Irradiation of Methyl Diazomalonate in Solution. Reactions of Singlet and Triplet Carbenes with Carbon–Carbon Double Bonds[1]

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Abstract: Direct and sensitized irradiation of methyl diazomalonate gives singlet and triplet biscarbomethoxycarbene, respectively. The reactions of these species with carbon–carbon double bonds are described. Cyclopropanes are formed with substantial retention of stereochemistry from the singlet but with complete loss from the triplet. Additions to allene, norbornadiene, and benzene are also achieved. The reactions of several triplet carbenes with dienes are reported, but even in systems thought to be favorable to 1,4 addition, only the normal cyclopropanes could be found. Reactions with carbon–hydrogen single bonds are also described. Singlet carbene reacts by direct insertion, but the triplet abstracts hydrogen to give radical pairs which undergo recombination and disproportionation.

Myriad descriptions of the properties of carbenes have appeared over the last 10 years.[3a–z] These reviews have been accompanied by an even greater number of descriptions of the properties of individual carbenes. However, relatively few of these accounts have dealt with the problem of distinguishing the two possible electronic states of carbenes, singlets and triplets. A notable exception among the reviews is the discussion by Gaspar and Hammond[4] of the spin states of carbenes. Although it was recognized early that singlet and triplet carbenes might be chemically distinguishable[5,6] and evidence adduced to that effect,[3r,5–8] the properties of the two different states are still not well differentiated. Admonitions to this effect[3m,4] echo earlier[9] warnings that precious little analogy existed for the properties under discussion. Much of the ambiguity exists because of the difficulty in being certain which spin state is being observed. The arguments traditionally presented as to how each spin state should behave are, in the last analysis, based largely upon intuition. As clearly pointed out by Gaspar and Hammond,[4] such arguments gain a sufficient degree of credibility only when the properties of both spin states of a given carbene have been observed. Unfortunately, in only three cases has this ideal been approached. Studies of singlet and triplet methylene,[10–14] fluorenylidene,[15] and dicyanocarbene[16] have been made. None of these examples provides an unequivocally clear picture of the properties of both singlets and triplets.[17]

No entirely satisfactory comparison of the two possible spin states of a carbene in solution is available. In the light of this it seemed sensible to test the various criteria currently in wide use as diagnostics for spin

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[1] (a) Preliminary accounts have appeared: M. Jones, Jr., A. Kulczycki, Jr., and K. F. Hummel, *Tetrahedron Lett.*, 183 (1967); M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *ibid.*, 1391 (1967). For a preliminary account of the chemistry of methyl diazomalonate in the gas phase, see D. C. Richardson, M. E. Hendrick, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 3790 (1971). (b) We wish to express our thanks to the National Science Foundation for support of this work in the form of NSF GP-5257, GP-12759, and GP-30797X, and two Undergraduate Participation Fellowships to A. K., Jr. A generous grant from the Lilly Research Laboratories also contributed to the support of this work. Parts of this work are taken from the A. B. Theses of D. S. M., A. K., Jr., K. F. H., and P. M. H., Princeton University, 1965, 1966, 1967, and 1968. Further portions are extracted from the Ph.D. Thesis of M. E. H., Princeton, 1971.

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[3] (a) P. Miginiac, *Bull. Soc. Chim. Fr.*, 2000 (1962); (b) E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963); (c) E. Chinoporos, *Chim. Chron. A*, **28**, 168 (1963); (d) H. W. Wanzlick, *Angew. Chem.*, **74**, 129 (1962); (e) C.-C. Kuo, *Hua Hsueh Tung Pao*, 27 (1962); *Chem. Abstr.*, **58**, 12377 (1963); (f) W. E. Parham and E. E. Schweizer, *Org. React.*, **13**, 55 (1963); (g) H. Kloosterziel, *Chem. Weekbl.*, **59**, 77 (1963); (h) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (i) H. M. Frey, *Progr. React. Kinet.*, **2**, 131 (1964); (j) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964; (k) W. Kirmse, *Progr. Org. Chem.*, **6**, 164 (1964); (l) J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964); (m) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964); (n) J. I. G. Cadogan and M. J. Perkins in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, Chapter 9; (o) C. W. Rees and C. E. Smithen, *Advan. Heterocycl. Chem.*, **3**, 57 (1964); (p) B. J. Herold and P. P. Gaspar, *Fortschr. Chem. Forsch.*, **5**, 89 (1965); (q) G. G. Rozantsev, A. A. Fainzil'berg, and S. S. Novikov, *Russ. Chem. Rev.*, **34**, 69 (1965); (r) G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968); (s) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967); (t) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes," Appleton-Century-Crofts, New York, N. Y., 1969; (u) W. Kirmse, *Chem. Unserer Zeit*, **3**, 184 (1969); (v) W. Kirmse, "Carbene, Carbenoide und Carbenanaloge," Verlag-Chemie, Weinheim, 1969; (w) R. A. Moss, *Chem. Eng. News*, **47**, 30 (June 16, 1969); (x) D. Bethell, *Advan. Phys. Org. Chem.*, **7**, 153 (1969); (y) A. M. van Leusen and J. Strating, *Quart. Rep. Sulfur Chem.*, **5**, 67 (1970); (z) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

[4] See P. P. Gaspar and G. S. Hammond in ref 3h, p 235 ff.

[5] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

[6] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

[7] R. M. Etter, H. S. Skovronek, and P. S. Skell, *ibid.*, **81**, 1008 (1959). See ref 3r and 8.

[8] M. Jones, Jr., W. J. Baron, and Y. H. Shen, *ibid.*, **92**, 4745 (1970).

[9] W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958), and footnotes in ref 4.

[10] R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965).

[11] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 1015 (1962).

[12] R. J. Cvetanović, H. E. Avery, and R. S. Irwin, *J. Chem. Phys.*, **46**, 1993 (1967).

[13] T. W. Eder and R. W. Carr, Jr., *J. Phys. Chem.*, **73**, 2074 (1969).

[14] D. F. Ring and B. S. Rabinovitch, *Int. J. Chem. Kinet.*, **1**, 11 (1969).

[15] M. Jones, Jr., and K. R. Rettig, *J. Amer. Chem. Soc.*, **87**, 4013, 4015 (1965).

[16] E. Ciganek, *ibid.*, **88**, 1979 (1966).

[17] Our original manuscript contained a detailed justification of this view. Many of the arguments can be found among the reviews in ref 3.

state. We have therefore studied the direct and photosensitized decomposition of methyl diazomalonate in solution. Reported properties of the carbene **1**

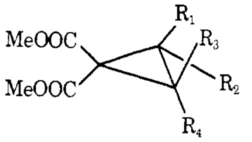
$$(CH_3OOC)_2CN_2 \xrightarrow{h\nu} \underset{\mathbf{1}}{(CH_3OOC)_2C:}$$

derived from this compound are confined to studies of the reaction with the carbon–hydrogen bond[18,19] and occasional accounts of addition reactions,[20] usually copper catalyzed.[21,22]

It was first necessary to determine if cyclopropanes could be formed in reasonable yields and without complicating side products. Some of the olefins used as acceptors for **1** and a few representative yields are shown in Table I. Compounds **2–6** were formed in comparable yields. The structures of the products were proven by elementary and spectral analysis, with the emphasis on nuclear magnetic resonance (nmr). Beyond simple consistency of the spectra with the assigned structures, the most important point was the absence of signals in the region associated with vinyl hydrogen or hydrogen α to two ester groups. Dimethyl malonate absorbs at τ 6.74, Meldrum's acid[23] at τ 6.34, and a variety of compounds produced in this work at τ 6.6–6.9. (Spectra of the cyclopropanes formed in this work can be found in the Experimental Section.) In the cyclopropanes **2–12** no signals were found in this region, save those from methoxy groups. The compounds **4**, **5**, and **6** do show vinyl absorption at τ 5.2, 4.4, and 4.5–5.1, respectively. The presence of a terminal methylene group in **4** and **5** is confirmed further by bands in the infrared spectra at 900 and 908 cm^{-1}, respectively.[24] Similarly, **6** shows bands appropriate for a vinyl group at 922 and 904 cm^{-1}. Affirmation of the cyclopropane ring is found in the presence of bands in the infrared at 990–1030 cm^{-1}, a position often associated with the three-membered ring.[25] Addition to the double bond is accompanied by insertion into the available carbon–hydrogen bonds. In no case is the yield of carbon–hydrogen insertion product comparable to that of the cyclopropane.

Table I. Reaction of **1** with Olefins

Olefin	Yield, %	Product
3,3-Dimethyl-1-butene		**2**
1-Pentene		**3**
2,3-Dimethyl-1,3-butadiene		**4**
Allene		**5**
1,3-Butadiene		**6**
2,3-Dimethyl-2-butene	28	**7**
2-Methyl-2-butene	43	**8**
cis-2-Butene	23	**9** + **10**
trans-2-Butene	16	**10**
cis-4-Methyl-2-pentene	40	**11** + **12**
trans-4-Methyl-2-pentene	24	**12**

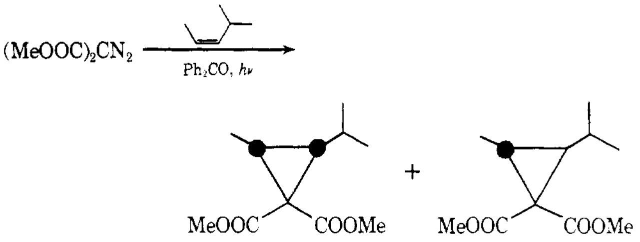


2, $R_1 = (CH_3)_3C$; $R_2 = R_3 = R_4 = H$
3, $R_1 = CH_2CH_2CH_3$; $R_2 = R_3 = R_4 = H$
4, $R_1 = CH(CH_3){=}CH_2$; $R_2 = CH_3$; $R_3 = R_4 = H$
5, $R_1, R_2 = CH_2$; $R_3 = R_4 = H$
6, $R_1 = CH{=}CH_2$; $R_2 = R_3 = R_4 = H$
7, $R_1 = R_2 = R_3 = R_4 = CH_3$
8, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
9, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
10, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
11, $R_1 = CH(CH_3)_2$; $R_3 = CH_3$; $R_2 = R_4 = H$
12, $R_1 = CH(CH_3)_2$; $R_4 = CH_3$; $R_2 = R_3 = H$

Investigation of the addition to cis olefins where more than one cyclopropane may be formed revealed that while the addition is predominately cis, about 10% of the isomeric cyclopropane is also formed (see Table II). In an attempt to induce intersystem crossing from the singlet to the triplet, the photolysis of methyl diazomalonate in *cis*-4-methyl-2-pentene was run in varying concentrations of hexafluorobenzene. Unlike the fluorenylidene case,[15] it is not until very large amounts of hexafluorobenzene have been added that the amount of trans cyclopropane increases significantly (Figure 1). Indeed, initially, the amount of cis cyclopropane increases slightly. We feel that a likely source of this increase is excited methyl diazomalonate. Excited diazo compound could produce trans cyclopropane by addition to the double bond followed by loss of nitrogen and closure. Rotation about the critical carbon–carbon bond might be allowed at several points along the reaction coordinate. As hexafluorobenzene is added to the mixture, excited diazo compound could play a decreasingly important role as fruitless collisions serve to deactivate it to the ground state. The chances of excited diazo compound meeting a receptive molecule will go down as the concentration of olefin decreases. Thus, added inert solvent can produce more cis cyclopropane until enough has been added so that all excited diazo compound has been deactivated and/or intersystem crossing begins. In any event, the direct photolysis does produce an intermediate which gives predominately cis addition to olefins.

