

KINETICS AND MECHANISMS OF CLEAVAGE OF ALLYLIC DERIVATIVES OF GROUP IVA ELEMENTS BY MERCURIC SALTS I. ALLYLSILANES

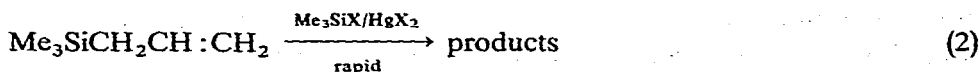
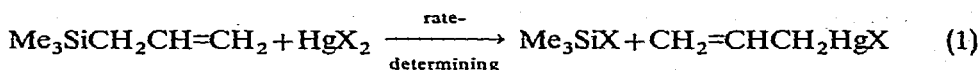
R. M. G. ROBERTS

Department of Chemistry, University of Essex, Wivenhoe Park, Colchester (Great Britain)

(Received October 30th, 1967)

SUMMARY

The kinetics and mechanism of cleavage of trimethylallyl silane and its derivatives by mercuric salts have been investigated in solvent acetonitrile. The reaction was followed by spectrophotometric and gas chromatographic methods. The stoichiometry of the reaction is not that of a simple bimolecular process, and is best represented by the reaction scheme:



A second molecule of substrate is rapidly attacked by Me_3SiX formed in the rate determining step. Separate examination of (2) revealed that reaction occurred in the absence of mercuric salts. Me_3SiX was not consumed during the process but acts as a catalyst, resulting in first order kinetic behaviour. Mercuric salts strongly catalyse this step, acting as Lewis acids, and enhancing the already polar nature of Me_3SiX .

Rate constants were calculated for (1) from chromatographic data, adopting the above reaction scheme. The reaction was found to be first order in both substrate and electrophile.

Spectrophotometric studies indicated that (1) proceeded via a π complex, the rate of decomposition of which corresponded with that obtained by chromatographic techniques, thus supporting the proposed mechanism. In addition, evidence is presented which supports an S_E2 rather than S_F transition state for (1).

INTRODUCTION

In 1959 Mazerolles and Lesbre¹ reported on the reactions of allylgermanes with mercuric bromide, hydrogen bromide, and bromine, but no attempt was made to elucidate the mechanism of these reactions. Allylic compounds are interesting mechanistically since it is possible to observe both anionotropic and cationotropic rearrangements. Anionotropy was the subject of an intensive investigation by Hughes,

Ingold and co-workers². However, relatively little work has been done in the field of cationotropy, particularly in organometallic systems. The purpose of this and subsequent papers³ is to investigate the mechanisms and range of reactivities of allyl-metal compounds with electrophiles.

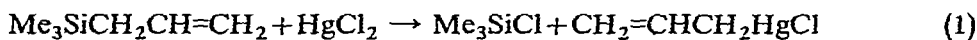
Electrophilic substitution of allylic carbon comprises two fundamental mechanistic types S_E and S'_E depending on the site of electrophilic attack. Each of these processes has unimolecular (S_{E1} , S'_{E1}) and bimolecular (S_{E2} , S'_{E2}) components with, in addition, four centre (S_F) and anion-catalysed mechanisms (S_{EC})^{4,5}.

Already some progress has been made in this field, notably by Sleezer, Winstein and Young⁶ who studied the acidolysis of allylmercurials, and by Kuivila and Verdone⁷ who investigated the protonolysis of allyltin compounds. Both found strong evidence of an S'_{E2} mechanism.

RESULTS AND DISCUSSION

Cleavage of allyl-metal bonds by electrophiles occurs in preference to alkyl-, vinyl- and phenyl-metal bonds for silicon^{8,9}, germanium¹⁰, tin¹¹, lead^{13,14} and mercury⁶. The substrates chosen for the investigation were thus trialkylallylsilanes. The cleavage was carried out in solvent acetonitrile to obviate complicating side reactions caused by the solvolysis of the halosilane products in solvent ethanol³, and to correlate reaction rates with those obtained for the germanium analogues³, thus gaining a measure of the relative electron releasing properties of trialkyl-silyl and -germanyl groups.

