H, NCH_2), 4.37 (m, 1 H, vinyl H), 4.34 (d, J = 10 Hz, 1 H, $CHCl_2$), 4.1 (bs, 1 H, NH), 2.67 (m, 5 H, ArH); ir ($CHCl_3$) 3440, 3395, 1660, 1382, 1373, 910 cm^{-1}.

***N*-Benzyl-*cis*-2-(dichloromethyl)-5,5-dimethylene-3-cyclopentene-1-carboxamide (26).** The dichloroketone **8**[21] (1 g, 5 mmol) in 3 ml of ether was treated with 0.53 g (5 mmol) of benzylamine for 30 min. A quantitative yield of amide **26**, mp 138–140 °C, was obtained: NMR (Me_2SO-d_6) τ 9.1–9.5 (m, 4 H), 7.05 (d, J = 8 Hz, 1 H, 1-H), 6.15 (m, 1 H), 5.73 (d, J = 5.5 Hz, 2 H, CH_2Ph), 4.34 (d of d, 1 H), 4.53 (d of d, 1 H), 3.6 (d, J = 10 Hz, 1 H, $CHCl_2$), 2.71 (m, 5 H), 1.7 (br, NH); ir (CCl_4) 1630 cm^{-1}. Anal. Calcd for $C_{16}H_{17}ONCl_2$: C, 62.0; H, 5.48. Found: C, 61.81; H, 5.31.

Zinc Reduction of 8. A mixture of 1.2 g of **8**, 0.5 g of zinc dust (activated by treatment with 10% HCl), and 1 g of glacial acetic acid in 30 ml of ether was stirred for 4 days. Workup yielded an oil which by NMR consisted mainly of monochloroketone **25a**: τ 8.6–9.5 (m, 4 H), 6.72 (d of d, J = 7 Hz and 3 Hz, 1 H, CHC=O), 5.93 (m, 1 H), 4.98 (d of d, J = 8.5 Hz and 3 Hz, 1 H, CHCl), 4.3 (d of d, J = 5.5 and 2 Hz, 1 H), 4.5 (d of d, J = 5.5 Hz, 1 H); ir 1782 cm^{-1}.

Further reduction with zinc led to a mixture of **25a** and **25b**, ir 1770 and 1785 cm^{-1}.

Acknowledgment. Support of this work by a grant from the National Science Foundation and the National Cancer Institute is gratefully acknowledged.

References and Notes

(1) (a) Cycloadditions. 22. For the previous paper in this series, see A. Hassner, D. Tang, and J. Keogh, *J. Org. Chem.*, **40**, 2102 (1976). (b) Work performed in part at the University of Colorado, Boulder, Colo.
(2) J. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Am. Chem. Soc.*, **87**, 5257 (1965).
(3) For leading references, see: (a) K. N. Houk, *J. Am. Chem. Soc.*, **95**, 7287 (1973); (b) R. M. Cory and A. Hassner, *Tetrahedron Lett.*, 1245 (1972); (c) A. Hassner, V. K. Fletcher, and D. P. G. Hamon, *J. Am. Chem. Soc.*, **93**, 264 (1971); (d) W. T. Brady and J. P. Hieble, *J. Org. Chem.*, **36**, 2033 (1971); (e) M. Rey, S. Roberts, A. Dieffenbacker, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970).
(4) (a) R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, **7**, 221 (1968); (b) W. T. Brady, *Synthesis*, 415 (1971).
(5) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).
(6) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970; R. Sustmann, A. Ansmann, and F. Vahienholt, *J. Am. Chem. Soc.*, **94**, 8099 (1972).
(7) See, for example, (a) W. T. Brady and R. Roe, Jr., *J. Am. Chem. Soc.*, **93**, 1662 (1971); (b) W. Weyler, Jr., L. R. Byrd, M. C. Caserio, and H. W. Moore, *ibid.*, **94**, 1027 (1972).
(8) L. H. Keith, *Tetrahedron Lett.*, 3 (1971).
(9) H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971).
(10) A. Hassner and D. P. G. Hamon, unpublished.
(11) V. R. Fletcher and A. Hassner, *Tetrahedron Lett.*, 1071 (1970).
(12) These results were reported in preliminary form in ref 3b.
(13) (a) R. E. Davis and M. R. Wilcott, III, *J. Am. Chem. Soc.*, **94**, 1744 (1972); (b) M. R. Wilcott, III, R. E. Lenkinski, and R. E. Davis, *ibid.*, **94**, 1742 (1972).
(14) H. Kwart and J. A. Ford, Jr., *J. Org. Chem.*, **24**, 2060 (1959).
(15) (a) G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Lett.*, 4497 (1968); (b) J. E. Baldwin and J. A. Kapecki, *J. Am. Chem. Soc.*, **92**, 4868, 4874 (1970); (c) R. Huisgen, L. A. Feiler, P. Otto, and G. Binsch, *Chem. Ber.*, **102**, 3444, 3460 (1969).
(16) A cyano group deshields a vicinal proton cis to it on a cyclobutanone ring,[7b] further substantiating structure **15** and explaining the reversal of NMR positions of 1- and 5-H from that in compound **7**. However, a similar reversal in adduct **14**, while it probably results from a conformational placement of the 1-H in the shielding and the 5-H in the deshielding regions of the *exo*-phenyl, is not as easily explained.
(17) W. E. Heyd and C. A. Cupas, *J. Am. Chem. Soc.*, **93**, 6086 (1971).
(18) A. P. Krapcho and R. Donn, *J. Org. Chem.*, **30**, 641 (1965).
(19) W. J. Bailey and M. Madoff, *J. Am. Chem. Soc.*, **76**, 2707 (1954).
(20) (a) R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967); (b) G. Kaufman, F. Cook, J. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).
(21) L. Makosza. Polish Patent 55 771, Jan 1966; *Chem. Abstr.*, **70**, 106 047 (1970).
(22) While work was in progress (see ref 12), the preparation and structure proof for **8** was reported by P. R. Brook and J. M. Harrison, *J. Chem. Soc., Perkin Trans. 1*, 778 (1974).
(23) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Am. Chem. Soc.*, **90**, 4762 (1968).
(24) This hypothesis has been elaborated further by: (a) H. E. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971); and (b) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).
(25) L. A. Paquette and L. M. Leichter, *J. Am. Chem. Soc.*, **94**, 3653 (1972).
(26) 20 ft × $\frac{3}{8}$ in. 15% XE-60 on Chromosorb; flow rate: 200 ml/min; column temperature: (a) 130 °C, (b) 150 °C, (c) 140 °C.
(27) L. I. Smith and H. H. Hoehn, "Organic Syntheses", Collect. Vol. 3, Wiley, New York, N.Y., 1955, p 356.
(28) Silica gel PF-254, 20 × 20 cm × 2 mm. Eluting solvents: (a) 99/1 Skellysolve B/ethyl acetate; (b) 6× with 99/1 ethyl acetate/Skellysolve B and 1× with 95/5; (c) 1/1 chloroform/ethyl acetate; (d) chloroform.
(29) Prepared by A. Miller in our laboratory.

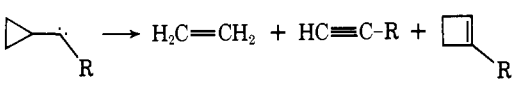
The Stereochemistry of the Intramolecular Reactions of Cyclopropylcarbenes[1]

Robert R. Gallucci and Maitland Jones, Jr.*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received March 30, 1976*

Abstract: The direct irradiation of the *cis*-dimethylcyclopropyl diazo ester (**6**) gives *cis*-2-butene, *cis*-3,4-dimethyl-1-carbomethoxycyclobutene, and methyl propiolate. The trans diazo ester (**6a**) behaves similarly. Thus both the ring expansion and fragmentation reactions proceed with retention of stereochemistry. The benzophenone- or fluorenone-sensitized decompositions also lead to retention of stereochemistry to a very high degree. A number of explanations for the observed retention are put forward. The addition of 2,3-dimethylcyclopropylcarbomethoxycarbene (**9**) to isobutylene is also discussed.

