Chromyl Chloride Oxidations. VII. Kinetics and Mechanism of the Electrophilic Addition to Cycloalkenes[1-3]

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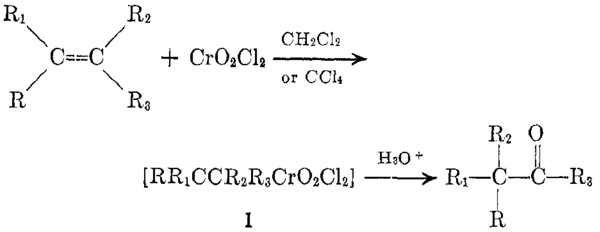
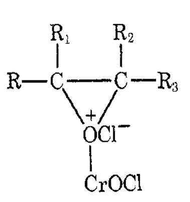
The rapid oxidation of cyclopentene, 1-methyl- and 1,2-dimethylcyclopentene, cyclohexene, 1-, 3-, and 4-methylcyclohexene, 1,3- and 1,4-dimethylcyclohexene, 1-acetylcyclohexene, cycloheptene, 1-methylcycloheptene, cyclooctene, cyclododecene, and bicyclo[2.2.1]hept-2-ene by chromyl chloride has been studied kinetically by means of a spectrophotometric stopped-flow system. The kinetics, which measure the rate of formation of the 1:1 chromyl chloride–cycloalkene adduct, follow the second-order rate law: $\nu = k[\mathrm{CrO_2Cl_2}][\text{cycloalkene}]$. The rate of oxidation increases with the increasing number of methyl groups at the carbon–carbon double bond. The relative rate of oxidation of 1-methylcyclohexene in carbon tetrachloride, chloroform, and methylene chloride is 1.00:4.05:17.4. Large negative entropies of activation ($\Delta S^{\ddagger} = -23.5$ to -42.7 eu) and low enthalpies of activation ($\Delta H^{\ddagger} = 3.21$–$10.6$ kcal/mol) are observed. A consideration of the effects of strain energies, stereochemistry, and ionization potentials on the rates is presented. Comparisons of the relative reactivities of chromyl chloride oxidations with other reactions involving symmetrical and unsymmetrical cyclic activated complexes suggest that the rate-limiting step involves a partially positively charged unsymmetrical three-membered cyclic activated complex. This conclusion does not necessarily hold for bicyclic systems.

The proposed mechanisms and observed products for the chromyl chloride oxidation of carbon–carbon single and double bonds have generated considerable controversy for many years.[4-26] Styrenes have been postulated as intermediates in the chromyl chloride oxidation of arylalkanes (Étard reaction),[17-27] and cycloalkenes have been suggested as intermediates in the oxidation of cycloalkanes.[12,14] Chromyl chloride reacts rapidly with alkenes,[4-11] cycloalkenes,[11-15,24] and styrenes[1,5,8,12,16-23] to give 1:1 chromyl chloride–unsaturate adducts **1** which can be converted to aldehydes and/or ketones in good to excellent yields by reductive hydrolysis with finely powdered zinc dust or with nascent sulfur dioxide.[7,8,23] For example, 2,4,4-trimethyl-1-pentene and 4,4-dimethyl-2-neopentyl-1-pentene are oxidized to 2,4,4-trimethylpentanal and 4,4-dimethyl-2-neopentylpentanal in 75.8 and 80.8% yields, respectively.[7,8,16] Table I shows the products from the chromyl chloride oxidation of some endocyclic and exocyclic cycloalkenes.[28]



(1)

Structure **2** has been suggested for the adduct **1**,[6,11-14]



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and structures **3** and **4** have been proposed as possible cyclic activated complexes for the rate-determining step in the chromyl chloride oxidation of styrenes.[1,20] Kinetic data from the oxidation of alkenes favor the unsymmetrical three-membered cyclic activated complex **4**.[9] Also, preliminary oxidation studies with cyclopentene, cyclohexene, and bicyclo[2.2.2]hept-2-ene suggested that the activated complex could resemble structure **3**, **4**, or **5**.[11]

In an attempt to further elucidate the mechanism of the chromyl chloride oxidation of cycloalkenes, we have examined the kinetics of chromyl chloride addition

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[1] Previous paper in series: F. Freeman and N. J. Yamachika, *J. Amer. Chem. Soc.*, **94**, 1214 (1972).

[2] Presented in part at the Symposium on the Reactivity of Olefins, Nice, France, Sept 29, 1971, and the Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif., Oct 18, 1971.

[3] Abstracted in part from the M.S. thesis of K. W. Arledge, California State College, Long Beach, Calif., 1971.

[4] W. H. Hartford and M. Darren, *Chem. Rev.*, **58**, 1 (1958).

[5] K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, p 69.

[6] S. J. Cristol and K. R. Eilar, *J. Amer. Chem. Soc.*, **72**, 4353 (1950).

[7] F. Freeman, P. J. Cameron, and R. H. DuBois, *J. Org. Chem.*, **33**, 3970 (1968).

[8] F. Freeman, R. H. DuBois, and T. G. McLaughlin, *Org. Syn.*, **51**, 4 (1971).

[9] F. Freeman, P. D. McCart, and N. J. Yamachika, *J. Amer. Chem. Soc.*, **92**, 4621 (1970).

[10] R. A. Stairs, *Can. J. Chem.*, **38**, 2028 (1960); R. A. Stairs, D. G. M. Diaper, and A. L. Gatzke, *ibid.*, **41**, 1059 (1963).

[11] F. Freeman and N. J. Yamachika, *Tetrahedron Lett.*, 3615 (1969).

[12] C. N. Rentea, I. Necsoiu, M. Rentea, A. Ghenciulescu, and C. D. Nenitzescu, *Tetrahedron*, **22**, 3501 (1966).

[13] V. Psemetchi, I. Necsoiu, M. Rentea, and C. D. Nenitzescu, *Rev. Chim. (Bucharest)*, **14**, 1567 (1969).

[14] C. D. Nenitzescu, *Bull. Soc. Chim. Fr.*, 1349 (1968).

[15] L. V. Sulima and I. P. Gragerov, *J. Gen. Chem. USSR*, **29**, 3787 (1959).

