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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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.

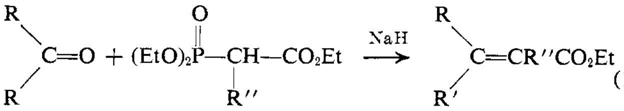
Major attention has been directed to the special properties which are manifested by the cyclopropyl group upon photochemical excitation. Evidence for auxochromic properties of cyclopropanes has been documented, for example, in the ultraviolet absorption spectra of arylcyclopropanes,[3] of alkenylcyclopropanes,[4] 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.

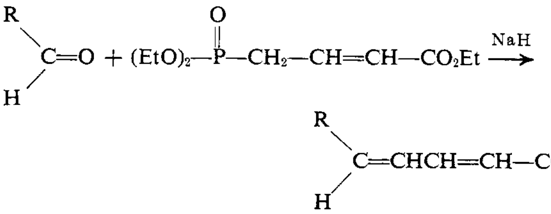
In connection with our detailed investigation of the photolytic properties of simple α,β-unsaturated esters[1a] and their cyclopropyl derivatives,[1b,c] we have had occasion to examine the ultraviolet absorption spectra of a systematic series of cyclopropyl-substituted olefinic esters. The data reported 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.



(1)



(2)

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(1) Photochemistry of α,β-Unsaturated Esters. IV. For papers I, II, and III in this series, see (a) M. J. Jorgenson, *Chem. Commun.*, **7**, 137 (1965); (b) M. J. Jorgenson and C. H. Heathcock, *J. Am. Chem. Soc.*, **87**, 5264 (1965); and (c) M. J. Jorgenson, *ibid.*, **88**, 3463 (1966), respectively.

(2) NSF Undergraduate Summer Institute Participant, 1967.

(3) (a) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86**, 4628 (1964); (b) A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

(4) C. H. Heathcock and S. R. Poulter, *ibid*,, **90**, 3766 (1968).

(5) (a) E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962); (b) R. H. Eastman and S. K. Freeman, *J. Am. Chem. Soc.*, **77**, 6642 (1955); (c) S. Julia, M. Julia, S. Tschen, and P. Graffin, *Bull. Soc. Chim. France*, 3207 (1964); S. Julia, M. Julia, and P. Graffin, *ibid.*, 3218 (1964), and references therein.

(6) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **89**, 3449 (1967), and references therein.

(7) J. Pete, *Bull. Soc. Chim. France*, 357 (1967).

(8) N. H. Cromwell and G. V. Hudson, *J. Am. Chem. Soc.*, **75**, 872 (1953).

(9) J. F. Music and F. A. Matsen, *ibid.*, **72**, 5256 (1950).

(10) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966).

(11) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966).

(12) W. S. Wadsworth, Jr., and W. D. Emmons, *ibid.*, **83**, 1733 (1961).

Table I. Ultraviolet Absorption and Proton Magnetic Resonance Chemical Shifts of Cyclopropylacrylic Esters and Model Esters

