenation of (+)-α-cyperone (I) was found by Simonsen and his co-workers [1] to give a tetrahydro-derivative, $[\alpha]_{5461}$ +14·8°. The same homogeneous product (II) has now been obtained from (+)-β-cyperone (III). Since (+)-α-cyperone has the configuration (I),[2] hydrogenation of (+)-β-cyperone at the 5 : 6-double bond must take place from the α-face of the molecule. Concomitant saturation of the 4 : 10-double bond through the same absorbed complex will lead to the *trans*-tetrahydro-ketone (II*a*). Analogous steroid and similar mono- and di-unsaturated ketones, however, yield *cis*-, *trans*-, or mixed products depending on the other substituents. Intermediate desorption to give a *cis*-fused product (II*b*) or the more stable form (II*c*) thus cannot be excluded.

Partial reduction of β-cyperone preferentially at the 5 : 6-double bond has also been

* Part IV, *J.*, 1955, 2423.

[1] Bradfield, Hegde, Rao, Simonsen, and Gillam, *J.*, 1936, 667.
[2] McQuillin, *J.*, 1955, 528.

examined. In an analogous case Woodward *et al.*[3] were able to reduce the terminal bond of a dienone by using a palladised strontium carbonate catalyst in benzene. In another instance [4] reduction of a steroid dienone by zinc in acetic acid has been reported. We have compared these two methods. In our case the former required modification in order to achieve reasonably selective reduction; partial poisoning of the catalyst by lead acetate (cf. Lindlar [5]) was found to be effective. Addition of pyridine which has been found to be useful in controlled reduction of acetylenic [6] and of ethylenic bonds of differing reactivity [7] was found on the other hand to assist complete reduction of β-cyperone to alcohols.

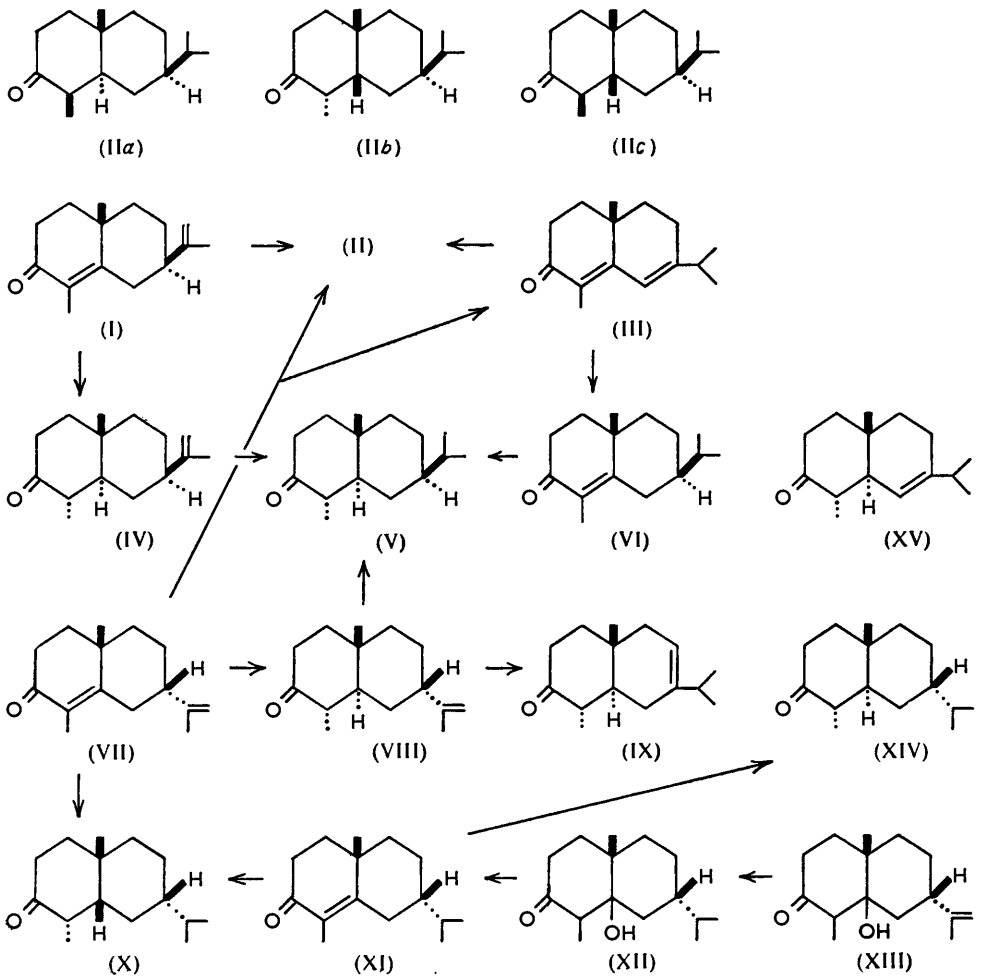
Both methods led to the same dihydro-derivative which for the following reasons may be shown to be (VI). Reduction of (+)-α-cyperone by means of lithium in liquid ammonia leads to a single product which on analogy with similar steroid reductions [8] may be given the *trans*-fused structure (IV); the 4-methyl substituent is presumed to take up the more stable configuration. Catalytic reduction of the side chain of this product (IV) gave a new tetrahydro-cyperone (V), which could also be obtained from the dihydro-compound (VI) by long treatment with zinc and acetic acid. Partial reduction of β-cyperone, catalytically or by zinc and acetic acid, must therefore lead to the product (VI) in which the *iso*propyl side chain adopts the stable 6β-orientation. Similarly reduction at the bridge-head by zinc and acetic acid must, as with lithium in ammonia, lead to the stable *trans*-fused product (V).