[16] F. Freeman, R. H. DuBois, and N. J. Yamachika, *Tetrahedron*, **25**, 3441 (1969).

[17] K. B. Wiberg, B. Marshall, and G. Foster, *Tetrahedron Lett.*, 345 (1962).

[18] C. N. Rentea, M. Rentea, I. Necsoiu, and C. D. Nenitzescu, *Rev. Chim. (Bucharest)*, **12**, 1495 (1967).

[19] I. Necsoiu, A. Ghenciulescu, M. Rentea, C. N. Rentea, and C. D. Nenitzescu, *ibid.*, **12**, 1503 (1967).

[20] F. Freeman and N. J. Yamachika, *J. Amer. Chem. Soc.*, **92**, 3730 (1970).

[21] G. G. Henderson and T. Gray, *J. Chem. Soc.*, **85**, 1041 (1904).

[22] A. L. Gatzke, R. A. Stairs, and D. G. M. Diaper, *Can. J. Chem.*, **46**, 3695 (1968).

[23] A. Ghenciulescu, I. Necsoiu, M. Rentea, and C. D. Nenitzescu, *Rev. Chim. (Bucharest)*, **14**, 1543 (1969).

[24] D. H. R. Barton, P. J. L. Daniels, J. F. McGhie, and P. J. Palmer, *J. Chem. Soc.*, 3675 (1963).

[25] H. C. Duffin and R. B. Tucker, *Tetrahedron*, **24**, 389 (1968).

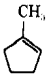
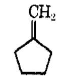
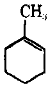
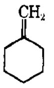
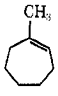
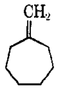
[26] O. H. Wheeler, *Can. J. Chem.*, **36**, 667 (1958).

[27] A. Étard, *C. R. Acad. Sci.*, **84**, 127 (1877).

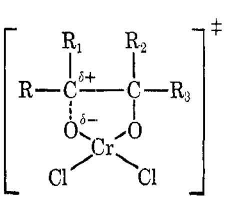
[28] Isolation and/or nonreductive hydrolysis of the hygroscopic and amorphous organometallic complex **1** give(s) rise to a variety of side reactions including chlorination, isomerization, oxidation of the initial product, and carbon–carbon double bond cleavage.[7,8,15]

TABLE I

PRODUCTS OF THE CHROMYL CHLORIDE OXIDATION OF CYCLOALKENES

Endocyclic cycloalkene	Overall yield, %	(% Yield) Products (% Yield)	Overall yield, %	Exocyclic cycloalkene
	56[a]	(84.6) 2-Methylcyclopentanone (72.0) (1.4) Cyclopentanecarboxaldehyde (17.5) (4.2) 2-Chloro-2-methylcyclopentanone (4.7) (9.9) 2-Methylcyclopentan-3-one (5.8)	40[a]	
	68[b]	(52.5) 2-Methylcyclohexanone (29.1)[a] Cyclohexanecarboxaldehyde (47.1)[a] (38.5) 1-Methylcyclopentanecarboxaldehyde (23.8)[a] (9.3) 2-Chloro-2-methylcyclohexanone		
	60[a]	(52.8) 2-Methylcycloheptanone (31.5) (3.9) Cycloheptanecarboxaldehyde (28.3) (26.4) 1-Methylcyclohexanecarboxaldehyde (25.3) (11.1) 2-Methylcyclohepten-3-one (5.7) 2-Chloro-2-methylcycloheptanone Cycloheptanone (12.4) Cyclooctanone (2.5)	68[a]	

[a] Reference 12. [b] Reference 11.



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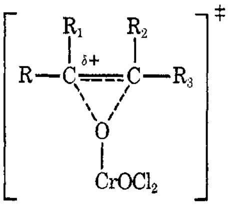

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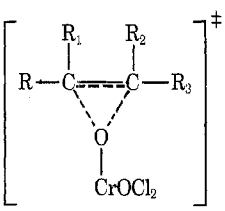

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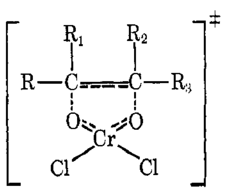

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to (oxidation of) carbon-carbon double bonds in a variety of cycloalkenes. The kinetics, which measure the rate of formation of the chromyl chloride-cycloalkene adduct **1**, were determined in a spectrophotometric stopped-flow system owing to the very fast rates of oxidation.[1,9,20,29]

Experimental Section

Solutions of cycloalkene and chromyl chloride, in specially purified solvents,[9] were prepared immediately prior to use.

Cycloalkenes.—The cycloalkenes were obtained commercially: cyclopentene,[30] 1-methylcyclopentene,[30] 1,2-dimethylcyclopentene,[31] cyclohexene,[32] 1-methylcyclohexene,[33] 3-methylcyclohexene,[30] 4-methylcyclohexene,[30] 1,3-dimethylcyclohexene,[31] 1,4-dimethylcyclohexene,[31] 1-acetylcyclohexene,[30] cycloheptene,[30] 1-methylcycloheptene,[30] cyclooctene,[34] cyclododecene (mixture of *cis* and *trans* isomers),[34] and bicyclo[2.2.1]hept-2-ene.[30] The cycloalkenes were refluxed for at least 2 hr with $LiAlH_4$,[35] in order to remove any peroxides, before distillation.

Solvent Purification.—Carbon tetrachloride,[36] chloroform,[36] and methylene chloride[36] were purified as previously described.[9]

Chromyl chloride (Alfa Inorganics, Inc.) was distilled and the middle fraction, bp 114.5–115.5°, was used.

Kinetic Measurements.—The rapid rate of oxidation was followed by observing the disappearance of chromyl chloride in a stopped flow reactor[1,9,11,20,29] at 415 and 440 mμ[37,38] under pseudo-first-order conditions (large excess of cycloalkene). Some runs with bicyclo[2.2.1]hept-2-ene were also performed under second-order conditions owing to the extremely fast rate of reaction. The pseudo-first-order rate constants (k_ψ) were obtained from the slopes of plots of $-\ln\,[\log\,(T_\infty/T)]$ *vs.* time. T_∞ is the per cent transmission at a point just before the chromyl chloride-cycloalkene adduct **1** begins to precipitate. All rate constants given in the tables are the average of two or more determinations, and were calculated on a CDC 3300 computer.[39] A Forma Model 2095-2 refrigerated and heated bath circulator was used to maintain constant temperature (±0.02°).

