Photochemistry of α,β-Unsaturated Esters. VII. The Photolytic Behavior of Vinylcyclopropanecarboxylates[1]

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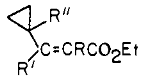
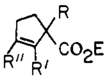
Abstract: Upon direct photolysis esters **1–6** undergo the following reactions: fragmentation to carbenes (followed by their collapse to allenes, furans and cyclopropenes), rearrangement to cyclopentenes and ring expansion to bicyclo[2.1.0]pentanes. Ring opening to dienic esters and deconjugation, a reaction characteristic of simple α,β-unsaturated esters, are not important general pathways. In methanol-O-*d* double bond migration in **2** to give ethyl 3-cyclopropyl-3-butenoate (**26**) becomes the prominent reaction course. Sensitized photolyses yield only cyclopentenes. The photolytic course is strongly influenced by double bond substituents. Possible conformational origins of this effect and other mechanistic aspects of these reactions are considered.

The photochemical reactions of simple cyclopropane derivatives have been recognized to be those occurring with scission of one or two of the strained bonds, in accord with theoretical predictions.[2] Among the structural consequences of this behavior which have been encountered in simple cyclopropane derivatives are geometrical isomerization,[3] ring opening to olefins,[3j,4] fragmentation to carbenes,[5] and when conjugated with an olefinic bond, rearrangement to cyclopentenes,[6] the photochemical counterpart of the familiar thermal vinylcyclopropane rearrangement.[7]

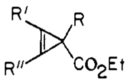
As part of our inquiries into the photolytic behavior of α,β-unsaturated esters, we have investigated the chemical response to ultraviolet radiation of cyclopropyl olefinic esters. In preliminary reports[8,9] we have communicated that this system is exceptionally reactive, undergoing manifold photochemical transformations, unique among cyclopropyl compounds. In addition to the reactions enumerated above,[10] we uncovered the first example of a novel ring expansion reaction affording bicyclo[2.1.0]pentanes. Because of the behavioral versatility of cyclopropane in this chemical environment, an excellent opportunity presented itself for an investigation of stereoelectronic factors, which determine the partitioning of the excited state of cyclopropane into various chemical pathways. To this end we have scrutinized in detail the photochemical behavior of esters **1–6**.



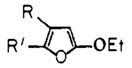
1, $R = R' = R'' = H$
2, $R = R'' = H; R' = CH_3$
3, $R = R' = CH_3; R'' = H$
4, $R' = R'' = H; R = CH_3$
5, $R = H; R' = R'' = CH_3$
6, $R = R'' = H$; R' = cyclopropyl



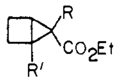
7, $R = R' = R'' = H$
8, $R = R'' = H; R' = CH_3$
9, $R = R' = CH_3; R'' = H$
10, $R' = R'' = H; R = CH_3$
11, $R = H; R' = R'' = CH_3$
12, $R = R'' = H$; R' = cyclopropyl
13, $R = R'' = H$; R' = propenyl



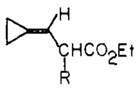
14, $R = R'' = H; R' = CH_3$
15, $R = R' = CH_3; R'' = H$
16, $R = CH_3, R' = R'' = H$
17, $R = H, R' = R'' = CH_3$
18, $R = R' = H$; R'' = cyclopropyl



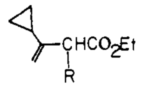
19, $R = R' = H$
20, $R = CH_3; R' = H$
21, $R = H; R' = CH_3$



22, $R = CH_3; R' = H$
23, $R = R' = CH_3$



24, $R = H$
25, $R = CH_3$



26, $R = H$
27, $R = CH_3$

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(1) Paper VI in this series: M. J. Jorgenson, *J. Am. Chem. Soc.*, **91**, 198 (1968).

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

(3) For recent examples, see (a) D. W. Setzer, B. S. Rabinowitch, and E. G. Spittler, *J. Chem. Phys.*, **35**, 1840 (1961); (b) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964); (c) H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 954 (1968); (d) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, 90, 4892 (1968); (e) J. E. Bell, *ibid.*, **87**, 4966 (1965); (f) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, 86, 2532 (1964); (g) G. S. Hammond and R. S. Cole, *ibid.*, **87**, 3256 (1965); (h) S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, *2957* (1968); (i) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); (j) G. W. Griffin, E. J. O'Connel, and H. A. Hammond, *ibid.*, **85**, 1001 (1963); (k) W. G. Brown and J. F. Neumer, *Tetrahedron*, **22**, 473 (1966); (l) B. Nann H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **48**, 1680 (1965).

(4) (4) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963); (b) L. D. Hess and J. N. Pitts, *J. Am. Chem. Soc.*, 76, 485 (1954), **89**, 1973 (1967); (c) L. D. Hess, J. L. Jacobson, K. Schaffner, and J. N. Pitts, Jr., *ibid.*, **89**, 3684 (1967); (d) R. E. K. Winter and R. F. Lindauer, *Tetrahedron Letters*, 2345 (1967); (e) W. G. Dauben and G. W. Shaffer, *ibid.*, 4415 (1967); (f) P. J. Kropp and H. J. Kraus, *J. Org. Chem.*, **32**, 4118 (1967); (g) P. J. Kropp. *Advan. Org. Photochem.*, **1**, 1 (1967).

(5) (a) D. B. Richardson, L. R. Durett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, *J. Am. Chem. Soc.*, **87**, 2763 (1965); (b) P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, 30, 539 (1965); (c) C. L. Currie, S. J. H. Okabe, and J. R. McNesby, *J. Phys. Chem.*, 67, 1494 (1963); (d) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (London), 1562 (1966); (e) M. Jones, Jr., W. H. Sachs, A. Kulczycki, Jr., and F. J. Waller, *J. Am. Chem. Soc.*, **88**, 3167 (1966); (f) M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6798 (1967).

(6) (a) P. J. Kropp, *ibid.*, **89**, 1126 (1967); (b) M. Jones, *ibid.*, **89**, 4237 (1967); (c) H. Prinzbach and E. Druckey, *Tetrahedron Letters*, 2959 (1965); (d) for a review, see R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

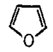
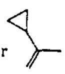
(7) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147 (1966), and references therein.

(8) M. J. Jorgenson and C. H. Heathcock, *J. Am. Chem. Soc.*, **87**, 5264 (1965).

(9) M. J. Jorgenson, *ibid.*, **88**, 3463 (1966).

(10) Geometrical isomerization and other consequences of ring substitution will be considered in a later publication.

Table I. Product Distribution from Photolyses of Esters **1–6**

Compd					 or 	Acyclic products	Isolated yields, %
1[a]	**7** (50%)		**19** (20%)		**24** (10%)	*b*	*b*
1[c]	**7** (23%)		Traces		**24** (62%)	Ethyl 3,4-hexadienoate (**34**) (11%), ethyl 3,5-hexadienoate (**33**), and ethyl 2,3-butadienoate (3%)	30
2[a,d]	**8** (70%)	**14** (8%)	**20** (2.6%)		**26** (17%)	*cis*- and *trans*-ethyl 3-methyl-3,5-hexadienoate (3.5%)	60
3[a,e]	**9** (10%)	**15** (24%)[f]		**22** (48%)	**27** (10%)	*g*	48
4[c,h]	**10** (6%)	**16** (25%)		**23** (14%)	**25** (20%)	Ethyl 2-methyl-2,4-hexadienoate and ethyl 2-methyl-3,4-hexadienoate (15%); *cis*- and *trans*-ethyl 2-methyl-2,5-hexadienoate (13%); two unidentified dienic esters (10%); ethyl 2-methyl-2,3-butadienoate (5%)	22
5[a]	**11** (60%)	**17** (40%)					60
6[a]	**12** (88%) **13** (12%)	**18** (traces)					67

[a] Ether. [b] 0.5-g scale, yields not obtained and minor products not identified. [c] Hexane. [d] Product **20** not formed in hexane or methanol, more **26** and acyclic products formed in methanol. [e] Similar distribution of products in hexane, benzene, or methanol; yields are poor in the latter solvent. [f] When corrected for the amount of cyclopropane ester formed from reduction of **15**, this value is raised to about 32%. [g] Minor amounts of other products, probably acyclic, were indicated by vapor phase chromatography, but were not characterized. [h] Similar product distribution in ether.

Results

Ester **1–6** possess strong $\pi \rightarrow \pi^*$ absorption maxima ranging from 217 to 250 mμ; these maxima incorporate auxochromic effects exerted by the cyclopropyl group, when compared to the appropriate alkyl group, ranging from -3.5 to $+26$ mμ.[11] The weak $n \rightarrow \pi^*$ transition, expected to lie in the 240-mμ region,[12] is occluded by the strong $\pi \rightarrow \pi^*$ excitation in all cases. Geometrical isomerization, which has been noted to be an efficient process in other systems,[13] proceeded much faster, by a factor of at least 10, than irreversible transformation to product. Product origin from stereochemically distinct ground states, or from individual electronic excited states of a discrete electronic configuration, cannot be ascertained experimentally for these reasons.

Irradiations were generally not carried to completion, as some of the photoproducts were found to be thermally and/or photochemically labile. Yields could be maximized when the irradiation was arrested at the 50–75% conversion state and starting material was recovered. Structure and distribution of products, as well as total yields of isolated material, are compiled in Table I. All photolyses were conducted under similar conditions, employing a Hanovia 450-W lamp and Vycor filter. The effect of variation of reaction conditions will be detailed separately.

Independent syntheses established the structures of cyclopentenecarboxylates **9**[14] and **10**.[15] Ester **8** was obtained from the thermal vinylcyclopropane rearrangement of **2**. Structures for esters **7**, **11**, **12**, and **13** follow by analogy from their origin, and from their distinctive spectral properties, which resemble those of esters **8**, **9**, and **10**. Structural assignment to cyclopropene ester **17** was secured by spectral comparison with an authentic sample.[16] Ester **14** was hydrogenated in the presence of palladium on charcoal, furnishing solely ethyl *cis*-2-methylcyclopropanecarboxylate; the latter was prepared by an unambiguous route.[17] Structures for cyclopropene esters **15** and **16** were adduced from their characteristic spectra (Table II). These include the substituent sensitive "double bond stretching" vibration occurring at high frequency[18] and the low field vinyl proton nmr absorption, both typical for cyclopropenes. Cyclopropene **15** was hydrogenated in the presence of palladium on charcoal, providing ethyl *trans*-1,2-dimethylcyclopropanecarboxylate, with less than 5% of the *cis* isomer formed. Only trace amounts of **18** were formed in the photolysis of **6**; its presence in the product mixture was inferred from the 1800-cm^{-1} vibration in the infrared spectrum.

The 2-ethoxyfurans **19–21** exhibited distinctive nmr spectral features (Table III) which could be utilized for structure assignment. Furan **19** was synthesized by an established route.[19] Furan **21** was prepared by pyrolysis of the known 2-methyl-2,5-diethoxydihydrofuran,[20] in order to rule out its presence as a photoproduct of ester **2**. The nmr spectra of **20**, in comparison with those of **19** and **21**, clearly permit the assignment of **20** as 4-methyl-2-ethoxyfuran.

Analogous to the conversion of **3** to **22**,[9] ester **4** was found to yield the two geometrical isomers of bicyclo-

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

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

(13) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(14) R. Granger and H. Techer, *Compt. Rend.*, **250**, 1282 (1960).

(15) C. Ounannes, M. Dvolaitzky, and J. Jacques, *Bull. Soc. Chim. France*, 776 (1965).

