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ALKALINE CLEAVAGE OF *ortho*-, *meta*- AND *para*-CARBORANYL(12)-TRIMETHYLSTANNANES

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SUMMARY

Alkaline cleavage of *o*-, *m*- and *p*-carboranyltrimethylstannanes in CH_3OH with KOH and in CD_3OD with KOD has been investigated.

The values of the rate constants obtained in CD_3OD were found to be in agreement with those in CH_3OH, and varied in the order *ortho* ≫ *meta* > *para*. A mechanism for the cleavage reaction has been suggested.

During the course of extensive investigations into the alkaline cleavage of Group IV derivatives, Eaborn and co-workers have shown that the trends exhibited during these reactions differ from those observed in the acid cleavage reactions classified as S_E2[1–6].

On the basis of these kinetic studies four possible mechanisms have been suggested[6–8]:

(1). Simultaneous attack of the OR^- ion on the tin atom with cleavage of the carbon–tin bond.

(2). Rapid formation of a penta-coordinate tin intermediate followed by a rate-determining cleavage of the carbon–tin bond.

(3). The rate-determining formation of a penta-coordinate tin intermediate followed by the rapid cleavage of the carbon-tin bond.

(4). Electrophilic attack by the solvent at the carbon atom and nucleophilic attack at the tin atom proceeding at comparable rates.

Mechanisms (1) and (2) may be explained in terms of an S_E1 (N) reaction[8].

If electrophilic attack on the carbanion or on any other intermediate occurs during the fast stage of the process, no deuterium kinetic isotope effect will be observed.

Eaborn and co-workers[9] have shown, however, that a pronounced kinetic isotope effect does occur during the alkaline cleavage of compounds of the type $XC_6H_4SnMe_3$ in mixtures of methanol and O-deuteriomethanol, the hydrogen atom being incorporated into the cleavage product almost four times faster than deuterium. This observation seems to support the existence of mechanism (4). However, such an ionic mechanism seems hardly likely in compounds of the type $ArSnMe_3$[8]. In this series, an anomaly has been observed in the substituent effect[6,7] and in addition it has been shown that in the alkaline cleavage of aryltrimethylsilanes the experimental

points obtained for the benzyl and phenyl derivatives do not fit into the relationship $\log k_2 = f(pK_a)$[8].

It is therefore of interest to study the nature of alkaline cleavage in *o*-, *m*- and *p*-carboranyltrimethylstannanes in which the carbon atom is formally in a hexa-coordinated state and the formation of a hepta-coordinated intermediate and cleavage of the C–Sn bond as implied by mechanism (4) is therefore unlikely. In addition, the "special state" of the carbon atom in carboranes suggests that electrophilic attack by the proton would be possible only at the free carboranyl anion.

Studies of the alkaline cleavage were carried out using KOH in methanol at different alkali concentrations and over a wide range of temperatures. The quantity of carboranes formed during the cleavage reactions was estimated by the use of GLC employing an internal standard.

The results obtained for the alkaline cleavage of *o*-, *m*- and *p*-carboranyl-stannanes are listed in Table 1.

TABLE 1

CLEAVAGE REACTIONS OF *o*-, *m*- AND *p*-CARBORANYLTRIMETHYLSTANNANES WITH KOH IN METHANOL[a]

$C_2B_{10}H_{11}Sn(CH_3)_3$ (0.05 *M*)	*Temp.* (°C)	*KOH* (*M*)	$10^5 k^b$ (s^{-1})	$10^5 k_2{}^c$ ($l \cdot mole^{-1} \cdot s^{-1}$)	*Average* $10^5 k_2$ ($l \cdot mole^{-1} \cdot s^{-1}$)
para	20	0.5	5.5±0.3	11	11.9
		0.7	8.5±0.4	12.1	
		1	12.2±0.5	12.2	
	30	0.5	17.8±0.9	35.6	36.4
		0.7	27.2±0.3	38.8	
		1	35±2	35	
	40	0.05		112±3	107
		0.5	57±3	113	
		0.7	68±4	98	
		1	110±3	110	
	50	0.5	140±10	286	286
meta	10	0.5	40±2	80	77
		0.7	52±2	74	
		1	77±3	77	
	15	0.43	57±5	132	129
		0.7	85±9	121	
		1	133±10	133	
	20	0.05		193±9[d]	198
		0.5	93±4	186	
		0.7	125±5	178	
		1.09	250±20	229	
	25	0.5	145±9	290	290
ortho	−40	0.5	93±8	186	186
	−50	0.5	38±5	76	76