Results

Table II summarizes the kinetic data for the chromyl chloride addition to (oxidation of) cyclohexene to give the cycloalkene-chromyl chloride adduct **1**. The

TABLE II

KINETIC DATA FOR THE CHROMYL CHLORIDE OXIDATION OF CYCLOHEXENE AT 10.0° [a]

[Cyclohexene], $\times 10^3 M$	$[CrO_2Cl_2]$, $\times 10^4\,M$	k_ψ,[b] sec^{-1}	k_2,[c] M^{-1} sec^{-1}
4.9	4.5	0.006	1.20
9.9	4.5	0.011	1.10
14.8	4.5	0.016	1.09
24.7	4.5	0.020	1.05
29.6	4.5	0.031	1.02
34.6	4.5	0.037	1.20
39.5	4.5	0.048	1.21
39.5[d]	3.9	0.041	1.05
39.5[d]	5.9	0.041	1.02
39.5[d]	7.9	0.046	1.18
39.5[d]	9.9	0.052	1.31
39.5[d]	11.8	0.053	1.35

[a] Carbon tetrachloride solvent, λ = 415 mμ. [b] Pseudo-first-order rate constant. [c] Second-order rate constant = k_ψ/[cyclohexene]. [d] λ = 440 mμ.

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(29) K. B. Wiberg and R. D. Geer, *J. Amer. Chem. Soc.*, **87**, 5202 (1965); **88**, 5827 (1966).

(30) Aldrich Chemical Co., Inc.

(31) Chemical Samples Co.

(32) Matheson Coleman and Bell.

(33) K & K Laboratories, Inc.

(34) Sample from Columbian Carbon Co., Inc.

(35) Metal Hydrides Inc.

(36) Mallinckrodt Chemical Works.

(37) O. H. Wheeler, *Can. J. Chem.*, **38**, 2137 (1960).

(38) A. Bartecki, *Rocz. Chem.*, **38**, 1455 (1964).

(39) K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, New York, N. Y., 1965, p 165.

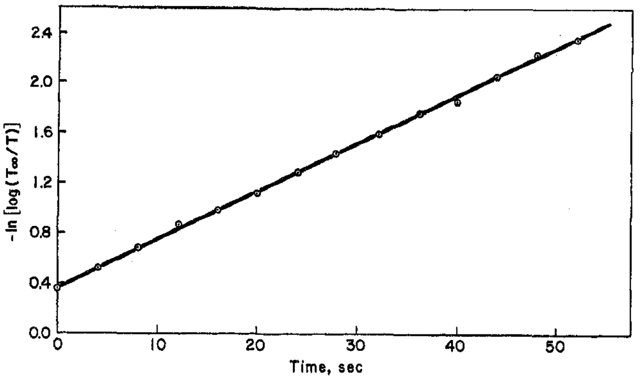


Figure 1.—First-order plot for the reaction of 1-methylcyclohexene with chromyl chloride in carbon tetrachloride; $[CrO_2Cl_2] = 4.5 \times 10^{-4}\ M$, [1-methylcyclohexene] $= 4.2 \times 10^{-3}\ M$, $\lambda = 415$ mμ, $T = 0°$.

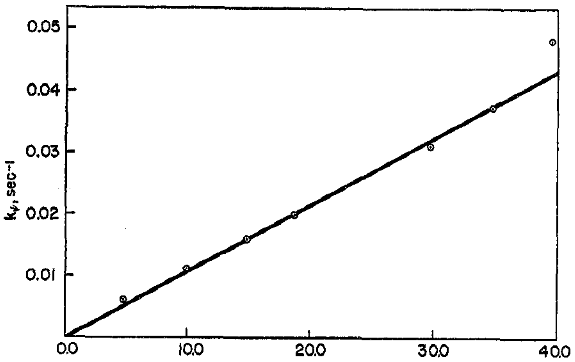


Figure 2.—Effect of cyclohexene concentration on the pseudo-first-order rate constants (k_ψ) for the chromyl chloride oxidation of cyclohexene in CCl_4 at 10.0°.

constancy of the value of the second-order rate constant ($k_2 = k_\psi/$[cyclohexene]), at constant chromyl chloride concentration, over an eightfold range of cyclohexene concentration suggests a first-order dependence on the cycloalkene. It is also seen from Table II that at constant cyclohexene concentration, the pseudo-first-order rate constant (k_ψ) does not alter appreciably over a threefold range of chromyl chloride concentration at 440 mμ. With a tenfold excess of 1-methylcyclohexene good first-order plots were obtained (Figure 1). Thus, further support is given for the first-order dependence on chromyl chloride. Additional support for the first-order dependence on cycloalkene is seen in a plot of k_ψ against cyclohexene concentration (Figure 2) or 1-methylcyclohexene concentration (Figure 3) which gives a straight line that passes through the origin. These data suggest the following rate law.

$$\frac{-d[CrO_2Cl_2]}{dt} = k[\text{cycloalkene}][CrO_2Cl_2] \qquad (2)$$

Effect of Solvents on Rates.—Table III shows the effects of carbon tetrachloride, chloroform, and methylene chloride on the rate of chromyl chloride oxidation of 1-methylcyclohexene at 10.0°. Several empirical parameters for estimating solvent polarity are also presented.

Effect of Strain Energies on Rates.—The effects of strain energy on the chromyl chloride oxidation of the lower cycloalkenes are presented in Table IV.

