

spatial arrangement of the atoms and bonds that have to be rearranged in the key step of the fragmentation of II and IX, respectively. In the ajmaline series, the hydrogen at C-2 is sufficiently close to C-17 to lead to its migration with simultaneous aromatization of the dihydroindole to an indole system ($I \rightarrow Ib$, see above). In the 2-epi series, this hydrogen is, however, *trans* and far away from C-17, thus blocking that process. Aromatization is only possible by rearranging the C-2, C-3 bond to a C-3, C-17 as implied in the process $IX \rightarrow IXa$. It should be noted, however, that the bonds broken and the bonds rearranged are spatially the same (around C-2) in both processes which thus are very closely related although leading to entirely different fragments. These two groups of epimers thus represent a rather unique example in which the stereochemistry at one center so completely changes the fragmentation of a carbon skeleton. The effect is here so drastic because of the very rigid arrangement of the polycyclic ring system.

Experimental

Mass Spectra.—The conventional spectra were taken with a single-focusing mass spectrometer (CEC 21-103C) equipped with a heated inlet system operated at 175°; ionizing current 10 or 50 μ a., ionizing voltage 70 v.

The high-resolution spectra were obtained with a double-focusing mass spectrometer (CEC 21-110), using a photographic plate for recording. The samples were introduced directly into the ion source and perfluorokerosene was used as the mass standard; ionizing current 100 μ a., ionizing voltage 70 v. All the line positions were measured and then converted to accurate masses and corresponding elemental compositions with the aid of a computer.¹³ A selected group of these values is shown in Fig. 1-6.

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Three-Membered Rings. I. Conjugative Properties and Electronic Spectra of Arylcyclopropanes, Oxiranes, and Thiiranes¹

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The ultraviolet spectra of a series of *p*-substituted phenylcyclopropanes, styrene oxides, and styrene sulfides have been examined with regard to chromophoric enhancement as measured by the effect of the *p*-substitution on the "primary" ($^1A_{1g} \rightarrow ^1B_{1u}$) electronically forbidden transition in benzene. It is shown that, relative to benzene, oxirane and thiirane are electron withdrawing, whereas cyclopropane is electron donating. Thus *p*-methoxy substitution was observed to shift conjugatively and enhance the ultraviolet "primary" absorption bands of phenyloxirane and thiirane but had little effect on phenylcyclopropane; *p*-nitro substitution showed the reverse effect. These observations are in agreement with second-order resonance effects and clarify some of the conflicting observations and conclusions concerning the unsaturation properties of the three-membered ring systems.

The electronic spectra of molecules containing three-membered rings adjacent to unsaturated groups have provided an effective method of demonstrating the conjugative properties arising from the unsaturation character of these rings.² These effects in cyclopropane have been documented by a variety of physical³ and chemical⁴ techniques and have been described theoretically by Coulson⁵ and Matsen⁶ and their co-workers.

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(3) (a) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947); (b) V. T. Aleksanian, Kh. E. Sterin, M. Yu. Lukiva, I. L. Saforova, and B. A. Kayon'skii, *Optika i Spektroskopija*, **7**, 114 (1959); (c) I. M. Klotz, *J. Am. Chem. Soc.*, **66**, 88 (1944).

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Spectroscopic evidence of the electronic interaction of oxirane with adjacent unsaturated groups has been contributed by Rogers^{3a} and more recently by Cromwell⁷ and co-workers who demonstrated that both oxirane and azirane are capable of transmitting as well as extending electronic effects in variously substituted chalcone oxides and imines.⁷ However, a contradictory effect was noted by Cromwell in the case of *p*-methoxy substitution on the β -phenyl ring and was not satisfactorily explained. Also the failure of the cyclopropyl ring to transmit conjugation in some systems as reported by Eastman⁹ and Mariella¹⁰ was unexplained. These apparent anomalies may on the one hand reflect the difficulty of interpretation of the perturbations of the

