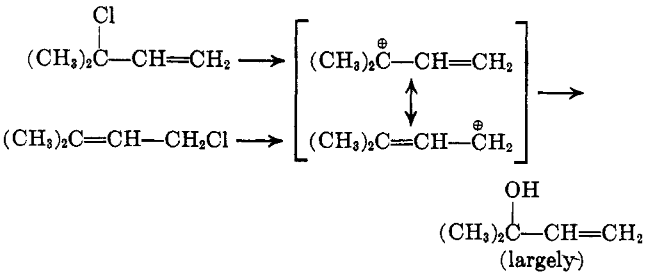
resonance effect. If this is the case then the electron-donating power of the methyl groups relative to that of the vinyl group will be greater in the transition state than in the carbonium ion. By the principle of microscopic reversibility this will also be true in the reverse reaction, the combination of the carbonium ion with a nucleophile. It would therefore be expected that the methyl groups will stabilize the transition state involving reaction of the carbonium ion at the tertiary carbon atom, where they are attached directly to the positively charged carbon atom, more than the transition state involving reaction at the primary carbon atom, where the methyl groups can supply electrons to the reaction center only by a sterically inhibited resonance interaction through a carbon–carbon double bond. This argument thus provides an explanation for the fact that, under conditions where the SN2 mechanism is discouraged, both 1,1-dimethylallyl and 3,3-dimethylallyl halides hydrolyze to give considerably more 1,1-dimethylallyl alcohol than 3,3-dimethylallyl alcohol,[68] in spite of the fact that the latter alcohol is almost undoubtedly the more stable of the two.[69] An electrostatic argument could be given to explain the reaction of the mesomeric carbonium ion at either the primary or tertiary carbon atom. The electron-donating methyl groups will tend to take positive charge upon themselves in the carbonium ion. This positive charge at one end of the allylic system will tend to attract the $\pi$ electrons so as to make the adjacent (tertiary) carbon atom less positive



than the more distant primary carbon atom. This tendency to reduce like charges on adjacent atoms could thus give the primary carbon atom the largest positive charge and make it the principal reaction site. However, it can also be pointed out that the positive charges on the methyl groups will place the tertiary carbon atom nearer the *center* of positive charge. All in all it seems difficult to make an *a priori* prediction of the electrostatic effect of the larger charge on the primary carbon atom relative to the somewhat smaller charge on the tertiary carbon atom, augmented by additional charges on two of the groups attached to it.

**Conclusion.**—None of the explanations for orientation in reactions of mesomeric ions and radicals seems capable of explaining all the existing data. Unfortunately, very few experiments designed to assess the relative importance of the various possible explanations seem to have been carried out. Nevertheless, the author believes that the principle of least motion, which follows automatically from an accepted method of applying transition-state theory to the effect of structure on reactivity, may often be a factor of major importance in such reactions.

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[69] P. B. D. de la Mare, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 37.

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# Conjugation Effects on the Low-Intensity Electronic Transition of Small-Ring Carbonyl Compounds[1,2]

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Ultraviolet absorption studies of the low-intensity $n-\pi^*$ transition of *cis* and *trans* pairs of arylaroylethylenimines have been investigated. The isomer which has its carbonyl absorption maximum at longer wavelength and with a greater intensity in the ultraviolet range is the one to which the *trans* configuration has been assigned. The difference in light absorptions for the two geometrical isomers in this series are reasonably large. The results of spectral studies with the related ethylene oxide and cyclopropyl ketones were compared. Evidence is presented which demonstrates that the importance of three-ring carbonyl hyperconjugation in the $n-\pi^*$ transition is a function of the heteroatom present in the small-membered ring. The conjugative effects of the three-membered ring is discussed in terms of enhanced contributions of second-order resonance structures to the hybrid in the excited state.

The electronic spectra of molecules containing three-membered rings adjacent to a carbonyl group have provided an effective method of demonstrating the conjugative properties arising from the unsaturation character of these rings.[5,6] The nature of the electrical interaction between the small ring and the carbonyl group has been described as a type of hyperconjugation which results from orbital overlap of the bent bonds of the small ring with the $\pi$ orbitals of the attached carbonyl group.[7] The three-membered ring is known to possess a somewhat delocalized electronic system.[8] These delocalized electrons lie in the plane of the ring and have been attributed to the overlap

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[1] Supported in part by a research grant (NSF-GP-3972) of the National Science Foundation.