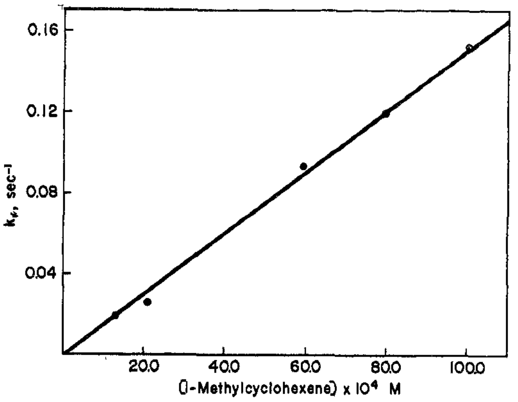


Figure 3.—The linear dependence of the pseudo-first-order rate constants on increasing concentration of 1-methylcyclohexene at constant chromyl chloride concentration in CCl_4 at 10.0°.

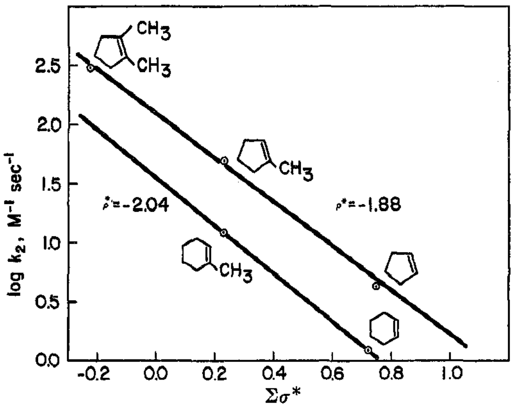


Figure 4.—Relations between rate constants and substitution of methyl groups at carbon–carbon double bonds of cyclopentene and cyclohexene.

TABLE III

EFFECT OF SOLVENTS ON THE RATE OF CHROMYL CHLORIDE OXIDATION OF 1-METHYLCYCLOHEXENE[a]

Solvent	k_2,[b] M^{-1} sec^{-1}	Relative rate	μ[c,d]	ϵ[d,e]	E_T[f]	Z[g]	S[h]
CCl_4[i]	12.1	1.00	0.00	2.24	32.5	52.4	−0.245
$CHCl_3$[j]	49.1	4.05	1.15	4.81	39.2	63.2	−0.200
CH_2Cl_2[k]	211	17.4	1.55	9.08	41.1	64.2	−0.189

[a] $[CrO_2Cl_2] = 4.05 \times 10^{-4}\ M$, $\lambda = 415$ mμ, $T = 10.0°$. [b] Second-order rate constant $= k_\psi/$[1-methylcyclohexene]. [c] Dipole moment. [d] J. A. Riddick and E. Toops, Jr., "Organic Solvents," Vol. VII of "Techniques of Organic Chemistry," A. Weissberger, Ed., Interscience, New York, N. Y., 1965. [e] Dielectric constant. [f] K. Dimroth, C. Reichardt, T. Siepman, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963). [g] E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958). [h] S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960). [i] [1-Methylcyclohexene] $= 42.1 \times 10^{-4}\ M$. [j] [1-Methylcyclohexene] $= 93.0 \times 10^{-4}\ M$. [k] [1-Methylcyclohexene] $= 21.9 \times 10^{-4}\ M$.

Thermodynamic Parameters and Relative Rates.—The rates of the chromyl chloride oxidation of 15 cycloalkenes were determined at several temperatures. Table V summarizes the data for the activation parameters and the relative rates (to cyclohexene) of oxidation, and Figure 4 shows the relation between rates and substitution of methyl groups at the carbon–carbon double bonds of cyclopentene and cyclohexene.

Relation between Rates of Oxidation and Ionization Potentials.—A correlation between ionization potentials and logarithm of relative rates (to 1-hexene) for the

Table IV

Effect of Strain Energies on the Chromyl Chloride Oxidation of Cycloalkenes

Cycloalkane	$-\Delta H$,[a] kcal/mol	Total[b] strain, kcal/mol	$-\Delta H$,[c] kcal/mol	k_2,[d] M^{-1} sec^{-1}	Cycloalkene
Cyclopentane	793.52[e]	6.5	25.7[f]	4.51	Cyclopentene
Cyclohexane	944.48[e]	0.0	27.10[f]	1.10	Cyclohexene
Cycloheptane	1108.2[e]	6.3	25.85[f]	4.72	Cycloheptene
Cyclooctane	1269.2[e]	9.6	23.62[f]	4.84	*cis*-Cyclooctene
Cyclododecane	1884.2[e,g]	3.4[h]	20.67[f]	1.25[i]	*cis*-Cyclododecene

[a] Heat of combustion for gaseous hydrocarbons to give liquid water at 25.0°. [b] Calculated by subtracting (number of CH_2 groups × 157.4) from the observed heat of formation. [c] Heat of hydrogenation in acetic acid solution at 25.0°. [d] Second-order rate constant for chromyl chloride oxidation at 10.0° [e] S. Kaarsemaker, and J. Coops, *Recl. Trav. Chim. Pays-Bas,* 71, 261 (1952); J. Coops, H. van Kamp, W. A. Lambgrets, B. J. Visser, and H. Dekker, *ibid.*, 79, 1226 (1960). [f] R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957). [g] Solid state. [h] K. B. Wiberg, *J. Amer. Chem. Soc.*, **87**, 1070 (1965). [i] Mixture of cis and trans isomers.

Table V

Relative Rates and Thermodynamic Parameters for the Chromyl Chloride Oxidation of Some Cycloalkenes[a]

Registry no.	Cycloalkene	k_2,[b] M^{-1} sec^{-1}	Relative rate	$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol
110-83-8	Cyclohexene	1.10	1.0	10.1	23.6	16.5
591-49-1	1-Methylcyclohexene	12.1	11	3.21	42.2	14.9
591-48-0	3-Methylcyclohexene	3.95	3.6	9.90	20.7	15.7
591-47-9	4-Methylcyclohexene	1.35	1.2			
2808-76-6	1,3-Dimethylcyclohexene	36.1	32.8	10.6	14.0	14.5
2808-79-9	1,4-Dimethylcyclohexene	15.1	13.7	7.80	25.5	14.9
932-66-1	1-Acetylcyclohexene	0.15	0.14	8.50	32.1	17.4
142-29-0	Cyclopentene	4.51	4.1[c,d]	8.90[d]	23.5[d]	
693-89-0	1-Methylcyclopentene	48.6	44.2	5.07	32.8	14.2
765-47-9	1,2-Dimethylcyclopentene	299	273	4.39	31.5	13.2
628-92-2	Cycloheptene	4.72	4.3	6.69	31.7	15.5
1453-25-4	1-Methylcycloheptene	182	165			
931-88-4	Cyclooctene	4.84	4.4	3.55	42.7	15.4
1501-82-2[e]	Cyclododecene	1.25[e]	1.1	8.26	28.8	16.3
498-66-8	Bicyclo[2.2.1]hept-2-ene	562	511			

[a] Carbon tetrachloride solvent, $T = 10.0°$, $\lambda = 415$ mμ. [b] Second-order rate constant = $k_{\psi}/$[cycloalkene]. [c] Relative rates at 5.0° and 15.0° = 4.9 and 4.5, respectively. [d] Reference 11. [e] Mixture of cis and trans isomers.