The isomeric tetrahydro-ketones (II) and (V) gave closely similar, but differing, infrared spectra, and derivatives of the same melting point but differing rotation. The former ketone, regarded as a primary product of hydrogenation, *trans* (II*a*) or *cis* (II*b*), will possess the less stable configuration at $C_{(4)}$. Enolisation towards $C_{(4)}$ will be sterically impeded in a *trans*- and facilitated in a *cis*-product,[9] and the rate in each case relatively reduced by the equatorial disposition of the hydrogen atom concerned.[10] Our material was not appreciably changed by vigorous acid or alkaline treatment or catalytically. A structure (II*c*) formed by spontaneous inversion during hydrogenation or subsequent manipulation is perhaps more likely than extreme resistance [10b] to inversion of a *trans*-ketone (II*a*).

The ketol (XIII), previously described,[2] was smoothly hydrogenated to a crystalline dihydro-ketol (XII), and then dehydrated by alcoholic potassium hydroxide to the unsaturated ketone (XI), which in turn could be reduced by lithium in liquid ammonia to a tetrahydro*epi*cyperone (XIV). The di- and the tetra-hydro*epi*cyperone (XI) and (XIV) were shown to be different from (VI) and (V) respectively and their corresponding derivatives. The 6α-configuration of the side chain must therefore be undisturbed during these transformations; the ketol (XIII) was recovered unchanged after refluxing with palladised charcoal in alcohol in absence of hydrogen. This is of some importance in view of the behaviour of (+)-*epi*-α-cyperone (VII) on hydrogenation. A crystalline tetrahydro-*epi*-α-cyperone has previously been described.[2] The proportion of this crystalline product, now shown to be (X), has been found to vary considerably with the ratio of catalyst used. It is accompanied by a liquid ketone from which the tetrahydro-6β-*iso*propyl ketone (II) can be isolated as the oxime in high yield. This inversion of the side chain to the stable 6β-configuration was confirmed in the hydrogenation of the dihydro-*epi*-ketone [2] (VIII) to a single product identical physically, in its infrared spectrum, and in its derivatives with (V). Hydrogenation of the dihydro-ketone (XI), however, led to the crystalline tetrahydro-ketone (X) in high yield.