Despite many previous investigations[2,3] and wide use in synthesis,[4-6] the ring-expansion and fragmentation reactions of cyclopropylcarbenes are still imperfectly understood, and several problems are outstanding. Thus, although gas-phase reactions show relatively more fragmentation than their solution counterparts, the introduction of an inert moderator into the gas-phase reaction is sometimes without effect.[7] In unsymmetrically substituted cyclopropylcarbenes it is the less-substituted and, therefore, stronger bond that migrates in the ring expansion. This is curious, although an explanation based

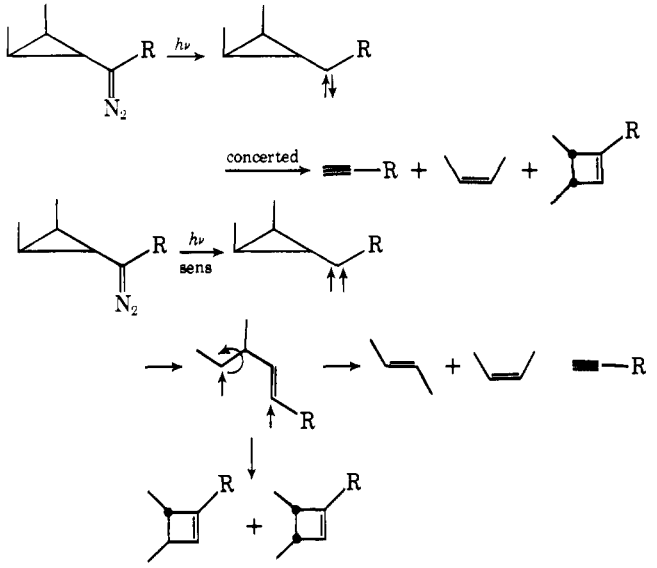


upon steric effects has been put forward[8,9] and electronic factors briefly investigated as well.[10] A third puzzling aspect is the absence of the products of hydrogen migration where they might well be expected to be major products.[11-13] Other seemingly anomalous reactions continue to appear.[14]

Obviously, knowledge of the mechanism of the rearrangement is central to an understanding of the problems mentioned

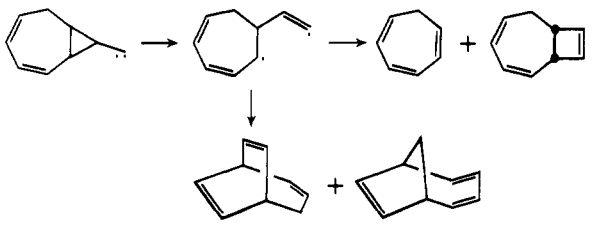
above. Is the reaction concerted or are intermediates involved? In particular, how does the reaction change as a function of the spin state of the carbene? Although the singlet carbene seemed likely to rearrange in a concerted fashion, we thought the triplet might be prone to ring opening in analogy to the behavior of the cyclopropyl radical[15] (Scheme I). We have focused upon

Scheme I



the introduction of a stereochemical label in the hopes of probing further into the mechanism of the rearrangement.

Retention of stereochemistry has been observed on occasion[10,16,17] and thus one might be inclined to favor a concerted reaction, at least for the singlet carbene. However, these reports clash with earlier data which implicate a nonconcerted pathway. For instance, the products obtained from the pyrolysis of the lithium salt of bicyclo[5.1.0]octa-2,4-diene-8-carboxaldehyde tosylhydrazone can best be explained by opening of the carbene to a delocalized diradical which closes at all possible positions.[18] Comparable results have been obtained in related systems,[19,20] and loss of stereochemistry has been re-

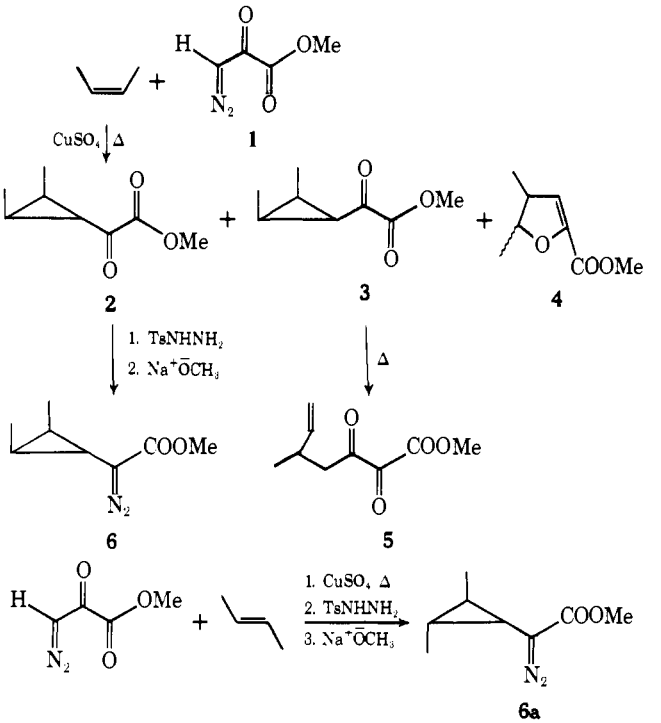


ported by Guarino and Wolf in a very simple system.[21] In this work, the gas-phase decomposition of *trans*-2,3-dimethylcyclopropyldiazomethane gave along with the expected product of stereospecific reaction *trans,trans*-hexa-2,4-diene, almost 20% *cis,trans*-hexa-2,4-diene which must arise from conrotatory opening of *cis*-3,4-dimethylcyclobutene. The fragmentation to 2-butenes was found to be more stereospecific, as only 4–5% *cis*-2-butene was obtained from the trans precursor. If we make the assumption that any diradical pathway would give approximately equal amounts of stereoisomers, then the reported products indicate a high degree of nonstereospecificity in the reaction. This is especially true as it is the trans isomer that is the less likely to lose its original stereochemistry in a diradical.[40] In any event the work of Guarino and Wolf provides a contrast to the later reports of stereospecific rearrangement in solution.[10,16,17]

We were led by these contrasts to investigate the stereochemistry of both ring expansion and fragmentation as a function of spin state. We chose to work in solution where the complicating factor of hot-molecule reactions should be absent and chose as starting materials the *cis*-dimethylcyclopropyl diazo ester **6** and its trans counterpart **6a**. We hoped that the ester group would function both to stabilize the diazo compound and make the photosensitized generation of the triplet carbene easy. Isolation of the diazo compound would allow us to avoid the mechanistic hazards inherent in treating tosylhydrazones with base.[22,23]

Oxoacetates **2** and **2a** were obtained through the $CuSO_4$-catalyzed addition of methyl diazopyruvate (**1**) to *cis*- and *trans*-2-butene (Scheme II). The crude mixture, which con-

Scheme II



sisted of **2, 4,** and **5** in relative yields of 66.0, 4.6, and 29.4%, was purified by preparative gas chromatography (GC). Under conditions of the GC separation the syn, cis isomer **3** rearranged to compound **5**.[24] This rearrangement facilitated the separation of the syn and anti isomers **2** and **3** and confirmed the structure of **2**. Reinjection of **2** into the gas chromatograph under the same conditions used in the preparative separation produced neither **4** nor **5**. Keto ester **2a** also rearranged under gas chromatographic conditions to **5** and was purified by column chromatography on silica gel. Compound **4** may arise directly from the reaction mixture or through the decomposition of the syn, cis isomer **3**. The exact stereochemistry of the dihydrofuran **4** was not determined.

The keto esters **2** and **2a** were converted to their tosylhydrazones in high purity and the corresponding diazo compounds prepared[25] (Scheme II). Although yields of the diazo compounds produced by this method were low, higher temperatures, or longer reaction times, resulted in an unacceptably large amount of ring expansion product mixed with the diazo ester. In no case was more than 5% 3,4-dimethyl-1-carbomethoxycyclobutene present. Pyrolysis of the dry lithium salt of the tosylhydrazones[26] did not give diazo esters of acceptable purity.