Table II. Stereochemistry of Addition of **1** to Olefins

Olefin	Conditions	% **11**	% **12**
cis-4-Methyl-2-pentene	Direct $h\nu$	92	8
trans-4-Methyl-2-pentene	Direct $h\nu$	10	90
cis-4-Methyl-2-pentene	$h\nu/Ph_2C{=}O$	10	90
trans-4-Methyl-2-pentene	$h\nu/Ph_2C{=}O$	14	86



11 **12**

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[18] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **83**, 1989 (1961). See also ref 48.

[19] M. R. Willcott, III, Ph.D. Thesis, Yale University, New Haven, Conn., 1963; *Diss. Abstr.*, **26**, 5730 (1964).

[20] J. A. Berson, D. R. Hartter, H. Klinger, and P. W. Grubb, *J. Org. Chem.*, **33**, 1669 (1968).

[21] R. Breslow, R. Winter, and M. Battiste, *ibid.*, **24**, 415 (1959).

[22] H. Musso and U. Biethar, *Chem. Ber.*, **100**, 119 (1967).

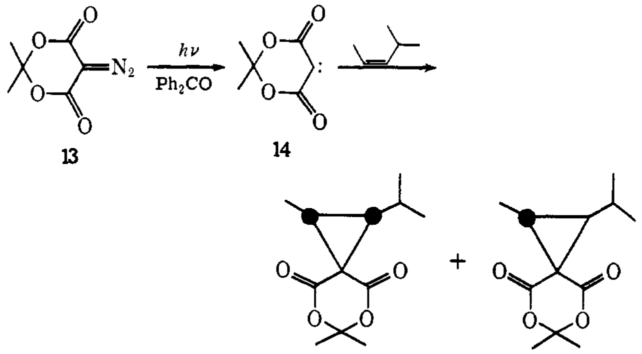
[23] D. Davidson and S. A. Bernhard, *J. Amer. Chem. Soc.*, **70**, 3426 (1948).

[24] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 34.

[25] H. Weitkamp, H. Hasserodt, and F. Korte, *Chem. Ber.*, **95**, 2280 (1962).

Sensitization of the decomposition with benzophenone produces dramatic changes in the mode of addition. The relative extinction coefficients of the diazo compound and benzophenone in the region >3000 Å allows >98% of the light to be absorbed by the sensitizer. Table II contrasts the results of the sensitized and direct irradiations. The species produced in the sensitized reaction yields nearly the same mixture of cyclopropanes from either cis or trans olefin.[26] Less than 2% of isomerization of solvent could be detected, and the adducts themselves were shown to be stable to the reaction conditions.

When the sensitized and unsensitized photolyses of the diazo compound related to Meldrum's acid[28] (**13**)



13 **14**

cis-**15** *trans*-**15**

are compared, a change of a different nature can be noticed. Direct irradiation of **13** in olefins produces very little adduct (1–2%). Indeed, we can isolate very little product of any kind. The sensitized decomposition is very different and here adducts can be isolated in relatively good yield. The direct decomposition produces so little adduct that the stereochemistry of the addition reaction could not be reliably determined. In contrast, the stereochemistry of the sensitized decomposition is exactly what one would expect from a triplet intermediate. These results are summarized in Table III.

Table III. Decompositions of **13** in Olefins

Olefin	Conditions	Yield, %	% cis	% trans
cis-2-Butene	$h\nu$	~2		
	$h\nu$/Ph$_2$C=O	26	14	86
trans-2-Butene	$h\nu$	~2		
	$h\nu$/Ph$_2$C=O		15	85
cis-4-Methyl-2-pentene	$h\nu$	Very small		
	$h\nu$/Ph$_2$C=O	17	4	96
trans-4-Methyl-2-pentene	$h\nu$	Very small		
	$h\nu$/Ph$_2$C=O		6	94

The structures of the adducts were confirmed by an independent synthesis shown below for **15**. The spectra of the adducts are also in accord with the assignments (see Experimental Section).

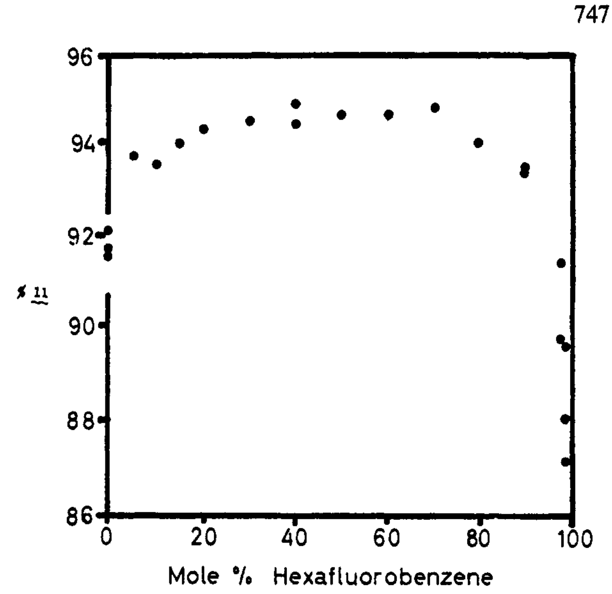
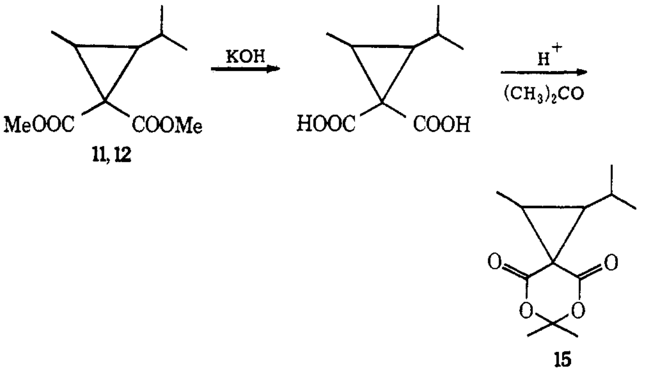


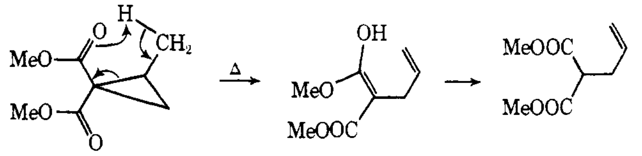
Figure 1. Addition of **1** to *cis*-4-methyl-2-pentene in hexafluorobenzene.



11, 12

15

A freely rotating intermediate produced by addition of triplet biscarbomethoxycarbene or **14** would be expected to give a mixture of cyclopropanes reflecting the thermodynamic stabilities of the products. An attempt to determine this ratio in the malonate case by thermally interconverting the two adducts was thwarted by a new but not unprecedented[29–31] rearrangement. An account of the thermal isomerizations of **2**, **7**, **8**, **9**, and **11** has appeared.[32] The mechanism proposed[32]



is unexceptional and derives support from the observation that 1,1-biscarbomethoxy-2-*tert*-butylcyclopropane (**2**) is stable at 300°.

When allowed to choose between pairs of olefins, stabilized carbenes are often able to discriminate.

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[26] The rationalization of the lack of stereospecificity in carbene reactions is usually one in which addition of triplet methylene takes place in two steps, the rate of rotation in the intermediate competing favorably with the rate of closure to cyclopropane. Alternatively, Hoffmann[27] has pointed out that singlet methylene plus ethylene correlates with a trimethylene in its lowest singlet state and thus with the ground state of cyclopropane. The net result is rapid closing of an initially formed trimethylene. Triplet methylene, on the other hand, correlates with a triplet excited state of trimethylene in which rotation is most easy. Operationally the two explanations are difficult to distinguish, and we shall phrase our arguments in terms of the former.

(27) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(28) B. Eistert and F. Geiss, *Chem. Ber.*, **94**, 929 (1961).

(29) D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel, *Proc. Chem. Soc.*, 415 (1964).

(30) R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, **87**, 2281 (1965).

(31) M. Jones, Jr., and W. Ando, *ibid.*, **90**, 2200 (1968).

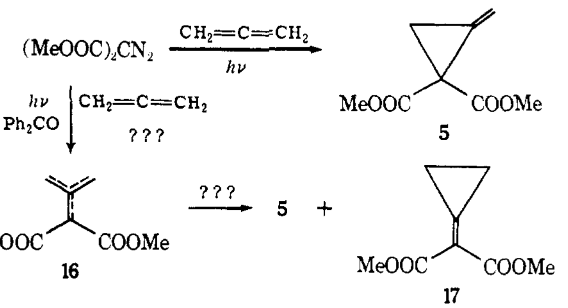
(32) W. Ando, *Tetrahedron Lett.*, 929 (1969).