(16) R. K. Armstrong, *J. Org. Chem.*, **31**, 619 (1966). We thank Dr. Armstrong for providing us with the infrared spectrum of ester **17**.

(17) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **82**, 2372 (1960). We are indebted to Professor Applequist for furnishing us with a sample of *cis*-2-methylcyclopropanecarboxamide, from which the ethyl ester was prepared.

(18) Strong dependence of this vibration on methyl substitution has been noted before: (a) G. Closs, *Advan. Alicyclic Chem.*, **1**, 73 (1966), and references therein; (b) E. Ciganek, *J. Am. Chem. Soc.*, **88**, 1979 (1966); (c) H. Lind and A. J. Deutschman, Jr., *J. Org. Chem.*, **32**, 326 (1967).

(19) D. G. Manley and E. D. Amstutz, *ibid.*, 21, 516 (1956).

(20) J. Fakstorp, D. Raleigh, and L. E. Schniepp, *J. Am. Chem. Soc.*, **72**, 869 (1950).

Table II. Spectral Characteristics of Cyclopropene Carboxylates

Compd	$\nu^{CCl_4,b}$ cm^{-1}	Proton chemical shift, τ CCl$_4$^{a}			
		Vinyl proton	Allylic CH$_3$	C$_1$ proton	C$_1$ CH$_3$
14	1820	3.75 (m)	7.85 (d, J = 1.2)	8.0 (d, J = 1.6)	
15	1800	3.67 (broad, s)	7.95 (d, J = 1.4)		8.75 (s)
16	1720	3.08 (s)			8.68 (s)
17	1920		7.95 (s)	8.10 (s)	

[a] s = singlet, d = doublet, m = multiplet. [b] These characteristic cyclopropene frequencies have been interpreted as arising from coupling of skeletal with ring substituent vibrations.[18a]

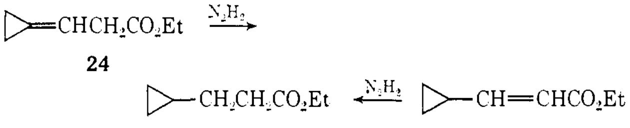
Table III. Nmr Spectra of 2-Ethoxyfurans

Compd	τ, ring protons^a	Assignment	τ ring CH$_3$^{b}
Parent (**19**)	3.2 (d of d, $J \sim$ 1 and 2 cps)	H$_5$	
	3.85 (d of d, $J \sim$ 2 and 3 cps)	H$_4$	
	4.93 (d of d, $J \sim$ 1 and 3 cps)	H$_3$	
4-Methyl (**20**)	3.50 (m)	H$_5$	8.08 (unsym d, $J \sim$ 1.5 cps)
	5.10 (d, $J \sim$ 1 cps)	H$_3$	
5-Methyl (**21**)	4.35 (m)	H$_4$	7.90 (unsym d, $J \sim$ 1.5 cps)
	5.15 (d, $J \sim$ 3 cps)	H$_3$	
3-Methyl	$\sim$4.2 (d, $J \sim$ 2 cps)^c	H$_4$	$\sim$8.0 (s)^c
	$\sim$3.2 (d, $J \sim$ 2 cps)^c	H$_5$	

[a] The following coupling constants can be derived from these data: $J_{H_3,H_4} \sim$ 3 cps, $J_{H_4,H_5} \sim$ 2 cps, $J_{H_3,H_4} \sim$ 1 cps; these values are similar to those reported for furan [G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.*, **84**, 583 (1962)], where corresponding values are 3.3, 1.75, and 0.85 cps; s = singlet, d = doublet, m = multiplet. [b] The following long-range coupling constants involving methyl substituents are evident: $J_{H_5,Me_4} \sim$ 1 cps, $J_{H_4,Me_5} \sim$ 1.5 cps, $J_{H_3,Me_5} \sim$ 0. [c] Predicted values, based on the analysis of nmr spectra of furans **19–21**.

[2.1.0]pentane **23**. The two isomers of **22** and **23** were formed photochemically in nearly a 1:1 ratio. Stereochemical assignments to these isomers have been made[21] and their thermal properties studied by us.[21,22] Both isomers of **22** were found to be hydrogenated stereoselectively to the isomeric ethyl 1,2-dimethylcyclopentanecarboxylates,[23] whose stereochemistry we have unambiguously assigned.[24]

Methylenecyclopropane esters **24** and **25**, as well as 3-cyclopropyl-3-butenoates **26** and **27**, were characterized spectrally. Ester **24** was hydrogenated in the presence of diimide to ethyl 3-cyclopropylpropanoate (28);[25] the latter was also prepared in a similar fashion from ester **1**.[26]



Acyclic products from the irradiation of esters **1**, **2**, and **4** were accorded structure assignments on the basis of spectral criteria (*cf.* Experimental Section). Allenic[27] or conjugated environments for double bonds could be deduced from characteristic infrared double bond stretching frequencies and from the chemical shift and coupling behavior of protons in the nmr spectrum. The formation of ethyl 2-methyl-2,3-butadienoate as a photolysis product of **4** could be confirmed by comparison of the infrared spectra of an isolated sample of this ester with that of authentic material.[28]

Yields of cyclopropenes, ethoxyfurans, and allenic esters diminished with time during the irradiation. The largest conversion to these products was achieved when irradiation was conducted on a small scale, so that total irradiation time was kept short. Since the products were not isolated from these small-scale irradiations, the maximum attainable yields of labile products from these irradiations are not known. It is significant that in all irradiations in which fragmentation is a dominant pathway, total yields of isolated products were low. Unsubstituted 2-cyclopropenecarboxylates are unknown.[29] For this reason, yields of monomeric products which should include ethyl 2-cyclopropenecarboxylate were very low in the irradiation of ester **1**; the material balance was compensated for by the formation in high yield of polymeric material. In hexane the amount of ethylene trapped[26] corresponded to a fragmentation pathway taken by **1** to the extent of 2%, predicting 6–7% of fragmentation products in the isolated material. Comparison of the amount of ethylene trapped in the photolysis of ester **4** with the amount of cyclopropene **16** isolated in this reaction revealed that less than half of the expected ethylene was trapped by this method. The conclusion can be drawn that at least 4% of ester **1** reacted *via* a fragmentation pathway, and probably more, since cyclopropene **16** is not immune to further reaction under the photolysis conditions; isolated yields are most certainly lower than actual yields. Inspection of Table I reveals that the highest yields of photoproducts are obtained in those photolyses which do not proceed significantly

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(21) M. J. Jorgenson, T. J. Clark, and J. Corn, *J. Am. Chem. Soc.*, 90, 7020 (1968).

(22) M. J. Jorgenson and T. J. Clark, *ibid.*, 90, 2188 (1968).

(23) M. J. Jorgenson, *Tetrahedron Letters*, 4577 (1968).

(24) M. J. Jorgenson, A. J. Brattesani, and A. F. Thacher, *J. Org. Chem.*, 34, 1103 (1969).

(25) Mr. John Sieh carried out this experiment.

(26) This aspect of the work was carried out with assistance from Mr. Brattesani.

(27) Terminal allenic esters possess a characteristic doublet at 1930 and 1960 cm^{-1} and absorption at 850 cm^{-1} [J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, 22, 207 (1957); D. R. Taylor, *Chem. Rev.*, 67, 317 (1967)]. These absorptions were evident for the esters assigned to be ethyl 2,3-butadienoate and ethyl 2-methyl-2,3-butadienoate. Nonterminal allenes possess only one absorption band in the 1900–2000-cm^{-1} region.

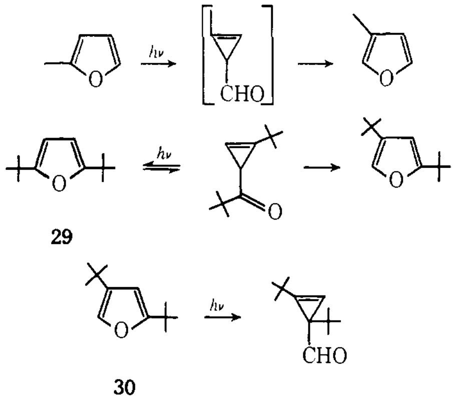
(28) We thank Dr. Colin Day of Oxford University for kindly furnishing us with an infrared spectrum.

(29) The methyl ester has been trapped and hydrogenated at low temperatures [W. von E. Doering, G. Laber, R. Bonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956)].

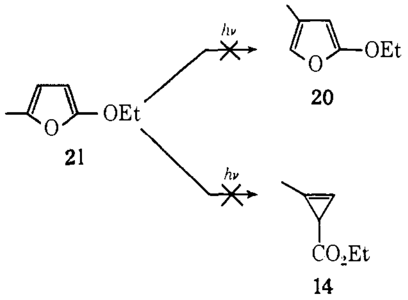
via fragmentation (*e.g.*, ester **2**) or which yield relatively stable cyclopropenes (*i.e.*, esters **3** and **5**).

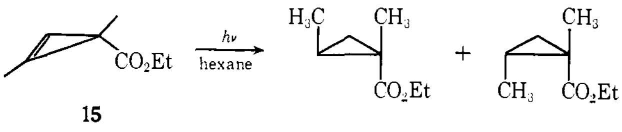
Discussion

Primary Origin of Photoproducts. The selectivity with which either furan or cyclopropene products are formed from esters **1**, **3**, **4**, and **5** argues against a photointerconversion of these products. However, it was important to establish that ethoxyfurans **19** and **20** and cyclopropenyl esters **14–18** were generated directly from the starting ester, in view of reported cases where photochemical interchanges between furan and cyclopropene derivatives have been observed.[30-32] For example, it has been reported that 2-methylfuran undergoes a photorearrangement in the vapor phase to 3-methylfuran,[30] *via* a postulated 2-methyl-2-cyclopropenecarboxaldehyde. More relevant to our situation, van Tamelen and Whitesides[32] have noted a similar rearrangement in the liquid phase for *t*-butylfurans, **29** and **30**, and proof for the intermediacy of cyclopropenes was presented.

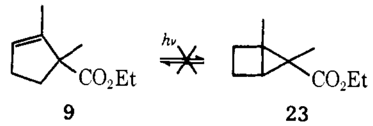


When 5-methyl-2-ethoxyfuran (**21**), λ_{max} 225 mμ, was irradiated in hexane with a Vycor filter, it did not rearrange to furan **20** nor to the cyclopropene ester **14**, expected in analogy with the work on *t*-butylfurans.[32] Only polymeric material was obtained upon prolonged irradiation. Cyclopropene **15** (ϵ *ca.* 1000 at 210 mμ), on the other hand, did react to furnish two new products, formed in approximately equal amounts; these were shown to be identical with the products of hydrogenation of the cyclopropene **15**, namely, *cis*- and *trans*-ethyl 1,2-dimethylcyclopropanecarboxylate.[33,34] The possibility that the allenic esters ethyl 2,3-butadienoate and ethyl 2-methyl-2,3-butadienoate were derived photochemically from cyclopropene precursors was not probed, but analogy for such a reaction exists in the case of ketones.[32] Thermal interconversion between allenic, cyclopropene, and furan products during photolysis or during isolation was ruled out.

