70.5, 73.5, 80.2, 86.9, 108.4, 109.0, 113.8, 119.6, 127.0, 127.6, 130.0, 141.4, 150.0, 151.2, 151.3, 151.8, 154.7, 169.4, 170.4; ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3 H), 2.10 (s, 3 H), 2.15 (s, 3 H), 2.44 (s, 3 H), 4.27 (s, 3 H), 4.48 (m, 3 H), 6.33-6.01 (m, 5 H), 6.88 (dd, 1 H), 7.22 (d, 1 H, J = 2.9 Hz), 7.82 (dd, 1 H, J = 3.9, 1.8 Hz), 8.08 (s, 1 H); UV (EtOH) λ_{max} 310 nm (ϵ 3.0 × 10^4), 326 (ϵ 2.8 × 10^4), 336 (2.7 × 10^4), 352 (ϵ 2.4 × 10^4), 250 (ϵ 8.3 × 10^3); fluorescence (EtOH) excitation 350 nm and emission 400 nm; mass spectrum, m/z (relative intensity) 537 (M^+, 1.7), 308 ($Pur^+ + CH_2O$, 3.4), 280 (14.1), 279 (39.9), 278 (Pur^+, 100.0), 259 ($sugar^+$, 1.5), 199 (1.7), 157 (9.1), 139 (68.3).

2-Phenylinosine (11). To 50 mL of dry ethanol saturated with ammonia gas at ice-salt bath temperatures was added 0.267 g (0.546 mmol) of **2**. The solution was stirred at ice-salt bath temperatures for 1 h and at 25 °C for 23 h. The solvent was removed under reduced pressure and the residue was lyophilized. The deprotected nucleoside (0.186 g) in 400 mL of water was photolyzed as described for **2** for 34 h. The solvent was removed under reduced pressure and the residue chromatographed on silica gel plates that were developed in 4:1 ethyl acetate:methanol. The band at R_f 0.22 gave 0.157 g (0.455 mmol, overall yield = 83.4%) of **11** as a light yellow crystalline compound: mp 98-101 °C; ^{13}C NMR ($CDCl_3$) δ 61.2, 70.3, 73.9, 85.5, 87.2, 122.8, 127.8, 128.5, 131.2, 132.0, 139.2, 148.5, 153.3, 157.2; ^{1}H NMR ($CDCl_3$) δ 3.72-3.54 (m, 2 H), 4.20 (m, 1 H), 4.58 (m, 1 H), 5.14 (m, 1 H), 5.97 (d, 1 H, J = 5.9 Hz), 7.60 (m, 3 H), 8.12 (m, 2 H), 8.37 (s, 1 H), 11.2 (s, 1 H); UV (EtOH) λ_{max} 290 nm (ϵ 5.8 × 10^3), 260 (4.9 × 10^3); fluorescence (EtOH) excitation 366 nm and emission 456 nm; mass spectrum, m/z (relative intensity) 254 ($Pur^+ + C_3H_2O$, 10.9), 240 ($Pur^+ + CHO$, 20.0), 225 ($Pur^+ + CH_2$, 22.7), 213 (20.0), 212 (96.4), 211 (Pur^+, 42.7).

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Registry No. **1**, 5987-76-8; **2**, 71122-76-4; **3**, 92220-51-4; **4**, 90596-68-2; **5**, 92220-52-5; **6**, 92220-53-6; **7**, 92220-54-7; **8**, 90596-69-3; **9**, 92220-56-9; **10**, 92220-55-8; **11**, 32447-14-6; guanosine, 118-00-3; 2,3,5-tri-*O*-acetylguanosine, 6979-94-8; 2-amino-6-chloro-9β-(2,3,5-tri-*O*-acetyl-D-ribofuranosyl)purine, 16321-99-6; benzene, 71-43-2; *N*-methylpyrrole, 6973-60-0; 2-methylfuran, 534-22-5; thiophene, 110-02-1; pyridine, 110-86-1; 2-phenyl-6-chloro-9β-(ribofuranosyl)purine, 56489-65-7.

Cycloaddition Reactions of Strained Ring Systems. Photochemistry of 1-Phenyl-2-carbomethoxy-3,3-dimethylcyclopropene[1]

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The sensitized irradiation of 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene produced two novel photodimers. The minor product can be explained in terms of an initial bond formation to give a diradical intermediate. Collapse of the diradical furnishes a tricyclohexane which undergoes a subsequent cycloreversion to give a 1,4-cyclohexadiene derivative. The major photodimer is derived by cyclopropyl ring opening of the initially produced diradical followed by cyclization to give a bicyclo[1.1.0]butane derivative. Direct irradiation of 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene afforded a mixture of 1-carbomethoxy-3,3-dimethyl-1-phenylallene, 1-carbomethoxy-3-methyl-2-phenylbutadiene, and 2-carbomethoxy-3-methyl-1-phenylbutadiene. The formation of the three products can be rationalized in terms of a vinylcarbene intermediate which inserts into the adjacent methyl group. The product distribution favors cleavage of the carbomethoxy substituted σ-bond of the cyclopropene ring. This regioselectivity can be attributed to a funneling of the excited singlet state of the cyclopropene to the energy surface of the higher lying carbene state. The photochemical and thermal behavior of several hydroxyalkyl substituted cyclopropenes derived from 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene was also studied and the results obtained were compared to the reactions in the carbomethoxy series.

Cyclopropene[2] was first prepared some 60 years ago but, despite its unusual structure exhibiting high Baeyer strain, the molecule received minimum attention until the late 1950s. Since that time chemical and theoretical interest has been considerable and a number of reviews have appeared describing the thermal[3] and photochemical behavior[4] of this highly strained class of hydrocarbons. Suitably substituted cyclopropenes suffer the ene reaction[5,6] and also readily undergo dimerization,[7-12] cycloaddition,[13,14] and complexation with transition metals[15] as a means of releasing strain. Our research group has been involved over the past few years in a program of synthesizing unusual polycyclic ring systems which makes use of the cycloaddition behavior of cyclopropenes as the primary strategy.[13] [4 + 2] cycloaddition across the double bond in cyclopropene proceeds quite readily since it reduces ring strain by 26 kcal/mol.[16,17] The transition-state energy for this reaction, however, is very sensitive to steric

[†] Alexander von Humboldt Senior Fellow, University of Wurzburg, 1983-1984.

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(2) Demyanov, N. Y.; Doyarenko, M. N. *Bull. Acad. Sci. Russ.* **1922**, *16*, 297.
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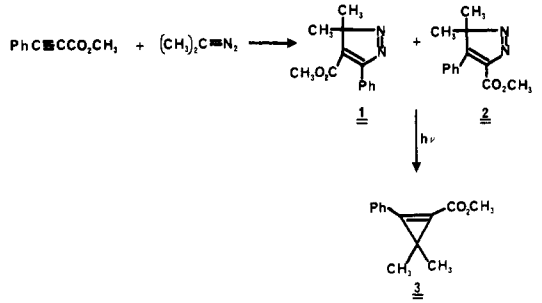
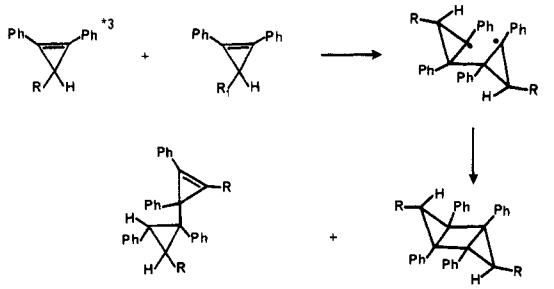
factors as is indicated by the observation that 3,3-disubstituted cyclopropenes do not undergo ready Diels–Alder cycloadditions.[18] We envisioned that one way of enhancing the reactivity of a 3,3-disubstituted cyclopropene would be to place an electron-withdrawing substituent on the π-bond. FMO theory predicts that attachment of a carbomethoxy group on an alkene will lower the energy of the LUMO and thereby enhance the cycloaddition rate.[19,20] During the course of our studies with 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene we uncovered some novel chemistry which differs from the previously reported behavior of related systems. We report here the results of these studies.[21]

Results and Discussion

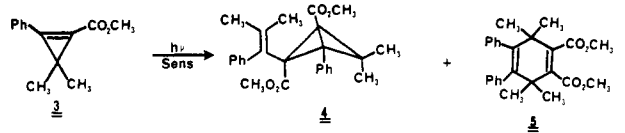
The photolysis of 3*H*-pyrazoles is a well-known method for preparing cyclopropenes.[22] 1-Phenyl-2-carbomethoxy-3,3-dimethylcyclopropene (**3**) was synthesized by treating 2-diazopropane with methyl phenylpropiolate according to the general procedure of Franck-Neumann and Buchecker.[23] The 1,3-dipolar cycloaddition reaction proceeded readily at 25 °C to give a mixture of 3*H*-pyrazoles **1** (71%) and **2** (29%) which could be separated by silica gel chromatography. Irradiation of either isomer using Pyrex filtered light afforded cyclopropene **3** in 85% yield.



