# A Direct Synthesis of Spiro-Activated Cyclopropanes from Alkenes via the Irradiation of Isopropylidene Diazomalonate

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Abstract: Direct irradiation of isopropylidene diazomalonate (**14**) in the presence of several alkenes afforded the corresponding spiro-activated cyclopropanes in high yield. The potentially valuable synthetic intermediates **8–10** have been prepared in this way from olefins **18–20**. A high degree of stereoselectivity was observed in cyclopropanations of the sterically biased alkenes **18, 19,** and **21.** Cyclopropanation of *cis-* and *trans*-2-butene was stereospecific. Insertion into C–H bonds was seldom observed. Lewis acids were found to influence both the rate of photodecomposition of **14** and the efficiency of addition of the resultant carbene (**13**) to double bonds.

Nucleophilic opening of activated cyclopropanes (homoconjugate addition) is an extremely attractive method for the construction of a variety of complex natural products.[1-4] In general, intramolecular openings (e.g., **1 → 2**) proceed in high yield under relatively mild conditions.[3-7] Unfortunately, most simple activated cyclopropanes (e.g., **3**) are rather lethargic in intermolecular openings. Recently, Danishefsky and his collaborators studied the nucleophilic opening of several cyclic acylals (e.g., **5**) with a variety of nucleophiles. They observed

1　　　　　　　　　　　2
quantitative

(1)

3　　　　　　　　　　　4

5

6
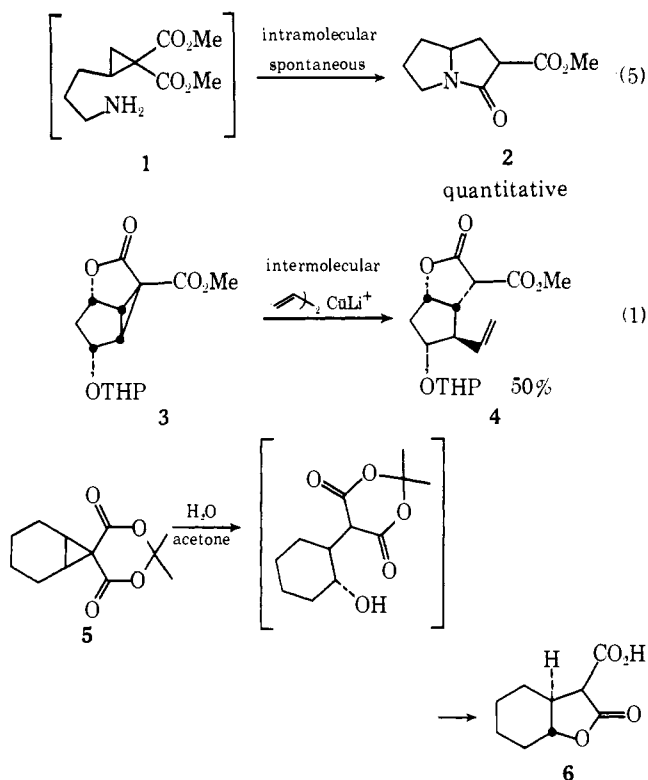
that activated cyclopropanes of this type were several orders of magnitude more reactive and coined the term spiro-activation to describe this enhanced reactivity.[8-10] Representatives of this class of compounds were first prepared by the reaction of diazomethane with isopropylidene benzylidene malonate.[11]

These compounds were prepared from the corresponding 1,1-dicarbomethoxycyclopropanes (e.g., **7a**) by saponification to the diacids (e.g., **7b**) which were then subjected to treatment with isopropenyl acetate and sulfuric acid to effect closure to the cyclic acylal. Alternatively the acylals have been synthe-

7a, R = CH₃
7b, R = H
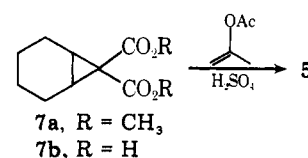
sized by treatment of the diacids with acetone, acetic anhydride, and sulfuric acid.[12]

In practice, this procedure is limited to the synthesis of spiro-activated cyclopropanes which are not labile to strong acid or base.

