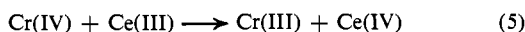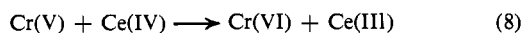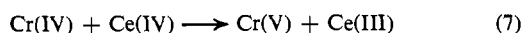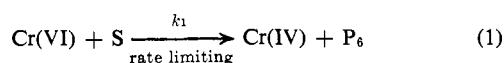after ten half-lives for the chromic acid oxidation has passed.

Figure 2 shows the effect of cerium(III) and cerium-(IV) on the product composition in the oxidation of phenyl-*tert*-butylcarbinol[7] by chromium(VI). In the absence of added cerium ion, chromic acid oxidation of this substrate produces both the normal product, pivalophenone (64%), and cleavage products, benzaldehyde (36%) and *tert*-butyl alcohol. When the amount of cerium is approximately 50 times less than that of the chromium(VI), the amount of cleavage product is reduced to the minimal amount of 5%. Reduction of the cleavage reaction to one-half that without cerium present requires a [Cr(VI)] to [Ce] ratio of 10,000.

These results show that the reactive chromium(IV) species, formed in the rate-limiting step in chromic acid oxidations, can be effectively removed by reaction with very small amounts of either cerium(IV) or cerium(III). Scheme IV adequately explains our data.

Scheme IV

$$Cr(VI) + S \xrightarrow[\text{rate limiting}]{k_1} Cr(IV) + P_6 \qquad (1)$$

$$Cr(IV) + Ce(IV) \longrightarrow Cr(V) + Ce(III) \qquad (7)$$

$$Cr(V) + Ce(IV) \longrightarrow Cr(VI) + Ce(III) \qquad (8)$$

$$Cr(IV) + Ce(III) \longrightarrow Cr(III) + Ce(IV) \qquad (5)$$

The combination of steps 7 and 8 with three times reaction 1 and two times reaction 5 gives eq 9, according

$$2Cr(VI) + 3S \longrightarrow 3P_6 + 2Cr(III) \qquad (9)$$
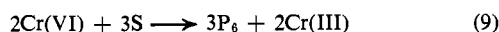
to which chromium(VI) is the only oxidant reacting with the organic substrate. The added cerium compounds thus act as a catalyst effecting the disproportionation of the intermediate chromium species chromium(IV) and chromium(V) into the stable valence states of chromium.

Further work is in progress and will be reported in detail.

(7) Under identical conditions the second-order rate constant for oxidation of phenyl-*tert*-butylcarbinol by cerium(IV) was 150 times less than that for the corresponding chromic acid oxidation. Both benzaldehyde (62%) and pivalophenone (38%) were produced in the cerium(IV) oxidation.

* Author to whom inquiries should be sent.

Michael P. Doyle, Raymond J. Swedo, Jan Roček*
Department of Chemistry, University of Illinois at Chicago Circle
Chicago, Illinois 60680
Received September 1, 1970

π–π* Region Cotton Effects of Cyclic Conjugated Dienes and Enones. Interpretation in Terms of Allylic Axial Chirality Contributions[1]

Sir:

Although the Cotton effects of optically active 1,3-cyclohexadienes[2] and heteroannular transoid con-

(1) Part of a presentation at the 1970 Midwest Regional American Chemical Society Meeting, Lincoln, Neb., Oct 28–30, 1970.

jugated dienes[3] in the 230–280-nm (π–π* transition) region correlate well with the helicity or chirality of the chromophore (positive when the planes of the two double bonds are skewed in a right-handed helix; negative when left-handed),[4] heteroannular cisoid conjugated dienes apparently have had to be excluded from this treatment.[5] Likewise, while optical rotatory dispersion (ORD) and circular dichroism (CD) curves of transoid α,β-unsaturated cyclic ketones in the same spectral region generally conform[6] to the transoid diene chirality rule,[3] they are frequently complicated by strong overlapping optical transitions of opposite sign.[7]

Similarly, a proposed extension[6a] of the homoannular cisoid diene chirality rule[2] to cisoid conjugated enones, while evidently widely accepted,[6b,7,8] has not been firmly validated. Indeed, nmr[9] and even other ORD–CD data[8b] (for the longer wavelength n–π* transition) are available showing that such an extension is probably incorrect for at least two of the cases (cholest-5-en-4-one and cholest-4-en-6-one) originally cited[6a] to illustrate it.