[a] Constants were estimated by the method of least squares, confidence limits being estimated from the experimental curve, the probability *R* being equal to 0.95. The average experimental error between individual experiments did not exceed 10%. For the *o*-carboranyl series the average experimental error was ca. 20%, as every point on the kinetic curve was determined from a separate run. [b] $k_1 = (2.303/t) \cdot \log(C_0/C)$. [c] $k_2 = k_1/[OH^-]$. [d] $k_2 = [1/(C_0 \cdot t)] \cdot (C_0/C - 1)$.

Values of the second-order rate constants obtained for *m*- and *p*-carboranyl derivatives were found to fit the kinetic curve quite well, to be independent of the initial concentrations employed and to be the same irrespective of whether the experiments were carried out with pseudo-unimolecular conditions (excess alkali) or with initial equimolecular concentrations of reagents. The value of k_2 obtained for *o*-carboranyltrimethylstannane is only approximate, due to its very large value, although individual values of k_2 agreed amongst each other quite well when the experiments were repeated. The various thermodynamic parameters (Table 2) were determined from the dependence of k_2 on temperature.

TABLE 2[a]

THERMODYNAMIC PARAMETERS

Compound	$\Delta H^{\neq}$ (*kcal·mole*$^{-1}$)	$\Delta S^{\neq}$ (*kcal·mole*$^{-1}$ *deg.*$^{-1}$)
o-$C_2B_{10}H_{11}Sn(CH_3)_3$ (I)	8.8	−32.6
m-$C_2B_{10}H_{11}Sn(CH_3)_3$ (II)	14.9	−19.96
p-$C_2B_{10}H_{11}Sn(CH_3)_3$ (III)	19.2	−10.95

[a] The activation energies estimated by the method of least squares for the three compounds were found to obey the relationships:
$\log k_2 = 6.08 - 2053.7/T$ for compound (I)
$\log k_2 = 8.85 - 3387.0/T$ for compound (II)
$\log k_2 = 10.82 - 4323.8/T$ for compound (III)

From the data obtained (Table 1), the rate constant for the alkaline cleavage of C–Sn in carboranyl derivatives is seen to vary in the order *ortho* ≫ *meta* > *para* with corresponding values of $k_{rel}^{20°}$ of 1020, 17 and 1.

This variation in the rate of reaction appears to be associated with an increasing enthalpy of activation which is only partially compensated by the change in the entropy of activation.

A linear relationship exists between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with a value of β approximately equal to 500 *K*; as the series of compounds studied is very small, however, it is not possible to claim unambiguously that there is a compensation effect. However, the existence of a certain compensation dependence between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ could be put forward as an argument for a common reaction mechanism for the particular series of *o*-, *m*- and *p*-carborane derivatives studied. The reactivity order observed corresponds to the stability of the carboranyl anions. A linear relationship also exists between the rate constants k_2 and the pK_a values of the carborane isomers:
$\log k_2 = 3.63 - 0.19\ pK_a$. (See Fig. 1.)

In fact, the data obtained suggest that the rate-determining step is the ionisation of the C–Sn bond [mechanism (1) or (2)] followed by a fast reaction with the solvent[8]. It is not possible, however, on kinetic grounds to make a clear-cut distinction between these two mechanisms. Furthermore, it is not possible to completely exclude mechanism (3), although the ready coordination of tin with nucleophiles in compounds involving strong electron-accepting groups makes this mechanism unlikely.