During the course of our research on the total synthesis of natural products we wished to examine the homoconjugate addition of organometallic reagents to the spiro-activated cyclopropanes **8–12.**

8　　　　　　　　　　　9

10　　　　　11　　　　　12
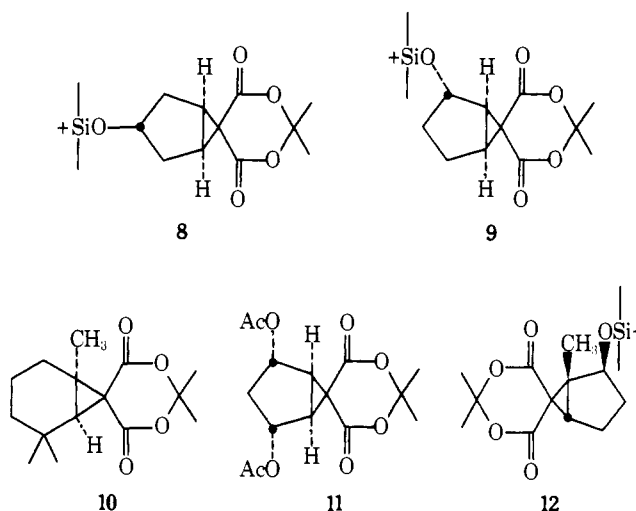
Therefore, we sought a neutral method for the synthesis of these cyclopropanes, which would be compatible with their varied functionality and structural features. Conceivably these compounds could be prepared directly by the addition of carbene **13** to the corresponding olefin. Direct and sensitized irradiation of isopropylidene diazomalonate (**14**) in the presence of alkenes[12] and hydroxylic solvents[13] have been reported. The benzophenone-sensitized photodecomposition of **14** in either (*E*)- or (*Z*)-2-butene with a medium-pressure mercury arc and a Pyrex filter furnished the desired cyclopropanes **15** and **16** as a thermodynamic mixture albeit in low yield (26%). Direct irradiation of **14** in alkenes through Pyrex produced only 1–2% of addition products.[12]

The ultraviolet absorption spectrum of **14** in methanol reveals an n → π* transition at 332 nm (ϵ_{332} 225) and a π → π*

Table I. Direct Irradiation of **14** with Alkenes at 253.7 nm

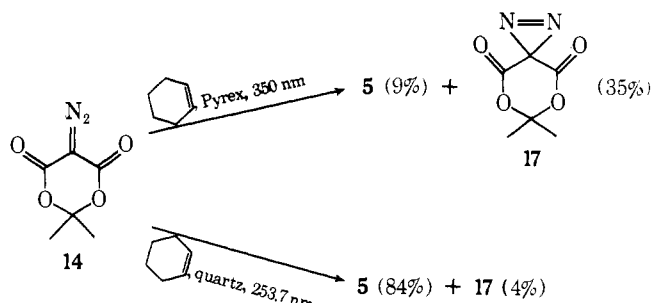| alkene	mol alkene/ mol **14**	cyclo- propane	isolated yield, %
1-cyclohexene	20	**5**[10]	84
1-cyclohexene	1.2	**5**[10]	66
trans-2-butene	10	**15**	79
cis-2-butene	10	**16**	87
4-*tert*-butyldimethylsilyloxy-1-cyclopentene (**18**)	0.66	**8**	70[a,b]
3-*tert*-butyldimethylsilyloxy-1-cyclopentene (**19**)	0.66	**9**	73[a,c]
1,3,3-trimethyl-1-cyclohexene (**20**)	0.66	**10**	64[a,d]
cis-3,4-methylenedioxy-1-cyclopentene (**21**)	0.66	**22**	68[a,c]
1-methyl-1-cyclohexene	2	**23**	76
1-hexene	10	**24**	83
1-hexene	2	**24**	59
bicyclo[2.2.1]hept-2-ene	2	**25**	40[e]
1-methylenecyclohexane	2	**26**	83
2-methyl-1,3-butadiene (**27**)	2	**28** + **29**	72[f]
1-phenyl-1-cyclohexene	0.66	**30**	54[a,f,g]
cis-3,5-diacetoxy-1-cyclopentene (**31**)	0.66	**11**	0
2,4-dioxabicyclo[3.2.1]oct-6-ene (**32**)	0.66	**33**	0
trans-3-*tert*-butyldimethylsilyloxy-5-methoxy-1-cyclopentene (**34**)	0.66	**35**	0
4-*tert*-butyldimethylsilyloxy-2-cyclopenten-1-one (**36**)	0.66	**37**	0
3-*tert*-butyldimethylsilyloxy-2-methyl-1-cyclopentene (**38**)	0.66	**12**	0

