process, the rate constant for that transfer is given by eq 11 where

$$k_{et} = \frac{2\pi}{h}\beta^2 F\rho \qquad (11)$$

β is the electronic matrix element for the mixing of the initial and final states, F is the Franck–Condon factor for the transition, and ρ is the density of final states. The latter two parameters are clearly intimately related. The above considerations suggest the possibility that endothermic triplet energy transfer to the nonplanar π systems under consideration may, at least in part, be faster than predicted by the Sandros equation (eq 10) as a consequence of a high available T_1 vibrational level density relative to the planar systems which appear to conform with this equation. Structural features, including symmetry, which result in a high density of

low-frequency vibrations in S_1 and T_1 may well lead to a similar situation in S_0, a situation which would also facilitate operation of the "hot band" mechanism.

We raise the above possibility more as a query than as a proposal. It is worth pointing out that if "nonvertical" behavior was essentially a vibrational state density phenomenon, there should be a whole range of degrees of "nonvertical" behavior, that of *cis*-stilbene, the 1,2-diphenylpropenes, and CHT being extreme enough to readily allow experimental detection.

Upper Excited State(s) in the Methylenecyclopropane/Trimethylenemethane System. Photolysis of (*E*)- and (*Z*)-2,3-Diethyl-2-methylmethylenecyclopropane at 185 nm

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Abstract: From the photolysis of the title compounds in solution at 185 nm, it is possible to obtain all the possible methylenecyclopropane rearrangement products in about equal amounts. This contrasts with the thermal rearrangement which leads to mostly (>80%) one rearranged product. It is suggested that the photochemical rearrangement proceeds from a $\pi \rightarrow \pi^*$ excited state of methylenecyclopropane to the energy surface of a high-lying excited state of trimethylenemethane such as the $^1A'_1$ state (D_{3h} symmetry) but mixes with the lower ($^1A_1$) surface and leads to products. The other important photochemical process leads to an olefin and acetylene with retention of the stereochemistry.

The intense theoretical interest that has been displayed in recent years in the ground and excited states of trimethylenemethane (TMM)[1] has resulted in numerous experimental investigations of the thermal transformation:[2]
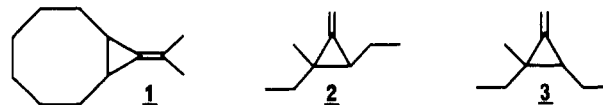

methylene-cyclopropane   TMM
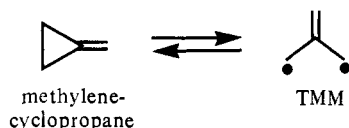
Although several studies on the photochemistry of methylenecyclopropane have been reported (see below),[3] they have provided very limited insight into the equilibrium given above.

Gas-phase photolysis at 147 and 124 nm of methylenecyclopropane itself resulted in total fragmentation of the molecule.[4] Many investigations have been carried out in solution with radiation of wavelength >200 nm on derivatives of methylenecyclopropane and especially those with conjugating phenyl groups.[5] Both the fragmentation reaction (1a) and the methylenecyclopropane rearrangement (1b) were observed under these conditions.

(1)
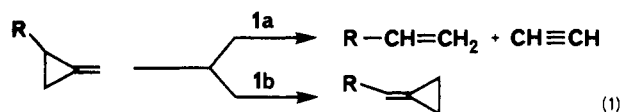
In view of the extended chromophoric systems that these reactants contained, very little information concerning the identity of the excited state(s) that was (were) involved can be obtained. In the first study of a methylenecyclopropane without conjugating groups, Gilbert and Luo[6] photolyzed **1** with radiation >200 nm and showed that it fragmented to cyclooctene and dimethylvinylidene $(CH_3)_2C=C:$, the latter being identified by either trapping with cyclohexene or by the isolation of its rearrangement product.

These results will be discussed later in this article. A key result on the photolysis of a monocyclic methylenecyclopropane was reported by Takeda et al.[7] They found that irradiation of methylenecyclopropane itself in a low-temperature matrix with "ultraviolet light" (presumably radiation >200 nm) did not lead to the ESR spectrum of trimethylenemethane in its triplet ground

(1) Yarkony, D. R.; Schaeffer, H. F. *J. Am. Chem. Soc.* **1974**, *96*, 3754.

(2) For a review, see: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981.