The direct irradiation of the cis and trans diazo esters **6** and **6a** in benzene for 3 h through Pyrex proceeded in a straightforward manner. As expected, the only major products were 2-butene and methyl propiolate, arising from the fragmentation reaction, and the dimethylcarbomethoxycyclobutene produced by ring expansion. In both cases complete retention of stereochemistry was observed (Table I, Scheme III).

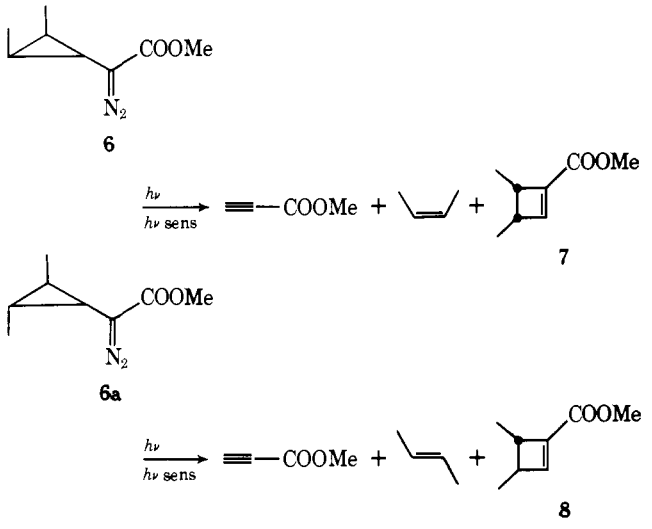
Under gas chromatographic conditions where known mix-

Table I. Yields of Rearrangement and Fragmentation Products[a]

Run	Diazo ester	Sensitizer	% 7	% 8	% *cis*-2-butene	% *trans*-2-butene
A	*cis*-**6**	Fluorenone	96.5 (41.5)[c]	3.5	99	1
B	*trans*-**6a**	Fluorenone	1.7	98.3 (40.2)	Tr	100
C	*cis*-**6**	Benzophenone	98.2	1.8	*b*	
D	*trans*-**6a**	Benzophenone	0	100 (52.2)	*b*	
E	*cis*-**6**		100 (47.2)	0	100	0
F	*trans*-**6a**		0	100 (46.3)	0	100

[a] Runs A, B, E, and F were performed in duplicate without appreciable variation in the numbers shown. [b] Isomerization of products under reaction conditions. 0% = none to within the limits of detection, ca. 0.5%. [c] Absolute yields of dimethylcyclobutene esters are in parentheses.

Scheme III



tures of butenes could be cleanly separated[27] only the 2-butene isomer corresponding to retention of stereochemistry was seen. That is, *trans*-diazo ester **6a** gave *trans*-2-butene and *cis*-diazo ester **6** yielded *cis*-2-butene. No other volatile olefinic products were detected.

The products remaining in solution were separated and collected by preparative gas chromatography. Methyl propiolate was identified as a product in both irradiations by coinjection and comparison of spectra with those of an authentic sample. The ring-expanded products from both the cis and trans diazo esters **6** and **6a** were identified by their nuclear magnetic resonance (NMR) and infrared (ir) spectra. The absolute stereochemistry of the disubstituted carbomethoxycyclobutenes was assigned on the basis of the magnitude of the coupling constants of the nonolefinic cyclobutyl protons. A value of 4.5 Hz was measured for the product arising from the ring expansion of the cis diazo ester **6** and 1.4 Hz for the corresponding product from the trans diazo compound **6a.** The larger coupling constant was assigned to the *cis*-3,4-dimethyl-1-carbomethoxycyclobutene (**7**) where the dihedral angle between the cyclobutyl protons is small, and the smaller coupling constant assigned to the *trans*-3,4-dimethyl-1-carbomethoxycyclobutene (**8**) where the angle between the cyclobutyl protons is larger. Agreement with the values determined for cyclobutene itself (J_{cis} = 4.65 Hz, J_{trans} = 1.75 Hz) is excellent.[28]

Further indication that the stereochemistry was assigned correctly comes from the behavior of **7** and **8** upon injection into the gas chromatograph. Under conditions where the *cis*-dimethylcarbomethoxycyclobutene was stable, the trans isomer opened completely to the 3-carbomethoxy-*trans,trans*-hexa-2,4-diene (injector temperature 140 °C, column 120 °C). NMR spectra of crude reaction product showed no hexadiene, and the trans cyclobutene ester (**8**) could be collected unchanged from the gas chromatograph under more gentle conditions. This behavior is in agreement with similar observations made by Winter[29] on the relative stabilities of *cis*- and *trans*-3,4-dimethylcyclobutene.

Coinjection of the *cis*- and *trans*-dimethylcarbomethoxycyclobutenes **7** and **8** into the gas chromatograph showed that they could easily be separated from each other and the 3-carbomethoxy-*trans,trans*-hexa-2,4-diene. The absolute yields of cyclobutenes are shown in Table I. Accurate absolute yields of the methyl propiolate could not be obtained since under gas chromatographic conditions where the components of the crude mixture could be separated, partial decomposition occurred. All products, except as already discussed, were shown by suitable control experiments to be stable under photolysis and separation conditions. The diazo esters **6** and **6a** when injected into the gas chromatograph also rearranged with retention of stereochemistry to **7** and **8,** respectively. No products corresponding to loss of original stereochemistry were seen.

The benzophenone-sensitized irradiations of diazo esters **6** and **6a** were performed with a 10:1 ratio of benzophenone to diazo ester. The products were analyzed as in the unsensitized irradiations. The triplet carbene was expected to rearrange to a diradical intermediate which would give rise to a mixture of isomeric products (Scheme I). Gas chromatographic analysis showed that the cyclobutenes were formed with almost complete retention of stereochemistry, as only a trace of *trans*-3,4-dimethyl-1-carbomethoxycyclobutene (**8**) could be detected in the irradiation of the cis diazo ester **6** (Table I). Unfortunately the 2-butenes were found to isomerize under the reaction conditions, so the stereospecificity of the fragmentation reaction could not be determined. Control experiments showed that esters **7** and **8** did polymerize upon prolonged sensitized irradiation, but the amount of compound consumed was negligible in 3-h irradiations. No interconversion, fragmentation, or ring opening of the cyclobutene esters could be detected under the reaction conditions. Methyl propiolate was also found to be stable.

A different sensitizer that would not isomerize the 2-butenes but would sensitize the diazo ester decomposition was neces-

Table II. Variation in the Amount of Adduct as a Function of Sensitizer Concentration

Diazo ester [6]		Adduct % **10**[a]
	[Fluorenone]	
1	10	25.2
1	1/2	24.3
1	1/4	21.8
1	1/20	16.3
1	0	3.5
	[Benzophenone]	
1	3	25.9

[a] Percent relative to the amount of *cis*-3,4-dimethyl-1-carbomethoxycyclobutene (**7**).

sary. Fluorenone has a lower triplet energy than benzophenone (53.3 vs. 68.5 kcal/mol)[30] and would neither react directly with the carbene nor interfere with the product analysis. A report in the literature indicated that prolonged irradiation of *cis*-2-pentene in benzene with equal amounts of fluorenone led to much less isomerization than a similar irradiation using benzophenone.[31] Dilute solutions of *cis*- and *trans*-2-butene were irradiated for 3 h under the usual reaction conditions in the presence of a large excess of fluorenone. Gas chromatographic analysis showed no interconversion of olefins.

The question of whether or not fluorenone could efficiently sensitize the decomposition of a diazo ester to a triplet carbene was addressed in other experiments. The first was to examine the effect fluorenone sensitization had on the relative amounts of *cis*- and *trans*-2,3-dimethyl-1,1-dicarbomethoxycyclopropane produced by the addition of dicarbomethoxycarbene to *cis*-2-butene. This system was chosen as a test case because it has been well studied with other triplet sensitizers.[32] A solution of dimethyl diazomalonate in benzene with a large excess of *cis*-2-butene was irradiated for 3 h. The ratio of cis to trans adduct in the unsensitized photolysis was 93.5/6.5. Fluorenone sensitization (10:1) changed the cis/trans adduct ratio to 28.0/72.0. This compares favorably with the benzophenone-sensitized (4:1) value of 19.0/81.0.[33] No interconversion of products took place under the reaction or analysis conditions.