Cyclopropene photochemistry has been unusual in the rich variety of different types of photochemical transformations encountered. Electronically excited singlet states of cyclopropenes generally react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinylcarbenes, while triplet states generated by sensitization techniques give high yields of dimers.[3] Photophysical studies including quantum yield measurements and isotope effects are consistent with the interpretation that the triplet-induced dimerization process occurs in a stepwise fashion via a diradical intermediate.[10] Earlier observations by DeBoer indicate that there are severe steric constraints associated with the triplet dimerization reaction.[10] Thus, 1,2-diphenylcyclopropenes, where both 3-positions are substituted with alkyl groups, do not dimerize.



In contrast to these findings we have observed that the sensitized irradiation of **3** in benzene afforded a mixture of two dimers. Moreover, the structure of the major photodimer is significantly different from previously reported examples. The major photodimer is assigned as 1,2-dicarbomethoxy-3-phenyl-4,4-dimethyl-2-(2-methyl-1-phenyl-1-propenyl)bicyclo[1.1.0]butane (**4**) on the basis of its characteristic NMR spectrum (90 MHz, $CDCl_3$) which showed four distinct methyl signals at δ 1.23, 1.58, 1.69, and 2.20, two methoxy signals at 3.54 and 3.87, as well as an aromatic multiplet (6.86–7.49). Unequivocal proof of this assignment derives from a single-crystal X-ray structure analysis. Crystals of **4** were monoclinic with space group $P2_1/C$ and with a = 14.951 (3) Å, b = 10.402 (3) Å, c = 14.075 (3) Å, β = 90.36 (2)°, Z = 4, d = 1.227 g cm^{-3}. The structure was solved by direct methods and



refined by full-matrix least squares with isotropic thermal parameters. Convergence was achieved with R = 0.058 for 943 observations and 121 variables.[24] The structure of the minor photodimer **5** (14%) was assigned on the basis of its straightforward spectral data (see Experimental Section). Thermolysis of dimer **4** resulted in the formation of two new products (**6** and **7** (1:1 ratio)) whose structures were deduced from their spectroscopic properties. These same two compounds were also formed by heating cyclopropene **3** at 175 °C for 72 h. Structures **6** and **7** could be readily interconverted by thermolysis or sensitized photolysis. Extended irradiation of the mixture produced cyclohexadiene **8** as the exclusive photoproduct. This chemistry is summarized in Scheme I.

The photochemistry of cyclopropene derivatives has been shown to be remarkably dependent on the multiplicity of the excited state involved.[13,14] The formation of the vinylcarbene in the direct irradiation experiments can be viewed as the result of heterolytic cleavage and simultaneous rotation of the disubstituted methylene carbon.[25,26] Both electrons occupy an in plane σ orbital with only two electrons in the conjugated π-orbital. A conceivable explanation which could account for the formation of dimer **4** involves generation of vinylcarbene **9** from the singlet state of **3** (i.e., light leakage) followed by a subsequent cycloaddition across the cyclopropene π-bond. This

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(24) We wish to thank Professor George R. Newkome and Dr. F. R. Fronczek, Louisiana State University, for the single X-ray structure determination of dimer **4**. Details will be reported elsewhere.
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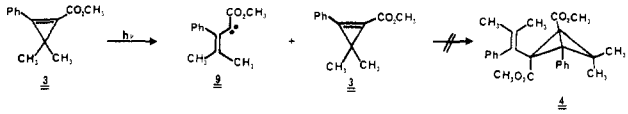
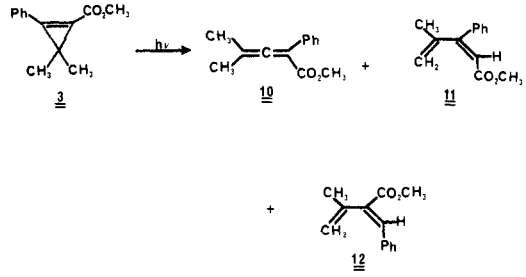
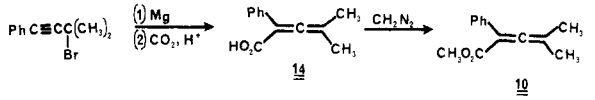


sequence of reactions was discounted, however, by the fact that no signs of dimer 4 could be found in the direct photolysis of 3.

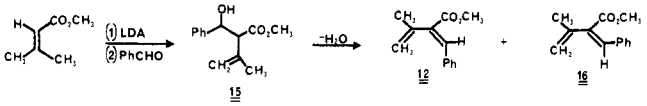
The direct irradiation of 3 followed an entirely different course from the sensitized photolysis and produced a mixture of 1-carbomethoxy-3,3-dimethyl-1-phenylallene (10, 49%), 1-carbomethoxy-3-methyl-2-phenylbutadiene (11, 30%), and 2-carbomethoxy-3-methyl-1-phenylbutadiene (12, 20%). The product structures were in accord with the NMR, UV, IR, and mass spectral data (see Experimental Section).



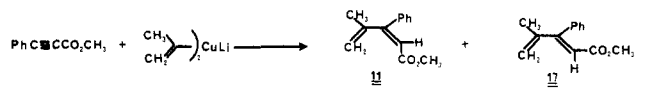
Additional support for the various photoproducts was made by comparison with independently synthesized samples. Allene 10 was prepared by treating propargyl bromide 13 with magnesium turnings and quenching the Grignard reagent with carbon dioxide.[27] Esterification of the resulting allenic acid 14 with diazomethane afforded 10 in high yield.



Preparation of an authentic sample of butadiene 12 was accomplished by the dehydration of hydroxybutenoate 15.



This material was prepared by treating methyl 3-methylcrotonate with base followed by reaction of the resulting carbanion with benzaldehyde according to the general procedure of Heathcock and Dugger.[28] Dehydration of 15 with Burgess' reagent[29] produced a 1:1 mixture of (*E*)- and (*Z*)-2-carbomethoxy-3-methyl-1-phenyl-1,3-butadienes which could be separated by silica gel chromatography. The *E* isomer was identical with the diene isolated from the photolysis of cyclopropene 3. The structure of the remaining butadiene was also confirmed by comparison with an authentic sample. Treatment of 2-propenyl cuprate reagent[30] with methyl phenylpropiolate produced a mixture of the (*E*)- and (*Z*)-stereoisomers which could be separated by column chromatography. The (*E*) isomer proved to be identical with photoproduct 11 obtained from the photolysis of 3.



(27) Ford, J. H.; Thompson, C. D.; Marvel, C. S. *J. Am. Chem. Soc.* **1935**, *57*, 2619.
(28) Dugger, R. W.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1181.
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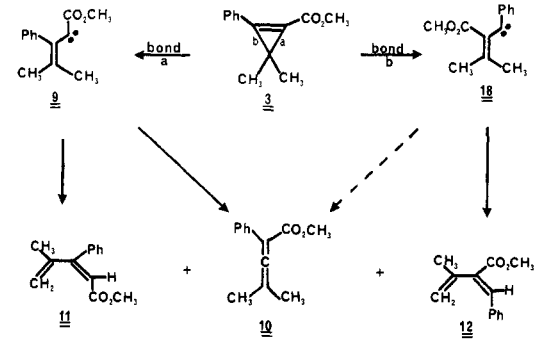
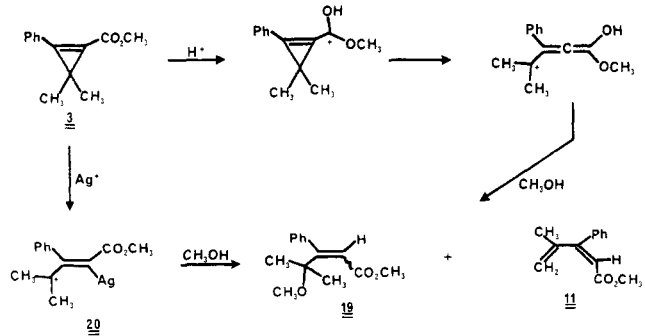
Ring opening of an unsymmetrically substituted cyclopropene such as 3 can occur in either of two directions to generate vinylcarbenes 9 or 18. Insertion of the carbene carbon onto the adjacent methyl group will produce dienes 11 and 12. The formation of allene 10 can be explained



