The Chirality of Olefin Complexes

By A. I. SCOTT* and A. D. WRIXON

(*Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut* 06520)

Summary Certain complexes of optically active olefins exhibit Cotton effects, the signs of which may be useful in determining olefin stereochemistry.

THE assignment of absolute stereochemistry to chiral olefins by the octant rule[1] may on occasion require additional verification. Thus, alkenes with few substituents may possess $\pi \rightarrow \pi^*$ dichroic maxima which are rather inaccessible (185—190 nm.), or other chromophoric interference may occur in the $\pi \rightarrow \pi^*$ region of olefin absorption. For such cases it is still pertinent to relate the sign of the Cotton effects of chromophoric derivatives of olefins to their relative and absolute configurations. We now describe three methods (A)—(C) of potential value which together with the chirality rules for *epi*-sulphides[2] may serve as useful adjuncts for such assignment.

(A) *Optically-active intermolecular charge transfer* (*C.T.*) *transitions.* In principle it should be possible to detect optical activity in the C.T. bands of donor–acceptor molecules.[3] A brief report[3a] on the C.T. circular dichroism of tetracyanoethylene (TCNE)–camphor solutions suggested that a study of TCNE–olefin complexes might reveal anomalous dispersion in the visible region. Obvious advantages of this method would be the expected sensitivity of the C.T. transition energy to the alkyl substitution pattern of the olefin system,[4] the quantitative recovery of olefin and the minimal distortion of alkene geometry in the complex. Our preliminary observations show that solutions of optically-active olefins (10^{-1} M) in methylene chloride saturated with TCNE do in fact exhibit c.d. maxima in the region 440—520 nm. corresponding to the previously observed[4] electronic C.T. transitions (Table 1). No attempt has been made in the present study to assign accurate $\Delta\epsilon$ values to these solutions but an interesting correlation has emerged between the olefin geometry and the signs of the C.T. and $\pi \rightarrow \pi^*$ Cotton effects. Thus, a reversal of sign between the $\pi \rightarrow \pi^*$ and the C.T. transitions is observed for the *trans*-olefins, (−)-*trans*-cyclo-octene and 3β-hydroxycholest-5-ene whilst the *cis*-olefins, cholest-2-ene and (+)-α-pinene retain the same sign for the original and C.T. transitions (Table 1). The C.T. circular dichroism of (*R*)-(−)-*trans*-cyclo-octene–TCNE and cholesterol–TCNE

TABLE 1. *TCNE–olefin complexes*

Olefin	Sign of $\pi \rightarrow \pi^*$ Cotton effect 200 nm	λ_{max}TCNE–olefin solution (nm)	Sign of Cotton effect of TCNE–olefin solution
Cholest-2-ene	+	440	+
3-Methylcholest-2-ene	+	520	+
4,4-Dimethylcholest-2-ene		470	+
(+)-α-Pinene	+	510	+
3β-Hydroxycholest-5-ene	+	440 (325)	− (+)
(−)-*trans*-cyclooctene	−	470	+
(−)-β-Pinene	+	460	−
(−)-Menthol*		325	−
Cholestan-3β-ol*		370	+
Cholestan-3β-ol acetate*		330	−

* Model compounds.

TABLE 2

Cotton effects of Pt^{II}*–Olefin Complexes*

Olefin	Quadrants of Pt complex	Predicted Cotton effect (440 nm)	Observed Cotton effect
Cholest-1-ene		−	−
Cholest-2-ene		−	+ (weak)
3-Methylcholest-2-ene		−	−
4,4-Dimethylcholest-2-ene		− +	−(460 nm) +(410 nm)
Cholest-3-ene		+	+
(+)-β-Pinene		−	−
Phyllocladene		+	+
3β-Hydroxyandrost-16-ene		+	+

are shown in Figure 1. In the case of hydroxyalkenes a second optically-active transition due to hydroxy–TCNE interaction can be discerned at 325 nm. The same optically-active band is present in solutions of saturated alcohols containing TCNE as shown by the dichroic maximum of 3β-cholestanol and menthol (Table 1). With the principle of C.T. dichroism established for "transparent" chromophores it should now be possible to observe the Cotton effects of diverse u.v. transitions, since the chromophores in the present study have been "shifted" by some 200—300 nm.