[3] Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.
[4] Fieser, Rajagopalan, Wilson, and Tishler, *ibid.*, 1951, **73**, 4133.
[5] Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.
[6] Ruzicka and Müller, *ibid.*, 1939, **22**, 755.
[7] (*a*) Hershberg, Oliveto, Gerold, and Johnson, *J. Amer. Chem. Soc.*, 1951, **73**, 5073; (*b*) Oliveto, Weber, and Hershberg, *ibid.*, 1954, **76**, 4482.
[8] (*a*) Sondheimer, Mancera, Rosenkranz, and Djerassi, *ibid.*, 1953, **75**, 1282; (*b*) Barton, Ives, and Thomas, *J.*, 1954, 903.
[9] Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21; Taylor, *ibid.*, p. 250; Baddeley, *Ann. Reports*, 1954, **51**, 154.
[10] (*a*) Corey, *Experientia*, 1953, 9, 329; (*b*) Bladon, Henbest, Jones, Lovell, Wood, Woods, Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2921; Crawshaw, Henbest, and Jones, *J.*, 1954, 733.

It is evident that these inversions require migration of the double bond of the *iso*propenyl substituent before hydrogenation. Migration of this kind on a catalyst surface is well known,[11] and on nickel at 95° for example all the hydrogen atoms of propene are equivalent for deuterium exchange.[12] Hydrogenation of the compound (VII) or (VIII) was very slow in comparison with that of (I) or (III), and the occurrence of bond migration was established by refluxing the 6-*epi*-ketone (VIII) with palladised charcoal in alcohol. In the product

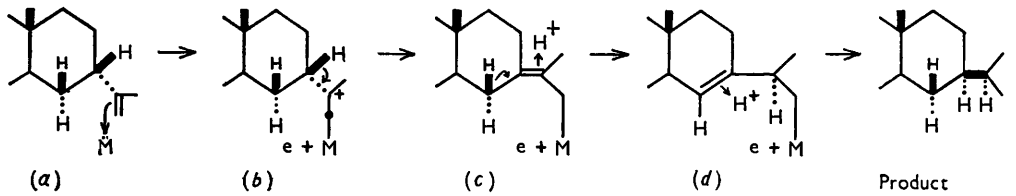


terminal methylene absorption at 890 cm.$^{-1}$ had been replaced by strong bands at 809 and 843 cm.$^{-1}$ (>C:CH– [13]) together with a new band at 1177 cm.$^{-1}$ (Pr^i); [14] this isomerised ketone may be (XV) or, more probably, (IX). By the same treatment *epi*-α-cyperone (VII) was quantitatively converted into β-cyperone whilst under the same conditions α-cyperone (I) was isomerised to β-cyperone (III) to the extent of only 25%.

The driving force in these cases is clearly the energy release as the large 6α-*iso*propenyl substituent achieves an essentially equatorial configuration, migration of the double bond conferring trigonal symmetry on $C_{(6)}$. In the 6-*epi*-series absorption on to the catalyst from the α-face of the molecule will be impeded and absorption from the β-face is likely to

[11] Braude and Linstead, *J.*, 1954, 3544; Fukushima and Gallagher, *J. Amer. Chem. Soc.*, 1955, **77**, 139.
[12] (*a*) Twigg, *Trans. Faraday Soc.*, 1939, **35**, 934; (*b*) see Bond, *Quart. Rev.*, 1954, **8**, 279, for discussion.
[13] Sheppard and Simpson, *ibid.*, 1952, **6**, 1.
[14] *Idem, ibid.*, 1953, **7**, 19.

be weak owing to the disposition of, and compression in, the remainder of the molecule. If the process of absorption at the *iso*propenyl centre is regarded as being initiated as in (*a*), the state of association first formed can clearly promote isomerisation to the thermo-



dynamically more stable and more easily absorbed structure *via* (*b*), (*c*), and (*d*). These steps are largely inoperative in the case of (+)-α-cyperone where the β-orientated *iso*propenyl group is already equatorial, and the molecule is therefore capable of being absorbed directly on to the catalyst without prior isomerisation.