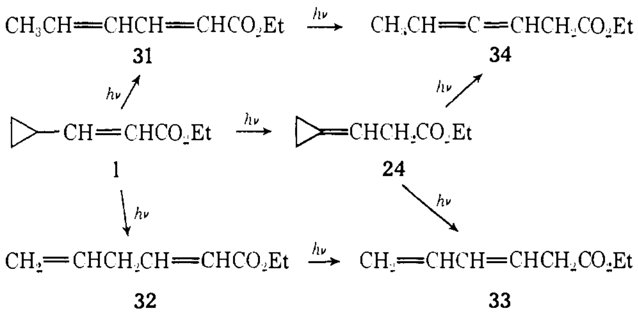




Direct photolysis in hexane (Vycor filter) of cyclopentene ester **9** led only to slow polymerization. Under these conditions bicyclo[2.1.0]pentane **23** reacted slowly to furnish a number of unidentified products in low yield, none of them being cyclopentene **9**. In view of these results, it is unlikely that cyclopentenes are formed from bicyclo[2.1.0]pentanes, or that the converse is true. These conclusions are also supported by the fact that bicyclo[2.1.0]pentanes are formed rather selectively, being conspicuously absent in the photolysis of esters **1**, **2**, **5**, and **6**.



Acyclic products are most likely formed from secondary photolytic processes, involving the intermediacy of conjugated dienic esters. For example, a two-photon pathway *via* esters **31** and **32** is logical for the formation of the acyclic esters ethyl 3,5-hexadienoate (**33**) and ethyl 3,4-hexadienoate (**34**) from ester **1**. Less likely, product formation might arise from photolysis of ester **24**. In a control experiment, the related ester **25** was found not to furnish ethyl 2-methyl-3,4-hexadienoate and ethyl 2-methyl-2,5-hexadienoate upon irradiation.



The formation of dienic esters **31** and **32** involves photolytic cleavage of the cyclopropane ring, a well-precedented reaction.[4] The subsequent deconjugation reactions of **31** and **32** are examples of the familiar iso-

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[30] H. Hiraoka and R. Srinivasan, *J. Am. Chem. Soc.*, 90, 2720 (1968).

[31] R. Srinivasan, *ibid.*, 89, 1758, 4812 (1967).

[32] E. E. van Tamelen and T. H. Whitesides, *ibid.*, 90, 3896 (1968).

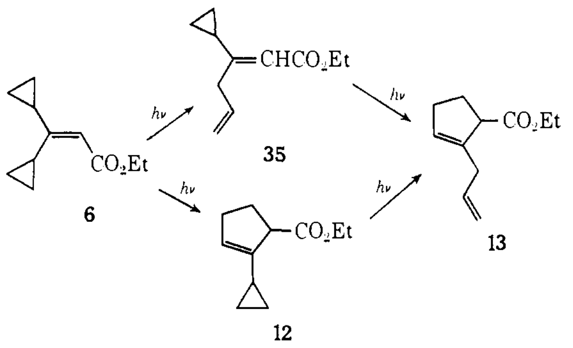
[33] The two isomers could be readily distinguished by their nmr spectra. Thus, the *cis* isomer exhibited absorption due to one proton at τ 9.75, while the *trans* isomer showed absorption due to one proton at a lower field at τ 9.28. In the complex τ 9 region also, the spectra were strikingly similar to those published for the corresponding *cis* and *trans* methyl esters [T. V. Van Auken ad K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, 84, 3736 (1962)] whose stereochemical assignment was subsequently corroborated by an independent method [D. E McGreer, N. W. K. Chiu, and R. S. McDaniel, *Proc. Chem. Soc.*, 415 (1964)]. The characteristic higher field chemical shift of one of the ring methylene protons in the *cis* compared to the *trans* isomer in 1,2-dimethylcyclopropanes bearing an electron-withdrawing substituent at C_1 has been observed by us in a number of other systems (unpublished results from these laboratories).

[34] (a) At the temperatures of their formation it is unlikely that cyclopropenes convert thermally to ethoxyfurans, as has been found for phenyl-substituted cyclopropenyl esters [R. Breslow and D. Chipman, *Chem. Ind.* (London), 1105 (1960)]. Further irradiations at Dry Ice temperatures furnished a higher percentage of furan product than was found at room temperatures. (b) For analogy of such photochemical reductions, see P. J. Kropp and H. J. Kraus, *J. Am. Chem. Soc.*, 89, 5199 (1967).

merization reaction of α,β-unsaturated esters to β,γ-unsaturated esters, which we have found to be general for such esters.[35,36] This photochemical deconjugation also embraces reactions which occur with the abstraction of cyclopropyl (*e.g.*, **1** → **24**) or vinyl hydrogens. As an example of the latter, we have found that ethyl 6,6-dimethyl-2,4-heptadienoate is smoothly transformed into its allenic isomer.[37]

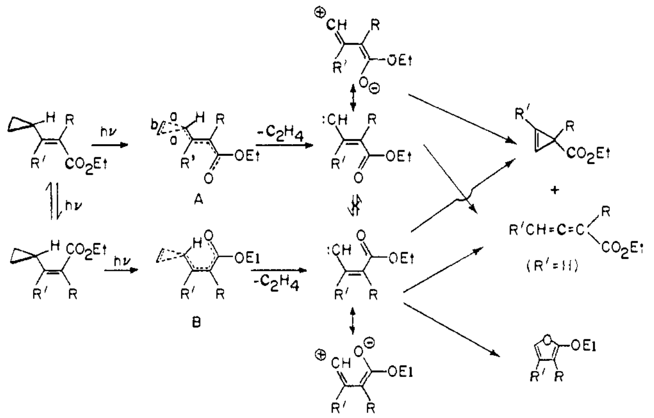
$$(CH_3)_3CCH{=}CHCH{=}CHCO_2Et \xrightarrow{h\nu} (CH_3)_3CCH{=}C{=}CHCH_2CO_2Et$$

The origin of ester **13** is uncertain. It could be formed from a subsequent reaction of ester **12**, or might be a photolysis product of the intermediate ester **35**, formed from a cyclopropane cleavage reaction of ester **6**. In the latter case, ester **35** must necessarily react as soon as it forms, since no **35** is detectable during the reaction of **6**. In view of the low efficiencies with which cyclopropylacrylic esters **1**–**6** react, it is highly unlikely that ester **35** constitutes an exception. Irradiation of ester **12** led to a slow consumption of starting material and formation of polymeric products only.



Photochemical Fragmentation. This mode of reaction is surprisingly general for cyclopropylacrylic esters.[38] As Table I indicates, cyclopropene products are formed more frequently than furans, and allenes are produced only when they possess a terminal double bond. The simplest pathway which gives rise to these products is depicted in Scheme I, where symmetrically bisected *s-trans* conformation[39] A (*trans* ester) and B (*cis* ester) have both cyclopropane bonds weakened in the excited state, because of favorable overlap of the orbitals constituting these bonds with the π systems. Loss of ethylene (trapped as the dibromide in our experiments) and formation of a vinylogous carbethoxycarbene is an expected consequence. The two carbenes formed from the *cis* and *trans* isomers have different geometries. If their lifetime is short, rotation about the central bond is unlikely,[41] so that each carbene should give rise to a discrete set of products. The carbene derived from excited state A can insert into the double bond, to give cyclopropene, as well as into the vinyl C–H bond (R′ = H) to give allene ester,[42] while carbene derived from B can afford both of these products as well as ethoxyfuran, derived from insertion into the ester carbonyl.

Scheme I



It is worth noting that the fragmentation reaction takes exclusively that course which leads to ethylene and a resonance stabilized carbene. No fragmentation into methylene and a dienic ester, a pathway analogous to the formation of methylene from arylcyclopropanes,[5a] is observed. The direction of bond scission follows from the geometry of excited states A and B, where bonds a and not a and b, as would be required for fragmentation into methylene, are weakened.

The preference for the formation of cyclopropenes over that for furans is puzzling, since the photostationary state favors both geometrical isomers to similar extents in all irradiations. It is possible that the substitution pattern about the double bond in the starting material governs the fate of the carbene derived from excited state B. Esters **3**, **4**, and **5** would lead to furans possessing at least two substituents on adjacent carbons, so that the carbene may prefer, for steric reasons, to collapse to cyclopropene instead.

Solvent effects play an important role on the course of the fragmentation reaction. The enhanced incursion of the fragmentation pathway for **1** in ether to give furan is striking. Sensitized photolysis did not lead to fragmentation products. These results are consonant with previous conclusions[5a] that methylene generated from photofragmentation of arylcyclopropanes is extruded as a singlet, and hence from a singlet excited state of the cyclopropane precursor.

Vinylcyclopropane Rearrangement. The formation of cyclopentene products is a general reaction of esters **1**–**6**, though the facility with which these are formed varies significantly with structure. The amounts of cyclopentene products formed are high for esters **1**, **2**, **5**, and **6**, low for esters **3** and **4**. The ability to undergo photochemical vinylcyclopropane rearrangement is clearly related to the presence of an α-methyl substituent in the cyclopropylacrylic ester.

The pronounced effect of a *cis* substituent in vinylcyclopropane on the energetics of the thermally induced

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[35] M. J. Jorgenson, *Chem. Commun.*, 137 (1965).

[36] M. J. Jorgenson and L. Gundel, *Tetrahedron Letters*, 4991 (1968).

[37] We thank Mr. A. Miller for the preparation of this ester and Mr. D. Dahlhauser for conducting the photolysis.

[38] It has also been found to take place in ring-substituted cyclopropylacrylic esters, though this reaction mode is not a general one in these cases (unpublished results from these laboratories).

[39] The *s-cis* conformation is not appreciably populated in vinylcyclopropane[40] and we have shown[11] that these conformations are unimportant for cyclopropylacrylic esters, as well.

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

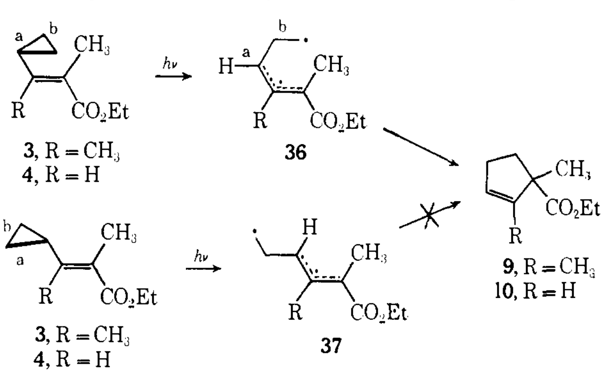
[41] Simple carbenes extruded in similar photofragmentations have been shown to react as singlets[5a] so that these carbenes should be short-lived and thus incapable of undergoing restricted rotation.

[42] When reaction to give allene products requires insertion into a carbon–carbon bond, the expected allene is not formed. Insertion into carbon–carbon bonds by carbenes is not a general pathway [W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964)].

rearrangement to cyclopentene is a well-recognized phenomenon.[7,43] Steric interference to coplanarity of the intermediate *s-cis* diradical, and hence to its stabilization by resonance, adequately accounts for the absence of cyclopentene products in the pyrolysis of *cis*-2-substituted cyclopropylethylene derivatives. (The less energetic diradical of *s-trans* geometry will be unproductive toward cyclopentene formation, reverting to starting material or partaking of alternative reaction pathways.)

