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

II. ALLYLGERMANES

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SUMMARY

The kinetics and mechanism of cleavage of triethylallylgermane and its derivatives by mercuric salts in solvents acetonitrile and ethanol have been investigated. Cleavage in acetonitrile is a simple bimolecular electrophilic substitution of mercury for germanium. The reaction was more than one hundred times faster than that of the corresponding silanes. Traces of water in the solvent had a profound effect on reaction rates.

Lower reaction rates were observed in solvent ethanol, and the reactivity sequence $Et_3Sn \gg Et_3Ge > Et_3Si$ was found, reflecting the relative electron releasing properties of the groups. The reaction was, however, complicated in its later stages by acidolysis of the product mercurial.

Evidence for an "open" (S_E2) rather than cyclic (S_F) transition state is presented together with a discussion of cationotropic rearrangement mechanisms.

INTRODUCTION

The cleavage of allylsilanes by mercuric salts has been reported in some detail[1]. The present paper extends concepts developed in this work to the cleavage of allylic germanes.

RESULTS AND DISCUSSION

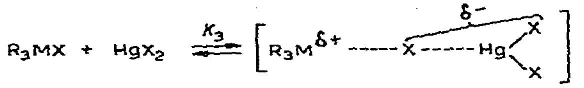
A rather complex mechanistic pattern was found in the silane series as shown below

$$R_3MCH_2CH{=}CH_2+HgX_2 \overset{K_1}{\rightleftarrows} [\pi\ \text{complex}]_{Hg} \xrightarrow[\text{determining}]{\text{rate}} R_3MX+CH_2{=}CHCH_2HgX \quad (1)$$

$$R_3MCH_2CH{=}CH_2+R_3MX \overset{K_2}{\rightleftarrows} [\pi\ \text{complex}]_{M} \xrightarrow{\text{rapid}} \text{products} \quad (2)$$

$M = Si$; $R = Me, Et$; $X = OAc, Cl, Br, I$

Step (2) was strongly catalysed by mercuric salts which acted as Lewis acids, enhancing the polarisation of the halosilane product. This in turn facilitates attack on the allylic double bond to form a complex.



$$R_3MX + HgX_2 \overset{K_3}{\rightleftharpoons} \left[R_3M^{\delta+}\text{-----}\overset{\delta-}{X}\text{-----}Hg\begin{smallmatrix}X\\ X\end{smallmatrix}\right] \qquad (3)$$

Preliminary tests in the germanes series revealed that process (2) only occurred in highly polar media such as DMSO, and is not important in solvents acetonitrile, ethanol, and dioxane. The degree of intervention of (2) depends on the values K_1, K_2 and K_3. These in turn are governed by the nature of the solvent and M. Strongly electron releasing groups such as Et_3Ge[2] would increase K_1 and K_3. Thus allyl–metal bond cleavage of Et_3Ge compounds should be enhanced relative to Et_3Si compounds.

One might expect that step (2) would also be facilitated by a change from silicon to germanium. However, the formation of the complex in this step involves p–d interactions between the allylic double bonds and metal d orbitals of suitable symmetry. The value of this overlap integral largely determines the stability of the complex. In changing from silicon to germanium d orbital overlap appears to be less effective, thus reducing the stability of the complex. Thus highly polar solvents are necessary to promote step (2) for allylgermanes, compensating for the loss of stability of the complex by increasing K_3.

As expected, allylgermanes reacted much faster than their silicon analogues. Since wide variations in mechanism occurred in the solvents chosen for the investigation, the work will be reported under solvent headings.

Cleavage of allylgermanes by mercuric salts in acetonitrile

Cleavage in this solvent was rapid and not complicated by process (2). In all cases simple bimolecular kinetic equations were obeyed, the reaction being first order with respect to both substrate and electrophile. The reaction rate was extremely sensitive to traces of water and only solvent of high purity gave reproduceable results

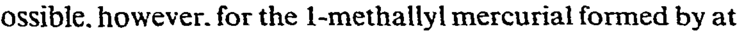
TABLE 1

SECOND ORDER RATE CONSTANTS k_2 ($l \cdot mole^{-1} \cdot sec^{-1}$) AS A FUNCTION OF CONCENTRATION OF Et_3GeCH_2-$CH{=}CHR$ AND $HgBr_2$ IN ACETONITRILE AT 24.9°

Run	R	$[Et_3GeCH_2CH{=}CHR]$ ($10^4 M$)	$[HgBr_2]$ ($10^4 M$)	k_2
86	H	0.75	0.75	35
93	H	0.75	0.75	35
94	H	0.75	0.75	35
85	H	1.50	1.50	43
87	H	2.25	2.25	39
88	H	0.75	1.50	49
90	H	0.75	2.25	46
102[a]	H	1.00	1.00	0.73
104[b]	H	1.00	1.00	45
98, 99[c]	CH_3	1.00	1.00	110

[a] Solvent 98% v/v aq. MeCN. [b] $HgCl_2$ as electrophile. [c] Mean of two determinations.

