Halogenated Ketenes. XIV. Substituent Effects in Unsymmetrical Alkylhaloketene–Cyclopentadiene Cycloadditions[1]

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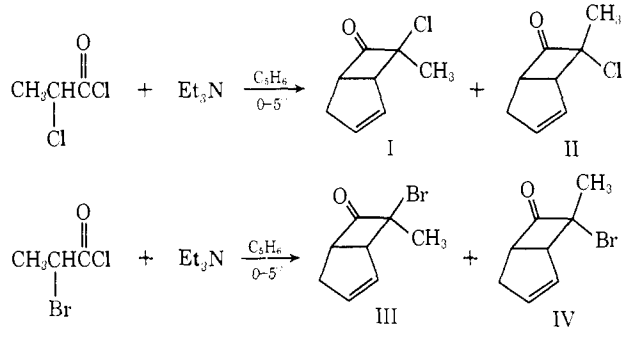
Contribution from the Department of Chemistry, North Texas State University, Denton, Texas. *Received January 17, 1970*

Abstract: The dehydrohalogenation of 2-haloalkanoyl halides with triethylamine in the presence of cyclopentadiene produces a distribution of *endo*-alkyl and *exo*-alkyl 1,2-cycloadducts. The isomers are the result of *in situ* cycloaddition of the alkylhaloketene with cyclopentadiene. The isomer distributions are dependent upon the nature of the substituents of the alkylhaloketene, the solvent media, and the reaction temperature. When the alkyl portion of the alkylhaloketene is systematically increased from methyl to *t*-butyl, the amount of the *endo*-alkyl isomer produced increases. The distributions are consistent with a concerted cycloaddition involving an orthogonal approach of the ketene and olefin as dictated by the principle or orbital symmetry conservation. The halogen of the alkylhaloketene is responsible for the strong solvent dependency of the *endo*/*exo*-alkyl isomer distributions. An application of the *endo*/*exo* isomer ratio distributions is suggested for distinguishing between concerted ketene–olefin cycloadditions and two-step processes.

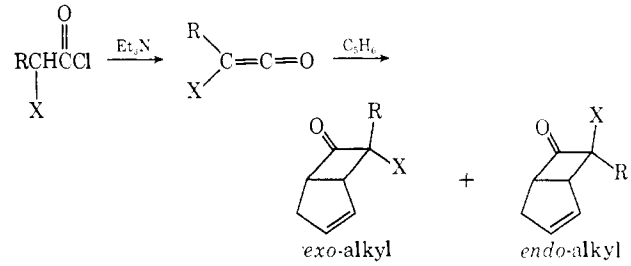
In preceding papers in this series, we have reported that the dehydrohalogenation of 2-halopropanoyl halides with triethylamine in the presence of cyclopentadiene produces both the *endo*- and *exo*-methyl 1,2-cycloaddition isomers.[2,3] Recent results indicate that the ratio of *endo*-methyl to *exo*-methyl cycloadduct isomers is not influenced by the residual double bond in cyclopentadiene.[4] However, it was noted that the isomer distribution of the cycloadducts is strongly dependent upon the solvent media. When 2-chloropropanoyl chloride was dehydrochlorinated in the presence of cyclopentadiene in hexane at 0–5°, an *endo*-/*exo*-methyl (I/II) distribution of 4.3 was observed as compared to an *endo*/*exo* distribution of 0.59 when acetonitrile was employed as the solvent. The dehydrochlorination of 2-bromopropanoyl chloride in the presence of cyclopentadiene yielded an *endo*-/*exo*-methyl (III/IV) distribution of 0.71 in hexane at 0–5° which became 0.14 in acetonitrile.



The purpose of this paper is to relate some findings which indicate that alkylhaloketenes react with cyclopentadiene by a concerted process involving an orthogonal approach of ketene and diene and show that the strong solvent dependency on the *endo*-/*exo*-alkyl isomer distribution is due to the halogen of the alkylhaloketene.