Singlet carbenes generally act as electrophiles[33–38] although the bulkier ones are subject to steric hindrance.[34–38] In contrast to the large amount of data reported on singlet relative rates, only fragmentary information is available for triplets. Diphenylcarbene is reported[7] to add to 1,3-butadiene and 1,1-diphenylethylene 100 times faster than to *cis*-2-butene. This comparison is not wholly satisfactory, as diphenylcarbene reacts with *cis*-2-butene primarily by hydrogen abstraction, not addition.[3r,8] Triplet fluorenylidene has been shown to add to butadiene faster than to *cis*-4-methyl-2-pentene,[15] but the comparison was only qualitative.[39] These changes in relative rate have been universally rationalized on the basis that allylic resonance would have little effect upon a species adding in one step but a large effect on the triplet, which must add to an olefin to give an intermediate. Our data support the generalization that triplets do add faster to dienes than to unconjugated olefins. Table IV shows two substantial differences between the direct photolysis and the sensitized. There is a three- to fourfold increase in the relative rate of addition to dienes over monoolefins. We feel the earlier arguments adequate to explain this increase. Secondly, there is a decrease in the relative rates of addition to certain olefins. Thus, additions to 2,3-dimethyl-2-butene and *cis*-4-methyl-2-pentene are slower in the sensitized reactions than in the direct decompositions. In the absence of further supporting data, we do not know if this is a general effect. Analysis of the reactions was by gas–liquid partition chromatography (see Experimental Section) and all peaks were calibrated for differences in thermal conductivity by injection of known mixtures.

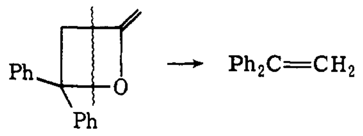
Table IV. Relative Rates of Addition of Singlet and Triplet **1** to Olefins

	Singlet **1**	Triplet **1**
2,3-Dimethyl-2-butene	0.88	0.33
2-Methyl-2-butene	1.0	1.0
1-Pentene	0.47	0.46
3,3-Dimethyl-1-butene	0.48	0.48
cis-4-Methyl-2-pentene	0.55	0.15
trans-4-Methyl-2-pentene	0.23	0.13
2,3-Dimethyl-1,3-butadiene	1.3	4.4
1,3-Butadiene		4.5

Four other addition reactions deserve special mention. Unsensitized decomposition of methyl diazomalonate in allene gives **5** as the only isolable product. Analysis of the crude reaction mixture by nmr spectroscopy also showed no peaks attributable to additional compounds. One might have hoped that the sensitized reaction, proceeding through triplet **1**, would lead to the trimethylenemethane **16**, and then to **5** and **17**. A similar scrambling of a label has been seen in the gas-phase addition of dideuteriomethylene to allene[40] but the most likely explanation for the scrambling involves hot molecule rearrangements, not spin state. In our work, the sensitized decomposition gave only **5** and 1,1-diphenylethylene in the ratio 12:1. The latter product probably arises *via* the oxetane **18**, as shown below. Oxetane formation has been previously observed on irradiation of solutions of benzophenone in allenes.[41] An attempt to prepare **17** independently by pyrolysis of **5** at 500° (0.3 Torr) failed, as **19** appeared as the sole product. This reaction finds remote precedent in the rearrangement of diphenylmethylenecyclopropanes[42] and vinylmethylenecyclopropanes.[43,44]



$$(MeOOC)_2CN_2 \xrightarrow[h\nu,\ Ph_2CO]{CH_2=C=CH_2} \underset{(12)}{5} + \underset{(1)}{Ph_2C=CH_2}$$



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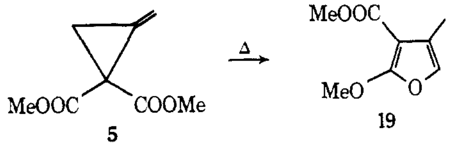

The formation of only the ring-substituted product **5** in the reaction of **1** with allene appears to be typical of triplet carbenes. Thus, diphenylcarbene, triplet fluorenylidene, and triplet carbomethoxycarbene all react analogously.[45] The last case is of some interest, as triplet carbomethoxycarbene has not received wide attention.[46] The results of benzophenone-sensitized

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(33) P. S. Skell and R. M. Etter, *Chem. Ind.* (*London*), 624 (1958).

(34) R. A. Moss, *J. Org. Chem.*, **31**, 3296 (1966).

(35) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Amer. Chem. Soc.*, **85**, 2754 (1963).

(36) G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965).

(37) M. Jones, Jr., A. M. Harrison, and K. R. Rettig, *ibid.*, **91**, 7462 (1969).

(38) R. A. Moss, in "Carbenes," M. Jones, Jr., and R. A. Moss, Ed., Interscience, New York, N. Y., 1972.

(39) Quantitative work of J. D. Walton fixes the ratio of rates of addition of triplet fluorenylidene to 2,3-dimethylbutadiene and *cis*-4-methyl-2-pentene as ~22.5.

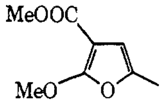
(40) W. von E. Doering, J. C. Gilbert, and P. A. Leermakers, *Tetrahedron*, **24**, 6863 (1968).

(41) H. Gotthardt, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, **33**, 2774 (1968).

(42) M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and R. A. Butler, *Tetrahedron Lett.*, 845 (1970).

(43) T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, **90**, 4749 (1968).

(44) (a) A. C. Day, C. G. Scales, O. J. R. Hodder, and C. K. Prout, *Chem. Commun.*, 1228 (1970). (b) See also M. E. Hendrick, *J. Amer. Chem. Soc.*, **93**, 6337 (1971) for an account of the formation of the related i from triplet **1** and methylacetylene.



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(45) M. E. Hendrick, Ph.D. Thesis, Princeton University, Princeton, N. J., 1971.

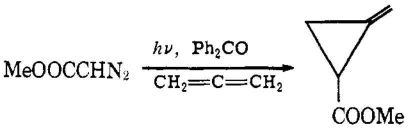
(46) See, however, footnote 3 in T. DoMinh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1766 (1970).

and unsensitized decompositions of methyl diazoacetate in the 2-butenes are appended below in Table V. Substantial, but not complete, loss of stereospecificity occurs. It might be noted that although the results of the unsensitized reactions are only in general agreement with the early report of Doering and Mole,[47] they do well with the later work of Neil.[48]

Table V. Stereochemistry of Addition of Carbomethoxycarbene to Olefins

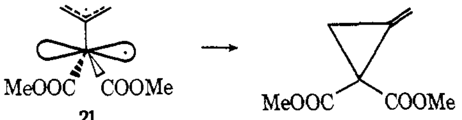
Olefin	Conditions	Cyclopropane Cis-anti	 Cis-syn	 Trans
cis-2-Butene	Direct $h\nu$	1.0	0.56	0.07
trans-2-Butene	Direct $h\nu$	1.0		13.4
cis-2-Butene	$Ph_2C=O/h\nu$	1.0	0.25	2.5
trans-2-Butene	$Ph_2C=O/h\nu$	1.0	0.10	9.5

The sensitized decompositions of methyl diazomalonate and methyl diazoacetate in allene clearly proceeded faster than the unsensitized, and yet only the adducts **5** and **20** could be isolated or detected in the crude products.



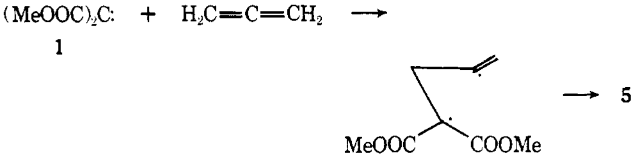
20

The failure to observe **17** has several possible explanations. (1) Instead of undergoing energy transfer to the diazo compound, triplet benzophenone might be undergoing quenching in some other way. However, added benzophenone does increase the rate of decomposition of the diazo compound, and given that energy transfer from benzophenone to methyl diazomalonate occurs under other conditions, we doubt the validity of this first possibility. (2) Perpendicular trimethylenemethanes may be involved. If so, the logical choice is **21**, which has the electron in the lone orbital well delocalized over the two ester groups. Intermediate **21** can close only to **5**. But triplet trimethylenemethanes are known to be planar,[49] and although the corresponding singlet states may be in the perpendicular arrangement,[50] there is no reason to suspect their presence in these reactions. (3) Regardless of the trimethylenemethanes formed, it might be that a preference to close to products bearing the ester groups on the ring exists. There is indirect evidence that trimethylenemethanes will not close exclusively to ring-substituted products. Recent reports of the direct and sensitized photolyses of substituted 4-methylene-1-pyrazolines have shown that sensitization favors formation of the ring-substituted products.[51-53] These products are by no means the sole ones, however, as they are in the carbene–allene reactions. (4) Finally, addition might occur only at the terminal position of the allene, which would require exclusive formation of **5**.

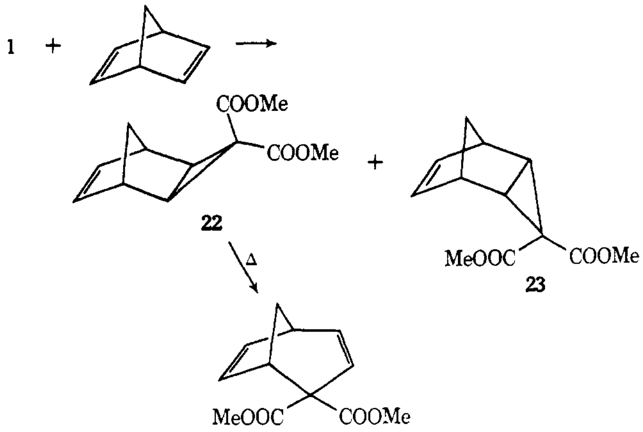


21 **5**

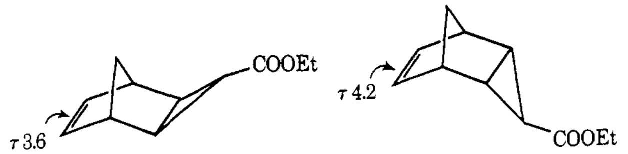
Addition to the terminal position in the allene finds some support in the preference of triplet **1** for monosubstituted olefins as revealed by relative rate studies (see Table IV), and in the absence of compelling evidence for another explanation, we favor this one.