(3) Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. R. *J. Am. Chem. Soc.* **1982**, *104*, 967 and earlier references therein.
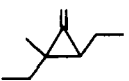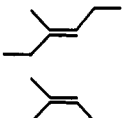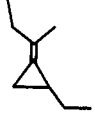
(4) Hill, K. L.; Doepker, R. D. *J. Phys. Chem.* **1972**, *76*, 3153.

(5) (a) Kende, A. S.; Goldschmidt, Z.; Smith, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 7606. (b) Gilbert, J. C.; Gros, W. A. *Ibid.* **1976**, *98*, 2019.

(6) Gilbert, J. C.; Luo, T. *J. Org. Chem.* **1981**, *46*, 5237. See also footnote 14 in: Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 1.

(7) Takeda, K.; Yoshida, H.; Hayashi, K.; Okamura, S. *Bull. Inst. Chem. Res. Kyoto Univ.* **1967**, *45*, 55.

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Table I. Photolysis Products and Yields of Compounds **3** and **2**[a-c]

| 3		2
12.0%		33.3%
22.1%		6.0%
16.2%[d]		15.0%[d]
	8 + 9	
13.0%		15.3%
	7	
12.0%		18.3%
	6	
19.0%	**3** **2**	13.0%

[a] At 50% conversion of starting material. [b] 185 nm (10^{-2} M in pentane). [c] Mass balance was ~80% for both isomers. [d] It is presumed that this is a mixture of **8** and **9** in unknown ratio. It could not be resolved into two components even on a 120 m long capillary chromatographic column.

state ($^3A'_2$). They were able to generate this spectrum in another experiment in which methylenecyclopropane was kept in a low-temperature matrix and irradiated with fast electrons.
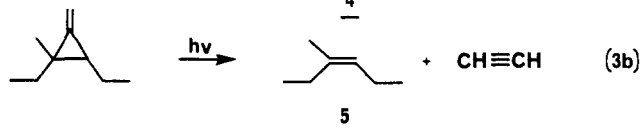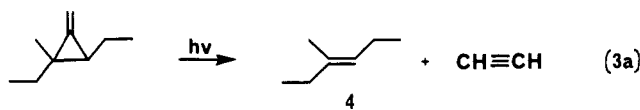
We report here on a solution-phase photodecomposition study in the far-ultraviolet of two methylenecyclopropanes (**2** and **3**) with suitable stereochemical labels to determine the course of their transformations.
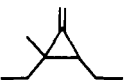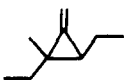
Results

Photolysis of a solution of either **2** or **3** in pentane with 185-nm radiation gave rise to fragmentation and methylenecyclopropane rearrangement, as well as interconversion. The product analysis shown in Table I was at 50% conversion. When values at lower and higher conversion were monitored, it was found that the ratios of the isomeric methylenecyclopropanes were unchanged with conversion, but the olefinic C_7 products were formed stereospecifically at low (<10%) conversion. The interconversion reactions (2a and 2b) can therefore be viewed as relatively slow
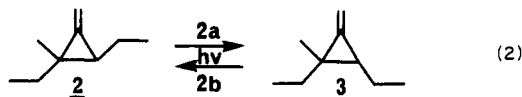

pathways in comparison to the fragmentation reactions (3a and 3b) although they occur in parallel.

Table II. Pyrolysis Products and Yields from Compounds **2** and **3**[a-c]

3		2
8%[d]		8%[d]
3%		3%
71%		63%

[a] Pyrolysis at 198 °C (oil bath, sealed tubes). [b] Not checked for geometrical isomerization. [c] ~75% conversion. [d] See comment *d* in Table I.

Of the methylenecyclopropane rearrangement products, the separation and identification of the stereoisomers **6** and **7** from both **2** and **3** suggest that **8** and **9** were probably also formed but
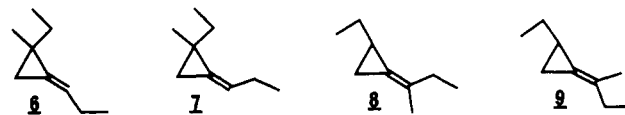
could not be separated. The quantum yields for the disappearance of **2** or **3** via all observed pathways were 0.29.[8]

Pyrolyses of **2** and **3** in sealed tubes led to the analytical results shown in Table II. These results were invariant with changes in the conversion from about 20% to 75%.

