236. *The Steric Course of Alkylation of Enols from Some* cyclo*Hexanones and of Hydrogenation of Selin-4-en-3-ones in Neutral and Alkaline Solution.*

By R. Howe and F. J. McQuillin.

Alkylation of 2 : 5-substituted *cyclo*hexanones is shown to occur preferentially on the face of the molecule where the 5-substituent already is. Hydrogenation of (+)-α- and (+)-*epi*-α-cyperone in alkaline ethanol has been used to characterise a series of *cis*-dihydro- and *cis*-tetrahydro-derivatives and to obtain information about the processes involved; by using alkaline ethanol as solvent, it is possible to hydrogenate preferentially the double bond of the CH:CH·CO group without saturation of the isolated 11 : 12-olefinic double bond.

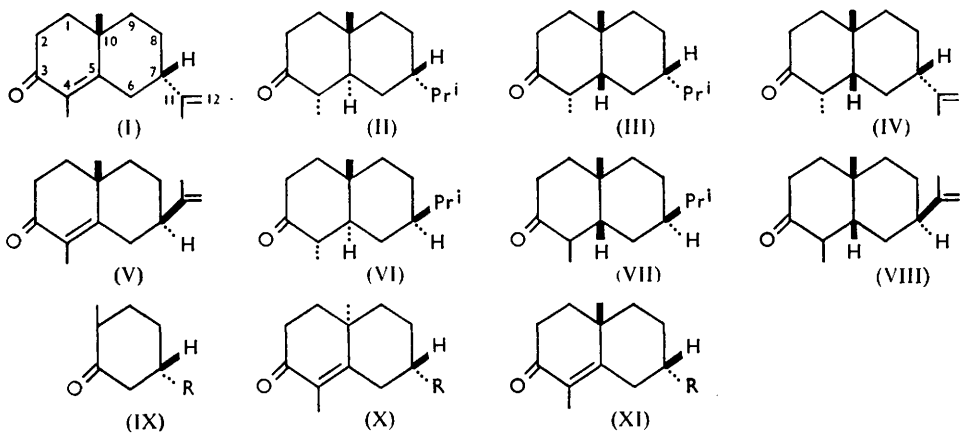
We have earlier reported [1] the reduction of (+)-*epi*- (I) and natural (+)-α-cyperone (V). Later work disclosed that the two *cis*-tetrahydro-ketones (III) and (VII) described contained some 5 : 10-*trans*-material. By hydrogenating the cyperones in alkaline solution we have now been able to obtain these two *cis*-tetrahydro-ketones in a pure state and also the two *cis*-dihydro-derivatives (IV) and (VIII), thus completing the series of four tetrahydro- and four dihydro-cyperones having the 4-methyl substituent in the stable configuration. The remaining pair of 11 : 12-dihydro-cyperones was described earlier.[1] In the course of this work we have also obtained information on (i) the effect of the side-chain orientation at $C_{(7)}$ on the proportions of *cis*- and *trans*-products formed on hydrogenation, (ii) a parallel influence of the 4-methyl substituent, (iii) the effect of acidity and alkalinity in determining the relative rates of hydrogenation of an enone and an isolated olefinic double bond, and also in influencing the mobility of the olefinic bond at a catalyst surface (cf. Howe and McQuillin [1]), (iv) the stereochemistry of the tetrahydrocyperone synthesised by Bradfield, Jones, and Simonsen.[2] The last point will first be considered.