In this report, on the basis of new plus existing data,[2,3,6,7] we wish to propose a fundamentally different approach to the interpretation of the π–π* region Cotton effects of these various systems utilizing the olefin chirality concept of Yogev, Amar, and Mazur.[10] Rather than the inherent dissymmetry or chirality of the chromophore (when nonplanar), this approach considers *asymmetric perturbations of the double bond components of the chromophore through excited-state interactions with their allylic axial or pseudoaxial bonds as the primary factor controlling the sign of the Cotton effect* (but not necessarily its magnitude).[11]

(2) (a) A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.*, **83**, 4661 (1961); (b) A. W. Burgstahler, H. Ziffer, and U. Weiss, *ibid.*, **83**, 4660 (1961); (c) H. J. C. Jacobs and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **84**, 932 (1965); (d) U. Weiss, H. Ziffer, and E. Charney, *Tetrahedron*, **21**, 3105 (1965); (e) E. Charney, *ibid.*, **21**, 3127 (1965); (f) H. Ziffer, U. Weiss, and E. Charney, *ibid.*, **23**, 3881 (1967).

(3) E. Charney, H. Ziffer, and U. Weiss, *ibid.*, **21**, 3121 (1965).

(4) A possible exception to the cisoid diene chirality rule has been reported recently by S. Bory and C. R. Engel, *Bull. Soc. Chim. Fr.*, 3043 (1970). See also P. Crabbé, *Proc. Nat. Acad. Sci. U. S.*, **66**, 4 (1970).

(5) Reference 2d, p 3107, and private communication from Dr. Weiss.

(6) (a) C. Djerassi, R. Records, E. Bunnenberg, K. Mislow, and A. Moscowitz, *J. Amer. Chem. Soc.*, **84**, 870 (1962); (b) J.-C. Bloch and S. R. Wallis, *J. Chem. Soc. B*, 1177 (1966); (c) *cf.* W. B. Whalley, *Chem. Ind. (London)*, 1024 (1962).

(7) (a) L. Velluz, M. Legrand, and R. Viennet, *C. R. Acad. Sci., Paris*, **261**, 1687 (1965); (b) K. Kuriyama, M. Moriyama, T. Iwata, and K. Tori, *Tetrahedron Lett.*, 1661 (1968); (c) H. Ziffer and C. H. Robinson, *Tetrahedron*, **24**, 5803 (1968).

(8) (a) R. E. Ballard, S. F. Mason, and G. W. Vane, *Discuss. Faraday Soc.*, **35**, 43 (1963); (b) G. Snatzke, *Tetrahedron*, **21**, 413, 439 (1965); (c) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, Calif., 1965, pp 194–196; (d) L. Velluz, M. Legrand, and M. Grosjean, "Optical Circular Dichroism," Academic Press, New York, N. Y., 1965, pp 131–134; (e) J. H. Brewster, *Top. Stereochem.*, **2**, 64 (1967); (f) C. W. Deutsche, D. A. Lightner, R. W. Woody, and A. Moscowitz, *Annu. Rev. Phys. Chem.*, **20**, 419 (1969).

(9) D. Lavie, S. Greenfield, Y. Kashman, and E. Glotter, *Israel J. Chem.*, **5**, 151 (1967); *cf.* R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963).