 [a] Isolated yields based on alkene; all others based on **14**. *[b]* 13% of the corresponding cis cyclopropane was also produced bringing the total yield to 83%. *[c]* Exclusive formation of the trans cyclopropane was observed in this reaction. *[d]* A significant amount (ca. 30%) of carbene C–H insertion products was obtained with this alkene. No insertion products were isolable with any other alkenes in this series. *[e]* Both exo and endo cyclopropanes were produced. *[f]* Addition of free-radical inhibitor (2,6-di-*tert*-butylphenol) was necessary to prevent polymerization of the alkene. *[g]* Prolonged irradiation times were required in this case owing to competitive light absorption by the alkene.

transition at 249 nm (ϵ_{249} 9400). We decided to investigate the photodecomposition of **14** under irradiation at these wavelengths.[14] Direct photolysis of **14** in a large excess of cyclohexene through Pyrex in a Rayonet reactor equipped with 350-nm bulbs resulted in the production of the desired cyclopropane **5**[10] in 9% yield. In addition, the interesting diazirine **17** was isolated in 35% yield.[15,16] The low efficiency observed
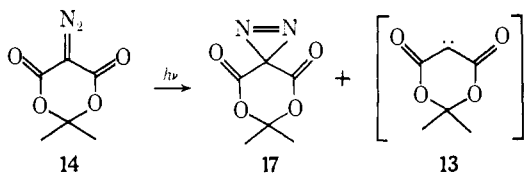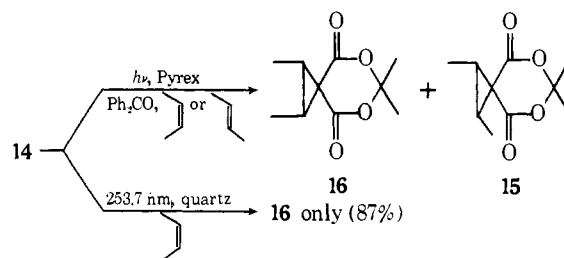

in the conversion of **14** to cyclopropane **5** at this wavelength might well be due to the relatively low extinction coefficient of the n → π* transition at 332 nm. Absorption in the π → π* region of **14** is ca. 42 times stronger in intensity than the n → π* band suggesting that the smooth decomposition of isopropylidene diazomalonate to carbene **13** would become more efficient at wavelengths near 249 nm.[18] Indeed, when **14** was subjected to direct irradiation at 253.7 nm through quartz with 20 equiv of cyclohexene cyclopropane **5** was obtained in 84% yield.

At this wavelength the yield of diazirine **17** fell to 4%. A better indication of the increased efficiency associated with this process was furnished by reducing the amount of cyclohexene to 1.2 equiv. Under these conditions, even after inclu-

sion of an inert cosolvent,[19] the yield of **5** fell to only 66%.

