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Kinetics of the Siloxyvinylcyclopropane Rearrangement Using a Micro Stirred Flow Reactor[1]

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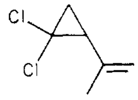
The kinetics of the thermal rearrangement of 1-(1-(trimethylsiloxy)cyclopropyl)cyclopentene (**3**), 5-methyl-1-(1-(trimethylsiloxy)cyclopropyl)cyclopentene (**5**), 1-cyclopropyl-1-(trimethylsiloxy)ethylene (**7**), and 1-((*Z*)-2-methyl-1-(trimethylsiloxy)cyclopropyl)cyclopentene (**9**) was investigated on a micro stirred flow apparatus. Siloxyvinylcyclopropanes **3**, **5**, and **7** rearrange cleanly to their respective cyclopentyl enol silyl ethers with a calculated $\Delta G^{\ddagger}$(350 °C) of 43.8 kcal/mol for **3**, 42.9 kcal/mol for **5**, and 51.3 kcal/mol for **7**. Siloxyvinylcyclopropane **9** rearranged to 4-cyclopentylidene-4-(trimethylsiloxy)but-1-ene (**10**) via the homo 1,5 hydrogen shift with a calculated $\Delta G^{\ddagger}$(350 °C) of 39.2 kcal/mol. A comparison of the $\Delta G^{\ddagger}$'s for the rearrangement of siloxyvinylcyclopropanes is made with those of other substituted vinylcyclopropanes.

Introduction and Background

In the 20 years since its discovery, the vinylcyclopropane rearrangement has been the subject of many mechanistic and theoretical studies.[3] Attempts to study the mechanism by attaching various substituent labels have met with much frustration in that, in addition to the rapid randomization of the carefully labeled substrate,[4] the substituent itself may have a direct effect upon the reaction path. Methyl labels on the cyclopropane ring can convert rapidly to an orientation cis to the vinyl group where they undergo the homo 1,5 hydrogen shift much faster than the rearrangement to the cyclopentene.[5] Labels on the vinyl group cis to the cyclopropyl often sterically prevent the reaction from proceeding.[6,7]

Heteroatoms placed on the vinylcyclopropane moiety have drastically varied effects on the rearrangement, depending upon their location. These substituent effects must be taken into account in any mechanistic rationale and in planning any synthesis which utilizes the rearrangement. Dichloride **1** thermalizes at a lower temperature than the parent vinylcyclopropane, whereas monochloride **2** after 4 h at 350 °C is recovered unchanged; raising the temperature to over 400 °C results in polymerization.[7] Qualitative observations with compounds **3** and **5** suggested the trimethylsiloxy group facilitated the rearrangement and an approximate 9 kcal/mol lowering of the E_a was estimated.[8] But placement of the trimethylsiloxy group in a different position, as in **7**, hampers the rearrangement as indicated by the requirement of much higher temperatures or longer contact times to achieve reasonable conversions.[9] Before an understanding of the source of these effects can emerge, a quantitative study is necessary.



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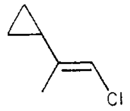

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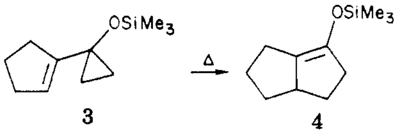

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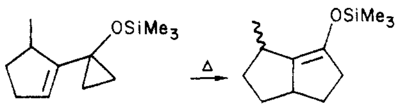

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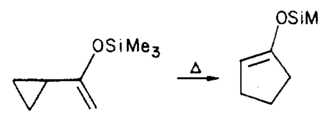
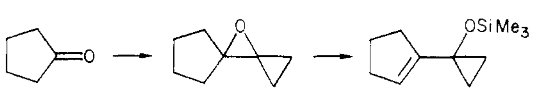
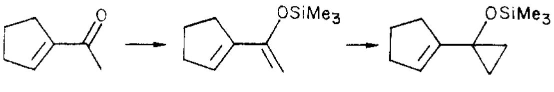


7 8

In addition the siloxyvinylcyclopropane rearrangement is a synthetically very important process for the annulation of five-membered rings in that the product is a regiospecific enolate equivalent,[10] easily allowing further elaboration.[9,11] The two main routes into siloxyvinylcyclopropanes employ either the lithium diethylamide opening of oxaspiropentanes[9] (eq 1) or the silver Simmons–Smith reaction on enol silyl ethers[11] (eq 2).