by either a 1,2-phenyl shift from 9 or a 1,2-carbomethoxy shift from 18. More than likely, 10 is produced from vinylcarbene 9 since we are unaware of any examples of a 1,2-carbomethoxy shift to a carbene center. There is some difficulty in interpreting the regioselectivity of ring opening for this reaction. Cyclopropene to vinylcarbene conversions are known to be reversible both thermally[31] and photochemically.[32] This means that the product distribution may reflect different rates of return to cyclopropene for the two possible carbenes rather than selectivity of ring opening. Nevertheless, the fact that structures 10 and 11 are found in much larger quantities than 12 suggests that cleavage of the carbomethoxy substituted bond is the preferred process. This is similar to earlier results encountered by Padwa[33] and Zimmerman[34] who found that an unusual substituent effect operates in the photorearrangement of a series of unsymmetrically substituted cyclopropenes. In all the cases studied, product distribution reflects favored cleavage of the alkyl substituted rather than the phenyl substituted σ bond. This unusual regioselectivity was attributed to a funneling of the excited state of the cyclopropene to the energy surface of the higher lying carbene state.[33] Thus the preferential formation of 10 and 11 from cyclopropene 3 is perfectly compatible with the earlier observations.

In contrast with the photochemical results, exposure of cyclopropene 3 to acidic methanol resulted in the formation of butadiene 11 and methoxy ether 19. No signs of



allene 10 or the isomeric butadiene 12 could be detected in the crude reaction mixture. Treatment of 3 with an

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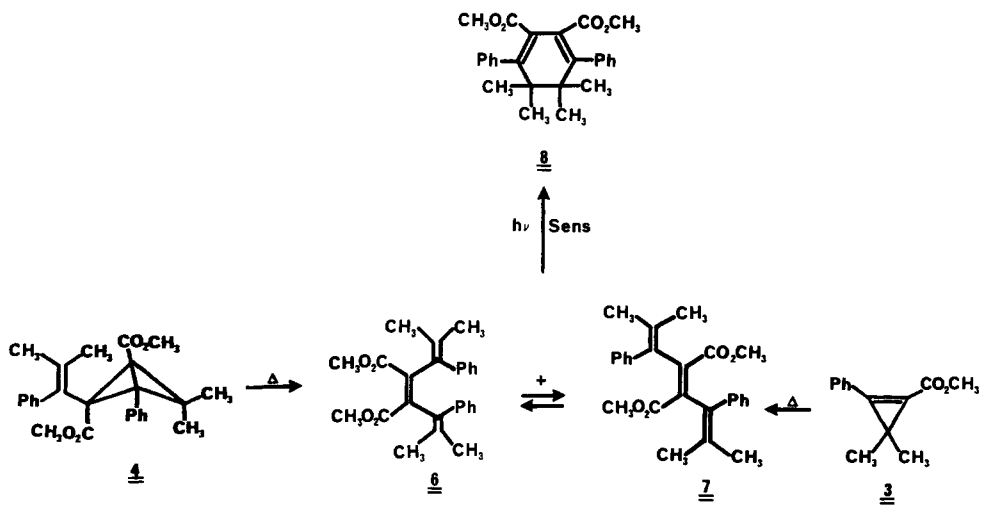
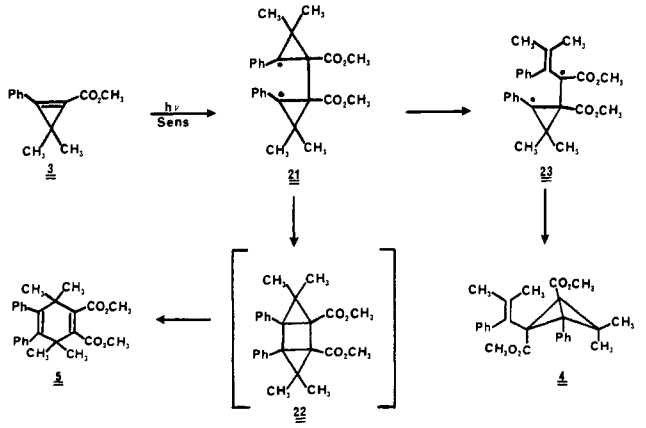
(34) Zimmerman, H. E.; Aasen, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 2342; *J. Org. Chem.* **1978**, *43*, 1493.

Scheme I

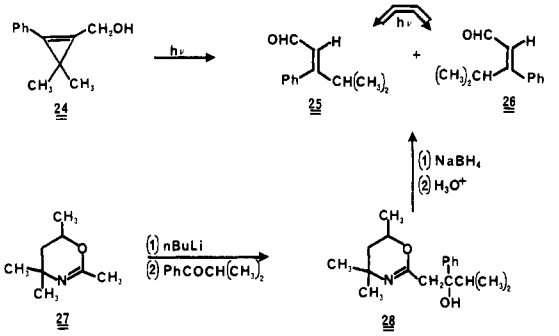


excess of silver perchlorate in methanol also resulted in the selective cleavage of the carbomethoxy substituted σ-bond producing compounds **11** and **19**. The regioselectivity of the cleavage reaction can be explained by assuming an initial protonation of the carbomethoxy group followed by rapid opening of the cyclopropene ring. The resulting cation can either lose a proton to give butadiene **11** or react with methanol to produce **19**. In line with earlier evidence for the intermediacy of a metal-bonded carbonium ion–metal complexed carbene hybrid intermediate in the transition metal promoted rearrangement of strained ring systems,[35,36] it is tempting to suggest the involvement of a related species in the silver-induced rearrangement of cyclopropene **3**. Thus, we propose that silver ion behaves as a very specific Lewis acid that attacks the cyclopropene ring to yield argentio carbonium ion **20**.[37] This species then reacts with methanol to produce structure **19**.

The results obtained from the direct irradiation experiments clearly demonstrate that the formation of dimer **4** from the sensitized photolysis of **3** can not be explained by addition of the initially generated vinylcarbene across the cyclopropene π-bond. An attractive rationalization for the formation of the photodimers is that bond formation from the triplet state occurs in a stepwise fashion to generate diradical **21**. Simple collapse of **21** with carbon–carbon bond formation furnishes tricyclohexane **22** which undergoes a subsequent cycloreversion to give **5**. In addition, diradical **21** can undergo cyclopropyl ring opening to give **23** which subsequently cyclizes to give bicyclobutane **4**. The diradical formed from 1,2,3-trisubstituted cyclopropenes rapidly couples before it has a chance to undergo cyclopropyl ring opening and consequently only tricyclohexane dimers are found in the triplet-sensitized irradiation of these systems.[10] At higher temperatures the bicyclobutane dimer **4** is converted to hexatrienes **6** and **7**. This transformation presumably proceeds via the intermediacy of biradical **23**.[38]



Earlier work in our laboratory has established that vinylcarbenes generated from the irradiation of diphenyl substituted cyclopropenes can be trapped by methanol to give methoxy substituted ethers.[13,33] As a continuation of our investigations in this area, we were particularly interested in determining whether the insertion reaction would also occur when the alcohol and the cyclopropene ring were constrained to be within the same molecule. In order to probe this possibility, we carried out a study dealing with the photochemistry of a hydroxy substituted cyclopropene. As our first model we chose to investigate the photochemistry of 1-(hydroxymethyl)-2-phenyl-3,3-dimethylcyclopropene (**24**). This material was prepared by the Dibal reduction of cyclopropene **3**. Irradiation of **24** in benzene under a nitrogen atmosphere led to a 2:1 mixture of the *Z* (**25**) and *E* isomers of 3-phenyl-4-methyl-2-penten-1-al (**26**). These two compounds were interconverted on further irradiation. The structures of the aldehydes were confirmed by comparison with authentic samples prepared by treating the carbanion derived



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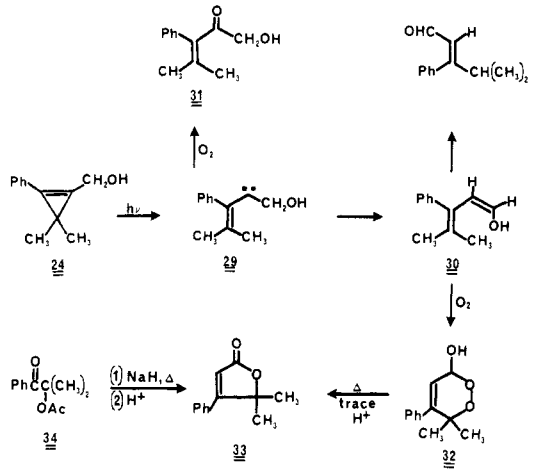
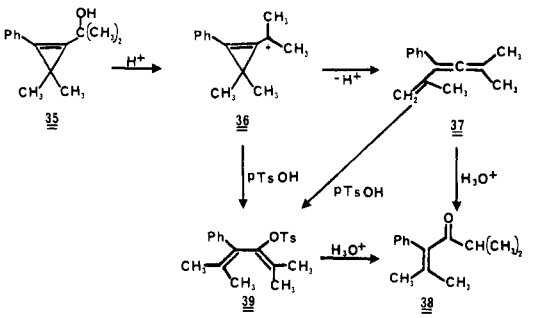
Scheme II



from oxazine **27** with isobutyrophenone according to the general procedure of Meyers and co-workers.[39] The resulting adduct **28** was reduced with sodium borohydride followed by oxalic acid hydrolysis to give a mixture of **25** and **26**.