Singlet **1** adds to norbornadiene to give two products, **22** and **23**, in the ratio 68/32. On incautious gas chromatography, a third compound, **24**, also appears, but this is not present in the crude reaction mixture and is not a primary product. Triplet **1** gives the same two products in the slightly changed ratio of 79/21. Assignment of structure was by inspection of spectra (see Experimental Section for details). The stereochemistry was fixed as **22** = exo and **23** = endo by analogy to the monoesters **25** and **26** synthesized by Sauers and Sonnet,[54] with particular emphasis given the chemical shift of the vinyl protons.



22 **23** **24**



25 **26**

22, τ 3.6 23, τ 4.4

Rearrangement to **24** takes place at 140–180° only from the exo compound **22** and finds direct analogy in the related rearrangements discovered by Franz and Osuch[55] and Klumpp and coworkers.[56] No sign of the product of 2 + 4 addition of **1** to norbornadiene could be found even in the triplet case.

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[47] W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

[48] T. C. Neil, Ph.D. Thesis, Pennsylvania State University, University Park, Pa., 1964.

[49] P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **90**, 2715 (1968).

[50] (a) M. J. S. Dewar and J. S. Wasson, *ibid.*, **93**, 3081 (1971); (b) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

[51] T. Sanjiki, H. Kato, and M. Ohta, *Chem. Commun.*, 496 (1968).

[52] T. Sanjiki, M. Ohta, and H. Kato, *ibid.*, 638 (1969).

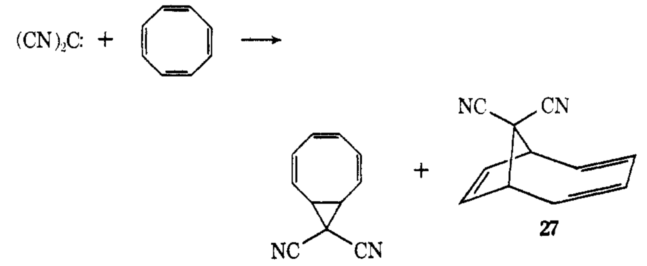
[53] S. D. Andrews and A. C. Day, *ibid.*, 667 (1966).

[54] R. R. Sauers and P. E. Sonnet, *Tetrahedron*, **20**, 1029 (1964).

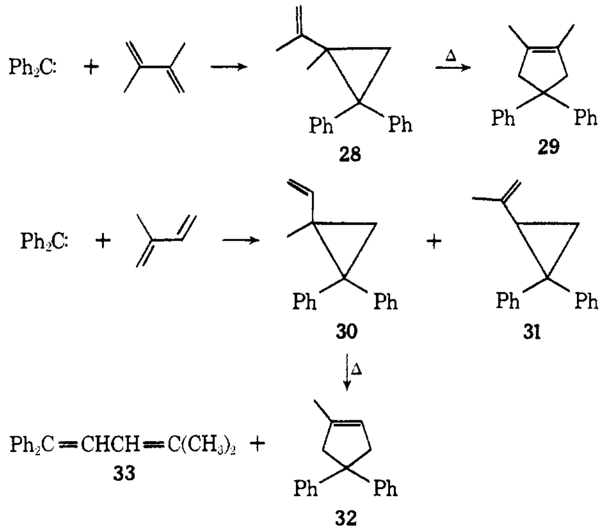
[55] J. E. Franz and C. Osuch, *Chem. Ind. (London)*, 2058 (1964).

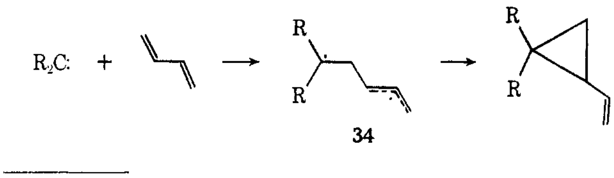
[56] G. W. Klumpp, J. W. F. K. Barnick, A. H. Veefkind, and F. Bickelhaupt, *Recl. Trav. Chim., Pays-Bas*, **88**, 766 (1969).

Among the more puzzling aspects of carbene chemistry is the small number of 1,4 additions known. Indeed, we can find only a single example that seems certain to be a bona fide 1,4 addition. This is the formation of 9,9-dicyanobicyclo[4.2.1]nona-2,4,7-triene (**27**) in the thermal reaction of dicyanocarbene with cyclooctatetraene.[57] Other claims of 1,4 additions have been made,[58–61] but they either involved a gas-phase reaction with a high probability of hot molecule isomerizations,[58,62,63] a copper-catalyzed reaction,[59,60] or conditions so harsh as to raise the serious possibility of rearrangement of a primary product.[61]



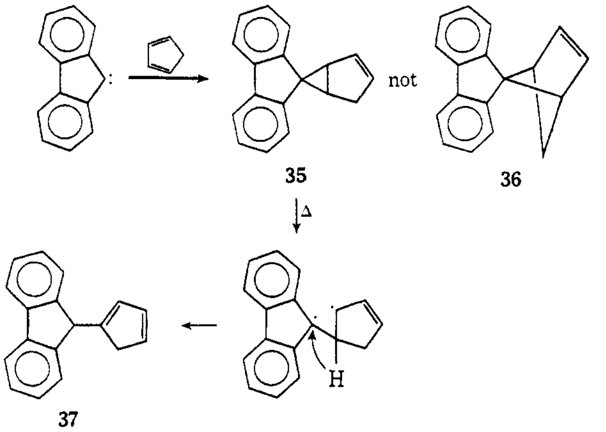
One might well expect a triplet to be more likely to undergo 1,4 addition than a singlet, as the intermediate diradical might not be restricted to 1,2 closure. Even with triplets, however, acyclic dienes yield only 1,2 adducts. As shown below, the products of the hypothetical 1,4 additions (**29** and **32**) could be made by thermal rearrangements of **28**, **30**, and **31** and were shown to be absent in the reaction mixtures. Acyclic dienes might fail to give 1,4 adducts because addition of the carbene to the trans form would give **34**, which could close only to a 1,2 adduct. Obviously, cyclic dienes avoid this problem.

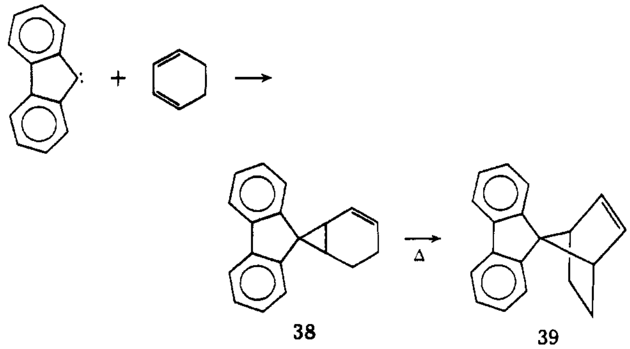




The reaction of carboethoxycarbene with cyclopentadiene has been carefully studied,[64] and particular attention turned to the question of 1,4 product. None could be found either on direct photolysis of ethyl diazoacetate or copper-catalyzed decomposition. The triplet was not investigated.[64]

Fluorenylidene, a carbene which reacts as a mixture of spin states, was found to add to cyclopentadiene to give only **35** and to add to cyclohexadiene to give **38**. No trace of the hypothetical 1,4 adducts **36** and **39** could be found.[64a] The assignment of the structure **35** rather than **36** depends heavily on the absence of a typical norbornadiene "triplet" at $\tau \sim 4$ in the nmr spectrum. Other bicyclo[2.1.1]hexenes do show such a signal.[65–67] Adduct **38** could be thermally rearranged to **39**, a material highly prone to decomposition, which could not be obtained in analytically pure form. Adduct **35** gave only the product of hydrogen shift. The assignment of structure **39** depends on the consistency of the nmr spectrum and the appearance of an apparent triplet at τ 3.58. Compound **39** is not present in the crude reaction mixture from irradiation of diazofluorene in cyclohexadiene–hexafluorobenzene.





1,2-Dimethylenecyclohexane, which incorporates the relevant features of a cyclic diene without requiring the

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(57) A. G. Anastassiou and R. P. Cellura, *Tetrahedron Lett.*, 5267 (1970).

(58) V. Franzen, *Chem. Ber.*, **95**, 571 (1961).

(59) J. A. Berson and E. S. Hand, *J. Amer. Chem. Soc.*, **86**, 1978 (1964).

(60) T. V. Domareva-Mandel'shtam and I. A. D'yakonov, *J. Gen. Chem. USSR*, **34**, 3896 (1964).

(61) H. Nozaki, M. Yamabe, and R. Noyori, *Tetrahedron*, **21**, 1657 (1965).

(62) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962).

(63) B. Gryzbowska, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4402 (1961); 3826 (1962).

(64) J. Warkentin, E. Singleton, and J. F. Edgar, *Can. J. Chem.*, **43**, 3456 (1965).

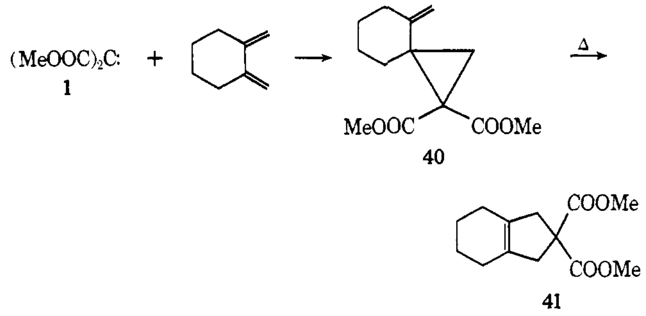
(64a) NOTE ADDED IN PROOF. Diphenylcarbene also gives a 1,2 adduct with cyclopentadiene: H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969).

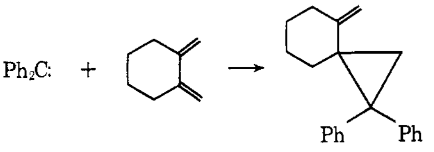
(65) J. Meinwald and B. E. Kaplan, *J. Amer. Chem. Soc.*, **89**, 2611 (1967).