Allylsilanes react far slower than their germanium counterparts. Moreover, the stoichiometry of the reaction of trimethylallylsilane with mercuric halides is not that of the simple electrophilic substitution represented below. Trimethylallylsilane



was completely consumed during the reaction to give yields of trimethylchlorosilane and allylmercuric chloride of 52 and 51 % respectively together with a low boiling product X. Vapour phase chromatograms of reaction mixtures confirmed this product analysis.

Two direct analytical methods were employed, gas-liquid chromatography (GLC) and ultraviolet spectroscopy.

Kinetics by GLC

The technique is described elsewhere. Reaction mixtures always showed three peaks in addition to the solvent, corresponding to $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$, Me_3SiCl , and X. The peak heights of the latter two products increased smoothly with reaction time at the expense of the allylsilane peak which eventually disappeared. This clearly demonstrates that the reaction traced occurs in solution and not in the injection tube or column.

In addition, $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ and Me_3SiCl were found to react at a measurable rate in the absence of HgCl_2 to give X and Me_3SiCl , whilst traces of mercuric salt greatly accelerated the reaction. The chlorosilane was not consumed during the reaction and thus acts catalytically (Table 1).

Table 1 clearly shows that the allylsilane reacts according to a first order rate

TABLE I

FIRST AND SECOND ORDER RATE CONSTANTS (k_1, sec^{-1} ; $k_2, \text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$) FOR THE REACTION OF $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (0.001 M) AND Me_3SiCl (0.01 M) IN MeCN AT 35.0° (5 μl injection)

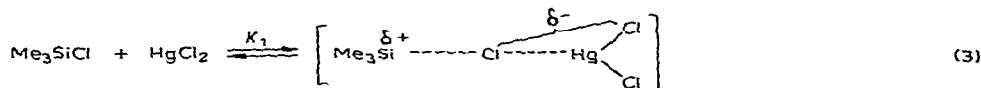
Time (sec)	Peak height $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	Peak height Me_3SiCl	$\log[a/(a-x)]$	$10^4 k_1$	$x/(a-x)$	$10^2 k_2$
0	4.31	5.90	0.000			
600	3.36	5.92	0.108	4.1	0.283	4.7
1200	2.55	5.85	0.228	4.4	0.690	5.8
1800	2.07	6.10	0.318	4.1	1.08	6.0
2400	1.60	6.00	0.430	4.1	1.69	7.0
3030	1.22	5.75	0.548	4.2	2.53	8.3
3600	0.97	5.68	0.647	4.1	3.44	9.6
4860	0.58	5.60	0.870	4.1	6.43	13.2
∞	0.00					

law, with k_1 of $4.1 \times 10^{-4} \text{sec}^{-1}$. When the reaction was performed using a fivefold excess of lithium chloride, the reaction rate was reduced by a factor of 7.

Since $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ is quite stable in acetonitrile in the absence of chlorosilane the following reaction scheme is postulated:



The intermediate complex may be a π complex with silicon acting as a π electron acceptor. The strong catalytic effect of mercuric salts can be attributed to an enhanced polarisation of the chlorosilane by the mercuric salt acting as a Lewis acid:

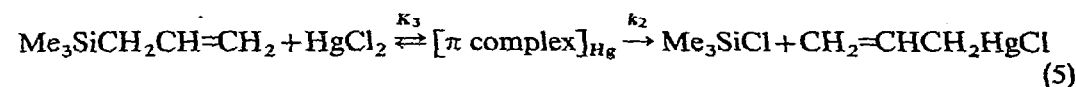


This increases the electrophilicity of silicon and promotes attack on the double bond. Similarly the retardation produced by added halide ion can be explained by the formation of a penta-covalent complex, with consequent reduction in the electrophilicity of the chlorosilane. Armed with this knowledge, the reaction of the allylsilane with mercuric chloride can be formulated in greater detail.



In the initial stages of the reaction Me_3SiCl is formed in the presence of a large excess of mercuric chloride, thus enhancing (3), and reducing the electrophilicity of the mercuric chloride.

