able assistance with certain preparative aspects of this work is also acknowledged.

(15) Alfred P. Sloan Research Fellow, 1968–1970.

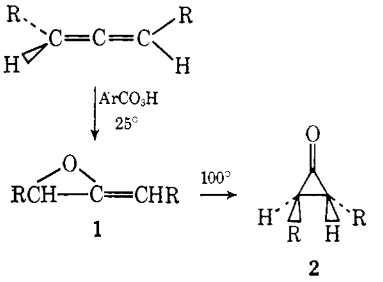
J. K. Crandall,[15] W. H. Machleder
Contribution No. 1617, Department of Chemistry
Indiana University, Bloomington, Indiana 47401
Received August 14, 1968

1,3-Di-*t*-butylallene Oxide. Isolation and Isomerization to *trans*-2,3-Di-*t*-butylcyclopropanone

Sir:

We wish to report the preparation and characterization of an allene oxide, a type of species which has been suggested as an intermediate, but which has hitherto eluded isolation.[1]

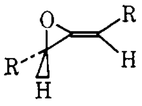
Reaction of excess 1,3-di-*t*-butylallene with *m*-chloroperbenzoic acid in hexane followed by removal of the *m*-chlorobenzoic acid by filtration and bulb-to-bulb distillation of the filtrate gave a distillate showing one major and three minor peaks, all of retention time longer than the allene by glpc (SE 30 on Chromosorb W). Collection of the major peak afforded a colorless liquid to which is assigned the allene oxide structure **1** on the basis of the following evidence: nmr (CCl_4) δ 0.98 (s, 9 H), 1.08 (s, 9 H), 3.25 (s, 1 H), 4.82 (s, 1 H); ir (CCl_4) 2960 (s), 2900 (s), 2860 (s), 1795 (m, broad), 1475 (s), 1465 (s), 1395 (m), 1365 (s), 1260 (w), 1200 (m), 1125 (m), 1085 (s), 980 (s), 940 (m), 930 (m), 920 (m), 870 (m), 710 (m) cm^{-1}; mass spectrum at 80 eV: *m/e* (relative intensity), 168 (4.3), 140 (8.6), 126 (20.7), 125 (29.3), 109 (8.6), 97 (27.6), 83 (81), 70 (84.5), 69 (89.7), 57 (100). The mass spectrum of the compound is similar to that of *trans*-2,3-di-*t*-butylcyclopropanone (**2**),[2] differing principally in the relative intensity of several ions. The glpc retention time of **1** on SE 30 is also the same as that of **2**. However, the infrared, nmr, and ultraviolet spectra of **1** collected from glpc showed that **2** was not present. Upon heating to 100°, the allene oxide **1** does isomerize to the cyclopropanone **2** (time for 50% isomerization, ~5 hr), identical ir and uv spectra with those of an authentic sample.

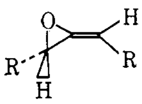


(1)

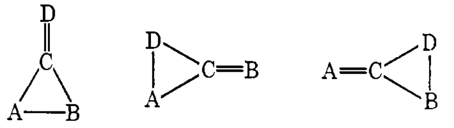
R = *t*-butyl

Two epoxides of 1,3-di-*t*-butylallene are possible, **1a** and **1b**. The simplicity of the nmr spectrum of **1** is suggestive that it is a single species.


1a


1b

The type of small-ring isomerism depicted in eq 2 (**3**–**5**)[3] is known in the all-carbon system[4] and has been suggested in some examples containing heteroatoms.[5] The results of the present study provide an example of eq 2 in a heterocyclic system in which both isomers (**1** and **2**) are isolable species and establish that the cyclopropanone form is the more stable of the two in this case.[6]



(2)

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(1) See J. K. Crandall and W. H. Machleder, *Tetrahedron Lett.*, 6037 (1966), and references cited therein. See also, J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, **90**, 7347 (1968). We wish to thank Professor Crandall for sending us a copy of his paper prior to publication.

(2) J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967).

(3) For **3**, **4**, and **5**, the appropriate number of substituents are assumed to be attached to A, B, and D, corresponding to the usual valence states of these atoms.