(Table 1). In all runs, reaction was quantitative. An average value of the 2nd order rate constant of 39 $l\cdot mole^{-1}\cdot sec^{-1}$ was obtained. A value of k_2 of 110 $l\cdot mole^{-1}\cdot sec^{-1}$ was obtained for triethyl 3-methallylgermane, reflecting the $+I$ effect of the methyl substituent. Product analysis revealed an 88 % yield of 3-methallyl mercuric bromide. This suggests that substitution has occurred by an S_E2 rather than S'_E2 mechanism. It is possible, however, for the 1-methallyl mercurial formed by attack at C_3, to undergo a rapid rearrangement to the more thermodynamically stable 3-methallyl derivative



$$CH_2{=}CH{-}CH(HgBr){-}CH_3 \rightleftharpoons BrHg{-}CH_2{-}CH{=}CH{-}CH_3 \quad (4)$$

The site of electrophilic attack can only be determined by examining the products of cleavage of the 1-methallylgermane. So far, all attempts to synthesise this compound have failed, though the corresponding silane has apparently been prepared[3]. The details of this synthesis were not reported.

Grignard syntheses from 1-methallyl halides always result in the formation of the 3-methallyl Grignard indicating that a dynamic equilibrium similar to (4) is set up, the position of equilibrium lying far to the right. It is probable that allylic mercurials behave in an analagous fashion. Therefore, in spite of the observed products, an S'_E2 process cannot be ruled out. It is reasonable to suppose that, like the silane analogues, the allylgermanes react via a complex. The formation of such a complex could not be traced in the case of the germanes because of the high reaction rate and the consequently low concentrations of reagents employed. For anionotropic rearrangements, the S_N2 mechanism is always more probable than the S'_N2 process. This has been attributed to the repulsion of the incoming nucleophile at C_3 by the electron cloud of the allylic double bond. In the case of cationotropy, where the attacking species is electron deficient, the situation is reversed and S'_E2 processes should predominate over S_E2. This has already been demonstrated by Sleezer, Winstein and Young[4] for the acidolysis of allylmercurials, and by Kuivila and Verdone[5] for the acid cleavage of allyltin compounds. Returning to the present work, evidence for an S'_E2 mechanism can be gleaned from a more detailed discussion of the effect on reaction rate of a 3-methyl substituent. The ratio $k_2(Me)/k_2(H)$, [where the substituent at C_3 appears in parentheses] has values of 2.8 and 4.3 for solvents acetonitrile and ethanol respectively (*vide infra*). If substitution proceeded without rearrangement, that is by an S_E2 mechanism, this ratio would be close to unity since the 3-methyl substituent, being remote from the reaction centre would not appreciably alter the electron density at C_1. The values obtained, therefore, point towards an S'_E2 mechanism, in which the methyl group attached directly to the reaction centre would facilitate reaction. In addition, it was noted that in the case of the silanes where complex formation could actually be observed, the rate of formation was much greater for the 3-methallylsilane than for the allylsilane[6]. Although somewhat indirect, the evidence favours mechanism S'_E2 rather than S_E2.

By comparing the relative rates of cleavage of triethylallylsilanes and -germanes a value of $k_2(Ge)/k_2(Si)$ of 167 was obtained. This, coupled with the fact that under identical conditions, triethylallyltin reacts at a rate too fast to be measured, leads to the reactivity sequence

$$Et_3Sn \gg Et_3Ge > Et_3Si$$

This is the expected order for a reaction demanding electrons at the reaction centre and reflects the relative electron releasing properties of these groups.

Cleavage of allylgermanes in ethanol

Product analysis showed only a 25% yield of allylmercuric bromide, but following the course of the reaction spectrophotometrically by the disappearance of mercuric salt, the reaction could be followed to well over 50%. Thereafter, a side reaction occurred in which mercuric bromide was produced. Deviations from both first and second order plots occurred after 50% reaction. Data calculated on the initial stages of the reaction clearly indicated that the first step is a simple bimolecular process (Table 2). As expected the 3-methallyl compound reacted faster than the unsubstituted allylgermane. Change of electrophile revealed the reactivity sequence

TABLE 2

FIRST AND SECOND ORDER RATE CONSTANTS (k_1, sec^{-1}; k_2, l·mole^{-1}·sec^{-1}) FOR THE REACTION OF $Et_3GeCH_2CH{=}CHR$ AND $HgBr_2$ IN ABSOLUTE ETHANOL AT 25.0±0.1°