(10) A. Yogev, D. Amar, and Y. Mazur, *Chem. Commun.*, 339 (1967). Although certain obvious limitations in connection with non-conjugated exomethylene steroids have been found [M. Fétizon and I. Hanna, *ibid.*, 462 (1970)] for this rule and its octant counterpart [A. I. Scott and A. D. Wrixon, *Tetrahedron*, **26**, 3695 (1970)], it has proved extremely useful for a number of endocyclic applications [*e.g.*, see A. W. Burgstahler, J. N. Marx, and D. F. Zinkel, *J. Org. Chem.*, **34**, 1550, 3716 (1969)].

(11) The comparatively large amplitudes reported[2a,c,d] for the ORD curves of such dienes as pyro- and isopyrocalciferol, which molecular models indicate have a nearly planar chromophore, seem to contradict the proposed[2e,8f] dependence of the intensity of the Cotton effect on the

Figure 1. 1,3-Cyclohexadiene chirality. Helix indicates sense of chromophore chirality; signs + (right-handed) and − (left-handed) designate allylic axial chirality contributions.
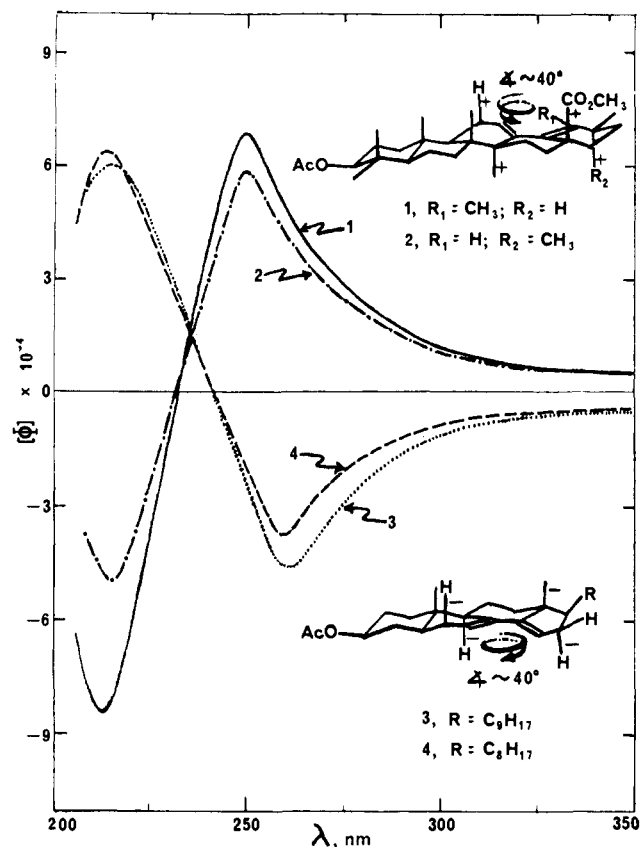
Figure 2. ORD curves of typical heteroannular cisoid conjugated dienes: **1** measured in isooctane and curve supplied by Dr. U. Weiss; **2–4** measured in *n*-hexane in a 1.0-cm cell with a Cary Model 60 recording spectropolarimeter.

In contrast to 1,3-cyclohexadienes (Figure 1), in which the chirality of the chromophore is the same as that imposed by the C-5 and C-6 pseudoaxial bonds on their respective adjacent double bonds, typical hetero-annular cisoid conjugated dienes (Figure 2) have chirality contributions of the allylic pseudoaxial bonds that are *opposite* to the chirality of the *diene system*. Thus in the case of homoannular cisoid dienes the two approaches necessarily agree in predicting the sign of the Cotton effect, but with heteroannular cisoid dienes they do not. The positive ORD curves (Figure 2) of the conformationally unambiguous dienes methyl vanguerolate acetate (**1**)[12] and methyl 3β-acetoxy-12,18-oleadien-28-oate (**2**)[13] on the one hand, and the negative

skewness of the chromophore. From a wide variety of examples[2,3,6,7] plus additional measurements of our own, it appears to us that high rotational strengths in cyclic conjugated systems are more directly dependent on the number and nature of exocyclic double bonds present.

