Tetrahedron, 1965, Vol. 21, pp. 163 to 178. Pergamon Press Ltd. Printed in Northern Ireland

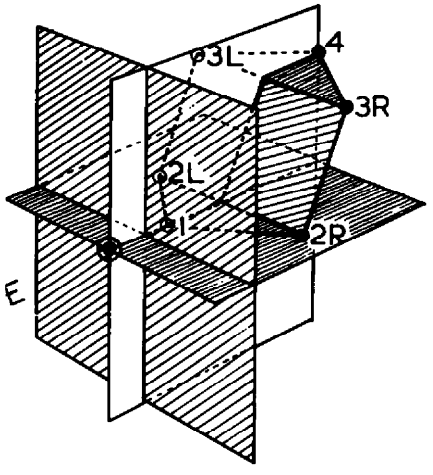
ROTATORY DISPERSION CURVES OF CYCLOPROPYL-KETONES AND EPOXY-KETONES†

CARL DJERASSI, W. KLYNE, T. NORIN, G. OHLOFF and E. KLEIN[1]

(*Received* 14 *September* 1964)

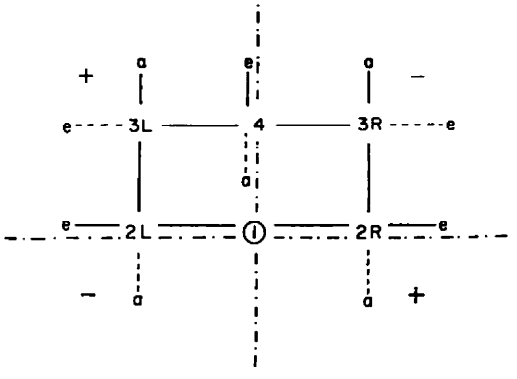
Abstract—The optical rotatory dispersion curves of a wide variety of epoxy ketones and cyclopropyl ketones are reported and discussed; the results are analysed in terms of the Octant Rule. It is shown that cyclopropane and ethylene oxide (oxiran) rings make contributions to the Cotton Effect at ca. 290 mμ which are *opposite* in sign to those made by alkyl groups.

THE Octant Rule[2] has provided a satisfactory generalization relating the stereochemistry of saturated ketones (carrying alkyl and halogen substituents) and the sign and magnitude of their Cotton effects for the n → π* transition (~290 mμ); this is summarized in formulae I and II.



I

Cyclohexanone
(Showing symmetry planes)



II

Octant projection of cyclohexanone (I, viewed from point E). Signs shown are those for alkyl substituents in the *back* octants (remote from point E).

† This paper forms Part CI of the Stanford series on Optical Rotatory Dispersion by Djerassi and colleagues; for previous paper see Part C, K. M. Wellman, W. S. Briggs and C. Djerassi, *J. Amer. Chem. Soc.* in press. It also forms Part 13 of the Westfield series by Klyne and colleagues; for previous paper see Part 12, R. Gardi, R. Vitali and A. Ercoli and W. Klyne, *Tetrahedron* (in Press).

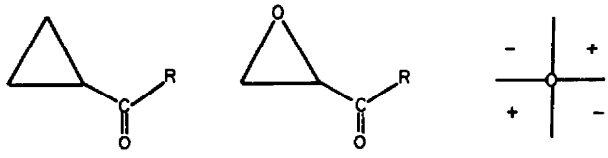
[1] Addresses. (C.D.) Stanford University, Stanford, California; (W.K) Westfield College, London, N.W.3; (T.N.) Kungl. Tekniska Högskolan, Stockholm; (G.O.) Firmenich et Cie., Genève, *formerly* Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr); (E.K.) Max-Planck-Institut.

C.D. acknowledges with thanks support for the work at Stanford from the National Cancer Institute of the National Institutes of Health, Bethesda, Md. He is indebted to Mrs Ruth Records for many of the ORD curves. W.K. is indebted to the Department of Scientific and Industrial Research for a grant, to the Wellcome Trust for the loan of a spectropolarimeter, and to Miss Jane Jackson and Miss Wendy Robertson for many of the ORD curves.

[2] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.* **83**, 4013 (1961).

Numerous applications of the Octant Rule in these series are collected in two papers.[3] The Rule has been extended in a generalized form to inherently dissymmetric chromophores.[4]

Over the past few years, examples have been collected in two of our laboratories which show that cyclopropyl and ethylene oxide (oxiran) rings adjacent to carbonyl (as in III and IV) make contributions to the Cotton effect (for the n → π* transition) of sign (as in V) *opposite* to those made by ordinary alkyl groups.



III IV V

Signs for cyclopropyl and oxiran substituents in *back* octants. "Reversed" Octant Rule.