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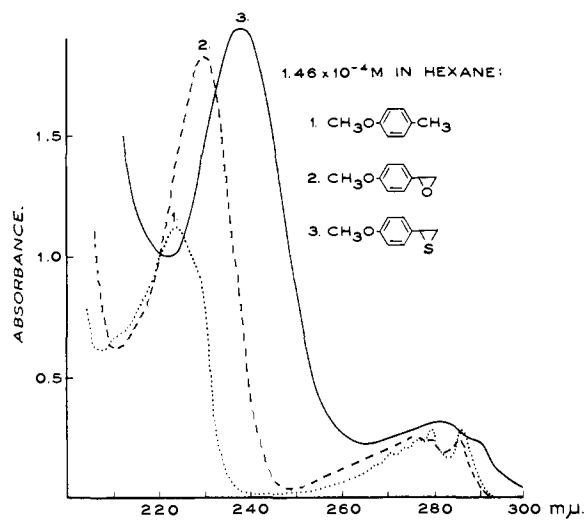


Figure 1.

complex chromophore systems involved or may reflect real electronic differences in the cyclopropyl and oxirane (azirane) rings in these systems.

The spectroscopic evidence from a series of *p*-substituted aryl-oxiranes, cyclopropanes, and thiiranes presented here shows that the three-membered rings are electronically different. Thiirane and oxirane behave as electron acceptors whereas cyclopropane behaves as an electron donor relative to benzene.

Experimental

Materials.—*p*-Methoxystyrene oxide was prepared from *p*-methoxystyrene *via* the dibromide according to the method of Guss.¹¹ The sample was purified by repeated crystallization from petroleum ether (b.p. 30–60°) to give colorless needles, m.p. 16.5–17° (lit.¹¹ 20 ± 2°), n_D^{20} 1.5393; infrared λ_{max}^{KB} 11.4 μ . This sample showed no change in infrared or ultraviolet spectra after storage at 4° for 48 hr. Phenylcyclopropane,¹² *p*-nitrophenylcyclopropane,¹² and *p*-nitrostyrene oxide, m.p. 84–85° (lit.¹³ 84.2–85.4°), have been described previously. *p*-Methylanisole, *p*-nitrotoluene, and *p*-methoxyphenylcyclopropane were either obtained from commercial sources or the spectral data were obtained from the literature. The three styrene sulfides are described elsewhere.¹⁴

Ultraviolet Spectra.—The wave length maxima and molar absorptivities and certain half-widths of the displaced and enhanced "primary" absorption band of benzene in variously sub-

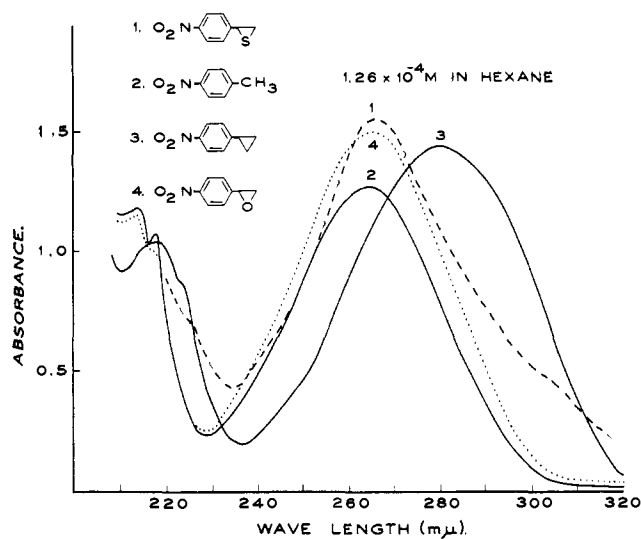


Figure 2.

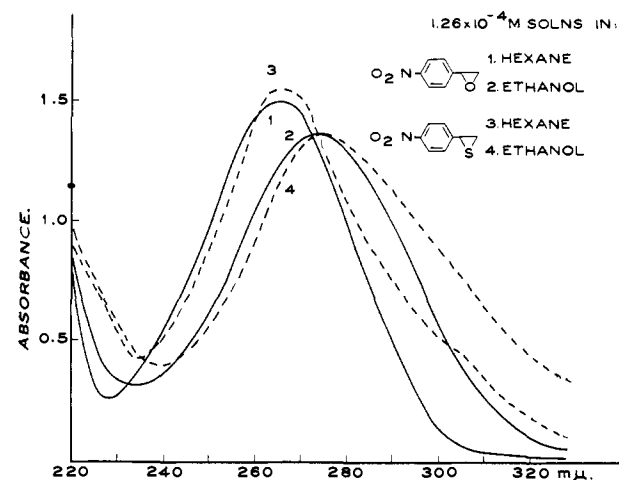


Fig. 3.—Solvent effect on the ultraviolet spectra.