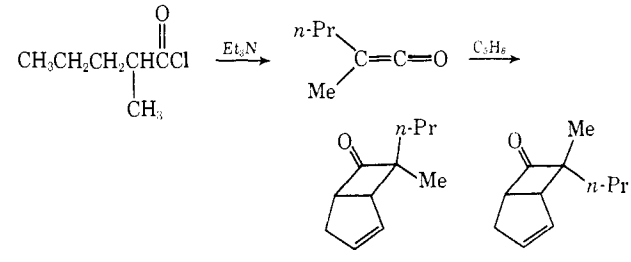
Results

The dehydrohalogenation of 2-chloro- and 2-bromoalkanoyl halides with triethylamine in the presence of cyclopentadiene has been examined in more detail in an effort to understand more fully the cyclobutanone isomer distributions previously reported. The alkyl substituent of the alkylhaloketene has been varied in an



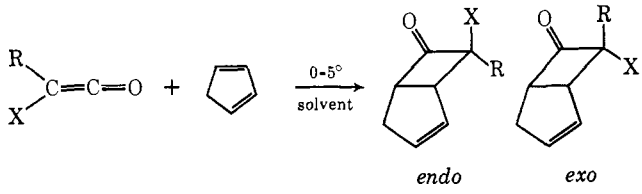
effort to determine the effect on the isomer distribution. Also, the effect of the solvent on the isomer distributions was determined by effecting each preparation in both hexane and acetonitrile. The results are shown in Table I.

Methyl-*n*-propylketene, an unsymmetrical dialkylketene, was prepared by the dehydrochlorination of 2-methylpentanoyl chloride and allowed to undergo an *in situ* cycloaddition with cyclopentadiene. The isomer



(1) Paper XII: W. T. Brady, F. H. Parry, III, R. Roe, Jr., E. F. Hoff, Jr., and L. Smith, *J. Org. Chem.*, **35**, 1515 (1970).
(2) W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966).
(3) W. T. Brady and B. M. Holifield., *Tetrahedron*, **23**, 4251 (1967).
(4) W. T. Brady, R. Roe, Jr., E. F. Hoff, Jr., and F. H. Parry, III, *J. Amer. Chem. Soc.*, **92** 146 (1970).

Table I. Substituent and Solvent Affects on Isomer Distributions



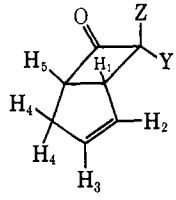
endo *exo*

R	X	Solvent	*endo/exo*	% yield
CH_3	Cl	Hexane	4.3	75
C_2H_5	Cl	Hexane	5.3	77
i-C_3H_7	Cl	Hexane	10	71
CH_3	Cl	Acetonitrile	0.59	62
C_2H_5	Cl	Acetonitrile	1.1	77
i-C_3H_7	Cl	Acetonitrile	1.1	55
CH_3	Br	Hexane	0.71	63
C_2H_5	Br	Hexane	1.6	70
i-C_3H_7	Br	Hexane	2.8	78
t-C_4H_9	Br	Hexane	~100	11
CH_3	Br	Acetonitrile	0.14	60
C_2H_5	Br	Acetonitrile	0.27	54
i-C_3H_7	Br	Acetonitrile	0.56	49
t-C_4H_9	Br	Acetonitrile	~100	54
n-C_3H_7	CH_3	Hexane	1.4	8
n-C_3H_7	CH_3	Acetonitrile	1.4	81

distribution *was not* dependent upon the polarity of the solvent in which the reaction was conducted as revealed in Table I. However, the yield of this reaction was found to be very dependent upon the polarity of the solvent.

As indicated in Table I, both the *endo*- and *exo*-alkyl isomers were produced in these *in situ* cycloaddition reactions. The isomer distributions were determined by vpc and further verified by nmr. Table II