From these considerations it seems probable that the species actually hydrogenated in the case of (VII) is β-cyperone (III) and in the case of (VIII) an isomer, probably (IX). Since the crystalline tetrahydro-*epi*-α-cyperone (X) is formed by the catalytic reduction of the dihydro-*epi*-α-cyperone (XI) having the 6α-*iso*propyl substituent, the reduction will most probably take place from the β-face, to give the *cis*-tetrahydro-6α-*iso*propyl ketone (X) as indicated.

Certain regularities may be noted among the molecular-rotational differences (ΔM_{5461}) in the cyperones. In the natural series, reduction of the *iso*propenyl group is accompanied by a positive change (+33°) which is greater (+80°) in the presence of the αβ-unsaturated ketone system. In the *epi*-series, the corresponding changes are negative (−61°, −86° respectively).

Experimental

Ultraviolet spectra were measured on a Hilger Uvispectrometer. Infrared absorption spectra were measured on a Grubb-Parsons double-beam spectrometer on liquid films of 0·05 mm. thickness. Ultraviolet spectra and [α] are for solutions in EtOH and $CHCl_3$ respectively unless otherwise stated.

Catalytic Reduction of (+)-α-*Cyperone* (I).—(+)-α-Cyperone in ethanol with palladised charcoal (20%) took up ~2 mols. of hydrogen to give (+)-*decahydro*-4 : 9β-*dimethyl*-3-*oxo*-6β-iso*propylnaphthalene* (II), b. p. 95°/0·1 mm.; after chromatography on alumina and elution with light petroleum, it had n_D^{20} 1·4860, $[\alpha]_{5461}$ +10·5° (*c*, 4·3) (Found: C, 81·2; H, 12·0. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%). The 2 : 4-*dinitrophenylhydrazone* formed orange-yellow needles, m. p. 151—152° (from ethanol), $[\alpha]_D$ +37° (*c*, 0·54), $\lambda_{max.}$ 370 mμ (log ε 4·38 in $CHCl_3$) (Found: C, 63·1; H, 7·5. $C_{21}H_{30}O_4N_4$ requires C, 62·7; H, 7·5%). The *oxime* formed needles, m. p. 118—119° (from methanol–water), $[\alpha]_{5461}$ −67° (*c*, 3·4) (Found: C, 76·2; H, 11·4. $C_{15}H_{27}ON$ requires C, 76·0; H, 11·4%).

Catalytic Reduction of (+)-β-*Cyperone* (III).—(+)-β-Cyperone, reduced as above gave, after chromatography, a colourless oil, b. p. 95°/0·1 mm., n_D^{20} 1·4859, $[\alpha]_{5461}$ +11·6° (*c*, 8·0) (Found: C, 80·8; H, 11·7%). The 2 : 4-dinitrophenylhydrazone formed orange-yellow needles, m. p. and mixed m. p. 151—152°, from ethanol.

Partial Reduction of (+)-β-*Cyperone* (III).—(i) (+)-β-Cyperone (0·2 g.) was refluxed with zinc dust (1·0 g.) in glacial acetic acid (7 c.c.) for 18 hr. The recovered oil, b. p. 95°/0·1 mm., n_D^{17} 1·5070, $[\alpha]_{5461}$ +78° (*c*, 3·0), $\lambda_{max.}$ 249·5 (log ε 3·9) and 300 mμ (log ε 2·3), was carefully chromatographed on alumina with light petroleum, and from the later fractions, by use of ultraviolet absorption analysis, (+)-1 : 2 : 3 : 5 : 6 : 7 : 8 : 9-*octahydro*-4 : 9β-*dimethyl*-3-*oxo*-6β-iso*propylnaphthalene* (VI) was obtained as a colourless oil, b. p. 85—90°/0·05 mm., n_D^{20} 1·5118, $[\alpha]_{5461}$ +151·6° (*c*, 3·4), $\lambda_{max.}$ 249·5 (log ε 4·18) and 300 mμ (log ε 2·15) (Found: C, 81·5; H, 11·0. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9%). The 2 : 4-*dinitrophenylhydrazone* formed stout red needles, m. p. 164°, from ethanol (Found: C, 63·2; H, 7·3. $C_{21}H_{28}O_4N_4$ requires C, 63·0; H, 7·0%). The *oxime* formed needles, m. p. 118° (from methanol), $[\alpha]_{5461}$ +188° (*c*, 0·9) (Found: C, 76·5; H, 10·5. $C_{15}H_{25}ON$ requires C, 76·6; H, 10·6%).