Simonsen and his co-workers, by alkylation of (−)-tetrahydrocarvone (IX*a*) with ethyl β-chloropropionate, followed by a Reformatsky condensation with ethyl α-bromopropionate, obtained a dihydrocyperone which was characterised by hydrogenation to a crystalline tetrahydro-ketone, m. p. 102—103°, $[\alpha]_{5461}$ +22·2°, as the main product. Through the courtesy of the late Sir John Simonsen we have been able to show, by comparison of the semicarbazones, that this substance is the same as the *cis*-tetrahydro-*epi*-α-cyperone (III) (m. p. 98°, $[\alpha]_{5461}$ +23·2°) which we obtained [1] by hydrogenation of the ketone (XI*a*). The discrepant melting point of the ketones has been shown to be due to the presence in both preparations of a little of the corresponding *trans*-tetrahydro-*epi*-α-cyperone (II), which we obtained earlier (m. p. 67°) by reduction of the ketone (XI*a*) with lithium in liquid ammonia. Rigorous crystallisation of our *cis*-tetrahydro-*epi*-α-cyperone has now raised the melting point to 108° ($[\alpha]_{5461}$ +24·0°). This material gives a 2 : 4-dinitrophenylhydrazone, m. p. 123°; the same derivative of the *trans*-ketone, m. p. 67°, has m. p. 222° and from a mixture of the two derivatives the latter, which is much the less soluble, separates readily on crystallisation from ethyl acetate. The 2 : 4-dinitrophenylhydrazone, m. p. 221—223°, reported by Bradfield, Jones, and Simonsen proved to be identical with the latter which was also obtained from the 2 : 4-dinitrophenylhydrazone of lower-melting specimens of our *cis*-tetrahydro-*epi*-α-cyperone.

This identification of the ketones (II) and (III) establishes (XI) as the stereochemical structure of the principal product of Simonsen's synthetic method. By the somewhat different Mannich-base metho-salt condensation, (−)-dihydrocarvone (IX*b*) was previously shown [3] to yield the ketones (X*b*) and (XI*b*) in a ratio of ~1 : 4. By the same method

[1] Howe and McQuillin, *J.*, 1956, 2670.
[2] Bradfield, Jones, and Simonsen, *J.*, 1936, 1137.
[3] McQuillin, *J.*, 1955, 528; Howe and McQuillin, *J.*, 1955, 2423.

Abe, Harukawa, Ishikawa, Miki, and Toga [4] obtained from the (±)-ester (IX*c*) a product in which the corresponding (11-epimeric) isomers (XI*c*) predominated. Thus in these three alkylations, involving the *cyclo*hexenolate ion derived from the ketones (IX*a*, *b*, and *c*), the alkyl group becomes attached to the face of the molecule already carrying the substituent R, to give on cyclisation mainly the sterically less stable isomer. Other instances may be noted: Johnson, Christiansen, and Ireland,[5] using a monocyclic but heavily substituted *cyclo*hexanone, report a predominance of the isomer formed by methylation on the face carrying the largest aryl substituent. In cyanoethylation of structurally similar tricyclic ketones two groups of workers [6, 7] report the less hindered as the predominant product, whilst a third group [8] found an excess of the more hindered isomer. Heusler, Ueberwasser, and Wieland [9] draw attention, however, to the known reversibility



(*a*) R = Pr^i, (*b*) R = ·CMe:CH$_2$, (*c*) R = ·CHMe·CO$_2$Me.

of Michael-addition alkylation and to the importance of experimental conditions and the nature of the addend [10] in presenting examples of exclusive formation of either isomer. Sarett and his co-workers [11] obtained exclusively the more stable isomer in some examples of substitutive alkylation. Bromination and deuteration preferentially from the more hindered side of an enol which have also been noted and discussed, particularly by Corey and Sneen,[12] disclose a tendency which may be related to examples of alkylation where the more hindered product is obtained.

Of the tetrahydro-*epi*-α-cyperones, m. p. 67° and 108°, noted above, the former, obtained by lithium in liquid ammonia reduction, is regarded as the 4α-methyl-*trans*-ketone (II); the latter, which is resistant to alkali-isomerisation, is therefore the 5 : 10-*cis*-isomer (III) having the 4-methyl substituent in the stable configuration corresponding to the conformation (XVI; R = Pr^i, R′ = H). The *cis*- (III) and the *trans*-isomer (II) are formed in the ratio *ca.* 17 : 3 in hydrogenation of the ketone (XI*a*); *inter alia*, the 7α-side-chain will impede *trans*-hydrogenation.