(66) J. Meinwald and H. Tsuruta, *ibid.*, **91**, 5877 (1969).

(67) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

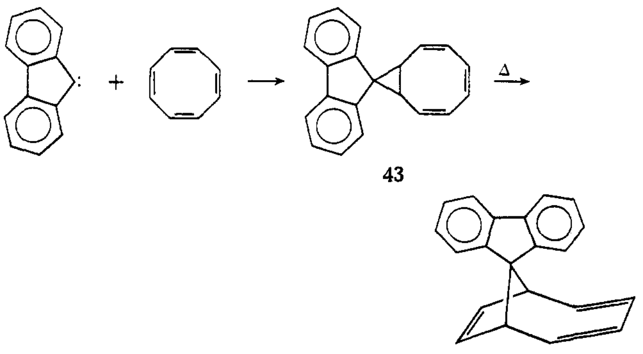
formation of a highly strained product, also gives only 1,2 additions with both **1** and diphenylcarbene. Pyrazolines are not formed and the products of the hypothetical 1,4 additions could be made as shown.



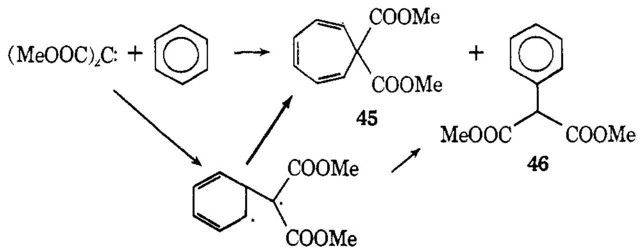


It occurred to us that cyclooctatetraene might be unique in its ability to form 1,4 adducts. Dicyanocarbene and cyanonitrene had produced a 1,4 adduct.[57,68] Although fluorenylidene had been allowed to add to cyclooctatetraene,[69] the 1,4 adduct was apparently not sought.

In our hands, fluorenylidene gave only **43**, which could be easily rearranged to **44**. This conversion finds analogy, as do the characterizations of **43** and **44**, in the work of Schönleber,[70] who observed the related reactions of cyclopentadienylidene and its adduct to cyclooctatetraene. Thus dicyanocarbene remains the lone carbene possessing the ability to undergo 1,4 addition. We suspect the source of its unique quality must be sought in the cyano groups rather than the reaction partner.



Benzene also acts as an acceptor for **1**, a report to the contrary notwithstanding.[71] Photolysis of methyl diazomalonate in benzene gave **45** and **46** in the ratio 2.7:1.[72] The photosensitized reaction gave the same two products in the ratio 1.6:1. The increased amount of the phenylmalonate **46** is consistent with a mechanism involving a diradical which can either close to the norcaradiene related to **45** or undergo hydrogen shift to **46**.



The second most frequently studied property of carbenes is the insertion into carbon–hydrogen bonds. We have attempted to complement the earlier study of Doering and Knox[18] on the direct photolysis of diazomalonic ester by examining the sensitized decomposition in saturated hydrocarbons. Table VI compares the relative rates of insertion into the tertiary, secondary, and primary carbon–hydrogen bonds for both the direct[18] and sensitized reactions. The sensitized decomposition yields a slightly more selective intermediate than does the direct. Rough composite values for the tertiary–secondary–primary ratios of singlet and triplet biscarbomethoxycarbene are 15–40:5:1 and 20–50:6:1, respectively. This is in general keeping with the data of Ring and Rabinovitch[73] on abstraction of hydrogen by triplet methylene, although our effects seem to be smaller. Comparison is perilous, however, because of the large differences in reaction conditions in the two cases. It is certainly evident that the yields of "insertion products" are sharply reduced in the sensitized decomposition. Were the mechanism of the "insertion" to be in reality a totally different process, this would not be at all surprising. A hydrogen abstraction–recombination process would be expected to give new products derived from the radicals generated by abstraction. Such products do appear as shown below. Direct irradiation produces an intermediate that gives only insertion products with no free-radical products. The sensitized decomposition gives lower yields of "insertion products" and the products expected from free-radical dimerization and hydrogen abstraction.

Table VI. Relative Rate of Insertion of **1** into Carbon–Hydrogen Bonds

Hydrocarbon	Ratio	Singlet **1**	Triplet **1**
n-Pentane	Sec:prim	5.4	6.9
n-Butane	Sec:prim	4.8	5.2
i-Butane	Tert:prim	39	52
2,3-Dimethylbutane	Tert:prim	13	20

Identification of many of the products of the insertion reactions was not simple, as the nmr spectra were not definitive. Accordingly, the products of insertion of **1** into *n*-pentane (**48–50**), *n*-butane (**51** and **52**), and isobutane (**53**) were synthesized from the appropriate alkyl bromides and dimethyl sodiomalonate. In other cases (**54**, **55**, **56**) the structures were clear from the spectra and syntheses were not done.

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(68) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968).

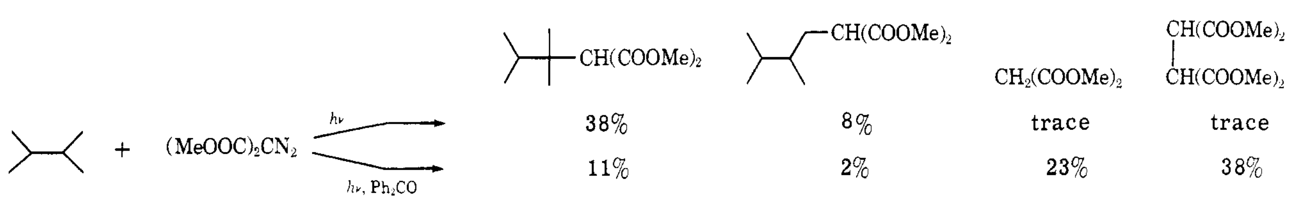
(69) H. Dürr and H. Kober, *Justus Liebigs Ann. Chem.*, **740**, 74 (1970).

(70) D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969).

(71) E. Ciganek, *J. Org. Chem.*, **30**, 4366 (1965).

(72) Analysis of the reaction mixture was greatly aided by an nmr spectrum of authentic[20] **45**, which was kindly provided by Professor J. A. Berson of Yale University.

(73) D. F. Ring and B. S. Rabinovitch, *Can. J. Chem.*, **46**, 2435 (1968).



$$(MeOOC)_2CH_2 \xrightarrow[RBr]{Na} (MeOOC)_2CHR \xleftarrow[RH]{\Delta} (MeOOC)_2CN_2$$

48, R = $CH(CH_2CH_3)_2$
49, R = $CH_3CHCH_2CH_2CH_3$
50, R = $CH_2CH_2CH_2CH_2CH_3$
51, R = $CH_2CH_2CH_2CH_3$
52, R = $CH_3CHCH_2CH_3$
53, R = $CH_2CH(CH_3)_2$
54, R = $C(CH_3)_3$
55, R = $C(CH_3)_2CH(CH_3)_2$
56, R = $CH_2CH(CH_3)CH(CH_3)_2$

Experimental Section

General. Infrared spectra were measured on a Perkin-Elmer Model 237B Grating Infrared Spectrometer. Nmr spectra were measured on a Varian Associates A-60-A instrument. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., Spang Microanalytical Laboratory, Ann Arbor, Mich., Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Atlantic Microlab, Inc., Atlanta, Ga. Gas chromatographic analyses and collections were performed on a Varian Aerograph A-90-P instrument using the following columns: A, 3 m, 5% Carbowax 20M on 45–60 mesh Chromosorb P; B, 3 ft, 10% Dow Corning 550 silicone oil on 60–80 mesh Chromosorb P; C, 6 ft, 20% Dow Corning 710 silicone oil on 40–60 mesh Chromosorb P; D, 2 m 10% Carbowax 20M on 60–80 mesh Chromosorb P; E, 3 m, 30% $AgNO_3$–glycerine on 40–60 mesh Chromosorb P; F, 2 m, 10% Dow Corning 710 silicone oil on 60–80 mesh Chromosorb P; G, 2 m, 10% Dow Corning 710 silicone oil on 40–60 mesh Chromosorb P; H, 1 m, 20% Dow Corning 710 silicone oil on 40–60 mesh Chromosorb P; J, 1 ft, 10% FFAP on 60–80 mesh Chromosorb P.

Direct Decomposition of Methyl Diazomalonate (MDM) in 3,3-Dimethyl-1-butene. A solution of 400 mg of MDM in 10 ml of 3,3-dimethyl-1-butene was cooled with running water and irradiated through Pyrex with two G. E. Sunlamps for 19 hr. After distillation of solvent, the yellow residue was purified by gas chromatography on column A operated at 175°. The major product (retention time 19 min) was collected and characterized.[74]

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.38; H, 8.73.

Direct Decomposition of MDM in 1-Pentene. A solution of 400 mg of MDM in 20 ml of 1-pentene was cooled with running water and irradiated through Pyrex for 17 hr with two G. E. Sunlamps. Gas chromatography on column A at 139° showed one major product (retention time 26 min), identified as **3**.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 7.60. Found: C, 60.13; H, 7.93.

Direct Decomposition of MDM in 2,3-Dimethyl-2-butene. A solution of 101 mg. of MDM in 4.3 ml of 2,3-dimethyl-2-butene was sealed in a Pyrex test tube and irradiated under nitrogen for 7.5 hr with two G.E. Sunlamps. Gas chromatography on column A gave 41.3 mg (28.2%) of a volatile major product, mp 28–30°, identified as **7** (retention time 17 min). A minor product (retention time 37 min) was collected in 10.7% yield (15.7 mg) and identified as 1,1-dicarbomethoxy-3,4-dimethyl-3-pentene (**47**) by spectral analysis.

Anal. (**7**) Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.21; H, 8.47. (**47**) Found: C, 61.49; H, 8.50.

Direct Decomposition of MDM in 2-Methyl-2-butene. A solution of 180 mg of MDM in 8.5 ml of 2-methyl-2-butene was sealed under nitrogen in a Pyrex tube and irradiated for 7.5 hr with a G.E. Sunlamp. Gas chromatography on column A at 140° gave 99 mg of the major product (retention time 14.5 min), which was identified as **8**.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.73; H, 8.06.