(ii) A palladium–strontium carbonate catalyst (2%) was prepared according to Woodward *et al.*[3] The catalyst (1 g.) in water (10 c.c.) was reduced in hydrogen. A solution of lead

acetate (5 mg.) in water (10 c.c.) was then added with shaking and after 1 hour's warming on the water-bath the catalyst was filtered off and dried (cf. Lindlar [5]).

(+)-β-Cyperone (366 mg.) in benzene (20 c.c.) with the above catalyst (310 mg.) took up ~1 mol. of hydrogen in 8·5 hr. The recovered oil, b. p. 90°/0·1 mm., $\lambda_{max.}$ 250 (log ε 4·03) and 301 mμ (log ε 3·02), was chromatographed on alumina (15 g.) and eluted with light petroleum in 50 c.c. portions to give 8 fractions. Fractions 2—7, having similar refractive indices, were combined and distilled, giving (+)-1 : 2 : 3 : 5 : 6 : 7 : 8 : 9-octahydro-4 : 9β-dimethyl-3-oxo-6β-*iso*propylnaphthalene (VI), b. p. 90°/0·1 mm., n_D^{20} 1·5143, $[\alpha]_{5461}$ +171° (*c*, 4·45), $\lambda_{max.}$ 250 (log ε 4·12) and 300 mμ (log ε 3·1), *i.e.*, containing ~5% of (+)-β-cyperone. The 2 : 4-dinitrophenylhydrazone formed needles, m. p. 166°, from ethanol, mixed m. p. 164°. The oxime formed needles, m. p. and mixed m. p. 118°.

Reduction of (+)-α-*Cyperone by Lithium in Liquid Ammonia.*—(+)-α-Cyperone (0·63 g.) in dry ether (20 c.c.) was added to a solution of lithium (0·13 g.) in liquid ammonia (150 c.c.). After 40 min. ammonium chloride (0·9 g.) was added and the ammonia allowed to evaporate. Recovered by the addition of water and ether, the product formed an oil, b. p. 90°/0·1 mm., which after chromatography on alumina and elution with light petroleum gave (−)-10α-*decahydro*-4α : 9β-*dimethyl*-3-*oxo*-6β-iso*propenylnaphthalene* (IV), b. p. 90°/0·1 mm., n_D^{20} 1·5016, $[\alpha]_{5461}$ −20·0° (*c*, 4·8) (Found : C, 81·4; H, 10·6%). The 2 : 4-*dinitrophenylhydrazone* formed orange-yellow needles, m. p. 170°, from ethanol (Found : C, 63·0; H, 7·4%). The *oxime* formed needles, m. p. 140° (from methanol), $[\alpha]_{5461}$ −146° (*c*, 4·0) (Found : C, 76·9; H, 10·8%).