Related arguments can be developed to account for the unfavorable ring closure to cyclopentene encountered in esters **3** and **4**. In a diradical mechanism, diradical **36**, formed upon excitation of that conformer which approximated an *s-cis* geometry,[39] will close to cyclopentenes, while diradical **37**, derived from the symmetrical *s-trans* conformation, is unproductive. Interconversion between diradicals **36** and **37** is unlikely; allyl radicals are known to preserve their configuration.[44,45]

Although the stability arguments developed here are similar for both the thermal and photochemical rearrangement, a significant difference exists. While the facility of the thermal reaction will be a direct function of the energetics of the transition state, in the photochemical case the overriding factor, which may determine the partitioning of the photochemically excited molecule into this pathway, could be the ground-state conformer population of the molecule. Any diradical formed will have the same geometry as its ground-state precursor.[45] The proportion of photoproduct which will have the cyclopentene structure will therefore be directly related to the population of that conformer which can lead to diradical **36**. It is not known exactly what the conformational preference of cyclopropylacrylic esters is.[11,39] By analogy with conformational conclusions reached for vinylcyclopropane[40] and for some of its alkyl derivatives,[43] it is reasonable to assume that in most cyclopropylacrylic esters the conformational minima correspond also to the *s-trans* and a nonsymmetrical *s-cis* or *gauche* conformation with a dihedral angle between 70 and 80°. Only the *gauche* conformer can lead to cyclopentene products; as the simplest explanation of the α-methyl effect one could therefore invoke a decrease in the *gauche* conformer population for esters **3** and **4**.



3, R = CH_3
4, R = H

36

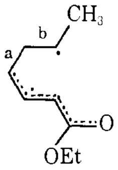
9, R = CH_3
10, R = H

3, R = CH_3
4, R = H

37

The question as to whether ring closure to cyclopentene is a concerted or a diradical process is an interesting and important one. There is little doubt that the thermal rearrangement proceeds *via* a diradical,[7,43] as is predicted by the simplest application of Woodward–Hoffmann rules[46] to sigmatropic shifts.[47,48] For a rearrangement treated as an electrocyclic reaction, it has been calculated[49] that a concerted process should also be forbidden. Since symmetry arguments are reversed for reactions occurring in the first excited state,[50] a concerted process, either sigmatropic or electrocyclic, should be permitted. Attempts to probe into this question by utilizing ring-substituted cyclopropylacrylic esters failed; double bond and ring *cis–trans* isomerization took place at a much faster rate than ring closure to cyclopentenes, so that the original stereochemistry was lost.[51] Since ring isomerization occurs *via* opening of bond a to a diradical (**36a**), this observation could be construed as an argument against the intervention of diradicals in cyclopentene formation.[52] However, an alternative hypothesis, namely that diradical **36a** undergoes rotation around bond b and reclosure to the ring-isomerized starting material at a much faster rate than closure to cyclopentenes, is equally tenable.

Photosensitization produced only cyclopentene products.[53] Significantly, and in contrast to the direct photolysis, both esters **3** and **4** readily furnished cyclopentenes **9** and **10**, respectively.



36a

Photochemically induced vinylcyclopropane rearrangements are common in cyclic systems.[6d] Vinylcyclopropane[54] and (2,2-dimethyl-1-phenylcyclopropyl)-2-methyl-1-propene[55a] have been reported not to undergo a vinylcyclopropane rearrangement, so that our examples constitute the first cases of successful photochemical rearrangements brought about in flexible systems.

Ring Expansion to Bicyclo[2.1.0]pentanes. This pathway is highly selective, being followed only by esters

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(43) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem.*, **80**, 592 (1968).

(44) (a) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961); (b) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964).

(45) It is not certain that a photochemically generated allylic diradical will exhibit the same stereochemical stability as one which is produced thermally.

(46) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(47) Thermal sigmatropic 1,3 shifts will occur in a sterically prohibited antarafacial manner. However, since migration of a carbon bond is involved in cyclopentene formation, a suprafacial process with concomitant inversion at the migrating carbon is permitted.[48]

(48) J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5504 (1968).

(49) M. J. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

(50) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 396, 2511 (1965).

(51) Unpublished results from these laboratories.

(52) Related arguments concerning the thermal rearrangement have been presented [M. R. Willcott and V. H. Cargle, *J. Am. Chem. Soc.*, **89**, 723 (1967)].

(53) Photosensitization of the vinylcyclopropane rearrangement has been reported by Kropp[6a] in the case of $(+)$-2-carene-4α-methanol.

(54) J. Meinwald and G. W. Smith, *J. Am. Chem. Soc.*, **89**, 4923 (1967).

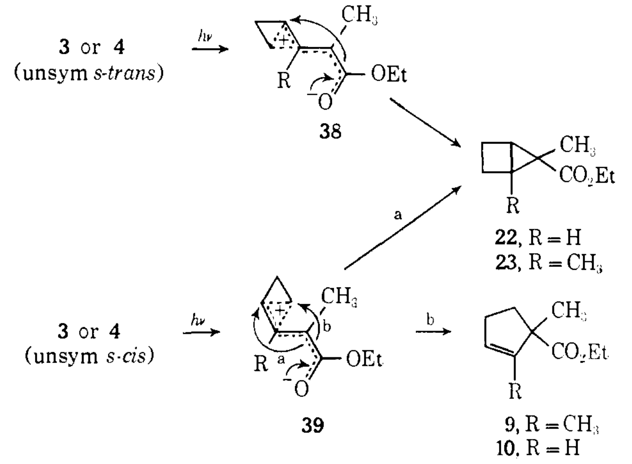
(55) (a) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5970 (1968). (b) Successive methyl substitution on the double bond of the cyclopropylacrylic ester chromophore has been shown[11] to diminish the auxochromic contribution of the cyclopropane ring. This effect is particularly evident in the case of ester **4**, where the bathochromic shift has decreased to 15 mμ from a value of 23 mμ in the parent **1**. A conformational interpretation for this effect has been advanced.[11]

3 and **4**. Photosensitization of **3** and **4**, under conditions where **23** proved to be photostable, while producing cyclopentenes **9** and **10**, failed to generate bicyclo[2.1.0]pentane products. The origin of bicyclo[2.1.0]pentanes **22** and **23** from the excited singlet state is implicated by these results.

In the previous section we have elaborated on the importance of ground-state conformer population in determining the structure and distribution of photoproducts. Two possible explanations can be devised to accommodate the high selectivity of bicyclo[2.1.0]pentane formation. If the effect of the α-methyl group is interpreted in conformational terms,[55b] and if it is a change in conformer population which causes the appearance of bicyclo[2.1.0]pentane products in **3** and **4**, then it is necessary to stipulate that the particular conformation which gives rise to these products is absent in esters **1**, **2**, **5**, and **6**. It was assumed above that cyclopropylacrylic esters exist in a conformational equilibrium which is qualitatively similar to that of simple vinylcyclopropanes. However, this analogy, because of the vastly different electronic structures of these two systems, need not be compelling.[56a] An additional conformer, of nonsymmetrical *s-trans* geometry, with a dihedral angle in the vicinity of 160°, is a reasonable postulate for esters **3** and **4**, since such a geometry minimizes the nonbonded interactions between the α-methyl group and the cyclopropylcarbinyl hydrogen present in the symmetrical *s-trans* conformations of esters **3** and **4**. This conformation sacrifices maximum conjugative overlap of the cyclopropane bonds, but still provides stabilization by unsymmetrical "participation" of one of the cyclopropane bonds in the ground and/or excited states. The formation of bicyclo[2.1.0]pentanes only from **3** and **4** *via* **38** is thus accountable.

The interpretation advanced above presupposes that bicyclo[2.1.0]pentanes and cyclopentenes have different conformational origins. In this scheme, cyclopentene could arise upon direct photolysis from the triplet state, whereas singlet states give rise to bicyclo[2.1.0]pentanes. Another interpretation, equally consonant with experimental facts, presumes that both products are derived in the direct photolysis from the same excited singlet state and that it is the fate of this common intermediate which is affected by the presence of the α-methyl group. If an energy barrier exists for the collapse to product, then the presence of the α-methyl substituent could serve to increase the activation energy to cyclopentene closure (path b in **39**) in **3** and **4** compared to **1**, **2**, **5**, and **6**, thereby causing bicyclo[2.1.0]pentane formation (path a in **39**) to become a competitive or alternative process.

The conformationally different species (**38** and **39**)[56b] which have been invoked in the two interpretations are stabilized by unsymmetrical participation of the cyclopropane ring; this depiction is akin to that employed in rationalizing the high reactivity of cyclopropylcarbinyl derivatives; special stability is derived from such nonclassical ions.[57] If we specify the $\pi \rightarrow \pi^*$ electronic configuration for the lowest singlet state,[58] the formation of vibrationally or electronically excited dipolar intermediates, which derive stabilization of the positive charge by the cyclopropane ring, is reasonable. Further reaction of the dipolar species formally corresponds to a cyclopropylcarbinyl → cyclobutyl rearrangement.[9,59] An $n \rightarrow \pi^*$ excited state would possess a cyclopropylcarbinyl carbon which is much less electron deficient than it is in the ground state, so that stabilization by cyclopropane would be relatively unimportant.[60]



Since our first report of the observation of the photochemical ring expansion of a vinylcyclopropane derivative, Kristinsson and Hammond[55] have noted that a more complex derivative, (2,2-dimethyl-1-penylcyclopropyl)-2-methylpropene undergoes, upon direct photolysis, rearrangement to 2,2,5,5-tetramethyl-3-phenylbicyclo[2.1.0]pentane.

Finally, attention should be drawn to the formal analogy of the ring closure modes of vinylcyclopropane to those of 1,3-dienes.[61] The formation of cyclobutenes bears mechanistic similarities to the formation of cyclopentenes. (The reported[62] inability of 1,1,3-trisubstituted 1,3-dienes to undergo this reaction is reminiscent of our *cis*-methyl effect in the ring closure to cyclopentene.[63]) The "bond switching" reaction leading to bi-

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(56) (a) The different magnitudes of the vicinal coupling constants between the β-vinyl proton and the cyclopropylcarbinyl proton in vinyl cyclopropanes and cyclopropylacrylic esters, of similar degree of substitution, attest to a different character of the conformational equilibrium in the two systems.[11] (b) These are depicted for the *trans* isomers only. The ratio of two geometrical isomers of 22 and 23 formed corresponds remarkably well to the photostationary ratio of the geometrical isomers of 3 and 4, implying that each geometrical isomer of the starting ester selectively gives rise to one of the two stereoisomers of bicyclo[2.1.0]pentanes.

(57) For a good summary, see H. G. Richey in "Carbonium Ions," Vol. 3, G. A. Olah and P. R. Schleyer, Ed., Interscience Publishers, Inc., New York, N. Y., 1969.

(58) The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorption bands are of comparable energies for all cyclopropylacrylic esters;[11] for esters 3 and 6 λ_{max} for $\pi \rightarrow \pi^*$ transitions probably correspond to lower energies than λ_{max} for $n \rightarrow \pi^*$ excitation.[12]

(59) Rearrangements *via* cyclopropylcarbinyl cations during photolysis have been invoked [H. E. Zimmerman, *Advan. Photochem.*, 1, 190 (1963)]. A nonclassical bicyclobutaonium ion was considered in the photochemical reaction of 2,3-homotropone [L. A. Paquette and O. Cox, *J. Am. Chem. Soc.*, 89, 5633 (1967)].

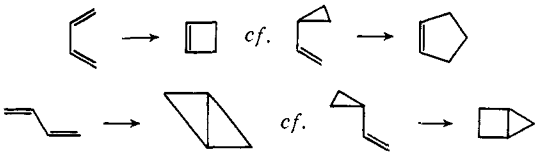
(60) In the same vein, the excited state leading to ethylene extrusion (Scheme I) can be envisaged to be of the $\pi \rightarrow \pi^*$ configuration, having its positive charge delocalized in a symmetrical nonclassical cyclopropyl cation.

(61) R. Srinivasan, *Advan. Photochem.*, 4, 113 (1966). In this comparison the cyclopropane ring is equated to a double bond, a very appropriate comparison because of the many similarities in the reactivity of these two functionalities.