Table II. Nmr Spectra of Some Unsymmetrical Ketoketone–Cyclopentadiene Adducts



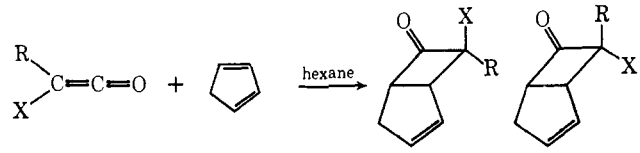
Z	Y	H_1	H_2 and H_3	H_4	H_5
Cl	Cl	4.08	5.9	2.68	4.25
CH_3 (1.28)	CH_3 (0.93)	3.15	5.8	2.52	3.95
CH_3 (1.77)	Cl	3.62	5.9	2.65	3.95
Cl	CH_3 (1.47)	3.65	5.9	2.64	4.28
CH_3 (1.91)	Br	3.55	5.8	2.60	4.03
Br	CH_3 (1.58)	3.75	5.8	2.62	4.26
C_2H_5	Cl	3.60	5.9	2.63	3.94
Cl	C_2H_5	3.70	5.9	2.62	4.27
C_2H_5	Br	3.54	5.8	2.60	3.90
Br	C_2H_5	3.70	5.8	2.60	4.26
i-C_3H_7	Cl	3.65	5.9	2.65	3.95
Cl	*i*-C_3H_7	3.64	5.9	2.60	4.20
i-C_3H_7	Br	3.66	5.8	2.68	3.97
Br	*i*-C_3H_7	3.76	5.9	2.58	4.27
Br	*t*-C_4H_9	3.90	5.9	2.61	4.39
CH_3 (1.28)	*n*-C_3H_7	3.15	5.8	2.50	3.95
n-C_3H_7	CH_3 (0.95)	3.15	5.8	2.50	3.95

records some of the nmr data and reveals a surprisingly easy spectral method for distinguishing the isomers of the alkylhaloketene cycloadducts.

The isomers of the methyl-*n*-propylketene–cyclopentadiene adduct were distinguished by a method previously described,[2] *e.g.*, the chemical shift of the methyl singlet since the *endo*-methyl signal is about δ 0.3 upfield from the *exo*-methyl resonance.

The temperature of the cyclobutanone preparations was varied and the effects are shown in Table III.

Table III. Temperature Effect on the Isomer Distribution



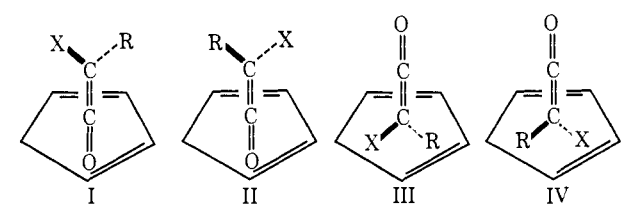
endo *exo*

R	X	Temp, °C	*endo/exo*
CH_3	Cl	0–5	4.3
CH_3	Cl	25	4.5
CH_3	Cl	40	4.7
CH_3	Br	0–5	0.71
CH_3	Br	25	1.1
CH_3	Br	40	1.4
i-C_3H_7	Br	0.5	2.8
i-C_3H_7	Br	25	6.7
i-C_3H_7	Br	40	7.4
n-C_3H_7	CH_3	0–5	1.4
n-C_3H_7	CH_3	40	1.6

Discussion

The *in situ* cycloaddition of alkylhaloketene with cyclopentadiene produces most interesting results when the size of the alkyl group is varied as shown in Table I. As the alkyl group is systematically increased from methyl, ethyl, isopropyl to *t*-butyl, the *endo*-alkyl isomer increases, *i.e.*, as the alkyl group becomes larger, more of that isomer is produced where this substituent is *endo*.

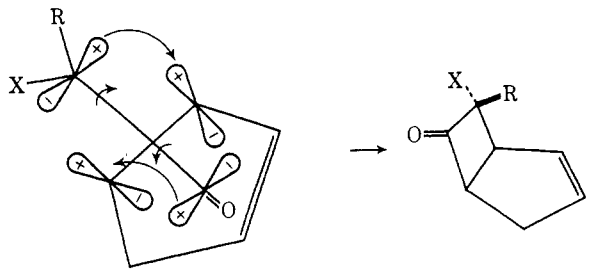
These results are most easily understood by employing the principle of orbital symmetry conservation. The ketene cycloaddition to an olefin is allowed to be a thermally concerted process only when the approach of the reactants is orthogonal whereby the ketene plays an antarafacial role ($\pi 2_s + \pi 2_a$).[5] There are four possible orthogonal approaches in the system under investigation.[6] It is apparent that orientations I and



I II III IV

II are sterically preferred. As the size of the alkyl substituent increases, it would seem that geometry II would be preferred. Completion of the cycloaddition process in II leads to the alkyl group being *endo* and in I the alkyl group becomes *exo*. Thus, the observed increased formation of the *endo*-alkyl isomer when the alkyl substituent is increased is most consistent with the principle of orbital symmetry conservation.

(5) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969).
(6) The ketene is arbitrarily drawn on the top of the cyclopentadiene molecule.