These results are in sharp contrast to the reported properties of carbene **13** generated via irradiation using a medium-pressure mercury arc and Pyrex filter.[12,13] Benzophenone-sensitized photodecomposition of **14** in cyclohexene using a quartz cell at 253.7 nm resulted in an intractable mixture of products in low yield.[20] We have also found that direct irradiation of **14** at 253.7 nm in either *cis*- or *trans*-2-butene af-

fords the corresponding cyclopropanes **15** and **16** with complete retention of geometry.[15] These results suggest the intermediacy of a singlet carbene.[21]

In light of the very respectable yields secured in the photochemical spirocyclopanations described above we undertook an extensive examination of the reaction of **13** with a variety of alkenes. The results of this study are compiled in Table I.

Inspection of the yields obtained in the cyclopropanation of many alkenes in Table I suggests a noteworthy degree of generality. Of particular interest is the selectivity with which **13** adds to alkenes **18**, **19**, and **21**. In the case of **18** only 15% of the cis adduct was formed whereas with **19** and **21** the trans adduct was the exclusive product.[22]

The cyclopropanation of **27** resulted in the formation of **28** and **29** as a 70/30 mixture, respectively.[15]

The preference for the more highly substituted double bonds by the electronically deficient species **13** is not unexpected. This is again reflected by the higher yield obtained in the cyclopropanation of 1-methyl-1-cyclohexene as compared to 1-hexene. Further evidence for an electronically deficient **13** is the unfortunate inertness of alkenes **31**, **32**, and **34**, which possess two allylically disposed oxygen functions,[23] and the enone **36**.

The acid-catalyzed decomposition of diazo alkanes and diazo esters has been known for many years. Recently, much interest has been diverted to the Lewis acid mediated intramolecular carbon alkylations of unsaturated diazo ketones.[24–26] In these and related reactions the electrophilicity of the α-diazocarbonyl system is markedly enhanced.[27,28] We therefore examined the influence of Lewis acids on the photodecomposition of **14** and the subsequent addition of **13** to alkenes.[29,30] Addition of the relatively weak Lewis acids zinc chloride and boron trifluoride etherate promoted an increase in both the rate with which **13** was generated and the efficiency of its addition reactions. Unfortunately, this enhancement of reactivity was not dramatic enough to effect cyclopropanation of the olefin **31**. The degree of increased electrophilicity of the cyclopropanating agent is reflected in improved yields for representative alkenes (Table II).

We found the improved yields obtained from the Lewis acid catalyzed additions of **13** to mono- and 1,2-disubstituted alkenes to be fairly general and gratifying. In addition, the frustratingly low yield furnished in the case of 1-methyl-1-cyclohexene appears to be representative of the poor yields secured in the catalyzed addition of **13** to trisubstituted olefins.

In view of the inherent simplicity and the scope of the direct photochemical cyclopropanations reported here we believe that this method will provide a powerful tool for the synthesis of natural products.

Experimental Section

Infrared spectra were recorded on a Beckman IR 4210 infrared spectrophotometer. NMR spectra were taken on Varian T-60 and Varian HR-220 spectrometers, using tetramethylsilane as internal standard. Mass spectra were determined on a AEI-MS9 mass spectrometer. Melting points were determined using a Fisher-Johns apparatus and are uncorrected. All alkenes used in this study were available commercially with the exception of 1,3,3-trimethyl-1-cyclohexene (**20**),[33] *cis*-3,4-methylenedioxy-1-cyclopentene (**21**),[34] 4-*tert*-butyldimethylsilyloxy-1-cyclopentene (**18**), and 3-*tert*-butyldimethylsilyloxy-1-cyclopentene (**19**). The preparation of the latter two alkenes by the silylation of the corresponding alcohols[36] is given below. Isopropylidene diazomalonate (diazo Meldrum's acid) was prepared by the method of Eistert and Geiss.[32]