stituted aryl oxiranes, thiiranes and cyclopropanes, and the parent alkylbenzenes, are presented in Table I. All spectra (except as noted) were recorded on either a Model 11 or Model 14 Cary spectrophotometer. *p*-Methoxystyrene oxide and sulfide were rather unstable in polar solvents. The absence of absorbance changes at the maxima for 0.5 hr. after the spectrum was recorded was taken as evidence of stability to assure validity of the data.

In Fig. 1 and 2 are presented the definitive characteristics of the spectra which correlate the bands with the displaced "primary" band of benzene. In Fig. 3 are presented the spectra of the solvent-sensitive *p*-nitrostyrene sulfide and oxide in ethanol and hexane.

Discussion

The benzene chromophore adjacent to the three-membered rings is particularly useful in establishing the extent of electron delocalization. The electronically forbidden "primary" band at 210 $m\mu$ ($^1A_{1g} \rightarrow ^1B_{1u}$)¹⁵ is uniquely subject to enhancement such that conjugative effects are readily identified and are distinguishable from inductive effects.¹⁶ The spectroscopic effects have been summarized by Goodman and Shull¹⁷ and

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TABLE I

SPECTROSCOPIC DATA ON STYRENE OXIDES AND SULFIDES AND ARYL-CYCLOPROPANES AND ALKANES^a (*p*-XC₆H₄Y)

Y	—X = H—		—X = OCH ₃ —			—X = NO ₂ —		
	λ_{max} , $m\mu$	$\epsilon \times 10^{-3}$	λ_{max} , $m\mu$	$\epsilon \times 10^{-3}$	$\nu_{1/2}^b$	λ_{max} , $m\mu$	$\epsilon \times 10^{-3}$	$\nu_{1/2}^b$
Oxiranyl	212	4.7 ^c	230	12.4	3.40	265	11.9	5.72
Thiiranyl	226	8.5	238	13.3	4.25	266	12.0	5.83
Cyclopropyl	220	8.4	225 ^d	7.5	..	280	11.0	5.91
Methyl	206	3.2	223 ^e	7.7	3.02	264 ^f	10.4	5.77

^a These data are for the displaced primary absorption band of benzene; determined in hexane or isoctane on a Cary Model 11 spectrophotometer. ^b In $cm^{-1} \times 10^{-3}$. ^c Ref. 3a. ^d R. Ya. Levina, Yu. S. Shabarov, and V. K. Potapov, *J. Gen. Chem. U.S.S.R.*, **29**, 3196 (1959). ^e J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **37**, 1294, 1305 (1959). ^f W. Brown and H. Regan, *J. Am. Chem. Soc.*, **69**, 1032 (1947).

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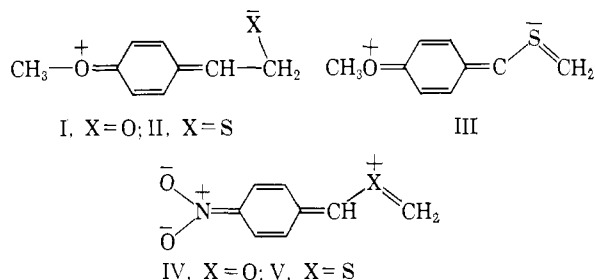
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found to be in general agreement with a molecular orbital perturbation treatment, as was earlier described by Matsen⁶ for the less sensitive 250-m μ forbidden transition (¹A_{1g}-¹B_{2u}). The theoretical description by Nagakura¹⁸ of the spectra of substituted benzenes with electron-attracting or -donating groups indicated that interpretation of the spectra in terms of the contributions of resonance structures with separation of charge contributing more to the excited states is in good qualitative agreement with his more rigorous quantum mechanical "charge-transfer" treatment. Rogers^{3a} and Cromwell⁷ have described the conjugative and electronic effects of the three-membered rings in terms of enhanced contributions of second-order resonance structures to the hybrid in the excited states.