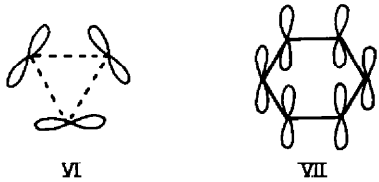
This paper summarizes the experimental evidence regarding these rotatory dispersion curves, and outlines some theoretical considerations which show that these experimental findings fit the predictions of theory.

Some preliminary comments have already been published in a paper on the sesquiterpene, thujopsene, by one of us (Norin[5]). Legrand *et al.*[6] comment on the fact that cyclopropyl and oxiran ketones show circular dichroism curves of sign *opposite* to those expected on the ordinary Octant Rule, but do not discuss the situation in detail.

THEORETICAL CONSIDERATIONS

We are greatly indebted to Prof. A. Moscowitz (University of Minnesota) for suggesting this qualitative treatment of the problem, and for many valuable discussions. We are also grateful to Prof. K. Mislow (Princeton University) for helpful suggestions.

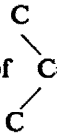
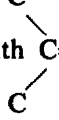
The cyclopropane and oxiran groups have somewhat delocalized electron systems, which can couple with the electronic system of the carbonyl group. These delocalized electrons lie in the plane of the three-membered ring (as in VI).

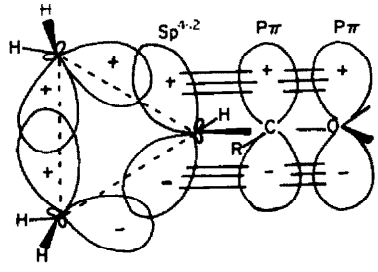


VI VII

[3] C. Djerassi and W. Klyne, *J. Chem. Soc.* 4929 (1962); 2390 (1963).
[4] A. Moscowitz, K. Mislow, M. A. W. Glass and C. Djerassi, *J. Amer. Chem. Soc.* **84**, 1945 (1962); E. Bunnenberg, C. Djerassi, K. Mislow and A. Moscowitz, *Ibid.* **84**, 2823 (1962).
[5] T. Norin, *Acta Chem. Scand.* **17**, 738 (1963).
[6] M. Legrand, R. Viennet and J. Caumartin, *C.R. Acad. Sci.* **253**, 2378 (1961).

The delocalized orbitals may be described (Ingraham[7]) as $sp^{4\cdot12}$ hybridized orbitals; two such orbitals are associated with each atom of the three-membered ring. It should be noted that the lines joining the ring-atoms (dashed lines in VI) are *not* σ bonds, but merely indicate the shape of the molecule. Evidence for the delocalized orbitals has been put forward from theoretical,[8,9] magnetic susceptibility,[10] UV,[11,12] IR[11] and NMR[13] studies.

This cyclopropane geometry (VI) contrasts sharply (cf. Kosower[12]) with that of the π orbitals of benzene (one p_π orbital per carbon atom), which lie above and below the ring system (VII). For maximum interaction with a carbonyl group the plane of the three-membered ring should therefore lie perpendicular to the plane of  , i.e., *parallel* to the π orbital of the C=O group, (VIII). We may contrast with this the requirements for conjugation between C=O and C=C or an aromatic ring, which should be *coplanar* with  . In the geometrical situation shown in VIII, the delocalized orbital of the three-membered ring overlaps the non-bonding $n = 2p_y^0$ orbital on oxygen (cf.[4]).



VIII

Cyclopropylketone
(based on Fig. 26 in Ingraham, Ref.[7])

The electric dipole transition moment for the $n \rightarrow \pi^*$ transitions, which is symmetry-forbidden in simple ketones, is no longer forbidden in the ketones carrying three-membered rings.

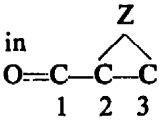
[7] L. I. Ingraham in *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) pp. 518–521. Wiley, New York (1956).
[8] A. D. Walsh, *Trans. Faraday Soc.* **45**, 179 (1949).
[9] C. A. Coulson and W. Moffitt, *Phil. Mag.* **40**, 1 (1949).
[10] J. R. Lacher, J. W. Pollock and J. D. Park, *J. Chem. Phys.* **20**, 1047 (1952).
[11] R. H. Eastman, *J. Amer. Chem. Soc.* **76**, 4115, 4118 (1954); **77**, 6643 (1955).
[12] E. M. Kosower and M. Ito, *Proc. Chem. Soc.* 25 (1962).
[13] A. D. Cross, *J. Amer. Chem. Soc.* **84**, 3206 (1962); D. H. Williams and N. S. Bhacca, *Ibid.* **85**, 2861 (1963); T. Shono, T. Morikawa, A. Oku and R. Oda, *Tetrahedron Letters* 791 (1964); K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.* **83**, 1226 (1961).