(62) R. Srinivasan, *J. Am. Chem. Soc.*, 84, 4141 (1968).

(63) Recent work [A. A. Bothner-By and D. Jung, *ibid.*, 90, 2342 (1968); A. A. Bothner-By and D. F. Koster, *ibid.*, 2351 (1968)] on the conformational preference of 1,1,3-trisubstituted dienes has revealed that these exist primarily as skew conformers. This could then be the reason for the observed photochemical inertness of 2,4-dimethyl-1,3-pentadiene.[62]

cyclo[1.1.0]butanes is related to the formation of bicyclo[2.1.0]pentanes from vinylcyclopropanes.

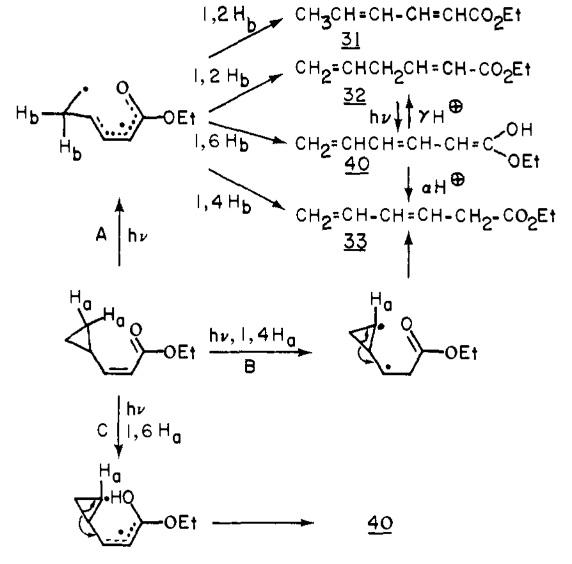


A dichotomy exists in the mechanistic interpretation of the origin of cyclobutenes and bicyclo[1.1.0]butanes. On the one hand both products have been rationalized as arising from the singlet excited states of *s-cis* and *s-trans* conformers, respectively;[62] on the other hand, it has been conjectured[64] that bicyclobutane products originate *via* a diradical mechanism, a concerted mode being considered improbably on orbital symmetry grounds. It is not clear whether orbital symmetry constraints permit a concerted mechanism for the formation of bicyclo[2.1.0]pentanes from vinylcyclopropanes, and whether a particular conformation is required for its formation.

Ring Cleavage. Cyclopropane ring opening is a familiar thermal and photochemical process. This reaction has received particular attention in the case of cyclopropyl conjugated ketones;[4b,c,e] the details of the photochemical ring opening mechanism have not been firmly established.

In a previous section we have advanced the interpretation that the acyclic dienic esters derived from the photolysis of ester **1** could be formed as secondary photoproducts *via* **31** and **32** or **24**. Other pathways, proceeding *via* distinctly different primary cleavage processes, can be envisaged; these are depicted for *cis* ester **1** in Scheme II. The first step in pathway A is part of the commonly accepted mechanism for the cleavage of cyclopropyl ketones.[4b,c] In the case of the *cis* ester **1** this diradical can react *via* four different routes: to give intermediate esters **31** or **32** *via* 1,2-hydrogen shifts, to give trienol **40** *via* a 1,6-hydrogen shift, or to furnish **33** directly *via* a 1,4-hydrogen shift. Two pathways (B and C) involve the abstraction, by the carbonyl and double bond, respectively, of a ring hydrogen.[65] The first of these leads directly to **33**, while the latter furnishes the trienol **40**. It should be noted that all of these pathways could take place concertedly; for mechanism B and C a specific conformation (probably-unsym *s-cis*) is required for the hydrogen abstraction reaction. It is evident that photoproducts need not arise from a two photon reaction, but can be generated directly from the cyclopropylacrylic ester *via* a one-photon pathway in all three reaction modes; those occurring with a 1,6-hydrogen shift will be sterically precluded in the *trans* esters.

Scheme II



The effect of structure on this photochemical pathway deserves comment. Acyclic esters are conspicuously absent in the photolysis of esters **5** and **6**, amount to but a few per cent of product in esters **2** and **3** but constitute a significant proportion of product in the case of esters **1** and **4**. Photosensitization of ester **4** yields no acyclic products.[66]

Photochemical Deconjugation. In striking contrast to simple α,β-unsaturated esters,[35,36] this isomerization reaction is found to be relatively unimportant in cyclopropylacrylic esters. Overwhelming preference for the abstraction of an allylic methyl, rather than cyclopropyl, hydrogen is manifested in esters **2** and **3**. When deconjugation is permitted only into the exocyclic position, methylenecyclopropane products are formed, as in **1** and **4**. Since the hydrogen abstraction reaction in α,β-unsaturated esters has been shown to occur stereospecifically from the excited singlet state of the *cis* isomer,[36,67] by analogy, the *cis* isomers of **1** and **4** are required for their transformation into **24** and **25**. Since this reaction occurs very efficiently in simple conjugated esters, but products from this reaction mode are not, with the exception of irradiation of **1** in hexane, prominently distributed among the photoproducts, it is tempting to suggest that cyclopropylacrylic esters react predominantly *via* a different excited state. From the absorption spectra of esters **1–6**,[11] it is evident that in contrast to simple α,β-unsaturated esters,[68] the two singlet states are close in energy. Different ordering of the two singlet states, as a function of solvent and substitution, is to be expected. The striking difference in product distribution observed for ester **1** in ether *vs.* hexane could thus be explained.

Deconjugations involving the abstraction of a non-allylic δ-hydrogens have been observed for simple α,β-unsaturated esters.[35] It was hoped that in the case of cyclopropylacrylic esters, as well, this reaction mode might be occurring as a competitive one to the unfavorable deconjugation into the exocyclic position. Such a reaction course would be expected to lead to bicyclo[1.1.1]butane products, *e.g.*, **41** from **1**; however, no bicyclo[1.1.0] products have yet been detected in the photolysis of any cyclopropylacrylic esters.

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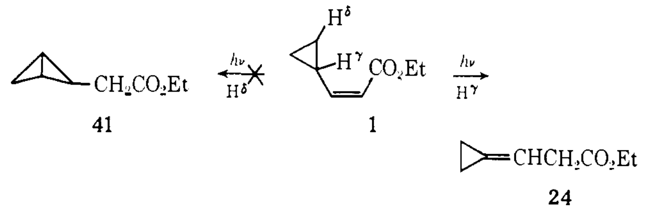
[64] R. Srinivasan, *J. Am. Chem. Soc.*, 90, 4498 (1968).

[65] A 1,4-hydrogen abstraction scheme of this type was first drawn attention to as a viable mechanism for cyclopropane ring opening by Padwa [A. Padwa and W. Eisenhardt, *J. Am. Chem. Soc.*, 90, 2443 (1968)]. Such a mechanism was advanced by these authors for the ring opening of aziridinyl ketones.

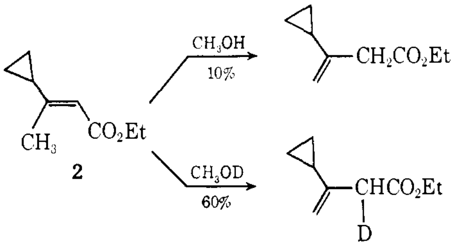
[66] In another example, cyclopropane ring opening to diene occurred only upon direct irradiation.[6a]

[67] J. A. Barltrop and J. Wills, *Tetrahedron Letters*, 4987 (1968).

[68] Simple acyclic α,β-ethylenic esters cannot have the $\pi \rightarrow \pi^*$ state as their lowest excited singlet, since in the absence of the strong stabilizing effect of the cyclopropane substituent, the two singlets are found to differ appreciably in energy (λ_{max} $\pi \rightarrow \pi^*$ *ca.* 200–220 mμ; λ_{max} $n \rightarrow \pi^*$ *ca.* 240 mμ).



Reaction of ester **2** in methanol-O-*d* led to an increase in the rate at which the β,γ isomer **26** was formed, so that the photoproduct was composed of (α-deuterated) **26** to the extent of 60% rather than 10%, as found in ordinary methanol. This deuterium solvent isotope effect is in accord with that observed by us for several other simple α,β-unsaturated esters.[69] Esters **3** and **4** did not change their reaction course in methanol-O-*d*.



Photochemistry of Cyclopropyl Conjugated Enones. Because the photochemistry of acyclic unsaturated ketones is related to that of corresponding esters,[70,71] we have probed into the photochemical behavior of 4-cyclopropyl-3-penten-2-one (**42**). Aside from facile *cis–trans* isomerization, no reaction could be induced upon direct or sensitized photolysis. The ketone proved to be rather stable, undergoing only slow polymerization.

Of the various expected reactions, the failure to yield deconjugation product, *i.e.*, 4-cyclopropyl-4-penten-2-one, is in accord with our previously noted [70,71] observation that primary allylic hydrogens are not photochemically relocated in simple ethylenic ketones. The fact that ketone **42** does not afford the characteristic photoproducts obtained for the corresponding ester **2** might be attributed to a different excited state which ketone **42** compared to esters **1–6** populate. From the absorption spectrum, the lowest excited singlet state in conjugated ketones is clearly n → π^*. Because ketone **42** has its $\pi \rightarrow \pi^*$ absorption maximum displaced bathochromically (λ_{max} 258 mμ), this will lead to a smaller energy gap between the two singlet levels, compared to simple α,β-unsaturated ketones, but the lowest singlet is probably still n → π^*. Since we favor $\pi \rightarrow \pi^*$ singlet for the origin of fragmentation product and bicyclo[2.1.0]pentanes from esters **1–6**, the finding that ketone **42** does not yield these products is in line with this interpretation.[72] Since ketone **42** upon sensitization does not form cyclopentenes, it is tempting to suggest that the electronic configuration of the lowest triplet state also differs for ketone **42** from that of esters **1–6**.

Experimental Section[73]

Preparation of Ethyl Cyclopropylacrylates. The method of Wadsworth and Emmons[74] was employed for the synthesis of these esters. Experimental modifications are described for individual syntheses.

