The data in Table I are of practical value since they allow a choice in the wavelengths of the Cotton effects and thus greatly facilitate measurements when the alcohol itself has an optically active absorption, *e.g.*, benzenoid, enone, overlapping that of the benzoate chromophore.[10]

The optical rotatory power or rotational strength $R_{\pi\pi^*}$ is proportional to the imaginary part of the scaler product of the electric transition moment and magnetic transition moment[11] (eq 1). Since the intramolecular charge-transfer transition

$$R_{\pi\pi^*} = Im[(\psi_\pi|\mathbf{P}|\psi_{\pi^*})(\psi_{\pi^*}|\mathbf{M}|\psi_\pi)] \qquad (1)$$

$$\psi_\pi{}^0\ (=\sum_r C_{\pi r}(\chi_{2p_z})_r) \rightarrow \psi_{\pi^*}{}^0\ (=\sum_r C_{\pi^* r}(\chi_{2p_z})_r)$$

has its electric transition moment along the y axis,[12] the magnetic transition moment directed along the y axis makes a contribution to the optical rotation. If the atomic orbital of the π-molecular orbital is approximated by the Slater type orbital, the magnetic moment operation for the atomic orbital can be evaluated, for example, as in eq 2.[13,14] The rotational strength

$$\mathbf{M}\chi_{2p_z} = \frac{e\hbar}{2mci}[\mathbf{i}\chi_{2p_y} - \mathbf{j}\chi_{2p_x}] \qquad (2)$$

calculated by first-order perturbation then becomes

$$R_{\pi\pi^*} = Im\left[\frac{-\mathbf{j}e\hbar}{2mci}(\psi_\pi{}^0|\mathbf{P}|\psi_{\pi^*}{}^0)\left\{\sum_{j\neq\pi^*}\frac{\int\psi_j{}^0V\psi_{\pi^*}{}^0\mathrm{d}\tau}{E_{\pi^*}{}^0 - E_j{}^0} \times \int\psi_j{}^0\sum_r C_{\pi r}(\chi_{2p_x})_r\mathrm{d}\tau - \sum_{i\neq\pi}\frac{\int\psi_i{}^0V\psi_\pi{}^0\mathrm{d}\tau}{E_\pi{}^0 - E_i{}^0} \times \int\psi_i{}^0\sum_r C_{\pi^* r}(\chi_{2p_x})_r\mathrm{d}\tau\right\}\right]$$

where $\psi_i{}^0$ and $\psi_j{}^0$ are either the orbitals introduced by the electrostatic perturbation V mainly due to the incomplete screening of nuclei of asymmetric substituents and are limited to those having nonzero overlap integrals with χ_{2p_z} (electrostatic perturbation) or the orbitals of asymmetric substituent itself which overlap with $\psi_{\pi^*}{}^0$ and $\psi_\pi{}^0$ orbitals (overlap perturbation).[11,15]

If it is assumed that the two oxygen atoms have similar electronic properties and are effectively perturbed because of the proximity of the asymmetric center, the rotational strength $R_{\pi\pi^*}$ will be governed by the oxygen orbitals, χ_{2p_z} and χ_{2p_x}. The first term of the magnetic transition moment then becomes

$$\sum_{j\neq\pi^*}\underbrace{\frac{\int\psi_j{}^0V\{C_{\pi^*O_1}(\chi_{2p_z})_{O_1} + C_{\pi^*O_2}(\chi_{2p_z})_{O_2}\}\mathrm{d}\tau}{E_{\pi^*}{}^0 - E_j{}^0}}_{A} \times \underbrace{\int\psi_j{}^0\{C_{\pi O_1}(\chi_{2p_x})_{O_1} + C_{\pi O_2}(\chi_{2p_x})_{O_2}\}\mathrm{d}\tau}_{B}$$