Run	R	$[Et_3GeCH_2CH{=}CHR]$ ($10^2 M$)	$[HgBr_2]$ ($10^2 M$)	10^4k_1	10^2k_2	% reaction followed
9	H	1.00	1.00	2.4	3.1	40
31	H	1.00	1.00	2.5	2.9	40
12	H	1.00	2.00	6.9	3.7	51
14	H	1.00	3.00	11.0	3.9	41
13	H	1.00	4.00	14.0	3.0	50
8	H	0.50	1.00	3.0	3.4	43
15	H	2.00	2.00	9.0	3.6	32
19	H	3.00	2.00	6.3	3.8	38
					av. 3.5	
24	CH_3	0.50	0.50	4.9	13.7	33
25	CH_3	0.75	0.75	10.9	16.2	37
22	CH_3	1.00	1.00	16.0	16.0	33
26	CH_3	1.50	1.50	19.2	14.9	33
23	CH_3	2.00	2.00	25.0	13.9	28
					av. 14.9	

$$Hg(OAc)_2 \gg Cl > Br > I$$

a result which parallels that found for the cleavage of allylsilanes[1]. Added lithium bromide in equimolar quantities strongly retards reaction. These observations are again in keeping with an S_E2 rather than S_F mechanism.

Product analysis on the cleavage of the 3-methallylgermane by mercuric bromide yielded 25% 3-methallylmercuric bromide which would suggest an S_E2 rather than $S_E'2$ mechanism though the same reservations apply as in solvent acetonitrile.

Nature of side reaction

There are three possible routes whereby mercuric bromide may be formed during the reaction

$$2\,\mathrm{RHgBr} \rightleftarrows \mathrm{R_2Hg}+\mathrm{HgBr_2} \tag{5}$$

$$\mathrm{Et_3GeBr}+\mathrm{RHgBr} \rightarrow \mathrm{Et_3GeR}+\mathrm{HgBr_2} \tag{6}$$

$$\left\{\begin{array}{ll}\mathrm{Et_3GeBr}+\mathrm{HOEt} \rightarrow \mathrm{Et_3GeOEt}+\mathrm{HBr} & (7)\\ \mathrm{HBr}+\mathrm{RHgBr} \rightarrow \mathrm{RH}+\mathrm{HgBr_2} & (8)\end{array}\right.$$

(R = allyl)

(5) is the well known symmetrisation reaction. Normally the equilibrium lies well to the left, but if sequestering agents such as ammonia[4] or halide ions are used, the equilibrium can be displaced to the right. Since bromide ions are produced by the solvolysis of triethylbromogermane, (5) is a possibility. However, a relatively large bromide ion concentration ($\sim 4\ M$) is needed to affect the equilibrium, and since the concentration of the reaction solution is at most $2 \times 10^{-2}\ M$, scheme (5) is improbable.

(6) is essentially the reverse of the forward reaction studied. Normally one would not expect $\mathrm{Et_3GeOEt}$, produced by the ethanolysis of $\mathrm{Et_3GeBr}$, to compete favourably with mercuric bromide as an electrophile, but the production of $\mathrm{Br^-}$ during the course of the reaction would favour the formation of $[\mathrm{HgBr_3}]^-$ and protonation of the oxygen atom in the ethoxygermane would increase its electrophilicity. Because (6) is an equilibrium we should only expect to follow the course of the reaction to 25 % completion and not, as is observed, to greater than 50 % completion, which is beyond the position of equilibrium. Hence (6) is not thermodynamically feasible. Recent work by Kreevoy[5] has shown that allylic mercurials are readily acidolysed giving support to postulate (7, 8). To test these hypotheses, the following experiments were carried out in EtOH, the rate of production of $\mathrm{HgBr_2}$ being measured in each case.

$$\mathrm{Et_3GeBr}+\mathrm{RHgBr} \rightarrow \mathrm{HgBr_2}\ \text{formed} \tag{9}$$

$$\mathrm{Et_3GeOEt}+\mathrm{RHgBr}+\mathrm{Br^-} \rightarrow \text{no}\ \mathrm{HgBr_2}\ \text{formed} \tag{10}$$

$$\mathrm{RHgBr}+\mathrm{Br^-} \rightarrow \text{no}\ \mathrm{HgBr_2}\ \text{formed} \tag{11}$$

If (5) were valid, all three reactions should have yielded $\mathrm{HgBr_2}$. If (6) were valid, both (9) and (10) would have produced $\mathrm{HgBr_2}$. If (7) were valid only (9) should show reaction.

The experimental observations demonstrate clearly that the competing side reaction is the acidolysis of the mercurial produced during the reaction.