[2] Photochemical Transformations of Small-Ring Carbonyl Compounds, part IX. For part VIII. see A. Padwa and R. Hartman, *J. Am. Chem. Soc.*, **88**, 1518 (1966).

[3] National Institutes of Health Predoctoral Fellow, 1964–.

[4] National Science Foundation Undergraduate Research Participant, 1964–.

[5] R. A. Raphael, "Chemistry of Carbon Compounds," Vol. IIA, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1953, pp 25–28.

[6] L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice Hall, Inc., Engelwood Cliffs, N. J., 1963, pp 320–326.

[7] N. H. Cromwell, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **19**, 214 (1958).

[8] For a summary of leading references see A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

of bent-bonding orbitals.[9] When atoms with $\pi$-bonding electrons such as a carbonyl group are attached to the carbon atom of these bent bonds, some over lapping and interaction between the bent bonds and the $\pi$ orbital occurs. Evidence for such delocalization has been contributed by Rogers[10] and more recently by Cromwell and co-workers[11] who demonstrated that both oxirane and azirane are capable of transmitting as well as extending electronic effects in variously substituted chalcone oxides and imines. Additional evidence for this delocalization has also been put forward from theoretical,[12] magnetic susceptibility,[13] kinetic,[14] infrared,[15] and nmr studies.[16,17]

Following Walsh's prediction of special geometric requirements for such interactions,[12] Cromwell reported that for maximum conjugative interaction, the plane of the three-membered ring should lie parallel to the $\pi$ orbital of the carbonyl group.[18a] Experimental evidence was obtained in the case of the *cis* and *trans* forms of arylaroylethylenimines,[18b] ethylene oxides,[18c] and cyclopropyl carbonyl compounds.[19] It has been shown that in these series the *cis* isomers absorb at a somewhat lower wavelength and with less intensity than the *trans* compounds. The results have been rationalized in terms of a steric inhibition of hyperconjugation in the *cis* isomers.[18a] The assignment of configuration on the basis of ultraviolet absorption spectra is in complete agreement with the configurational assignments made by other methods.[20]

While the $\pi$–$\pi^*$ transition of the carbonyl group in small-ring carbonyl compounds has been thoroughly studied and is reasonably well understood, the low-intensity n–$\pi^*$ electronic transition of these compounds has received little attention. In the present study the effects of molecular structure and solvent on the low-intensity n–$\pi^*$ transition of small-ring carbonyl compounds have been examined. In particular, the effect of substitution in the acyl and aryl portion of the molecule, the effect of solvent polarity, and the effect of the heteroatom present in the small ring on the energy of the transition of these systems has been investigated. The spectroscopic evidence from a series of arylaroylethylenimines, $\alpha,\beta$-epoxy ketones, and benzoylcyclopropanes presented here shows that the three-membered rings are electronically different.

## Results and Discussion

It is well recognized that the weak absorption band of ketones and aldehydes occurring in the 280–360-m$\mu$ region arises from excitation of a nonbonding 2p electron to the antibonding $\pi$ orbital. This has been designated as the n–$\pi^*$ state by Kasha.[21] After electron promotion the excited n–$\pi^*$ state has two electrons in the bonding $\pi$ orbital, one in the antibonding $\pi^*$ orbital, and the remaining 2p electron still localized on oxygen. Since it is the two bonding electrons which make the molecule planar, the n–$\pi^*$ excited state still retains planarity and has the remaining 2p electron localized in an orbital orthogonal to the plane of the carbonyl double bond. The criteria which have been used in the identification of n–$\pi^*$ transitions are (a) intensity (since it is symmetry forbidden), (b) "hypsochromic shift" of the maximum with increasing polarity of the medium, (c) "hypsochromic shift" of the maximum caused by electron-supplying substituents attached directly to the $\pi$ system, and (d) obliteration of vibrational fine structure upon changing from nonpolar to polar solvents.[22–24] The band near 325 m$\mu$ in the spectra of the small-ring carbonyl compounds, as is shown below, satisfies all of these requirements and thus is definitely an n–$\pi^*$ transition.