4-*tert*-Butyldimethylsilyloxy-1-cyclopentene (18). To 4.0 g (67 mmol) of imidazole and 5 g (35 mmol) of *tert*-butyldimethylsilyl chloride in 7 mL of dry dimethylformamide was added 2.52 g (30 mmol) of 1-cyclopenten-4-ol.[35] The mixture was stirred at 35 °C for 15 h, cooled, diluted with 50 mL of water, and extracted with two 25-mL portions of ligroin (bp 20–40 °C). The combined ligroin solutions were washed successively with 25 mL of water and 25 mL of brine and were dried over anhydrous sodium sulfate. The residue left after evaporation of the solvent was evaporatively distilled at 60 °C and 50 Torr to afford 5.46 g (92%) of **18**: IR (CCl₄) cm⁻¹ 3029–2829 (C–H), 1610 (C=C), 1468 and 1459 (*gem*-dimethyl); NMR (CDCl₃) δ 0.05 (s, 6, CH₃), 0.90 (s, 9, CH₃), 2.43 (m, 4, CH₂), 4.53 (m, 1, CH), 5.63 (broad s, 2, vinyl); mass spectrum (70 eV) *m/e* 198.

3-*tert*-Butyldimethylsilyloxy-1-cyclopentene (19). 1-Cyclopenten-3-ol[37] (2.52 g, 30 mmol) was subjected to the procedure given above to furnish 5.34 g (90%) of **19**: IR (CCl₄) cm⁻¹ 3027–2826 (C–H), 1612 (C=C), 1468 and 1459 (*gem*-dimethyl); NMR (CDCl₃) δ 0.05 (s, 6, CH₃), 0.90 (s, 9, CH₃), 1.70–2.33 (m, 4, CH₂), 4.93 (m, 1, CH), 5.83 (m, 2, vinyl); mass spectrum (70 eV) *m/e* 198.

The following is a typical experimental procedure for the uncatalyzed direct photochemical cyclopropanation of alkenes.

Cyclopropane 8. A solution of 594 mg (3 mmol) of **18** and 765 mg (4.5 mmol) of **14** in 1.2 mL of dry dichloromethane was placed in a septum-sealed quartz cell and irradiated in a Rayonet reactor fitted out with 253.7-nm bulbs. The photolysis was judged complete when the absence of **14** was revealed by TLC (in this case 72 h). The residue left after evaporation of the solvent was taken up in 20 mL of ether and filtered through a glass plug. The product was chromatographed on an Altex medium-pressure LC (silica gel Woelm 32–63 m) with 1:4 ethyl acetate–cyclohexane to afford 238 mg (70%) of **8**: IR (CCl₄) cm⁻¹ 1796 and 1772 (C=O), 1381 and 1372 (*gem*-dimethyl), 1012 (cyclopropane); NMR (CCl₄) δ 0.05 (s, 6, CH₃), 0.87 (s, 9, CH₃), 1.59 (s, 3, CH₃), 1.66 (s, 3, CH₃), 1.81 (m, 2, CH₂), 2.05 (m, 1, CH₂), 2.22 (m, 1, CH₂), 3.22 (m, 1, cyclopropyl), 3.70 (m, 1, cyclopropyl), 4.21 (m, 1, CH); high-resolution mass spectrum (70 eV), 340.1697 (calcd, 340.1706).

Chromatographic elution of a second band furnished the minor (cis) cyclopropane, 44 mg (13%): IR (CCl₄) cm⁻¹ 1798 and 1774 (C=O), 1383 and 1375 (*gem*-dimethyl), 1010 (cyclopropane); NMR (CCl₄) δ 0.05 (s, 6, CH₃), 0.85 (s, 9, CH₃), 1.56 (s, 3, CH₃), 1.63 (s, 3, CH₃), 1.90 (m, 2, CH₂), 2.12 (m, 2, CH₂), 3.13 (m, 1, cyclopropyl), 3.59 (m, 1, cyclopropyl), 4.36 (m, 1, CH); high-resolution mass spectrum (70 eV), 340.1697 (calcd, 340.1706).