Direct Decomposition of MDM in *cis*-2-Butene. A solution of 87 mg of MDM in 8 ml of *cis*-2-butene was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. Sunlamp for 7 hr. Preparative gas chromatography on column A gave 28 mg of the major product **9** (retention time 17 min). *Ca.* 5 mg of a minor product, **10**, could also be isolated (retention time 11 min).

Anal. (**9**) Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.13; H, 7.75. (**10**) Found: C, 58.07; H, 7.50.

Direct Decomposition of MDM in *trans*-2-Butene. A solution of 107 mg of MDM in 7 ml of *trans*-2-butene was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 7 hr. Preparative gas chromatography on column A at 140° gave 24 mg of **10** (retention time 11 min).

Direct Decomposition of MDM in *cis*-4-Methyl-2-pentene. Analytical Run. A solution of 33.6 mg of MDM in 1.4 ml of *cis*-4-methyl-2-pentene was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. Sunlamp for 2 hr. Gas chromatography on column A at 122° showed a major peak (retention time 27 min) identified as **11** and a minor peak (retention time 18 min) identified as **12**. The ratio of **11**:**12** was 11.6 (92.1% **11**).

Anal. (**11**) Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.42; H, 8.67. (**12**) Found: C, 61.65; H, 8.33.

Variation of 11:12 with Irradiation Time. An irradiation of a solution of 37 mg of MDM in 1.3 ml of *cis*-4-methyl-2-pentene was monitored by gas chromatography on column A. Over a 3-hr interval the ratio of **11**:**12** was constant within 0.5%.

Variation of 11:12 with Concentration of MDM. When the ratio of MDM to olefin was varied from 0.33 mmol of MDM per 100 mmol of olefin to 2.7 mmol per 100 mmol, the ratio **11**:**12** was constant within 0.5%. When larger amounts of MDM were used, slightly larger amounts of **12** appeared. Thus, 5.4 mmol of MDM per 100 mmol of olefin gave **11**:**12** = 9.7 (90.6% **11**).

Direct Decomposition of MDM in *cis*-4-Methyl-2-pentene. Preparative Run. A solution of 186 mg of MDM in 12.3 ml of *cis*-4-methyl-2-pentene was sealed in a Pyrex tube under nitrogen and irradiated with two G.E. Sunlamps for 6 hr. After distillation of the solvent, preparative gas chromatography on column A gave 99 mg of cyclopropanes.

Direct Decomposition of MDM in *trans*-4-Methyl-2-pentene. A solution of 186 mg of MDM in 14 ml of *trans*-4-methyl-2-pentene was irradiated under nitrogen in a Pyrex tube for 6 hr with two G.E. Sunlamps. After distillation of solvent, preparative gas chromatography on column A at 121° gave 61.5 mg of **12** (retention time 18 min) and 6.8 mg of **11** (retention time 18 min).

Direct Decomposition of MDM in 2,3-Dimethyl-1,3-butadiene. A solution of 300 mg of MDM in 10 ml of 2,3-dimethyl-1,3-butadiene was sealed in a Pyrex tube under nitrogen and irradiated with two G.E. Sunlamps for 24 hr. After distillation of the solvent, gas chromatography on column B at 128° gave **4** (retention time 11 min).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.17; H, 7.74.

Direct Decomposition of MDM in 1,3-Butadiene. A solution of 50 mg of MDM in 1 ml of 1,3-butadiene was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. Sunlamp for 7 hr. Gas chromatography on column C at 150° revealed one major peak corresponding to **6** (retention time 8 min).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.53; H, 6.67.

Direct Decomposition of MDM in Allene. A solution of 100 mg of MDM in 15 ml of allene was sealed under nitrogen in a thick-walled Pyrex Carius tube and irradiated for 9 hr with two G.E. Sunlamps. Gas chromatography on column D at 140° gave **5** (retention time 18 min).

Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.25; H, 6.00.

Direct Decompositions of MDM in *cis*-4-Methyl-2-pentene and Hexafluorobenzene. a. Runs with MDM Proportional to Olefin. Irradiations were run under nitrogen in sealed Pyrex tubes. All

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(74) Tables of infrared and nmr spectra are found at the end of the experimental section.

tubes used in a given run were irradiated with the same light source for the same amount of time. The products were analyzed by gas chromatography on column A at 140°. The results of a typical run in which the ratio of MDM to olefin was 5.4 mmol of MDM per 100 mmol of olefin are plotted in Figure 1.

b. Runs with the Amount of MDM Constant. When a small, constant amount of MDM was used, thus effectively increasing the ratio of MDM to olefin at high hexafluorobenzene concentrations, curves indistinguishable from that in Figure 1 were obtained.

c. Effect of MDM Concentration at 50 and 90% Hexafluorobenzene Concentration. Changes of MDM concentration by a factor of 8 at these values of added hexafluorobenzene gave **11**:**12** ratios constant within 0.5%.

Competition Runs. Roughly equimolar mixtures of 2-methyl-2-butene and the other olefins were made up in Pyrex tubes. To the mixture was added 5 mg of MDM and the tubes were sealed under nitrogen and irradiated with a G.E. Sunlamp for 2 hr. Analytical gas chromatography on column A at 140° served to separate all the adducts except for the product of addition of **1** to *trans*-4-methyl-2-pentene (**12**), which was related to the standard through a separate competition with 1-pentene. Peak areas were measured by means of a planimeter. The values were corrected for the varying thermal conductivities of the adducts by amounts determined by analyses of known mixtures of the adducts.

Sensitized Decomposition of MDM in *cis*-4-Methyl-2-pentene. A solution of 24 mg of MDM and 180 mg of benzophenone in 2.5 ml of *cis*-4-methyl-2-pentene was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. Sunlamp for 3 hr. Gas chromatography on column A at 140° revealed **12** and **11** in the ratio 9.0 (90% trans).

Sensitized Decomposition of MDM in *trans*-4-Methyl-2-pentene. A solution of 25 mg of MDM and 182 mg of benzophenone in 2.5 ml of *trans*-4-methyl-2-pentene was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. Sunlamp for 2.5 hr. Gas chromatography on column A at 140° revealed **12** and **11** in the ratio 6.2 (86% trans).

Sensitized Competition Runs. Solutions of 10 mg of MDM and 70 mg of benzophenone in *ca.* 10 ml of an equimolar mixture of 2-methyl-2-butene and another olefin were sealed under nitrogen in Pyrex tubes and irradiated with a G.E. Sunlamp for 3–4 hr. As before (see direct decomposition), *trans*-4-methyl-2-pentene was related to 2-methyl-2-butene *via* a competition with another olefin.

Control Experiments. a. Check for Isomerization of Adducts. A solution of 180 mg of benzophenone and 23.4 mg of **11** in 2.5 ml of *cis*-4-methyl-2-pentene was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. Sunlamp for 4 hr. Gas chromatographic analysis on column A at 140° revealed no isomerization to **12** and no decrease in the size of the peak due to **11**.

b. Check for Isomerization of Solvent. Solvent recovered from an irradiation in *cis*-4-methyl-2-pentene was checked for conversion to the trans isomer by gas chromatography on column E at 20°. Less than 2% isomerization could be detected.

c. Check for Effect of Oxygen. Identical solutions of 10 mg of MDM and 200 mg of benzophenone in 2.5 ml of *cis*-4-methyl-2-pentene were prepared. One was sealed under nitrogen and the other was saturated with oxygen and sealed under oxygen. The two samples were irradiated for 4 hr with a G.E. Sunlamp and analyzed by gas chromatography on column A at 140°. No difference between the two reactions was apparent.

Sensitized Decomposition of MDM in Allene. A solution of 400 mg of MDM and 500 mg of benzophenone in 8 ml of allene was irradiated under nitrogen in a sealed Pyrex tube for 12 hr with two G.E. Sunlamps. After removal of the solvent, gas chromatography on column D at 140° showed two peaks in the ratio of 12:1. The larger of these was shown to be **5**, and the smaller was diphenylethylene.

Pyrolysis of 5. *Ca.* 25 mg of **5** was evaporated through a 1 ft × 18 mm Quartz tube maintained at 460° and 0.3 Torr. Gas chromatography on column D at 140° and examination of the nmr spectrum of the crude pyrosylate revealed only **19** as product.

Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.21; H, 6.03.

Direct Decomposition of MDM in Benzene. A solution of 1 g of MDM in 20 ml of benzene was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 12 hr. After removal of the solvent, analysis of the crude reaction mixture by nmr showed **45** and **46** in the ratio of 2.7:1.

Sensitized Decomposition of MDM in Benzene. A solution of 1 g of MDM in 20 ml of benzene was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 12 hr. After removal of the solvent, analysis of the crude reaction mixture by nmr showed **45** and **46** in the ratio of 1.6:1.

Direct Decomposition of MDM in Norbornadiene. A solution of 1 ml of MDM in 20 ml of freshly distilled norbornadiene was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 12 hr. After removal of the solvent, gas chromatography on column F operated at 145° showed three compounds: **24** (retention time 32 min), **22** (retention time 42 min), and **23** (retention time 50 min). The first of these was shown not to be present in the crude reaction mixture by nmr spectroscopy.

Anal. (**24**) Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.69; H, 6.34. (**23**) Found: C, 64.76; H, 6.30. (**22** + **24**) Found: C, 64.88; H, 6.27.

Sensitized Decomposition of MDM in Norbornadiene. A solution of 1 g of MDM and 1 g of benzophenone in 20 ml of freshly distilled norbornadiene was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 12 hr. After removal of the solvent, gas chromatography on column F at 145° showed **24**, **22**, and **23** as above. Once more **24** was shown to be absent in the crude reaction mixture.

Direct Decomposition of 13 in Olefins. The following procedure is typical. A solution of 200 mg of **13** in 20 ml of *cis*-2-butene was sealed under nitrogen in a Pyrex tube and irradiated for 12 hr with a medium pressure mercury arc. After removal of the solvent, gas chromatography on column G at 142° showed only very small amounts of adducts. Irradiations in *trans*-2-butene, *tert*-butylethylene, and *cis*- and *trans*-4-methyl-2-pentene gave similar results.