Evidence will be presented later that the first stage in the cleavage of the allyl-silicon bond by mercuric chloride occurs via a π complex. Thus, as the reaction proceeds, the chlorosilane competes successfully with mercuric chloride for the π electrons in the double bond. The overall reaction may now be formulated as:



This readily explains the observed 50% yields. Just how far (5) goes to completion depends on values of the equilibrium constants K_1 , K_3 , K_4 .

The value of the rate constant, k_2 , for the cleavage of the C-Si bond by HgCl_2 can now be evaluated using the method described elsewhere. Table 2 lists the values of k_2 so obtained. The constancy of these values supports the above thesis, an average value of k_2 of $0.083 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$ being obtained.

TABLE 2

VALUES OF k_2 ($\text{l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$) FOR THE REACTION OF $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (a) AND HgCl_2 (b) IN ACETONITRILE AT 35.0°

Run	$[a]=[b]$ ($10^3 M$)	k_2 (from eqn. 7)	k_2 (from eqn. 8)	Yield of Me_3SiCl (%)
38	1.00	0.080	0.088	49.3
39	1.14	0.081	0.094	50.8
40	1.33	0.076	0.080	48.4
41	1.60	0.075	0.082	51.5
42	1.78	0.083	0.095	50.6
43	2.00	0.078	0.083	49.0
		av. 0.079	0.087	

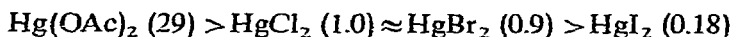
Addition of an equimolar amount of Et_4NCl strongly retarded reaction. The reaction was carried out at different temperatures and the Arrhenius plot of data listed in Table 3 yielded values of E_a of 12.0 kcal/mole and $\log A$ of $7.31 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$.

TABLE 3

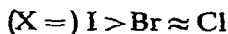
THE EFFECT OF TEMPERATURE ON k_2 ($\text{l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$)

Temp. ($^\circ\text{C}$)	$10^2 k_2$	Temp. ($^\circ\text{C}$)	$10^2 k_2$
25	4.2	35	8.3
30	5.6	43.7	13.7

Change of mercuric salt revealed the following reactivity sequence (relative rates in parenthesis):



The sequence suggests an S_E2 rather than S_F mechanism since the formation constants of $[\text{HgX}_3]^-$ and $[\text{HgX}_4]^{2-}$ are in the order:



By this token an S_F mechanism, which relies on nucleophilic assistance to carbon-metal bond fission, should be enhanced by a change from chloride to iodide. In addition, the presence of added halide should enhance S_F reaction whereas strong retardation is observed.

Triethylallylsilane showed a similar reaction pattern. A value of $k_2(\text{Et})/k_2(\text{Me})$ of 0.85 was obtained which could be interpreted as a small steric effect.

Evidence of π complex formation

When equimolar solutions (10^{-3} M) of $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ and mercuric bromide are mixed, a rapid increase in absorption occurs over and above that due to products and factors. λ_{max} could not be determined due to solvent cut off at $265 \text{ m}\mu$.

Clearly a complex has been formed. Parallel experiments using a variety of allylic compounds instead of allylsilanes gave similar results. At greater concentrations, the allylsilane/ HgBr_2 complex decomposed according to a first order rate law, whereas the allylic halides did not react further. This evidence indicates that a π complex has been formed. The rate of formation of the complex was some thirty times that of the destruction. The method of evaluating the rate constants of complex formation was essentially that described by Frost and Pearson¹⁵. Brevity precludes a detailed discussion of these results.

TABLE 4

VALUES OF k_1 (sec^{-1}) FOR THE DECOMPOSITION OF THE COMPLEX AND k_2 ($\text{l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$) FOR THE REACTION OF $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ AND HgCl_2 AS A FUNCTION OF CONCENTRATION OF REACTANTS IN ACETONITRILE AT 35°

Run	$[\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2]$ (10^2 M)	$[\text{HgCl}_2]$ (10^2 M)	$10^3 k_1$	k_2
266 U	0.30	0.30	0.29	0.075
263 U	0.40	0.40	0.58	0.068
265 U	0.50	0.50	0.61	0.074
264 U	0.60	0.60	0.80	0.083
220 U	1.00	1.00	0.76	0.069
221 U	1.50	1.50	1.30	0.075
222 U	2.00	2.00	2.37	0.075
223 U	2.50	2.50	3.72	0.080
226 U	1.00	2.50	2.73	0.090
230 U	2.50	1.00	0.80	0.069
				av. 0.076