(B) d → d *Transitions of platinum*(II)*–olefin complexes.* Preliminary studies[5] have indicated that a quadrant rule correctly predicts the absolute configuration of Pt^{II} complexes formed by dissolving a chiral olefin in an alcoholic solution of sodium tetrachloroplatinate. This technique has now been extended to a range of steroidal and terpenoid olefins, as shown in Table 2. With the assumption that platinum complexes on the more accessible face of the ligand, the quadrant rule predictions are correct in all cases with the exception of cholest-2-ene which shows extremely weak positive circular dichroism at 440 nm. (predicted *negative*). On the other hand, 3-methylcholest-2-ene (Table 2) conforms

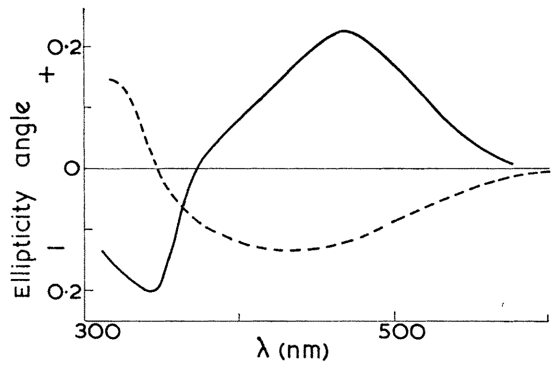


FIGURE 1. *The c.d. of* 10^{-1}M *solutions of* (−)-trans-*cyclo-octene* (———) *and of cholesterol* (- - - - - -) *in saturated* CH_2Cl_2–TCNE *solution at* 25°.

to the rule and sign reversal in the case of cholest-2-ene may indicate a special effect which will be discussed in a later paper. The c.d. curve and quadrant diagram for cholest-3-ene are shown in Figure 2.

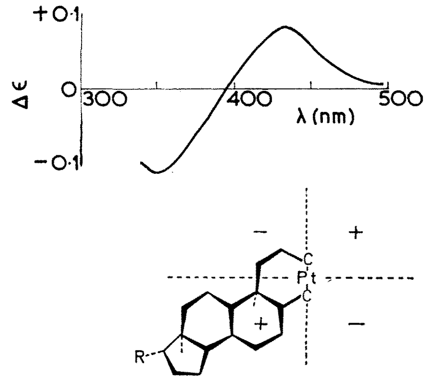
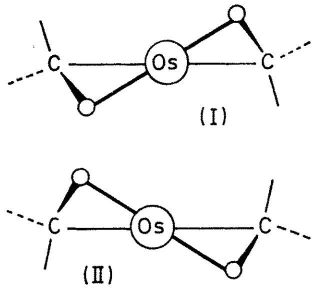


FIGURE 2. *The c.d. curve* (MeOH) *and quadrant diagram for cholest-*3*-ene* Pt^{II} *complex.*

C) *Osmate esters*. An important advance in the study of lefin chirality was made when Djerassi[6,7] observed that the smate esters of steroidal glycols prepared from the corre:ponding olefin exhibited anomalous o.r.d. curves, thus paving the way for configurational assignments. If, as in the case of Pt^{II} complexes, it is assumed that the approach of OsO_4 takes place from the less hindreed face of the molecule we find that the sign of the Cotton effect measured on a number of osmate esters as their pyridine complexes conforms to a chirality rule similar to that developed for the cuprammonium derivative of 1,2-diols.[8,9]