Discussion

Analysis of the results in Table I in terms of the photochemistry of cyclopropanes in solutions in the far-ultraviolet shows the following pathways:
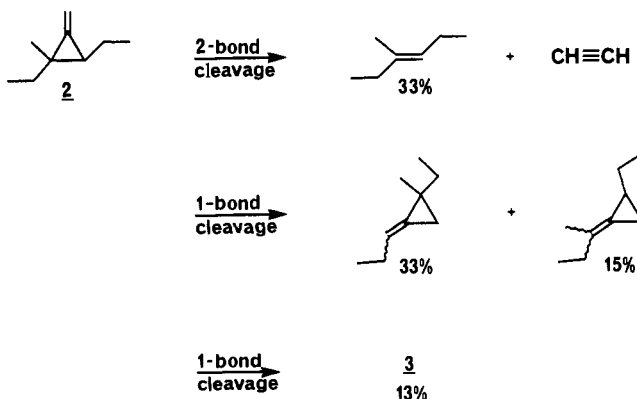
The ratio of two-bond cleavage to one-bond cleavage is somewhat lower than in monocyclic cyclopropanes,[9] but the methylenecyclopropane rearrangement which is viewed here as a result of one-bond cleavage introduces a low-energy pathway that is not available in saturated alkyl cyclopropanes. The photochemical interconversion of **2** → **3** is a novel process which is not observable in either **10** or **11** or any other fused, bicyclic alkanes containing a strained cyclopropane ring system. Although it can be formally viewed as a process which involves a one-bond

(8) This quantum yield should be viewed as a lower limit since the interconversion of **2** and **3** was not taken into account.

(9) Srinivasan, R.; Baum, T.; Ors, J. A. *Tetrahedron Lett.* **1981**, *22*, 4795.

10   **11**   **12**
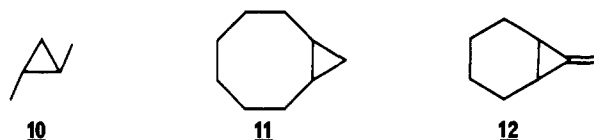
cleavage, its absence in **10** or **11** suggests a role for the olefinic group in the present instance which must await further research.

A comparison of the results of the photolysis of **2** and **3** to another methylenecyclopropane, **12**,[10] indicates that the relative extent of two-bond and one-bond cleavages in both is comparable.

CH≡CH

2-bond cleavage 39%   **12**   hv 185nm   minor products ~13%   1-bond cleavage   33%
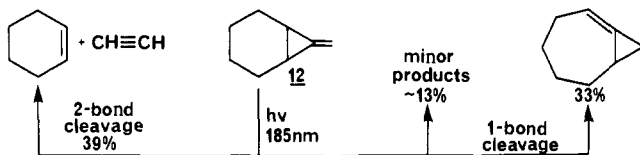
The most striking result from the present work is the observed lack of regioselectivity in the photochemical methylenecyclo-propane rearrangement whereas the thermal rearrangement fully exemplifies the regioselectivity that others have found earlier in similar systems.[11] The thermal rearrangement has been explained as involving a twisted orthogonal singlet $^1B_1$ excited state of trimethylenemethane that is 17.6 kcal/mol above the triplet ground state [$^3A'_2$] of TMM.[3] Reclosure from this orthogonal state can proceed only regioselectively, since both the planar $^1B_2$ and $^1A_1$ states through which loss of regiochemistry can occur are cal-culated to be placed 0.5–4.0 kcal/mol above the $^1B_1$ state.

Both the discordance between the results of thermolysis and photolysis in the present work and the earlier results of Takeda and his co-workers[7] rule out the simple possibility that photolysis of methylenecyclopropane can lead to either the $^1B_1$ or the $^3A'_2$ states of TMM.

Calculations on the electronically excited states of methyl-enecyclopropane (MCP) and trimethylenemethane (TMM) were carried out by using a recent version of the INDO/S-CI program of Zerner.[12] For MCP, the experimental geometry was used.[13] For TMM, standard bond lengths and angles were assumed: methylene HCH angles = 120°; all r_{CC} = 1.40 Å; all r_{CH} = 1.10 Å. Molecular orbitals for MCP were obtained by the restricted Hartree–Fock (RHF) method for closed shells while restricted open-shell (ROHF) calculations were performed on TMM. Triplet molecular orbitals were used for both triplet and singlet states in the configuration interaction (CI) calculations. The CI-active orbital space consisted of all single and double excitations from the filled to the unfilled molecular orbitals.