(1)



(2)

It was our interest in the various applications of the siloxyvinylcyclopropane rearrangement that prompted us to look into the kinetics of the rearrangement utilizing the

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[1] E. Vedejs and E. S. C. Wu, *J. Am. Chem. Soc.*, **97**, 4706 (1975).

[2] Natural Sciences Div., New College of USF, Sarasota, FL 33580.

[3] N. P. Neureiter, *J. Org. Chem.*, **24**, 2044 (1959); C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 4896 (1960); S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968); M. Schneider and I. Merz, *Tetrahedron Lett.*, 1995 (1974); R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967); W. v. E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **96**, 1168 (1974); **97**, 5512 (1975); R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970; J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, **94**, 8917 (1972).

[4] G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **98**, 6705 (1976); P. H. Mazzocchi and H. J. Tamburin, *ibid.*, **92**, 7220 (1970); **97**, 555 (1975); R. A. Clark, *Tetrahedron Lett.*, 2279 (1971); M. R. Willcott and V. H. Cargle, *J. Am. Chem. Soc.*, **89**, 723 (1967); **91**, 4130 (1969).

[5] R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 221 (1964).

[6] A. J. Berlin, L. P. Fisher, and A. D. Ketley, *Chem. Ind. (London)*, 509 (1965).

[7] A. D. Ketley, A. J. Berlin, E. Gorman, and L. P. Fisher, *J. Org. Chem.*, **31**, 305 (1966).

[8] B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 289, 5298, 5311 (1973). For application in the total synthesis of aphidicolin, see B. M. Trost, Y. Nishimura, and K. Yamamoto, *J. Am. Chem. Soc.*, **101**, 1328 (1979).

[9] S. A. Monti, F. G. Cowherd, and T. W. McAnich, *J. Org. Chem.*, **40**, 858 (1975).

[10] Other vinylcyclopropanes which produce enol derivates: B. M. Trost and D. E. Keeley, *J. Am. Chem. Soc.*, **98**, 248 (1976); A. A. Ozorio, *Diss. Abstr. B*, **33**, 641 (1972).

[11] C. Girard, P. Amice, J. P. Barnier, and J. M. Conia, *Tetrahedron Lett.*, 3329 (1974).

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Table I. Activation Parameters for the Rearrangement of Several Siloxyvinylcyclopropanes

compd	E_a, kcal/mol	log A	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	$\Delta G^\ddagger$(350 °C), kcal/mol
3	44.3 ± 3.4	13.3 ± 1.2	43.0	−1.24	43.8 ± 0.2
5	47.2 ± 2.1	14.6 ± 0.7	45.9	4.84	42.9 ± 0.2
7	63.1 ± 4.7	17.3 ± 1.4	61.7	16.7	51.3 ± 1.6
9	39.3 ± 1.5	13.1 ± 0.6	38.2	−1.69	39.2 ± 0.4

micro stirred flow apparatus.[1] This method was easily applied since the siloxy compounds were volatile, underwent a very clean pyrolysis, and were easily differentiated and integratable by gas chromatography. Flow reactors provide a convenient method of obtaining kinetic data on gas-phase thermolysis reactions.[12]

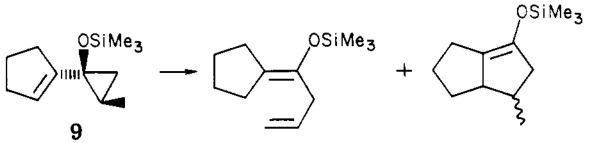
The stirred-flow method assumes that the reactor effluent is representative of the steady-state concentrations of the starting material and of the product within the reactor. The kinetics is performed by varying the flow rate through the reactor and the temperature and observing the ratio of starting material to product, [A]/[B]. The flow rate, U, is expressed in milliliters/second at the reactor exit and therefore must be temperature corrected[13] to the reactor temperature since it is measured with a soap-film flow meter at ambient temperature. The kinetic expression is simple[13] as shown in eq 3–5, where V = reactor volume. A plot of U/V against the ratio of starting material to product yields a straight line with k_1 as the slope. Any extraneous reactions of the product or starting material do not interfere with the determination of k_1; they affect only the intercept.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{3}$$

$$k_1[\mathrm{A}] - [\mathrm{B}]U/V = 0 \text{ material balance for B} \tag{4}$$

$$\text{therefore } k_1[\mathrm{A}]/[\mathrm{B}] = U/V \tag{5}$$

Four siloxyvinylcyclopropanes were studied, **3**, **5**, **7**, and **9**. The product of the thermolysis of **9** produced the expected homo 1,5 hydrogen shift product **10** with only a minor trace of vinylcyclopropane rearrangement product **11**.