The cis and trans diazo esters **6** and **6a** were irradiated in benzene with a 20-fold molar excess of fluorenone under conditions similar to those used in the other photolyses. The products were identified and analyzed as previously described. Both the 2-butenes and the dimethylcarbomethoxycyclobutenes were formed with retention of stereochemistry. Only a trace of product corresponding to loss of original stereochemistry could be detected (Table I, Scheme III). Additional irradiation (1 h) of both a reaction mixture derived from the fluorenone-sensitized cis diazo ester irradiation and a crude reaction mixture from the sensitized trans diazo ester photolysis showed no change in the relative amounts of products present.

We were concerned initially as to whether or not the triplet carbene was actually formed in the fluorenone-sensitized irradiation. The simplest explanation for retention of stereochemistry in the sensitized irradiation was that no significant sensitization took place and the singlet carbene reaction was again observed. In order to establish the presence of the triplet carbene in the fluorenone-sensitized irradiation, addition of the *cis*-dimethylcyclopropylcarbomethoxycarbene (**9**) to *cis*-2-butene was attempted. In several direct and fluorenone-sensitized irradiations only carbene rearrangement products were observed, no adduct was found. Thus, the nonstereospecific addition of the dimethylcyclopropylcarbomethoxycarbene (**9**) could not be used as a criterion for the presence of the triplet carbene. A similar reaction using benzophenone as a sensitizer also failed to yield an adduct with *cis*-2-butene. The benzophenone- or fluorenone-sensitized addition of diazo ester **6** did yield an adduct (**10**) with isobutylene in analogy to the reaction reported for cyclopropylcarbomethoxycarbene[34] (Table II). In both the sensitized and unsensitized addition to isobutylene *cis*-3,4-dimethyl-1-carbomethoxycyclobutene (**7**) remained the major product. The ratio of the methyl propiolate to the cyclobutene, estimated from the integration of the crude NMR spectrum, did not vary to any dramatic extent, and the overall yield of products remained approximately the same. The adduct was isolated using preparative gas chromatography and gave a satisfactory spectroscopic analysis for **10.** In the unsensitized addition, the amount of adduct **10** relative to ester **7** was 3.5%. Addition of fluorenone increased the fraction of adduct to 25.2%. Benzophenone-sensitization resulted in a yield of adduct of 25.9% (Table II). The relative suppression of intramolecular rearrangements vs. intermolecular reactions in the sensitized as compared with the direct irradiation is good evidence for the presence of a triplet carbene. Similar enhancement of the intermolecular reaction over the intramolecular reaction in going from a singlet to a triplet carbene has been demonstrated several times.[34-36]

Table III. Ratio of Fragmentation to Ring Expansion

Diazo ester **6** Run	% **7**[a]	Diazo ester **6a** Run	% **8**[a]
A	66	B	85
C	65	D	80
E	67	F	80

[a] Relative to methyl propiolate.

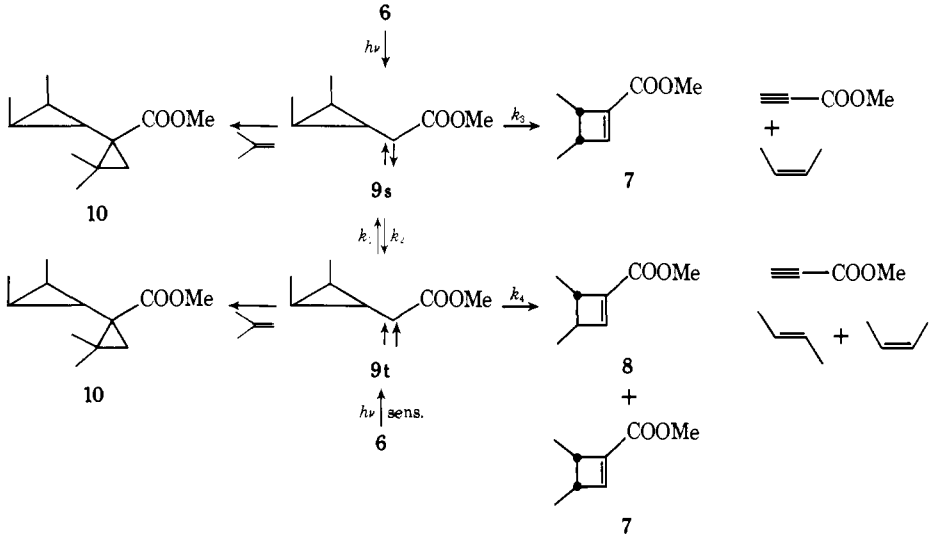
Under conditions where substantial amounts of adduct are formed with isobutylene, none is seen with *cis*-2-butene. The difference in the amount of adduct formed with a small change in olefin structure is striking. However, such an effect is not without precedent. The best studied case is that of diphenylcarbene where arguments have been made for the effect of both the electronic and steric nature of the olefin on the relative amounts of cyclopropanes produced.[37] Further work is underway to examine the dependence of cyclopropylcarbomethoxycarbene addition on olefin structure.

The ratios of fragmentation to ring expansion in the sensitized and unsensitized irradiations are shown in Table III. This ratio remains nearly constant in going from sensitized to unsensitized decomposition. The major factor influencing the relative amounts of fragmentation and ring expansion is the stereochemistry of the cyclopropyl ring. The cis diazo ester (**6**) shows slightly more fragmentation than the trans diazo ester (**6a**). The small difference in the fragmentation vs. ring expansion ratio for the cis and trans carbenes (**9** and **9a**) is real but not mechanistically interpretable at this time.

In the direct irradiation the rearrangement of the singlet carbene proceeds with retention of stereochemistry in both the fragmentation and ring expansion. The complete retention of stereochemistry in both the trans and, more importantly, the cis isomer is dramatic enough to indicate that the singlet carbene rearrangement takes place entirely by a concerted mechanism. This result eases the doubt caused by the small, but substantial, amounts of compound corresponding to loss of stereochemistry seen by others in the rearrangement of *cis*- and *trans*-2,3-dimethylcyclopropylcarbene.[17,21]

The fragmentation of singlet *trans*-2,3-dimethylcyclopropylcarbene has been described as a concerted, disrotatory nonlinear cheletropic process.[16] The same description may be

Scheme IV

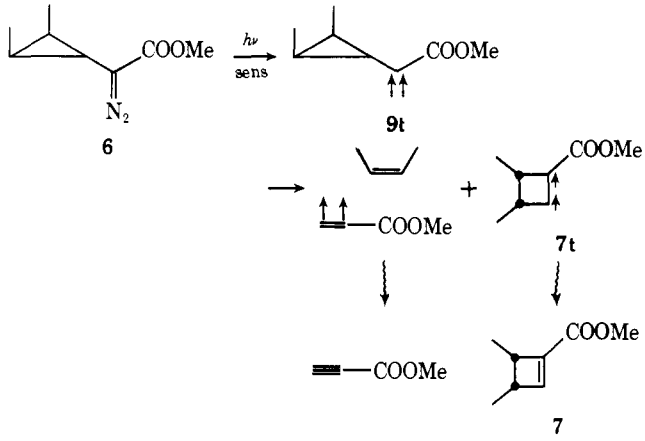


applied to the fragmentation of *cis*-2,3-dimethylcyclopropylcarbomethoxycarbene (**9**) and *trans*-2,3-dimethylcyclopropylcarbomethoxycarbene (**9a**) encountered in this work (Scheme IV). In this case it is satisfying to see the same high degree of specificity in product formation that was observed earlier.[10,16] The lower degree of stereospecificity seen by Guarino and Wolf[21] may be associated with the gas-phase conditions in which their carbenes were generated, or to the relative stability of carbene **9** (**9a**) compared with dimethylcyclopropylcarbene.