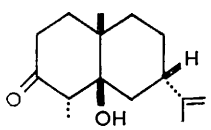
A similar structure (XII) and conformation (XVI; R = ·CMe:CH$_2$, R′ = OH) clearly

[4] Abe, Harukawa, Ishikawa, Miki, and Toga, *J. Amer. Chem. Soc.*, 1953, **75**, 2567; cf. Clemo and McQuillin, *J.*, 1952, 3839.
[5] Johnson, Christiansen, and Ireland, *J. Amer. Chem. Soc.*, 1957, **79**, 1995.
[6] Woodward, Sondheimer, Taub, Heusler, and MacLamore, *ibid.*, 1952, **74**, 4223.
[7] Wieland, Ueberwasser, Anner, and Miescher, *Helv. Chim. Acta*, 1953, **36**, 1231.
[8] Barkley, Knowles, Raffelson, and Thompson, *J. Amer. Chem. Soc.*, 1956, **78**, 4111.
[9] Heusler, Ueberwasser, and Wieland, *Helv. Chim. Acta*, 1957, **40**, 323.
[10] Szpilfogel, Van de Burg, Siegmann, and Van Dorp, *Rec. Trav. chim.*, 1956, **75**, 1043.
[11] Sarett, Johns, Beyler, Lukes, Poos, and Arth, *J. Amer. Chem. Soc.*, 1953, **75**, 2112.
[12] Corey and Sneen, *ibid.*, 1956, **78**, 6269.

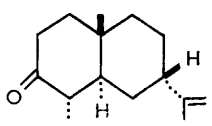
represent the ketol previously described [3] in its resistance to base-catalysed dehydration and inversion of the side-chain orientation at a hydrogenation catalyst.[1] Dehydration will involve an increase in compression; the side-chain is already equatorial.

The proportion (11 : 14) of *cis*- (VII) and *trans*-tetrahydrocyperone (VI) formed on hydrogenation of the 7β-substituted natural ketone (V) in ethanol contrasts with the predominantly *cis*-reduction of the 7α-substituted ketone (XI*a*) and illustrates the effect of the 7-substituent on the course of reduction. The 7β-substituted *trans*-tetrahydroketone (VI) has already been described.[1] The *cis*-ketone (VII) has now been obtained by hydrogenation in alkaline ethanol; alkali has been noted [13] to promote *cis*-reduction of steroid analogues. From the properties of these pure ketones the composition of the mixture obtained in neutral alcohol may be estimated.

The predominantly *trans*- and *cis*-reduction of (+)-α-cyperone (V) in neutral and alkaline ethanol respectively is in agreement with the mainly *trans*-reduction of (−)-α-santonin in neutral or acid media,[14,15] and with the reported *cis*-reduction of sodium santoninate [15] (effectively in alkaline solution). Under neutral conditions cholest-4-en-3-one and 1 : 2 : 3 : 5 : 6 : 7 : 8 : 9-octahydro-9-methyl-3-oxonaphthalene on the other hand are hydrogenated to *cis*-products.[16,17] The 4-methyl group of the sesquiterpene appears therefore to promote *trans*-reduction. This may arise from the very close proximity of the 4α-methyl and 7α-substituent in the first product (XVII) of 4β : 5β-addition of hydrogen. The reported *trans*-reduction [18] of 4-methylcholest-4-en-3-one is in agreement with this. In alkaline solution intervention of an enol will obviate this effect.



(XII)



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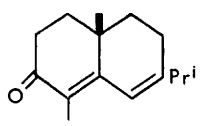

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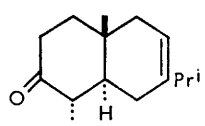
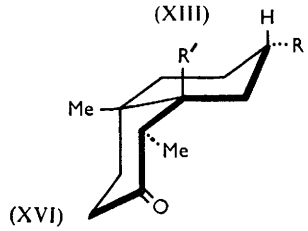
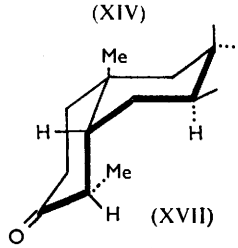


(XV)



(XVI)



(XVII)