TABLE 3. *Osmate esters*

Olefin	Chirality of chelate conformation	Sign of cotton effect at 480 nm
Cholest-1-ene[6]	*k*	+
Cholest-2-ene[6]	*k'*	−
Cholest-4-ene	*k'* for 4α, 5α *k* for 4β, 5β	+
3β-Acetoxycholest-5-ene[6]	*k*	+
Coprost-6-ene[6]	*k'*	−
3-Methylcholest-2-ene	*k'*	−
(−)-*trans*-cycloctene	*k'*	−
(−)-Butane-2,3-diol	*k*	+
(+)-Diethyl tartrate	*k'*	−
(+)-*trans*-cyclo-octane-1,2-diol	*k'*	−



(I) *k* chelate (II) *k'* chelate

Thus the *k* conformation[10] (I) of the osmate chelate ring is associated with a positive Cotton effect at 480 nm. whilst a negative c.d. or o.r.d. in this region is associated with a *k'* chelate conformation (II) (Table 3). These assignments were made using diol esters of known absolute stereochemistry *i.e.* derived from those steroids which are known to react with OsO_4 on the α-face, and correlated with (−)-butane-2,3-diol osmate, assuming in the latter case a pseudoequatorial disposition of the methyl groups. Two examples of the correlation method may be cited. The osmate ester derived either from (−)-*trans*-cyclo-octene[11] or from (+)-*trans*-cyclo-octane-1,2-diol[12] exhibits a negative c.d. (Δε −5) near 480 nm. indicating the *k'* chelate (II) and hence by placing the ring residue substituents in the pseudoequatorial conformation the (*R*)-configuration of (−)-*trans*-cyclo-octene follows. Again the cholest-4-ene system is known to give both coprostane and cholestane derivatives on hydrogenation.[13] By treatment of cholest-4-ene with OsO_4[14] we obtained as the main product an osmate ester with a positive Cotton effect leading to *k* chelate chirality and hence assignment of the configuration 4β, 5β to the corresponding diol.

In addition to these chirality rules for metal complexes we note that similar considerations may be applied to the conformational analysis of the di- and tri-thiocarbonates[15] and to thionocarbonates.[16]

(*Received, July* 28*th*, 1969; *Com.* 1153.)

---

[1] A. I. Scott and A. D. Wrixon, preceding communication.

[2] K. Kuriyama, T. Komeno, and K. Takeda, *Tetrahedron*, 1966, **22**, 1039.

[3] (a) G. Briegleb and H. G. Kuball, *Angew. Chem. Internat. Edn.*, 1964, **3**, 307; (b) R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe", Springer–Verlag, Berlin 1961.

[4] R. H. Bauer, *Analyt. Chem.*, 1963, **35**, 107.

[5] A. D. Wrixon, E. Premuzic, and A. I. Scott, *Chem. Comm.*, 1968, 639.

[6] E. Bunnenberg and C. Djerassi, *J. Amer. Chem. Soc.*, 1960, **82**, 5953.

[7] C. Djerassi, "Optical Rotatory Dispersion", McGraw–Hill, New York, 1960.

[8] S. T. K. Bukhari, R. D. Guthrie, A. I. Scott, and A. D. Wrixon, *Chem. Comm.*, 1968, 1580.

[9] *Cf.* K. M. Wellman, W. Mungall, T. G. Mecca, and C. R. Hare, *J. Amer. Chem. Soc.*, 1967, **89**, 3647.

[10] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620. We thank Professor Corey for a sample of the cyclo-octanediol.

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

[12] E. J. Corey and J. I. Shulman, *Tetrahedron Letters*, 1968, 3655.

[13] C. W. Shoppee, B. D. Agashe, and G. H. R. Summers, *J. Chem. Soc.*, 1957, 3107.

[14] R. Criegee, B. Marchand, and H. Wannowius, *Annalen*, 1942, **550**, 99.

[15] C. Djerassi, H. Wolf, D. A. Lightner, E. Bunnenberg, K. Takeda, T. Komeno, and K. Kuriyama, *Tetrahedron*, 1963, **19**, 1547; D. A. Lightner, C. Djerassi, K. Takeda, K. Kuriyama, and T. Komeno, *ibid.*, 1965, **21**, 1581.

[16] A. H. Haines and C. S. P. Jenkins, *Chem. Comm.*, 1969, 350.