As discussed previously, the increase in the amount of addition product occurring in going from the direct to the sensitized decomposition of cis diazo ester **6** in isobutylene is good evidence that the triplet carbene is formed in the fluorenone-a sensitized irradiation. The small change in the amount of isobutylene adduct formed as the amount of sensitizer is decreased by a factor of 40 (Table II) indicates that under photolysis conditions, where fluorenone to diazo ester ratios were 20:1, complete sensitization is occurring. The retention of stereochemistry in the sensitized photolysis products refutes our earlier thoughts that the triplet carbene might rearrange through a 1,4 diradical (Scheme I). It is possible, but very unlikely, that a diradical plays a major role in this stereospecific reaction. In order to explain retention of stereochemistry using such an intermediate it would have to be assumed that intersystem crossing and subsequent closure or fragmentation occurred faster than bond rotation. This seems a poor assumption in view of the behavior of other 1,4 diradicals. The addition of benzyne to *cis*- and *trans*-1,2-dichloroethylene proceeds with substantial loss of stereochemistry,[38] and 1,4 diradicals generated in other systems have been shown to close with loss of stereochemistry, especially in the triplet state.[39-41] The small amounts of nonstereospecific products produced in the sensitized irradiations may well arise from such a pathway. As discussed earlier, the 1,4-diradical intermediate plays a major role in the reactions of other cyclopropylcarbenes.[18,19] The reason for the difference in mechanism is unclear, but may have to do with the greater stability of the diradicals derived from the other cyclopropylcarbenes, or to the existence of alternate reactions of the triplet carbene **9t** in this instance.

Could the triplet carbene rearrange directly to triplet products which then relax to their singlet ground states without loss of stereochemistry (Scheme V)?[42] It is known that triplet 2-butenes lose stereochemistry in returning to the ground state,[43] and since the 2-butenes are formed stereospecifically in this case, it must be assumed that any triplet carbene fragmentation gives only singlet olefin and triplet methyl propiolate. It must also be assumed that the triplet carbomethoxy-

Scheme V



cyclobutene (**7t**) formed by the ring expansion of the triplet carbene does not ring open, react, or lose stereochemistry. Irradiation of cyclobutene **7** in the presence of benzophenone or fluorenone did not result in loss of stereochemistry or ring opening, but there is no guarantee that sensitization was achieved. Might the triplet carbomethoxycyclobutene **7t** be formed in the sensitized irradiation only to return to the ground state unchanged? The gas-phase reactions of triplet *cis*-3,4-dimethylcyclobutene indicate that it ring opens to a mixture of hexadienes whose composition varies widely with the pressure of inert gas in the system.[44] However, the extension of these results to the solution chemistry of **7** is unwise. Acetone-sensitized irradiation of cyclobutene gives mainly oxetane formation and radical addition neither of which is observed in this case. Ring opening is not observed.[45] A concerted triplet carbene rearrangement to give products in their excited states is an intriguing possibility and cannot be rigorously excluded in this case. However, such behavior has not been observed in other triplet carbene rearrangements. A further clarification awaits an investigation of the solution chemistry of triplet *cis*-3,4-dimethyl-1-carbomethoxycyclobutene (**7t**).

A plausible explanation which finds precedent in the behavior of other carbenes is that the singlet and triplet cyclopropylcarbomethoxycarbenes (**9s** and **9t**) are in equilibrium,[37] and what is observed in the sensitized irradiations are the rearrangement products of only the singlet carbene. If the triplet and singlet carbenes equilibrate, there are two possible explanations of why only singlet carbene products are observed. The first is that cyclopropylcarbomethoxycarbene is a ground state singlet and that the equilibrium between the singlet and triplet lies far in favor of the singlet carbene. That is, $k_1 \gg k_2$

and $k_1 > k_4$ (Scheme IV). The triplet carbene once formed undergoes rapid intersystem crossing to the singlet before it has a chance to react via the diradical pathway (k_4). Return to the triplet state is slow or impossible, and products arise from the concerted pathway (k_3) with retention of stereochemistry. A variation of this mechanism is that an appreciable equilibrium exists between the singlet and triplet carbenes ($k_1 \cong k_2$), and the ratio of products is determined by the relative magnitude of k_3 and k_4. To explain retention of stereochemistry in the products, k_3, the concerted pathway, would have to be of considerably lower energy than the diradical pathway k_4. Since the ground state of the cyclopropylcarbomethoxycarbene is not known with certainty,[46] a reasonable choice between these possibilities cannot be made.

We prefer the last mechanism in which singlet carbene plays the crucial role in both the direct and sensitized irradiations to other explanations. There is essentially no change in the ratio of fragmentation to ring expansion in going from direct to sensitized photolysis (Table III). This supports the contention that the products in both irradiations arise from the same intermediate, namely the singlet carbene. If the sensitized and direct irradiations involved product formation from different intermediates, these species would be required to give the same fragmentation to ring-expansion ratio; an unlikely event.

Of course it would be possible, as it nearly always is, to reword all of the mechanistic discussions to exclude carbenes in favor of singlet and triplet diazo compounds. We cannot rigorously exclude such a possibility, but can note that cyclopropylcarbenes have been generated in a variety of ways and that ring expansion is ubiquitous.[3,47] Thus the assumption that carbenes are the reactive intermediates in this case seems valid.

The variation in the amount of carbene addition to isobutylene in going from singlet to triplet carbene may arise from many factors depending on the relative magnitudes of the rate constants in Scheme IV. However, the equilibrium between singlet and triplet carbene (or the rate at which the triplet undergoes intersystem crossing to the singlet if the carbene is a ground state singlet) is not the fastest reaction in Scheme IV. If equilibrium were established faster than addition or rearrangement, the amount of adduct produced in the addition to isobutylene would be the same for the singlet and triplet carbenes. Since a difference in the yield of adduct is seen when starting with the singlet or triplet carbene, the rate of interconversion between these two species cannot be faster than the rate of other possible reactions.

Conclusion

One thing is clear; both the sensitized and direct irradiation of diazo esters **6** and **6a** give rise to products with retention of stereochemistry. The reaction most likely involves a concerted rearrangement. The specific nature of the pathway that the triplet cyclopropylcarbomethoxycarbene follows to give these products remains a subject of some doubt.

A direct rearrangement to triplet products which subsequently relax to their ground state without loss of stereochemistry is not ruled out, but a second, more likely, possibility is the formation of a singlet carbene from the triplet through intersystem crossing. If an appreciable equilibrium exists between the singlet and triplet carbenes, the predominance of the concerted rearrangement of the singlet over the triplet rearrangement can also explain the photolysis results.

Experimental Section

General. Nuclear magnetic resonance spectra were recorded at 60 MHz using a Varian A-60A spectrometer. All chemical shifts are measured in ppm from Me_4Si (δ). Infrared spectra were taken on a Perkin Elmer 237-B grating spectrophotometer. Mass spectra were run on an AEI MS-9 spectrometer. Gas chromatographic collections and analyses were performed on an Aerograph A90P chromatograph using the following columns: (A) 5 ft, 15% Carbowax 20M on 60/80 mesh Chromosorb P; (B) 6 ft, 10% Carbowax 20M on 60/80 mesh Chromosorb P; (C) 1 ft, 10% FFAP on 60-80 mesh Chromosorb P; and (D) 9 ft, 10% (v/v) saturated $AgNO_3$/ethylene glycol on 60/80 mesh Chromosorb P. Gas chromatographic analyses of dimethylcarbomethoxycyclobutenes were performed on a Varian Aerograph series 1520 chromatograph (we thank P. v. R. Schleyer for use of this machine) using column B. Yields were determined gas chromatographically and are corrected for relative detector responses. All photolyses were carried out with a Hanovia 450-W medium-pressure mercury arc shielded with Pyrex filters. Samples were cooled to ca. 15 °C. Unless further purification is indicated, material was used as received from the commercial sources. Melting points taken on a Thomas Hoover apparatus are uncorrected.