(−)-10α-*Decahydro*-4α : 9β-*dimethyl*-3-*oxo*-6β-iso*propylnaphthalene* (V).—(i) (−)-10α-Decahydro-4α : 9β-dimethyl-3-oxo-6β-*iso*propenylnaphthalene (IV) in ethanol with palladised charcoal (20%) slowly took up ~1 mol. of hydrogen to give (−)-10α-*decahydro*-4α : 9β-*dimethyl*-3-*oxo*-6β-iso*propylnaphthalene* (V), b. p. 90°/0·1 mm., n_D^{20} 1·4865, $[\alpha]_{5461}$ −5·0° * (*c*, 6·6) (Found : C, 80·9; H, 11·8%). The 2 : 4-*dinitrophenylhydrazone* formed orange-yellow needles, m. p. 151—152° (from ethanol), $[\alpha]_D$ −126° (*c*, 0·34), $\lambda_{max.}$ 370 mμ (log ε 4·38 in $CHCl_3$) (Found : C, 62·35; H, 7·75%). The *oxime* formed needles, m. p. 118—119° (from methanol), $[\alpha]_{5461}$ −126° * (*c*, 1·7) (Found : C, 76·0; H, 11·6%).

(ii) (+)-β-Cyperone (0·2 g.) was refluxed with zinc dust (1·0 g.) in glacial acetic acid (7·0 c.c.) for 60 hr. The recovered oil was carefully chromatographed on alumina with light petroleum, and the first fraction rechromatographed to give (−)-10α-decahydro-4α : 9β-dimethyl-3-oxo-6β-*iso*propylnaphthalene (V), b. p. 90°/0·1 mm., n_D^{20} 1·4895, $[\alpha]_{5461}$ −9° (*c*, 6·3) (Found : C, 81·5; H, 11·8%). The 2 : 4-dinitrophenylhydrazone formed orange-yellow needles, m. p. 152—153°, from ethanol, and the oxime needles, m. p. 119—120° (from methanol), $[\alpha]_{5461}$ −116° (*c*, 1·1), identical with the corresponding derivatives in section (i).

Attempted Isomerisation of (+)-*Decahydro*-4 : 9β-*dimethyl*-3-*oxo*-6β-iso*propylnaphthalene* (II).—This ketone, $[\alpha]_{5461}$ +10·5° (*c*, 4·3), was treated as follows and then recovered. (i) Refluxed (90 mg.) in methyl-alcoholic potassium hydroxide (10%; 5 c.c.) under nitrogen for 16 hr. : $[\alpha]_{5461}$ +9·2° (*c*, 8·4). (ii) Refluxed (80 mg.) with toluene-*p*-sulphonic acid (80 mg.) in glacial acetic acid (3 c.c.) for 18 hr. : $[\alpha]_{5461}$ +9·4° (*c*, 9·8). (iii) Refluxed (60 mg.) with palladised charcoal (20%; 100 mg.) in ethanol (5 c.c.) for 16 hr. : $[\alpha]_{5461}$ +9·6° (*c*, 4·5). (iv) The ketone (80 mg.) in dry ether (5 c.c.) was added with shaking to potassium amide (from 100 mg. of metal) in liquid ammonia (100 c.c.) and set aside for 1 hr. : $[\alpha]_{5461}$ +7·6° (*c*, 5·0).

Reduction of (+)-10α-*Decahydro*-4α : 9β-*dimethyl*-3-*oxo*-6α-iso*propenylnaphthalene* (VIII).—This ketone, prisms, m. p. 48° (from light petroleum), $[\alpha]_{5461}$ +23·1° (*c*, 5·1), prepared by the reduction of (+)-*epi*-α-cyperone by lithium in liquid ammonia (cf. Part III),[2] gave an *oxime* as needles, m. p. 107° (from methanol), $[\alpha]_{5461}$ −60° (*c*, 3·9) (Found : C, 76·7; H, 10·4%).

The ketone (VIII) in ethanol with palladised charcoal took up 1 mol. of hydrogen to give (−)-10α-decahydro-4α : 9β-dimethyl-3-oxo-6β-*iso*propylnaphthalene (V), b. p. 90°/0·1 mm., n_D^{20} 1·4886, $[\alpha]_{5461}$ −6·9° * (*c*, 9·3) (Found : C, 81·1; H, 12·0%). The 2 : 4-dinitrophenylhydrazone formed orange-yellow needles, m. p. and mixed m. p. 152—153°, from ethanol. The oxime formed needles, m. p. and mixed m. p. 118—119° (from methanol), $[\alpha]_{5461}$ −130° * (*c*, 3·1).