The formation of aldehydes **25** and **26** from the irradiation of **24** can be readily rationalized in terms of a vinylcarbene intermediate (i.e., **29**). As was discussed earlier, the major product derived from the photoinduced ring opening of a 1-phenyl-2-alkyl substituted cyclopropene always corresponds to the preferential cleavage of the alkyl σ-bond. Carbene **29** can undergo a 1,2-hydrogen shift to give dienol **30** which undergoes a subsequent 1,5-sigmatropic hydrogen migration. Support for this mechanism was obtained by carrying out the irradiation of **24** in the presence of oxygen. Under these conditions the formation of aldehydes **25** and **26** is completely suppressed. The major products that were isolated from the reaction corresponded to keto alcohol **31** (15%) and dioxane **32** (63%). The assignment of structure **32** was supported by its conversion to furanone **33**. This material was also prepared from the cyclization of 1-phenyl-2-acetoxy-2-methylpropan-1-one (**34**) with base.[40] Dioxane **32** is the result of a novel Diels–Alder reaction of dienol **30** with oxygen. Trapping of vinylcarbene **29** with oxygen to give **31** also competes to a minor extent with the 1,2-hydrogen shift reaction. This chemistry is summarized in Scheme II.

Attention was next turned to the chemical behavior of 1-phenyl-2-(2-hydroxy-2-propyl)-3,3-dimethylcyclopropene (**35**). Alcohol **35** was prepared by the reaction of cyclopropene **3** with methyllithium in ether. Unfortunately, all attempts to isolate a photoproduct from the direct or sensitized irradiation of **35** were unsuccessful and consequently further photochemical study of this system was abandoned. We did encounter, however, some interesting acid-induced reactions of this compound. Thus, treatment of **35** with Burgess' reagent resulted in the formation of allene **37**. The structure of **37** was readily established from its characteristic spectral properties (see Experimental Section) and by its conversion to 2,5-dimethyl-3-phenylhex-2-en-4-one (**38**). When the dehydration reaction was



carried out in benzene with *p*-toluenesulfonic acid, butadiene **39** was isolated in high yield. This material was also produced by treating allene **37** with *p*-toluenesulfonic acid. Subjection of **39** to aqueous hydrolytic conditions afforded ketone **38**. The rearrangement of **35** probably proceeds through a cyclopropenylcarbinyl ion (i.e., **36**) which readily undergoes a ring opening reaction to the observed products.

In conclusion, the photochemical and ground-state behavior of phenyl substituted cyclopropenes is especially rich in the varied types of reactions encountered. The subtle variation of behavior as a function of the nature of the substituent group attached to the π-bond continues to provide mechanistic challenge. Further studies on the photosensitized [2 + 2]-cycloaddition reactions of cyclopropene **3** are in progress and will be reported in due course.

Experimental Section

All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer 467 infrared spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz by using a Varian EM-390 spectrometer. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV.

Preparation of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (3). A mixture of 4-carbomethoxy-5,5-dimethyl-3-phenyl- (1) and 3-carbomethoxy-5,5-dimethyl-4-phenylpyrazole (2) was prepared according to the procedure of Franck-Neumann and Buchecker.[23] To a solution of 2-diazopropane in 200 mL of ether at −78 °C was added 20.26 g of methyl phenylpropiolate. The mixture was allowed to warm to room temperature and was stirred at 25 °C for 12 h. The ether was removed under reduced pressure and the reddish oil that was left was chromatographed on a 5 × 30 cm silica gel column using benzene as the eluent. The first component isolated contained 20.90 g (71%) of a yellow oil whose spectral properties were consistent with 4-carbomethoxy-5,5-dimethyl-3-phenylpyrazole (1): NMR (90 MHz, $CDCl_3$) δ 1.61 (s, 6 H), 3.78 (s, 3 H), and 7.33–8.10 (m, 5 H); IR (neat) 2960, 2230, 1725, 1633, 1493, 1440, 1350, 1293, 1205, 1090, 1027 cm^{-1}.

The second component isolated from the column contained 8.31 g (29%) of a yellow crystalline solid, mp 78–79 °C, whose structure was assigned as 3-carbomethoxy-5,5-dimethyl-4-phenyl-pyrazole (2): NMR (90 MHz, $CDCl_3$) δ 1.48 (s, 6 H), 3.78 (s, 3 H), 6.93–7.43 (m, 5 H); IR (KBr) 3090, 1730, 1465, 1388, 1350, 1255, 1170, 1110, 1012, 873 cm^{-1}.

A solution containing 3 g of the above mixture in 1.5 L of benzene was irradiated for 90 min with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure and the crude residue was chromatographed on a 2.5 × 10 cm silica gel column with hexane as the eluent. The major fraction contained 2.22 g (85%) of a clear oil whose structure was assigned as 1-carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (3): NMR (90 MHz, $CDCl_3$) δ 1.38 (s, 6 H), 3.78 (s, 3 H), 7.32–7.80 (m, 5 H); IR (neat) 2958, 2230, 1840,

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(41) A related set of acid-catalyzed rearrangements had previously been reported to occur in the solvolysis of 2-(trimethylcyclopropenyl)-2-propyl *p*-nitrobenzoate, see: Closs, G. L. "Advances in Alicyclic Chemistry"; Hart, H., Karabatsos, G. J., Eds.; Academic Press: New York, 1966; p 53.

1710, 1495, 1448, 1373, 1295, 1200, 1055, 925 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.08; H, 6.98.

Triplet-Sensitized Irradiation of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (3). A solution containing 300 mg of 3 and 30 mg of thioxanthenone was irradiated in 200 mL of anhydrous benzene with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. The photolysis was carried out under an argon atmosphere for 15 h. The crude mixture was percolated through a small silica gel column and was then chromatographed on a 1.5 × 60 cm silica gel column with a 5% acetone:hexane mixture as the eluent. The first component isolated contained 199 mg (67%) of a white crystalline solid, mp 118–119 °C, whose structure was assigned as 1,2-dicarbomethoxy-4,4-dimethyl-2-(2-methyl-1-phenyl-1-propenyl)-3-phenylbicyclo[1.1.0]butane (4) on the basis of the following spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.23 (s, 3 H), 1.58 (s, 3 H), 1.69 (s, 3 H), 2.20 (s, 3 H), 3.54 (s, 3 H), 3.87 (s, 3 H), 6.86–7.49 (m, 10 H); IR (KBr) 3460, 3075, 3040, 2980, 2940, 1730, 1710, 1600, 1440, 1380, 1245, 1180, 1120, 1080, 1040 cm^{-1}; MS, m/e 404 (M^+, base), 258, 257, 330, 329, 313, 298, 270, 255, 241. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.19; H, 6.99. Found: C, 77.24; H, 6.99.

The molecular structure of bicyclo[1.1.0]butane (4) was unequivocally established by an X-ray crystal structure analysis. The crystals of 4 were monoclinic with space group $P2_1/C$ and the unit cell parameters were a = 14.951 (3) Å, b = 10.402 (3) Å, c = 14.075 (3) Å, β = 90.36 (2)°, Z = 4, d = 1.227 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least squares with isotropic thermal parameters. Convergence was achieved with R = 0.058 for 943 observations and 121 variables. The final positional and thermal parameters are given in Tables 1–3 of the supplementary material section.