Table VI

Ionization Potentials and Log Relative Rates (to 1-Hexene) for the Chromyl Chloride Oxidation of Some Unsaturated Hydrocarbons

Unsaturate	k_2,[a] M^{-1} sec^{-1}	k_2/k_2(1-hexene)[b]	log $k_{2\,\mathrm{rel}}$[c]	Ionization potential, eV
2,3-Dimethyl-2-butene	287.5	4107	3.613	8.30,[e] 8.4,[f] >8.5[g]
Bicyclo[2.2.1]hept-2-ene	562[h]	8028.6	3.904	8.83,[i] 8.95,[j] 9.20[k]
Styrene	26.9[d]	384.3	2.584	8.43,[l] 8.47[m]
Cyclopentene	4.51[h]	64.4[h]	1.809	9.01,[m] 9.00,[l] 9.3[f]
Cyclohexene	1.22[h]	17.43[h]	1.241	8.72,[n] 9.2[f]
1-Pentene	0.09[d]	1.29	0.110	9.50[m]
cis-2-Pentene	1.11[d]	15.86	1.200	9.11[o]
trans-2-Pentene	1.01[d]	14.43	1.159	9.06[o]
1-Hexene	0.07[d]	1.00	0.000	9.45[e]

[a] Second-order rate constant = $k_{\psi}/[{>}C{=}C{<}]$ at 10.0°. [b] Second-order rate constant for oxidation of 1-hexene [c] Relative to 1-hexene. [d] References 3 and 9. [e] R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc. Ser. A*, **258**, 459 (1960). [f] J. L. Charlton, C. C. Liao, and P. de Mayo, *J. Amer. Chem. Soc.*, **93**, 2463 (1971). [g] R. J. Cvetanovic, *J. Chem. Phys.*, **30**, 19 (1959). [h] This work. [i] N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Amer. Chem. Soc.*, **92**, 19 (1970). [j] W. C. Steele, B. H. Jennings, G. L. Botyos, and G. O. Dudek, *J. Org. Chem.*, **30**, 2886 (1965). [k] D. A. Demeo and A. J. Yencha, *J. Chem. Phys.*, **53**, 4536 (1970). [l] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969). [m] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962). [n] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964). [o] J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **81**, 2064 (1959).

chromyl chloride oxidation of nine unsaturated hydrocarbons is shown in Table VI and Figure 5.

Comparison of the Ratio of Relative Reactivities.—Table VII shows a comparison of the ratio of relative reactivities for reactions proceeding *via* three-membered and five-membered cyclic activated complexes.

Discussion

The kinetic data above clearly show that the chromyl chloride oxidation of cycloalkenes is first order with respect to reductant and to oxidant. This also is consistent with the observed second-order rate law for the chromyl

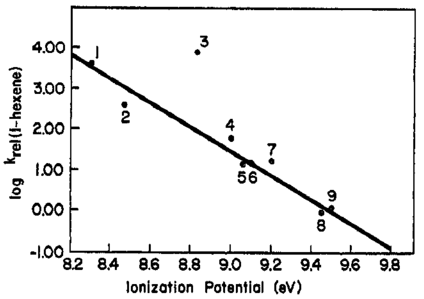
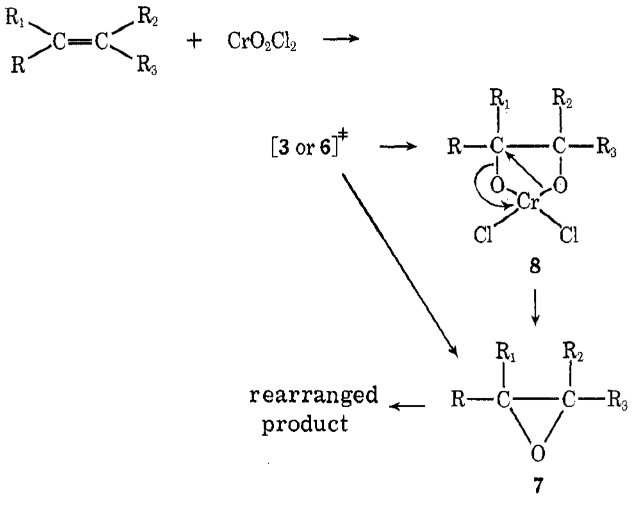


Figure 5.—Relation between log relative rate of chromyl chloride oxidation (to 1-hexene) and ionization potentials. The unsaturated compounds for the number points are as follows: 1, 2,3-dimethyl-2-butene; 2, styrene; 3, bicyclo[2.2.1]hept-2-ene; 4, cyclopentene; 5, *trans*-2-pentene; 6, *cis*-2-pentene; 7, cyclohexene; 8, 1-hexene; 9, 1-pentene.

chloride oxidation of alkenes[9] and styrenes.[1,20] Since structurally rearranged products are obtained from the oxidation of unsaturated hydrocarbons, it is reasonable to assume that positively charged product-determining intermediates are formed after the rate-determining steps. These intermediates could resemble **2** or they could be the corresponding epoxides.[1,40-45] Rearrangement of the epoxide **7** under the hydrolytic conditions would lead to the observed aldehydes and ketones.[7]

Although the intermediacy of epoxides **7** in the chromyl chloride oxidation of carbon–carbon double bonds remains to be demonstrated, it is possible that they could be formed from the proposed cyclic activated complexes **3–6**, from a cyclic chromium(IV) ester **8** (Scheme I), or from an intermediate carbonium ion **9** (Scheme II).