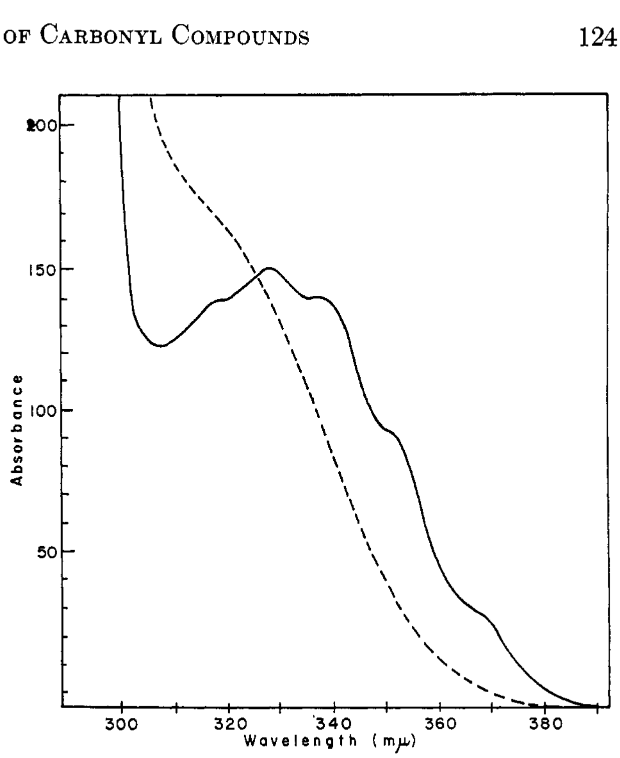

Figure 1.—The ultraviolet absorption spectrum of *cis*-1-cyclohexyl-2-phenyl-3-benzoylaziridine in (a) isooctane, ———; (b) 95% ethanol, - - - -.

The ultraviolet absorption spectrum of *cis*-1-cyclohexyl-2-phenyl-3-benzoylaziridine, as an example of this class of compounds, exhibits two distinct transitions. The higher energy $\pi$–$\pi^*$ transition possesses a broad structureless absorption band which maximizes in isooctane at 241 m$\mu$ ($\epsilon_{\max}$ 9870). The lower energy n–$\pi^*$ transition possesses a highly structured absorption band which exhibits a maximum in cyclohexane at 327 m$\mu$ ($\epsilon_{\max}$ 150). All of the other small-ring carbonyl compounds measured also showed considerable fine structure of the n–$\pi^*$ absorption band in cyclo-

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[9] C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

[10] M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947).

[11] See N. H. Cromwell, F. H. Schumacher, and J. L. Adelfang, *ibid.*, **83**, 974 (1961), for a bibliography of the extensive work in this field.

[12] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[13] J. R. Lacher, J. W. Pollock, and J. D. Park, *J. Chem. Phys.*, **20**, 1047 (1952).

[14] R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963).

[15] R. H. Eastman, *J. Am. Chem. Soc.*, **76**, 4115, 4118 (1954); **77**, 6643 (1955).

[16] D. H. Williams and N. S. Bhacca, *ibid.*, **85**, 2861 (1963).

[17] G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965).

[18] (a) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952); (b) N. H. Cromwell, *et al.*, *J. Am. Chem. Soc.*, **73**, 1044 (1951); (c) *ibid.*, **76**, 5752 (1954).

[19] (a) H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955); (b) N. H. Cromwell and R. Mohrbacher, *ibid.*, **79**, 401 (1957).

[20] A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, *ibid.*, **87**, 1050 (1965).

[21] M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

[22] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 179–187.

[23] A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold (Publishers) Ltd., London, 1954, Chapter 5.

[24] W. D. Closson and P. Haug, *J. Am. Chem. Soc.*, **86**, 2384 (1964), and references listed therein.