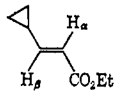
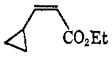
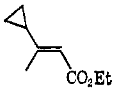
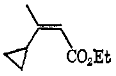
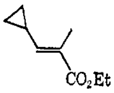
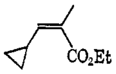
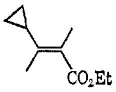
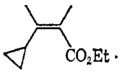
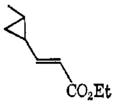
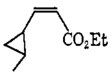
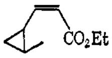
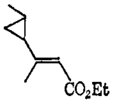
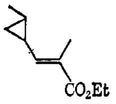
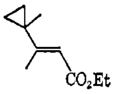
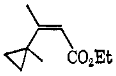
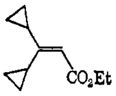
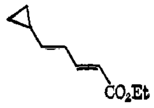
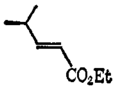
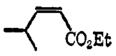
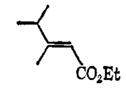
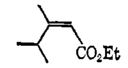
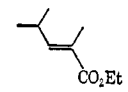
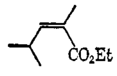
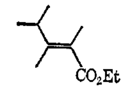
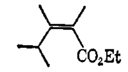
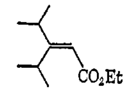
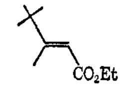
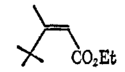
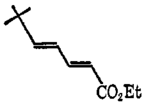
	Compound	λ_{max}^{EtOH}, mμ (log ϵ)[a]	Auxochromic effect, $\Delta\lambda$[b]	Chemical shifts, τ (Δ ppm)			
				H$_\alpha$	H$_\beta$	CH$_{3\alpha}$	CH$_{3\beta}$
1.		231 (4.20)	+23	4.25 (−0.03)	3.65 (+0.53)		
2.		232 (4.15)	+24	c	c		
3.		236 (4.10)[d]	+17	4.42 (−0.03)[e]			8.05 (+0.15)
4.		238 (4.10)	+19.5	4.40 (−0.10)[e]			8.50 (+0.25)
5.		234.5 (4.19)	+17.5		3.95 (+0.43)	8.10 (−0.10)	
6.		238 (4.09)	+20.5		4.87 (+0.49)	8.16 (0)	
7.		240 (4.07)	+15			8.05[f] (−0.15)	8.34[f] (+0.14)
8.		243 (4.07)	+19			8.17[f] (−0.05)	8.62[f] (+0.24)
9.		237 (4.20)	+29	4.30 (−0.02)	3.68 (+0.56)		
10.		237 (4.12)	+29	c	c		
11.		237 (4.12)	+29	c	c		
12.		240 (4.09)	+21.5	4.45 (0)[e]			8.05 (+0.15)
13.		239.5 (4.14)	+22.5		4.02 (+0.44)	8.15 (−0.05)	
14.		231 (4.08)	+13.5[h], 12.5[i]	4.30 (−0.07)[e,h] (−0.15)[e,i]			7.95 (+0.09)[h] (+0.05)[i]
15.		217 (4.17)	−3.5[h], −1.5[i]	4.37 (−0.08)[e,h] (−0.13)[e,i]			8.15 (−0.02)[h] (−0.10)[i]
16.		247 (4.13)	26.5	4.64 (−0.01)			
17.		278 (4.41)	17	c	c		
18.		208 (4.10)		4.28	3.12		
19.		208 (4.08)		c	c		

Table I (*Continued*)

Compound	λ_{max}^{EtOH}, mμ (log ε)[a]	Auxochromic effect, Δλ[b]	Hα	Hβ	$CH_{3\alpha}$	$CH_{3\beta}$
20. 	218.5 (4.20)		4.45[e]			7.90
21. 	218.5 (4.18)		4.50[e]			8.25
22. 	217 (4.13)			3.58	8.20	
23. 	217.5 (3.98)			4.38	8.16	
24. 	225 (3.89)				8.20[k]	8.20[k]
25. 	224 (3.80)				8.22[k]	8.38[k]
26. 	220.5 (4.16)		4.65[e]			
27. 	217.5 (4.13)		4.37[e]			7.86
28. 	220.5 (3.86)		4.45[e]			8.17
29. 	261 (4.49)		c	c	c	c

[a] λ_{max} values rounded off to 0.5 mμ; estimated accuracy ±0.5 mμ. [b] From comparison with appropriate isopropyl or *t*-butyl model esters. [c] First-order analysis impossible because of complex splitting pattern. [d] Reported λ_{max}^{EtOH} 234.5 mμ (ref 5c). [e] Approximate value, signal broad. [f] Assignments are somewhat arbitrary, based primarily on typical α-CH_3 chemical shift values for related esters. [g] Approximately 10–20% of the *cis*-1,2-cyclopropane geometrical isomer present. [h] By comparison with the *t*-butyl model **27** or **28**. [i] By comparison with the isopropyl models **20** or **21**. [j] Prepared according to ref 12. [k] Reported chemical shifts [I. Tömösközi, *Tetrahedron*, **22**, 179 [(1966)] τ 8.18 for ester **24** and 8.22 and 8.38 for α and β methyl, respectively, for ester **25**.