SCHEME I



If the addition of chromyl chloride to cycloalkenes is expected to be electrophilic in nature, then an increase of electron availability in the carbon–carbon double bond should increase the rate of reaction. Table

TABLE VII

RELATIVE REACTIVITIES OF CYCLOPENTENE (A), CYCLOHEXENE (B), AND BICYCLO[2.2.1]HEPT-2-ENE (C) IN REACTIONS INVOLVING THREE- AND FIVE-MEMBERED CYCLIC ACTIVATED COMPLEXES

Reaction	Temp, °C	Size of cyclic activd complex	k_2, M^{-1} min^{-1} A	B	C	Ratio of relative rates A/B	Δ^a	C/B	Δ^a	C/A	Δ^a
Chromyl chloride oxidation	$10^{b,c}$	3^b	4.51^d	1.10^d	562^d	4.1	1.0	511	1.0	125	1.0
Chromic acid oxidation	25^e	3	0.931	0.724	3.97	1.3	3.1	5.5	93	4.3	29
Epoxidation	$25.8^{f,g}$	3	$0.185\text{–}0.195^g$	0.129^g		1.5	2.7				
	25^h	3		$0.0192^{d,h}$	$0.0228^{d,h}$			1.2	426		
Bromine addition	25^i	3	0.040	0.030		1.3	3.1				
Dibromocarbene addition		3				1.25^j	3.3				
Silver complex formation	40^k	3	7.3	3.6	62	2.0	2.0	17	30	8.5	14.7
Diphenylnitrilimine cycloaddition	$\sim 80^{l,m}$	5				~12	0.34	284	1.8	~24	5.2
Benzonitrile oxide cycloaddition	20^n	5				19	0.22	1800	0.28	93	1.3
Phenyl azide cycloaddition	$25^{d,o}$	5	1.86×10^{-7}	0.033×10^{-7}	188×10^{-7}	57	0.07	5700	0.09	101	1.2
	$25^{d,p}$	5	1.83×10^{-7}	$(3.3 \times 10^{-9})^{d,o,q}$	2.15×10^{-5}	56	0.07	6500	0.08	115	1.1
Picryl azide cycloaddition	$25^{d,p}$	5	1.08×10^{-4}	2.55×10^{-6}	2.04×10^{-2}	42	0.1	8000	0.06	190	0.6

[a] Δ is the ratio of the chromyl chloride oxidation ratio and the ratio of the comparative reaction. [b] This work. [c] Reference 11. [d] Time unit is sec^{-1}. [e] 0.002 M sulfuric acid in 95% w/w acetic acid. A. K. Awasthy and J. Roček, *J. Amer. Chem. Soc.*, **91**, 991 (1969). [f] D. Swern, *Chem. Rev.*, **45**, 49 (1949). [g] Peracetic acid in acetic acid solution. J. Böeseken and J. Stuurman, *Recl. Trav. Chim. Pays-Bas*, **56**, 1034 (1937). [h] Perlauric acid in chloroform. K. D. Bingham, G. D. Meakins, and G. H. Whitham, *Chem. Commun.*, 445 (1966). [i] Acetic acid solvent. P. W. Robertson, J. K. Heyes, and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952). [j] Potassium *tert*-butoxide and bromoform. P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956). [k] Equilibrium constant (l./mol) for formation of silver nitrate–unsaturate complex in 1,2-dihydroxyethane. M. A. Muks and F. T. Weiss, *ibid.*, **84**, 4697 (1962). [l] Boiling benzene solvent except for cyclopentene. R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 819. [m] A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillick, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192 (1967); R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962). [n] Ether solvent. Table VII, ref *l*, p 826. [o] Carbon tetrachloride solvent. R. Huisgen, G. Szeimies, and L. Möbius, *Chem. Ber.*, **100**, 2494 (1967). [p] Chloroform solvent. A. S. Bailey and J. E. White, *J. Chem. Soc. B*, 819 (1966). [q] Carbon tetrachloride solvent. R. Huisgen, L. Möbus, G. Muller, H. Stangl, G. Szeimies, and J. M. Vernon, *Chem. Ber.*, **98**, 3992 (1965).

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[40] Epoxides have been isolated in the chromyl acetate oxidation of alkenes and styrenes,[41,42] and in the chromic acid oxidation of allylic alcohols,[43] cyclohexene,[44] and styrenes.[45]

[41] M. A. Davis and W. J. Hickinbottom, *J. Chem. Soc.*, 2205 (1958).

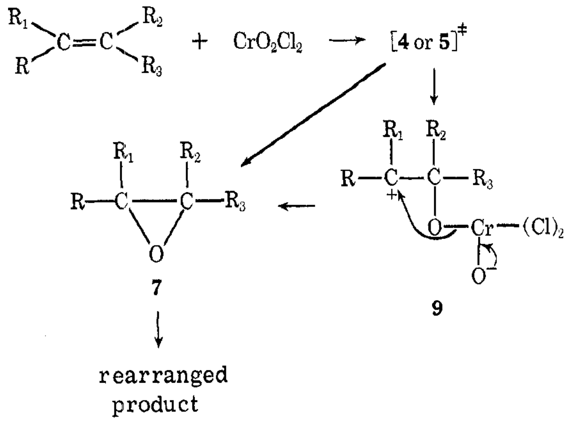
[42] W. A. Mosher, F. W. Steffgen, and P. T. Lansbury, *J. Org. Chem.*, **26**, 670 (1961).

[43] P. S. Kalsi, K. S. Kumar, and M. S. Wadia, *Chem. Ind. (London)*, 71 (1971).

[44] J. Roček and J. C. Drozd, *J. Amer. Chem. Soc.*, **92**, 6668 (1970).

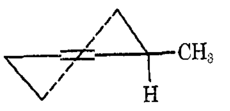
[45] W. J. Hickinbottom and G. E. M. Moussa, *J. Chem. Soc.*, 4195 (1957); G. E. M. Moussa, *J. Appl. Chem.*, **12**, 385 (1962).

