The Effect of Cyclopropyl Substitution on the $\pi \rightarrow \pi^*$ Transition of Simple Olefins

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Abstract: The ultraviolet spectra of 16 cyclopropyl olefins and 8 simple olefins have been measured. The cyclopropyl group imparts a bathochromic shift of from 8.0 mμ to more than 15 mμ, to the $\pi \rightarrow \pi^*$ transition of the olefin, when compared to the corresponding isopropyl model. Spectra of cyclopropyl olefins in which free rotation is not likely suggest that there is no conformational preference associated with the donor ability of the cyclopropyl group.

Considerable attention has been focused on the conjugative properties of the cyclopropane ring when joined directly to an unsaturated grouping.[3] Among these studies have been several concerned with the effect of the cyclopropyl group on the ultraviolet spectra of various systems.

Rogers measured the spectrum of phenylcyclopropane and noted that the primary benzene band had undergone a bathochromic shift of 20 mμ.[4] Goodman and Eastman confirmed these results and obtained similar results from several rigid systems containing the phenylcyclopropane chromophore, concluding that the effect shows no stereochemical preference.[5]

On the other hand, Kosower and Ito[6] examined two rigid cyclopropyl conjugated ketones and discovered a marked steric dependence on the bathochromic shift, which amounts to as much as 20–25 mμ.[7] Dauben and Berezin confirmed these results, and noted that a further additive bathochromic shift attends successive alkyl substitution on the basic cyclopropyl ketone chromophore.[8]

Others have noted that the spectrum of pyridine experiences a substantial bathochromic shift upon being substituted by cyclopropyl in the 2 position,[9] and that a similar shift occurs in the spectra of cyclopropyl-substituted 2,4-dinitrophenylhydrazones.[10,11]

Julia and coworkers have observed large bathochromic shifts in the spectra of β-cyclopropyl-α,β-unsaturated acids, nitriles, esters, aldehydes, and ketones.[12] In a more detailed study of β-cyclopropyl-α,β-unsaturated esters, Jorgenson confirmed the previously observed bathochromic shift, noted an additive effect of alkyl substitution on the basic chromophore, and presented evidence for a stereochemical bias on the conjugative effect of the cyclopropane group.[13]

Richey tabulated the ultraviolet spectra of a number of cyclopropyl carbonium ions and called attention to the intense, long-wavelength band which occurs in these spectra, but which is absent in the spectra of simple carbonium ions.[14]

Julia, *et al.*, have reported the spectra of two 1-cyclopropyl-1,3-dienes, and observed a bathochromic shift due to the cyclopropyl group of 6.5 and 9.5 mμ.[15]

Pete has summarized the available data on ultraviolet spectra of various cyclopropyl-substituted chromophores, including a number of cases in which a cyclopropane ring is joined to an isolated carbon–carbon double bond.[16] However, most of the data available for cyclopropyl olefins pertain to highly strained, polycyclic compounds, and do not admit to generalization, in light of the known influence of strain on ultraviolet spectra.[17]

Because of the paucity of data available on the effect of cyclopropyl substitution on the primary absorption band of simple, acyclic olefins, we have undertaken a systematic study of the ultraviolet spectra of a series of cyclopropyl olefins. The object of the study was to accurately ascertain the magnitude of any spectral shift imparted by the cyclopropyl group under conditions where strain energy in the ground state is roughly constant. We also sought to determine whether the basic vinylcyclopropane unit may be viewed as a chromophore in which successive alkylation would lead to a regular incremental shift in the absorption maximum, as in 1,3-dienes, bicyclic cyclopropyl ketones,[8] and acyclic cyclopropylacrylic esters.[13] We finally hoped to determine, from a study of the proper compounds, whether the magnitude of any shift imparted by the cyclopropyl group is related to the ground-state conformation of the vinylcyclopropane unit.

Results and Discussion

The ultraviolet spectral data for olefins **1**–**24** are tabulated in Table I. Representative sample spectra are depicted in Figure 1. As will be seen from the figure, the compounds studied show symmetrical curves, with readily detectable maxima.