9 **10** **11**

The results of the kinetic studies are presented in Table I as the least-squares-derived parameters from the Arrhenius and Eyring plots of the data; Figure 1 displays the Arrhenius plots of the data. The error propagation[14] is from the scatter in the least-squares regression analysis and 95% confidence limits are reported on all values. The value R^2 is the normal linear regression correlation coefficient. All pyrolyses were well behaved giving GC traces showing well-defined peaks with baseline separation except for **5** in which a small (3% vs. total peak areas) unidentified peak was present. Table I summarizes the activation parameters for the thermal rearrangement of the siloxyvinylcyclopropanes.

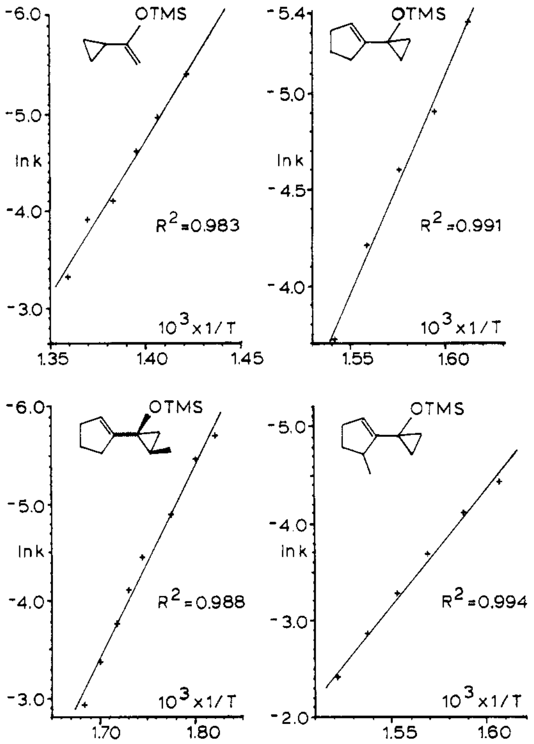


Figure 1. Arrhenius least-squares plots of the kinetic data.

Discussion

Since $\Delta G^\ddagger$ is far less influenced by systematic errors[15,16] than E_a or $\Delta H^\ddagger$ and $\Delta S^\ddagger$ and can be used to correlate the work done in different laboratories, the $\Delta G^\ddagger$(350 °C) values were calculated from the published data[17] and are presented in Table II along with $\Delta\Delta G^\ddagger$(350 °C) a measure of the substituent effect.

The first point to note is that the substituent effect for the 1′-trimethylsiloxy is very close to that of the 1′-methoxy **14**. Previous work[18] showed that there was no significant difference between the rates of rearrangement of the oxy-Cope and the siloxy-Cope. It also appears that a heteroatom at the 2′ position contributes to a greater lowering of the $\Delta G^\ddagger$ than at the 1′ position.

However, a heteroatom on the vinyl substituent as in **2** or **7** appears to raise the $\Delta G^\ddagger$ significantly. Several rationales for the high $\Delta G^\ddagger$ for **7** could be proposed: reduction of the π electrons' participation in the ring opening,[7] inductive destabilization of any radicaloid species with no possibility for mesomeric return, or the fact that in **3** there is significant relief of steric strain upon ring opening which is not present in **7**; all may operate to some degree. The reluctance of **7** to rearrange resulted in a much larger error in its $\Delta G^\ddagger$ since to obtain an adequate temperature range for the kinetics, temperatures approaching the upper limit of the stirred-flow apparatus had to be used.

With the exception of the natural reluctance of the rearrangement to proceed to a center with a cis vinyl sub-

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[12] L-U. Meyer and A. de Meijere, *Chem. Ber.* **110**, 2545 (1977).

[13] W. C. Herndon, *J. Chem. Educ.*, **41**, 425 (1964); W. C. Herndon, M. B. Henly, and J. M. Sullivan, *J. Phys. Chem.*, **67**, 2842 (1963).

