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BASE CLEAVAGE OF α-HALOSUBSTITUTED ALKYL GROUPS FROM GERMANIUM

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Summary

A kinetic study has been made of the base cleavage of di- and trihalomethyl(trimethyl)germanes (Me_3GeCHX_2, Me_3GeCX_3; X = Cl, Br) in n-propanol/water in the presence of ammonia buffer. Two processes leading to the Ge–C bond cleavage were detected, and their rate constants were determined. The results for the dihalomethyl(trimethyl)germanes are compared with those for the corresponding processes at silicon and tin centres.

Introduction

Over thirty years ago Hughes [1] drew attention to the analogy between nucleophilic substitution at silicon and that at a carbonyl centre and the same analogy was recently made by Dewar [2]. Experiments in this laboratory have confirmed that mechanistic similarity between $B_{AC}2$ type process at carbonyl carbon in $MeC(O)CX_3$ compounds and nucleophilic substitution at silicon and tin atoms in Me_3SiCHX_2 and Me_3SnCHX_2; (X = Cl, Br) compounds [3]. It has been now found that polyhalomethyl(trimethyl)germanes (Me_3GeCHX_2, Me_3GeCX_3) undergo reactions of the same type.

Results and discussion

The rate of solvolytic cleavage of polyhalomethyl(trimethyl)germanes in 8/2 v/v n-propanol/water can be determined by observing the change of haloalkane concentration by GLC using an internal standard. Thus, solutions of germanes in n-propanol/water solvent, containing ammonia buffer, LiCl *, and an internal standard [3] were kept at 25°C. Samples were withdrawn with Hamilton micro-

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* Ionic strength was maintained at 0.4 by the addition LiCl.

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TABLE 1

SOLVOLYSIS OF (POLYHALOMETHYL)TRIMETHYLGERMANES IN n-PrOH/H_2O 8/2 v/v; 25°C, μ 0.4

Compound	$10^7 \times k_2$ (l mol^{-1} s^{-1})	$10^7 \times k_3$ (l mol^{-1} s^{-1})
$Me_3GeCHCl_2$	0.03	0.04
$Me_3GeCHBr_2$	5.4	6.1
Me_3GeCCl_3	181	249
Me_3GeCBr_3	7922	67500

TABLE 2

COMPARISON OF THE DATA FOR CLEAVAGE OF DIHALOMETHYL GROUPS FROM SILICON, GERMANIUM AND TIN

Compound	$10^7 \times k_2$ (l mol^{-1} s^{-1})	$k_{2(rel)}$ [c]	$10^7 \times k_3$ (l mol^{-1} s^{-1})	$k_{3(rel)}$ [c]
$Me_3SiCHCl_2$ [a]	0.92	1	6.99	1
$Me_3GeCHCl_2$	0.03	0.033	0.04	0.006
$Me_3SnCHCl_2$ [b]	0.43	0.47	0.3	0.043
$Me_3SiCHBr_2$ [a]	107	1	169	1
$Me_3GeCHBr_2$	5.4	0.05	6.1	0.036
$Me_3SnCHBr_2$	4.37	0.04	5.12	0.030

[a] Ref. 4 [b] Ref. 5. [c] Rate relative to that of the corresponding silicon compound.

syringe at appropriate intervals of time and analysed by GLC. The first order rate constants k_1 were derived from the haloalkane/standard peak areas. The k_1 values were plotted against the ammonia concentration, as described earlier [4], and the two catalytic rate constants in eq. 1 were calculated. The results are shown in Table 1.

$$\text{Rate} = k_1[\equiv\text{Ge}-\text{C}] = \left\{ k_2 \frac{[NH_3]}{[NH_4Cl]} + k_3[NH_3]\frac{[NH_3]}{[NH_4Cl]} \right\}[\equiv\text{Ge}-\text{C}] \tag{1}$$

The features of the Ge–C bond cleavage processes considered in terms of the stepwise mechanism established for the other Group IV electrophilic centres [5], are as follows:

(1) The kinetic data are fully consistent with those obtained earlier for dihalomethylsilanes and dihalomethyltins, as can be seen from Table 2, which gives data for the simple base catalysis (k_2) and base/nucleophile catalysis (k_3) *.

(2) The contributions of the ammonlysis, (given by k_3/k_2, which has a value of 1.3 for $Me_3GeCHCl_2$ and 1.1 for $Me_3GeCHBr_2$) are between those for silicon analogues (7.6 for $Me_3SiCHCl_2$ and 1.6 for $Me_3SiCHBr_2$) and those for the tin analogues (0.7 for $Me_3SnCHCl_2$ and 1.2 for $Me_3SnCHBr_2$), with a slight relative

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* In contrast to the situation with the germanes and silanes, the main process for the dihalotins cleavage is the reaction catalysed by weak base (NH_3), the rate equation having the form.

$$k_1 = k_1[NH_3] + k_2[NH_3]/[NH_4Cl] + k_3[NH_3]^2/[NH_4Cl]$$

decrease in the reaction rate with nitrogen nucleophile for the less electronegative and softer dibromomethyl leaving group.