The second component isolated contained 42 mg (14%) of a white crystalline solid, mp 198–199 °C, which was identified as dimethyl 4,5-diphenyl-3,3,6,6-tetramethylcyclohexa-1,4-diene-1,2-dicarboxylate (5) on the basis of the following spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.31 (s, 12 H), 3.77 (s, 6 H), 6.80–7.13 (m, 10 H); IR (KBr) 3450, 3020, 2970, 1730, 1450, 1430, 1380, 1320, 1235, 1190, 1095, 1075, 1020 cm^{-1}; MS, m/e 404 (M^+), 389, 373, 357, 345 (base), 325, 314, 301, 299, 285, 271, 255, 241, 215, 178, 165; ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.51, 37.89, 51.93, 125.76, 126.76, 131.22, 139.06, 140.27, 141.25, 168.86. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.19; H, 6.99. Found: C, 77.14; H, 7.02.

Thermolysis of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (3). A 1.4-g sample of 3 was thermolyzed in 60 mL of cyclohexane at 175 °C. After heating for 72 h at 175 °C, the Carius tube was opened and the solvent was removed under reduced pressure. The crude yellow oil was subjected to medium-pressure chromatography on a 1.5 × 65 cm silica gel column with a 5% acetone:hexane mixture as the eluent. The first component isolated from the column contained 230 mg of recovered starting material. The second component isolated contained 435 mg (34%) of a crystalline material which was identified as dimethyl 2,7-dimethyl-3,6-diphenylocta-2,4(*Z*),6-triene-4,5-dicarboxylate (6) on the basis of its spectral properties: mp 76–77 °C; NMR (90 MHz, $CDCl_3$) δ 1.63 (s, 6 H), 1.78 (s, 6 H), 3.43 (s, 6 H), 7.18 (br s, 10 H); IR (KBr) 3450, 3080, 3020, 2970, 2930, 2870, 1765, 1725, 1490, 1435, 1385, 1230, 1155, 1015 cm^{-1}; UV (cyclohexane) 235 nm (ϵ 17 100), 287 nm (ϵ 3360); MS, m/e 404 (M^+, base), 389, 373, 357, 314, 298, 297, 285, 269, 255, 241, 228, 116; ^{13}C NMR (20 MHz, $CDCl_3$) δ 22.0 (q, 12 Hz), 22.6 (q, 120 Hz), 51.7 (q, 150 Hz), 126.3 (d, 160 Hz), 127.2 (d, 160 Hz), 129.8 (d, 160 Hz), 131.0 (s), 134.9 (s), 139.0 (s), 139.5 (s), 168.0 (s). Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.19; H, 6.99. Found: C, 77.10; H, 7.03.

The third component isolated from the column contained 380 mg (31%) of a crystalline material which was assigned as dimethyl 2,7-dimethyl-3,6-diphenylocta-2,4(*E*),6-triene-4,5-dicarboxylate (7) on the basis of its spectral properties: mp 87–88 °C; NMR (90 MHz, $CDCl_3$) δ 1.23 (br s, 6 H), 1.51 (s, 6 H), 3.64 (s, 6 H), 7.11 (br s, 10 H); IR (KBr) 3620, 3460, 3090, 3030, 2940, 2890, 1730, 1610, 1490, 1390, 1250, 1175, 1050, 1015, 970 cm^{-1}; UV (cyclohexane) 238 nm (ϵ 17 440), 283 nm (ϵ 4450); MS, m/e 404 (M^+, base), 389, 373, 357, 314, 298, 297, 285, 269, 255, 241, 228, 116; ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.2 (q, 120 Hz), 21.8 (q, 120 Hz), 51.5 (q, 150 Hz), 125.8 (d, 160 Hz), 126.9 (d, 160 Hz), 129.1 (q, 160 Hz), 136.5 (s), 139.5 (s), 140.8 (s), 168.3 (s). Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.19; H, 6.997. Found: C, 77.26; H, 7.00.

These same two compounds were also produced when a sample of dimer 4 was heated in cyclohexane at 175 °C for 72 h in a sealed Carius tube.

Triplet-Sensitized Irradiation of Dimethyl 2,7-Dimethyl-3,6-diphenylocta-2,4(*Z*),6-triene-4,5-dicarboxylate (6). A 100-mg sample of dimer 6 was irradiated in 15 mL of anhydrous benzene with a catalytic amount of thioxanthenone for 10 min with a 450-W Hanovia medium-pressure mercury arc lamp with a uranium filter sleeve. Removal of the solvent followed by silica gel chromatography gave *trans*-dimethyl 2,7-dimethyl-3,6-diphenylocta-2,4(*E*),6-triene-4,5-dicarboxylate (7). The remaining product isolated from the column product was identified as dimethyl 1,4-diphenyl-5,5,6,6-tetramethylcyclohexa-1,3-diene-2,3-dicarboxylate (8) on the basis of its spectral properties: mp 148–149 °C; NMR (90 MHz, CCl_4) δ 1.03 (br s, 12 H), 3.23 (s, 6 H), 7.04–7.40 (m, 10 H); IR (KBr) 3110, 2950, 2670, 2280, 1715, 1415, 1395, 1240, 1190, 1155, 875, 725 cm^{-1}; UV (cyclohexane) 288 nm (ϵ 4270), 227 (ϵ 4093); MS, m/e 404 (M^+), 313, 129, 105, 91 (base), 59. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.19; H, 6.99. Found: C, 76.99; H, 7.02.

Direct Irradiation of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (3). A solution containing 250 mg of 1-carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (3) in 180 mL of benzene was irradiated with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Corex filter sleeve under an argon atmosphere for 160 min. Removal of the solvent under reduced pressure left a dark yellow oil which was shown by NMR spectroscopy to contain a mixture of four components. These were identified as recovered starting material (3), 1-carbomethoxy-3,3-dimethyl-1-phenylallene (10) (49%), 1-carbomethoxy-3-methyl-2-phenylbutadiene (11) (30%), and 2-carbomethoxy-3-methyl-1-phenylbutadiene (12) (20%). The structures of these materials were assigned on the basis of their spectral data and by comparison with independently prepared samples.

Independent Synthesis of 1-Carbomethoxy-3,3-dimethyl-1-phenylallene (10). To a solution containing 2.0 g of phenylacetylene in 25 mL of ether was added 4.8 mL of a 2.7 M methylmagnesium bromide solution at 0 °C. The solution was stirred for an additional 15 min and then 0.96 mL of acetone was added dropwise. The solution was allowed to warm to room temperature and was then quenched with a saturated ammonium chloride solution and ice. The ether layer was washed with water and a saturated salt solution and was then dried over magnesium sulfate. Removal of the solvent under reduced pressure left 1.9 g (92%) of a light yellow oil which was shown to consist mostly of 1,1-dimethylphenylpropargyl alcohol: NMR (60 MHz) δ 1.6 (s, 6 H), 2.63 (br s, 1 H), 7.1–7.5 (m, 5 H). To a 0.5-g sample of the above alcohol in 25 mL of chloroform was slowly added 14 mL of phosphorus tribromide. The solution was stirred at room temperature for an additional hour. The solvent was then removed under reduced pressure and the crude residue was dissolved in ether, washed with a saturated sodium bicarbonate solution and a saturated salt solution, and was then dried over magnesium sulfate. The solvent was removed under reduced pressure and the product was distilled from potassium carbonate at 1 mm to give 0.471 g of 1,1-dimethylphenylpropargyl bromide in 68% yield; NMR (60 MHz, $CDCl_3$) δ 2.1 (s, 6 H), 7.1–7.4 (m, 5 H).

A sample containing 0.471 g of the above bromide in 30 mL of ether was treated with 0.051 g of magnesium. The resulting Grignard reagent was poured over crushed dry ice and then 30 mL of a 10% hydrochloric acid solution was added. The ether layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give 0.201 g (52%) of 3,3-dimethyl-1-phenylallenic acid (14) as a white solid: NMR (60 MHz, $CDCl_3$) δ 1.88 (s, 6 H), 7.1–7.6 (m, 5 H), 9.33 (br s, 1 H).