Sensitized Decomposition of 13 in *cis*-4-Methyl-2-pentene. A solution of 200 mg of **13** and 520 mg of benzophenone in 10 ml of *cis*-4-methyl-2-pentene was sealed under nitrogen in a Pyrex tube and irradiated for 18 hr with a medium pressure mercury arc. After removal of the solvent, gas chromatography on column H showed residual **13** and the cis and trans adducts of **14** to the olefin (retention times at 145° of 18 and 23 min, respectively). The total yield of adducts was 17%.

Synthesis of the Cis Adduct. 1,1-Dicarboxy-2-methyl-3-isopropylcyclopropane. A solution of 1.5 g of **11** in 13 ml of a 10% KOH solution in water was refluxed for 18 hr. The solution was acidified to pH 1 with 10% H_2SO_4 and extracted with 5 × 15 ml portions of ether. The ether washings were extracted with one 10-ml portion of water, dried over Na_2SO_4, and concentrated at the water pump. This yielded 1 g of crude diacid.

Synthesis of 15. The diacid synthesized above was dissolved in 0.6 ml of acetic anhydride and cooled to 0°. After addition of three drops of H_4SO_4, 0.5 ml of acetone was added and the solution was allowed to stand at room temperature for 12 hr. The solution was extracted with 2 × 10 ml portions of ether. The ether washings were dried and concentrated at the water pump to give a yellow oil. Preparative gas chromatography on column H at 145° gave **15** (mp 62–64°) in 22% yield, based on starting diester **11**. The trans isomer was made analogously (mp 63–66°).

Anal. (cis isomer **15**) Calcd for $C_{12}H_{18}O_4$: C, 63.70, H, 8.02. Found: C, 63.99; H, 8.25. (Trans isomer) Found: C, 63.70; H, 8.02.

Direct Decomposition of Methyl Diazoacetate (MDA) in *cis*-2-Butene. A solution of 100 mg of MDA in 10 ml of *cis*-2-butene was sealed under nitrogen in a Pyrex tube and irradiated for 12 hr with two G.E. Sunlamps. After removal of the solvent, gas chromatography on column D at 60° revealed the three adducts as shown in Table V.

Direct Decomposition of MDA in *trans*-2-Butene. A solution of 100 mg of MDA in 10 ml of *trans*-2-butene was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 12 hr. The reaction mixture was worked up as above.

Sensitized Decomposition of MDA in *cis*-2-Butene and *trans*-2-Butene. A solution of 100 mg of MDA and 200 mg of benzophenone in 10 ml of olefin was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 12 hr. The reaction mixtures were worked up as in the unsensitized runs.

Direct Decomposition of MDA in Allene. A solution of 100 mg of MDA in 10 ml of allene was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 12 hr. After removal of the solvent, gas chromatography on column D showed a single peak (retention time at 60° = 17 min).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.53; H, 7.28.

Sensitized Decomposition of MDA in Allene. A solution of 100 mg of MDA and 400 mg of benzophenone in 10 ml of allene was sealed under nitrogen in a Pyrex tube and irradiated with two G.E.

Table VII. Infrared Spectra in CCl_4

Compd	Ir, cm^{-1}
2	2950, 1730, 1432, 1332, 1260, 1212, 1145, 1100
3	2945, 1730 (vs), 1435, 1325, 1290, 1210, 1130
4	3082, 2990 (sh), 2965, 2900, 2845, 1740, 1650, 1438, 1385, 1346, 1313, 1271, 1237, 1195, 1117, 1076, 1065, 1004, 960, 900
5[a]	3060, 3000, 2950, 2900, 2849, 1728, 1434, 1385, 1315, 1278, 1180, 1145, 1108, 1028, 978, 911, 838, 818, 783, 686, 1078
6	3077, 2990, 2940, 2895, 2840, 1735, 1642, 1440, 1332, 1275, 1212, 1185, 1138, 1059, 1030, 995, 950, 922, 904
7	2949, 1730, 1452, 1430, 1380, 1225, 1190, 1165, 1120, 1080, 1060
8	2950, 1730, 1462, 1435, 1360, 1322, 1290, 1248, 1215, 1110, 1060, 1035, 925
9	2948, 1728, 1432, 1389, 1323, 1268, 1218, 1185, 1098, 1055, 1025
10	2950, 1450, 1435, 1728, 1385, 1337, 1297, 1270, 1215, 1140, 1100, 1071, 1019, 905
11	2950, 1730, 1485, 1437, 1390, 1370, 1325, 1292, 1250, 1215 (sh), 1223, 1197, 1142, 1060, 1030
12	2951, 1726, 1455, 1432, 1381, 1291, 1247, 1210, 1140, 1067, 990
cis-**15**	2951, 2910, 2855, 1732, 1457, 1406, 1386, 1375, 1361, 1321, 1288, 1279, 1209, 1185, 1100, 1072, 1049, 1013, 976, 949, 903
trans-**15**	3007, 2965, 1738, 1476, 1470, 1427, 1391, 1376, 1335, 1287, 1273, 1252, 1214, 1055, 983
35	3051, 2900, 2822, 1940, 1901, 1599, 1479, 1447, 1438, 1350, 1337, 1280, 1250, 1222, 1200, 1151, 1100, 1077, 1069, 1018, 987
40[a]	3035, 2988, 2922, 2850, 1225, 1638, 1404, 1370, 1300, 1263, 1225, 1190, 1150, 1132, 1100, 990, 927, 920, 898, 837
47	2949, 2900, 2850, 1752 (sh), 1740, 1430, 1340, 1225, 1190, 1150, 1032
48	3040, 2995, 2950, 2930, 2851, 1764, 1748, 1690, 1462, 1437, 1340, 1265, 1242, 1222, 1157, 1121, 1025
51	3010, 2988, 2949, 2918, 2855, 1765, 1745, 1469, 1438, 1383, 1347, 1300, 1287, 1259, 1234, 1197, 1159, 1118, 1062, 1025
52	3010, 2985, 2952, 2948, 2868, 2840, 1765, 1739, 1459, 1436, 1385, 1365, 1325, 1262, 1231, 1195, 1171, 1153, 1131, 1091, 1025
53	3020, 2980, 2945, 2856, 1762, 1741, 1469, 1436, 1369, 1325, 1274, 1246, 1194, 1154, 1125, 1050, 1025
54	3025, 3000, 2955, 2908, 2860, 2845, 1763, 1740, 1600, 1498, 1483, 1469, 1437, 1400, 1372, 1325, 1240, 1218, 1200 (sh), 1149, 1052, 1015
55	2960, 2875, 1767, 1740, 1431, 1436, 1390, 1383, 1372, 1340, 1308, 1209, 1242, 1200, 1154, 1125, 1064, 1035
56	2960, 2890, 1770, 1739, 1469, 1435, 1385, 1373, 1325, 1238, 1215, 1128, 1101, 1070, 1035

[a] Neat; sh = shoulder.

Table VIII. Nmr Spectra in CCl_4 (TMS Added as Internal Standard[a])

Compd	Nmr spectra in CCl_4, τ
2	6.33 (s, 6 H), 8.0–9.0 (m, 2 H), 9.1 (s, 9 H)
3	6.31 (s, 6 H), 7.9–9.3 (m, 10 H)
4	5.21 (broad s, 2 H), 6.30, 6.43 (2 s, 6 H), 8.2 (broad s, 3 H), 8.6–8.7 (m, 5 H)
5	4.38 (t of d's, 1 H), 4.44 (t of d's, 1 H), 6.30 (s, 6 H), 7.88 (d of d's, 2 H)
6	4.5–5.1 (m, 3 H), 6.29, 6.31 (2 s, 6 H), 7.21–7.72 (m, 1 H), 8.22–8.80 (m, 2 H)
7	6.40 (s, 6 H), 8.80 (s, 12 H)
8	6.35 (s, 6 H), 8.33 (q, 1 H), 8.81–8.90 (m, 9 H)
9	6.31 (s, 6 H), 8.1–8.5 (m, 2 H), 8.90 (d, 6 H)
10	6.30 (s, 6 H), 8.30 (m, 2 H), 8.90 (d, 6 H)
11	6.35 (s, 6 H), 8.2–8.6, 8.6–9.2 (m's, 12 H)
12	6.36 (s, 6 H), 8.87 (m, 12 H)
15	7.3–7.9 (m, 2 H), 8.25 (s, 6 H), 8.62 (d, 3 H), 8.98 (m, 7 H)
trans-**15**	7.4–8.1 (m, 2 H), 8.3 (s, 6 H), 8.65 (d, 3 H), 8.9–9.2 (m, 7 H)
19	3.37 (q, 1 H), 5.98 (s, 3 H), 6.28 (s, 3 H), 7.92 (d, 3 H), 4.4–4.6 (m, 2 H), 6.37 (s, 3 H), 7.6–7.9 (m, 1 H), 8.7–8.1 (m, 2 H)
22	3.6 (t, 2 H), 6.36 (s, 3 H), 6.41 (s, 3 H), 6.9–7.0 (m, 2 H), 8.2 (m, 2 H), 8.7–9.3 (m, 2 H)
23	4.39 (t, 2 H), 6.44 (s, 3 H), 6.52 (s, 3 H), 6.8–7.1 (m, 2 H), 7.6–7.8 (m, 2 H), 7.7–8.2 (m, 2 H)
24	3.6–4.0 (m, 2 H), 4.3–4.9 (m, 2 H), 6.29 (s, 3 H), 6.42 (s, 3 H), 6.5–6.8 (m, 1 H), 7.2–7.5 (m, 1 H), 7.9–8.1 (m, 1 H), 7.7–8.4 (m, 1 H)
28	2.5–3.0 (m, 10 H), 5.2–5.4 (m, 2 H), 8.08 (d, 1 H), 8.46 (s, 3 H), 8.82 (d, 1 H), 8.91 (s, 3 H)
30	2.5–3.0 (m, 10 H), 4.5–5.5 (m, 3 H), 8.2–8.9 (m, 2 H), 8.92 (s, 3 H)
31	2.5–3.0 (m, 10 H), 5.2–5.4 (m, 2 H), 7.6–8.0 (m, 1 H), 8.2–8.9 (m, 2 H), 8.56 (s, 3 H)
32	2.95 (broad s, 10 H), 4.62–4.8 (m, 1 H), 6.9–7.2 (m, 4 H), 8.2–8.4 (m, 3 H)
35	2.2–2.5 (m, 2 H), 2.7–3.3 (m, 6 H), 3.9–4.15 (m, 2 H), 6.95–7.5 (m, 4 H)
38	2.2–3.3 (m, 8 H), 4.0–4.6 (m, 2 H), 7.8–8.5 (m, 6 H)
39	2.2–3.1 (m, 8 H), 3.57 (t, 2 H), 7.25 (m, 2 H), 8.4–8.9 (m, 4 H)
40	5.30 (broad s, 1 H), 5.46 (broad s, 1 H), 6.32 (s, 3 H), 6.47 (s, 3 H), 7.6–7.9 (m, 2 H), 8.02 (d, 1 H), 8.0–8.7 (m, 6 H), 8.61 (d, 1 H)
42	2.5–3.1 (m, 10 H), 5.57 (broad s, 1 H), 5.80 (broad s, 1 H), 7.7–7.9 (m, 2 H), 8.21 (d, 1 H), 8.86 (d, 1 H), 7.9–9.0 (m, 6 H)
44	2.0–3.2 (m, 8 H), 3.5–4.2 (m, 4 H), 4.53 (d, 2 H), 6.95 (d, 2 H)
47	6.35 (s, 6 H), 6.65 (t, 1 H), 7.42 (d, 2 H), 8.4 (broad s, 9 H)
48	6.68 (s, 6 H), 6.79 (t, 1 H), 7.95–9.35 (m, 11 H)
49	6.31 (s, 6 H), 6.84 (d, 1 H), 8.4–9.3 (m, 11 H)
50	6.33 (s, 6 H), 6.69 (d, 1 H), 7.75–8.3 (m, 1 H), 8.4–9.3 (m, 10 H)
51	6.30 (s, 6 H), 6.78 (t, 1 H), 7.95–9.3 (m, 9 H)
52	6.33 (s, 6 H), 6.84 (d, 1 H), 7.5–8.2 (m, 1 H), 8.35–9.3 (m, 8 H)
53	6.32 (s, 6 H), 6.68 (t, 1 H), 8.0–9.2 (m, 9 H)
54	6.31 (s, 6 H), 6.87 (s, 1 H), 8.91 (s, 9 H)
55	6.32 (s, 6 H), 6.68 (m, 1 H), 8.0–9.0, 9.0–9.3 (m, 13 H)
56	6.38 (s, 6 H), 6.6 (s, 1 H), 8.4 (m, 1 H), 9.03 (s, 6 H), 9.15 (d, 6 H)