where $C_{\pi^*O_1} \approx C_{\pi^*O_2}$ and $C_{\pi O_1} \approx C_{\pi O_2}$. In the case of electrostatic perturbation, the sign of the term A depends on the position of the asymmetric substituent in the eight spaces divided by the nodal planes of the orbitals χ_{2p_z} and $\psi_j{}^0$ (Figure 1). On the other hand, the term B is fixed in sign without regard to the position of substituent. In the case of overlap perturbation, A will be of opposite sign in the two spaces divided by plane xy, and B also alters its sign in the four sectors divided by planes α, β, and yz. The same situation also holds for the second term. Therefore, the product of A and B, *viz.*, the rotational strength $R_{\pi\pi^*}$, alternates its sign, in rough approximation, from sector to sector as illustrated in Figure 1. Since the present qualitative discussion is based on a simple LCAO–MO treatment, and the orbital $\psi_j{}^0$ may dominantly be the lone-pair orbitals in the case of electrostatic perturbation, an unambiguous prediction of the absolute sign and a quantitative definition of the sector boundaries require more exact wave functions and knowledge pertaining to the asymmetric perturbation[16] and structures of lone-pair orbitals.

The fact that no Cotton effect is detected in the $\pi \rightarrow \pi^*$ transition at 280 mμ can be accounted for by the properties of the transition, namely, the wave function related to the ^1L_b transition is localized in the benzene ring, and therefore, owing to the large distance from the asymmetric center responsible for the perturbation, the rotational strength is almost zero. The same consideration applies to the ^1L_a transition. In contrast, due to the strong contribution of the COO group, the wave function related to the 230-mμ transition is effectively perturbed by the substituent and a Cotton effect is observed.[17]

Acknowledgments. We are indebted to Dr. Y. Amako of our department for helpful discussions.

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(10) See entry 15 in Table I, ref 1.

(11) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940); A. Moscowitz, *Advan. Chem. Phys.*, 4, 67 (1962).

(12) The direction of the transition moment of this band in benzoic acid is actually tilted by 6.5° from the y axis toward the carbonyl group.[7]

(13) J. C. Tai and N. L. Allinger, *J. Am. Chem. Soc.*, **88**, 2179 (1966).

(14) Y.-H. Pao and D. P. Santry, *ibid.*, **88**, 4157 (1966).

(15) G. Wagnière, *ibid.*, **88**, 3937 (1966).

(16) The various asymmetric perturbations have been discussed for the inherently symmetric system in ref 11 and 15.

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Perchlorotropone

Sir:

We have synthesized hexachlorotropone (II), the first perhalogenated tropone, by direct photoisomerization of hexachlorobicyclo[3.2.0]hepta-3,6-dien-2-one (I).[1] Although the photoisomerization of substituted tropones to bicycloheptadienones[2] and the further phototransformations of the products have been extensively studied,[3] to our knowledge the present case is the first example of the reverse reaction.

Irradiation of a dilute (1–2%) dichloromethane solution of I in a quartz vessel, using low-pressure mercury vapor lamps in a Griffin–Srinivasan reactor,[4]

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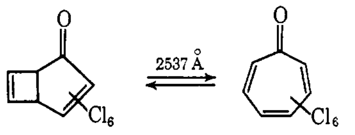
(1) A. Roedig and L. Hornig, *Ann.*, **598**, 208 (1956).

(2) (a) K. F. Koch, *Advan. Alicyclic Chem.*, **1**, 258 (1966); (b) D. J. Pasto in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 155 ff.

(3) O. L. Chapman and J. D. Lassila, *J. Am. Chem. Soc.*, 90, 2449 (1968), and references therein.

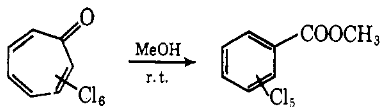


I II

leads in the course of 10–20 hr to an equilibrium mixture containing roughly equal amounts of I and II along with some polymer. The absorption curves of I and II overlap extensively, but the mercury resonance emission lies near a maximum (at 258 nm) in the absorption of I; isomerization occurs also at wavelengths above 300 nm, but the equilibrium concentration of II is lower. The course of the irradiation is best followed by taking the ir spectrum of the solution at intervals and working up the solution when the carbonyl band of II reaches a maximum. The tropone is less volatile and less soluble than I and may conveniently be isolated in 30–40% yield from the equilibrium mixture by high-vacuum fractional sublimation followed by recrystallization from hexane. The product is obtained as lemon-yellow blades or thin plates, mp 82.2–83.4°.