(12) D. H. R. Barton, H. T. Cheung, P. J. L. Daniels, K. G. Lewis, and J. F. McGhie, *J. Chem. Soc.*, 5163 (1962). The ORD curve (recorded at the National Institutes of Health in isooctane on a sample supplied by Professor Barton) was kindly made available to us by Dr. U. Weiss.

(13) D. H. R. Barton and C. J. W. Brooks, *J. Chem. Soc.*, 257 (1951). We are most grateful to Professor Barton for providing a sample for this determination.
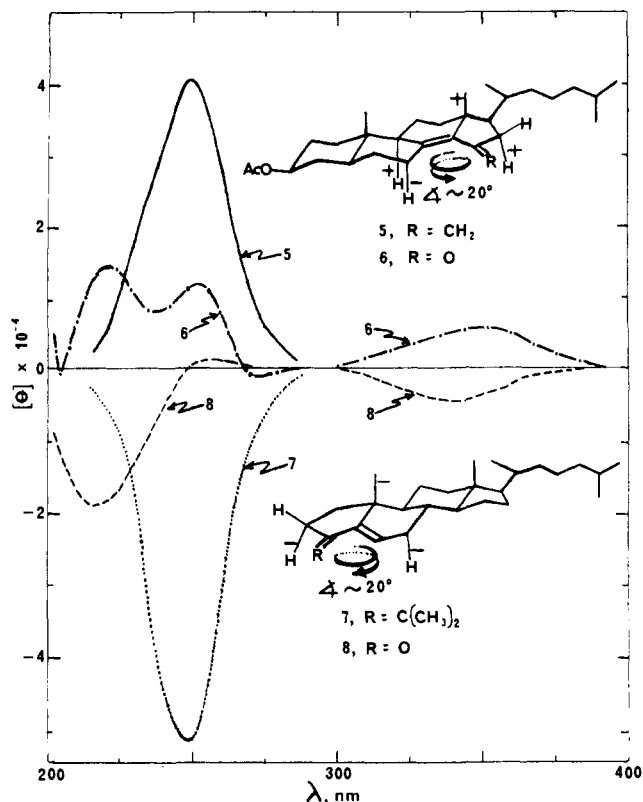
Figure 3. CD curves of heteroannular cisoid conjugated enones and related dienes having unambiguous chromophore chirality; measurements made in *n*-hexane in a 1.0-cm cell with a Cary Model 6001 CD accessory unit on a Cary Model 60 recording spectropolarimeter.

curves of ergosterol-B₃ acetate (**3**)[14] and 5α-cholesta-7,14-dien-3β-ol acetate (**4**)[14] on the other, are correctly predicted by the allylic axial chirality approach but not by the cisoid diene chirality rule.

Paralleling these findings are the antipodal CD curves (Figure 3) of 15-methylene-5α-cholest-8(14)-en-3β-ol acetate (**5**)[15] and 3-isopropylidene-A-norcholest-5-ene (**7**),[16] which we investigated at the suggestion of Dr. Ulrich Weiss of the National Institutes of Health. Dreiding models indicate that the geometry of the chromophore in **5** and in **7** is quite rigid, yet these dienes exhibit Cotton effects opposite to those required by the cisoid diene chirality rule but in agreement with the allylic axial chirality approach. Similar Cotton effect behavior is found for 6-methylenecholest-4-ene (positive) and 4-methylenecholest-5-ene (negative),[17] in which there is probably greater conformational mobility but practically identical allylic axial chirality.

When applied to cyclic conjugated enones, this approach suggests that the Cotton effect in the region of the ultraviolet maximum (230–260 nm) is usually dominated by allylic axial perturbations of the carbon–carbon double bond, while the Cotton effect in the

(14) Prepared by the method of D. H. R. Barton and G. F. Laws, *ibid.*, 52 (1954); *cf.* R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelly, *ibid.*, 1131 (1957).