The preparation and subsequent *in situ* cycloaddition of methyl-*n*-propylketene to cyclopentadiene produces both the *endo*- and *exo*-methyl isomers as shown in Table I. The isomer distribution of *endo*-/*exo*-methyl of 1.4 does not change as the solvent is varied from hexane to acetonitrile. However, the alkylhaloketene cycloadduct isomer distributions are very dependent upon the solvent as revealed in Table I. Although the role of the solvent in influencing the isomer distribution is not well understood, it is obvious that the solvent dependency of the alkylhaloketene cycloaddition isomer distribution is due to the halogen substituent. These data suggest that the alkylhaloketenes are unsymmetrically solvated.

It is pertinent to emphasize that the yields of dialkylketene cycloadditions with cyclopentadiene are about ten times greater in acetonitrile as compared to hexane. This is probably due to an enhanced rate in the more polar solvent since much more dimer is produced in hexane. Presumably, the more polar solvent solvates the transition state to a greater degree, thus lowering the energy of activation.

An examination of the nmr data in Table II reveals a very characteristic trend, *i.e.*, the chemical shift variation of H_5. When the halogen is *endo*, this H_5 absorption varies from δ 3.9 to 4.0 and when the halogen is *exo*, this absorption varies from 4.2 to 4.4. This H_5 resonance is split into two triplets by H_1. This is the result of cross ring deshielding of H_5 by the *exo*-halogen which was established by a comparison of the spectra of the cyclopentadiene adduct of dichloroketene with that of dimethylketene. When the halogen is *exo* (dichloroketene adduct), the chemical shift of H_5 is δ 4.25 whereas for *exo*-methyl (dimethylketene adduct), it is δ 3.95. There is an excellent correlation by comparing the chemical shift of H_5 of the methylhaloketene–cyclopentadiene adducts with the above. The structures of the methylhaloketene–cyclopentadiene adducts were unequivocally established previously by observing the shift in the *endo*-methyl resonance upon bromination and hydrogenation of the residual double bond in the cycloadduct.[2-4]

The synthesis and separation of the other alkylhaloketene–cyclopentadiene adduct isomers further demonstrates the deshielding effect of *exo*-halogen and illustrates how easily the isomers are distinguished by simply determining the chemical shift of H_5.

The effect of temperature on the *endo*-/*exo*-alkyl isomer distributions is more pronounced as the size of the alkyl substituent increases, as shown in Table III. Since the reactions to form the two isomers are kinetically controlled, the isomer ratios represent a ratio of the two rate constants. Therefore, the isomer dependence on temperature, particularly as the size of the alkyl substituent increases is expected.

Kinetic and stereochemical evidence is consistent with a concerted mechanism for ketene cycloaddition to olefins.[7-12] Nevertheless, if a two-step mechanism were operative in the cycloaddition of alkylhaloketenes and cyclopentadiene, then the *exo*-/*endo*-alkyl isomer distribution might be expected to be a test of this possibility. In this case an increasing proportion of *exo*-/*endo*-alkyl cycloadduct isomers would be expected as the steric bulk of the alkyl substituent of the alkylhaloketene increases. This expectation does, of course, assume that the second ring closing step is slow to the extent that steric factors would enter into the isomer distribution. This seems a reasonable assumption in view of the recent results of Huisgen and coworkers.[13] Nevertheless, the *exo*-/*endo*-alkyl isomer distribution actually decreases as the size of the alkyl group increases. Consequently, this ketene cycloaddition, like so many others, is best interpreted as occurring by a concerted process.

Experimental Section

Vapor phase chromatography was accomplished on an F & M Scientific Model 700 chromatograph employing a 10 ft × 0.25 in. column packed with 2% silicone fluid F-1265, QF-1 on Chromosorb G. Isomer distributions were determined by vpc peak area integrations and were checked with synthetic mixtures of the isomers. The isomer distributions were determined periodically during the addition of reagents in a particular preparation and were found to be identical with the distribution at the end of the run. Also, the isomer distributions were found to be unchanged upon reflux at distillation temperatures. Hexane and acetonitrile were dried over Linde 4A molecular sieves. All of the acid halides with the exception of 2-bromo-3,3-dimethylbutanoyl chloride were prepared from commercially available acids by standard procedures.

All of the proton nmr spectra were recorded on a Varian A-60 instrument employing tetramethylsilane as the internal standard. All of the spectra were recorded at 25°. The solutions were about 20% in carbon tetrachloride.