Phosphonoacetate (R'' = H), phosphonopropionates (R'' = CH_3), and phosphonocrotonates were utilized; the conditions were modified to maximize product yields in cases of reluctant reactivity.

Effect of Double Bond Substituents on Uv Maxima. Table I summarizes the measured ultraviolet absorption maxima for esters **1–17** and for 12 model compounds (esters **18–29**). The reported maxima correspond to the $\pi \rightarrow \pi^*$ transitional energies. The contribution from the weak $n \rightarrow \pi^*$ transition, reported to occur at 237 mμ in ethyl acrylate and known not to vary appreciably with structure,[13] can be considered to be negligible in all cases.

An evaluation of the effectiveness of a cyclopropyl group in extending conjugation can be made by comparison of the measured uv maxima of cyclopropylacrylic esters with those of the corresponding isopropyl or *t*-butyl derivatives. A compilation of these auxochromic effects (Δλ in Table I) reveals that maximum conjugation of 24 mμ, corresponding to a stabilization of the excited state by the cyclopropane relative to an isopropyl group of 14 kcal, is achieved in the parent system **1**. The effectiveness of the cyclopropane decreases with increasing substitution at the double bond, diminishing to 15 mμ in the case of the disubstituted ester **7**. A similar, but somewhat smaller, effect has been noted by Heathcock and Poulter[4] for vinylcyclopropanes. A dissection of substituent effects leads to the formulation of a rule (Table II) for the calculation of the ultraviolet maxima of cyclopropylacrylic ester. The rule predicts with good accuracy the absorption maxima of the α,β-disubstituted cyclopropylacrylic estes **7** and **8**; the calculated maxima of 239 mμ for ester **7** and 244 mμ for ester **8** agree well with the observed maxima of 240 and 243 mμ, respectively.

The effect of two cyclopropyl substituents at the β position is a bathochromic shift of 26.5 mμ. Comparison of ester **16** with ester **3** as the best available model, where a methyl group replaces the second cyclopropane, reveals that the effect of the second cyclopropane group amounts to only 10 mμ. A similar effect in the hydrocarbon series was noted by Heathcock and Poulter.[4]

The consequence of placing a cyclopropyl group into a conjugative location at the δ carbon of a dienic ester

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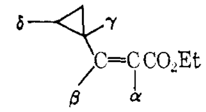
(13) W. D. Closson, S. F. Brady, and P. J. Orenski, *J. Org. Chem.*, **30**, 4026 (1965).

Table II. Summary of Substituent Effects in Calculation of Ultraviolet Absorption Maxima for Cyclopropylacrylic Esters



Parent system	*trans* ester	231 mμ
	cis ester	232 mμ
Olefinic methyl substituents		Increment, mμ
α (*trans* ester)		+3
(*cis* ester)		+6
β (*trans* ester)		+5
(*cis* ester)		+6
β cyclopropyl		+(16–17)
Cyclopropyl methyl substituents[a]		
γ (no substituents *cis* to ring)		−6
γ (substituents *cis* to ring)		−21
trans[b] δ		+(5–6)(+3)[c]
cis[b] δ		+5
Effect of additional double bond		+47

[a] These values refer to the special cases discussed in the text; these substitution effects should be greatly subject to the nature of the double bond substitution. [b] Refers to substitution with respect to the cyclopropane ring system. [c] Comparison of ester **12** with **3**.

is a bathochromic increment of 17 mμ. This corresponds to a stabilization energy of 6–7 kcal, a value which is only half of that found in the case of the parent ester **1**.

Effect of Cyclopropyl Substitution on Uv Maxima. It is evident from the data compiled for esters **9–13** that a methyl group on a methylene carbon of the cyclopropane is capable of exerting its electronic effect; the bathochromic effects noted here on the ultraviolet absorption maxima vary from 3 to 6 mμ.