Ethyl 3-cyclopropyl-2-propenoate (1), bp 96–101° (28 mm), was prepared in 73% yield from the reaction of 11.2 g of cyclopropanecarboxyaldehyde with a 10% excess of the sodium salt of triethylphosphonoacetate at 0° in 1,2-dimethoxyethane (glyme) followed by reaction at room temperature for 1 hr. Nmr spectra and glpc analyses revealed the product to be exclusively *trans* isomer.[75] *Anal.* Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.68. Found: C, 68.88; H, 8.84. **Ethyl 3-cyclopropyl-2-butenoate (2)**, bp 99–103° (18 mm) (lit.[76] bp 96–98 (20 mm)), was prepared in 82.8% yield from the reaction in glyme of methyl cyclopropyl ketone (42 g, 0.5 mole) with the sodium salt of triethylphosphonoacetate (125 g, 0.55 mole) followed by a reflux period of 40 hr. Nmr and glpc analysis revealed that the product consisted of *trans* and *cis* isomers in a ratio of 76:24; in addition some ethyl 3-cyclopropyl-3-butenoate (**26**) was also formed. Both the *cis* isomer and the β,γ isomers had lower boiling points and could be separated from the *trans* isomer by fractional distillation.[75] *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.07; H, 9.13. Found (*trans* isomer): C, 69.92; H, 9.22. Found (*cis* isomer): C, 70.23; H, 9.25. **Ethyl 2-methyl-3-cyclopropyl-2-butenoate (3)**, bp 105–110° (20 mm), was prepared in 45% yield from the reaction in glyme of cyclopropyl methyl ketone (42 g, 0.5 mole) with the sodium salt of triethylphosphonopropionate (86 g, 0.36 mole), followed by a reflux period of 120 hr. *cis* and *trans* isomers, in a ratio of 30:70, as well as 4% of the β,γ isomer **27**, were formed. When a 50% excess of ketone was employed and the reaction continued for a period of 8 days, the yield of product was raised to 49%.[75] *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.34; H, 9.82 (for a mixture of *cis* and *trans* isomers, which could not be separated by glpc.) **Ethyl 2-methyl-3-cyclopropyl-2-propenoate (4)**, bp 96–101° (28 mm), was obtained in 82% yield from the reaction in glyme of cyclopropanecarboxaldehyde (31.7 g, 0.45 mole) with the sodium salt of triethylphosphonopropionate (140 g, 0.61 mole) followed by reaction at room temperature for 1 hr. Nmr and glpc analyses indicated that the product was exclusively the *trans* isomer.[75] *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.84; H, 9.45. **Ethyl 3-(1-methylcyclopropyl)-2-butenoate (5)**, bp 94–96° (15 mm), was obtained in 60% yield in diglyme from the reaction of methyl 1-methylcyclopropyl ketone (6.7 g, 0.067 mole) with the sodium salt of triethylphosphonoacetate (23 g, 0.1 mole) followed by heating at 110° for 3 days and reflux for 4 days. The synthesis of **5** could not be accomplished in glyme even after prolonged reaction. Nmr analysis indicated that the product was pure *trans* isomer.[75] *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.57; H, 9.40. **Ethyl 3,3-dicyclopropyl-2-propenoate (6)**, bp 136–137° (17 mm), was obtained from the reaction in glyme of dicyclopropyl ketone (25 g, 0.25 mole) with the sodium salt of triethylphosphonoacetate (42 g, 0.2 mole) for a period of 1 week.[75] *Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.33; H, 8.98.

Preparation of 4-Cyclopropyl-3-penten-2-one (42).[77] To 3-cyclopropyl-2-butenoic acid (6.85 g, 0.054 mole, *cis*:*trans* ratio 15:85) in ether (100 ml) was added a 10% excess of powdered lithium hydride (Lithium Corp.) and the mixture stirred mechanically overnight. To the thick mass was added slowly methyllithium (0.0653 mole) in hexane. After stirring for 12 hr, the mixture was decomposed with a large excess of water. Extraction with ether afforded 3.1 g of crude ketone, whose composition by nmr spectral analysis was 90% ketone **42** as well as 10% of the dimethyl carbinol of **42**. (This carbinol underwent dehydration during vapor phase analysis, so that it could not be detected by this method.) Acidification of the aqueous layer afforded 1.8 g (26% recovery) of a solid acid, whose nmr spectral composition revealed it to be 80–90% starting material contaminated by 10–20% of the β,γ isomer, 3-

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[69] M. J. Jorgenson, *J. Am. Chem. Soc.*, **91**, 198 (1969).

[70] M. J. Jorgenson and N. C. Yang, *ibid.*, **85**, 1698 (1963).

[71] N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).

[72] The $\pi \rightarrow \pi^*$ state has been assigned to the lowest excited singlet for acetylenic esters, to explain the difference in behavior between these esters and their corresponding ketones: J. W. Wilson and V. S. Stubblefield, *J. Am. Chem. Soc.*, 90, 3423 (1968).

[73] Mass spectra molecular weight determinations were made for all new compounds; nmr spectra recorded for ethyl esters do not include the characteristic signal due to the ester ethyl protons.

[74] W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

[75] The principal nmr spectral features and the uv absorption spectra have previously been reported.[11]

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

[77] Mr. D. Dahlhauser and Miss T. Leung carried out the preparation of this ketone.

cyclopropyl-3-butenoic acid. Conversion to the methyl ester, by treatment with diazomethane, followed by glpc analysis, showed this mixture of esters to be 75% *trans*, 15% *cis*, and 10% β,γ-ester. Pure ketone **42** was obtained by distillation of the crude product, bp 87° (20 mm) (lit.[76] bp 86° (19 mm)), in 41% over-all yield (51% based on reacted acid.) The *cis*:*trans* composition of the ketone was 15:85. *Anal.* Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.62; H, 10.01. The product displayed the following characteristics: $\nu^{\mathrm{CCl_4}}$ 1680 and 1600 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 4.04 (broad singlet, 1 H), 7.98 (s, 3 H), 8.14 (s, 3 H), 8.2–8.8 (complex, 1 H), 9.2–9.4 (complex, 1 H); $\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (ϵ 13,100), (lit.[76] 257 mμ (ϵ 13,000)).

Photolysis of Ethyl 3-Cyclopropyl-2-propenoate (1). Ester **1** (10.20 g) was irradiated[78] in spectroquality hexane (150 ml) for a total of 9 days. The photolysis was interrupted at regular intervals to permit cleansing of the polymer-coated immersion well. Exit gases were bubbled through a bromine in carbon tetrachloride solution contained in a gas-washing bottle. After the photolysis was more than 75% complete, it was discontinued and the solvent fractionally distilled through a 40-cm Vigreux column. The residue was fractionated through a 23-plate spinning-band column; nine fractions ranging in boiling point from 68 to 83° (20 mm) were collected. Total distillable material amounted to 4.23 g, of which 1.92 g was shown to be recovered starting ester and its *cis* isomer. Total yield of photoproducts, based on reacted **1**, was 30.4%. The composition of each fraction was obtained by glpc analysis. For the combined fractions, the constitution and composition of photoproducts, in order of increasing retention time on a Carbowax column, were as follows: 3.2% of a mixture (approximately 40:60) of ethyl 2,3-butadienoate and ethyl 3,5-hexadienoate (**34**) [$\nu_{\max}^{\mathrm{CCl_4}}$ (for mixture) 1720 (s), 1730 (s), 1640 (m), 1930 (w), 1960 (w), and 920 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ (for mixture) 3.8–5.3 (*ca.* 4 H), 6.65 (broad triplet); the structural assignment to these esters is not a firm one]; 23% ethyl cyclopentene-2-carboxylate (**7**) [$\nu_{\max}^{\mathrm{CCl_4}}$ 1740 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 4.3 (broad singlet, 2 H), 6.55 (broad triplet, 1 H), 7.4–8.2 (broad, 4 H). (*Anal.* Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.44; H, 9.03)]; 11% ethyl 3,4-hexadienoate (**34**) [$\nu_{\max}^{\mathrm{CCl_4}}$ 1750 (s), 1970 (w); $\tau^{\mathrm{CCl_4}}$ 4.5–5.0 (broad, 2 H), 6.95 (doublet of doublets, 2 H), 8.2 (doublet of doublets, 3H)]; 62% β,γ ester **24** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1740 cm^{-1} (s); $\tau^{\mathrm{CCl_4}}$ 4.2 (multiplet, 1 H), 6.9 (doublet, J = 7 cps, split into triplet, J = 1 cps), 8.85–9.0 (broad singlet, 4 H) (*Anal.* Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: 68.57; H, 8.92)].

The *cis*:*trans* photostationary state ratio was 45:55. The *cis* isomer possessed a retention time higher than that of ester **24** but lower than that of *trans*-**1** [(*Anal.* Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.68. Found: C, 68.60; H, 8.88); $\tau^{\mathrm{CCl_4}}$ 3.3–3.9 (complex, 2 H), 6.8–7.4 (broad, 1 H), 8.9–9.8 (complex, 4 H)]. Time studies indicated that product **24** was formed slower than product **7** during the first 10% of the reaction, but that subsequently to that the formation of **7** was slowed down, so that the proportion of product changed in favor of **24**. Examination of the amount of ethylene trapped[26] as ethylene dibromide, by comparison of the intensity of the vapor phase signal of this solution with that of a solution of known concentration, revealed that 0.22 g of ethylene dibromide had formed during the photolysis; this corresponds to 0.0012 mole of ethylene, and therefore to 2% fragmentation of ester **1**, predicting 6% fragmentation products in the isolated material.

When 0.5 g of **1** was photolyzed in 50 ml of hexane for 5 hr, the distribution of photoproducts, at about 30% conversion, was approximately as follows: 45% **7**, 45% **24** with small amounts (less than 10%) of ethyl 3,4-hexadienoate, and trace amounts of 2-ethoxyfuran **19** formed.

Irradiation of 0.7 g of **1** in 50 ml of ether led after 7 hr (approximately 50% conversion) to the following distribution of photoproducts: about 20% **19**,[19] 50% **7**, 10% ethyl 3,4-hexadienoate; approximately 10% of a mixture of ethyl 2,3-butadienoate and ethyl 3,5-hexadienoate was formed as well.

Diimide Reduction of Ester 24. Formation of Ethyl Cyclopropylpropanoate (28).[26] Acetic acid (0.63 g) in absolute methanol (10 ml) was slowly added to a stirred solution, kept at 65° under a nitrogen atmosphere, of dipotassium azodicarboxylate (0.43 g) in methanol (20 ml) and ester **24** (0.225 g). The mixture was allowed to react at this temperature for 24 hr, at which time additional amounts of potassium dicarboxylate (0.43 g) in acetic acid (0.63 g) were added and the reaction allowed to proceed for a further period of 24 hr. Work-up of the reaction was accomplished by distillation of the methanol, addition of water (20 ml) to the solidified residue, extraction of the aqueous solution with ether, and evaporation of the ether. Vapor phase analysis indicated that the organic material consisted of starting material and hydrogenated ester in a ratio of 70:30. Ethyl 3-cyclopropylpropanoate was isolated by trapping and characterized spectrally: $\nu_{\max}^{\mathrm{CCl_4}}$ 1750 (s) cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 7.65 (unsymmetrical triplet, J = 7 cps, 2 H), 8.42 (unsymmetrical triplet, J = 7 cps, 2 H), 9.1–10.1 (broad, 5 H). *Anal.* Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.20; H, 10.14. The ester was found to be identical with the reduction product obtained by the same method from ester **1**.

Diimide Reduction of Ester 1. Formation of Ethyl Cyclopropylpropanoate (28).[25] This experiment was carried out under conditions similar to those employed for the reduction of ester **24**. Ester **1** (0.92 g, 0.0066 mole), dipotassium azodicarboxylate (2.58 g, 0.0133 mole), freshly distilled acetic acid (1.76 g, 0.029 mole), and methanol (50 ml) were allowed to react as above, for a total of 48 hr. At this time second portions of dipotassium azodicarboxylate (2.58 g) and acetic acid (1.76 g) were added, and the reaction continued to stir at 65° for an additional period of 24 hr. Work-up of the reaction mixture, as for the reduction of **24**, led to an ester mixture shown to consist of 97% reduced ester, ethyl 3-cyclopropylpropanoate, and 3% starting ester **1**. The product was shown to be identical with that derived from the reduction of ester **24**.

Preparation of 5-Methyl-2-ethoxyfuran (21).[79] Attempted isolation by trapping of 2-methyl-2,5-diethoxydihydrofuran, prepared according to a literature route,[20] revealed that dehydration occurred during this process. Pure **21** was conveniently isolated in this manner from a crude mixture of the reaction product containing 2-methyl-2,5-diethoxydihydrofuran. Pure **21** (*Anal.* Calcd for $C_7H_{10}O$: C, 66.65; H, 7.99. Found: C, 66.56; H, 7.76) had $\nu^{\mathrm{CCl_4}}$ 1600 and 1625 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 225 mμ (ϵ 4300); nmr data in Table I. In the mass spectrum strong peaks were prominent at *m/e* 43, 55, 83, and 97.