Those states that lie in the range of the 6.7-eV photon (=185 nm) are listed in Table III. Unfortunately, no experimental spectrum for MCP exists with which to compare the calculated values presented in Table III. The $\pi \rightarrow \sigma^*$ transition has a smaller oscillator strength but has a strongly antibonding orbital partic-ularly between the carbon–carbon and carbon–hydrogen bonds of the π moiety of MCP. The transition to this orbital would result in severely fragmented products. The $\sigma_a \rightarrow \pi^*$ transition has no oscillator strength but could provide a pathway to form acetylene and olefin.

CH₂ ‖ CH₂   +   HC≡CH
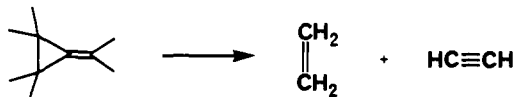
Excitation of an electron out of the σ_a orbital shown in **13** into the π^* orbitals would weaken the C–C side bonds of the cyclo-propane moiety as well as the C–H bonds attached to the double bond, thus promoting cleavage of the C–C side bonds and C–H

13
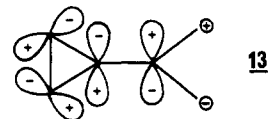
bonds, and lead to an olefin and an acetylene.

The $\pi \rightarrow \pi^*$ transition is calculated to be the most intense absorption and through a disrotatory ring opening as shown in Figure 1 could provide an energetically accessible excited-state TMM intermediate. The conrotatory ring opening given in Figure 2 also resulting from a $\pi \rightarrow \pi^*$ transition could provide still another pathway leading to a TMM excited state. Inspection of the low-lying electronic states of TMM shows that configurations which arise from either a conrotatory or disrotatory photochemical ring opening of MCP to TMM can give rise to either $2^1E'$ or $3^1E'$ excited states.[14] It is more likely that excited MCP would cross or mix with lower states of a TMM intermediate upon ring opening. The question comes down to whether or not there are any excited states of TMM which are energetically accessible in the 6.7-eV range. Calculations which were performed on the excited states of planar TMM are presented in Figure 3 and reveal some interesting trends. Neither the 2 E' nor the 3 E' excited states (6.1 and 6.9 eV, respectively, relative to the 1 $^1E'$ state) appear to be energetically accessible to the 6.7-eV photon since very accurate calculations indicate that the lowest singlet state (1 $^1E'$) of TMM is at least 1 eV higher in energy than MCP. However, our calculated value for the $^1A'_1$ (3.7 eV) agrees qualitatively with the 4.7-eV difference that was obtained by Yarkony and Schaeffer[1] using an ab initio treatment. Considering the qualitative nature of our calculations, the 2 $^1E'$ state may also be in an accessible region in terms of energy. A reasonable hypothesis is that the photochemical ring opening of MCP initially takes place along a higher potential energy surface of C_s or C_2 symmetry but then mixes with the lower $^1A'_1$ surface to form excited TMM and recloses to products. The intervention of planar states of D_{3h} symmetry could then explain the observed formation of all possible MCP rearrangement products in about equivalent yields. An alternative explanation of the regiorandomness of the products could be associated with the planar $^1A_1$ and $^1B_2$ singlet states of TMM. These two states could be implicated after initial excitation followed by rapid internal conversion. The ring opening of **2** or **3** could lead to four distinct planar TMM intermediates which could close to six distinct products explaining the regior-andomness.[15]