GEOMETRY OF STANDARD TYPES AND SUMMARY OF RESULTS

The following tables and diagrams illustrate the geometry of cyclopropyl and oxiran ketones in which the stereochemistry is fixed by fusion to other rings, and give a summary of results. They deal only with types that are readily available. Each pattern can, of course, exist in enantiomeric types.

Symbols and conventions

τ is the torsion angle (Klyne and Prelog[14]) for O.C.C.C. in



Projections are shown looking along the C1, C2 bond. (cf. formula VIII.)

θ is the angle between the plane of the three-membered ring and the *xz* plane of the carbonyl group.[2]

The symbol Δ is used in this paper to indicate a three-membered ring, *not* a double bond, or a difference.

In formulae IX–XII,

$Z = -CH_2-$ or $-O-$

E = Enantiomer of (cf. Ref.[3]).

Abbreviations

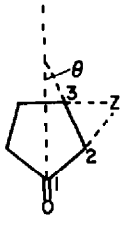
Conformations. a, anti; s, syn; p, periplanar; c, clinal (as in Ref.[14])

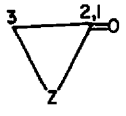
Octants (Back, unless stated otherwise). LL = lower left; LR = lower right; UL = upper left; UR = upper right; N = near.

FUSED RINGS

Bicyclo [3,1,0] *pattern*

Geometry





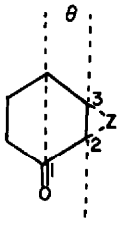
IX

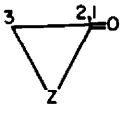
$\tau = 180°$ (ap),
$\theta \sim 25°$, Δ in (far) lower right octant

Results. For $Z = CH_2$ (Table 2A), the Octant Rule is "reversed". IX; ΔLR; negative C.E. *E*IX; ΔLL; positive C.E.

Bicyclo [4,1,0] *pattern*

Geometry





X

$\tau = 180°$ (ap),
$\theta = 0°$ (planes parallel),
Δ in (far) lower right octant.

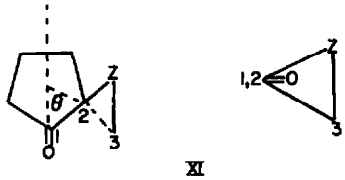
Results. For Z = O (Table 1A) and $Z = CH_2$ (Table 2A) the Octant Rule is "reversed". X; ΔLR; negative C.E. *E*X; ΔLL; positive C.E.

[14] W. Klyne and V. Prelog, *Experientia* **16**, 521 (1960).

SPIRAN RINGS

Spiro [4,2] *pattern*

Geometry



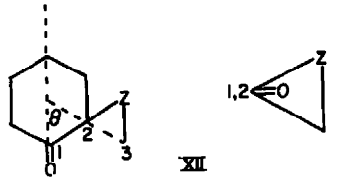
XI

$\tau = 30°$ (sp),
$\theta \sim 70°$,
Δ rather close to
xy-octant-plane.

Results (No cases yet available).

Spiro [5,2] *pattern*

Geometry



XII

$\tau = 0°$ (sp),
$\theta \sim 60°$,
Δ rather close to
xy-octant-plane.

The three-membered ring is in the *far* octant, but there is some orbital overlap in the near octant. Note that the three-membered ring is *syn* to the carbonyl oxygen here, whereas it is *anti* in the fused ring patterns (Tables 1A and 2A).

Results. $Z = CH_2$ (Table 2B). If Δ is considered as being in *near* octant, the Octant Rule is "reversed". XII; ΔNLR; positive C.E. *E*XII; ΔNLL; negative C.E. $Z = O$ (Table 1B). Values rather small; no clear evidence yet.

RESULTS

The results are summed up in two main Tables 1 and 2 for epoxy- and cyclopropyl-ketones, respectively, and are presented as molecular amplitudes (*a*). Additional results are given in Tables 3 and 4. Table 3 gives results for epoxy-aldehydes and epoxy-ketones in which the carbonyl group is in a side-chain; thus in both types, its conformation is not rigidly fixed. The sign of the Cotton effect when this is large might be used (with caution) to suggest a preferred conformation in the light of the "reversed" Octant Rule.