That the cyclopropane ring is capable of transmitting the electronic effect of alkyl substituents has been noted by Dauben and Berezin and a quantitative dissection of these bathochromic effects (3–7 mμ) has been made for rigid bicyclic ketones in terms of unsymmetrical conjugative participation of the cyclopropane bonds.[6] Large bathochromic increments (12–15 mμ) caused by substituents at the α position and more modest ones (5–6 mμ) at the β position are apparent from other literature data.[7] Esters **14** and **15** have a methyl substituent at the cyclopropylcarbinyl carbon, the α position in the above examples. Instead of strong bathochromic shifts, expected to result in ultraviolet maxima in the region of 240–250 mμ, the measured maxima were at startlingly low wavelengths. Ester **14** exhibited a maximum at 231 mμ, a wavelength which is 6 mμ lower than that of the model ester **3** which lacks the ring substituent. More dramatically, the conjugative effect of the cyclopropane vanishes entirely in ester **15**; the cyclopropane is found to have an electronic effect only comparable to that of a typical alkyl group in this ester.[14]

Conformation and Nmr Spectra of Cyclopropylacrylic Esters. Recently, the nature of the conformational equilibrium of flexible vinylcyclopropanes has been probed.[15–18] The best interpretation of the conformational equilibrium of the parent hydrocarbon is in terms of the presence of a low-energy *s-trans* conformation, the bisected conformer B (all R's = H), and a high-energy unsymmetrical conformer D or D′ (all R's = H).[17] It was concluded that the population of the *s-cis* conformer C is unimportant in the equilibrium.[19]

It is possible to interpret the uv spectra of the cyclopropylacrylic esters (except that of **15**) by treating these esters as vinylcyclopropane derivatives, whose carbethoxyl substituent has a purely steric effect on the conformational equilibrium. The presence of B and D as principal conformers follows in analogy with the case of vinylcyclopropane[17] and its alkyl derivatives.[18] In harmony with the accepted views on the steric requirements for the interaction of the cyclopropyl bonds with the π-electron system,[5a,6,7] it is assumed that for conformer D there exists, more or less effectively depending on the dihedral angle,[20,21] the opportunity for the conjugative interaction of one of the cyclopropane bonds (bond a in D, bond b in D′), while conjugation in conformations B and C should be at a maximum.[22]

The observation of the largest bathochromic effect in the *trans* series for ester **1** is consonant with the interpretation that the *s-trans* conformation B is populated to the largest degree in this ester. Substitution at the α and β positions, because of the introduction of steric effects, is expected to shift the equilibrium away from B toward D; the smaller bathochromic effects in esters **3** and **5** are accountable in these terms.

The varied effect of the cyclopropylmethyl substituent is best understood by recognizing that conformations D and D′ are not energetically equivalent in the case of esters **9–13** ($R_5 = CH_3$). Since the effect of the methyl group will be transmitted only in one of these (conformation D, *via* bond a), this effect will necessarily be strongly dependent on the proportion of the conformers present as D or D′.

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(14) It is tempting to ascribe the slight hypsochromic shifts observed for ester **15**, compared to its models, to an electron-withdrawing effect of the cyclopropane, when it is conformationally "frozen" into a nonconjugative geometry. A rate-retarding effect of the cyclopropane in a similar geometry was noted by Brown[10] in solvolytic studies. Other investigators, however, have evaluated the cyclopropyl group to be a slight electron donor [J. A. Landgrebe and J. D. Shoemaker, *J. Am Chem. Soc.*, **89**, 4465 (1967)], but in these systems the conformational freedom of the cyclopropane is not impaired.

(15) H. Günther and D. Wendisch, *Angew. Chem.*, **78**, 266 (1966).

(16) W. Lüttke and A. de Meijere, *ibid.*, **78**, 544 (1966).