Other mercuric halides behaved analogously thus offering a qualitative demonstration of the mechanism postulated in eqn. (5). However, as Table 4 shows, k_1 for the decomposition of the π complex varied with mercuric salt concentration. This initially surprising result can now be rationalised in terms of the mechanistic concepts developed above. Assuming step (6) to be rapid, as seems highly likely in view of the strong catalytic effect of HgCl_2 on (6), a method of evaluating k_2 can be devised. The rate constants so obtained (Table 4) show excellent agreement with those obtained from chromatographic data, thus further substantiating the postulates introduced above.

The reaction mechanism is then best formulated in terms of eqns. (5) and (6); although at present the exact nature of reaction (6) is not known.

EXPERIMENTAL

Preparation of starting materials

Trimethylallylsilane (b.p. $85\text{--}86^\circ$, n_D^{20} 1.4017) and triethylallylsilane (b.p. $64\text{--}66^\circ/12 \text{ mm}$, n_D^{20} 1.4441) were prepared by standard Grignard syntheses.

Solvent acetonitrile was purified by refluxing over P_2O_5 for 6 h and fractionating from anhydrous Na_2CO_3 . Mercuric salts were recrystallised from chloroform/acetone mixtures. Other salts employed were of reagent grade and used without further purification.

Kinetic techniques

(i) *Gas-liquid chromatography.* A Perkin Elmer F11 instrument was used with a polar column (DE 201, $2m \times \frac{1}{8}$ " o.d. stainless steel. Carbowax 1500 on Chromosorb W 15/85, 60–80 mesh. Column temp. 30° , injection temp. 250° , sensitivity 20×1). The reagents were mixed at reaction temperature, and $5 \mu l$ aliquots withdrawn through a serum cap at suitable time intervals and injected. The reaction mixture showed three peaks other than solvent (retention times in parentheses), a low boiling product X (30 sec), $Me_3SiCH_2CH=CH_2$ (62 sec) and Me_3SiCl (73 sec). All peaks were sharp and distinct. X did not appear in chromatograms of solutions of allyl- or chlorosilanes or allylmercuric chloride in acetonitrile, or in the solvent itself.

Calibration of standard solutions of both allyl- and chlorosilanes showed a linear dependence of peak height on concentration. Adopting the reaction schemes (5) and (6), the concentration of $Me_3SiCH_2CH=CH_2$ at reaction time t will be $(a-2x)$ mole- l^{-1} , since one mole of Me_3SiCl reacts with a further mole of substrate as soon as the chlorosilane is formed.

The rate of reaction can be evaluated from the decrease in $[Me_3SiCH_2CH=CH_2]$ and the increase in $[Me_3SiCl]$ and $[X]$, using values of peak height at $t = \infty$ to determine the final concentration of the products. Table 5 shows the agreement obtained for values of k_2 based on the rates of appearance or disappearance of the above species.

TABLE 5

RATE CONSTANTS k_2 ($l \cdot mole^{-1} \cdot sec^{-1}$) OBTAINED FROM: (a) DECREASE IN $[Me_3SiCH_2CH=CH_2]$, (b) INCREASE IN $[X]$, (c) INCREASE IN $[Me_3SiCl]$ IN ACETONITRILE AT 35.0°
 $[Me_3SiCH_2CH=CH_2] = [HgCl_2] = 1.00 \times 10^{-3} M$.