[14] Arrhenius least-squares analysis and error propagation done on a HP-25 calculator from equations taken from N. R. Draper and H. Smith, "Applied Regression Analysis", Wiley, New York, 1966. Eyring least-squares analysis and error propagation done on an IBM 1108 using a program written by G. R. Weisman from equations taken from C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry", Wiley, New York, 1954.

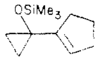
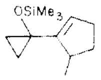
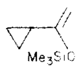
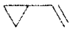
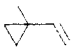
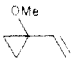
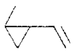
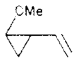
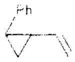
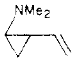
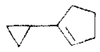
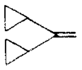
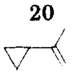
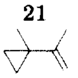
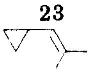
[15] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, pp 307–313.

[16] R. K. Harris, *Nucl. Magn. Reson.*, **2**, 216 (1973); A. Allerhand, F. Chen, and H. S. Gutowski, *J. Chem. Phys.*, **42**, 3040 (1965); W. Walter, E. Schaumann, and J. Voss, *Org. Magn. Reson.*, **3**, 733 (1971).

[17] For a general review see M. R. Willcott, R. L. Cargill, and A. B. Sears, *Prog. Phys. Org. Chem.*, **9**, 25 (1972).

[18] R. W. Thies, *J. Am. Chem. Soc.*, **94**, 7074 (1972).

Table II. Activation Parameters for the Thermal Rearrangement of Vinylcyclopropanes to Cyclopentenes and Approximate Empirical Substituent Effects (kcal/mol)

compd	log A	E_a	$\Delta G^{\ddagger}$ (350 °C)[a]	$\Delta\Delta G^{\ddagger}$ (350 °C)[b]
 **3**	13.3	44.3[c]	43.8	−4.5
 **5**	14.6	47.2[c]	42.9	−5.4
 **7**	17.3	63.1[c]	51.3	+3.0
 **12**	13.5 13.6	49.6[d] 49.7[e]	48.4 48.2	
 **13**	14.11	49.4[f]	46.6	−1.7
 **14**	13.43	44.7[g]	43.8	−4.5
 **15**	13.67 12.54[a]	48.7[h] 45.7[a]	47.1 47.1[i]	−1.2
 **16**	12.52	38.7[g]	40.4	−7.9
 **17**	13.38	41.0[g]	40.2	−8.1
 **18**	10.3	31.1[j]	38.9	−9.4
 **19**	14.01	51.3[k]	48.7	+0.4
 **20**	14.29	51.1[k]	47.7	−0.6
 **21**	13.89	50.9[l]	48.7	+0.4
 **22**	14.14	50.5[m]	47.5	−0.8
 **23**	13.79	50.0[n]	48.1	−0.2
 **24**	14.0	54.6[o]	52.0	+3.7

[a] Calculated from published values using equations found in ref 15. [b] $\Delta G^{\ddagger}$ (350 °C) of substituted $-\Delta G^{\ddagger}$ (350 °C) of **12** (48.3 kcal/mol). [c] This work. [d] M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961). [e] C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962). [f] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 959 (1964). [g] J. M. Simpson and H. G. Richey, *Tetrahedron Lett.*, 2545 (1973). [h] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1964). [i] W. R. Roth and J. Konig, *Justus Liebigs Ann. Chem.*, **688**, 28 (1965). [j] D. W. Shull, *Diss. Abstr. B*, 37, 775 (1976). [k] G. R. Branton and H. M. Frey, *J. Chem. Soc A*, 1342 (1966). [l] H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962). [m] H. M. Frey, *Adv. Phys. Org. Chem.*, 4, 147 (1966). [n] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 4188 (1964). [o] C. S. Eliot and H. M. Frey, *ibid.*, 345 (1965).

Table III. Instrument Parameters for Kinetic Runs

	temp, °C		retention times, min	
substrate	sample container	GLC column	substrate	product
3	60	150	7.0	9.0[a]
5	60	165	7.5[b]	10.2,[c] 11.8[d]
7	35	110	3.9	5.8[e]
9	60	165	8.0	9.9[f]

[a] Compound 4. [b] Minority impurity (3%) at 8.5 min. [c] Exo isomer of **6**. [d] Endo isomer of **6**. [e] Compound **8**. [f] Compound **10**.