(17) G. R. DeMare and J. S. Martin, *J. Am. Chem. Soc.*, **88**, 5033 (1966).

(18) S. Sarel, paper presented at the International Symposium on the Chemistry of Small Rings and Their Applications, Louvain, Belgium, Sept 12–15, 1967.

(19) (a) This interpretation of the conformational equilibrium differs with those derived less rigorously by others[15,16] and contrasts sharply with current views of the nature of the conformational equilibrium for cyclopropylcarbonyl compounds and cyclopropylcarbonium ions.[19b] (b) H. G. Richey in "Carbonium Ions," Vol. 2, G. A. Olah and D. R. Schleyer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968.

(20) No specific value is attached to the dihedral angle in D, as this value has been shown to differ with solvent[17] and substitution.[18] The dihedral angle of 79° derived for vinylcyclopropane in CCl_4[17] does not conform to the geometry which maximizes interaction of that bond with the π system. Because of the angle of bent of the cyclopropane bond orbitals (20–25°),[21] the optimum dihedral angle should be in the vicinity of 35–40°.

(21) D. Peters, *Tetrahedron*, **19**, 1539 (1963); C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962).

(22) Since comparison of both the uv data and nmr spectral data are made with structurally similar model esters, it can be safely concluded that the differences noted here are not due to conformational changes involving the carbethoxy group. The *s-cis vs. s-trans* relationship of the double bond with respect to the carboethoxy group, if it is governed primarily by steric factors, should remain constant between each cyclopropylacrylic ester and its model. This will be particularly true in the *trans* isomeric series, where the interactions of the *cis* substituents are identical. In the case of the *cis* esters this may not be strictly true, as the cyclopropyl substituent is only approximately modeled sterically by an isopropyl group, the latter surely being sterically more demanding.

The drastic reduction of the conjugative effect of the cyclopropane in ester **14** is satisfactorily rationalized in terms of a severe shift in the equilibrium from B toward D ($R_1 = R_2 = CH_3$; $R_3 = R_5 = H$; $R_4 = CO_2Et$). Because the interactions between the substituents R_2 and R_3 in ester **15** (CH_3 and CO_2Et, respectively) are even more pronounced than in ester **14**, an even stronger effect on the conformational equilibrium is to be expected. Since conjugative interaction should occur in conformers D and D , but since the measured uv spectrum of **15** reveals no such conjugation, we are compelled to stipulate a conformation for **15** in which all conjugative interaction is precluded. Such a conformation, since it relieves all crowding, clearly has geometry E (Figure 1). The orbitals of both cyclopropane bonds are almost orthogonal to the π system in E, so that the electronic interaction is at a minimum for this conformation. Whether all conjugation vanishes in such a spatial relationship has not been shown previously.[23]

The nmr spectral data (Table I) offer excellent reinforcement for the conformational interpretation advanced here. The characteristic anisotropic effect of the cyclopropane group[24] manifests itself in a strong shielding effect on the β substituent (typically, 0.45 ppm for hydrogen, 0.14–0.25 ppm for methyl) except for ester **15**. If the principal conformation of ester **15** is E, and no B is present, then the shielding on R_2 (CH_3) should be at a minimum. This is strikingly borne out by the observance of a slight deshielding effect instead of a shielding effect for the β-methyl group of ester **15**.

The magnitude of the coupling constants between the carbinyl hydrogen of the cyclopropane and the vicinal vinyl hydrogen ($J_{1,2}$) affords a quantitative estimate of the importance of conformation B in the equilibrium. The values determined for esters **1**, **4**, and **5** are 9.4, 10.0, and 10.3 cps, respectively; $J_{1,2}$ is found to be 6.5 cps for the model ester **18**. The consistently higher values of $J_{1,2}$ for cyclopropylacrylic esters serve as evidence that the cyclopropyl olefinic esters populate the *s-trans* conformation B to a larger extent than their isopropyl models. Taking the ideal value of 11–12 cps[25] for $J_{1,2}$ in B and recognizing that for conformations D and E this coupling constant should be small, the population of B can be estimated to be in the vicinity of 80–90% for esters **1**, **4**, and **5**.

