melted at 80–81°: $\lambda_{max}^{CF_3CO_2H}$ 314 mμ (log ε 4.21); $\tau_{CF_3CO_2H}$ 2.48 (m, 5H), 2.72 (1H), 7.65 (d, 1H), and 7.50–8.83 (m, 11H); τ_{CCl_4} 2.72 (m, 5H), 3.50 (1H), and 7.92–8.90 (m, 11H).

Anal. Calcd. for $C_{15}H_{17}NS_2$: C, 65.41; H, 6.22; S, 23.28. Found: C, 65.65; H, 6.35; S, 23.65.

Methylation of N,4-Diphenyl-2-imino-1,3-dithiole.—To 2 ml. of dimethyl sulfate was added 0.4 g. of **2a**, and the mixture was heated gradually to 140°, then allowed to cool slowly to room temperature. Glacial acetic acid (6 ml.) followed by 0.5 ml. of 70% perchloric acid was added. Dilution of the resulting solution with *ca.* 100 ml. of ether afforded 0.55 g. of a solid, which was collected, dried, and recrystallized once from 95% ethanol. It melted at 213–215°, and the mixture melting point with an authentic sample of N-methyl-N,4-diphenyl-2-imino-1,3-dithiolium perchlorate (**4**) was undepressed. The infrared and n.m.r. spectra of these compounds were identical.

Reaction of 2-Methylthio-4-phenyl-1,3-dithiolium Perchlorate with Ammonia in Acetonitrile.—1 (2.5 g., 7.65 mmoles) was dissolved in 75 ml. of acetonitrile and ammonia was allowed to bubble into the solution for 5 min. at room temperature. During the addition of ammonia the solution progressively changed color from yellow to black, with the appearance of some fine black solid. The solution was then heated gently for 20 min. and filtered to remove the insoluble black solid. An infrared spectrum of this solid indicated it to be ammonium perchlorate. The acetonitrile was stripped from the reaction mixture, leaving a black solid which was washed with ethyl acetate, dissolved in 10 ml. of 70% perchloric acid, heated for 5 min., and cooled; 40 ml. of ethyl acetate was added and the solution was filtered. The solid isolated was shown to be ammonium perchlorate. Similar experiments using ethanol, tetrahydrofuran, or aqueous ammonium hydroxide gave only tarry residues from which no crystalline solids could be isolated.

When 2.0 g. of 1 was stirred into 20 ml. of liquid ammonia, and the ammonia was allowed to evaporate slowly, the residue was a black tar containing crystals of ammonium perchlorate.

Terpenes. XVI. Optical Rotatory Dispersion Studies of Some Diterpenoid Derivatives Possessing a Bicyclo[2.2.2]octanone Ring System[1]

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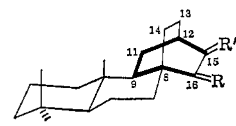
During the course of another investigation,[2] we had occasion to prepare a number of bicyclo[2.2.2]octanones derived from maleopimaric acid (the Diels–Alder adduct of abietic acid and maleic anhydride). Since the literature contains little information[3] on optical rotatory dispersion curves of optically active bicyclo[2.2.2]-octanones, we wish to record here our preliminary observations. An attempt to apply the octant rule[4] to these substances is described.

As in cyclopentanones,[5] in some cyclohexanones under the boat form the Cotton effect would be expected to arise mainly from the asymmetry of the cyclohexanone carbon atoms ("first-order effect"[5]) and only secondarily from the substituents ("second-order effect"[5]) attached to the cyclohexanone ring. The experimentally observed Cotton effects shown in Table I and Table II may therefore be interpreted as follows. If in compounds I and II the octant rule is applied to the cyclohexanone ring formed by C-8, C-9, C-11, C-12, C-15, and C-16, one finds that, in ketone I, C-11 is severely skewed in the positive upper left octant, and this effect is only partly counterbalanced by the negative contribution of substituent C-13 in the lower left octant, resulting in a positive Cotton effect. In ketone II, C-9 is strongly skewed in the negative upper right octant. Moreover, the negative contribution made by C-9 is enhanced by ring A, also in a negative octant, and this is only partly counterbalanced by the positive contribution of substituent C-14 in the lower right octant, resulting in a negative Cotton effect. Because of the "quasi-enantiomeric" relationship presented by ketones I and II, one would predict opposite Cotton effects for the two, and they exhibit similar intensities.

In compounds III–VI of Table II the octant rule is applied to the cyclohexanone ring formed by C-8, C-14, C-13, C-12, C-15, and C-16. In ketones III–V, C-15 is strongly skewed into the positive upper left octant, and the positive Cotton effect is still enhanced by the fused decalin moeity, also falling into a positive octant. Since the C-11 carbon atom in the lower left

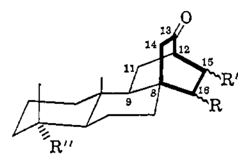
TABLE I



Compd.	R	R'	Cotton effect,[a] deg.
I	H_2	O	$[\Phi]_{308}$ = +3023
II	O	H_2	$[\Phi]_{312}$ = −3445

[a] The experimental molecular rotations of the peaks or troughs of the highest wave length are shown. In most cases both peaks and troughs were not obtained for a given compound since rotations could not be measured below ~300 mμ with the instrument used in this study.