(15) Prepared by Wittig synthesis from compound **6**.[14]

(16) R. M. Moriarty and E. S. Wallis, *J. Org. Chem.*, **24**, 1274 (1959); C. W. Shoppee and G. A. R. Johnston, *J. Chem. Soc.*, 2684 (1962); *cf.* D. N. Gupta, G. Schilling, and G. Just, *Can. J. Chem.*, **43**, 792 (1965).

(17) Prepared by Wittig synthesis from the corresponding ketones. A positive CD maximum has also been reported[7c] for 17β-acetoxy-6-methylen-4-androsten-3β-ol.

200–220-nm region evidently reflects the chirality contribution to the carbonyl group by the pseudoaxial bond on the α' carbon.

For example, in Figure 3 only the initial portion of the negative long-wavelength $\pi-\pi^*$ transition Cotton effect expected on the basis of the cisoid enone chirality rule[6a] for the left-handed enone chirality in 3β-acetoxy-5α-cholest-8(14)-en-15-one (6)[14] and the positive effect expected for the right-handed enone chirality in A-norcholest-5-en-3-one (8)[18] can be detected. The dominant lower wavelength Cotton effects exhibited by 6 and 8 are of opposite sign, in agreement with the allylic axial chirality approach.[19] Similar correlations extend (Table I) to cholest-5-en-4-one and cholest-4-en-

Table I. 200–220-nm Region Cotton Effects of Steroidal Enones

Chromophore	α'-Chirality contribution	Obsd Cotton effect
4-En-3-one[a−c]	2βH (+)	+
B-Nor-4-en-3-one[c]	2βH (+)	+
5-En-4-one[c]	3αH (−)	−
4-En-6-one[c]	7αH (+)	+
5-En-7-one[a,c]	8βH (−)	−
8(9)-En-7-one[a,c]	6βH (+)	+
8(14)-En-7-one[c]	6βH (+)	+
8(9)-En-11-one[a]	12αH (−)	−
9(11)-En-12-one[a]	13βMe (+)	+

[a] Reference 7a. [b] Reference 7b. [c] Reference 7c.

6-one as well as to other steroidal conjugated enones of reasonably certain conformation.

As anticipated, this allylic axial chirality interpretation of $\pi-\pi^*$ region Cotton effects is applicable to heteroannular transoid conjugated dienes[3,20] and to a variety of cyclic conjugated trienes and dienones, in addition to other cyclic conjugated dienes and enones. Results of these further studies will be reported shortly.

Acknowledgment. We are grateful to Mr. Hernan E. Cordova for preliminary experimental work and to Professors Pierre Crabbé, Albert Moscowitz, A. I. Scott, Günther Snatzke, and Oscar E. Weigang and Drs. Elliot Charney and Ulrich Weiss for valuable comments and suggestions.

(18) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 2528 (1952). We cordially thank Professor Shoppee for advice concerning the hypobromite oxidation of cholesterol (homogeneous conditions imperative) to the Diels acid used in the preparation of **8**.

(19) In contrast to **6**, 3β-acetoxy-5α-ergosta-8(14),22-dien-15-one[14] exhibits a substantial CD maximum (positive) only in the 220-nm region.

(20) The apparent "exception" of a steroidal 6,8(14)-diene to the transoid diene chirality rule (and hence to our approach) as suggested by ORD data[3] is not supported by CD measurements.

* Address correspondence to this author.