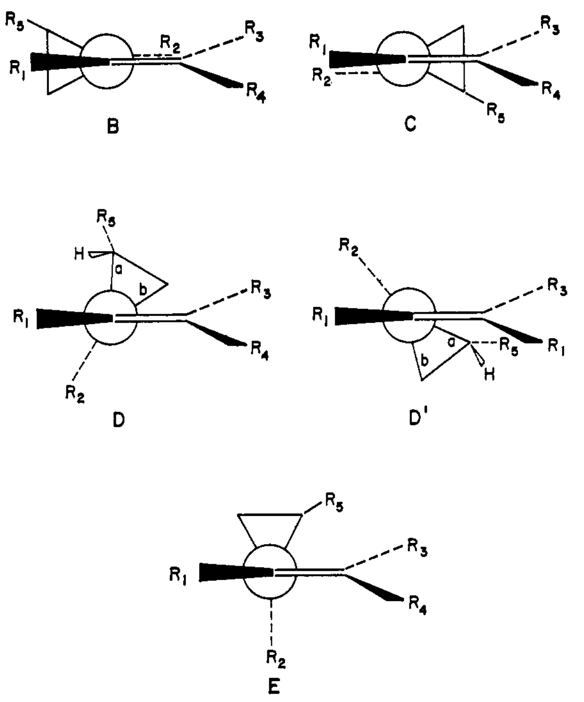

Figure 1.

The coupling constant is considerably higher for cyclopropylacrylic esters than for vinylcyclopropanes.[26] Values of 8–9 cps, depending on temperature, have been reported for vinylcyclopropane[15,16] and values of 6.5 and 7.0 cps have been measured for *trans*- and *cis*-propenylcyclopropane, respectively.[27] These values are much closer to $J_{1,2}$ in the corresponding isopropyl models ($J_{1,2}$ for 3-methyl-1-butene is 6.4 cps[25a]) than in the case of the ester derivatives above. It is evident that the driving force to assume the bisected conformation is considerably less for vinylcyclopropanes than it is for cyclopropylacrylic esters. This is paralleled by the conclusions reached by Heathcock and Poulter.[4] There exists a much less effective interaction of the cyclopropane with the double bond in vinylcyclopropanes than in our cyclopropylacrylic esters. Furthermore, in contrast to the strong dependence on conformational factors, in our esters the interaction in vinylcyclopropanes is not subject to steric control.[4] One reason for this difference, which suggests itself, is that in the cyclopropylacrylic esters there exists a charge separation in the ground state which is enhanced in the $\pi \rightarrow \pi^*$ excited state. This charge separation places some positive charge next to the cyclopropane ring so that stereochemical factors, which are known to enter into the stabilization of cyclopropylcarbinyl cations,[19b] will come into play both in the excited state as well as in the ground state. No such charge separation or charge transfer excitation exists for the hydrocarbon; the observed differences in conformational preference as well as in the effectiveness of cyclopropane conjugation could be due to such electronic factors.

Photolytic Reactivity of Cyclopropylacrylic Esters. Finally, it is of considerable interest to correlate, as a function of structure, the characteristics of the primary spectroscopic process, as manifested in the uv absorption spectra, with the chemical changes brought about

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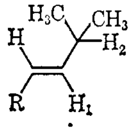
[23] The ultraviolet data can be interpreted equally well, if not more simply, by stipulating the presence of only conformations B and E for all cyclopropylacrylic esters. This analysis, however, ignores the conformational findings established for vinylcyclopropanes. However, because of different electronic considerations present in the esters, the analogy with the hydrocarbon systems should not be too compelling.

[24] J. Pierre and P. Arnaud, *Bull. Soc. Chim. France*, 1960 (1966), and references therein.

[25] (a) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Am. Chem. Soc.*, **84**, 2748 (1962); (b) E. W. Garbisch, Jr., *ibid.*, **86**, 5561 (1964).