Preparation of Methyl Diazopyruvate (1). The reaction of methyl oxalylchloride with an ether solution of diazomethane has been described elsewhere.[48] A pale-yellow powder precipitated from solution and was usually used without further purification. The diazopyruvate may be recrystallized from CCl_4 [mp 102.5–104 °C; (lit. 103–5 °C)]. Yields ranged from 67–73% (lit. 90%) NMR δ (C_6D_6) 3.28 (s, 3 H), 5.37 (s, 1 H); ir ($HCCl_3$) 2120, 1755, 1730, 1645, 1358, 1265 cm^{-1}.

Preparation of Oxoacetate 2. Methyl diazopyruvate (**1**) (7.5 g, 0.059 M) was dissolved in 30 ml of dry benzene and added to a large excess (ca. 40 ml) of dry *cis*-2-butene (99.0% min) in a 250-ml Fischer-Porter pressure bottle containing 9.35 g (0.059 M) of anhydrous $CuSO_4$. The bottle was sealed, wrapped in heating tape, and placed on a Paar shaker. The mixture was heated for 12 h at 75 °C with vigorous shaking. **Caution!** Shield apparatus and use a safety pressure release device. Both vigorous shaking and heating are necessary for the reaction to take place. A similar addition using a magnetic stirrer and an oil bath led to very low product yields. After shaking, the bottle was allowed to cool, and the excess butene was carefully allowed to boil off. The solution was then filtered and decolorized with activated charcoal. The products were purified by GC on column A at 135 °C. The crude reaction mixture consisted of three major components: **2**, **4**, and **5** (Scheme II). The relative yield of each: 66.0, 4.6, and 29.4%, respectively; absolute yield of **5**, 0.93 g and **2**, 2.41 g; overall yield, 35.4%. Yields of **2** and **5** in other runs varied from 33.6–44.0%. In some instances trace amounts of dimethyl oxalate and what was probably carbene dimer (CH_3OOC-CO-CH=CH-CO-$COOCH_3$) were isolated. **2**: ^1H NMR δ (CCl_4) 3.82 (s, 3 H), 2.07 (doublet of doublets, 1 H), 1.40–1.85 (m, 2 H), 1.16 (m, 6 H); ir (CCl_4), 2940, 1760, 1737, 1706, 1268, 1130, 1087 cm^{-1}. **5**: ^1H NMR δ ($CDCl_3$) 5.98–5.42 (m, 1 H), 5.16–4.78 (doublet of doublets, 2 H), 3.46 (s, 3 H), 2.65 (bs, 2 H), 0.94 (d, 3 H); ir (CCl_4) 2945, 1758, 1737, 1645, 1250, 1005, 990, 915 cm^{-1}. **4**: ^1H NMR, δ (CCl_4) 5.76 (d, 1 H), 4.42–4.96 (m, 1 H), 3.82 (s, 3 H), 1.32 (d, 3 H), 0.99 (d, 3 H); ir (CCl_4), 2960, 1745, 1630, 1470, 1440, 1304 cm^{-1}. "Dimer": ^1H NMR δ ($CDCl_3$) 6.87 (s, 2 H), 3.81 (s, 6 H); ir ($HCCl_3$) 2995, 1730, 1645, 1443, 1305, 1121 cm^{-1}.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found (**2**): H, 7.73. Found (**5**): C, 61.59; H, 7.73.

Preparation of Oxoacetate 2a. The $CuSO_4$-catalyzed carbene addition was performed as in the case of the cis isomer, using *trans*-2-butene (100%). Attempts to purify the crude mixture by gas chromatography led to rearranged product **5**. The crude reaction mixture, a yellow-orange oil, was purified by column chromatography on silica gel using an 80/20 cyclohexane/ethyl acetate solution as eluent. The desired product was the first material to come off the column; other compounds were not isolated. Yields of **2a** varied from 29.8–36.6%. **2a**: ^1H NMR δ ($CDCl_3$) 3.85 (s, 3 H), 2.49 (doublet of doublets, 1 H), 1.84–0.98 (m, 8 H); ir (neat) 2940, 1755, 1737, 1700, 1436, 1270, 1175 cm^{-1}; precise mass *m/e:* calcd for $C_8H_{12}O_3$ (**2a**): 156.078 638. Found: 156.077 171.

Preparation of Tosylhydrazones of 2 and 2a. Keto ester **2** (2.24 g, 0.143 M) was dissolved in 2 ml of methanol. A solution of 2.66 g (0.143 M) of recrystallized tosylhydrazide in 8 ml of methanol was added dropwise to the keto ester solution with stirring and gentle heating. The mixture was stirred at reflux for 2–6 h and cooled overnight; three crops of white crystals were isolated (total yield 4.41 g = 95%). NMR spectroscopy showed the tosylhydrazone to be present in two isomeric forms, thus an accurate value for the melting points could not be determined (*trans*-tosylhydrazone mp 75–77 °C, 83–84 °C; *cis*-tosylhydrazone mp 99.5–109 °C, 97–99 °C). Tosylhydrazone

of **2**: ^{1}H NMR δ ($CDCl_3$) 7.14–8.04 (AB quartet, 5 H) 3.76, 3.85 (s, 3 H), 2.43 (s, 3 H), 1.38–0.92 (m, 9 H); ir (KBr) 3238, 3200, 2951, 1720, 1695, 1594, 1575 cm^{-1}. Tosylhydrazone of **2a**: ^{1}H NMR δ ($CDCl_3$) 8.66 (bs, 1 H), 8.08–7.22 (AB quartet, 4 H), 3.82 (s, 3 H), 2.44 (s, 3 H), 1.31–0.62 (m, 9 H); ir (KBr) 3240, 3025, 2955, 1701, 1590, 1575 cm^{-1}.

Anal. Calcd for $C_{15}H_{20}N_2O_4S$: C, 55.55; H, 6.22; N, 8.64. Found for tosylhydrazone of **2**: C, 55.60; H, 6.26; N, 8.71. Found for tosylhydrazone of **2a**: C, 55.62; H, 6.25; N, 8.70.

Preparation of Diazo Esters 6 and 6a. Farnum's modification of the Bamford–Stevens reaction was used.[25] *cis*-Tosylhydrazone (1.37 g, 4.23 mmol) was dissolved in 14 ml of pyridine freshly distilled from CaH_2. Sodium methoxide (0.23 g, 4.23 mmol) was added in small portions with stirring at room temperature. Mild heating (30–40 °C) was sometimes used but tended to promote decomposition of the diazo compound. The mixture was stirred for 6–8 h, 20 ml of cold CCl_4 was added, and the reaction mixture was poured onto ice. The layers were separated and the aqueous layer extracted three times with cold CCl_4. The yellow organic layers were combined, extracted with ice water until all the pyridine was removed, and dried over $MgSO_4$ at 5 °C. The carbon tetrachloride was removed under reduced pressure. The remaining yellow oil was distilled using a short path column at room temperature and 0.1 mm Hg. The residue which remained was unreacted tosylhydrazone (0.33 g). The yield based on tosylhydrazone consumed was 38.7%. In a typical reaction the diazo ester was obtained in greater than 95% purity. The major impurity was *cis*- or *trans*-3,4-dimethyl-1-carbomethoxycyclobutene (**7** or **8**). Yields of **7** and **8** from the irradiation were corrected for the amount of cyclobutene present in the diazo compound. **6**: ^{1}H NMR δ (C_6D_6) 3.49 (s, 3 H), 1.02–0.73 (m, 9 H); ir (neat) 2938, 2065, 1703, 1435, 1274, 1125 cm^{-1}. **6a**: ^{1}H NMR δ (C_6D_6) 3.59 (s, 3 H), 1.22–1.50 (m, 1 H), 1.08–0.62 (m, 8 H); ir (neat) 2938, 2060, 1705, 1440, 1308, 1270, 1115 cm^{-1}.