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[1] Fellow of the Alfred P. Sloan Foundation.

[2] National Science Foundation Summer Fellow, 1966.

[3] For a review, see M. Y. Lukina, *Russ. Chem. Rev.*, 419 (1962).

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

[5] A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

[6] E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962).

[7] R. H. Eastman and S. K. Freeman, *J. Am. Chem. Soc.*, **77**, 6642 (1955).

[8] W. G. Dauben and G. H. Berezin, *ibid.*, **89**, 3449 (1967).

[9] R. P. Mariella, L. F. A. Peterson, and R. C. Ferris, *ibid.*, **70**, 1494 (1948).

[10] J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946).

[11] M. F. Hawthorne, *J. Org. Chem.*, **21**, 1523 (1956).

[12] S. Julia, M. Julia, S-Y. Tchen, and P. Graffin, *Bull. Soc. Chim. France*, 3207 (1964).

[13] M. J. Jorgenson and T. Leung, *J. Am. Chem. Soc.*, **90**, 3769 (1968).

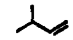
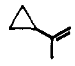
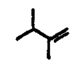
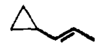
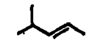
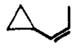
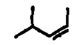
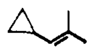
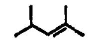
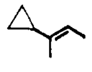
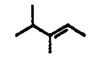
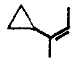
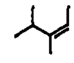
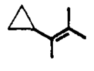
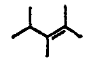
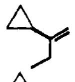
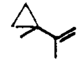
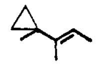
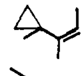
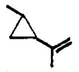
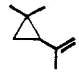
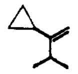
[14] H. G. Richey, Jr., in "Carbonium Ions," Vol. 2, G. Olah and P. von R. Schleyer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968.

[15] S. Julia, M. Julia, and P. Graffin, *Bull. Soc. Chim. France*, 3218 (1964).

[16] J. P. Pete, *ibid.*, 357 (1967).

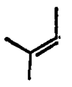
[17] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 203, 212.

Table I.

Compound	$\lambda_{max}^{C_6H_{12}}$, mμ	Log ε	Compound	$\lambda_{max}^{C_6H_{12}}$, mμ	Log ε	Shift, mμ[a]
1 	192.0	4.0	16 	<177.5	b	>+15.0
2 	196.0	3.99	17 	186.5	4.04	+9.5
3 	194.5	4.11	18 	181–183	4.04	+11.5–13.5
4 	192.5	4.19	19 	179.5–181.5	4.04	+11–13
5 	200.0	4.08	20 	191.0	4.01	+9.0
6 	193.5[d]	4.05	21 	185.5	4.07	+8.0
7 	196.0[d]	4.07	22 	186.5	4.00	+9.5
8 	198.0	4.10	23 	189.0	3.99	+9.0
9 	195.0	3.97				
10 	192.0	4.03				
11 	190.0[d]	4.03				
12 	189.0[d]	4.00				
13 	199.0	4.03				
14 	201.0	3.98				
15 	201.0	3.97	24 	195.5	4.0	+5.5

[a] Bathochromic shift due to cyclopropyl group, relative to isopropyl group. [b] There was no true maximum above 177.5 mμ, the spectroscopic limit of the instrument. However, the observed extinction coefficient at 178 mμ (log ε 3.99) suggests a wavelength maximum at approximately 177 mμ. [c] These numbers are the result of two determinations. The instrument is not very reliable below 183 mμ. [d] The geometry of olefins 6 and 7 was assigned on the basis of their nuclear magnetic resonance spectra.

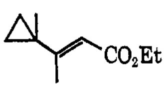
The data in Table I reveal that the maxima for the π → π* band of simple olefins **16–23** undergo bathochromic shifts of from 8.0 mμ to more than 15.0 mμ when isopropyl is replaced by cyclopropyl.[18] The 16-vinylcyclopropanes studied all absorb between 189 and 201 mμ, while the eight simple olefins all absorb at 191 mμ or less.