[26] Significance can be attached to this difference in size, since for the structural model assembly i the coupling constant ($J_{1,2}$) is 6.4–6.5 cps for the hydrocarbon (R = H),[25a] the ester ($R = CO_2Et$), or the ketone ($R = COCH_3$) (unpublished results), so that electronic and steric factors [M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963)] do not affect the vicinal coupling constants in this case.



i

[27] C. H. Heathcock and S. R. Poulter, unpublished results.

upon photolysis. The characteristic weakening of the cyclopropane bonds in the excited state, predicted by theory,[28] manifests itself in our case in photolytic fragmentation reactions, giving rise to carbene intermediates, or in cyclopropane bond cleavages leading to rearrangements.[1b,c] It is an intriguing corollary of the conclusions reached from the uv absorption spectrum concerning the conformation of ester **15** that this ester cannot have appreciable energy localized in its cyclopropyl bonds. As a consequence, the *cis* ester might not undergo the characteristic reactions of cyclopropylacrylic esters, although in this instance this consequence is impossible to establish, since the *trans* isomer with which it exists in a facile photochemical equilibrium does possess conjugative stabilization by the cyclopropane. The consequences on the photochemical reaction course in esters in which the cyclopropyl group is sterically insulated from exhibiting conjugative interaction in both geometrical isomers would be of great interest to examine, and we expect to pursue such studies.

A more detailed discussion of the photochemical behavior of cyclopropylacrylic esters will be presented in a subsequent publication.

Experimental Section

Measurement of Ultraviolet Absorption Spectra. The ultraviolet spectra of samples purified by vapor phase chromatography were measured on a Cary 14 spectrophotometer for compounds whose maxima occurred above 215 mμ. The spectra of esters **18** and **19** were measured on a Beckman Model DK-2A ratio recording spectrophotometer. The correspondence of maxima measured on these two spectrophotometers was checked and found to be excellent in the case of ester **1**. The maxima of absorption curves were determined from duplicate or triplicate runs. The average values reported in Table I are rounded off to 0.5 mμ.

Measurement of Nmr Spectra. The chemical shifts reported in Table I were obtained from measurement of the spectra on a Varian A-60 spectrometer, employing solutions of approximately 10–20% by volume in CCl_4 with internal TMS standard. Coupling constants were obtained and decoupling experiments were carried out on a Varian HA-100 spectrometer.

Preparation of Olefinic Esters.[29] The preparation of the cyclopropylacrylic esters **1–16** will be described in the full publication dealing with the photochemistry of these compounds. The model esters **19–29** and ester **17** were prepared as follows by way of the Emmons reaction,[12] employing various modifications, as stated in each case.

Ethyl 3,4-dimethyl-2-pentenoate (20), bp 80° (20 mm), was obtained in 75% yield after 24 hr in refluxing glyme. The ester mixture contained 10% of the *cis* isomer **(21)** which was readily separated by vapor phase chromatography. **Ethyl 2,4-dimethyl-2-pentenoates (22 and 23),** bp 94° (40 mm), were formed in 13% yield in a ratio of approximately 1:3 from the reaction of the sodium salt of triethyl phosphonopropionate[30] with isobutanal, in refluxing glyme over a period of 2 days. The two isomers were readily separated by vapor phase chromatography and their geometry was ascertained by the nmr spectral features reported in Table I. In addition, the isopropyl proton was characteristically shifted to lower field in isomer **23** from that in isomer **22**. **Ethyl 2,3,4-trimethylpentenoates (24 and 24),** bp 86–90° (38 mm), lit.[31] bp 78–86° (20 mm), were formed in 27.5% yield in a ratio of 1:4 from the reaction of triethyl phosphonopropionate and methyl isopropyl ketone in refluxing glyme over a period of 3 days. The two isomers were separated by vapor phase chromatography and their geometry was determined by nmr spectral analysis (*cf.* Table I). **Ethyl 3-isopropyl-4-methyl-2-pentenoate (26),** bp 90° (40 mm), was obtained in approximately 10% yield from the reaction in refluxing glyme over a period of 1 week. **Ethyl 3,4,4-trimethyl-2-pentenoate (27),** bp 103–105° (30 mm), lit.[32] bp 80–83° (12 mm), was formed in 73.4% in refluxing glyme for a period of 12 hr in the presence of excess ketone. The yields were inferior (59%) when no excess was employed.