Unsensitized Irradiations. The diazo ester **6** or **6a** was dissolved in ~1.0 ml of dry benzene. The sample was placed in a Pyrex tube fitted with a stopcock and degassed. The sealed tube was irradiated for 3 h using a medium-pressure Hanovia lamp. The concentration of diazo ester ranged from 0.026 to 0.212 g/ml. After the irradiation was complete (infrared spectra showed no diazo absorption), the sample was cooled, and the gaseous products were bubbled into toluene at −78 °C. This method of trapping the gaseous olefinic products was checked by the transfer of known mixtures of *cis*- and *trans*-2-butene in benzene. Within the limits of detection GC analysis showed the cis/trans ratio unchanged. Butenes were analyzed on column D at 25 °C.[27] The components remaining in solution were analyzed by gas chromatography and ^{1}H NMR spectroscopy. Separation of the crude reaction mixture was performed on column B at 125 °C. The collected products were shown to be methyl propiolate and *cis*- or *trans*-3,4-dimethyl-1-carbomethoxycyclobutene (**7** or **8**). The reactions usually proceeded in good yield (Table I) and showed very small, if any, amounts of other products. Absolute yields of cyclobutene ester were calculated by analytical gas chromatography using tetradecane (99.9%) as an internal standard. Under the GC conditions employed for the collection of reaction products ester **8** opened to the corresponding hexadiene [exact stereochemistry was not determined, but NMR spectra are consistent with the expected 3-carbomethoxy-*trans,trans*-hexa-2,4-diene (**11**)]. Under milder conditions using column C at 25 °C ester **8** could be isolated. Under GC conditions where yields were determined (column B at 60–75 °C), no ring opening was detected. Determination of the methyl propiolate yield by gas chromatography was not possible since under conditions where separation of the crude mixture could be achieved partial decomposition took place.

Sensitized Irradiations. The diazo ester was dissolved in benzene and either a 20-fold excess of recrystallized fluorenone or a tenfold molar excess of benzophenone was added. Total volume of the solution was ~7.0 ml. The concentration of diazo ester ranged from 0.009 to 0.026 g/ml. The degassed sample was irradiated (3 h, Pyrex tube) and worked up as in the unsensitized case. Yields were determined by gas chromatography. Relative amounts of methyl propiolate and dimethylcarbomethoxycyclobutene were determined from the crude ^{1}H NMR spectra and are shown in Table III along with the ratios for the unsensitized irradiations. **7**: ^{1}H NMR δ (C_6D_6) 6.81 (d, 1 H), 3.63 (s, 3 H), 3.42–2.50 (2 H), 1.22 (d, 3 H, J = 7.0), 0.98 (d, 3 H, J = 7.3); ir (CCl_4) 2950, 1730, 1600, 1425, 1300, 1245, 1140 cm^{-1}. **8**: ^{1}H NMR δ (C_6D_6) 6.79 (d, 1 H), 3.57 (s, 3 H), 2.77–1.94 (2 H), 1.31 (d, 3 H, J = 7.0), 1.04 (d, 3 H, J = 7.2); ir (CCl_4) 2950, 1725, 1600, 1437, 1280, 1270, 1245, 1125 cm^{-1}.[48] Methyl propiolate: ^{1}H NMR δ (C_6D_6) 3.29 (s, 3 H), 2.27 (s, 1 H); ir (neat) 3250, 2952, 2125, 1718, 1432, 1235, 983, 858, 755 cm^{-1}. 3-Carbomethoxy-*trans,trans*-hexa-2,4-diene (**11**): ^{1}H NMR δ (CCl_4) 6.23–5.56 (m, 3 H), 3.72 (s, 3 H), 1.84 (d, 3 H), 1.72 (d, 3 H); ir (CCl_4) 2950, 1730, 1435, 970 cm^{-1}.

Anal. Calcd for $C_8H_{12}O_2$ (**7**): C, 68.55; H, 8.63. Found: C, 68.30; H, 8.69.

Precise mass *m/e*: Calcd for $C_8H_{12}O_2$, **11**: 140.083 724. Found: 140.082 211.

Sensitized Addition of Dimethylcyclopropylcarbomethoxycarbene (9) to Isobutylene. Diazo ester **6** (0.0109–0.0441 g) was transferred to a Pyrex tube with a small amount of benzene; a large excess of isobutylene (~5 ml) was added along with the sensitizer. The tube was degassed, sealed, and irradiated for 3 h. The isobutylene was allowed to slowly boil off, and 3 ml of benzene was added. Gas chromatographic analysis, column B at 130 °C, showed a new peak in addition to carbomethoxycyclobutene (**7**) and methyl propiolate. The new peak was collected and identified as the adduct **10**. Relative yields of adduct **10** and **7** are shown in Table II as a function of sensitizer concentration. A similar set of experiments using *cis*-2-butene showed no adduct.

Adduct **10**: ^{1}H NMR δ (CCl_4) 3.66 (s, 3 H), 1.30–0.18 (m, 17 H); ir (CCl_4) 2940, 1730, 1435, 1130, 1110 cm−1.

Precise mass *m/e*: Calcd for $C_{12}H_{20}O_2$ (**10**): 196.146 321. Found: 196.145 005.

Fluorenone-Sensitized Addition of Dicarbomethoxycarbene to *cis*-2-Butene. Dimethyl diazomalonate[50] (0.320 g, 2.03 mmol) dissolved in 2.0 ml of dry benzene and 4 ml of *cis*-2-butene was irradiated for 3 h in a sealed Pyrex tube. The butene was allowed to boil off, and the samples were analyzed by gas chromatography, column B at 145 °C.

A similar experiment was performed using 0.485 g (3.07 mmol) of dimethyl diazomalonate and 5.01 g of recrystallized fluorenone (9:1) dissolved in 15 ml of dry benzene and 4 ml of *cis*-2-butene. The reaction mixture was analyzed under conditions identical with those above (see text for product ratios). The addition products were identified by coinjection with and comparison of the NMR spectra of authentic samples.[51] In three additional hours of irradiation under the reaction conditions, with a large excess of fluorenone (ca. 10:1), the products obtained from the unsensitized irradiation of dimethyl diazomalonate in *cis*-butene showed no change. Products were also stable under GC conditions.

Control Experiments. A solution of *cis*-3,4-dimethyl-1-carbomethoxycyclobutene (**7**) in benzene was irradiated for 2.5 h in a Pyrex tube under the usual reaction conditions. Both gas chromatographic and proton NMR analysis showed no change. *cis*-3,4-Dimethyl-1-carbomethoxycyclobutene (**7**) (0.252 g, 1.79 mmol) dissolved in 2 ml of benzene with 3.26 g (17.9 mmol) of recrystallized benzophenone was irradiated for a total of 14.5 h using a medium-pressure Hanovia lamp and a Pyrex filter. For the first 3 h samples were taken hourly. Analysis of the proton NMR spectra and GC trace after 3 h showed no substantial change in the amount of **7** or the presence of any new products. At longer reaction times the concentration of **7** was greatly reduced. Gas chromatographic analysis showed trace amounts of many unidentified products. After 14.5 h only a small amount of **7** remained. *trans*-3,4-Dimethylcyclobutene ester **8** showed similar behavior.

Cis diazo ester **6** (0.0670 g) and 1.436 g of recrystallized fluorenone (20:1) were dissolved in 8.0 ml of benzene and irradiated as described previously. The relative yield of products was determined (Table I) by GC analysis. The sample was resealed and irradiated for an additional hour. Gas chromatographic analysis showed no change in the product ratio.

A similar experiment performed using the trans diazo ester **6a** also showed no change in product distribution upon additional irradiation for 1 h.

A solution of methyl propiolate and benzophenone (1:10) in benzene was irradiated under the usual reaction conditions for 3 h. Gas chromatographic and NMR spectral analysis showed no reaction had occurred. Similarly no change was seen when a benzene solution of methyl propiolate/fluorenone (1:20) was irradiated for 3 h. Methyl propiolate was also stable under direct photolysis conditions.