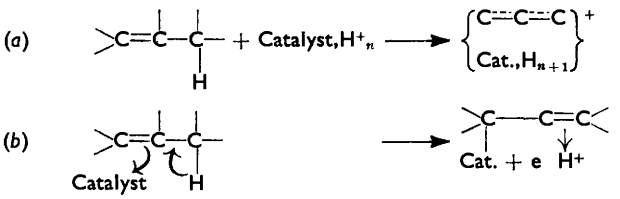
The effect of alkali on the hydrogenation of (+)-*epi*-α-cyperone (I) has also been examined. In neutral alcohol this ketone gives [1] as the major product a *cis*–*trans*-mixture of the 7β-ketones (VII) and (VI), together with a small amount of the uninverted *cis*-7α-ketone (III), accompanied by a minor proportion of the *trans*-isomer (II). The double-bond mobility responsible for inversion at position 7 appears to be impeded in an alkaline medium; under these conditions the principal product of hydrogenation proves to be the *cis*-7α-ketone (III). Hydrogenation of the dihydro-ketone (XIII) in alkaline ethanol similarly led to the uninverted product (II) in place of the 7β-*iso*propyl-ketone (VI) obtained [1] under neutral conditions. The formation of minor amounts of the inverted 7β-products in these experiments cannot, however, be excluded.

[13] See Slomp, Shealey, Johnson, Donia, Johnson, Holysz, Pedersen, Jensen, and Ott, *J. Amer. Chem. Soc.*, 1955, **77**, 1217.
[14] Kovaks, Herout, Horak, and Šorm, *Coll. Czech. Chem. Comm.*, 1956, **21**, 225; Yanagita and Tahara, *J. Org. Chem.*, 1955, **20**, 959; Tahara, *ibid.*, 1956, **21**, 222; Djerassi, Riniker, and Riniker, *J. Amer. Chem. Soc.*, 1956, **78**, 6362.
[15] Cocker and McMurry, *J.*, 1956, 4549.
[16] Grasshof, *Z. physiol. Chem.*, 1934, **223**, 249.
[17] Dauben, Rogan, and Blanz, *J. Amer. Chem. Soc.*, 1954, **76**, 6384.
[18] Meakins and Radig, *J.*, 1956, 4679.

(+)-*epi*-α-Cyperone (I) undergoes [1] bond migration to yield (+)-β-cyperone (XIV) when boiled in alcohol with palladised charcoal. The same result has now been obtained in an alkaline medium. We employed ethanolic potassium acetate; the use of alcoholic potassium hydroxide was examined, but not surprisingly, promoted extensive reduction of the carbonyl group. (+)-Dihydro-*epi*-α-cyperone (XIII), which undergoes a similar catalysed bond migration,[1] has now been shown also to lead to the same product, a ketone (XV), $[\alpha]_{4461}$ −72°, in both neutral alcohol and in ethanolic potassium acetate. This isomerised ketone (XV) and the parent (XIII) gave the same tetrahydro-ketone (VI) on hydrogenation.

In alcoholic alkali, hydrogenation of the 4 : 5-double bond of the enone system in both ketones (I) and (II) was found to be very much faster than that of the isolated 11 : 12-double bond. This enabled us to obtain the otherwise difficultly accessible *cis*-dihydro-ketones (IV) and (VIII); this method of selective hydrogenation may prove more widely useful.

Bream, Eaton, and Henbest [19] have discussed a number of examples of catalysed migration of olefinic bonds in steroids and have summarised the geometrical requirements of the reaction in a mechanism (*a*) involving acid catalysis. This has analogies in the known hydrogenolysis of allyl alcohols, with or without accompanying bond migration.[20, 21] Our previous results, obtained in neutral alcohol, were rationalised [1] in terms of a mechanism (*b*), and the present work was in part an attempt to distinguish between these alternatives. With this aim we have therefore examined the hydrogenation of (+)-*epi*-α-cyperone (I), also in acidified ethanol, which in a very rapid reaction gave the same mixture of 7-inverted and 7-uninverted products as in neutral alcohol, and in benzene which gave the mixture of 7-inverted ketones (VI) and (VII) in a very slow reaction.



These results indicate that hydrogenation and migration of an olefinic double bond are apparently proton-catalysed but not proton-dependent processes, to which, on present evidence, (*a*), (*b*), or other mechanisms may apply in different conditions.