(4) J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 2720 (1963); E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961), and references cited therein.

(5) J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 5091 (1966); I. Lengyell and J. C. Sheehan, *Angew. Chem.*, **80**, 27 (1968); F. D. Greene and J. F. Pazos, *J. Org. Chem.*, in press.

(6) The asymmetry present in the 1,3-di-*t*-butylallene oxide–*trans*-2,3-di-*t*-butylcyclopropanone system should permit a detailed examination of the stereochemistry of these interconversions on which we hope to report at a future date.

Ronald L. Camp, Frederick D. Greene
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received September 9, 1968

The Benzoate Sector Rule, a Method for Determining the Absolute Configurations of Cyclic Secondary Alcohols

Sir:

Brewster's benzoate rule,[1] which covers Freudenberg's phthalate rule[2] and Mills' rule,[3] is widely employed to determine the absolute configurations of cyclic secondary alcohols.[4,5] However, it is not applicable to certain types of compounds, such as those in which the carbinyl carbon is flanked by two methylene groups (entry 4 in Table I) and those in which one of the carbons adjacent to the carbinyl carbon is the bulkier and also more polar (Figure 1).[6]

We have found that the strong Cotton effect of benzoates due to $\pi \rightarrow \pi^*$ intramolecular charge-transfer transition[7] at *ca.* 225 mμ permits predictions of the

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(1) J. H. Brewster, *Tetrahedron*, **13**, 106 (1961); see also J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475, 5483, 5493 (1959).

(2) K. Freudenberg, "Stereochemie," Deuticke, Leipzig, 1933, p 696.

(3) J. A. Mills, *J. Chem. Soc.*, 4976 (1952).

(4) See the following for a slightly extended application of the benzoate rule: M. Miyamoto, K. Morita, Y. Kawamatsu, Y. Kawashima, and K. Nakanishi, *Tetrahedron*, **23**, 411 (1967).

(5) See the following for alcohol derivatives which give rise to Cotton effects: P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965, Chapter 11.

(6) See footnote 28 in K. Nakanishi, M. Ohashi, M. Tada, and Y. Yamada, *Tetrahedron*, **21**, 1231 (1965).

(7) N. Harada and K. Nakanishi, *J. Am. Chem. Soc.*, **90**, 7351 (1968).

Table I. Rotations of Benzoates

No.	Compound[a,b]	Predicted sign	ORD[c] a (extrema in mμ)	CD[c] Δε (mμ)	Solvent[d]
1	5α-Cholestane 1β- (C)	−	−100 (234/222)		M–D
2	5α-Androst-2-ene 17β-acetate 1α- (C)	+	+258 (236/218)		M
3	Cholest-4-ene 3β-	−	−200 (236/217)		E
4	Cholest-5-ene 3β-	+	+120 (235/215)		M–D
5	*A*-Homocholest-4a-ene 3α- (I)	+	+238 (235/212)		M–D
6	*A*-Homocholest-4a-ene 3β- (I)	−	−170 (238/218)		M
7	5α-Cholest-7-ene 3β-acetate 6α-	+	+194 (235/215)		H
8	5α-Cholest-7-ene 3β-acetate 6β-	−	−154 (234/221)	−9.00 (227)	H
9	5α-Cholestane 7β-	+	+ 48 (235/222)		M
10	Cholest-5-ene 3β-acetate 7β-	+	+189 (232/222)	+4.46 (225)	M–D
11	Rockogenin 3β-acetate 12β- (T)	− ?[e]	+109 (232/215)	+2.89 (220)	M–D
12	Methyl 7-deoxycholate 3α-acetate 12α- (W)	+ ?[e]	−138 (235/212)		M
13	3-Methoxyestradiol 17β- (W)	+	+344 (232/218)	+4.63 (225)	M
14	*Cf.* 3-methoxyestradiol (W)			+2.01 (226)	M
15	3-Methoxyestradiol 17β-*p*-methoxybenzoate (W)[f]	+		+2.42 (250)	M–D
16	Lanostane 3β-	+	+142 (235/217)		H
17	Isopropylidenetaxinol 5α-[g]	+	+160 (235/215)	+4.32 (225)	M–D