TABLE II



Compd.	R	R'	R''	Cotton effect,[a] deg.
III	H	H	CH_3	$[\Phi]_{310}$ = +1713
IV	H	H	CO_2CH_3	$[\Phi]_{310}$ = +1608
V	β-CO_2CH_3	α-CO_2CH_3	CO_2CH_3	$[\Phi]_{319}$ = +941
VI	β-CO_2CH_3	β-CO_2CH_3	CO_2CH_3	$[\Phi]_{303}$ = −4664
VII	Double bond at C-15–C-16		CO_2CH_3	$[\Phi]_{315}$ = +24327

[a] The experimental molecular rotations of the peaks or troughs of the highest wave length are shown. In most cases both peaks and troughs were not obtained for a given compound since rotations could not be measured below ~300 mμ with the instrument used in this study.

(1) Paper XVI in the series from Oklahoma State University. The work at Oklahoma State University was supported by the National Science Foundation (GP-233).

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octant makes a smaller negative contribution, a positive Cotton effect is observed for these ketones.

A comparison of the curves of V and VI is particularly interesting. The *trans* diester V, the thermodynamically more stable product, can be prepared from VI by refluxing in base followed by reesterification with diazomethane. Such an inversion of configuration of a carboxyl grouping is reminiscent of similar changes of stereochemistry performed with 16,17-dicarboxy steroids.[6] This epimerization at C-15 of VI into V is accompanied by a change in the sign of the Cotton effect and can thus be readily followed by optical rotatory dispersion. A possible explanation for the negative Cotton effect observed for VI may be that the unfavorable steric and electronic repulsions of the *cis* C-15 and C-16 carbomethoxy groups in VI induce a conformational modification of the ring system. Further work is, however, desirable in order to permit a safe interpretation for the inversion of the Cotton effect which is observed in going from VI to V.

Finally, in the ethylenic ketone VII, the sign of the Cotton effect is in agreement with the structure and stereochemistry proposed for the β,γ-unsaturated keto chromophore.[3] Indeed, a positive Cotton effect is to be expected[3] if the absolute configuration of this chromophore is as indicated in formula VII. Furthermore, as indicated in Table II, the β,γ double bond greatly enhances the magnitude of the Cotton effect, as previously observed in cases where a nonbonding orbital can overlap the π-system of the neighboring carbonyl chromophore.[3,7,8]

Experimental

All optical rotatory dispersion curves were obtained in methanol (c 0.05–0.15) using the Rudolph photoelectric spectropolarimeter beginning at 700 mμ and continuing to 300 mμ. The preparation and characterization of all compounds used has been described[1] and analytically pure samples were used. In the case of compound VI, both the trough (−4664°) and the peak (+1280°) were obtained in methanol solution, and the curve was unchanged after the addition of a trace of hydrochloric acid, indicative of no hemiketal formation.[9]

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Terpenes. XVII.[1] Studies on the Ozonolysis of Methyl Maleopimarate and the Epoxidation of Trimethyl Maleopimarate and Fumaropimarate

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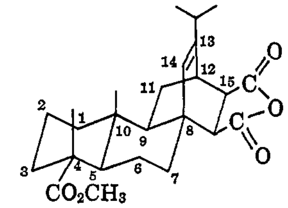
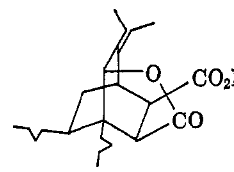
In 1936 Wienhaus and Sandermann[2] reported that ozonolysis of methyl maleopimarate (I), the Diels–Alder adduct obtained from levopimaric acid methyl ester and maleic anhydride, gave a methyl ester,



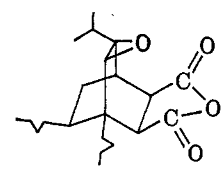
I



II

$C_{25}H_{34}O_8$, m.p. 250°. Several years later Ruzicka and LaLande,[3] after careful re-examination of the reaction, found in addition to the above-mentioned product two other isomeric monomethyl esters of molecular formula $C_{25}H_{34}O_6$, m.p. 289–290° and m.p. 226–227°.[4] The latter workers found that the dimethyl ester of the product of m.p. 226–227° was identical with the dimethyl ester of the product obtained on oxidation of maleopimaric acid with alkaline permanganate. Recent work from our laboratory[5,6] has shown that this product is correctly represented by structure II.

Ruzicka and LaLande[3] concluded that the product of m.p. 289–290° was an acid lactone ester and suggested two possible structures.[4] However, our work does not support the previously assigned structures, and instead we propose structure III for this product.


III

The infrared spectrum of III showed the characteristic five-membered ring anhydride type carbonyl absorption at 1773 and 1842 cm.$^{-1}$ and, in addition, its n.m.r. spectrum showed the proton at C-14 as a singlet centered at δ 3.20 and the isopropyl methyl groups appeared as a pair of doublets (J = 7 c.p.s.) centered at δ 0.72 and 1.07. The most convincing evidence for structure III came from the observation that it could also be prepared from I by treatment with trifluoroperacetic acid[7]; however, other peracids such as monoperphthalic or *m*-chloroperbenzoic were ineffective. The stereochemistry of the epoxide ring in III was assigned on the basis of arguments presented below.

Epoxide III was partially converted into the epoxy triester IV by refluxing in alkali followed by re-esterification with diazomethane. Compound IV was also readily prepared by epoxidation of trimethyl fumaropimarate (V) with trifluoroperacetic acid. A comparison of the n.m.r. spectra of III and IV was of interest. Surprisingly, one of the isopropyl methyl groups in IV is deshielded to a considerable extent (δ 1.32) as compared with those in III. The anhydride ring in III was opened only with great difficulty. Thus, the

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