TABLE 1A. EPOXY-KETONES: FUSED RINGS
Conformations—See note (a)

Formulae	Compound type	Position of epoxide O in octant	Cotton effect: Found *a*	Cotton effect: Sign predicted on "Reversed Octant Rule"	Source and ref.
	STEROIDS AND TRITERPENES				
XIII	3-Oxo-4α,5α-epoxide	LR	−178D −203M	−	F, D K
—	4β-Methyl-4α,5α-epoxide (b)	LR	−179M	−	H, K, 15
—	7-Oxo-5α,6α-epoxide	LL	+122M	+	Ki, K
XIV	3-Oxo-4β,5β-epoxide (Androstane series)	UR	+162D +142M	+	Hb, D K
—	(Cholestane series)		+176D +145M +138M	+	D K D
—	(Spirostan series)		+179D	+	D
—	4α-Methyl-4β,5β-epoxide (b)	UR	+109M	+	H, K, 15
—	7-Oxo,5β,6β-epoxide	?	−16M	?	Ki, K
XV	3-Oxo-1α,2α-epoxide(5α) (Steroid)	LL	+93D	+	T, D
	3-Oxo-1α,2α-epoxide(5α) (Triterpene)	LL	+141M	+	J, K
XVI	3-Oxo-1β,2β-epoxide(5β)	UL	−90D	−	D
—	7-Oxo-8α,9α-epoxide(5α)	LR	−59M	−	D
	SESQUITERPENE				
XVII	Dihydrosantonin epoxide (3-oxo-4α,5α-epoxy)	LR	−104!M	−	Hn, D, 16
	MONOTERPENES				
XVIII	(+)-Epoxide from (−)-piperitone	UR	+121M		O, D, 17
XIX	(−)-Epoxide from (−)-verbenone	UR	+50M		O, D, 17
XX	(+)-Epoxide from (−)-carvone	LL	+43M		O, D, 17
EXX	Enantiomer of above	LR	−42M		O, D, 17

[15] J. M. Coxon, M. P. Hartshorn and D. N. Kirk, *J. Chem. Soc.* 2461 (1964).
[16] J. B. Hendricksen and T. L. Bogard, *J. Chem. Soc.* 1678 (1962).
[17] E. Klein and G. Ohloff, *Tetrahedron* **19**, 1091 (1963). For recent work on the O.R.D. curves of similar ketones *without* epoxide rings, see G. Ohloff, J. Osiecki and C. Djerassi, *Chem. Ber.* **95**, 400 (1962).

Possible conformations

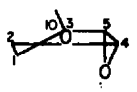
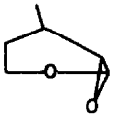
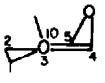
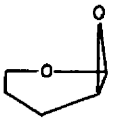
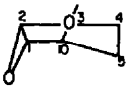
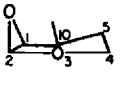
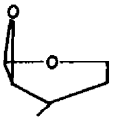
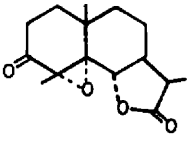
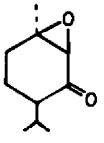
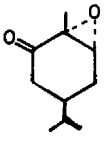
	P near planar	B half-boat
XIII		
XIV		
XV		
XVI		
XVII		
XVIII		
XIX		
XX		

TABLE 1B. EPOXY-KETONES: SPIRAN TYPE

Formula	Compound	Cotton effect Found *a*	Source and ref.
XXI	(+)-Epoxide from (+)-pulegone (c)	+45M +35E	O, D, 17 R, 20
—	(−)-Epoxide from (+)-pulegone (c)	−13M −33E	O, D, 17 R, 20
XXII	(−)-Epoxide from (−)-pinocarvone (60% pure)	−13M	O, D, 17
XXIII	7-Oxo-8α,14α-epoxide; 5α-steroid	−30M	D
XXIV	13β,18β(?)-Epoxy-12-oxohopane*	+101M	J, K, 21

* Configuration allotted provisionally here.

TABLE 2A. CYCLOPROPYL-KETONES
Three-membered ring parallel to carbonyl group

Formulae	Compound	Three-membered ring in octant	Cotton effect Found *a*	Cotton effect Predicted sign on "Reversed Octant Rule"	Source and ref.
	Bicyclo[3,1,0]-types				
XXV	Sabina ketone	LR	−205!M	−	N, K, 5
XXVI	Dihydroumbellulone	LR	−69D −93M	−	E, D, 11, 22 E, K
XXVII	Tricyclic ketone from umbellulone	LR	+217!D	+	E, D, 11, 22
XXVIII	Thujopsene ketone	LL	+276M +142H	+	Er, K, 23
XXIX	Dihydrolumisantonin	LL	+220C +220M	+	Jg B, K, 24, 25
XXX	1,5-Cyclo-2-oxo-10α-steroids ("lumi" compounds from 1,4-dien-3-ones)				
	17β-Hydroxyandrostane type	LL	+228C +280C*	+	Jg, 24
	Cholestane type	LL	+292!M +170H	+	G, K
	Bicyclo[4,1,0]-types				
XXXI	(+)-Carone		+59M +43H		N, K
XXXII	Thujopsene derivative		ca.+200†	+	Nz, 26
XXXIII	4α,5-Methylene-3-oxo-5α-steroid		−164M	−	Da, D
XXXIV	4β,5-Methylene-3-oxo-5β-steroid		+124M	+	Da, D

* Compound with H instead of Me at C—1. † Estimated from first extremum.