Time (sec)	Peak ht. $Me_3SiCH_2CH=CH_2$	$\log\left(\frac{a-x}{a-2x}\right)$	$10^2 k_2$	Peak ht. X	$\log\left(\frac{a-x}{a-2x}\right)$	$10^2 k_2$	Peak ht. Me_3SiCl	$\log\left(\frac{a-x}{a-2x}\right)$	$10^2 k_2$
0	1.98			0.00			0.00		
2515	1.43	0.078	7.1	0.50	0.077	7.1	0.18	0.070	6.4
3765	1.12	0.141	8.5	0.80	0.147	9.0	0.27	0.122	7.5
4880	0.93	0.193	9.1	0.85	0.163	7.7	0.32	0.158	7.5
6210	0.74	0.264	9.7	0.98	0.206	7.7	0.38	0.208	7.7
7290	0.67	0.294	9.3	1.10	0.256	8.1	0.46	0.300	9.4
8320	0.56	0.356	9.9	1.30	0.365	10.1	0.50	0.366	10.1
∞	0.00			1.79			0.69		

A more accurate method of computing k_2 was devised using peak height ratios, thus obviating the errors incurred by injection. Since peak heights (p) varied linearly with concentration, the following relationships hold:

$$\begin{aligned} [Me_3SiCH_2CH=CH_2] &= a - 2x = f_1 \cdot p_1 \\ [Me_3SiCl] &= x = f_2 \cdot p_2 \\ [X] &= x = f_3 \cdot p_3 \end{aligned}$$

f_1 and f_2 were obtained from calibration of standard solutions of the reagents. f_3 was derived from infinity readings on a number of reaction mixtures, assuming $x = \frac{1}{2}a$.

$$\therefore x/(a-2x) = f_2 \cdot p_2 / f_1 \cdot p_1 = \phi_1 \quad (7)$$

$$x/(a-2x) = f_3 \cdot p_3 / f_1 \cdot p_1 = \phi_2 \quad (8)$$

The rate equation for cleavage of the carbon-silicon bond by HgCl_2 at equimolar concentrations is given by: $\log(a-x)/(a-2x) = ak_2t/2.303$

From (6) and (7),

$$\log(a-x)/(a-2x) = \log(1 + \phi_1) = \log(1 + \phi_2) \quad (9)$$

thus enabling two sets of data for computing k_2 . Table 2 shows the values of k_2 obtained using this method.

(ii) *Spectroscopic method.* The reagents were mixed at the reaction temperature in a thermostatted 4 cm silica cell in a Unicam SP 500 instrument. solvent being used as a reference. The reaction was followed at 270 μm . From (5)

$$\begin{aligned} [\pi \text{ complex}]_{\text{Hg}} &= K_3 \cdot [\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2] \cdot [\text{HgCl}_2] \\ &= K_3 \cdot (a-2x) \cdot (b-x) \end{aligned}$$

at $t=0$: $[\pi \text{ complex}]_{\text{Hg}}^0 \propto (D_0 - D_\infty)$. at $t=t$: $[\pi\text{-complex}]_{\text{Hg}} \propto (D_t - D_\infty)$

$$\therefore \frac{D_t - D_\infty}{D_0 - D_\infty} = \frac{(a-2x) \cdot (b-x)}{a \cdot b} \quad (10)$$

A plot of $D_0 - D_\infty$ against ab was found to be linear, demonstrating the validity of Beers Law for the π complex. x can be calculated from (10) using:

$$x = \frac{2b+a}{4} - \frac{1}{2} \left\{ \frac{(2b+a)^2}{4} + 2a \cdot b \left[\frac{(D_t - D_\infty)}{(D_0 - D_\infty)} - 1 \right] \right\}^{\frac{1}{2}} \quad (11)$$

TABLE 6

VALUES OF k_2 ($\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$) FOR THE CLEAVAGE OF $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (a) BY MERCURIC CHLORIDE (b) IN ACETONITRILE AT 35.0°
 $[a] = [b] = 4.00 \times 10^{-3} \text{ M}$.

Time (sec)	D_t	x (10^3 M)	$x/(a-x)$	k_2
0	0.414			
240	0.362	0.22	0.026	0.063
360	0.342	0.31	0.039	0.063
480	0.322	0.40	0.052	0.063
600	0.302	0.50	0.067	0.065
720	0.281	0.61	0.087	0.070
840	0.262	0.70	0.104	0.072
960	0.244	0.77	0.119	0.072
1080	0.228	0.89	0.147	0.077
∞	0.089			

Using (11) 2nd order rate constants for C–Si bond fission can be computed (Table 6). The value of k_2 agrees well with that derived from chromatographic data.