Albert W. Burgstahler,* Rodney C. Barkhurst

*Department of Chemistry, The University of Kansas
Lawrence, Kansas 66044*

Received August 26, 1970

Effects of Polar Substituents on Photoreduction and Quenching of Fluorenone by Dimethylanilines[1]

Sir:

Photoreduction of aromatic ketones by aliphatic amines is characterized by moderately high quantum

yields and low sensitivity to diffusion-controlled quenchers and to concentration of amine.[2] These reactions may proceed by rapid charge-transfer interactions,[2−5] for which rate constants, k_{ir}, may exceed 10^9 M^{-1} sec^{-1}, followed either by transfer of α hydrogen and formation of radicals, k_h, or by charge destruction and quenching, k_e (eq 1). Quantum yields would be

$$\text{Ar,ArC}{=}\text{O*}(\text{T}_1) + \text{RCH}_2\text{NR}_2 \xrightarrow{k_{ir}} [\text{Ar,Ar}\overset{.}{\text{C}}{-}\overset{-}{\text{O}} \quad \text{RCH}_2\overset{.+}{\text{NR}_2}]$$

$$\text{Ar,Ar}\overset{.}{\text{C}}{-}\text{OH} + \text{R}\overset{.}{\text{C}}\text{HNR}_2 \qquad \text{Ar,ArC}{=}\text{O}(\text{S}_0) + \text{RCH}_2\text{NR}_2 \qquad (1)$$

proportional to the fraction $f = k_h/(k_h + k_e)$, the rate constant for abstraction of hydrogen, $k_H = fk_{ir}$. It is of interest to examine effects of polar substituents on k_{ir} and on f. We report now on photoreduction and quenching of fluorenone by para-substituted dimethylanilines. Fluorenone is photoreduced by tertiary amines[6−8] in hydrocarbon solution, and this reaction, unlike that of benzophenone,[2] is not complicated by light-absorbing transients.

The dimethylanilines were obtained commercially or prepared by methylation of the corresponding anilines, and after purification had physical properties corresponding to literature values. Fluorenone was from Eastman, mp 83°. *trans*-Stilbene was from Pilot Chemicals, mp 124°. Aliquots, 3 ml, were degassed and irradiated in Pyrex under argon in 1-cm square tubes fitted with Teflon stopcocks, either on a turntable by a G.E. H-85-A3 lamp fitted with Corning 7380 filters, or by a Bausch and Lomb 38-86-01 monochromator at 405 nm. Analyses for fluorenone were made at 405 nm. Quantum yields were determined at 405 nm by ferrioxalate actinometry.[9] The pinacol, mp 182–185°, was obtained in essentially quantitative yield from photoreduction of fluorenone by dimethylaniline and by *p*-carbethoxy- and *p*-methyldimethylanilines. Solutions of 0.003 M fluorenone and 0.003–0.01 M dimethylaniline in benzene were irradiated on the turntable, and rates were converted to quantum yields. Linear plots of $1/\varphi$ vs. inverse concentration of amine[10] lead to intercepts, $k_{ir}/\varphi_{isc}k_H$, in which φ_{isc} is the quantum yield for formation of triplet,[11] ~ 0.93. The ratio of slope to intercept is k_d/k_{ir}, where k_d is the rate constant for self and solvent deactivation of the triplet. Solutions of 0.003 M fluorenone, 0.01 M dimethylaniline, and 0.001–0.01 M stilbene were irradiated on the turntable. Linear plots of the ratio of unquenched to quenched rates against concentration of quencher have slope = $k_q/(k_{ir}(\text{Am}) + k_d)$. Values of k_{ir} were based on $k_q =$

(2) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968).

(3) S. G. Cohen and J. I. Cohen, *ibid.*, **89**, 164 (1967); *J. Phys. Chem.*, **72**, 3782 (1968).

(4) S. G. Cohen and N. Stein, *J. Amer. Chem. Soc.*, **91**, 3690 (1969).

(5) S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, 837 (1970).

(6) R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 1265 (1967).

(7) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968); 2125 (1969).

(8) G. Davis, P. A. Carapellucci, K. Szoc, and J. D. Gresser, *J. Amer. Chem. Soc.*, **91**, 2264 (1969).

(9) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(10) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

(11) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).