Table IV. Kinetic Data for Thermal Rearrangement of 3

T, K	$k \times 10^3$	ln k	R^2
620.0	4.7095	−5.35818	0.999
627.0	7.4201	−4.90357	0.995
634.5	10.0423	−4.60095	0.994
641.5	14.8435	−4.21019	0.997
648.5	24.2265	−3.72031	0.996

Table V. Kinetic Data for Thermal Rearrangement of 5

T, K	$k \times 10^3$	ln k	R^2
622.0	11.9702	−4.42534	0.993
629.5	16.3405	−4.11411	0.992
636.5	25.0564	−3.68662	0.998
643.5	37.5687	−3.28158	0.998
650.0	56.7684	−2.86878	0.994
657.0	89.0427	−2.41864	0.997

stituent displayed by the high $\Delta G^{\ddagger}$ for **24**, alkyl substituents on the double bond do not make a large perturbation on the $\Delta G^{\ddagger}$ of the arrangement.

Finally, the $\Delta G^{\ddagger}$ for the thermolysis of **9** (3.6 kcal/mol below that of **3**) reflects the lower barrier for the isomerization followed by a homo 1,5 hydrogen shift than for the rearrangement to cyclopentene. The $\Delta G^{\ddagger}$(350 °C) for the thermolysis of **15** to *cis*-1,4-hexadiene is 44.0 kcal/mol, 3.1 kcal/mol below the $\Delta G^{\ddagger}$(350 °C) for the rearrangement to 3-methylcyclopentene.[17] The $\Delta G^{\ddagger}$(350 °C) of **9** is 4.8 kcal/mol below that of **15** for the isomerization and homo 1,5 hydrogen shift, thus displaying a similar substituent effect for trimethylsiloxy as was found for **3** and **5**.

Experimental Section

Apparatus. For a detailed description of the apparatus see ref 1. The quartz reactor was conditioned at 375 °C for several days, first with norbornadiene vapors and then with *O*,*N*-bis(trimethylsilyl)acetamide.

Stirred-Flow Kinetics. Compounds **3–6** and **9** were prepared by the method of Trost and Bogdanowicz;[8] compounds **7** and **8** were prepared by the method of Monti and co-workers.[9] All compounds were purified by GLC and directly collected into a bent length of 4-mm tubing; one end was then sealed, the compound centrifuged into the closed end, and the tubing cut ca. 1.5 cm above the closure and placed in the apparatus (see ref 1).

With the reactor at ca. 200 °C and then at 400 to 450 °C, the GLC conditions were optimized to yield baseline separation and minimal tailing on the starting material and product peaks. A 15 ft × $^1/_8$ in. 20% Dow-Corning 710 silicon oil on Chromosorb W column was employed at 40 psi with a flow rate of ca. 4 mL/min. Table III summarizes pertinent instrument parameters. The system was allowed to equilibrate overnight at the lowest kinetic run temperature. Equilibration times between flow-rate changes were 20–40 min and between temperature changes 2–3 h. All runs were performed from lower to higher temperatures and from faster to slower flow rates in order to minimize the equilibration time. All flame-ionization response factors of the isomers were automatically assumed to be unity.

Product identification was done by injection of known samples on the kinetics column or on an almost identical column (8 ft ×

Table VI. Kinetic Data for Thermal Rearrangement of 7

T, K	$k \times 10^3$	ln k	R^2
703.0	4.4526	−5.41426	0.995
710.5	7.0403	−4.95610	0.999
716.5	9.8611	−4.61916	0.999
722.3	16.5136	−4.10357	0.995
730.0	19.9017	−3.91695	0.997
736.0	36.2569	−3.31713	0.984

Table VII. Kinetic Data for Thermal Rearrangement of 9

T, K	$k \times 10^3$	ln k	R^2
548.0	3.3525	−5.69851	0.847
554.4	4.2474	−5.46145	0.979
562.5	7.5062	−4.89203	0.960
572.5	11.6534	−4.45216	0.992
577.0	16.2270	−4.12107	0.995
581.5	23.0012	−3.77221	0.996
587.5	34.4480	−3.36830	0.997
593.5	53.1226	−2.93515	0.981