Products

Trimethylallylsilane (4.8 g 0.042 moles) in dry MeCN (200 ml) were treated with mercuric chloride (11.4 g. 0.042 mole) in dry MeCN (200 ml) and allowed to stand overnight. The reaction mixture was fractionally distilled, using a cold trap at -78° for low boiling products. Two fractions were collected, b.p. $56-79^\circ$ 3.92 g and b.p. $79-81^\circ$, 4.7 g. Both fractions showed strong C–Si stretching and deformation frequencies at 1269 cm^{-1} and 1052 cm^{-1} respectively, but no double bond stretching frequencies. NMR spectra of both fractions showed three proton absorbances at 8.13 τ (MeCN), 9.64 τ (Me_3SiCl) and 10.01 τ , the latter being another reaction product of step (6).

Unfortunately, silanes readily form azeotropes with acetonitrile¹⁶, rendering the isolation of individual silanes impossible by fractional distillation. Gas-liquid chromatograms of both fractions indicated a total yield of Me_3SiCl of 52%, which is in good agreement with the value of 50% obtained from chromatographic rate data (Table 2).

In addition, 0.8 g of a low boiling liquid was recovered from the cold trap. A solution of the compound in acetonitrile showed two proton absorbances at 8.13 τ (MeCN) and 9.92 τ . The latter was thus shown to be different from Me_4Si ($\tau = 10.0$). As yet the product has not been identified, though it certainly possesses Si–C bonds. However, the identification of X is not essential to the evaluation of the rate of cleavage of C–Si bonds by mercuric salts.

The residue was pumped dry and extracted with hot chloroform ($2 \times 500\text{ ml}$). Removal of solvent yielded 5.9 g (51%) allylmercuric chloride m.p. 108° .

ACKNOWLEDGEMENTS

The author wishes to thank the Science Research Council for a research fellowship.

REFERENCES

- 1 P. MAZEROLLES AND M. LESBRE, *C. R. Acad. Sci., Paris*, 248 (1959) 2018.
- 2 C. K. INGOLD, *Structure and Mechanism*, Bell, London, 1963.
- 3 R. M. G. ROBERTS, *J. Organometal. Chem.*, 12 (1968) 97.
- 4 M. H. ABRAHAM AND J. A. HILL, *J. Organometal. Chem.*, 7 (1967) 11.
- 5 H. B. CHARMAN, E. D. HUGHES, C. K. INGOLD AND H. C. VOLGER, *J. Chem. Soc.*, (1961) 1142.
- 6 P. D. SLEEZER, S. WINSTEIN AND W. G. YOUNG, *J. Amer. Chem. Soc.*, 85 (1963) 1890.
- 7 H. G. KUIVILA AND J. A. VERDONE, *Tetrahedron Lett.*, (1964) 119.
- 8 L. H. SOMMER, L. J. TYLER AND F. C. WHITMORE, *J. Amer. Chem. Soc.*, 70 (1948) 2872.
- 9 D. GRAFSTEIN, *J. Amer. Chem. Soc.*, 77 (1955) 6650.
- 10 A. D. PETROV AND V. F. MIRONOV, *Angew. Chem.*, 73 (1961) 59.
- 11 S. D. ROSENBERG, E. DEBRECZENI AND E. L. WEINBERG, *J. Amer. Chem. Soc.*, 81 (1959) 972.
- 12 P. AUSTIN, *J. Amer. Chem. Soc.*, 53 (1931) 3514.
- 13 H. GILMAN, E. B. TOWNE AND H. L. JONES, *J. Amer. Chem. Soc.*, 55 (1933) 4689.
- 14 M. M. KREEVOY, *J. Amer. Chem. Soc.*, 81 (1959) 1099.
- 15 A. A. FROST AND R. G. PEARSON, *Kinetics and Mechanism*, Wiley, New York, 1961, p. 186.
- 16 R. O. SAUER AND E. M. HADSELL, *J. Amer. Chem. Soc.*, 70 (1948) 4258.