SCHEME II

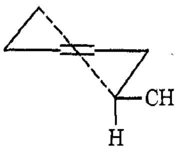


V shows that 1-methylcyclohexene is oxidized 12 times as fast as cyclohexene. In contrast, the electron-attracting acetyl group on the cyclohexene ring slows the rate by a factor of approximately seven. It is also seen that 1-methylcyclopentene and 1,2-dimethylcyclopentene are approximately 11 and 66 times as reactive as cyclopentene. In these respects the chromyl chloride oxidation closely resembles electrophilic reactions (*e.g.*, bromine addition, chromic acid oxidation, epoxidation) which involve three-membered cyclic activated complexes.

It is of interest to note that 3-methyl- and 4-methylcyclohexene (**10**, **11**) are oxidized slightly faster than cyclohexene. In contrast, remote alkyl substituents retard the rates of epoxidation with *m*-chloroperbenzoic acid[46] and the addition of 2,4-dinitrobenzenesulfenyl chloride[47] to various cyclohexene derivatives. The similarity in the rates of oxidation among cyclohexene, **10**, and **11** precludes an evaluation of the contribution of conformation, inductive, and steric effects. Inductive effects at the carbon–carbon double bond are indeed important, as is shown in the linear free energy of log k *vs.* $\Sigma\sigma$ (Figure 4),[48,49] and the steric and conformation factors in **10** and **11** could be small, since the methyl groups are probably in the equatorial positions.[9,50] The lesser enhancing effect of the methyl group in the four position is also seen when the rates of oxidation for 1,3-dimethyl- and 1,4-dimethylcyclohexene are compared.



10



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The relations between rate constants and substitution of methyl groups at the carbon–carbon double bonds of cyclopentene and cyclohexene are shown in Figure 4. A ρ^* of -2.04 is obtained from the two-point line for cyclohexene and 1-methylcyclohexene, and a ρ^* of -1.88 ($r = 0.997$, $s = 0.093$) is obtained for 1-methyl- and 1,2-dimethylcyclopentene.[49,50] These values are comparable to those reported for the chromyl chloride oxidation of alkenes ($\rho^* = -2.63$)[9] and styrenes ($\rho^+ = -1.99$),[20] and are compatible with activated complexes with a small degree of carbonium ion character.[20,51] Consequently, the observed ρ^* values for the chromyl chloride oxidation of cycloalkenes are not inconsistent with the formulation of unsymmetrical **3** or **4** as the activated complex.

A plot of ionization potential, which is a measure of electron availability, *vs.* log $k_{\mathrm{rel(1\text{-}hexane)}}$ (Figure 5 and Table VI) is also compatible with an electrophilic attack of chromyl chloride at the carbon–carbon double bond. In qualitative terms, cyclopentene, cyclohexene, and bicyclo[2.2.1]hept-2-ene might not be expected to give an excellent fit to the line owing to torsional strain, bond angle bending strain, and nonbonding interactions. However, it is seen that only the bicyclic system shows a large deviation from the line. Consequently, the possibility of a change in mechanism for the oxidation of bicyclo[2.2.1]hept-2-ene must also be considered.

In Table III it is noted that solvents which are empirically regarded as having higher polarity cause an increase in the rate of oxidation. This result is consistent with the development of a partially charged cyclic activated complex (**3** or **4**) in the transition state region from initially neutral cycloalkene and chromyl chloride.

Table IV shows the complex relation between strain energies and rate constants in the chromyl chloride oxidation of cycloalkenes. Since the heat of hydrogenation reflect strain energies in *both* the unsaturated and saturated compounds, interpretation of these data must be done with care. Garbisch and coworkers[52] have calculated that cyclopentene and bicyclo[2.2.1]-hept-2-ene are more strained than cyclohexene by approximately 3.7 and 9.7 kcal/mol, respectively. A considerable amount of this strain is relieved in reactions involving cyclic four-, five-, or six-membered activated complexes.[53] Therefore, the comparable rate constants for oxidation of cyclopentene and cyclohexene suggest that there is not a significant relief of strain and that the activated complex probably shows a close resemblance to **4**. Alternatively, the very small rate difference may be due to an activated complex which closely resembles the reactants.[54,55]

An examination of the relative rates and the ratios of reactivities in Table VII reveals that the chromyl chloride oxidation of cyclopentene and cyclohexene is remarkably similar to other reactions leading to cyclic three-membered activated complexes. In contrast, the bicyclo[2.2.1]hept-2-ene–cyclohexene ratio appears

(46) B. Rickborn and S. Y. Lwo, *J. Org. Chem.*, **30**, 2212 (1965).

(47) H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961).

(48) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556.

(49) The $\Sigma\sigma^*$ for the cycloalkenes was calculated as follows: in cyclohexene the C=C was considered as having two *n*-butyl groups (-0.26) and two hydrogens (0.98) = $\Sigma\sigma^* = 0.72$. In this manner $\Sigma\sigma^*$ values of 0.23, 0.75, 0.26, and -0.23 were calculated for 1-methylcyclohexene, cyclopentene, and 1-methyl- and 1,2-dimethylcyclopentene, respectively. Perchance treating cycloalkenes as substituted ethenes is an oversimplication, since chromyl chloride oxidations presumbably proceed *via* a highly ordered activated complex and there may be small but significant variations in activation parameters owing to steric effects and *I* strain. However, it is also recognized that chromyl chloride oxidations are not particularly susceptible to steric effects.[9]

(50) A. I. Scott and A. D. Wrixon, *Tetrahedron*, **27**, 4787 (1971).

(51) ρ^+ values larger than -3 are generally observed in reactions with a large degree of carbonium ion character in the activated complex.

(52) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Peterson, and C. M. Sprecher, *J. Amer. Chem. Soc.*, **87**, 2932 (1965).

(53) Table VII, ref *e*.

(54) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(55) R. E. Erickson and R. L. Clark, *Tetrahedron Lett.*, 3997 (1969).

to suggest a five-membered cyclic activated complex (**3** or **6**) for the bicyclic system.[53]

3, **4**, **5**, or **6** would require the large negative entropies of activation (−23.5 to −42.7 eu) tabulated in Table V. $\Delta S^{\ddagger}$ values of this magnitude have been observed for reactions, *e.g.*, epoxidation, 1,3-dipolar cycloadditions, with rigid orientation requirements in the activated complex.