The above acid was added to 50 mL of an ether solution of diazomethane at 0 °C. The solution was allowed to warm to room temperature over a 1-h period and was then allowed to stir for an additional 1 h. Removal of the solvent under reduced pressure left 0.23 g of a light yellow oil which was distilled at 100 °C (0.5 mm) to give 0.22 g (99%) of 1-carbomethoxy-3,3-dimethyl-1-phenylallene (10) as a clear oil. The structure of this material was assigned on the basis of its spectral properties: NMR (60 MHz, $CDCl_3$) δ 1.88 (s, 6 H), 3.75 (s, 3 H), 7.17–7.54 (m, 5 H); IR (neat) 2975, 1944, 1750, 1700, 1601, 1480, 1420, 1270, 1160,

1030, 885 cm^{-1}; UV (95% ethanol) 250 nm (ϵ 8480); MS, m/e 202 (M^+, base), 143, 128, 84. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.01; H, 7.03. This material was identical in every detail with a sample of **10** obtained from the photolysis of **3**.

Independent Synthesis of 2-Carbomethoxy-3-methyl-1-phenyl-1,3-butadiene (12). A 0.7-g sample of methyl 2-(phenylhydroxymethyl)-3-methyl-3-butenoate (**15**) was prepared according to a procedure developed by Heathcock and Dugger.[28] The above compound was taken up in 25 mL of tetrahydrofuran and 0.76 g of Burgess' reagent[29] was added. The mixture was heated at reflux overnight. The solvent was partially removed under reduced pressure and the residue was taken up in ether. The ether solution was washed twice with water and then with a saturated salt solution and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude residue was chromatographed on a 1.5 × 60 cm 10% silver nitrate impregnated silica gel column with a 5% ether:hexane mixture as the eluent. The first component isolated from the column contained 200 mg (29%) of (*E*)-2-carbomethoxy-3-methyl-1-phenyl-1,3-butadiene (**12**). This material was identical in all respects with the photoproduct obtained from the irradiation of 1-carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (**3**) and possessed the following spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.92 (t, J = 1 Hz, 3 H), 3.70 (s, 3 H), 4.90 (d, J = 1 Hz, 1 H), 5.13 (d, J = 1 Hz, 1 H), 7.47 (s, 1 H), 7.16–7.63 (m, 5 H); IR (neat) 2990, 1715, 1615, 1450, 1275, 1230, 1100, 955 cm^{-1}; UV (95% ethanol) 279 nm (ϵ 16 060); MS, m/e 202 (M^+), 143, 128, 91. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.04; H, 7.01.

The second component isolated contained 1.87 mg (28%) of (*Z*)-2-carbomethoxy-3-methyl-1-phenyl-1,3-butadiene (**16**): NMR (60 MHz, $CDCl_3$) δ 2.05 (br s, 3 H), 3.70 (s, 3 H), 5.07 (s, 1 H), 5.20 (br s, 1 H), 6.63 (s, 1 H), 7.30 (br s, 5 H); IR (neat) 2990, 1715, 1615, 1450, 1275, 1230, 1100, 955 cm^{-1}; UV (95% ethanol) 279 nm (ϵ 16 060); MS, m/e 202 (M^+), 143, 128, 91. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.16; H, 6.95.

Independent Synthesis of 1-Carbomethoxy-3-methyl-2-phenyl-1,3-butadiene (11). In a 250-mL round-bottom flask was placed 0.1 g of a 2% lithium:sodium mixture in 50 mL of ether under a nitrogen atmosphere. The suspension was mechanically stirred as 0.5 mL of 2-bromopropene was added dropwise. The mixture was stirred at room temperature for 20 min and the solution was then filtered through a porous frit into a 100-mL round-bottom flask under a positive pressure of nitrogen. The lithiate was cooled −20 °C and 0.317 g of cuprous iodide was added at once.[30] To the black cuprate reagent which formed was added 0.207 g of methyl phenylpropiolate. This mixture was stirred at −20 °C for 1 h and was then quenched with a 1:1 ammonium hydroxide:ammonium chloride solution. The organic layer was separated, washed with a saturated salt solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure to leave behind 0.277 g of a crude residue which was chromatographed on a 10% silver nitrate impregnated 1.5 × 65 cm silica gel column with a 5% ether:hexane mixture as the eluent. The first component isolated contained 113 mg (43%) of a clear oil whose structure was assigned as (*E*)-1-carbomethoxy-3-methyl-2-phenyl-1,3-butadiene (**11**). This material was identical in every detail with the photoproduct obtained from the irradiation of 1-carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (**3**): NMR (90 MHz, $CDCl_3$) δ 1.87 (t, J = 1 Hz, 3 H), 3.64 (s, 3 H), 4.84 (m, 1 H), 5.17 (m, 1 H), 6.03 (s, 1 H), 7.22–7.60 (m, 5 H); IR (neat) 3100, 2979, 1717, 1642, 1613, 1582, 1502, 1462, 1390, 1294, 1192, 1038, 138 cm^{-1}; UV (95% ethanol) 256 nm (ϵ 10 450); MS, m/e 202 (M^+), 143, 128, 115, 77. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.15; H, 7.02.

The second component isolated from the column contained 106 mg (39%) of a clear oil which was identified as (*Z*)-1-carbomethoxy-3-methyl-2-phenyl-1,3-butadiene (**17**) on the basis of the following spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.98 (s, 3 H), 3.43 (s, 3 H), 4.85 (s, 1 H), 5.27 (s, 1 H), 5.98 (s, 1 H), 6.97–7.40 (m, 5 H); IR (neat) 3100, 2979, 1717, 1642, 1613, 1582, 1502, 1462, 1448, 1390, 1374, 1294, 1220, 1192, 1077, 1038, 1022, 938, 818, 740 cm^{-1}; UV (95% ethanol) 256 nm (ϵ 10 450); MS, m/e 202 (M^+), 143, 128, 115, 77. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.15; H, 7.02.

Preparation of 1-(Hydroxymethyl)-2-phenyl-3,3-dimethylcyclopropene (24). A 1.5-g sample of 1-carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (**3**) in 25 mL of hexane was cooled to −78 °C. To this solution was added dropwise 9.2 mL of a 25% Dibal-H solution in toluene. The solution was stirred for 1 h at −78 °C and was then quenched with an ammonium chloride solution. The thick emulsion that formed was filtered through diatomaceous earth and was then washed with ether. The filtrate was extracted with ether and the combined organic layers were washed with water and a saturated salt solution and dried over magnesium sulfate. The solvent was removed under reduced pressure and the resulting yellow oil (1.13 g) was assigned as 3.3-dimethyl-1-(hydroxymethyl)-2-phenylcyclopropene (**24**) (86%) on the basis of the following spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.26 (s, 6 H), 2.88 (s, 1 H), 4.58 (s, 2 H), 7.02–7.48 (m, 5 H); IR 3375, 3100, 3050, 2950, 2880, 1844, 1738, 1688, 1600, 1577, 1490, 1450, 1368, 1258, 1178, 1072, 1058, 1008, 910, 830, 756, 691 cm^{-1}; UV (95% ethanol) 268 nm (ϵ 12 980).

Direct Irradiation of 1-(Hydroxymethyl)-2-phenyl-3,3-dimethylcyclopropene (24). A 200-mg sample of the above cyclopropene was irradiated with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Corex filter sleeve under an argon atmosphere for 45 min in benzene. The solvent was removed under reduced pressure. Percolation of the crude mixture through a 2.5 × 10 cm silica gel column gave two products which were identified as the cis and trans isomers of 3-phenyl-4-methyl-2-penten-1-al (**25** and **26**). The yellow oil contained 111 mg (56%) of a 2:1 mixture of the cis (**25**) and trans aldehydes (**26**). These structures were verified by comparison with authentic samples.

A sample of 2,4,4,6-tetramethyldihydro-1,3-oxazine (**27**) was prepared according to the procedure of Meyers and co-workers.[39] In a 250-mL round-bottom flask at −78 °C was placed 7.42 g of 2,4,4,6-tetramethyl-1,3-oxazine (**27**) in 100 mL of anhydrous tetrahydrofuran. To this solution was added 42 mL of a 1.44 M solution of *n*-butyllithium over a 1-h period. The mixture was stirred at −78 °C for an additional hour and then 7.9 g of isobutyrophenone was added dropwise over a 30-min period. This mixture was allowed to warm to room temperature and was then poured over ice–water and acidified to pH 2–3 with concentrated hydrochloric acid. This solution was extracted with pentane and the pentane solution was washed with a 40% sodium hydroxide solution. The aqueous solution was extracted with ether and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 13.88 g of a clear oil.

