An Asymmetric Synthesis of (−)-Humulene 1,2-Epoxide employing an Optically Active Humulene–Platinum Complex

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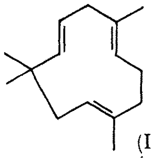
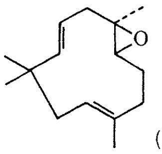
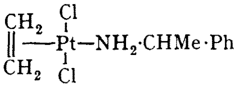
IT is not yet known how generally susceptible metal–olefin complexes are to epoxidation with peroxy-acids, but potentially this presents a route for the asymmetric synthesis of epoxides from substituted olefins, by prior coordination to a metal atom bearing an optically active ligand. During attempts to prepare optically active humulene (I),[1] by the method of complex formation developed by Cope *et al.*,[2] it has now been found that the strong complexing tendency of humulene with platinum may be used in an asymmetric synthesis of humulene 1,2-epoxide (II).

When humulene is treated with (III), (−)-*trans*-dichloro(ethylene)-α-methylbenzylamineplatinum(II),[2] in a 1 : 3 ratio in dichloromethane at room temperature an immediate evolution of ethylene occurs. Removal of the solvent followed by trituration of the residue with petroleum gives a yellow solid, m.p. 80—100°, $[\alpha]_D^{21}$ −15·4°. The integrated n.m.r. spectrum of this material is consistent with the structure of the 1 : 3 adduct (IV). Epoxidation of (IV) with peroxylauric acid in chloroform gives optically inactive humulene and humulene 1,2-epoxide (II), $[\alpha]_D^{20}$ −3·2°, optical yield 10·3% (this value is based on $[\alpha]_D$ −31·2°, the rotation of naturally occurring humulene 1,2-epoxide isolated from *Zingiber zerumbet* Smith[3]).

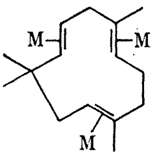

(I)



(II)


$\begin{matrix}\mathrm{CH_2}\\ \Vert\\ \mathrm{CH_2}\end{matrix}\!-\!\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{Pt}}}\!-\!\mathrm{NH_2{\cdot}CHMe{\cdot}Ph}$

(III)



(IV) M=Pt $(Cl_2)NH_2{\cdot}CHMe{\cdot}Ph$

Other humulene–platinum complexes can be obtained by varying the ratio of the reactants. A complex, m.p. 110—112°, $[\alpha]_D^{23}$ −15°, results from humulene and (III) in a 1 : 2 ratio. The integrated n.m.r. spectrum of this material is consistent with the structure of a 1 : 2 adduct although it is not clear which double bonds are involved in complex formation. Epoxidation with peroxylauric acid in chloroform gives (−)-(II) in 37% optical yield. Similarly, epoxidation of the complex obtained from humulene and (III) in a 1 : 1 ratio gives (−)-(II) in 22% optical yield. So far, we have not been able to obtain optically active humulene from any of these platinum complexes. It has been estimated from n.m.r. measurements that humulene is about as conformationally mobile as *trans*-cyclodecene,[4] a compound which also could not be obtained in optically active form.[5]

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[1] The humulene used in these experiments was isolated from commercial "caryophyllene" by the method of R. P. Hildebrand and M. D. Sutherland, *Austral. J. Chem.*, 1961, **14**, 272.

[2] A. C. Cope, C. R. Ganellin, H. W. Johnson, jun., T. V. Van Auken, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 1963, **85**, 3276.

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[4] Sukh Dev, J. E. Anderson, V. Cormier, N. P. Damodaran, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1968, **90**, 1246.

[5] A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 1965, **87**, 3644.