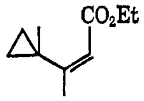
25

The effect of methyl substitution on the basic vinylcyclopropane chromophore is erratic. Compound **6**, a dimethylated vinylcyclopropane, absorbs at 193.5 mμ, while compound **5**, also dimethylated, absorbs at 200 mμ.[19] Alkylation at the 2 position of the ring is slightly more effective than alkylation on the double bond (*cf.* **13** and **14** with **2**).

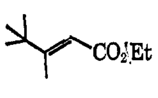
Alkylation at the 1 position on the cyclopropane ring imparts a hypsochromic shift of from 3.5 to 7 mμ (*cf.* **10** with **2**, **11** with **6**, and **12** with **7**). An analogous hypsochromic shift attending C_1 methylation was observed by Jorgenson in the spectra of β-cyclopropylacrylic esters, and has been explained on conformational grounds.[13] In the two substituted acrylates i and ii, the ultraviolet maxima occur at 231 and 217



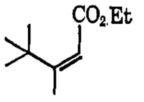
i



ii



iii



iv

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[18] The choice of isopropyl-substituted olefins **16–23** as reference compounds was influenced by a desire to minimize steric effects as much as possible. Such effects may, however, not be significant, since 2-methyl-2-butene (**25**) has λ_{max} 185.5 mμ, compared to λ_{max} 185.5 mμ for *trans*-3,4-dimethyl-2-pentene (**22**) and λ_{max} 186.5 mμ for *cis*-3,4-dimethyl-2-pentene (**21**).

[19] However, the bathochromic shift in the spectrum of **5** may reflect a special "*gem*-dimethyl effect," not previously recognized. Compare, for example, the spectra of olefins **21** and **22** with that of **20**. Similarly, it has been reported that in the vapor phase isobutylene absorbs at longer wavelength (λ_{max} 179, 184, 188 mμ) than either *cis*-2-butene (λ_{max} 175 mμ) or *trans*-2-butene (λ_{max} 178 mμ).[20]

[20] American Petroleum Institute Catalog of Ultraviolet Spectral Data, API Research Project 44, Serial No. 559, 557, and 558.

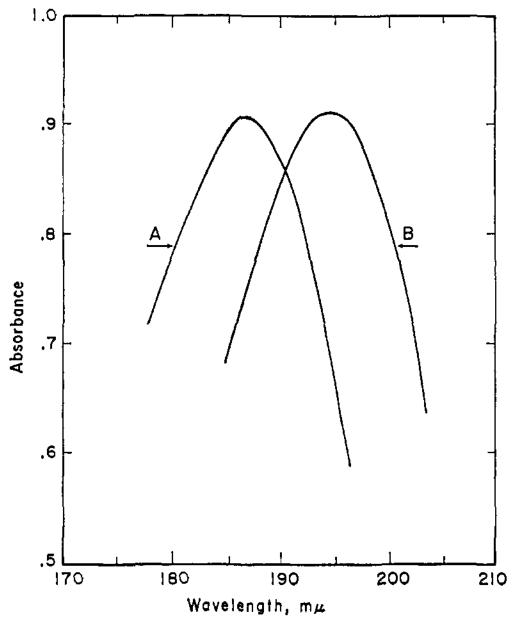

Figure 1. Ultraviolet spectra of 2,3-dimethyl-1-butene (A) and 2-cyclopropylpropene (B) in cyclohexane.

mμ, compared to 217.5 and 220.5 mμ for the model esters iii and iv.[13] The absence of cyclopropyl conjugation in ester ii was attributed to steric factors which force the cyclopropane ring into a conformation which makes conjugation impossible.[13] The fact that **11** and **12** show maxima at almost the same wavelength suggests that stereochemical requirements in simple cyclopropyl olefins are nil.