In a 600 mL beaker was placed 100 mL of tetrahydrofuran, 100 mL of 95% ethanol, and 13.88 g of the above hydroxyoxazine (**28**). The solution was cooled to −35 °C and the pH of the mixture was adjusted to pH 7 with hydrochloric acid. A 20-g sample of sodium borohydride was dissolved in 5 mL of water containing a drop of a 40% sodium hydroxide solution and this mixture was added to the above solution. The pH of the solution was maintained between 6–8 by the addition of a few drops of hydrochloric acid when needed. The solution was stirred for 1 h, was then poured into 100 mL of water, and made basic with a 40% sodium hydroxide solution. The mixture was extracted with ether, washed with a saturated salt solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 9.45 g of the tetrahydrooxazine.

The crude tetrahydrooxazine was heated at reflux for 2 h in 100 mL of water containing 20 g of oxalic acid. The solution was cooled, extracted with ether, washed with sodium bicarbonate, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 2.79 g of *trans*-3-phenyl-4-methyl-2-penten-1-al (**26**) which showed the following spectral properties: NMR (90 MHz, CCl_4) δ 1.03 (d, J = 7 Hz, 6 H), 2.73 (m, J = 7 Hz, 1 H), 5.98 (d, J = 8 Hz, 1 H), 7.12–7.50 (m, 5 H), 9.39 (d, J = 8 Hz, 1 H); IR (neat) 3070, 2985, 2950, 2895, 1667, 1610, 1575, 1500, 1478, 1454, 1410, 1400, 1325, 1192, 1168, 1130, 1065, 1035, 965, 905, 821, 790, 745 cm^{-1}; MS, m/e 174 (m^+, base), 159, 131, 122, 105, and 77; UV (cyclohexane) 235 nm (ϵ 6700).

A 100-mg sample of *trans*-3-phenyl-4-methyl-2-penten-1-al (**26**) was irradiated for 15 min in 180 mL of benzene with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Corex filter sleeve. Upon completion of the irradiation, the solvent was removed under reduced pressure. The resulting oil consisted

of a 3:1 mixture of trans (**26**) and cis aldehydes (**25**). The cis aldehyde (**25**) showed the following spectral properties: NMR (90 MHz, CCl_4) δ 1.20 (d, J = 7 Hz, 6 H), 3.73 (septet, J = 7 Hz, 1 H), 5.80 (d, J = 8 Hz, 1 H), 7.10–7.50 (m, 5 H) and 10.2 (d, J = 8 Hz, 1 H).

Direct Irradiation of 1-(Hydroxymethyl)-2-phenyl-3,3-dimethylcyclopropene (24) under an Oxygen Atmosphere. A 200-mg sample of the above (hydroxymethyl)cyclopropene (**24**) was photolyzed with a 550-W Hanovia medium-pressure mercury arc lamp equipped with a Corex filter sleeve for 25 min. A stream of pure oxygen was passed through the solution during the course of the photolysis. The solvent was removed under reduced pressure leaving behind a clear oil which contained two major products as evidenced by thin layer analysis. The oil was chromatographed on a 2 × 20 cm silica gel column with a 5% acetone:hexane mixture as the eluent. The first component isolated contained 32 mg (15%) of a light yellow oil which was assigned as 1-hydroxy-4-methyl-3-phenylpent-3-en-2-one (**31**) on the basis of its spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 2.12 (s, 3 H), 3.08 (s, 1 H), 3.72 (s, 2 H), and 6.98–7.40 (m, 5 H); IR (neat) 3440, 3030, 3000, 2900, 1945, 1700, 1650, 1600, 1470, 1415, 1347, 1268, 1150, 1015, 725 cm^{-1}; MS, m/e 190 (M^+), 159 (base), 131, 91; UV (cyclohexane) 244 nm (ϵ 9100). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.43. Found: C, 75.88; H, 7.47.

The second component isolated from the column contained 142 mg (63%) of a crystalline solid, mp 98–99 °C, which was assigned as 6,6-dimethyl-3,5-dihydro-3-hydroxy-5-phenyl-1,2-dioxane (**32**) on the basis of its spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.2 (s, 3 H), 1.6 (s, 3 H), 3.45 (s, 1 H), 5.48 (d, J = 4 Hz, 1 H), 5.78 (d, J = 4 Hz, 1 H) and 7.17–7.48 (m, 5 H); IR (KBr) 3260, 2975, 2925, 1475, 1430, 1390, 1360, 1340, 1250, 1170, 1065, 875 cm^{-1}; MS, m/e 206 (M^+), 174 (base); UV (95% ethanol) 226 nm (ϵ 7000). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.85; H, 6.85.

Thermolysis of 6,6-Dimethyl-3,6-dihydro-3-hydroxy-5-phenyl-1,2-dioxane (32). A 22-mg sample of dioxane **32** was dissolved in a 4:1 mixture of benzene-d_6:pyridine-d_5 and the solution was placed in a thick-walled NMR tube. The mixture was degassed via three freeze-pump-thaw cycles and sealed. The tube was heated at 155 °C for 30 min. Removal of the solvent gave 15 mg (75%) of a crystalline solid, mp 93–94 °C, whose structure was identified as 5,5-dimethyl-4-phenyl-2(5*H*)-furanone (**33**) on the basis of the following spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.67 (s, 6 H), 6.25 (s, 1 H), and 7.50–7.68 (br s, 5 H); IR (KBr) 2930, 1700, 1575, 1463, 1426, 1342, 1240, 1090, 960, 912, and 840 cm^{-1}; UV (cyclohexane) 263 nm (ϵ 5600); MS, m/e 188 (M^+), 173, 145, 102 (base). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.65; H, 6.45.

The structure of this material was further verified by an independent synthesis. A 15-g sample of isobutyrophenone was placed in 100 mL of glacial acetic acid and 5.59 g of bromine was added dropwise to the solution. This mixture was heated at 100 °C for 12 h. The solution was allowed to cool and was then poured over ice. Ether was added and the organic phase was extracted with a saturated sodium bicarbonate solution containing a pinch of sodium sulfite. The solution was then dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude α-bromo ketone contained 13.59 g (60%) of a clear oil: NMR (90 MHz, CCl_4) δ 1.97 (s, 6 H) and 7.27–8.27 (m, 5 H); IR (neat) 3090, 3000, 2950, 1680, 1600, 1580, 1460, 1390, 1270, 1170, 1100, 970, 880, 780 cm^{-1}.

A 13.59-g sample of the above α-bromo ketone was combined with 10 g of potassium acetate in 100 mL of ethanol and was heated at reflux for 20 h. After cooling, the salts were filtered and the solvent was concentrated under reduced pressure. The residue was taken up in ether and washed several times with water. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was rapidly distilled and the fraction boiling between 80–86 °C (0.5 mm) contained 1.35 g (11%) of a colorless oil which was assigned the structure of 1-phenyl-2-acetoxy-2-methylpropan-1-one (**34**) on the basis of the following spectral properties: NMR (90 MHz, $CDCl_3$) δ 1.56 (s, 6 H), 1.73 (s, 3 H), and 7.10–7.95 (m, 5 H); IR (KBr) 2990, 1735, 1685, 1600, 1450, 1370, 1250, 1150, 1020, 963, 895, 845, 710 cm^{-1}; UV (cyclohexane) 240 nm (ϵ 5200) and 278 nm (ϵ 800); MS, m/e 206 (M^+), 163, 105 (base), 77, and 59. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.74; H, 6.88.

A 180-mg sample of **34** was added to 40 mL of tetrahydrofuran containing 180 mg of potassium hydride. This mixture was stirred at room temperature for 12 h. The solution was cooled to 0 °C and the reaction was quenched with ice. The solvent was concentrated under reduced pressure. The mixture was extracted with ether, the extracts were washed with a 10% hydrochloric acid solution and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The semicrystalline solid contained a mixture of the desired butenolide as well as the 4-hydroxy lactone. This mixture was taken up in 50 mL of dry benzene, a catalytic amount of p-toluenesulfonic acid was added, and the mixture was heated at reflux for 12 h. The benzene solution was cooled, washed with a 10% sodium hydroxide solution, and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude oil was percolated through a 1 × 10 cm silica gel column with a 5% acetone:hexane mixture as the eluent. The semicrystalline product obtained was recrystallized from petroleum ether to give 80 mg (47%) of a crystalline solid, mp 93–94 °C, whose structure was assigned as 5,5-dimethyl-4-phenyl-2(5*H*)-furanone (**33**) on the basis of the following data: NMR (90 MHz, $CDCl_3$) δ 1.67 (s, 6 H), 6.23 (s, 1 H), and 7.50–7.68 (br s, 5 H); IR (KBr) 2930, 1700, 1575, 1463, 1426, 1342, 1240, 1090, 960, 912, and 840 cm^{-1}; UV (cyclohexane) 263 nm (ϵ 5600); MS, m/e 188 (M^+), 173, 145, 102 (base). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.65; H, 6.45.