Spectral Data for Spiro-Activated Cyclopropanes. 15: IR (CCl₄) cm⁻¹ 1800 and 1776 (C=O), 1384 and 1377 (*gem*-dimethyl), 989 (cyclopropane); NMR (CCl₄) δ 1.22 (d, 3, *J* = 1 Hz, CH₃), 1.37 (d, 3, *J* = 7 Hz, CH₃), 1.58 (s, 3, CH₃), 1.64 (s, 3, CH₃), 2.63 (m, 2, cy-

Table II. Lewis Acid Catalyzed Reaction of **13** with Alkenes

alkene	mol alkene/ mol **14**	mol catalyst/ mol **14**	cycloprop- ane	isolated yield, %
1-cyclohexene	2	0.046 (ZnCl₂)	**5**	72[a]
1-cyclohexene	2	0.092 (ZnCl₂)	**5**	88[a]
1-cyclohexene	2	0.184 (ZnCl₂)	**5**	>95,[a] 84
1-hexene	2	0.5 (BF₃· Et₂O)	**24**	82
1-methyl-1-cycloh- exene	2	0.5 (ZnCl₂)	**23**	11

[a] NMR yields; all others isolated yields based on **14**.

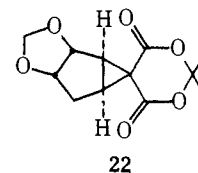clopropyl); high-resolution mass spectrum (70 eV), 198.0896 (calcd, 198.0892).

16: mp 45–47 °C; IR (CCl₄) cm⁻¹ 1799 and 1780 (C=O), 1381 and 1389 (*gem*-dimethyl), 994 (cyclopropane); NMR (CCl₄) δ 0.98 (d, 3, *J* = 6 Hz, CH₃), 1.12 (d, 3, *J* = 6 Hz, CH₃), 1.57 (s, 3, CH₃), 1.62 (s, 3, CH₃), 2.82 (m, 1, cyclopropyl), 3.63 (m, 1, cyclopropyl); high-resolution mass spectrum (70 eV), 198.0896 (calcd, 198.0892).

9: IR (CCl₄) cm⁻¹ 1801 and 1782 (C=O), 1390 and 1381 (*gem*-dimethyl), 1028 and 1012 (cyclopropane); NMR (CDCl₃) δ 0.07 (s, 6, CH₃), 0.87 (s, 9, CH₃), 1.60 (s, 3, CH₃), 1.65 (s, 3, CH₃), 1.78–2.20 (m, 4, CH₂), 3.37 (m, 1, cyclopropyl), 3.72 (d, 1, *J* = 7 Hz, cyclopropyl), 4.48 (d, 1, *J* = 3 Hz, CH); high-resolution mass spectrum (70 eV), 340.1707 (calcd, 340.1705).

10: IR (CCl₄) cm⁻¹ 1798 and 1770 (C=O), 1781 and 1773 (*gem*-dimethyl), 1019, 999, and 988 (cyclopropane); NMR (CDCl₃)[38] δ 0.92 (s, 1, CH₃), 0.96 (s, 2, CH₃), 1.17 (s, 1, CH₃), 1.22 (s, 2, CH₃), 1.02–1.68 (m, 6, CH₂), 1.37 (s, 1, CH₃), 1.40 (s, 2, CH₃), 1.55 (broad s, 6, CH₃), 1.60 (s, 3, CH₃), 3.08 (broad s, 1, cyclopropyl); high-resolution mass spectrum (70 eV), 266.1510 (calcd, 266.1518).