[a] Position of the benzoate group follows compound name. [b] We are greatly indebted for the supply of samples from: C, Dr. P. Crabbé, Syntex S. A.; I, Professor, Shô Itô, Tohoku University; T, Dr. K. Takeda, Shionogi Co.; W, Dr. T. Wada, Teikoku Hormone Co. [c] ORD and CD measurements were performed using a Jacso ORD/UV-5 spectropolarimeter with CD attachment. [d] E, ethanol; D, dioxane; H, *n*-hexane; M, methanol; M–D, methanol–dioxane (9:1). [e] The predicted signs are uncertain due to ambiguity in the benzoyloxy group conformation and rotatory contribution of the 21-Me group. Interpretations associated with the 12-OBz group require further clarification. [f] The CD Cotton effect is shifted to 250 mμ by introduction of the *p*-OMe; the Cotton effect due to ring A at 226 mμ could not be observed. clearly. [g] See Figure 1.

absolute configurations of a variety of cyclic *sec*-hydroxyl groups including those mentioned above ("benzoate sector rule"); benzoates also absorb at *ca.* 195 and 280 mμ, but Cotton effects could not be observed with these transitions.

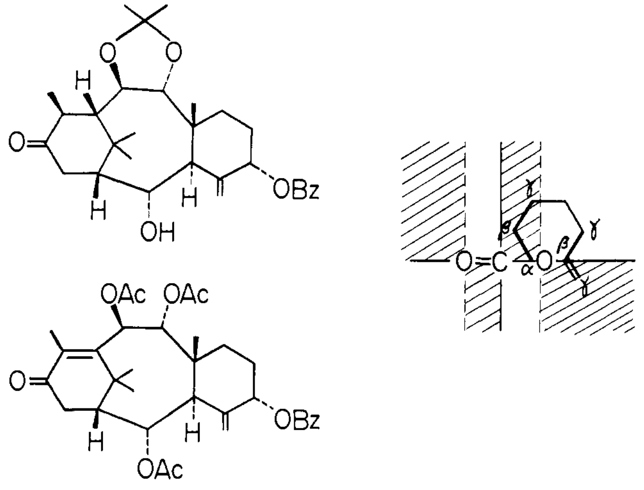

Figure 1. The benzoate sector for taxinine derivatives.

The sectors are set up as shown in Figure 2. The space is divided into four sectors by symmetry planes A and B,[8] and further into eight sectors by two additional planes, C and D, perpendicular to A and passing through the two oxygen atoms. The preferred conformation of the benzoyloxy group is assumed to be the one in which it lies staggered between the carbinyl hydrogen and the smaller substituent.[9]

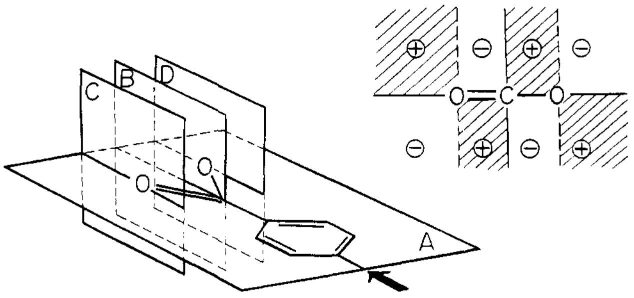

Figure 2. The beonzoate sectors. The benzoate is viewed from the direction of the arrow.

The benzoate is viewed from the *para* position (arrow in Figure 2), and the rotatory contributions of α,β and β,γ bonds are considered: the sector rule states that bonds falling in the shaded and unshaded sectors in Figure 2 make, respectively, positive and negative contributions to the sign of the 230-mμ Cotton effect. This alternation in signs of contributions of the sectors is corroborated by theoretical considerations.[7] The contribution of a double bond would be larger than that of a single bond because of the larger polarizability, and hence the sector which carries a β,γ-double bond, if any, will make the dominant contribution (Figure 1); similarly, the sector carrying a γ,δ-double bond will define the sign of the Cotton effect when this is the unsaturation closest to the carbinyl carbon (entries 4–6). Pertinent examples of application of the benzoate sector rule, mostly from steroids, are listed in Table I.