In this work we have employed the palladised charcoal " catalyst-d " of Linstead and Thomas [22] which was washed until it gave a neutral reaction in water.

Experimental

[α] are for solutions in chloroform.

(+)-3-*Oxo*-4 : 5 : 7β(H)-*eudesmane* (III) *and Comparison with the Material of Bradfield, Jones, and Simonsen.*—This ketone is best prepared by hydrogenation of (+)-3-oxo-7β-(*H*)-eudesm-4-ene (XI*a*) as previously described.[1] The hydrogenation product (from alcohol with palladised charcoal) was obtained by chromatography and crystallisation (from pentane) as fractions showing apparently sharp m. p.s between 89° and 100°. Repeated crystallisation from pentane gave needles, m. p. 108°, unchanged by further crystallisation, $[\alpha]_{5461}$ +24·0° (*c* 4·5) (Found: C, 80·8; H, 11·85. Calc. for $C_{15}H_{26}O$: C, 81·1; H, 11·7%). The 2 : 4-*dinitrophenylhydrazone* formed orange prisms, m. p. 123° from ethanol (Found: C, 62·5; H, 7·6. $C_{21}H_{30}O_4N_4$ requires C, 62·7; H, 7·5%). The *oxime* described previously [1] as an oil was obtained with m. p. 77—78° (from aqueous methanol), $[\alpha]_{5461}$ −68·5° (*c* 2·94) (Found: C, 75·8;

[19] Bream, Eaton, and Henbest, *J.*, 1957, 1974.
[20] Dauben and Hance, *J. Amer. Chem. Soc.*, 1955, **77**, 2451.
[21] Henbest and Jones, *J.*, 1948, 1798.
[22] Linstead and Thomas, *J.*, 1940, 1127.

H, 11·5. $C_{15}H_{27}ON$ requires C, 76·0; H, 11·4%). The semicarbazone formed prisms, m. p. 213—214° (decomp.) from aqueous methanol, $[\alpha]_{5461}$ −16·0° (*c* 0·9) (Found: C, 68·75; H, 10·7. Calc. for $C_{16}H_{29}ON_3$: C, 68·8; H, 10·4%). The semicarbazone obtained by Bradfield, Jones, and Simonsen,[2] kindly made available by Dr. L. N. Owen, had m. p. 210° (decomp.), $[\alpha]_{5461}$ −13·0° (*c* 0·8), and showed no depression of the m. p. on admixture with our sample.

(−)-3-*Oxo*-4 : 7β(H)-*eudesmane* (II).—After removal of the crystalline ketone, m. p. 108° (above), the remaining material was distilled to give an oil, b. p. 90°/0·1 mm. [0·172 g. from 0·8 g. of (+)-dihydro-*epi*-α-cyperone], $[\alpha]_{5461}$ +2·9° (*c* 4·8). This material gave a 2 : 4-dinitrophenylhydrazone, m. p. 189—194° raised by crystallisation from ethyl acetate to 222 224° (Found: C, 62·85; H, 7·7%), and did not depress the m. p. of the 2 : 4-dinitrophenylhydrazone, m. p. 222—223°, reported by Bradfield, Jones, and Simonsen or that of the derivative of authentic (−)-3-oxo-4 : 7β(*H*)-eudesmane (II) prepared earlier.[1]

Attempted Isomerisation of (+)-3-*Oxo*-4 : 5 : 7β(H)-*eudesmane* (III).—This ketone, m. p. 108° (50 mg.), in ethanol (4 c.c.) with potassium hydroxide (0·5 g.) in water (1 c.c.) was recovered (43 mg.; m. p. and mixed m. p. 108°) after 6 hours' refluxing under nitrogen.