Catalytic Reduction of (−)-*Cyperone Ketol* (XIII).—(−)-Cyperone ketol (XIII) in ethanol with palladised charcoal (20%) took up 1 mol. of hydrogen to give (−)-*decahydro*-10-*hydroxy*-4 : 9β-*dimethyl*-3-*oxo*-6α-iso*propylnaphthalene* (XII) as prisms, m. p. 64—65° (from light

* These values of $[\alpha]_{5461}$ are regarded as being the most reliable and agree quite well with those given on p. 2675.

petroleum), $[\alpha]_{5461}$ −57° (*c*, 3·8) (Found: C, 75·8; H, 11·3. $C_{15}H_{26}O_2$ requires C, 75·6; H, 10·9%).

Attempted Isomerisation of (−)-*Cyperone Ketol* (XIII).—(−)-Cyperone ketol (0·2 g.) in ethanol (20 c.c.) was refluxed with palladised charcoal (60 mg.) for 60 hr. The product was recovered quantitatively as prisms, m. p. and mixed m. p. 106° (from light petroleum).

Dehydration of (−)-*Dihydrocyperone Ketol* (XII).—(−)-Dihydrocyperone ketol (0·35 g.) in methyl-alcoholic potassium hydroxide (10%; 5 c.c.) was refluxed under nitrogen for 8 hr. The cooled solution was diluted with water and neutralised with dilute hydrochloric acid. The product, isolated in ether, gave on distillation (+)-1 : 2 : 3 : 5 : 6 : 7 : 8 : 9-*octahydro*-4 : 9β-*dimethyl*-3-*oxo*-6α-iso*propylnaphthalene* (XI), b. p. 90°/0·1 mm. (0·3 g.), n_D^{20} 1·5190, $[\alpha]_{5461}$ +136° (*c*, 3·8), $\lambda_{max.}$ 250·0 mμ (log ε 4·2) (Found: C, 81·8; H, 11·4%). The 2 : 4-*dinitrophenylhydrazone* formed scarlet needles, m. p. 194°, from ethanol (Found: C, 63·2; H, 7·15%). The *oxime* was a viscous oil, b. p. 110°/0·1 mm., $[\alpha]_{5461}$ +124° (*c*, 3·4) (Found: C, 76·4; H, 10·9%).

(−)-10α-*Decahydro*-4α : 9β-*dimethyl*-3-*oxo*-6α-iso*propylnaphthalene* (XIV).—A solution of (+)-1 : 2 : 3 : 5 : 6 : 7 : 8 : 9-octahydro-4 : 9β-dimethyl-3-oxo-6α-*iso*propylnaphthalene (0·18 g.) in dry ether (10 c.c.) was added to one of lithium (0·04 g.) in liquid ammonia (75 c.c.). After 40 min., ammonium chloride (0·25 g.) was added and the ammonia allowed to evaporate. Recovered by the addition of water and ether, the product formed an oil, b. p. 95°/0·1 mm., which crystallised to give (−)-10α-*decahydro*-4α : 9β-*dimethyl*-3-*oxo*-6α-iso*propylnaphthalene* (XIV) as prisms, m. p. 66—67° (from light petroleum), $[\alpha]_{5461}$ −4·6° (*c*, 7·6) (Found: C, 81·15; H, 12·0%). The 2 : 4-*dinitrophenylhydrazone* formed yellow needles, m. p. 221°, from ethanol (Found: C, 62·7; H, 7·8%). The *oxime* formed prisms, m. p. 101—102° (from methanol–water), $[\alpha]_{5461}$ −91° (*c*, 3·0) (Found: C, 75·65; H, 11·55%).