[20] W. Reusch and C. K. Johnson, *J. Org. Chem.* **28**, 2557 (1963).

[21] H. Fazakerley, T. G. Halsall and E. R. H. Jones, *J. Chem. Soc.* 1877 (1959).

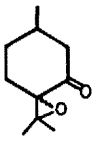
[22] C. Djerassi, R. Riniker and B. Riniker, *J. Amer. Chem. Soc.* **78**, 6377 (1956).

[23] T. Norin, *Acta Chem. Scand.* **15**, 1676 (1961).

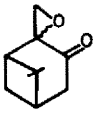
[24] K. Weinberg, E. C. Utzinger, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **43**, 236 (1960); H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni and O. Jeger, *Ibid.* **45**, 2346 (1962).

[25] D. H. R. Barton and P. T. Gilham, *J. Chem. Soc.* 4596 (1960).

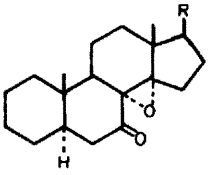
[26] T. Nozoe, H. Takeshita, S. Itô, T. Ôzeki and S. Seto, *Chem. Pharm. Bull. Japan* **8**, 936 (1960).



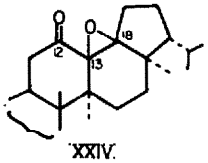
XXI



XXII

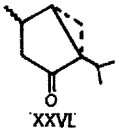


XXIII

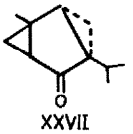


XXIV

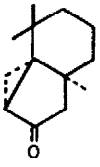
XXV



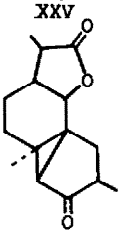
XXVI



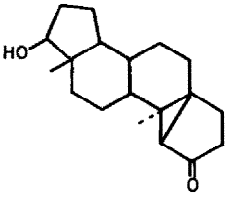
XXVII



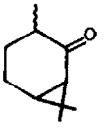
XXVIII



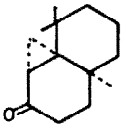
XXIX



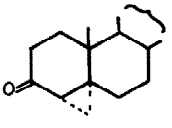
XXX



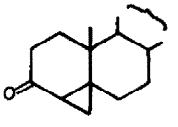
XXXI



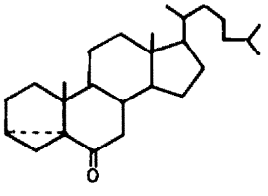
XXXII



XXXIII



XXXIV



XXXV

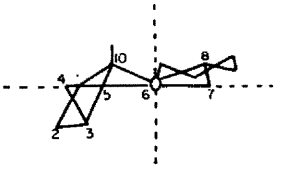
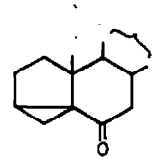


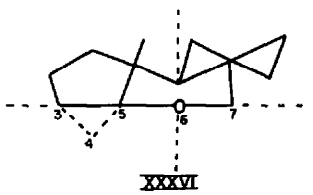
TABLE 2B. CYCLOPROPYL-KETONES

Three-membered ring *spiro* to carbonyl-carrying ring

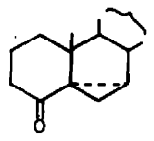
Formulae	Compound	Three-membered ring in octant	Cotton effect: Found *a*	Cotton effect: Predicted sign on "Reversed Octant Rule"	Source and ref.
XXXV	3α,5-Cyclo-5α-cholestan-6-one	NLL	−45!D	−	D
XXXVI	3β,5-Cyclo-5β-cholestan-6-one	NLL	−106!D −127M	−	Da, D H, K
XXXVII	5,7α-Cyclo-5α-cholestan-4-one	NLR	+40M +40M	+	S, K, 27 P, D

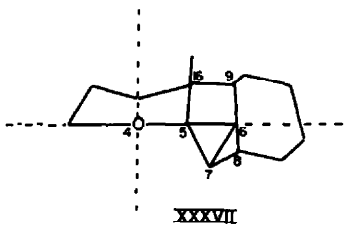
[27] G. H. R. Summers, *Proc. Chem. Soc.* 24 (1960).