Cleavage in DMSO

Only a 50 % yield of bromogermane was found in this solvent. This result parallels that obtained for the silane analogues and is explained by the intervention of (2) in the reaction scheme described above. In view of this complication, no detailed kinetics were attempted.

EXPERIMENTAL

Triethylallylgermane (b.p. 60–62°/10 mm, n_D^{20} 1.4595) and triethyl-3-methallylgermane (b.p. 76–78°/14 mm, n_D^{20} 1.4639) and trimethylallyltin (b.p. 128–130°, n_D^{20} 1.4725) were prepared in good yield by standard Grignard synthesis. Both allyl- and 3-methallylmercuric bromides were prepared by direct mercuration of the corresponding bromide, using finely divided mercury and *m*-chloroperoxybenzoic acid, and irradiating with UV light.

Acetonitrile was purified by refluxing over P_2O_5 for 6 h and distilling from anhydrous sodium carbonate. The solvent was fractionated again just prior to use. Ethanol and DMSO were purified by standard procedures.

Mercuric halides were recrystallised from acetone/chloroform mixtures and mercuric acetate from ethanol.

Kinetic techniques

For solvent ethanol, the reaction was followed measuring the rate of disappearance of mercuric salt by spectrophotometric means. Aliquots (5 ml) of the reaction mixture were quenched in 0.04 *M* KI solution (10 ml) at 0°, whence the allylmercuric halide was quantitatively precipitated. The method was checked using synthetic mixtures of mercuric bromide and allylmercuric bromide. The mixture was filtered at 0° and suitably diluted with KI solution. The absorbance of the diluted

TABLE 3

VALUES OF k_2 (l·mole^{-1}·sec^{-1}) FOR THE REACTION OF $Et_3GeCH_2CH{=}CH_2$ (0.01 *M*) WITH $HgBr_2$ (0.01 *M*) IN ETHANOL AT 25.0±0.1°

Time (sec)	D_t-D_∞	10^3x (mole·l^{-1})	$x/(a-x)$	10^2k_2
0	0.611		0.000	
240	0.571	0.66	0.071	3.0
360	0.544	1.10	0.124	3.4
480	0.532	1.29	0.148	3.1
600	0.524	1.43	0.167	2.8
720	0.510	1.65	0.198	2.8
840	0.491	1.96	0.244	2.9
960	0.486	2.05	0.258	2.7

TABLE 4

VALUES OF k_2 (l·mole^{-1}·sec^{-1}) FOR THE REACTION OF $Et_3GeCH_2CH{=}CH_2$ ($a=7.5\times10^{-5}$ *M*) AND $HgBr_2$ ($b=7.5\times10^{-5}$ *M*) IN ACETONITRILE AT 24.9±0.1°

Time (sec)	D_t	10^4x^a (mole·l^{-1})	$x/(a-x)$	k_2
0	0.532	0.262	0.54	40
180	0.373	0.379	1.02	37
360	0.302	0.441	1.43	35
540	0.265	0.485	1.83	33
720	0.238	0.526	2.35	35
900	0.213	0.572	3.21	39
1080	0.185	0.575	3.28	35
1260	0.183	0.603	4.10	37
1440	0.167			
	0.091			

[a] Calculated from the equation $x=1.65\times10^{-4}(7100b-D_t)$, which itself was derived from calibration data.

sample was measured at 323 mμ [λ_{max} for $(HgI_4)^{2-}$]. Solutions of mercuric bromide in KI obeyed Beer's law over the concentration range used in the work. Table 3 shows a typical run.

For solvent acetonitrile, a new technique had to be developed since the solutions used were too dilute (10^{-4} *M*). Aliquots (5 ml) were quenched in a mixture of 0.04 *M* KI (10 ml) and carbon tetrachloride (20 ml). The KI removed all the unreacted mercuric bromide as $[HgI_4]^{2-}$ plus a small quantity of allylmercuric bromide which was corrected for. The layers were separated and the absorbance of the KI layer measured at 323 mμ. Calibrations were made, using synthetic mixtures of allylmercuric bromide and mercuric bromide. Table 4 shows a typical run.

Products

Triethyl-3-methallylgermane (1.00 g, 0.0046 mole) in absolute ethanol (5 ml) at 0° was treated with mercuric bromide (1.8 g, 0.005 mole) in ethanol (10 ml) at 0°. A white precipitate occurred immediately. This was filtered off, washed with a little cold ethanol and sucked dry. More solid was recovered from the mother liquor on concentration. The combined yield was recrystallised from pentane to give 0.38 g (25 %), m.p. 88–89°. A mixture of the product and an authentic specimen of 3-methallylmercuric bromide melted at 88–89°, and the infrared spectrum of the product was identical with that of 3-methallylmercuric bromide.

For solvent acetonitrile, a similar procedure yielded 88 % 3-methallylmercuric bromide.

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