In general, the cyclopropyl group seems to exert its strongest effect on lightly substituted olefins (*cf.* **1**, **3**, and **4** with **16**, **18**, and **19**), a result compatible with the observations of Jorgenson on the spectra of cyclopropyl acrylic esters.[13]

The effect of a second cyclopropyl group (*cf.* **15** with **24**) is diminished, again in analogy to the observations of Jorgenson.[13]

Thus, when linked directly to an olefinic grouping, the cyclopropane ring behaves as a moderately powerful auxochrome. The bathochromic shifts observed in this study are comparable in magnitude to those observed in 1-cyclopropyl-1,3-dienic systems,[15] but are much less than the shifts observed in β-cyclopropyl-α,β-unsaturated carbonyl systems.[12,13] Finally, the donor ability of the cyclopropyl group in cyclopropyl olefins seems not to be a function of conformation, contrary to the results observed in cyclopropyl ketones[6,8] and β-cyclopropylacrylic esters,[13] but analogous to the behavior of phenylcyclopropanes.[5]

Experimental Section

Cyclopropyl olefins 1–10, 13, 14, and 24 were prepared in connection with another study. The synthesis and characterization of these compounds will be communicated separately. All compounds were purified by preparative vpc and have been characterized by elemental analysis, mass spectral molecular weight, and absorption spectra. The geometry of the double bond in compounds **6** and **7** was assigned on the basis of their nmr spectra. The 1,4 CH_3–CH_3 coupling in **7** was markedly greater than the analogous coupling in **6**, a result compatible with the assigned geometry.[21]

Olefins 16–23 were obtained from Chemical Samples Co. Columbus, Ohio, and were checked by vpc for purity before being used.

cis- **and** *trans-***2-(1-Methylcyclopropyl)-2-butenes (11 and 12).** 1-Methylcyclopropyl methyl ketone (5.0 g, 51 mmoles) was added to an ether solution of ethylidinetriphenylphosphorane, prepared under nitrogen from ethyltriphenylphosphonium bromide (22.4 g, 60 mmoles) and 55 mmoles of butyllithium in hexane. After stirring for several hours, the ether was replaced with 100 ml of tetrahydrofuran,[22] and refluxing was continued overnight. The tetrahydrofuran solution was diluted with 250 ml of pentane, and the resulting mixture was washed four times with 250-ml portions of water. The pentane solution was dried over potassium carbonate and then concentrated by heating on a steam bath under an air condenser. The residue was distilled through an 18-in., spinning-band column to give 1.50 ml of the mixture of olefins **11** and **12**, bp 99–106°. Analysis by vpc (20% Carbowax 20M on Chromosorb, 10 ft × $^3/_8$ in. at 70°) showed two components in a ratio of 20:1 (in order of increasing retention time).

The major component had a molecular ion peak at *m/e* 110 in its mass spectrum. Its infrared spectrum (in CCl_4 solution) has maxima at 3100, 3000, 2950, 2850, 1450, 1370, 1040, 1020, and 935 cm^{-1}. Its nmr spectrum consisted of a four-proton multiplet at δ 0.35–0.65, a three-proton singlet at δ 1.06, a six-proton multiplet at δ 1.63, and a broad, one-proton multiplet at δ 5.1.

The minor component had a weak molecular ion peak at *m/e* 110 in its mass spectrum. Its infrared spectrum (in CCl_4 solution) has maxima at 3070, 3000, 2950, 2850, 1440, 1370, 1020, and 930 cm^{-1}. Its nmr spectrum consisted of two-proton multiplets at δ 0.35 and 0.55, a three-proton singlet at δ 1.14, a broadened doublet (J = 7 cps) at δ 1.55, a sharp singlet at δ 1.60 (combined integral = six protons), and a one-proton broadened quartet at δ 5.3. The minor product was assigned structure **11** (*cis*-methyl groups) due to the absence of observable 1,4 coupling between the methyl groups.[21]