Experimental Section

Infrared spectra were recorded in carbon tetrachloride solution on an Acculab 6 spectrometer and are reported in reciprocal centimeters. Proton NMR spectra were recorded in carbon tetrachloride solution on an IBM Instruments NR-80 spectrometer (benzene-d_6 used as an internal lock and reference) or on a Varian T-60A spectrometer (chloroform or TMS were used as internal references) and are reported in parts per million (ppm) chemical shifts. The 300-MHz proton NMR were re-corded on a Nicolet spectrometer (TMS internal reference) at Rocke-feller University, New York. Mass spectra were recorded on a Hew-lett-Packard 5995 gas chromatography/mass spectrometer equipped with a 3% OV-101 glass column (0.25 in. × 6, 12 or 24 ft in length) and are reported in decreasing order of abundances. Analytical and preparative chromatography were carried out on a Hewlett-Packard 5750B or Per-kin-Elmer 3920B gas chromatograph equipped with a thermal conduc-tivity detector and/or flame ionization detector, with a 0.25-in. column containing UCW-982 on 80/100 Supelcoport, 24 ft in length. Attempts to separate compounds **2** and **3** were carried out on a 75-m capillary column (Perkin-Elmer 3920) but proved to give no better resolution. Three hundred megahertz proton NMR provided the best method for determining the amount of structural isomerization of **2** and **3** at 50% apparent conversions of starting materials, by VPC.

Apparatus. All photolyses were carried out on a semipreparative scale in pentane (Baker Photrex grade) in a water-jacketed Pyrex reaction vessel (50- or 120-mL volume) with a gas inlet tube and a side arm with a 14/20 tapered ground glass joint. The setup was fitted with a reflux

(10) Baum, T.; Srinivasan, R., unpublished results.

(11) Gajewski, J. J. *J. Am. Chem. Soc.* **1968**, *90*, 7178; **1971**, *93*, 4450. Gajewski, J. J.; Chou, S. K. *Ibid.* **1977**, *99*, 5696.

(12) Prof. Michael Zerner, INDO/S-CI, Quantum Theory Project, University of Florida.

(13) Laurie, V. W.; Stigliani, W. M. *J. Am. Chem. Soc.* **1970**, *92*, 1485.

(14) The detailed symmetry of the reaction pathway for the ring opening of MCP cannot be assessed without additional detailed calculations.

(15) We are indebted to the referee who suggested this idea to the authors.

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Table III. Excitation Energies for Low-Lying States of Methylenecyclopropane

transition	excitation energy, eV	oscillator strength
$\pi \rightarrow \pi^*$	6.68	0.604
$\sigma_a \rightarrow \pi^{*a}$	6.85	0.000
$\pi \rightarrow \sigma^{*b}$	6.90	0.005