Catalytic Reduction of (+)-epi-α-*Cyperone* (VII).—(+)-*epi*-α-Cyperone in ethanol with palladised charcoal (20%) took up ~2 mols. of hydrogen to give a product, b. p. 90°/0·1 mm., n_D^{16} 1·4885, $[\alpha]_{5461}$ +10·5° (*c*, 4·3), which partially crystallised and by chromatography on alumina gave in the first light petroleum eluates (+)-10β-decahydro-4α : 9β-dimethyl-3-oxo-6α-*iso*propylnaphthalene (X) as prisms, m. p. 97—98° (from light petroleum), $[\alpha]_{5461}$ +23·2° (*c*, 3·8) (cf. Part III [2]). The *oxime* was a viscous oil, b. p. 110°/0·1 mm., $[\alpha]_{5461}$ −67° (*c*, 4·2) (Found: C, 75·9; H, 11·55%).

After the crystalline tetrahydro-ketone (X) had been removed, the residual oil, $[\alpha]_{5461}$ +8·3° (*c*, 5·5), was converted into the oxime, m. p. 113—115°, $[\alpha]_{5461}$ −49° (*c*, 4·2). Three crystallisations from methanol–water (9 : 1) gave an oxime as needles, $[\alpha]_{5461}$ −64° (*c*, 2·1), identical with that of (+)-decahydro-4 : 9β-dimethyl-3-oxo-6β-*iso*propylnaphthalene (II), m. p. and mixed m. p. 118—119°, unchanged by further recrystallisation.

(+)-10β-*Decahydro*-4α : 9β-*dimethyl*-3-*oxo*-6α-iso*propylnaphthalene* (X).—A solution of (+)-1 : 2 : 3 : 5 : 6 : 7 : 8 : 9-octahydro-4 : 9β-dimethyl-3-oxo-6α-*iso*propylnaphthalene (XI) in ethanol with palladised charcoal (20%) slowly took up ~1 mol. of hydrogen to give a product which largely crystallised and by chromatography on alumina gave in the first light petroleum eluates (+)-10β-decahydro-4α : 9β-dimethyl-3-oxo-6α-*iso*propylnaphthalene (X) as prisms, m. p. and mixed m. p. 97—98° (from light petroleum).

Isomerisation of (+)-epi-α-*Cyperone* (VII).—(+)-*epi*-α-Cyperone (85 mg.) in ethanol (7·6 c.c.) was refluxed with palladised charcoal (20%; 170 mg.) for 20 hr., to give (+)-β-cyperone as a pale yellow oil, b. p. 90°/0·1 mm., $[\alpha]_{5461}$ +659° (*c*, 3·6), $\lambda_{max.}$ 300 mμ (log ε 4·42). The oxime formed needles, m. p. and mixed m. p. 139°, from methanol.

Isomerisation of (+)-α-*Cyperone* (I).—(+)-α-Cyperone (56 mg.) in ethanol (5 c.c.) was refluxed with palladised charcoal (20%; 112 mg.) for 20 hr., to give on recovery a pale yellow oil, b. p. 90°/0·1 mm., $[\alpha]_{5461}$ +235° (*c*, 3·6), $\lambda_{max.}$ 300 (log ε 3·87) and 250 mμ (log ε 4·10), *i.e.*, containing ~25% of (+)-β-cyperone.

Isomerisation of (+)-10α-*Decahydro*-4α : 9β-*dimethyl*-3-*oxo*-6α-iso*propenylnaphthalene* (VIII).—This ketone (70 mg.) in ethanol (5 c.c.) with palladised charcoal (90 mg.) was refluxed for 11 hr. The product was a pale yellow oil, b. p. 90°/0·1 mm., $[\alpha]_{5461}$ +50° (*c*, 7·7), $\nu_{max.}$ 1704, 1177, 843, and 809 cm.$^{-1}$.

One of us (R. H.) thanks the Department of Scientific and Industrial Research for an award. We thank Dr. Sukh Dev for a gift of (+)-α-cyperone and Mr. R. E. Dodd and Miss S. Robinson for the infrared determinations.

KING'S COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE UPON TYNE, 1.

[*Received, February 14th*, 1956.]