Hydrogenation of (+)-α-*Cyperone in Alkaline Ethanol.*—(i) (+)-α-Cyperone (1 g.) in ethanol (20 c.c.) containing potassium hydroxide (0·4 g.), shaken with palladised charcoal, absorbed 1 mol. of hydrogen during 0·5 hr. The product, b. p. 95°/0·1 mm., n_D^{20} 1·4980, [α] +28·8°, showed no absorption due to an enone group in the ultraviolet or infrared spectrum. Strong absorption at 890 cm.$^{-1}$ indicated, however, that the *iso*propenyl group was intact. It was purified *via* the *oxime* which was obtained with m. p. 96° (from methanol), [α] +89·5° (*c* 2·8) (Found: C, 76·45; H, 10·5. $C_{15}H_{25}ON$ requires C, 76·6; H, 10·6%). Hydrolysis by the previously described method[3] gave (+)-3-*oxo*-4α : 5β(H)-*eudesm*-11-*ene* (VIII), b. p. 95°/0·1 mm., n_D^{20} 1·5000, $[\alpha]_{5461}$ +29·1° (*c* 9·1) (Found: C, 82·0; H, 11·3. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9%). The 2 : 4-*dinitrophenylhydrazone* formed needles (from ethanol), m. p. 157° (Found: C, 62·7; H, 7·2. $C_{21}H_{28}O_4N_4$ requires C, 63·0; H, 7·0%).

(ii) Further hydrogenation of this substance with palladised charcoal in alcohol afforded (+)-3-*oxo*-4α : 5β(H)-*eudesmane* (VII), b. p. 95°/0·1 mm., n_D^{20} 1·4894, $[\alpha]_{5461}$ +30·4° (*c* 2·9) (Found: C, 81·4; H, 12·0. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%) [*oxime*, m. p. 108° (from aqueous methanol), [α] +28·8° (*c* 2·26) (Found: C, 75·6; H, 11·7. $C_{15}H_{29}ON$ requires C, 75·95; H, 11·4%); 2 : 4-*dinitrophenylhydrazone*, m. p. 155° (Found: C, 62·9; H, 7·2. $C_{21}H_{32}O_4N_4$ requires C, 62·7; H, 7·5%)].

Hydrogenation of (+)-epi-α-*Cyperone in Alkaline Ethanol.*—(i) (+)-*epi*-α-Cyperone (0·515 g.) in 2% ethanolic potassium hydroxide (25 c.c.) with palladised charcoal (300 mg.) absorbed 1 mol. of hydrogen in 5 hr. The product crystallised and was chromatographed on alumina, to give (+)-3-*oxo*-4 : 5 : 7β(H)-*eudesm*-11-*ene* (IV), as needles, m. p. 92—93° (from pentane), $[\alpha]_{5461}$ +26·0° (*c* 3·94) (Found: C, 81·9; H, 11·1. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9%). The *oxime* formed plates, m. p. 107° (from aqueous methanol), $[\alpha]_{5461}$ −73·2° (*c* 4·0) (Found: C, 76·7; H, 10·85. $C_{15}H_{25}ON$ requires C, 76·6; H, 10·6%); the 2 : 4-*dinitrophenylhydrazone* had m. p. 194° (from ethyl acetate–ethanol; after chromatography on alumina) (Found: C, 62·75; H, 7·05. $C_{21}H_{28}O_4N_4$ requires C, 63·0; H, 7·0%).

(ii) In a similar experiment in 10% alcoholic potassium hydroxide, (+)-*epi*-α-cyperone (0·4 g.) was hydrogenated to saturation in 120 hr. The product, on chromatography, gave the crystalline mixture of *cis*- and *trans*-7α-*iso*propyl-ketones (II) and (III), m. p. 97°, $[\alpha]_{5461}$ +21·2° (0·11 g.).

Hydrogenation of (+)-epi-α-*Cyperone in Acid Ethanol.*—The ketone (0·4 g.) in ethanol (20 c.c.) containing 1 drop of concentrated hydrochloric acid and palladised charcoal absorbed 2 mols. of hydrogen in 24 min. The product, by chromatography, gave a little of the crystalline mixture, m. p. 97—98°, of the *cis*- and *trans*-7α-*iso*propyl-ketones (II) and (III), and fractions eluted later gave the oxime, m. p. 117°, of the mixture of *cis*- and *trans*-7β-*iso*propyl-ketones (VI) and (VII) undepressed on admixture with the specimen prepared previously.[1]

Hydrogenation of (+)-epi-α-*Cyperone in Benzene.*—The ketone hydrogenated in benzene with palladised charcoal absorbed a little less than 2 mols. in 3 days. Chromatography removed a little unreduced material to give a fully reduced product, n_D^{20} 1·4864, $[\alpha]_{5461}$ +5·0° (*c* 6·3). Further chromatography gave no crystalline material, but the oxime of the mixture of *cis*- and *trans*-7β-*iso*propyl-ketones (VI) and (VII), m. p. 117°, $[\alpha]_{5461}$ −63° (*c* 2·6), could be isolated in good yield.