As seen from the data of Table I and Fig. 1 and 2, oxirane, thiirane, and cyclopropane are capable of extending the conjugation of a phenyl or *p*-substituted phenyl group in the sense that the perturbations of the benzene chromophore agree with those of well-verified electron-delocalizing substituents if the oxirane and thiirane are electron accepting and the cyclopropane is electron donating. Thus the characteristic 223-m μ band of *p*-methylanisole (the displaced and enhanced primary 210-m μ band) shows a conjugative shift to longer wave length, $\Delta\lambda_{\max}$ 7 m μ , and is increased in intensity greater than 50% when the methyl group is replaced by oxirane and even greater bathochromic and hyperchromic effects occur with a thiirane substituent. In contrast, no corresponding enhancement of *p*-nitrostyrene oxide or sulfide is observed relative to *p*-nitrotoluene. In the cyclopropyl compounds, on the other hand, the spectrum of *p*-methoxyphenylcyclopropane is not conjugatively altered from that of *p*-methylanisole, whereas *p*-nitrophenylcyclopropane shows a large shift and enhancement of oscillator strength in the characteristic 264-m μ transition of *p*-nitrotoluene to a maximum at 280 m μ . (The 264-m μ band of *p*-nitrotoluene corresponds with the shifted and enhanced 210-m μ band of benzene.^{16c}) Oxirane and thiirane extend the conjugation of the electron-donating anisole system but do not extend a nitrobenzene system. This can be explained if charge-separation structures in oxirane and thiirane with a negative charge on the oxygen (I) and sulfur (II, III) make significant contributions to the excited states; structures with a positive charge on these three-membered ring heteroatoms are unimportant. The greater conjugative effect of thiirane (in

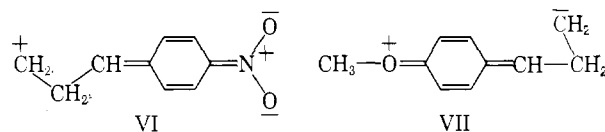


(18) S. Nagakura, *J. Chem. Phys.*, **23**, 1441 (1955).

spite of its lesser electronegativity) is consistent with the additional decet structure, III.

The absence of appreciable conjugative shifts with a *p*-nitro group indicates that structures such as IV and V do not make important contributions in these oxirane or thiirane systems. This is in contrast with the behavior of conjugated ethers or thioethers where the heteroatom assumes a positive charge but is similar to the behavior of a carbonyl system and is a way of expressing the nature of the unsaturation in the "ring" otherwise ascribed to ring strain¹⁹ or bent bonds associated with hybrid orbitals with enriched *p*-character.

The cyclopropyl group in contrast acts primarily as an electron donor as indicated by its significant interaction with the nitrobenzene chromophore and its failure to extend the conjugation of anisole as seen in Table I and Fig. 1 and 2. Thus it may be taken that structures such as VI make significant contributions to the arylcyclopropane system, and contrariwise structures giving the cyclopropyl group a negative charge such as VII are unimportant. Thus the resonance de-



scription is valid if the electron-donor and -withdrawal capacities are properly assessed.

The opposing electronic properties of the oxirane or thiirane and cyclopropane rings also explain the seemingly anomalous observations of enhancement reported by some authors^{7,9,10} and the "damping out" of conjugation reported by others.⁹

The spectrum shift found in styrene sulfide with the λ_{\max} at 226 m μ is also consistent as is the more diffuse character of the spectrum which fits qualitatively the superposition of the spectrum of ethylene sulfide²⁰ or benzyl alkyl sulfide²¹ upon the expected spectrum of styrene sulfide.

The long wave length asymmetry of the *p*-nitrostyrene sulfide as seen in Fig. 2 is the only apparently inconsistent note in this description of the pattern of effects. The differential solvent effect on this band as shown in Fig. 3 indicates that the long wave length shoulder arises from a transition distinct from that correlated with the primary benzene band. This is best indicated by comparison with *p*-nitrostyrene oxide in Fig. 3 which retains symmetry in both solvents. It is probable that the weak long wave length absorption arises from the independent thiirane ring excitation.^{20,21}

Acknowledgment.—The authors wish to thank Mr. Michael Hrenoff for determining some of the ultraviolet spectra.

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