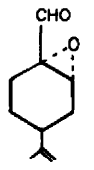


XXXVI



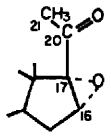


XXXVII

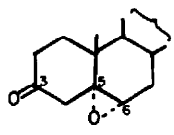


XXXVIII

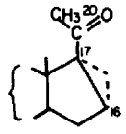
XXXIX



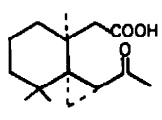
XL



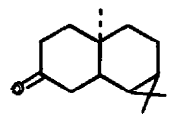
XLI



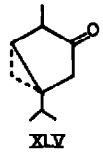
XLII



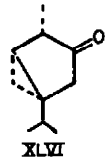
XLIII



XLIV



XLV



XLVI

TABLE 3. MISCELLANEOUS EPOXY-KETONES

Formula	Compound	Cotton effect *a*	Source and ref.
	Epoxides in which Carbonyl is in a Side-Chain		
XXXVIII	(−)-Epoxide from (−)-perilla-aldehyde	−1M	O, D, 17
XXXIX	(−)-Epoxide from (−)-myrtenal	+18M	O, D, 17
XL	16α,17α-Epoxy-20-oxosteroid	−4M	D
—	16β,17β-Epoxy-20-oxo-17α-steroid	(+)M*	D
—	16α,17α-Epoxy-21-acetoxy-20-oxosteroid	+6!D	T, D
	Non-Conjugated Epoxide		
XLI	5α,6α-Epoxy-3-oxosteroid(e)	−197!D −182 M	D D

* Weak positive Cotton effect on strong plain negative background.

TABLE 4. MISCELLANEOUS CYCLOPROPYL-KETONES

Formula	Compound	Cotton effect *a*	Source and ref.
	Side-Chain ketones		
XLII	16α,17α-Methylene-20-oxosteroid	ca. + 60D	Sa, D
XLIII	Degradation product from thujopsene	ca. −130	Nz, 26
	Non-conjugated ketones(f)		
XLIV	Nor-maalione	+84M	Bü, 28
XLV	(−)-Thujone	23M	N, K
XLVI	(+)-Isothujone	+4M	N, K

[28] G. Büchi, M. Schach von Wittenau and D. M. White, *J. Amer. Chem. Soc.* **81**, 1968 (1959).

Comments on Tables

Table 1*A*

(a) In many of these epoxyketones, the cyclohexanone ring to which the epoxide ring is fused, may well take up one of two conformations (formulae XIII-XVI). Present evidence and inspection of models does not appear to enable us to decide between these.

B = half-boat; P = near-planar—cf. the "one atom out of a plane" conformation suggested for the A-ring of triterpenes by Allinger[18] and by Ourisson.[19]

(b) The conformations of the 4-methyl-4,5-epoxy-3-oxosteroids are allotted as a result of the present work.

Table 1*B*

(c) The configurations of the epoxides from (+)-pulegone were allotted by Reusch and Johnson[20] on the basis of the "Ketone Octant Rule". The present work suggests that these configurations should be reversed.

Table 2*A*

(d) The geminal dimethyl group of (+)-carone (XXXI) may contribute strongly to the observed Cotton effect and a "reversed" effect of the conjugated cyclopropane ring is therefore not observed.

Table 3

(e) The large negative amplitude for the 5α, 6α-epoxy-3-oxosteroid does not seem easy to explain at present; it may be due to some form of long-range overlap.

[18] N. L. Allinger and M. DaRooge, *J. Amer. Chem. Soc.* **84**, 4561 (1962).
[19] J. M. Lehn, J. Levisalles and G. Ourisson, *Bull. Soc. Chim. Fr.* 1096 (1963).

Table 4

(f) As might be expected, non-conjugated cyclopropane rings make no special contribution to the Cotton effect of a carbonyl group.

Sources

The first symbol refers to the source of the sample.

B = Prof. D. H. R. Barton, Imperial College, London.
Bü = Prof. G. Büchi, M. I. T., Boston, Mass.
C = Dr. B. Camerino, Farmitalia, Milan.
D = Prof. C. Djerassi, Stanford, Calif.
Da = Prof. W. G. Dauben, Berkeley, Calif.
E = Dr. R. H. Eastman, Stanford, Calif.
Er = Prof. H. Erdtman, Stockholm.
G = Dr. P. D. Gardner, Austin, Texas.
H = Dr. M. P. Hartshorn, Christchurch, N.Z.
Hb = Prof. H. B. Henbest, Belfast.
Hn = Dr. J. B. Hendricksen, Los Angeles, Calif.
J = Prof. Sir Ewart Jones, Oxford.
Jg = Prof. O. Jeger, E. T. H., Zurich.
K = Prof. W. Klyne, Westfield College, London.
Ki = Dr. D. N. Kirk, Christchurch, N.Z.
N = Dr. T. Norin, Stockholm
Nz = Dr. T. Nozoe, Tohoku University, Sendai, Japan
O = Dr. G. Ohloff, formerly Max-Planck Institut, Mülheim-Ruhr, *now* Firmenich & Cie, Genève.
P = Dr. D. Peterson.
R = Dr. W. Reusch and Dr. C. K. Johnson, Michigan State University.
S = Dr. G. H. R. Summers, Swansea.
Sa = Prof. A. Sandoval, National University, Mexico.
T = Prof. C. Tamm, Basel.