Preparation of 1-Phenyl-1-(2-hydroxy-2-propyl)-3,3-dimethylcyclopropene (35). A 4.5-g sample of 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene (**3**) in 30 mL of anhydrous ether was added dropwise to a 100-mL solution of methyllithium (45 mmol) in ether at 0 °C. The mixture was allowed to warm to room temperature and was quenched with a cold ammonium chloride solution. The aqueous layer was extracted with ether, the ether layers were combined and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude yellow oil was percolated through 5 × 15 cm column of silica gel with a 5% acetone:hexane mixture as the eluent. The only product obtained contained 2.88 g (65%) of a yellow oil whose structure was assigned as 1-phenyl-2-(2-hydroxy-2-propyl)-3,3-dimethylcyclopropene (**35**) on the basis of the following spectral properties: NMR (90 MHz, CCl_4) δ 1.34 (s, 6 H), 1.48 (s, 6 H), 1.98 (br s, 1 H), and 7.20–7.56 (m, 5 H); IR (neat) 3370, 2975, 1830, 1705, 1600, 1490, 1450, 1370, 1280, 1180, 1080, 1035, 960, 923, 875, 860, 800, and 775 cm^{-1}; UV (95% ethanol) 268 nm (ϵ 14 400); MS, m/e 202 (M^+), 201, 159, 145, 129, 128, 105, and 59 (base). Anal. Calcd for $C_{14}H_{18}O$: C, 83.11; H, 8.99. Found: C, 82.92; H, 9.00.

Acid-Induced Rearrangement of 1-Phenyl-2-(2-hydroxy-2-propyl)-3,3-dimethylcyclopropene (35). A 0.21-g sample of the above cyclopropene was refluxed in 25 mL of anhydrous benzene which contained 0.2 g of p-toluenesulfonic acid for 20 min. The reaction was quenched with a cold sodium bicarbonate solution and extracted with benzene. The benzene layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude oil was subjected to silica gel flash chromatography with a 5% acetone:hexane mixture as the eluent. The major product contained 0.21 g (59%) of a viscous oil which could be crystallized from petroleum ether. The crystalline product, mp 97–98 °C, was assigned as 2,5-dimethyl-4-phenyl-3-(*o*-tosyl)-2,4-hexadiene (**39**) on the basis of the following spectral properties: NMR (90 MHz, CCl_4) δ 1.53 (s, 3 H), 1.70 (s, 3 H), 1.80 (s, 3 H), 1.87 (s, 3 H), 2.37 (s, 3 H) and 6.57–7.63 (m, 9 H); IR (KBr) 2950, 1600, 1490, 1440, 1360, 1290, 1175, 1070, 1040, 935, and 800 cm^{-1}; UV (95% ethanol) 223 nm (ϵ 23 800); MS, m/e 356 (M^+), 201, 184, 169, and 91 (base). Anal. Calcd for $C_{21}H_{24}SO_3$: C, 70.74; H, 6.80; S, 8.99. Found: C, 70.82; H, 6.83; S, 8.95.

A 200-mg sample of cyclopropene **35** was refluxed in 25 mL of methanol with a few drops of concentrated sulfuric acid for 1 h. The reaction was allowed to cool and was then concentrated under reduced pressure. The crude product was taken up in ether, washed with a saturated sodium bicarbonate solution, and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resultant yellow oil was percolated through 2 × 15 cm column of silica gel with a 5% acetone:hexane mixture as the eluent. The major product (100 mg, 49%) was obtained

as a light oil and was assigned as 2,5-dimethyl-3-phenylhex-2-en-4-one (38) on the basis of the following spectral characteristics: NMR (90 MHz, CCl_4) δ 0.9 (d, J = 7 Hz, 6 H), 1.65 (s, 3 H), 1.85 (s, 3 H), 2.45 (septet, J = 7 Hz, 1 H), and 7.03–7.45 (m, 5 H); IR (neat) 2975, 1685, 1600, 1490, 1445, 1380, 290, 1190, 1155, 1050, 1030, 930, 845, 775, 715 cm^{-1}; UV (cyclohexane) 237 nm (ϵ 8900), 243 nm (ϵ 8800), 248 nm (ϵ 8100), 254 (ϵ 6200), and 260 nm (ϵ 3800); MS, m/e 202 (M^+), 159, 131 (base), and 91. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.89; H, 8.99.

A 0.85-g sample of 1-phenyl-2-(2-hydroxy-2-propyl)-3,3-dimethylcyclopropene (35) was stirred in 50 mL of dry tetrahydrofuran with 0.925 g of Burgess' reagent[29] and 0.6 mL of triethylamine at room temperature for 12 h. The crude mixture was concentrated under reduced pressure and the residue was taken up in ether and washed twice with water. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was percolated through 2 × 10 cm of silica gel with hexane as the eluent. The major product contained 300 mg (38%) of a light yellow oil whose structure was identified as 1,1-dimethyl-3-phenyl-3-(2-propenyl)allene (37) on the basis of the following spectral properties: NMR (90 MHz, CCl_4) δ 1.75 (s, 6 H), 1.87 (s, 3 H), 4.78 (br s, 1 H), 4.95 (br s, 1 H), and 7.13–7.30 (m, 5 H); IR (neat) 2920, 1950, 1735, 1620, 1600, 1493, 1447, 1378, 1365, 1310, 1210, 1175, 1077, 1043, 1020, 973, 893, 765, 730, and 700 cm^{-1}.

A 200-mg sample of allene 37 was heated at reflux in 25 mL of dry benzene with 210 mg of *p*-toluenesulfonic acid for 15 min. The reaction was cooled, extracted with a saturated sodium bicarbonate solution, and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was percolated through 2 × 15 cm silica gel with a 5% acetone:hexane mixture as the eluent. The major product isolated contained 120 mg (30%) of a light oil which was identical in all respects with a sample of 2,5-dimethyl-4-phenyl-3-(*o*-tosyl)-2,4-hexadiene (39) which had been previously isolated.

A 130-mg sample of allene 37 was also heated at reflux in 25 mL of methanol with a few drops of concentrated sulfuric acid for 1 h. The reaction mixture was allowed to cool and was then concentrated under reduced pressure. The crude mixture was dissolved in ether, extracted with a saturated sodium bicarbonate solution, and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The major product contained 60 mg (42%) of a light oil whose structure was identical in all respects with a sample of 2,5-dimethyl-3-phenylhex-2-en-4-one (38).

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Supplementary Material Available: Table of fractional coordinates for non-hydrogen atoms of 1,4-dicarbomethoxy-2,2-dimethyl-3-phenyl-4-(1-phenyl-2-methylprop-1-enyl)bicyclo-[1.1.0]butane (4) (4 pages). Ordering information is given on any current masthead page.

Use of Solid Acids To Catalyze the Cis/Trans Photoisomerization of α,β-Unsaturated Carbonyl Compounds[1]

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The cis/trans isomerization of solutions of ethyl cinnamates, 1 and 2, 4-phenylbut-3-en-2-ones, 3 and 4, and cinnamonitriles, 5 and 6, has been examined in the presence of heterogeneous acids such as the aluminosilicates and Nafion. The proportion of the cis isomer present in the photostationary-state mixtures of 1 and 2 and 3 and 4 is dramatically enhanced when heterogeneous acids are present, a finding that is of preparative significance. The origin of this type of perturbation of the photostationary states of unsaturated esters and ketones has been examined in detail and it is shown that the primary factor involved is the preferential adsorption of the trans vs. the cis isomers.

The photoinduced cis/trans isomerization of olefins is a ubiquitous reaction that is of considerable use in the preparation of the thermodynamically less stable cis isomers.[3] One detrimental feature of these reactions from a preparative point of view is that the photostationary states reached frequently contain approximately equal amounts of both isomers and this necessitates separation and recycling steps. In 1981, Lewis and Oxman reported that the position of the photostationary states reached with α,β-unsaturated esters can be dramatically altered if a Lewis acid is present in the solution.[4] For example, irradiation of a benzene solution of ethyl cinnamate containing less than a molar equivalent of ethyl aluminum dichloride yielded a photostationary state containing 85% of the cis isomer. In the absence of the Lewis acid only 42% of the cis isomer was present at the photostationary state.

Recently an increasing amount of attention has been given to the use of surfaces to modify the course of a

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