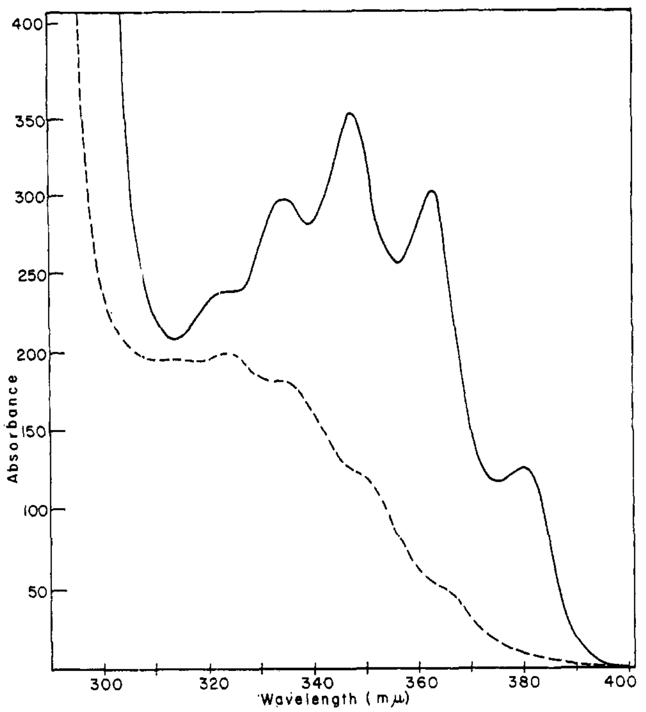
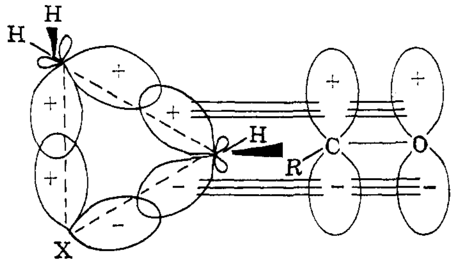


Figure 2.—The ultraviolet absorption spectrum of 1-cyclohexyl-2-phenyl-3-*p*-toluylaziridine in cyclohexane: (a) *trans*, ———; (b) *cis*, - - - -.

hexane and isooctane. A typical example of this band in a nonpolar medium is shown in Figure 1. On changing to more polar solvents the fine structure vanished and the low-intensity absorption band moved to shorter wavelength. In the spectra of the other benzoylaziridines examined, the fine structure for the *trans* isomer is always more pronounced than for the *cis* isomer (see Figure 2). All of the ethylene oxides and cyclopropylcarbonyl compounds, however, showed a splitting pattern with only occasional shoulders and minor asymmetries.

The molar absorptivities ($\epsilon$) of the *cis* benzoylaziridines range from 150–200, whereas the *trans* isomer's absorptivities are markedly enhanced, most of them falling between 300–400. In the case of a typical *trans*-benzoylaziridine [1-cyclohexyl-2-phenyl-3-benzoylaziridine in cyclohexane, $\lambda_{\max}$ 349 m$\mu$ ($\epsilon_{\max}$ 297)] the oscillator strength ($f$) of the transition was estimated as 0.0048. The expression $f = 4.315 \times 10^{-9}\int_{15{,}000\,\mathrm{cm}^{-1}}^{\nu_{\max}(\mathrm{cm}^{-1})} \epsilon_{\max}\, d\nu$ was used in order to decrease contribution of end absorption to the calculated value. This is about eight times that of typical benzoyl ketones, but still well within the range of "symmetry-forbidden" n–$\pi^*$ transitions.