1,1-Dicyclopropylethylene (15). Compound **15** was prepared in a manner strictly analogous to that used for the syntheses of compounds **11** and **12**. The sample had the same boiling point and infrared spectrum as those reported for Ketley and McClanahan for this material.[23]

2-Methyl-1-cyclopropylpropene (5). Isopropyl bromide (59 g, 0.48 mole) in 50 ml of dry ether was added dropwise to 12 g (0.50 g-atom) of magnesium turnings in 70 ml of ether, with stirring under a nitrogen atmosphere. The Grignard reagent was then added by drops to cyclopropanecarboxylic acid chloride (40 g, 0.38 mole) in 100 ml of anhydrous ether with 2 g of ferric chloride at −65°.[24] The reaction mixture was stirred in a Dry Ice bath for 3 hr and then warmed to room temperature. Ice water was added, and the aqueous phase was separated and washed several times with ether. The combined ether phases were washed several times with saturated aqueous sodium bicarbonate and dried over anhydrous potassium carbonate. The ether was evaporated on a steam bath and the residue distilled at reduced pressure to yield cyclopropyl isopropylketone, 30 g, 68%, bp 84–97° (110 mm) (lit.[25] 141.0–141.4° (761 mm)).

Anal. Calcd for $C_7H_{12}O$: C, 74.75; H, 10.79. Found: C, 74.74; H, 10.92.

Cyclopropyl isopropyl ketone (11.5 g, 103 mmoles) was treated with 1.1 g (30 mmoles) of lithium aluminum hydride in 100 ml of ether. The mixture was stirred 20 hr. Saturated aqueous ammonium chloride was added to liberate the carbinol. Distillation of the crude product yielded 7.2 g (70%) of cyclopropylisopropylcarbinol. The nmr spectrum showed bands at δ 0.2–0.9 (multiplet, five protons), 1.0 (d, J = 7 cps, six protons), 1.7 (multiplet, one proton), 2.6 (doublet of doublets, J = 6 cps, 8 cps), and 3.7 (singlet, one proton).

Cyclopropylisopropylcarbinol (5.0 g, 44 mmoles) was treated with 6 ml (65 mmoles) of phosphorus oxychloride in 30 ml of pyridine. The solution was heated 1 hr at 95° and then poured over ice. The mixture was extracted with pentane; the pentane was washed several times with dilute aqueous HCl, aqueous sodium bicarbonate, then water and dried over potassium carbonate. The pentane was removed by evaporation through an air condenser and the residue was distilled. A mixture of products was obtained, 0.60 g, bp 113–116° (bath temperature 130°).

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(21) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(22) F. Sondheimer and S. Wolfe, *Can. J. Chem.*, **37**, 1870 (1959).

(23) A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, **30**, 940 (1965).

(24) J. Cason and K. W. Kraus, *ibid.*, **26**, 1768 (1961).

(25) P. Bruylants, *Bull. Soc. Chim. Belges*, **36**, 519 (1927).

Vpc analysis (Carbowax 20M, 5 ft × $^1/_4$ in., 70°) separated five products: hydrocarbon **5**, approximately 60%, a small amount of a second product with slightly longer retention time, two rearranged chlorides (no cyclopropyl absorption in ir, molecular ions in the mass spectrum at 132 and 134), and a fifth product with retention time about the same as the other two chlorides.

Compounds **5** was characterized by its mass spectrum (m/e 96), ir spectrum, ν_{max} 3080, 3000–2850, 1450, 1370, 1060, 1040, 1010, and 950 cm^{-1}; and nmr spectrum, δ 1.65, 1.7 (broad singlets, six protons), 0.1–0.8 (multiplet, four protons), 1.3 (broad multiplet, one proton), and 4.5 (doublet, one proton).

Ultraviolet Spectra. Spectra were determined with a Beckman Model D, K-2A "Ratio Recording" spectrophotometer.[8,26]

Spectroquality reagent grade cyclohexene, supplied by Matheson Coleman and Bell, was used as the solvent for all spectral measurements.