7-Chloro-7-(2-propyl)bicyclo[3.2.0]hept-2-en-6-one. To a solution of 25 g (0.25 mol) of triethylamine, 68 g (1.0 mol) of cyclopentadiene, and 150 ml of dry hexane at 0–5°, 31 g (0.20 mol) of 2-chloro-3-methylbutanoyl chloride in 25 ml of dry hexane was added dropwise over a 1-hr period. After the addition was complete, the mixture was stirred 1 additional hr while warming to room temperature. A theoretical amount of salt was removed from the reaction mixture by filtration. The filtrate was concentrated by rotary evaporation. Vpc analysis of the residue revealed an *endo*-/*exo*-isopropyl isomer distribution of 10. Vacuum distillation through a 6-in. Vigreux column yielded 26 g of crude product (71%) at 66–74° (0.2 mm). Analysis by vpc of the crude distillate showed the isomer distribution to be unchanged. Both isomers showed characteristic carbonyl absorptions in the ir at 1800 cm^{-1} (s) and carbon–carbon unsaturation at 1607 cm^{-1} (w). That portion of the nmr spectrum not recorded in Table II is indicated: (*endo*-isopropyl isomer) δ 2.1 (m, 1 H), 0.97 (d, 3 H), and 1.08 (d, 3 H); (*exo*-isopropyl isomer) 2.0 (m, 1 H), 0.95 (d, 3 H), and 1.10 (d, 3, H).

Anal. Calcd for $C_{10}H_{13}OCl$: C, 65.0; H, 7.1. Found: C, 64.75; H, 6.91.

7-Bromo-7-(2-propyl)bicyclo[3.2.0]hept-2-en-6-one. A 40-g (0.20 mol) portion of 2-bromo-2-methylbutanoyl chloride in 25 ml of hexane was added dropwise over a 1-hr period to a solution of 25 g (0.24 mol) of triethylamine, 68 g (1.0 mol) of cyclopentadiene, and 150 ml of dry hexane at 0–5°. After the addition was complete,

(7) W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967).
(8) W. T. Brady and H. R. O'Neal, *ibid.*, **32**, 2704 (1967).
(9) R. Huisgen, J. A. Feiler, and P. Otto, *Tetrahedron Lett.*, 4485 (1968).
(10) R. Montaigne and L. Ghosez, *Angew. Chem. Intern. Ed. Engl.*, 7, 221 (1968).
(11) R. Huisgen, L. A. Feiler, and S. Binsch, *ibid.*, **3**, 753 (1964).
(12) G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Lett.*, 4497 (1968).
(13) R. Huisgen and P. Otto, *J. Amer. Chem. Soc.*, **91**, 5922 (1969).

the mixture was stirred 1 additional hr while warming to room temperature. After removal of the amine salt by filtration, the solvent was evaporated and the *endo*-/*exo*-isopropyl isomer distribution was 2.8 as indicated by vpc. Vacuum distillation through a 6-in. Vigreux column yielded 37 g of crude product (78%) at 61–73° (0.1 mm). The isomer distribution had not changed after distillation. The isomers were separated by vpc and both isomers showed the characteristic carbonyl absorptions in the ir at 1800 cm^{-1} (s) and carbon–carbon unsaturation at 1607 cm^{-1} (w). That portion of the nmr spectrum not recorded in Table II is as follows: (*endo*-isopropyl isomer) δ 1.9 (m, 1 H), 1.0 (d, 3 H), and 1.1 (d, 3 H).

Anal. Calcd for $C_{10}H_{13}OBr$: C, 52.24; H, 5.77. Found: C, 52.30; H, 5.67.

2-Bromo-3,3-dimethylbutanoyl Chloride. A solution consisting of 126 g (1.0 mol) of 3,3-dimethylbutanoic acid, 160 g (1.0 mol) of bromine, and 5 ml of phosphorus trichloride was heated at 70–80° for 24 hr or until the reaction mixture no longer showed the red color of bromine. The reaction solution was cooled in an ice bath and treated with 207.5 g (1.0 mol) of phosphorus pentachloride. Upon heating at reflux for 2 hr, the crude acid chloride could be removed by distillation at 108–110° (30 mm) to yield 138 g (61%), nmr (CCl_4) δ 4.42 (s, 1 H) and 1.18 (s, 9 H).