The long wavelength carbonyl absorption of arylaroylethylenimines displays an enhanced intensity which reflects a strengthened n–$\pi^*$ transition. The intense absorption in the ultraviolet spectrum suggests the prevalence of conformations in which the orientation of the $\pi$ electrons of the three-membered ring relative to electrons of the carbonyl group is geometrically favorable for enhancement. The carbonyl bands in the absorption spectrum of $\beta,\gamma$-unsaturated ketones have also been noted to feature extraordinarily intense absorption whose amplitudes in the n–$\pi^*$ region are orders of magnitude greater than those of other carbonyl compounds.[25,26] It thus seems that the virtually identically strengthened n–$\pi^*$ absorption of both $\beta,\gamma$-unsaturated ketones and arylaroylethylenimines are a consequence of a small amount of admixed $\pi$ character in the n–$\pi^*$ transition. The over-all effect of a double bond being situated in the vicinity of the carbonyl group will be the creation of an extended $\pi$ system that utilized the $\pi$ orbitals of both components and is diene like in conception. As Moscowitz, *et al.*, point out,[26] the situation is severely altered when the bond containing the p orbitals is twisted with respect to the carbonyl group. There will, in general, still be an extended $\pi$ system, but that $\pi$ system can now overlap with the electrons in the nonbonding orbital. The effect is to mix some $\pi$ character in with the nonbonding orbital and this small amount of admixed $\pi$ character causes the n–$\pi^*$ transition to take on certain features of an allowed $\pi$–$\pi^*$ transition. Consequently, the electric dipole transition moment of the n–$\pi^*$ transition, which is symmetry forbidden in simple ketones, is no longer forbidden in these systems. In the case of arylaroylethylenimines, for maximum interaction, the plane of the three-membered ring should lie parallel to the $\pi$ orbital of the carbonyl group.[27] In this geometrical position, the delocalized orbitals of the three-membered ring are in a sense analogous to the positioning of the double bond in $\beta,\gamma$-unsaturated ketones and overlap of the three-membered ring with the nonbonding electrons occurs. Although the approach to coplanarity of the nonbonding orbital of the carbonyl group with the three-membered ring is somewhat difficult to conceive of in either case, this should be less sterically restricted in the case of the *trans* structure. This *trans* arrangement provides for a more extensive polycentric molecular orbital than is possible with the more sterically hindered *cis* isomer and accounts for the larger molar absorptivity of the *trans* structure.[18,27]



X = C,O,N

Evidence has been obtained demonstrating that in a given pair of $\beta$-substituted ethylenimine ketone stereoisomers, the isomer possessing the *trans* structure exhibits an absorption maximum in the $\pi$–$\pi^*$ transition at longer wavelengths than does the *cis* isomer.[18] This comparison has now been extended in this series to the n–$\pi^*$ transition. Although the difference in light absorptions is small for the $\pi$–$\pi^*$ transition (3–5 m$\mu$), this difference is quite marked for the n–$\pi^*$ electronic transition. Comparison of the aroyl n–$\pi^*$ maximum of the *trans* isomer with the aroyl maximum of the analogous *cis* structure (Table I) shows that the difference in position is in the order of 22–27 m$\mu$. This large difference in position of the n–$\pi^*$ absorption

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[25] H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

[26] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

[27] N. H. Cromwell and G. Hudson, *ibid.*, **75**, 872 (1953).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRAL MAXIMA FOR SUBSTITUTED 2-BENZOYLAZIRIDINES AND RELATED COMPOUNDS IN CYCLOHEXANE