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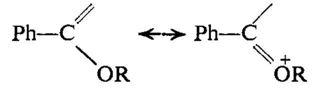
[8] In the present treatment the two oxygens of the ester group are assumed to be similar because of the resonance structures. For example,



$$\text{Ph—C}(\text{=O})\text{—OR} \longleftrightarrow \text{Ph—C}(\text{—O}^-)\text{=}\overset{+}{\text{O}}\text{R}$$

the C=O and C—O bond lengths in an A/B *cis* steroid 3α-*p*-bromobenzoate are 1.18 and 1.32 Å, respectively: J. S. McKechnie and I. C. Paul, *J. Am. Chem. Soc.*, **90**, 2144 (1968).

[9] The staggered conformation adopted for the benzoate sector rule is supported to a certain extent by microwave data, although these strictly apply to the gaseous state; *e.g.*, methyl formate: R. F. Curl, *J. Chem. Phys.*, **30**, 1529 (1959); ethyl formate: J. M. Riveros and E. B. Wilson, *ibid.*, **46**, 4605 (1967).

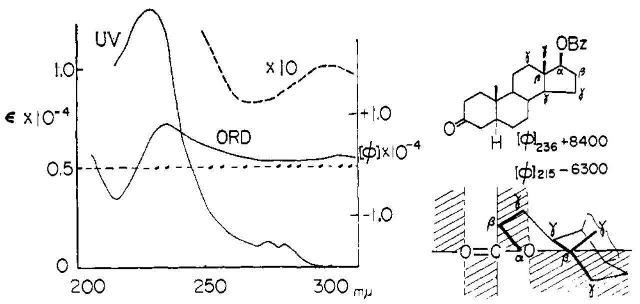


Figure 3. The benzoate Cotton effect of 3-oxoandrostane 17β-benzoate (EtOH). The Cotton effect of the ketone group is evident in the curve on the 10-fold expanded scale.

The presence of saturated ketone groups does not interfere with the interpretation, since Cotton effects due to ketone and benzoate groups differ greatly in position and intensity (Figure 3): the amplitude of the 290-mμ ketone Cotton effect is usually 5–50, whereas that of the 225-mμ benzoate group is 100–300. Correct predictions can be made in some cases even when the strongly optically active enone group is present, *e.g.*, the difference curve between the ORD curves of taxinine A[10,11] and its benzoate (Figure 1) (both with a = *ca.* 2000 around 250 mμ) clearly shows the expected positive Cotton effect centered at 225 mμ, $a = +165$. Where results are ambiguous because of overlap of the substrate and benzoate absorptions, the benzoate absorption can be shifted to longer wavelengths by appropriate *para* substituents[7] (*e.g.*, entry 15).

Although the scope of application of the present benzoate sector rule still remains to be clarified, a limiting case is when the asymmetric perturbation of the benzoate chromophore is insufficient to give rise to a Cotton effect, such as in cholestan-3β-ol and isoborneol (*endo*-OH); otherwise it appears to be widely applicable.[12]

Acknowledgments. We are grateful to Drs. P. Crabbé, Shô Itô, K. Takeda, and T. Wada for generous gifts of the samples listed in Table I.

(10) The absolute configuration of taxinine has been established by chemical correlations and X-ray analysis: M. Dukes, D. H. Eyre, J. W. Harrison, and B. Lythgoe, *Tetrahedron Letters*, 4765 (1965), and M. Shiro, T. Sato, H. Koyama, Y. Maki, K. Nakanishi, and S. Uyeo, *Chem. Commun.*, 98 (1966), respectively.

(11) H. C. Chiang, M. C. Woods, Y. Nakadaira, and K. Nakanishi, *ibid.*, 1201 (1967).

(12) This work has been supported in part by the National Institutes of Health, Public Health Service Research Grant No. CA 08394.

(13) Tanabe Pharmaceutical Co., Saitama, Japan.

N. Harada, Mo. Ohashi,[13] K. Nakanishi
Department of Chemistry, Tohoku University
Sendai, Japan

Received July 12, 1968

Optical Rotatory Power of the Benzoate Group

Sir:

The benzoate sector rule, a method for determining the absolute configuration of cyclic secondary alcohols, has been described in the preceding communication.[1] The theoretical aspects of the sector rule is discussed in the following.