7-Bromo-7-(2-methyl-2-propyl)bicyclo[3.2.0]hept-2-en-6-one. The dehydrochlorination of 2-bromo-3,3-dimethylbutanoyl chloride with triethylamine in the presence of cyclopentadiene was conducted by the same general procedure as described above. The cycloadduct was distilled through a 24-in. Vigreux column at 66–67° (0.4 mm): ir 1800 (C=O) and 1607 cm^{-1} C=C); nmr other than that described in Table II, δ 1.12 (s, 9 H). Only one isomer, the *endo*-*t*-butyl isomer, was obtained as evidenced by nmr and vpc.

Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.3; H, 6.17; mol wt, 243. Found: C, 54.54; H, 6.19; mol wt (by mass spectroscopy), 243.

7-Methyl-7-propylbicyclo[3.2.0]hept-2-en-6-one. The same general procedure was employed as described above for the dehydrochlorination of 2-methylpentanoyl chloride with triethylamine in the presence of cyclopentadiene. The cycloadduct distilled at 95–98° (2.5 mm): ir 1800 (C=O) and 1609 cm^{-1} (C=C); nmr other than that described in Table II, δ 1.4 (m, 4 H) and 1.05 (m, 3 H). An *endo*-/*exo*-*n*-propyl isomer distribution of 1.4 was obtained as evidenced by the nmr spectrum and vpc of the reaction solution prior to distillation.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.4; H, 9.80. Found: C, 80.2; H, 10.17.

Other Cycloadditions. All the other cycloadditions were effected as previously described except for changing the solvent and/or temperature.

Acknowledgment. Support for this investigation by the Robert A. Welch Foundation and the National Science Foundation (GP-7386) is gratefully acknowledged. The authors also wish to express their gratitude to Professor Roald Hoffmann for private communications concerning these results.

Chromyl Chloride Oxidations. V. Kinetics and Mechanism of the Electrophilic Addition to Alkenes[1,2]

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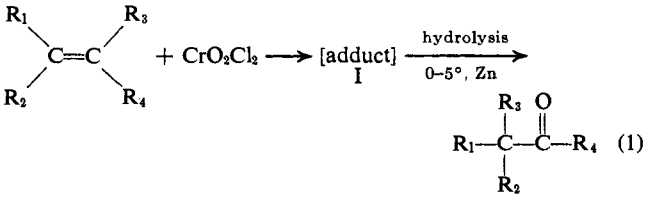
Contribution from the Department of Chemistry, California State College, Long Beach, California 90801. *Received December 31, 1969*

Abstract: The kinetics of the chromyl chloride oxidation of 15 alkenes, to give the chromyl chloride–alkene adduct, have been studied by spectrophotometric stopped-flow techniques. A first-order dependence on the concentration of each reactant was observed. The reactions are little affected by steric factors and are characterized by low enthalpies of activation ($\Delta H^{\pm}$ = 5.4–7.2 kcal/mol) and large negative entropies of activation ($\Delta S^{\pm}$ = −27.4 to −40.7 eu). An increase in alkyl substitution at the carbon–carbon double bond leads to large rate enhancements. An excellent correlation is obtained with Taft's σ^* values, and good correlations are also obtained with various forms of the extended Hammett equation. Comparison of the relative reactivities of chromyl chloride oxidations with other electrophilic alkene reactions (bromine and chlorine addition, chromic acid oxidation, epoxidation) suggest that the rate-determining step involves a partially positive charged cyclic three-membered ring activated complex.

The nature of the products from the chromyl chloride oxidation of carbon–carbon double bonds in alkenes,[5–7] cycloalkenes,[8–10] and styrenes[9,11,12] has been a subject of great controversy in recent years. For example, it has been reported that excess chromyl chloride oxidizes alkenes to chlorohydrins in low yields.[5,6] However, more recent product studies[7] (Table I) have shown that when a 1:1 molar ratio of chromyl chloride and alkene is used, the major oxidation products are carbonyl compounds which arise from hydride or alkyl migration (eq 1). In order to



(1)

(1) Previous paper in series: F. Freeman and N. J. Yamachika, *J. Amer. Chem. Soc.*, in press.

(2) Presented in part before the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 25, 1970.

(3) Abstracted in part from the M.S. thesis of P. D. McCart, California State College, Long Beach, Calif., 1969.

(4) Petroleum Research Fund Scholar, 1968–1970.

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