**22:** mp 105–107 °C; IR (CCl₄) cm⁻¹ 1795 and 1778 (C=O), 1381 and 1373 (*gem*-dimethyl), 1006 (cyclopropane); NMR (CDCl₃) δ 1.58 (s, 3, CH₃), 1.64 (s, 3, CH₃), 1.90 and 2.40 (m, 2, CH₂), 3.41 (m,

22

1, cyclopropyl), 3.89 (d, 1, *J* = 10 Hz, cyclopropyl), 5.05 (m, 1, CH), 5.21 (d, 1, *J* = 4 Hz, CH), 5.29 and 5.52 (s, 1, CH₂); high-resolution mass spectrum (70 eV), 254.0789 (calcd, 254.0790).
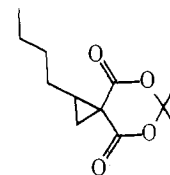
23: IR (CCl₄) cm⁻¹ 1789 and 1770 (C=O), 1381 and 1373 (*gem*-dimethyl), 998 (cyclopropane); NMR (CDCl₃) δ 1.17–2.03 (m, 8, CH₂), 1.40 (s, 3, CH₃), 1.58 (s, 3, CH₃), 1.63 (s, 3, CH₃), 3.70 (m,
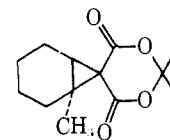
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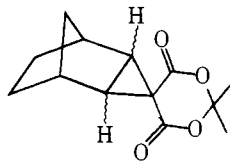1, cyclopropyl); high-resolution mass spectrum (70 eV), 180.0784 (calcd mass (−acetone, 58), 180.0786).

24: IR (CCl₄) cm⁻¹ 1796 and 1776 (C=O), 1381 and 1374 (*gem*-dimethyl), 990 (cyclopropane); NMR (CDCl₃) δ 0.90–1.55 (m,

24

9, CH$_2$ and CH$_3$), 1.60 (s, 3, CH$_3$), 1.65 (s, 3, CH$_3$), 2.60–3.60 (m, 3, cyclopropyl); high-resolution mass spectrum (70 eV), 226.1204 (calcd, 226.1205).

25 (as a mixture of exo and endo cyclopropanes): IR (CCl$_4$) cm^{-1} 1799 and 1772 (C=O), 1386 and 1378 (*gem*-dimethyl), 989 (cyclopropane); NMR (CDCl$_3$) δ 1.27–1.73 (m, 8, CH and CH$_2$), 1.57

25

(s, 3, CH$_3$), 1.63 (s, 3, CH$_3$), 2.65–3.28 (m, 2, cyclopropyl); high-resolution mass spectrum (70 eV), 236.1050 (calcd, 236.1048).

26: IR (CCl$_4$) cm^{-1} 1793 and 1771 (C=O), 1379 and 1370 (*gem*-dimethyl), 1020 and 989 (cyclopropane); NMR (CDCl$_3$) δ 1.43–1.87 (m, 10, CH$_2$), 1.58 (s, 3, CH$_3$), 1.65 (s, 3, CH$_3$), 2.65 and
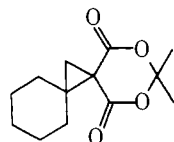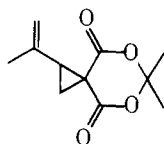

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3.10 (two d, 1, $J \approx 15$ Hz, cyclopropyl); high-resolution mass spectrum (70 eV), 180.0784 (calcd (−acetone, 58), 180.0786).

28 and **29** (as a 70:30 mixture): IR (CCl$_4$) cm^{-1} 1797 and 1772 (C=O), 1630 (C=O), 1389 and 1381 (*gem*-dimethyl, 1029 and 992 (cyclopropane); NMR (CDCl$_3$) δ 1.32 (s, 2.1, CH$_3$), 1.53 (s, 2.1,
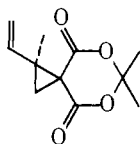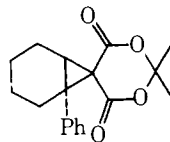

28   **29**

CH$_3$), 1.55 (s, 0.9, CH$_3$), 1.65 (s, 2.1, CH$_3$), 1.67 (s, 0.9, CH$_3$), 1.78 (m, 0.9, CH$_3$), 2.90 and 3.25 (two d, 0.7, $J = 14$ Hz, cyclopropyl), 3.40–3.60 (m, 0.9, cyclopropyl), 4.95–5.37 (m, 1.4, vinyl), 5.77–6.30 (m, 0.9, vinyl); high-resolution mass spectrum (70 eV), 210.0884 (calcd, 210.0892).