We conclude from the kinetic studies and the comparative rate data that the activated complex for the chromyl chloride oxidation of cycloalkenes can be represented by the partially charged unsymmetrical structure **4**.[56] **4** is consistent with the rapid rate of oxidation in solvents of low polarity and with the ρ^* of approximately −2.0. In this postulated mechanism, which is similar to the one proposed by Bartlett[57-59] for epoxidation, oxygen transfer from chromyl chloride occurs by a concerted process. That is, as the two new σ bonds are being formed, the oxygen–chromium bond is being broken.[60] After the rate-determining step, this mechanism could lead to a product-determining epoxide intermediate (Scheme II). Activated complexes similar to **4** and **5** have also been proposed for the chromic acid[44] and chromyl acetate[42] oxidation of carbon–carbon double bonds.[40,56]

The limited comparative rate data suggest that the activated complex for the chromyl chloride oxidation of bicyclo[2.2.1]hept-2-ene *probably* has a close resemblance to **3** or **6**. Additional studies on more bicyclic systems are in process in order to fully elucidate the mechanism.

Registry No.—Chromyl chloride, 7791-14-2.

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[56] The symmetrical species **5** and **6** could have sufficient carbonium ion character to satisfy $\rho^* \cong -2.0$. It is also recognized that the oxidation is a process in which there is a net flow of electrons from the substrate through the oxidant. This results in the inevitable development of a partial positive charge either on the carbon atoms of the double bond or on the oxygen atom, and of a partial negative charge on the chromium atom undergoing a valency change or on its ligands.

[57] P. D. Barteltt, *Rec. Chem. Progr.*, **11**, 47 (1950).

[58] A $\rho = -1.20$ has been obtained for the epoxidation of stilbenes with peroxybenzoic acid: B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955); Y. Ogata and I. Tabushi, *J. Amer. Chem. Soc.*, **83**, 3440 (1961).

[59] D. Swern, "Organic Peroxides," Vol. II, Wiley, New York, N. Y., 1971, p 355.

[60] Concerted closure of the two incipient σ bonds does not necessarily mean that the development of the bonds has proceeded to the same degree in the activated complex. Any difference between the bond-making rates during the activation process would lead to a partial charge at the more substituted carbon atom.

Silation of Dichloromethyllithium in the Presence of Excess *n*-Butyllithium

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The silation of a −100° solution of 2 equiv of *n*-butyllithium and 1 equiv of methylene chloride in THF–hexane with trimethylchlorosilane leads to a complex product mixture of butyltrimethylsilane (**3**), dichloro(trimethylsilyl)methane (**1**), bis(trimethylsilyl)chloromethane (**4**), bis(trimethylsilyl)dichloromethane (**2**), tris(trimethylsilyl)methane (**5**), 1,1-di(trimethylsilyl)-1-chloropentane (**6**), and tris(trimethylsilyl)chlorosilane (**7**). Experimental evidence is presented that indicates that successive silation of monolithio intermediates is occurring rather than production of dilithiodichloromethane.

It has been reported[1] that additions of *n*-butyllithium to cold (−100°) solutions of methylene chloride and trimethylchlorosilane in tetrahydrofuran (THF) give respectable yields of dichloro(trimethylsilyl)methane (**1**) and bis(trimethylsilyl)dichloromethane (**2**), depending on the quantity of reagents used (eq 1 and 2). In repeating this second reaction, we found it

$$1Me_3SiCl + 1CH_2Cl_2 + 1BuLi \xrightarrow[51\%]{THF,\ -100^\circ} \underset{\mathbf{1}}{Me_3SiCHCl_2} \quad (1)$$

$$2Me_3SiCl + 1CH_2Cl_2 + 2BuLi \xrightarrow[40\%]{THF,\ -100^\circ} \underset{\mathbf{2}}{Me_3SiCCl_2SiMe_3} \quad (2)$$

to be quite complex, regardless of whether the reaction was done *in situ* as Bamford and Pant describe or if the intermediate, dichloromethyllithium ($LiCHCl_2$), was preformed prior to addition of trimethylchlorosilane.

When trimethylchlorosilane was added last to a cold solution of 2 equiv of *n*-butyllithium to 1 equiv of methylene chloride in THF as the solvent, compound **2** was formed in approximately 50% yield (based on vpc). The other 50% of the reaction products was composed of compounds **1** and **3**–**7**. The silated products were isolated by preparative gas chromatography and characterized by infrared, nmr, and mass spectra,[2] elemental analysis, and comparisons to previously reported properties[1,3-7] (see Experimental Section for details and relative amounts). Additional structure proof of compound **2** was provided by its hydride reduction to a mixture of **4** and bis(trimethylsilyl)methane (**8**).[3] (Compound **4**, unlike **2**, reduces only very slowly with lithium aluminum hydride.)

Me_3SiBu **3**

$(Me_3Si)_2CHCl$ **4**

$(Me_3Si)_3CH$ **5**

$(Me_3Si)_2CClBu$ **6**

$(Me_3Si)_3CCl$ **7**

$(Me_3Si)_2CH_2$ **8**

$(Me_3Si)_4C$ **9**

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[1] W. R. Bamford and B. C. Pant, *J. Chem. Soc. C*, 1470 (1967).

[2] D. R. Dimmel, C. A. Wilkie, and F. Ramon, *J. Org. Chem.*, **37**, 2665 (1972).

[3] R. L. Merker and M. J. Scott, *J. Organometal. Chem.*, **4**, 98 (1965).

[4] R. Müller and G. Seitz, *Chem. Ber.*, **91**, 22 (1958).

[5] R. Mueller and S. Reichel, *ibid.*, **99**, 793 (1966).

[6] G. Fritz and J. Grobe, *Z. Anorg. Allg. Chem.*, **309**, 77 (1961).

[7] V. F. Mironov and N. A. Pogonkina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 182 (1955); *Chem. Abstr.*, **50**, 1574*d* (1956).