(3) Decomposition of the unstable intermediates $[ROGe(Me_3)CHX_2]^-$ and $[H_2NGe(Me_3)CHX_2]^-$ is the rate determining step in the reactions with RO^- and H_3N. The rates are markedly greater for the better polybromomethyl leaving groups; the relative rates for $CHBr_2/CHCl_2$ and $CHBr_3/CHBr_3$ being as follows k_2 $(CHX_2)_{rel.}$ 180; k_2 $(CX_3)_{rel.}$ 44; k_3 $(CHX_2)_{rel.}$ 152; k_3 (CX_3), 271.

(4) (Dichloromethyl)trimethylgermane (Table 2) is less reactive than the corresponding silicon and tin derivatives. (Dibromomethyl)trimethylgermane is also less reactive than the analogous silane but fairly close in reactivity to the analogous tin compound. It should be emphasised, however, that the observed low reactivity of organotins arises from the fact that the general catalysis route k_1 is favoured in the medium used [5].

As the reactivities of dihalomethylsilanes and phenylethynylsilanes are of the same order [6], it is of interest that the increase in the rate constant for the simple base catalysed process on going from the germanium to the silicon derivative, involving factors of 31 and 20 for the dichloromethyl- and (dibromomethyl)trimethyl compounds are consistent with the corresponding factor of 34 observed for (phenylethynyl) trimethyl-silane and -germane in the reaction with RO^- ($R = H$, Me) [7].

Experimental

The methods used for rate measurements have been described previously [3].

(Dibromomethyl)trimethylgermane

A solution of bromoform (25.3 g (0.1 *M*)) in 100 ml THF was cooled to −90°C and 0.1 *M* i-PrMgCl in 50 ml of THF was added during 15 min at −80°C. After addition of 20 g (0.1 *M*) Me_3GeBr in 40 ml THF at the same temperature the mixture was stirred for 0.5 h at −80°C then allowed to warm to room temperature and hydrolysed with saturated NH_4Cl. The organic layer was separated, dried over Na_2SO_4, and distilled to give 22.6 g $Me_3GeCHBr_2$, b.p. 72°C/60 mmHg with 78% yield. MS *m/e*: 296 (M^+). Found: C, 16.48; H, 3.40; Br, 55.11. $C_4H_{10}Br_2Ge$ calcd.: C, 16.54; H, 3.47; Br, 55.00%.

(Dichloromethyl)trimethylgermane

This was prepared as described above for $Me_3GeCHBr_2$ but using $CHCl_3$ instead of $CHBr_3$; 55% yield, b.p. 65°C/30 mmHg/(Lit. 150–160°C [8]). MS (*m/e*): 208 (M^+). Found: C, 24.01; H, 4.89; Cl, 35.25. $C_4H_{10}Cl_2Ge$ calcd.: C, 23.82; H, 4.96; Cl, 35.19.

(Tribromomethyl)trimethylgermane

$Me_3GeCHBr_2$, 11.5 g (0.04 *M*) was treated with 7.55 g (0.04 *M*) of *N*-bromosuccinimide in the presence of 0.2 g of benzoyl peroxide in 50 ml CCl_4 at 100°C for 1 h. The solution was filtered then evaporated, and the crude product was crystallized from n-propanol. Me_3GeCBr_3, 15.4 g, was obtained in 90% yield, m.p. 109°C. MS *m/e*: 376(M^+). Found: C, 12.92; H, 2.54; Br, 64.79. $C_4H_9Br_3Ge$ calcd.: C, 13.00; H, 2.46; Br, 64.90.

(Trichloromethyl)trimethylgermane

A mixture of 2.6 g (0.11 *M*) Mg, 23 g (0.15) CCl_4 and 14.8 g (0.075 *M*) Me_3GeBr was stirred under argon and 30 g (0.16 *M*) HMPT was slowly added, the temperature being kept below 60°C. The mixture was then stirred for 4 h at 45°C. 100 ml Et_2O was added, and the mixture hydrolysed with dilute HCl. The organic layer was separated and dried over $MgSO_4$. After removal of the Et_2O the product was crystalized from n-propanol to give 10 g of Me_3GeCCl_3 with 56% yield, m.p. 95°C Lit. 25°C [9]. MS *m/e*: 244(M^+). Found: C, 20.30; H, 3.89; Cl, 45.00. $C_4H_9Cl_3Ge$ calcd.: C, 20.35; H, 3.84; Cl, 45.05%.

References

1 E.D. Hughes, Quart. Revs., 5 (1951) 245.
2 M.J.S. Dewar and E. Healy, Organometallics, 1 (1982) 1705.
3 W. Stańczyk, J. Chmielecka and J. Chojnowski, J. Org. Chem., 47 (1982) 3757.
4 J. Chojnowski and W. Stańczyk, J. Organomet. Chem., 73 (1974) 41.
5 W. Stańczyk and J. Chojnowski, J. Organomet. Chem., 193 (1980) 31.
6 J. Chmielecka, J. Chojnowski, C. Eaborn and W. Stańczyk, J. Chem. Soc. Perkin Trans., in press
7 C. Eaborn and D.R.M. Walton, J. Organomet. Chem., 4 (1965) 217.
8 W.F. Mironow, S.A. Michajlanc and T.K. Gar, Zh. Obsch. Khim. 39 (1969) 397.
9 J. Satgé, C. Couret and J. Escudié, J. Organomet. Chem., 24 (1970) 633.