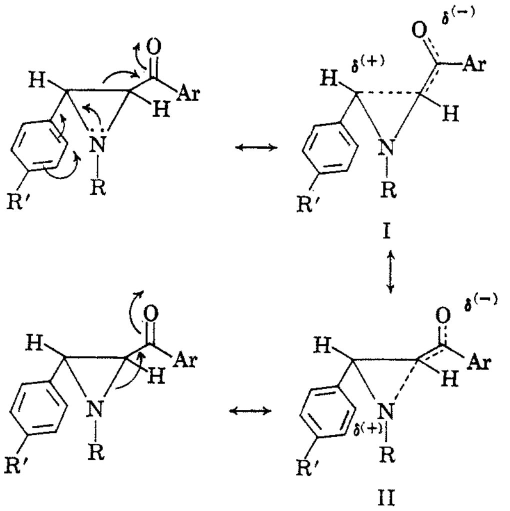
| Compound | $\lambda_{max}$, m$\mu$ | $\epsilon \times 10^{-3}$ |
|---|---|---|
| *cis*-1-Cyclohexyl-2-phenyl-3-benzoylaziridine | 327 | 0.150 |
| *trans*-1-Cyclohexyl-2-phenyl-3-benzoylaziridine | 349 | 0.297 |
| *cis*-1-Cyclohexyl-2-phenyl-3-*p*-toluylaziridine | 323 | 0.186 |
| *trans*-1-Cyclohexyl-2-phenyl-3-*p*-toluylaziridine | 347 | 0.320 |
| *cis*-1-Cyclohexyl-2,3-dibenzoylaziridine | 324 | 0.206 |
| *trans*-1-Cyclohexyl-2,3-dibenzoylaziridine | 351 | 0.524 |
| *cis*-1-Cyclohexyl-2-phenyl-3-*p*-phenylbenzoylaziridine | 331 | 0.186 |
| *trans*-1-Cyclohexyl-2-phenyl-3-*p*-phenylbenzoylaziridine | 351 | 0.734 |
| *cis*-1-Benzyl-2-phenyl-3-benzoylaziridine | 324 | 0.147 |
| *trans*-1-Benzyl-2-phenyl-3-benzoylaziridine | 347 | 0.281 |
| *cis*-1-Benzyl-2-phenyl-3-*p*-toluylaziridine | 323 | 0.162 |
| *trans*-1-Benzyl-2-phenyl-3-*p*-toluylaziridine | 344 | 0.263 |
| *cis*-1-Benzyl-2-*p*-tolyl-3-benzoylaziridine | 325 | 0.147 |
| *trans*-1-Benzyl-2-*p*-tolyl-3-benzoylaziridine | 346 | 0.274 |
| *cis*-1-Benzyl-2,3-dibenzoylaziridine | 324 | 0.257 |
| *trans*-1-Benzyl-2,3-dibenzoylaziridine | 348 | 0.410 |
| *cis*-1-Methyl-2-phenyl-3-benzoylaziridine | 326 | 0.142 |
| *trans*-1-Methyl-2-phenyl-3-benzoylaziridine | 348 | 0.287 |
| *cis*-1-Methyl-2-phenyl-3-*p*-phenylbenzoylaziridine[a] | ... | ... |
| *trans*-1-Methyl-2-phenyl-3-*p*-phenylbenzoylaziridine | 350 | 0.489 |
| *trans*-2-Phenyl-3-benzoylaziridine | 311 | 0.338 |
| *cis*-Chalcone oxide | 322 | 0.090 |
| *trans*-Chalcone oxide | 326 | 0.197 |
| Acetophenone | 316 | 0.042 |
| Phenyl cyclopropyl ketone | 310 | 0.050 |
| *cis*-1-Phenyl-2-benzoylcyclopropane | 319 | 0.167 |
| *trans*-1-Phenyl-2-benzoylcyclopropane | 315 | 0.226 |
| *trans*-1-Phenyl-2-*p*-toluylcyclopropane | 313 | 0.261 |
| 1,1-Diphenyl-2-benzoylcyclopropane | 322 | 0.227 |

[a] The n–$\pi^*$ absorption maximum for this compound is buried beneath the $\pi$–$\pi^*$ absorption band.

maximum of the small-ring stereoisomers provides still another independent confirmation of the assignment of stereochemistry.

We conclude that the magnitude of the molar absorptivity and the position of the n–$\pi^*$ absorption maximum is critically dependent on the relative disposition of the carbonyl group and the three-membered ring, and that there is an electrical interaction, especially in the excited state, of the $\beta$ substituent with the carbonyl group through the ring electrons. It is difficult, however, to describe clearly by structural formulas the nature of this electronic interaction. The modified Lewis structures shown below are used in a manner similar to that suggested by Cromwell[18] to describe pictorially the resonance representation of such electron interactions.