[a] The σ_a orbital looks similar to the antisymmetric combination of the Walsh orbital of cyclopropane (see Figures 1 and 2). [b] The σ^* orbital is strongly antibonding between the carbon atoms of the methylenecyclopropane π bond and consists mainly of carbon 2s orbitals.
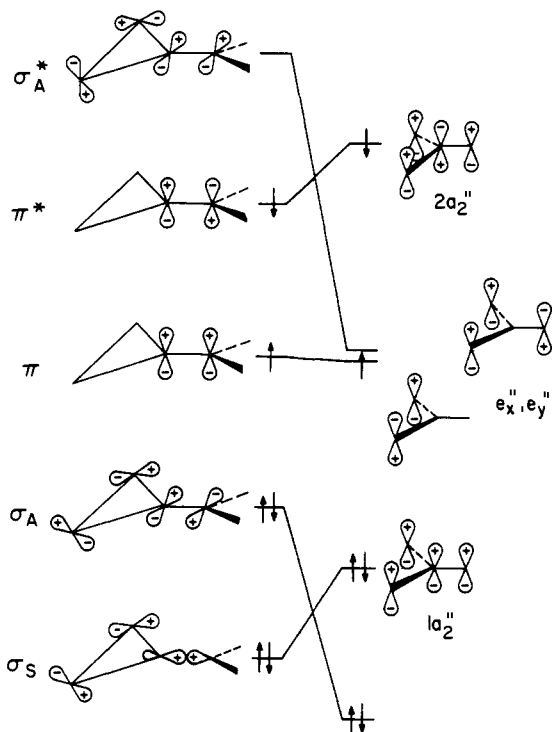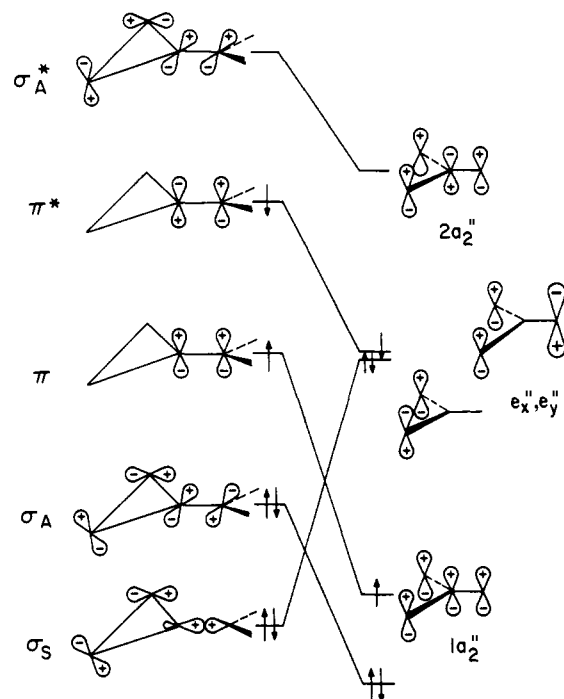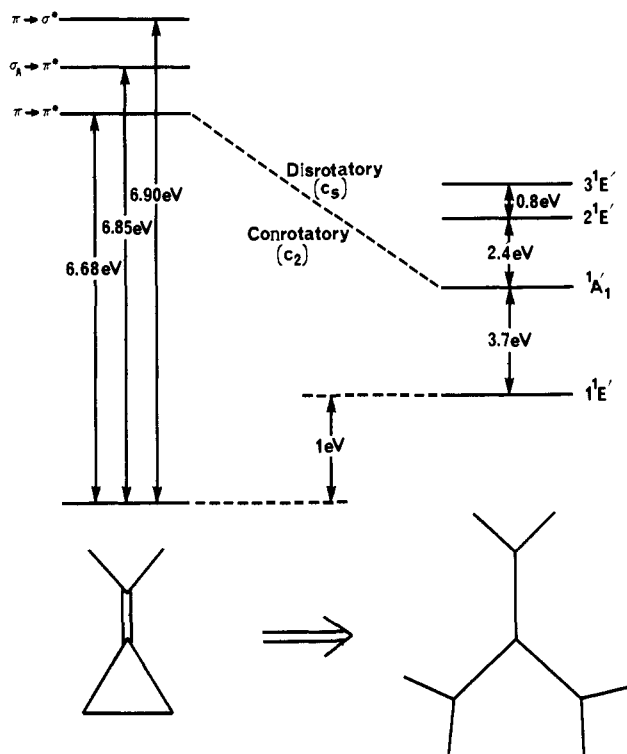

Figure 1. Correlation diagram showing the disrotatory photochemical opening of methylenecyclopropane to trimethylenemethane.

Figure 2. Correlation diagram showing the conrotatory photochemical opening of methylenecyclopropane to trimethylenemethane.

Figure 3. Calculated energy levels in the excited states of methylenecyclopropane and trimethylenemethane.

condenser, a magnetic stirring bar, an immersion well, and drying tube. The reactor was cleaned by washing with dilute aqueous HCl, several washes with water, three acetone rinses, and oven drying (105 °C). The light source was a 10-W Osram HNS 10W/U OZ low-pressure mercury resonance lamp (185- + 254-nm bands). In all photolyses, the lamps were given a warm-up time of 10 min and then cooled by a flow of nitrogen gas during photolysis.

Starting Materials. (*Z*)-1,2-Diethyl-1-methyl-3-methylenecyclopropane (3). The synthesis of 3 was achieved by the method of Arora and Binger[16] from 99% *cis*-3-methylhex-3-ene (Wiley), 1,1-dichloroethane, and 1.5 M methyllithium in ether at -40 °C. The resulting *syn*- and *anti*-1-chloro-1-methyl-2,3-diethyl-2-methylcyclopropanes were isolated by distillation on a Vigreaux column at reduced pressure and dehydrohalogenated by potassium *tert*-butoxide in Me₂SO at 80–90 °C. The desired product was isolated and purified by VPC in 99% geometrical purity: PMR (300 MHz) δ 5.20 (d, 2 H), 1.38 (m, 4 H), 1.13 (s, 3 H), 1.2–0.85 (7 H); IR 3050, 2950, 2920, 2864, 1770, 1735, 1452, 1372, 1152, 883 cm⁻¹; MS, *m/z* 27 (base), 39, 41, 67, 29, 538 79, 28, 91, 55; mol wt by mass spectrum 124.