30: mp 135–137 °C; IR (CDCl$_3$) cm^{-1} 1797 and 1766 (C=O), 1597 and 1573 (aromatic), 1382 and 1374 (*gem*-dimethyl), 1007 (cyclopropane); NMR (CDCl$_3$) δ 1.32 (s, 3, CH$_3$), 1.50 (s, 3, CH$_3$),

30

1.47–2.55 (m, 8, CH$_2$), 4.13 (m, 1, cyclopropyl), 7.27 (m, 5, aromatic); high-resolution mass spectrum (70 eV), 242.0942 (calcd, (−acetone, 58), 242.0943).

The following are typical experimental procedures for the Lewis acid catalyzed cyclopropanation of alkenes by **13**.

Cyclopropane 5.[10] A solution of 170 mg (1 mmol) of **14** and 164 mg (2 mmol) of cyclohexene in 0.25 mL of dry dichloromethane was placed in a septum-sealed quartz cell under a nitrogen atmosphere and 0.1 mL of 1.84 M zinc chloride in tetrahydrofuran was added by syringe. This solution was irradiated with 253.7-nm light until complete consumption of **14** was indicated by TLC (17 h). The reaction mixture was then taken up in 25 mL of ether, washed successively with three 10-mL portions of water and 15 mL of brine, and dried over anhydrous sodium sulfate. The product was purified as before by column chromatography to furnish 188 mg (84%) of **5**.

Cyclopropane 24. A solution composed of 170 mg (1 mmol) of **14** and 168 mg (2 mmol) of 1-hexene in 0.35 mL of dry dichloromethane was placed in a septum-sealed quartz cell under a nitrogen atmosphere and 62 μL (0.5 mmol) of distilled boron trifluoride etherate added by

syringe. This solution was irradiated with 253.7-nm light until complete consumption of **14** was revealed by TLC (15.5 h). The reaction mixture was then taken up in 25 mL of ether, extracted successively with two 10-mL portions of 5% aqueous sodium bicarbonate, two 10-mL portions of water, and 10 mL of brine, and dried over anhydrous sodium sulfate. The product was purified as before to afford 185 mg (82%) of **24**.

Diazirine 17. A solution of 170 mg (1 mmol) of **14** and 1.64 g (20 mmol) of cyclohexene in 2 mL of ether was introduced to a Pyrex cell and irradiated with 350-nm light for 36 h. The volatile organics were then evaporated and the residue was purified as before. The first band consisted of 17 mg (9%) of **5**. The second furnished 49 mg (35%) of **17**: mp 82–84 °C; IR (CCl$_4$) cm^{-1} 1769 (C=O), 1390 and 1380 (*gem*-dimethyl), 1287; NMR (CDCl$_3$) δ 1.95 (s, 6, CH$_3$); high-resolution mass spectrum (70 eV), 170.0325 (calcd, 170.0327).

The third band gave 29 mg (17%) of recovered **14**.

References and Notes

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(14) An attempt to prepare **13** from **14** by pyrolysis in the presence of copper bronze and cycloheptene gave only products derived from the decomposition of **14** and none of the desired cyclopropane.
(15) The assigned structure is supported by its (a) infrared and NMR spectra and (b) high-resolution mass spectrum.
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(20) In addition the photodecomposition of **14** in the presence of benzophenone at 253.7 nm was markedly slowed.
(21) Clearly, more refined experiments must be run before the intermediacy of a singlet could be firmly established.
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