The second symbol (where given) refers to the laboratory where the O.R.D. curves were determined.

D = Djerassi; K = Klyne.

The authors are all very grateful to the many colleagues who have generously provided reference samples.

Solvents. C, chloroform; D, dioxan; E, 95% ethanol; H, hexane; M, methanol.

EXPERIMENTAL

Rotatory dispersion curves were measured with Rudolf photoelectric spectropolarimeters: by C. Djerassi in the Department of Chemistry, Wayne State University, Detroit, Michigan, in the laboratories of Syntex S.A., Mexico City, and now in the Department of Chemistry, Stanford University, Stanford, California; and by W. Klyne at the Postgraduate Medical School, London W.12, in the Organic Chemistry Department, Imperial College of Science and Technology, London S.W.7. (by courtesy of Professor D. H. R. Barton, F.R.S.), and now in the Chemistry Department, Westfield College, London, N.W.3.

Experimental details are as in Djerassi (*Optical Rotatory Dispersion*, McGraw-Hill, New York, 1960) chap. 3 (solvent usually methanol or dioxan; tube 0·5 or 1 dm; 18–25°; *c*, 0·1 mg/cc or less).

The data for extrema (peaks and troughs) and amplitudes of curves are collected in the Table. Results are quoted as molecular rotations; some have been presented previously as specific rotations. The data for the extremum of longer wavelength are cited first in all cases, whether this extremum is a peak or a trough.

Solvents. C, chloroform; D, dioxan; E, 95% ethanol; H, hexane; M, methanol.

Formulae	Laboratory	Compound	Extrema [ϕ]	Extrema λ(mμ)	Extrema [ϕ]	Extrema λ(mμ)	Amplitude *a*	Solvent	Source and refs.
		STEROIDS AND TRITERPENES							
XIII	D	4α,5-Epoxy-5α-androstan-3-one, 17β-hydroxy	−8980	330	+8770	285	−178	D	F
—	K		−8750	325	+11500	280	−203	M	
—	K	4α,5-Epoxy-5α-cholestan-3-one, 4β-methyl	−6800	322	+11150	272	−179	M	H, 15
—	K	5,6α-Epoxy-5α-cholestan-7-one, 3β-acetoxy	+5540	336	−6630	292	+122	M	Ki
XIV	D	4β,5-Epoxy-5β-androstan-3-one, 17β-hydroxy	+8410	340	−7800	288	+162	D	Hb
—	K		+7300	330	−6900	285	+142	M	
—	D	4β,5-Epoxy-5β-cholestan-3-one	+8040	333	−9580	288	+176	D	
—	D		+7640	328	−6160	285	+138	M	
—	K		+7500	328	−7000	278	+145	M	
—	D	4β,5-Epoxy-5β-spirostan-3-one	+7530	338	−10400	283	+179	D	
—	K	4β,5-Epoxy-5β-cholestan-3-one, 4α-methyl	+5600	327	−5340	280	+109	M	H, 15
- -	K	5,6β-Epoxy-5β-cholestan-7-one, 3β-acetoxy	−1840	301	−280	274	−16	M	Ki

EPOXY-KETONES: FUSED RINGS (*Contd.*)

Formulae	Laboratory	Compound	Extrema [ϕ]	Extrema λ(mμ)	Extrema [ϕ]	Extrema λ(mμ)	Amplitude *a*	Solvent	Source and refs.
Steroids and triterpenes—(contd.)									
XV	D	1α,2α-Epoxy-3-oxo-5α-etianic acid, methyl ester	+6500	330	−2830	290	+93	D	T
—	K	1α,2α-Epoxylupan-3-one	+6760	322	−7160	277	+141	M	J
XVI	D	1β,2β-Epoxy-3-oxo-5β-etianic acid, methyl ester	−2620	333	+6360	280	−90	D	
—	D	8α,9α-Epoxy-7-oxo-5α-ergostane, 3β-acetoxy	−5420	330	+472	305	−59	M	
		SESQUITERPENE							
XVII	D	Dihydrosantonin epoxide (4α,5α-epoxy-3-oxo type)	−4190	300	−6200	290	−104!	M	Hn, 16
		MONOTERPENES							
XVIII	D	(+)-Epoxide from (−)-piperitone	+5800	325	−6350	280	+121	M	O,17
XIX	D	( )-Epoxide from (−)-verbenone	+2980	343	−2050	244	+50	M	O, 17
XX	D	(+)-Epoxide from (−)-carvone	+2320	322	−1770	284	+43	M	O, 17
*E*XX	D	*Enantiomer* of above	−2200	320	+1680	278	−42	M	O, 17