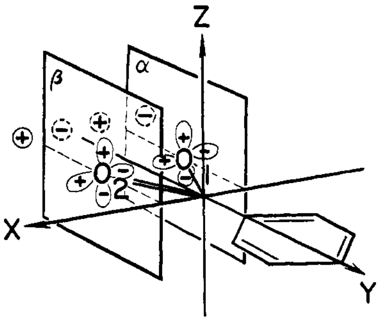


Figure 1. Signs of the upper sectors.

As the benzoate chromophore is inherently symmetric, the observed Cotton effect necessarily arises from the asymmetric perturbation of a substituent. The benzoate chromophore exhibits three π → π* absorption bands in the ultraviolet region, *i.e.*, at 280 mμ (ε 1000) due to the $^1A_{1g} \rightarrow {}^1B_{2u}(^1L_b)$ transition[2] of the benzene ring, at 230 mμ (ε 14,000) due to an intramolecular charge-transfer transition,[3-5] and at 195 mμ (ε 40,000) due to the $^1A_{1g} \rightarrow {}^1B_{1u}(^1L_a)$ transition.[6] In these transitions, the first and second absorption bands have the transition moments along the short and long axis of the benzoate chromophore,[7] respectively. The benzoates of optically active alcohols[8] exhibit a Cotton effect only at *ca.* 225 mμ; no Cotton effect was observed at the other absorption bands.

The fact that the observed Cotton effect is indeed due to the π → π* intramolecular charge-transfer transition and not due to an n → π* transition hidden in the strong absorption band was ascertained by observing the red shift caused by *para* substituents. As indicated in Table I, the shifts in the Cotton effect parallel those of the ultraviolet absorption maxima, and this provides strong support for the transition being π → π*. If the bands under consideration originated from an n → π* transition a blue shift would have been expected.[9]

Table I. Cotton Effects of *para*-Substituted Benzoates of Cholesterol[a]

Substituent	Uv λ_{max}, mμ	ORD, deg 1st extremum	ORD, deg 2nd extremum	a
$N(CH_3)_2$	311.2	$[\phi]_{316}$ +6100	$[\phi]_{270}$ −5400	+115
NH_2	293.8	$[\phi]_{300}$ +8100	$[\phi]_{262}$ −9500	+176
OCH_3	256.1	$[\phi]_{262}$ +9000	$[\phi]_{230}$ −9500	+185
Cl	240.2	$[\phi]_{248}$ +11,300	$[\phi]_{220}$ −9400	+207
H	229.2	$[\phi]_{235}$ +8400	$[\phi]_{215}$ −3600	+120
CN	239.5	$[\phi]_{245}$ +4600	$[\phi]_{216}$ −10,000	+146

[a] Solvent: methanol–dioxane (9:1).

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(1) N. Harada, Mo. Ohashi, and K. Nakanishi, *J. Am. Chem. Soc.*, **90**, 7349 (1968).

(2) P. Crabbé and W. Klyne, *Tetrahedron*, **23**, 3449 (1967).

(3) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *ibid.*, **23**, 1441 (1955); J. Tanaka and S. Nagakura, *ibid.*, **24**, 1274 (1956).

(4) J. Tanaka, S. Nagakura, and M. Kobayashi, *ibid.*, **24**, 311 (1956).

(5) Alternatively, this band has been assigned to the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition of the benzene chromophore: H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962.

(6) L. Verbit and Y. Inouye, *J. Am. Chem. Soc.*, **89**, 5717 (1967).

(7) J. Tanaka, *Bull. Chem. Soc. Japan*, **36**, 833 (1963).

(8) The benzoate sector rule so far only applies to cyclic secondary alcohols. However, primary alcohol benzoates also exhibit the 225-mμ Cotton effect, provided the optical center is not too far removed from the hydroxyl group; extension of the present rule is being carried out.

(9) The n → π* band has not been observed for benzoic acid but has been measured in various solvents for the *para*-substituted acetophenones.[4]