The structure of II was initially inferred from its spectroscopic properties: $\nu_{\max}$ 1695 (m), 1545 (m) cm^{-1} (C_2Cl_4); 1255 (m), 1172 (w), 1134 (s), 1029 (m), 887 (w), 718 (s), 708 (sh), 650 (w) cm^{-1} (CS_2); $\lambda\lambda_{\max}$ (cyclohexane; mμ (ϵ)) 269 (14,300) and 362 (2500) with shoulders or inflections at 262 (inflection, 13,400), 284 (inflection, 11,000), 347 (inflection, 2000), and 377 (sh, 2200). In particular, the observed low-frequency carbonyl absorption at 1695 cm^{-1} (compared to the starting material at 1751 cm^{-1}) and two-maxima electronic spectrum are characteristic of tropones.[5] The structure so assigned was then confirmed by a complete single-crystal X-ray structure analysis carried out by Dodge, *et al.*[6] The most striking feature of the structure of II is its nonplanarity, in contrast to tropone[7] and its simple derivatives[8] which are planar or very nearly so. The ring is boat shaped, the bow (C_7–C_1–C_2) being elevated 29° and the stern 24° relative to a line connecting points midway between C-2 and C-7, and C-3 and C-6. The distortion from planarity most likely occurs to relieve the crowding which the oxygen and six chlorines would generate around the periphery of a planar heptagon. Further evidence that II is a sterically strained molecule is seen in its high reactivity.

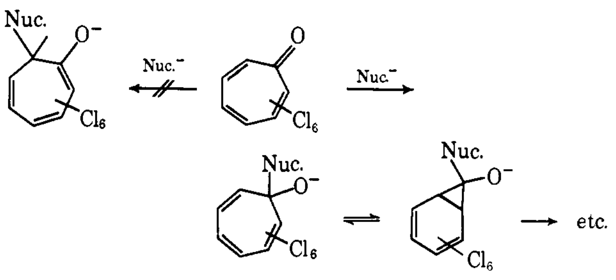
Perchlorotropone undergoes the well-known tropone-to-benzoate rearrangement with unprecedented facility. Merely on dissolution in methanol at room temperature it is converted immediately and quantitatively to methyl pentachlorobenzoate. This lability is approached only by certain polynitrotropolones,[9] whereas



2-chlorotropone and 2,3,5,7-tetrachlorotropone must be heated with alkali to effect rearrangement.[10] The reactivity of II as an acylating agent may be further contrasted with its aromatic isomer pentachlorobenzoyl chloride, which reacts with methanol only slowly at reflux.[11]

Exploratory experiments with other nucleophiles, such as amines and thiols,[12] suggest that their reactions with II proceed exclusively with rearrangement and that competing replacement of an α chlorine without rearrangement[10,13] is strongly disfavored.

The observed selectivity may be rationalized on the basis of the nonplanarity of II, which reduces the internal angle at C-1 and facilitates addition to the carbonyl while at the same time inhibiting the double-bond shift associated with attack at C-2.



Perchlorotropone is thermally unstable, rearranging above 200° to a mixture of pentachlorobenzoyl chloride and hexachlorobenzene. Similar transformations of 2-chloro- and 2-bromotropones, though at higher temperatures, have been reported by Mukai, *et al.*[14] As compound I is thermally more stable than II, its conversion to II cannot be effected thermally.

The further reactions of perchlorotropone and the synthesis and properties of related polyhalotropones are under study in this laboratory. Subsequent to our synthesis, Kusuda and West discovered an elegant nonphotochemical route to II[15] which appears more convenient for its preparation in quantity, but owing to the severity of the reaction conditions may be inapplicable to the preparation of related compounds.

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