EPOXY KETONES: SPIRAN-TYPE OXIDES

Formulae	Laboratory	Compound	Extrema [ϕ]	Extrema λ(mμ)	Extrema [ϕ]	Extrema λ(mμ)	Amplitude a	Solvent	Source and refs.
XXI	D	(+)-Epoxide from (+)-pulegone	+2100	314	−2520	274	+45	M	O, 17
—	D	(−)-Epoxide from (+)-pulegone	−504	320	+782	262	−13	M	O, 17
XXII	D	(−)-Epoxide from (−)-pinocarvone (60% pure)	−1450	327	−153	298	−13	M	O, 17
XXIII	D	8α,14-Epoxy-5α-cholestan-7-one, 3β-acetoxy	−4450	320	−1420	300	−30	M	O, 17
XXIV	K	13β,18β(?)-Epoxyhopan-12-one	+6550	315	−3539	277	+101	M	J, 21
		CONJUGATED CYCLOPROPYLKETONES Cyclopropane ring parallel to C=O							
		Bicyclo[3,1,0]-types							
XXV	K	Sabina ketone	−12350	297	+8200!	270	−205!	M	N, 5
XXVI	D	β-Dihydroumbellulone	−3360	312	+3500	275	−69	D	E, 11, 22
—	K		−4200	305	+5090	267	−93	M	
XXVII	D	Tricyclic ketone from umbellulone	−9250	307	+12400	275	−217!	D	E, 11, 22
XXVIII	K	Thujopsene ketone	−11690	298	−15870	261	+276	M	Er 23
—	K		+6460	313	−7750	268	+142	H	
XXX	K	1,5-Cyclo-10α-cholestan-2-one	+11700	307	−17550!	265	+292!	M	G
—	K		+6550	323	−10490	273	+170	H	
		Bicyclo[4,1,0]-types							
XXXI	K	(+)-Carone	+3870	308	−2080	265	+59	M	N
—	K		+3280	313	−1050	269	+43	H	
XXXIII	D	4α,5-Methylene-5α-cholestan-3-one	−5020	299	+11300	259	−164	M	Da
XXXIV	D	4β,5-Methylene-5β-cholestan-3-one	+5580	304	−6780	250	+124	M	Da

CYCLOPROPYL KETONES: SPIRAN TYPES
Three-membered ring *spiro* to carbonyl-carrying ring

Formulae	Laboratory	Compound	Extrema [φ]	Extrema λ(mμ)	Extrema [φ]	Extrema λ(mμ)	Amplitude a	Solvent	Source and refs.
XXXV	D	3α,5-Cyclo-5α-cholestan-6-one	−2550	318	+1980	295	−45!	D	
XXXVI	D	3β,5-Cyclo-5β-cholestan-6-one	−1770	315	+8780	276	−106!	D	Da
	K		−2430	308	+10300	270	−127	M	H
XXXVII	D	5,7α-Cyclo-5α-cholestan-4-one	+6840	295	+2800	268	+40	M	P
	K		+6150	295	+2120	270	+40	M	S, 27
		MISCELLANEOUS EPOXY-KETONES							
XXXVIII	D	(−)-Epoxide from (−)-perillaldehyde	−652	310	−515	270	−1	M	O, 17
XXXIX	D	(−)-Epoxide from (−)-myrtenal	−227	320	−2070	240	+18	M	O, 17
XL	D	16α,17-Epoxy-pregn-5-en-20-one, 3β-acetoxy	−446	330	+3	290	−4	M	
—	D	16β,17β-Epoxy-17α-pregn-5-en-20-one,3β-acetoxy	(Weak positive Cotton effect on strong plain negative background.)				(+)	M	
—	D	16α,17-Epoxy-pregn-5-en-20-one, 3β,21-diacetoxy	−430	320	−1050	280	+6!	D	T
XXIV	D	5,6α-Epoxy-5α-spirostan-3-one	−9840	325	+9840	290	−197!	D	
—	D		−9930	325	+8310	278	−182	M	
		OTHER CYCLOPROPYLKETONES							
XLII	D	16α,17-Methylene-5-en-20-one	+2520	300	0	280	ca. +60	D	Sa
XLIV		Nor-maalione	+3910	305	−2180	270	+84	M	Bü, 28
XLV	K	(−)-Thujone	−873	312	+1390	286	−23	M	N, 5
XLVI	K	(+)-Isothujone	+367	326	+13	267	+4	M	N, 5