Substitution of a methyl group into the *para* position of the benzene ring causes a small bathochromic shift in the wavelength of maximum absorption compared to the unsubstituted benzene ring. This can be explained if charge separation structures such as I with a negative charge on oxygen and a positive charge on carbon contribute to the excited state. Similarly, substitution of a cyclohexyl or phenyl group into the 1-position also causes a bathochromic shift in the wavelength of maximum absorption. This effect may be attributed to the importance of charge separation structures such as II to the excited state causing a smaller energy difference between the ground state and excited electronic state of the N-substituted aziridine as compared to the analogous energy difference in the unsubstituted case. Alternatively, it may be argued that the anomalous ultraviolet spectrum of *trans*-2-phenyl-3-benzoylaziridine (see Table I) is a result of intramolecular hydrogen bonding of the lone pair of electrons on the carbonyl oxygen with the hydrogen attached to the nitrogen atom of the three-membered ring. The formation of this hydrogen bond lowers the energy of the n orbital by an amount approximately equal to the energy of the hydrogen bond and hence this hydrogen bond must be broken in the process of promotion, thereby accounting for the anomalous blue shift in this case. At any rate, the n–$\pi^*$ absorption maximum is probably associated with the electronic vibrations and resonance in an ionized excited state of the entire small-ring system and has increasing difficulty in approaching coplanarity with the *cis* isomer.



It is interesting to contrast the above results and conclusions regarding the n–$\pi^*$ absorption spectrum of the arylaroylethylenimines with those of $\alpha,\beta$-epoxy ketones and cyclopropyl ketones. Our results show that these three-ring compounds have a much smaller effect on the carbonyl-associated chromophore in the excited state (compare values of *trans*-chalcone oxide in Table I with the related *trans*-arylaroylethylenimines). The spectroscopic evidence presented here shows that the three-membered rings are electronically different. As seen from the data of Table I, the arylaziridine ring causes a large bathochromic shift of the n–$\pi^*$ maximum compared to acetophenone. Comparison of the aroyl maximum of the chalcone oxide compounds demonstrate that the oxirane ring has a much smaller effect upon the position of the aroyl band maximum for the *trans* isomer. In the cyclopropyl compounds, on the other hand, the spectrum is not significantly different from that of acetophenone. These results can be explained if charge-separation structures such as I and II make significant contributions to the excited states for the arylaroylethylenimines and only minor contributions for the $\alpha,\beta$-epoxy ketone system. In the cyclopropyl system, charge-separation structures such as I and II are presumably unimportant. These observations are consistent with a recent report by Strait who demonstrated that three-membered rings may have different electronic properties as auxochromes.[28] The apparent anomalies may on the one hand reflect the difficulty of interpretation of the perturbations of the complex chromophore systems involved or may reflect real electronic differences in the nature of the rings in these systems.

## Experimental Section

**Materials.**—*cis*- and *trans*-1-cyclohexyl-2-phenyl-3-*p*-phenylbenzoylaziridine were supplied by Dr. N. Cromwell. *cis*- and *trans*-1-cyclohexyl- and -1-benzyl-2,3-dibenzoylaziridine were donated by Dr. H. Heine. *cis*- and *trans*-1-phenyl-2-benzoylcyclopropane, *trans*-1-phenyl-2-*p*-toluylcyclopropane, and 1,1-diphenyl-2-benzoylcyclopropane were donated by Drs. M. Newman and B. Ream. The other compounds were synthesized in this laboratory following procedures described in the literature.

**Measurements.**—The wavelength maxima and molar absorptivities of each small-ring carbonyl compound in cyclohexane are presented in Table I. The spectra were measured with a Cary recording spectrophotometer, Model 14, using matched 1-cm cells. The maxima were measured by running two or three times over the region of maximal absorption and averaging the values thus obtained. The maxima could be duplicated to at least ±5 A. The molar absorptivities ($\epsilon$) are probably accurate to within ±5%. All measurements were carried out using freshly prepared solutions. 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. Spectro Grade cyclohexane was used as the solvent in all cases.

**Acknowledgment.**—The authors wish to thank Dr. N. Cromwell, Dr. H. Heine, Dr. M. Newman, and Mr. B. Ream for supplying compounds used in this investigation. Support of this research by a grant from the National Science Foundation (Grant GP-3972) is acknowledged with appreciation.