(*E*)-1,2-Diethyl-1-methyl-3-methylenecyclopropane (2). The synthesis of 2 was achieved by the method of Arora and Binger[16] by the reaction of 98% *trans*-3-methylhex-3-ene (Wiley), 1,1-dichloroethane, and 1.5 M methyllithium in ether at -40 °C. The resulting *syn*- and *anti*-1-chloro-1-methyl-2,3-diethyl-2-methylcyclopropanes were isolated by distillation on a Vigreaux column at reduced pressure and dehydrohalogenated by potassium *tert*-butoxide in Me₂SO at 80–90 °C. The desired product was isolated and purified by VPC in 98% geometrical purity: PMR (300 MHz) δ 5.18 (d, 2 H), 1.37 (m, 4 H), 1.05 (s, 3 H), 1.1–0.85 (7 H); IR 3050, 2950, 2920, 2864, 1770, 2735, 1455, 1373, 1152, 885 cm⁻¹; MS, *m/z* 27 (base), 41, 29, 67, 29, 53, 79, 55, 91, 28; mol wt by mass spectrum 124.

Procedures. The photolysis solutions were purged by bubbling dried nitrogen for 20 min prior to irradiation, with vigorous stirring. Initial samples were extracted from the solution (after purging with nitrogen), and were taken at $t = 0$ for comparison with aliquots taken from the photolysates as a function of the time of irradiation. In most photolyses, aliquots were taken by syringe from the photolysate at 15, 30, 45, 60, 90, 120, 150, and 180 min of irradiation and monitored by VPC. In all quantitative photolyses, the VPC areas (H × 0.5 W) were calibrated with authentic samples of known concentration in pentane solution. Photoproducts were isolated by preparative VPC from concentrated photolysates and compared by spectral data to literature and/or authentic samples. Starting materials were reexamined after photolysis and compared

(16) Arora, S.; Binger, P. *Synthesis* **1974**, 801.

to spectral data prior to irradiation.

Direct Photolysis of 3 at 185 nm. VPC-purified **3** (342 mg, 2.76 mmol) in 100 mL of pentane was irradiated in a reactor with a Suprasil immersion well and Osram Hg lamp. Aliquots were monitored by VPC (50–120 °C program) as a function of the time of irradiation. At 10% conversion or less, (*Z*)-3-methylhex-3-ene was the only photofragmentation product observed. However, at conversions higher than 10%, both the *Z* and *E* isomers are observed. After 3 h of irradiation (50% conversion of **3** by VPC), the photolysate was concentrated by careful distillation in a water bath (40 °C). Photoproducts were isolated by preparative VPC and identified. Recovered starting material was examined by 300-MHz proton NMR to determine the extent of geometrical isomerization of **3** to **2**. The photolysis was calibrated by a 0.01 M pentane solution of (*Z*)-3-methylhex-3-ene.

Direct Photolysis of 2 at 185 nm. VPC-purified **2** (205 mg, 1.65 mmol) in 70 mL of pentane was irradiated in a reactor with a Suprasil immersion well and Osram Hg lamp. Aliquots were monitored as a function of the time of irradiation by VPC (50–120 °C program). At 10% conversion or less, (*E*)-3-methylhex-3-ene was the only photofragmentation product observed. However, at conversions higher than 10%, both *Z* and *E* isomers were present. After 3 h of irradiation (50% conversion of **2** by VPC) the photolysate was concentrated by careful distillation in a water bath (40 °C). The photoproducts were isolated by preparative VPC and identified. Recovered starting material was examined by 300-MHz proton NMR to determine the extent of geometrical isomerization of **2** to **3**. The photolysis was also calibrated with a 0.01 M pentane solution of (*E*)-3-methylhex-3-ene.

Quantitative Photolysis of 2 at 185 nm. VPC-purified **2** (181 mg, 1.46 mmol) in 50 mL of pentane was irradiated in a reactor with a Suprasil immersion well and Osram Hg lamp. The photolysis was conducted in the same manner as the preparative photolysis at 185 nm. After calibration by cyclooctene actinometry,[17] a quantum yield of 0.29 was calculated for the photoreaction of **2** at 185 nm. (This calculated quantum yield does not account for the geometrical isomerism that is shown to occur, and, therefore, the actual quantum yield would be slightly higher.)