Preparation of 2-Ethoxyfuran (19). The series of transformations leading to the formation of 5-ethoxyfuroic acid were followed as reported in the literature.[19] Furan **19** was conveniently generated in small amounts by injection of the acid into the vapor phase chromatograph at an injector temperature of about 300°, followed by trapping. It was characterized spectrally: $\nu_{\max}^{\mathrm{CCl_4}}$ 1525, 1580, 1610 cm^{-4} (sh); nmr spectra in Table I; in the mass spectrum, strong peaks at *m/e* 44 and 57 were prominent.

Photolysis of Ethyl 3-Cyclopropyl-2-butenoate (2).[79] A solution of ester **2** (49 g) in dry ether (850 ml) was irradiated[78] for a total of 216 hr. After distilling the ether through a Vigreux column, the residue was fractionated through a 23-plate spinning band column. A total of 11 fractions, ranging in boiling point from 70 (61 mm) to 103° (19 mm), were collected. Total distillable material amounted to 39.4 g; of this material 27.6 g was shown to be recovered starting material (*cis* and *trans* esters). Based on reacted starting material, the yield of photoproduct was calculated to be 60.5%. Composition of the photoproduct mixture in order of increasing retention time on a Carbowax column are as follows: 2.6% ethoxyfuran **20** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1570 and 1610 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 221 mμ (ϵ 5300) (for nmr data see Table I); prominent mass spectral peaks at *m/e* 41, 69, and 97; *Anal.* Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.7; H, *ca.* 10 (insufficient sample for more accurate analysis)]; 8.3% cyclopropene **14** [see Table II for spectral data; *Anal.* Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.60; H, 7.82; prominent mass spectral peaks at *m/e* 41, 43, 53 (100%), 55, 67, 69, 81, 83, 97, and 98]; 70% cyclopentene **8** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1660 (w) and 1740 cm^{-1} (s); $\tau^{\mathrm{CCl_4}}$ 4.62 (broad multiplet, 1 H), 6.82 (broad triplet, 1 H), 8.32 (broad singlet, 3 H) (*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.07; H, 9.13. Found: C, 69.93; H, 9.11); prominent mass spectral peaks at 41, 53, 77, 79, 80, 81 (100%), 82, 125]; 16.7% **26** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1730 (s) and 1640 cm^{-1} (w); $\tau^{\mathrm{CCl_4}}$ 5.30 (broad singlet, 2 H), 7.10 (broad singlet, 2 H), 9.2–9.7 (broad, 4 H) (*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.07; H, 9.13. Found: C, 70.17; H, 9.38); prominent peaks in the mass spectrum at *m/e* 41, 53, 67, 79, 80, 81, 98, 108, 109, 111, and 126]; 3.5% *cis*- and *trans*-ethyl 3-methyl-3,5-hexadienoate [$\nu_{\max}^{\mathrm{CCl_4}}$ 1730 (s), 1650 (w), 1600 (w), and 910 cm^{-1} (m); $\lambda_{\max}^{\mathrm{EtOH}}$ 233 mμ (ϵ ~ 20,000); $\tau^{\mathrm{CCl_4}}$ 3.2–6.2 (multiplets, 4 H), 7.06 (broad singlet, 2 H), 8.16 (broad singlet, 3 H); other isomer (probably *trans*) 3.5–5.3 (multiplets, 4 H), 6.92 (broad singlet, 2 H), 7.85 (unresolved doublet, 3 H)]. The photostationary state *cis*:*trans* ratio of **2** was 52:48.

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(78) Unless otherwise stated, photolyses were carried out at ambient temperatures under nitrogen atmosphere, employing a Hanovia Type L 450-W lamp and a Vycor filter. Progress of the photolysis was monitored by glpc analysis.

(79) These experiments were carried out in collaboration with Dr. Heathcock of these laboratories.[8]

When photolysis was conducted on a 1.0-g scale with cooling by means of a Dry Ice bath, 23% conversion occurred over a period of 5 hr. The composition of the photoproduct mixture was 90% **8**, 6% **20**, 1.3% **14**, and approximately 3% of the β,γ isomer **26**. Small-scale irradiation conducted at ambient temperatures in hexane afforded a ratio of products similar to that found in ether, but no furan could be detected.

The rates of reaction of ester **2** were determined, in consecutive runs carried out on identical scales and under the same conditions, in various solvents. The rates were very much the same in hexane and methanol; in the latter solvent, appreciably more acyclic products appeared to be formed. In methanol-O-*d* the rate of the reaction was approximately two to three times faster, and the product consisted to the extent of about 60% β,γ isomer **26**, shown to contain one deuterium at the α-carbon. Approximately 40% cyclopentene **8** was present, shown not to have deuterium incorporated; small amounts of cyclopropene **14** and acyclic esters were also formed. The results in methanol and methanol-O-*d* were reproducible.

Thermal Vinylcyclopropane Rearrangement of Ester 2. Formation of Cyclopentene 8.[79] A mixture of *cis* and *trans* ester **2** (268 mg) was heated at 350° in a sealed tube in the presence of 10 mg of hydroquinone. After 20 min 29% of the ester mixture had reacted to give **8** and after 70 min, when the composition of product **8** had increased to 68%, the pyrolysis was discontinued. Pure ester **8** was trapped (39 mg), characterized spectrally, and found to be identical with the photoproduct of ester **3**. On a 25 μl scale, pyrolyzed at 375° for 30 min with dimethyl glutarate as internal standard, it was shown that conversion of *trans* **2** was complete, giving a 95% yield of **8**, whereas 75% of *cis* **2** had reacted to furnish only 34% of **8**.

Catalytic Hydrogenation of Ester 14. Formation of Ethyl *cis*-2-Methylcyclopropanecarboxylate. Hydrogenation of **14** in the presence of palladium on charcoal in ethanol led to fast consumption of hydrogen and the formation of ethyl *cis*-2-methylcyclopropanecarboxylate (*Anal.* Calcd for $C_7H_{12}O_2$: C, 66.65; H, 7.99. Found: C, 66.56; H, 7.76). This ester exhibited identical vapor phase chromatographic retention times as its *trans* isomer, but the two had distinctly different ir and nmr spectra. The product of hydrogenation was found to be identical with a sample of ethyl *cis* 2-methylcyclopropanecarboxylate prepared by a literature procedure.[17]

Photolysis of Ethyl 2-Methyl-3-cyclopropyl-2-butenoate (3). A solution of 20 g of ester **3** was irradiated[78] in 450 ml of dry ether, for a total of 10 days, at which time approximately 90% of the starting ester had reacted. Concentration of the ether solvent by fractional distillation through a Vigreux column, followed by fractional distillation on a 23-plate spinning-band column, afforded a total of 10 g of distillable material, corresponding to a yield of 48%, based on reacted starting material. The composition of the photoproduct mixture was as follows, in order of increasing retention times on a Carbowax column: 4% ethyl *trans*-1,2-dimethylcyclopropane-1-carboxylate [$\nu_{\max}^{\mathrm{CCl_4}}$ 1725 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 8.75 (singlet, 3 H), 8.8–9.0 (broad, 5 H), 9.25 (complex, 1 H), identical with the major product of the hydrogenation of **15**]; 4% ethyl *cis*-1,2-dimethylcyclopropane-1-carboxylate [$\nu_{\max}^{\mathrm{CCl_4}}$ 1725 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 8.6–9.0 (complex), 9.75 (broad, 1 H), identical with the minor hydrogenation product of **15**]; 24% cyclopropene **15** [*cf.* Table II for spectral data (*Anal.* Calcd for $C_8H_{12}O_2$: C, 68.51; H, 8.63. Found: C, 68.51; H, 8.84); prominent mass spectral peaks at *m/e* 41, 43, 44. 53, 55, 67 (100%), 68, 69, 83, 95, 97, 111, and 112]; 10% cyclopentene **9** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1740 cm^{-1} (s); $\tau^{\mathrm{CCl_4}}$ 4.6 (broad 1 H), 7.35–7.92 (broad, 4 H), 8.32 (broad, 3 H) and 8.75 (broad, 3 H) (*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.30; H, 9.79), identical with a sample prepared by a literature route[14]]; 48% bicyclo[2.1.0]pentane **22**, *exo* and *endo* isomers[21] in ratio of 45:55 [*exo* isomer—$\nu_{\max}^{\mathrm{CCl_4}}$ 1725 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 7.90–8.50 (complex, 5 H), 8.73 (singlet, 3 H) and 8.86 (singlet, 3 H); *endo* isomer—$\nu_{\max}^{\mathrm{CCl_4}}$ 1725 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 7.90–8.50 (complex, 5 H), 8.70 (singlet, 3 H) and 8.80 (singlet, 3 H); prominent mass spectral peaks at *m/e* 41, 53, 55, 67, 79, 94, 95, 112, 125, 140, and 153 for *exo* isomer and 41, 53, 55, 67, 79, 91, 92, 94, 95, 96, 97, 107, 112, 123, 125, 140, and 153 for *endo* isomer]; 10% β,γ isomer **27** [$\nu_{\max}^{\mathrm{CCl_4}}$ 3100 (w), 1730 (s), 1630 (m) and 8.95 cm^{-1} (m, broad); $\tau^{\mathrm{CCl_4}}$ 5.30 (d, $J \sim 6$ cps, 2 H), 6.6 (quartet, $J = 7$ cps, 1 H), 8.7 (doublet, $J = 7$ cps, 3 H) and 9.2–9.7 (broad 4 H) (*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found, C, 71.07; H, 9.67); prominent mass spectral peaks at 41, 43, 53, 54, 67, 79, 92, 94, 95 (100%), 96, 111, 112, 125, 140, and 153].

Irradiation in hexane led to formation of products in a ratio similar to that in ether. In methanol the distribution of products did not differ appreciably from that formed in hexane or ether, but minor amounts of other photoproducts, whose structure was not elucidated, were also formed. Irradiations in methanol-O-*d* produced results identical with those in ordinary methanol. When Corex filtered light was utilized, the reaction was very slow in ether, but the products were formed in ratios similar to those formed when a Vycor filter was employed.

Hydrogenation of 15. Formation of Ethyl 1,2-dimethylcyclopropanecarboxylate. Ester **15** (100 mg) was hydrogenated in methanol (1 ml) over palladium on charcoal (30 mg). The uptake of hydrogen was rapid and stopped after 30 min. Vapor phase chromatographic analysis indicated that the product consisted of *trans*- and *cis*-ethyl 1,2-dimethylcyclopropanecarboxylate formed in a ratio of 95:5.