0.25 in. 20% Dow Corning 710 silicon oil on Chromosorb P) on a Varian Aerograph 90-P. All pyrolyses on the stirred-flow apparatus were extremely clean, yielding only a starting material and a product peak, except for **5** (containing a 3% impurity in the starting material) which pyrolyzed to *exo*- and *endo*-**6**. Compound **9** thermalized to **10** with very minor traces of **11** present. Peak areas were determined by disk integration. The flow rates were measured with a soap-film flow meter at 25 °C and cross checked with an electronic flow meter and by the position of the set screw on the carrier gas needle valve which had previously been calibrated with flow rate. Tables IV-VII summarize the specific kinetic data and Table I summarizes the activation parameters calculated from the Arrhenius and Eyring plots.[14]

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Registry No. **3**, 39834-22-5; **4**, 39834-25-8; **5**, 75751-13-2; **6** (isomer 1), 75751-14-3; **6** (isomer 2), 75751-15-4; **7**, 42161-96-6; **8**, 19980-43-9; **9**, 75751-16-5; **10**, 75751-17-6; **12**, 693-86-7; **13**, 16906-27-7; **14**, 49785-10-6; **15**, 24560-57-4; **16**, 75751-18-7; **17**, 19159-61-6; **18**, 75751-19-8; **19**, 694-89-3; **20**, 822-93-5; **21**, 4663-22-3; **22**, 3422-07-9; **23**, 54159-22-7; **24**, 1003-33-4.

Supplementary Material Available: Spectral data for compounds **4**, **5**, **6**, **9**, and **10** (3 pages). Ordering information is given on any current masthead page.

Metal-Catalyzed Organic Photoreactions. One-Step Synthesis of Chlorinated Ketones from Olefins by Photooxidation in the Presence of Iron(III) Chloride[1]

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Under photooxidation in pyridine in the presence of $FeCl_3$, mono- and disubstituted olefins gave α-chloro ketones, while tri- and tetrasubstituted olefins gave dichloro ketones with a C–C bond cleavage. The reaction was interpreted in terms of an electron-transfer mechanism occurring within the coordination sphere of the iron ion.

In our preceding paper,[2] we reported that $UO_2(OAc)_2$ caused the photoreactions of olefins to produce β-hydroxy hydroperoxides or bromohydrins as main products by reaction of molecular oxygen or polyhalomethanes, respectively. It was further revealed that the reaction proceeded by an entirely different mechanism from those known for the photoreaction of olefins, and we proposed a mechanism termed long-range electron transfer for the reaction. Our rationale for this mechanism was inter alia the findings that polyhalomethanes, as well as molecular oxygen, functioned as an electron acceptor and played an important role in initiating the reaction and that there existed a good correlation between reduction potentials of the halomethanes and their reactivities for the formation of the bromohydrins.

In our preliminary paper,[1] we reported that the photooxidation of olefins in the presence of $FeCl_3$ afforded α-chloro ketones or dichloro ketones, depending upon the type of the substrate olefins. In the present study, we investigated the photooxidation under various conditions with several types of olefin and found that the reaction could also be interpreted in terms of the long-range electron-transfer mechanism.

Results

Pyridine solutions of mono- and disubstituted olefins **1–16**, containing an appropriate amount of $FeCl_3$ and other additives as specified in Table I, were irradiated with Pyrex-filtered light for 30–180 min while oxygen gas was bubbled through. The evaporation of the solvent followed by extraction (workup I) gave α-chloro ketones or vinylogs **19–37** as the almost exclusive products (type A). On the other hand, tri- and tetrasubstituted olefins **17** and **18** afforded dichloro ketones **38** and **39**, respectively, under the same conditions. The reaction conditions and yields are summarized in the Table I. The structures of the most of the products were determined definitely on the isolated pure samples by comparison with the authentic samples, by chemical reactions, or by spectroscopic data. However, complete isolation was not accomplished with **24**, **30**, and *trans*-**35**, and these structures are speculative.

Most of these reactions are quite clean, and the amounts of byproducts are very small. We ascribe the unsatisfactory mass balance of the reaction to the escape of the starting olefins during the irradiation or workup proce-

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[1] Preliminary report: E. Murayama, A. Kohda, and T. Sato, *Chem. Lett.*, 161 (1978).

[2] E. Murayama, A. Kohda, and T. Sato, *J. Chem. Soc., Perkin Trans. 1*, 947 (1980).

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