***cis*-Ethyl 4-Methyl-2-pentenoate (19).** The *trans* ester **18**[12] was photochemically isomerized in ether solution to the *cis* ester. This isomerization was accompanied by β,γ isomerization, but the *cis* ester **19** exhibited a much lower retention time on a 20% Carbowax column and could be conveniently trapped, while the *trans* ester and the β,γ isomer had identical retention times.

***cis*-Ethyl 3,4,4-trimethyl-2-pentenoate (28)** was formed only in very small amounts in the Emmons reaction leading primarily to the *trans* ester **27**, and separation by vapor phase chromatography was difficult. It could be obtained readily upon photolysis of the *trans* ester. The trans ester (10 g) in ether (125 ml) was irradiated for 150 min with a Hanovia 450-W immersion lamp employing a Vycor filter. This time interval led to the establishment of a *cis–trans* photostationary state in a ratio of 27:73, while irreversible photoproducts were formed only to the extent of 4%. Fast distillation of the photomixture provided early fractions enriched in *cis* isomer (up to 70% *cis*). Final purification, resulting in pure *cis* isomer **28**, was accomplished by glpc separation on a 5-ft Dow 710 column.

Ethyl 6,6-Dimethyl-2,4-heptadienoate (29). The sodium salt of triethyl phosphonocrotonate (Aldrich Chemical) was generated by the reaction of triethyl phosphonocrotonate (10 g, 0.04 mol) with sodium hydride dispersion (2.34 g) in cooled glyme (100 ml), followed by addition of pivalaldehyde (4.2 g, 0.049 mol, 20% excess) which resulted in a slight rise in temperature. The solution was reacted at 40° for 1 hr. Work-up in the usual manner resulted in a 50.5% yield (3.7 g) of ester **29**, bp 127–129° (28 mm). Vpc analysis indicated the presence of primarily one isomer, whose nmr spectrum exhibited complex absorptions at τ 2.6–3.1 (one proton), 3.9–4.5 (three protons), quartet at 4.9 (two protons), triplet at 8.75 (three protons), and singlet at 8.90 (nine protons), compatible with the *trans–trans* geometry.

Ethyl 5-Cyclopropyl-2,4-heptadienoate (17). Approximately 0.5 g of impure cyclopropanecarboxaldehyde was treated with a large excess of the sodium salt of triethyl 4-phosphonocrotonate, as in the preparation of **29**, followed by reaction at room temperature for 5 hr. Work-up of the reaction afforded an apparent high yield of crude product which by vapor phase chromatographic analysis was shown to be quite pure. Analytically pure samples were obtained by trapping on a 10-ft 20% Carbowax column. The nmr spectrum (CCl_4) exhibited absorption corresponding to the β proton (deshielded by a carbethoxy group) as a doublet of doublets (at τ 2.9, complex absorption corresponding to three vinyl protons in the region τ 3.6–4.6, a quartet (two protons) at 4.9, a triplet (three protons) at 8.7, and complex absorption corresponding to five protons between 9 and 9.7.

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(28) R. Hoffman, *Tetrahedron Letters*, 3819 (1965).

(29) Mass spectral molecular weight determinations were obtained for all new compounds reported here.

(30) See Table I, footnote *k*.

(31) H. Vieregge, H. M. Schmidt, J. Renema, H. J. T. Bos, and J. F. Arens, *Rec. Trav. Chim.*, **85**, 929 (1966).

(32) R. Heilmann and R. Glenat, *Bull. Soc. Chim. France*, 1586 (1955).