References and Notes

(1) Support for this work by the Van't Hoff Fund and by the National Science Foundation through grants GP 30797X and MPS74-05690 is gratefully

acknowledged.
(2) M. Jones, Jr., and R. A. Moss, "Carbenes", Vol. I, Wiley, New York, N.Y., 1973, p 32–37.
(3) P. S. Skell and J. H. Plonka, *Tetrahedron*, **28**, 3571 (1972). The reactions of *cis*- and *trans*-2,3-dimethylcyclopropylcarbene generated by the addition of atomic carbon to various substrates have been explored by many groups (see ref 3 and 47). However, due to the vast differences in reaction conditions, the difficulty in assigning spin states and the possibility of reactions from vibrationally excited states, a comparison of these investigations and the results presented in this paper will not be made.
(4) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Am. Chem. Soc.*, **93**, 246 (1971).
(5) W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).
(6) W. R. Dolbier, Jr., O. T. Garza, and B. H. Al-Sader, *J. Am. Chem. Soc.*, **97**, 5038 (1975).
(7) P. B. Shevlin and A. P. Wolf, *J. Am. Chem. Soc.*, **88**, 4735 (1966).
(8) I. D. R. Stevens, H. M. Frey, and C. L. Bird, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968).
(9) C. L. Bird, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 707 (1967).
(10) S. S. Olin and R. M. Venable, *Chem. Commun.*, 104, 273 (1974).
(11) W. Kirmse and K.-H. Pook, *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966).
(12) G. Ohloff and W. Pickerhagen, *Helv. Chim. Acta*, **54**, 1789 (1971).
(13) L. Friedman and H. Schecter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).
(14) M. Oda, Y. Ito, and Y. Kitahara, *Tetrahedron Lett.*, 2587 (1975).
(15) C. Walling, *Mol. Rearrangements*, **1**, 441–442 (1963).
(16) J. A. Berson, W. Bauer, and M. M. Campbell, *J. Am. Chem. Soc.*, **92**, 7515 (1970); R. G. Bergman and D. H. White, private communication, 1972.
(17) A preliminary report on the pyrolysis of the tosylhydrazone salts of *cis*- and *trans*-2,3-dimethylcyclopropane-1-carboxaldehyde can be found in the thesis of M. B. Sohn, Princeton University, Princeton, N.J., 1972.
(18) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Am. Chem. Soc.*, **92**, 3118 (1970). See, however, T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *J. Org. Chem.*, **38**, 4095 (1973).
(19) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967).
(20) L. E. Sullivan, unpublished work, 1967.
(21) A. Guarino and A. P. Wolf, *Tetrahedron Lett.*, 655 (1969).
(22) W. Kirmse, B.-G. Bulow, and H. Schepp, *Justus Liebigs Ann. Chem.*, **691**, 41 (1966).
(23) P. K. Freeman and D. P. Kuper, *J. Org. Chem.*, **30**, 1047 (1965).
(24) W. Ando, *Tetrahedron Lett.*, 929 (1969).
(25) D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).
(26) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Am. Chem. Soc.*, **87**, 935 (1965).
(27) M. E. Bednas and D. S. Russell, *Can. J. Chem.*, **36**, 1272 (1958).
(28) I. Flemming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).
(29) R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965).
(30) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 298.
(31) G. S. Hammond, N. J. Turro, and P. A. Leemakers, *J. Phys. Chem.*, **66**, 1144 (1962).
(32) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Lett.*, 1391 (1967).
(33) T. Ford and M. Jones, Jr., unpublished results.
(34) M. B. Sohn and M. Jones, Jr., *J. Am. Chem. Soc.*, **94**, 8280 (1972).
(35) M. Jones, Jr., and W. Ando, *J. Am. Chem. Soc.*, **90**, 2200 (1968).
(36) Y. Yamamoto, S.-I. Murahashi, and I. Moritani, *Tetrahedron*, **31**, 2663 (1975).
(37) M. Jones, Jr., W. J. Baron, and Y. H. Shen, *J. Am. Chem. Soc.*, **92**, 4745 (1970).
(38) M. Jones, Jr., and R. H. Levin, *J. Am. Chem. Soc.*, **91**, 6411 (1969).
(39) L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Am. Chem. Soc.*, **95**, 2849 (1973); also L. M. Stephenson and T. A. Gibson, *J. Am. Chem. Soc.*, **94**, 4599 (1972), and references therein.
(40) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).
(41) F. D. Lewis, *J. Am. Chem. Soc.*, **92**, 5602 (1970).
(42) We thank H. D. Roth for helpful comments.
(43) P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, **5**, 70–79 (1968).
(44) R. Srinivasan, *J. Am. Chem. Soc.*, **91**, 7557 (1969).
(45) R. Srinivasan and K. A. Hill, *J. Am. Chem. Soc.*, **88**, 3765 (1966).
(46) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).
(47) A review of the reactions of cyclopropylcarbene generated by carbon atom reactions and diazo precursors can be found in the thesis of S. M. Kammula, Auburn University, Auburn, Alabama, 1974. See also P. C. Petrellis, G. W. Griffin, M. E. Hendrick, and M. Jones, Jr., *Chem. Commun.*, 1002 (1972).
(48) J. Ratusky and F. Sorm, *Chem. Listy*, **51**, 1091 (1957).
(49) We thank B. Snider for providing a sample of *trans*-3,4-dimethyl-1-carbomethoxycyclobutene used in obtaining ir data.
(50) J B. Hendrickson and W. A. Wolf, *J. Org. Chem.*, **33**, 3610 (1968).
(51) M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Am. Chem. Soc.*, **94**, 7469 (1972).

A Search for an α-Disulfoxide as an Intermediate in the Oxidation of an Aryl Thiolsulfinate[1]

Michael M. Chau and John L. Kice*

Contribution from the Department of Chemistry, Texas Tech University, Lubbock, Texas 79409. *Received May 17, 1976*

Abstract: The oxidation of *p*-fluorophenyl *p*-fluorobenzenethiolsulfinate (**1a**), ArS(O)SAr, to the corresponding thiolsulfonate, $ArSO_2SAr$ (**2a**), by peracetic acid, and other peracids, at −20 °C in chloroform has been studied by ^{19}F NMR. These studies show that the disulfide ArSSAr is *not* formed in detectable amounts during the course of the oxidation, thereby ruling out a mechanism for the oxidation of aryl thiolsulfinates by peracids proposed by Barnard and Percy (ref 8). Study of the oxidation of *p*-fluorophenyl benzenethiolsulfinate (**1b**), PhS(O)SAr, by the same reagent shows that the three different thiolsulfonates, $ArSO_2SAr$, $ArSO_2SPh$, and $PhSO_2SAr$, are all formed and in relative amounts consistent with *at least* 73% of the oxidation going via a pathway involving an α-disulfoxide, ArS(O)S(O)Ph, as an intermediate. The fact that α-disulfoxide ArS(O)S(O)Ar does not build up as an intermediate to a detectable level during the oxidation of **1a** means that it must be so thermally unstable that it has a half-life of less than 60 s at −20 °C. Since this suggests that $\Delta H^{\ddagger}$ for the decomposition of the α-disulfoxide is less than 20 kcal/mol, the S–S bond in an α-disulfoxide is apparently an extremely weak bond, much weaker than the S–S bonds in any of the other possible oxidized derivatives of disulfides.

Structures of **1–5** represent the various possible oxidized forms of an aryl disulfide that still retain the S–S bond. Compounds having all of these structures,[2-5] *except* **3**, *the α-disulfoxide*, are known, although some, such as the sulfinyl sulfones,[4b] **4**, are not very stable thermally.

Several attempts[6,7] to prepare an aryl α-disulfoxide have been made, but each has failed, and the product isolated has been the corresponding thiolsulfonate, **2**. Thus, Barnard[6] found that treating benzenesulfinyl chloride with zinc gave phenyl benzenethiolsulfonate (**2**, Ar = C_6H_5), rather than the α-disulfoxide. Similarly, although several groups[7,8] have felt that an α-disulfoxide was an initial oxidation product of the oxi-