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[26] R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, **27**, 345 (1962).

Cyclopropyl Conjugation in Olefinic Esters. Conformational Effects on Ultraviolet Absorption[1]

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Contribution from the Department of Chemistry, University of California at Berkeley, Berkeley, California 94720. *Received November 4, 1967*

Abstract: The ultraviolet absorption spectra of 17 cyclopropylacrylic esters and their respective models are reported. The effect of substitution on the spectral changes, ranging from a bathchromic effect of 29 mμ to a hypsochromic effect of 3 mμ, is evaluated in terms of the structure and population of possible conformers. The disappearance of a bathochromic effect in ester **15** is interpreted as support for the existence of a limiting geometrical requirement for cyclopropyl conjugative orbital overlap. Comparison of shielding effects on β substituents corroborates this interpretation. The magnitude of vicinal coupling constants indicates that cyclopropylacrylic esters populate the bisected conformation to a larger extent than corresponding vinylcyclopropanes.

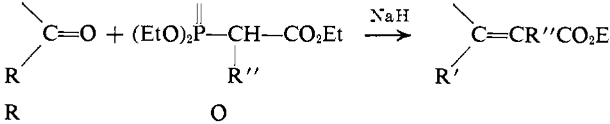
Major attention has been directed to the special properties which are manifested by the cyclopropyl group upon photochemical excitation. Evidence for auxochromic properties of cyclopropanes has been documented, for example, in the ultraviolet absorption spectra of arylcyclopropanes,[3] of alkenylcyclopropanes,[4] and of miscellaneous complex cyclopropyl ketones.[5,6] A compilation of these data has recently appeared.[7]

A stringent spatial relationship of the cyclopropane bond orbitals with respect to the π-electron system, the so-called parallel relationship, has been thought necessary for the manifestation of maximum conjugative properties both in the excited state[5–9] and in the ground state[10,11] of cyclopropane derivatives. In the case of rigid cyclopropyl ketones the observed spectra have been interpreted in such terms;[5a,6,7] however, for arylcyclopropanes[3b] and vinylcyclopropanes[4] geometric factors have been shown to be unimportant. It is apparent that this parallel relationship does not apply to all cyclopropane derivatives, but its precise scope of operation has not yet been defined.

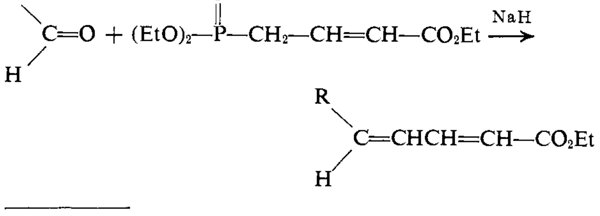
In connection with our detailed investigation of the photolytic properties of simple α,β-unsaturated esters[1a] and their cyclopropyl derivatives,[1b,c] we have had occasion to examine the ultraviolet absorption spectra of a systematic series of cyclopropyl-substituted olefinic esters. The data reported here on 17 such esters and their appropriate models permit a semiquantitative evaluation of various effects which influence the efficacy of cyclopropyl conjugation in the excited state. They also shed light on the question of the importance of conformational factors in the cyclopropyl conjugative interaction in olefinic esters.

Results and Discussion

Synthesis of Esters. The cyclopropylacrylic esters and their models were synthesized by the application of the Emmons reaction,[12] as formalized in eq 1 and 2.



$$\mathrm{RR'C{=}O + (EtO)_2\overset{\overset{O}{\|}}{P}{-}\underset{\underset{R''}{|}}{C}H{-}CO_2Et \xrightarrow{NaH} RR'C{=}CR''CO_2Et} \quad (1)$$



$$\mathrm{RHC{=}O + (EtO)_2{-}\overset{\overset{O}{\|}}{P}{-}CH_2{-}CH{=}CH{-}CO_2Et \xrightarrow{NaH} RHC{=}CHCH{=}CH{-}CO_2Et} \quad (2)$$

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