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[28] L. A. Strait, R. Ketcham, D. Jambotkar, and V. Shah, *J. Am. Chem. Soc.*, **86**, 4628 (1964).

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# Oxidation Products of Vitamin E and Its Model, 6-Hydroxy-2,2,5,7,8-pentamethylchroman. VIII. Oxidation with Benzoyl Peroxide[1]

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*Received October 14, 1965*

The reaction of benzoyl peroxide with *dl*-$\alpha$-tocopherol and its model, 6-hydroxy-2,2,5,7,8-pentamethylchroman, was studied. The major products were confirmed as the 5-benzoyloxymethyl derivatives and, in addition to the previously identified dimers and tocoquinones, trimers were identified as minor products. The decomposition of the 5-benzoyloxymethyl derivative of the model compound was studied under acidic and basic conditions and two new products were identified, compounds XI and XIII. Diels–Alder adducts of the derived quinone methide were also prepared.

In 1955, Inglett and Mattill[2] studied the oxidation of $\alpha$-tocopherol and its model, 6-hydroxy-2,2,5,7,8-pentamethylchroman, with benzoyl peroxide. The structure proposed for the product from the model was compound I, with the C-7 positional isomer also mentioned as a possibility. When $\alpha$-tocopherol was allowed to react with benzoyl peroxide, the products were reported to be $\alpha$-tocoquinone and another compound of unknown structure.

Recently, Goodhue and Risley[3,4] reported on the reaction of *d*-$\alpha$-tocopherol with benzoyl peroxide in various solvents. They reported that in hexane, benzene, or acetonitrile the product was 5-benzoyloxymethyl-$\gamma$-tocopherol (II), which was converted to the dimer III upon treatment with base. By using primary or secondary alcohols as solvents in this reaction products substituted in the 8a position with alkoxy groups (V) were obtained. In *t*-butyl alcohol the major product was dimer III.

We now wish to report on studies we have conducted on the oxidation of *dl*-$\alpha$-tocopherol and its model, 6-hydroxy-2,2,5,7,8-pentamethylchroman, with benzoyl peroxide and on some interesting chemical transformations of compound I. *dl*-$\alpha$-Tocopherol was oxidized with benzoyl peroxide at room temperature in benzene, and the benzoic acid produced was precipitated by the addition of petroleum ether rather than by washing with potassium hydroxide, as did Inglett and Mattill,[2] nor was the addition of sodium borohydride used to destroy the excess peroxide, as did Goodhue and Risley.[3]

The results obtained were in general agreement with those of the latter workers. A comparison of the crude reaction products by silica gel thin layer chromatography with the products obtained from the Goodhue and Risley method showed the presence of the same products. Separation of the reaction products by chromatography on a silica gel GF thick plate developed with petroleum ether–benzene (2:1) followed by the isolation of the separated products allowed their identification as trimers[5] A and B, dimer III, 5-benzoyloxymethyl-$\gamma$-tocopherol (II), and $\alpha$-tocoquinone. Treatment of the crude reaction products with base as in the isolation method used by Inglett and Mattill undoubtedly largely converts the 5-benzoyloxymethyl compound to dimer and trimer.[3,5]

We have confirmed that the major product produced upon treatment of the model chroman with benzoyl peroxide in benzene at room temperature is I, as postulated by Inglett and Mattill.[2] Treatment of this product with hydrochloric acid in benzene or with potassium hydroxide in ethanol yielded dimer IV and trimer VI *via* the presumed intermediate quinone methide. The production of these two products

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[1] For the preceding papers in this series, see W. A. Skinner and R. M. Parkhurst, *J. Org. Chem.*, **29**, 3601 (1964).

[2] G. E. Inglett and H. A. Mattill, *J. Am. Chem. Soc.*, **77**, 6552 (1955).

[3] C. T. Goodhue and H. A. Risley, *Biochem. Biophys. Res. Commun.*, **17**, 549 (1964).

[4] C. T. Goodhue and H. A. Risley, *Biochemistry*, **4**, 854 (1965).

[5] W. A. Skinner and P. Alaupovic, *J. Org. Chem.*, **28**, 2854 (1963).