Isomerisation of (+)-epi-α-*Cyperone in Ethanolic Potassium Acetate.*—(+)-*epi*-α-Cyperone

(0·15 g.) in ethanol (9 c.c.) and water (1 c.c.) with potassium acetate (1 g.) was heated under reflux with palladised charcoal (0·1 g.) in nitrogen for 20 hr. The product, n_D^{20} 1·5564, $[\alpha]_{5461}$ +583° (*c* 3·96), afforded (+)-β-cyperone oxime, m. p. and mixed m. p. 139°, $[\alpha]_{5461}$ +346° (*c* 1·06), in good yield.

Isomerisation of (+)-trans-4 : 5-*Dihydro*-epi-α-*cyperone in Ethanol and in Ethanolic Potassium Acetate.*—(i) The ketone (0·235 g.) in ethanol (10 c.c.) was refluxed with 20% palladised charcoal (250 mg.) for 100 hr., and on recovery gave a pale yellow ketonic oil, b. p. 90°/0·1 mm. Chromatography on alumina and elution with light petroleum gave the dihydro-ketone (XV), b. p. 90°/0·1 mm., n_D^{20} 1·4990, $[\alpha]_{5461}$ −72° (*c* 6·0), which showed no infrared absorption due to $>C{:}CH_2$ (Found: C, 82·1; H, 10·9. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9%). The 2 : 4-*dinitrophenylhydrazone* formed yellow needles, m. p. 154—155° (from ethanol), $[\alpha]_D$ −214° (*c* 1·9) (Found: C, 62·8; H, 7·4. $C_{21}H_{28}O_4N_4$ requires C, 63·0; H, 7·0%) (cf. ref. 1).

The isomerised ketone (XV) (37 mg.) in ethanol absorbed 1 mol. of hydrogen in 4·5 hr., to give a product which was converted directly into the oxime, m. p. and mixed m. p. 117—118°, $[\alpha]_{5461}$ −124·4° (*c* 2·2), of the tetrahydro-ketone (VI), identical with that obtained by direct reduction of the ketone (XIII) without prior isomerisation.[1]

(ii) The ketone (75 mg.) was refluxed with catalyst in aqueous ethanolic potassium acetate, as in the case of (+)-*epi*-α-cyperone. The product, n_D^{20} 1·4977, $[\alpha]_{5461}$ −75° (*c* 1·3), had the same infrared spectrum as the ketone (XV) obtained in neutral ethanol.

Reduction of (+)-trans-4 : 5-*Dihydro*-epi-α-*cyperone in Alkaline Solution.*—The ketone (0·148 g.) in 2% ethanolic potassium hydroxide (20 c.c.) with 20% palladised charcoal (0·3 g.) absorbed 1 mol. of hydrogen in 4 days. The product, b. p. 95°/0·2 mm., n_D^{20} 1·4970, $[\alpha]_{5461}$ −40·7° (*c* 2·73), showed no $>C{:}CH_2$ absorption. It gave a 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 223° (from ethyl acetate), identical with that of the tetrahydro-ketone (II). The mother-liquors, on chromatography, gave a 2 : 4-dinitrophenylhydrazone, m. p. 157°, $[\alpha]_D$ −163° (*c* 0·1), showing no depression on admixture with the 2 : 4-dinitrophenylhydrazone of the dihydro-ketone (XV). The low rotation indicates that this material probably contains some of the derivative [1] of the tetrahydro-ketone (VI) (2 : 4-dinitrophenylhydrazone, $[\alpha]_D$ −126°).

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