Photolysis of Ethyl 2-Methyl-3-cyclopropyl-2-propenoate (4). Ester **4** (20 g) was irradiated[78] in spectroquality hexane (500 ml) for a total of 3 weeks, with frequent interruptions to cleanse the immersion well of the deposited polymeric products. Fractional distillation through a 26-plate spinning-band column afforded a total of 9.8 g of distillable material of which 7.0 g was recovered *cis* and *trans* ester **4**; yield of product, based on converted starting material, was 22%. The composition of the product mixture, in order of increasing retention times of product, was as follows: less than 5% ethyl 2-methyl-2,3-butadienoate [$\nu_{\max}$ 1930 (w) 1960 (w) and 1715 (s), spectrally identical with an authentic sample],[28] 25% cyclopropene **16** [*cf.* Table II for spectral data (*Anal.* Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.37; H, 8.14); prominent mass spectral peaks of *m/e* 41, 53, 69, 81, 97 (100%), and 98]; 6% cyclopentene **10** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1740 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 6.40 (broad, 2 H), 7.5–7.8 (complex, 4 H), 8.75 (singlet, 3 H), identical with a sample prepared by an independent route[15]]; 13% of a 30:70 mixture of a *cis* and *trans* mixture of ethyl 2-methyl-2,5-hexadienoate [$\nu_{\max}^{\mathrm{CCl_4}}$ 1720 (s), 1640 cm^{-1} (m); $\tau^{\mathrm{CCl_4}}$ 4.0–5.4 (complex, 4 H). 6.4 and 6.9 (corresponding to allylic methylene hydrogens, broad triplets), 8.22 and 8.52 (corresponding to allylic methyl hydrogens, quartet, $J \sim 1$ cps (*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.86; H, 9.27); prominent peaks in the mass spectrum at *m/e* 79, 81 (100%), 109, and 111]; 15% of a 40:60 mixture of two allenic esters, believed to be ethyl 2-methyl-3,4-hexadienoate and ethyl 2-methyl-2,3-hexadienoate [for mixture: $\nu_{\max}^{\mathrm{CCl_4}}$ 1750 (s), 1720 (s). 1960 cm^{-1} (w); $\tau^{\mathrm{CCl_4}}$ 4.5–5.1 (complex, less than 2 H), 6.8–7.2 (broad, less than 1 H) 8.0 (broad multiplet, more than 1 H), 8.25 (sharp doublet, $J = 3$ cps) 8.4 (broad doublet) and 8.85 (doublet) in addition to absorption which occurred in the absorption region of the methyl of the ester group], 7% *exo*-bicyclo[2.1.0]pentane **23** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1720 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 7.8–8.6 (complex, 6 H), 8.9 (singlet, 3 H) (*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.96; H, 9.17); prominent mass spectral peaks at *m/e* 53, 67, 69, 79, 81 (100%), 111, 125, 126, and 139] 20% of the β,γ isomer **25** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1740 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 4.15–4.35 (multiplet, 1 H), 6.6–7.0 [broad, quartet, 1 H), 8.75 (doublet, $J = 7$ cps, 3 H), 8.8–9.0 (broad, 4 H) (*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.94; H. 9.21)]; 7% *endo*-bicyclo[2.1.0]pentane **23** [$\nu_{\max}^{\mathrm{CCl_4}}$ 1720 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 7.6–8.6 (complex, 6 H), 8.60 (singlet, 3 H) (*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.92; H, 9.32), prominent mass spectral peaks at *m/e* 41, 53, 81 (100%), 82, 97, 98, 111, 125, 126, and 139]. In addition about 10% of two unidentified alkenoic esters, one having retention time somewhat lower than *endo*-**23** and the other identical with that of *endo*-**26**, were isolated but not characterized. The *cis* isomer of starting material was produced in a 50:50 photostationary ratio with *trans* ester; the latter has a retention time lower than that of the *trans* isomer, but higher than that of photoproducts; it was isolated and characterized.[78] *Anal.* Calcd for $C_9H_{10}O_2$: C, 70.10; H, 9.15. Found: C, 70.45; H, 9.36. With the exception of products **23** and **25**, the photoproducts from this reaction were found to decompose upon standing.

In a repeat experiment, when the photolysis was conducted to more than 90% completion, the distribution of cyclopropene product **16** in the product mixture was approximately halved. The nitrogen swept exit gases were trapped in this experiment and the amount of dibromide formed was determined, as in the photolysis of ester **1**. It was found that the amount of ethylene trapped as the dibromide corresponded to 0.0016 mole and hence to 0.25 g of **4** undergoing the fragmentation reaction. This corresponds to less than half of the amount of cyclopropene product actually isolated in this photolysis.

The results of irradiations conducted on a small scale in ether or hexane were virtually identical. There was no change in product distribution when methanol-O-*d* was substituted for ordinary methanol.

Photolysis of Ethyl 3-(1-methylcyclopropyl)-2-butenoate (5). Ester **5** (6.3 g) was irradiated[78] in ether (600 ml) for a total of 23 hr. Approximately 80% of the starting material had reacted at this time. Only two photoproducts were indicated by glpc analysis; the *cis* isomer [(*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.08; H, 9.44); τ^{CCl_4} 4.40 (broad singlet, 1 H) 8.15 (doublet, J = 1 cps, 3 H), 8.80 (singlet, 3 H) and 9.15 (singlet, 4 H)] was formed in a photostationary equilibrium in a 60:40 ratio with *trans* isomer. Fractional distillation afforded a total of 4.1 g of distillable material of which 0.4 g was starting material; yield of photoproduct, based on converted starting material, was 60%. The two photoproducts were formed in a 40:60 ratio. The more abundant product was shown to be cyclopropene **17** by spectral comparison with authentic material[16] [(*Anal.* Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.76; H, 8.50); prominent peaks in the mass spectrum at *m/e* 41, 43, 67 (100%), 69, 95, 97, 111, and 112]. The more abundant product **11** has $\nu_{max}^{CCl_4}$ 1740 cm^{-1}; τ^{CCl_4} 6.77 (broad triplet, 1 H), 7.5–8.3 (complex, 4 H), 8.4 (broad singlet, 3 H) (*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.98; H, 9.27).

Photolysis of Ethyl 3,3-Dicyclopropyl-2-propenoate (6). Ester **6** (15 g) was irradiated[78] in ether (500 ml) for a total of 9 days, when approximately 90% of the ester had reacted. Fractional distillation, bp 110–133° (20 mm), afforded 10.83 g of photoproduct, of which 1.9 g was recovered starting material; product yield based on reacted starting material was 69%. The composition of photoproduct was 12% cyclopentene ester **13** [$\nu_{max}^{CCl_4}$ 1740 (s), 1640 (m), and 915 cm^{-1} (s); τ^{CCl_4} 4.0–5.2 (complex, 4 H), 6.8 (broad triplet, 1 H), 7.1 (broad singlet, 2 H), 7.5–8.5 (complex, 4 H); no λ_{max} above 210 mμ (*Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.19; H, 8.88); prominent mass spectral peaks at *m/e* 77, 79 (100%), 91, 92, 93, 105, 106, 107, 108, 109, 134, 135, and 151]; and 87% cyclopentene ester **12** [$\nu_{max}^{CCl_4}$ 1740 (s), 3100 cm^{-1} (w); τ^{CCl_4} 4.6 (broad singlet, 1 H), 6.65 (broad triplet, 1 H), 7.5–8.0 (complex, 4 H), 9.2–9.7 (complex, 4 H) (*Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.13; H, 8.76); prominent mass spectral peaks at *m/e* 79, 92, 93, 94, 106, 107, 108, 135, and 152].

At early stages of the photolysis, when only 1 g of ester **6** was employed, a fairly strong shoulder on the vapor phase retention time band of ester **13** could be seen. The ir spectrum of a mixture of **13** and this compound exhibited absorption at 1800 cm^{-1}, in addition to a strong carbonyl stretching vibration. This compound, tentatively assigned the cyclopropene structure **18**, disappeared upon further irradiation.

When a Corex filter was employed, slow transformation of ester **6** occurred (about 10% conversion after 9 days in a photolysis of 2 g of **6** in 40 ml of hexane) and the photoproduct consisted exclusively of ester **12**. Irradiation in methanol or methanol-O-*d* furnished **12** and **13** in proportions similar to those found in ether.

Photolysis of Ethyl 6,6-Dimethyl-2,4-heptadienoate.[37] A 0.5-g sample of this ester[11] was photolyzed[78] in spectroquality hexane (100 ml) for approximately 1 hr. A photostationary mixture of four geometrical isomers was quickly generated, but subsequent photolysis yielded only one new product. The allenic product, ethyl 6,6-dimethyl-3,4-heptadienoate, was isolated and characterized: $\nu_{max}^{CCl_4}$ 1950 (w), 1740 cm^{-1} (s); τ^{CCl_4} 4.7–5.0 (complex, four bands 2 H), 7.1 (four lines of equal intensity, probably doublet of doublets, J = 6 and 3 cps, 2 H) and 8.95 (singlet, 9 H) (*Anal.* Calcd for $C_{11}H_{18}O_2$: C, 72.48; H, 9.95. Found: C, 72.23; H, 10.02). The yield of this photolysis product was low.

Photolysis of 4-Cyclopropyl-3-penten-2-one (42). Ketone **42** (1.0 g) was irradiated[78] in hexane (50 ml) with Corex-filtered light. Slow formation of polymer was observed and after 24 hr no starting material remained. Similar results were obtained when irradiations were conducted with Vycor or Pyrex filtered light, or upon photosensitization employing triphenylene (E_T = 67 kcal) in benzene; in all cases facile generation of the photostationary state (*cis*:*trans* 40:60) was, aside from polymerization, the only photochemical reaction.

Photolysis of Ethyl 1,2-Dimethyl-2-cyclopropenecarboxylate (15). Ester **15** (110 mg) in hexane (5 ml) was irradiated in a quartz vessel, with Vycor filter, employing approximately one-sixth of theHanovia lamp arc. After 1 hr half of the ester had reacted, and after 4 hr none of the starting material remained. In addition to material of low retention time, which derived from the solvent, as established by irradiation of hexane alone, three new peaks appeared in the gas chromatograph. The two major peaks were trapped and were shown to be the *cis* and *trans* isomers of ethyl 1,2-dimethylcyclopropanecarboxylate. The third, minor peak was not identified. Yield of photoproduct appeared to be approximately 50%.

Control Photolyses.[78,80] Furan **21** (1 g) was photolyzed in ether (120 ml). No products were produced, but starting material slowly disappeared. After 21 hr all of **21** had reacted. Cyclopentene **9** (40 mg) was irradiated in hexane (3 ml) employing approximately one-eighth of the arc. Only polymeric material was formed; after 1 hr all of **9** had polymerized. Ester **12** (100 mg) was photolyzed in hexane (10 ml) employing approximately one-third of the arc. After 2 hr, half of **12** had reacted to give polymer. Ester **25** (15 mg) was irradiated in hexane (2 ml). After 2 hr all of **25** had reacted. Some product of lower retention time (about 10% yield) was formed but was not characterized. Photolysis of bicyclo[2.1.0]pentane **23** in hexane, Vycor filter, led to slow destruction of the ester and to minor amounts of photoproducts which were not characterized; cyclopentene **9** was not among these photoproducts.

Photosensitization Experiments. Ester **4** (0.5 g) was photolyzed in acetone (50 ml) employing Corex-filtered light. The *cis*:*trans* photostationary mixture (50:50) was generated within 20 min. In a much slower reaction, cyclopentene **10** was formed; approximately 20% ester **4** had converted to **10** after 10 hr. Product **10** was formed also when xanthone or benzophenone in benzene with Pyrex filter were employed as sensitizers. The yields of **10** after complete conversion of **4** were low in these cases (10–20%) because these sensitizers underwent chemical quenching with product. (The yields of **10** were found to decrease with time when ketone sensitizers were employed.) When triphenylene was used, cyclopentene **10** was formed in a slower reaction, but the yields of **10** were superior.

Sensitization with benzophenone of esters **2**, **3**, and **6** afforded similarly, but in poorer yield, cyclopentenes **8**, **9**, and **12**, respectively. Cyclopentene ester **7** reacted particularly rapidly when triphenylene or acetone were employed, to give high molecular weight products. The photostability of **8**, **9**, **10**, and **12** was somewhat higher under these conditions, so that these products could be isolated from the sensitized photolyses of their respective ester precursors.

Photolysis of bicyclo[2.1.0]pentane **23** in benzene in the presence of triphenylene as sensitizer produced no change.

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