[a] s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

Sunlamps for 12 hr. Work-up as above gave only a single peak on column D.

Irradiation of Diphenyldiazomethane in 2,3-Dimethylbutadiene. A solution of 1 g of diphenyldiazomethane in 10 ml of diene was irradiated with two G.E. Sunlamps for 12 hr, at which time the original purple color had faded to light yellow. After removal of the solvent the residue was chromatographed on alumina. Distilled hexane eluted 1.1 g of a colorless fragrant oil (93%).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.77; H, 8.19.

Rearrangement of 28 to 29. An nmr tube containing **28** in C_6D_6 was sealed under nitrogen and heated at 161°. Conversion to **29** was complete in 26 hr. Purification by alumina chromatography yielded pure material.

Anal. Found: C, 91.64; H, 8.16.

Irradiation of Diphenyldiazomethane in Isoprene. A solution of 1 g of diphenyldiazomethane in 10 ml of isoprene was irradiated with two G.E. Sunlamps for 12 hr, at which time the original purple color had faded to pale yellow. After removal of the isoprene, the residue was chromatographed on alumina–hexane to give 1.2 g (95%) of a colorless fragrant oil. Gas chromatography on column

D at 150° revealed two peaks, **30** and **31** (retention times 42 and 48 min, respectively).

Anal. (**30** + **31**) Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.02; H, 7.82.

Thermal Rearrangement of 30 and 31 to 32 and 33. An nmr tube containing **30** and **31** in C_6D_6 was sealed under nitrogen and heated at 152°. The conversion was complete in 21 hr. Gas chromatography on column B at 180° revealed two peaks **32** and **33** (retention times 16 and 20 min, respectively).

Anal. (**32**) Found: C, 92.32; H, 7.84.

Irradiation of Diazofluorene in Cyclopentadiene. A solution of 500 mg of diazofluorene in 24 ml of freshly distilled cyclopentadiene was irradiated with a G.E. Sunlamp for 4 hr at 0°. After removal of the solvent the yellow residue was recrystallized from cyclohexane to give white crystals, mp 158–158.5°. Gas chromatography on column F at 210° showed only one major peak, **35** (retention time 20 min) in addition to fluorenone.

Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 94.17; H, 6.14.

Thermal Rearrangement of 35 to 37. A solution of 200 mg of **35** in 20 ml of decalin (bp 194°) was refluxed for 21 hr. Most of the solvent was removed by distillation and the residue was chromatographed on alumina–hexane. White crystals, mp 111–116°, were isolated, and spectral analysis indicated structure **37**. Storage in air at room temperature for a few days resulted in decomposition.

Irradiation of Diazofluorene in 1,3-Cyclohexadiene. A solution of 300 mg of diazofluorene in 5 g of 1,3-cyclohexadiene was sealed under nitrogen in a Pyrex tube and irradiated with a medium pressure mercury arc for 20 hr. After removal of solvent, the residue was chromatographed on silica gel–hexane to yield 280 mg of a faintly evil-smelling yellow gum. Further chromatography on alumina–cyclohexane gave white crystals of **38**, mp 106–108°.

Thermal Rearrangement of 38 to 39. A solution of 100 mg of the fluorenylidene–1,3-cyclohexadiene adduct (**38**) in 0.5 ml of C_6D_6 was sealed under nitrogen and heated to 202°. The conversion to **39** was roughly half complete at 5 hr, at which time polymer formation became important and the reaction was stopped. Chromatography on silica gel–hexane gave crude **39**.

Irradiation of Diazofluorene in 1,3-Cyclohexadiene and Hexafluorobenzene. A solution of 100 mg of diazofluorene in 3.34 g of hexafluorobenzene and 0.16 g of 1,3-cyclohexadiene was sealed under nitrogen and irradiated with a medium pressure mercury arc for 10 hr. Nmr analysis of the residue from removal of the solvents revealed no **39**.

Direct Decomposition of MDM in 1,2-Dimethylenecyclohexane. A solution of 0.5 ml of MDM in 5.0 g of 1,2-dimethylenecyclohexane was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 14 hr. After removal of the diene, gas chromatography on column J at 100° revealed a single peak (retention time 27 min) corresponding to **40**.

Sensitized Decomposition of MDM in 1,2-Dimethylenecyclohexane. A solution of 0.5 ml of MDM and 0.5 g of benzophenone in 5.0 g of 1,2-dimethylenecyclohexane was sealed under nitrogen in a Pyrex tube and irradiated for 14 hr with two G.E. Sunlamps. After removal of the solvent, gas chromatographic analysis on column J at 100° revealed **40** and a new product (retention time 15 min). The new product was tentatively identified by spectral analysis as a dimer of 1,2-dimethylenecyclohexane.

Irradiation of Diphenyldiazomethane in 1,2-Dimethylenecyclohexane. A solution of 1.0 g of diphenyldiazomethane in 10 g of 1,2-dimethylenecyclohexane was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. Sunlamps for 12 hr. Chromatography on alumina–hexane gave, after removal of the diene, a low-melting solid, identified by nmr spectroscopy as **42**.

Irradiation of Diazofluorene in Cyclooctatetraene. A solution of 1 g of diazofluorene in 10 g of freshly distilled cyclooctatetraene was sealed under nitrogen in a Pyrex tube and irradiated with a medium pressure mercury arc for 48 hr. After removal of the cyclooctatetraene by vacuum distillation, chromatography on alumina–hexane gave *ca.* 0.7 g of **43**, mp 145–148°, lit.[69] 147°.

Anal. Calcd for $C_{21}H_{14}$: C, 93.99; H, 6.01. Found: C, 93.72; H, 5.89.

Thermal Rearrangement of 43 to 44. A solution of **43** in C_6D_6 was sealed in an nmr tube and heated at 160°. Analysis by nmr spectroscopy revealed that the reaction was over in *ca.* 45 min. Compound **44** could be recovered as pale yellow crystals, mp 136–137°.

Anal. Found: C, 93.54; H, 6.24.

Direct Decomposition of MDM in Saturated Hydrocarbons. The following typical procedure was used for all reactions. A solution of 100 mg of MDM in 10 ml of hydrocarbon was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. Sunlamp for 14 hr. Analysis was by gas chromatography on column D at 165°.

Sensitized Decomposition of MDM in Saturated Hydrocarbons. The following typical procedure was used for all reactions. A solution of 100 mg of MDM and 100 mg of benzophenone in 10 ml of hydrocarbon was sealed under nitrogen and irradiated with two G.E. Sunlamps for 14 hr. Analysis was by gas chromatography on column D at 165°.

Synthesis of the Alkylmalonic Esters. The following typical procedure was used for compounds **48–53**. To a room-temperature solution of 50 mg of Na in 2.5 ml of dry methanol was added 2.5 mmol of dimethylmalonate and 2.5 mmol of alkyl bromide. The solution was refluxed for 2 hr and 10 ml of water added. The solution was extracted with 3 × 1 ml hexane, dried over $MgSO_4$, and concentrated. Gas chromatographic analysis on column D at 165° revealed the products.

Analytical data on the unknown alkylmalonates are hereby given.

Anal. (**48**) Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.12; H, 8.94. (**49** + **50**) Found: C, 59.56; H, 8.66. (**51**) Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.55; H, 8.51. (**53**) Found: C, 57.32; H, 8.56. (**55**) Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.16; H, 9.45. (**56**) Found: C, 61.01; H, 9.30.