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(17) Schuchmann, H. P.; von Sonntag, C.; Srinivasan, R. *J. Photochem.* **1981**, *15*, 159.

Photolysis Products. (*Z*)-3-Methylhex-3-ene (**5**) was identified by comparison of its IR, PMR, mass spectrum, and VPC retention time with that of an authentic sample (Wiley 99%). The authentic compound was also used to calibrate the quantitative photolysis of **2** for the photofragmentation process.

(*E*)-3-methylhex-3-ene (**4**) was identified by comparison of its IR, PMR, mass spectrum, and VPC retention time with that of an authentic sample (Wiley 98%).

1-Isobutylidene-2-ethylcyclopropane (**8** + **9**) was identified by the following: IR 3025, 1770, 1452, 1372, 1180, 1067, 955 cm^{-1}; PMR δ 2.03 (2 H, m), 1.70 (br s, 3 H), 1.5–0.2 (11 H); MS, m/z 67 (base), 41, 27, 39, 29, 53, 55, 81, 109, 95; mol wt by mass spectrum 124.

syn-1-Ethyl-1-methyl-2-propylidenecyclopropane (**7**) was identified by the following: IR 3030, 1458, 1372, 1128, 1105, 1083, 1053 cm^{-1}; PMR δ 5.55 (m, 1 H), 2.02 (2 H, m), 1.28 (2 H, m), 1.1–0.7 (11 H); MS, m/z 67 (base), 41, 27, 39, 29, 53, 55, 81, 109, 96; mol wt by mass spectrum 124.

anti-1-Ethyl-1-methyl-2-propylidenecyclopropane (**6**) was identified by the following IR 3030, 1760 (w), 1455, 1372, 1287, 1052, 1000, 978, 942 cm^{-1}; PRM δ 5.64 (m, 1 H), 2.01 (2 H, m), 1.22 (2 H, m), 1.05–0.7 (11 H); MS, m/z 67 (base), 41, 27, 39, 29, 55, 53, 81, 109, 96; mol wt by mass spectrum 124, and from its predominance in the pyrolysis reaction.

Pyrolysis. Pyrolysis of 3 at 198 °C. VPC-purified **3** (200 mg, 1.61 mmol) was divided into three Pyrex tubes. The tubes were evacuated (with liquid nitrogen cooling), sealed with an oxygen–propane torch, and immersed in a heated silicon oil bath (198 °C). The pyrolysis samples were monitored by VPC (50–120 °C program) at 30, 60, and 90 min and compared to a $t = 0$ sample of **3**. The relative product ratios were calculated by VPC and were invariant (within experimental error) for each time interval of the pyrolysis.

Pyrolysis of 2 at 198 °C. VPC-purified **2** (193 mg, 1.56 mmol) was pyrolyzed exactly according to the procedure given above.

A Theoretical Study of Fluorine Atom and Fluoride Ion Attack on Methane and Silane

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Abstract: We have performed MNDO and ab initio calculations for reactions of fluorine atom attack on methane and silane and, in addition, fluoride ion attack on the same molecules in the case of MNDO. We modeled both substitution and abstraction reactions in each case. Results were compared with experimental data, where available. Comparisons show that MNDO usually does as well as the ab initio methods in reproducing experimental values for Δ*E*'s of these reactions, but MNDO predicts activation barriers too high in most cases. Nevertheless, MNDO does qualitatively agree with the ab initio result that, while carbon undergoes abstraction much more easily than substitution, silicon can undergo either substitution or abstraction quite easily. The analysis in the case of fluoride ion attack on silane is complicated by the predicted ease of formation of a stable trigonal-bipyramidal intermediate.

Silicon chemistry is increasingly important to many products of materials science including catalysts, semiconductors, organosilicon polymers, ceramics, glasses, and composites. Our special interest is silica surfaces and their interactions with organic molecules. In all of these applications an efficient, accurate, theoretical model for predicting silicon chemistry could produce

a great economy of effort. In particular, a detailed model of the mechanisms and products for silica polymerization would be of great help in tailoring silica materials for specific purposes. To this end, we began a combined theoretical and experimental program to study silicon reactions and silica surfaces several years ago.

Our goal is to perform theoretical calculations for rather large molecular systems without resorting to theoretical models which are expensive, time-consuming, and, thus, self-defeating for our

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