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For this reason, we have studied the alkaline cleavage of the three isomers in

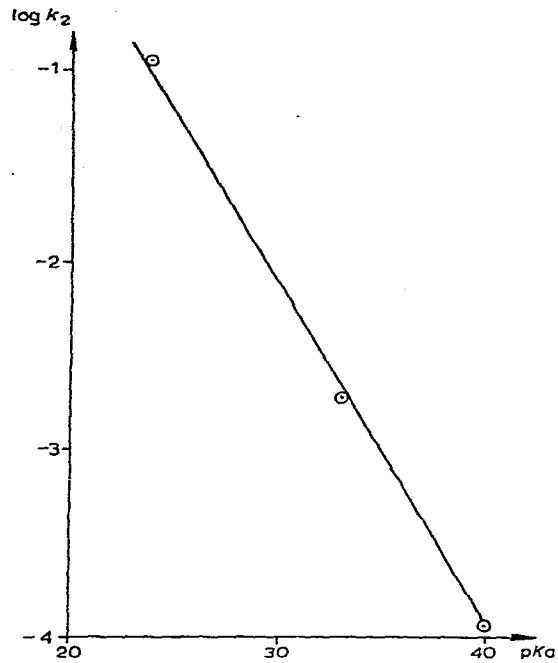

Fig. 1. The relationship between log k_2 and pKa of carboranetrimethylstannanes; pKa was taken from ref. 10, and $k_2^{20°}$ for *o*-carboranyltrimethylstannane was estimated from the Arrhenius relationship.

CD_3OD/KOD. The values of the rate constants obtained using this system were in agreement with those obtained in CH_3OH within the limits of experimental error (Table 3).

The results obtained indicate the absence of any appreciable kinetic isotope effect which it is suggested may be explained on the basis of the following mechanism:

$$o\text{-, } m\text{-, } p\text{-}HCB_{10}H_{10}C\text{-}Sn(CH_3)_3 + B^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$o\text{-, } m\text{-, } p\text{-}HCB_{10}H_{10}C^-[(CH_3)_3SnB] \xrightarrow[k_2]{CH_3OH}$$

$$o\text{-, } m\text{-, } p\text{-}HCB_{10}H_{10}CH + (CH_3)_3SnB$$

If $k_2 \gg k_{-1}$, then the overall rate of reaction may be expressed by the equation:

$$\text{Rate} = k_1 \cdot [Me_3SnR] \cdot [OH^-]$$

EXPERIMENTAL

o-, *m*- and *p*-Carboranyltrimethylstannanes were prepared according to the method previously described[11].

Rate measurements

To 0.1535 g (0.0005 mole) of *m*-, *p*-carboranyltrimethylstannanes in 9 ml of

TABLE 3

CLEAVAGE OF *o*-, *m*- AND *p*-CARBORANYLSTANNANES WITH KOD IN CD_3OD[a]

Compound	*Temp.* (°C)	$10^5 k_1$ (s^{-1})	$10^5 k_2$ ($l \cdot mole^{-1} \cdot s^{-1}$)
o-$C_2B_{10}H_{11}Sn(CH_3)_3$	−40	93	183
m-$C_2B_{10}H_{11}Sn(CH_3)_3$	20	92	183
p-$C_2B_{10}H_{11}Sn(CH_3)_3$	40	52	105

[a] Concentration of carboranylstannane 0.05 *M*, of KOD 0.5 *M*.

methyl alcohol was added 1 ml of a 60% CH_3OH/KOH solution containing different KOH concentrations for each series of experiments (0.56 g, 0.01 mole; 0.28 g, 0.005 mole; 0.392 g, 0.007 mole; 0.028 g, 0.0005 mole). Individual samples (0.5 ml) were neutralised with 1 ml of 1 *M* HCl and the cleavage products isolated by extraction with 1 ml of ethyl acetate. Complete extraction of carboranes was effected under these conditions.

Since the cleavage reactions of *o*-carboranyltrimethylstannane were studied at low temperature, a method involving the use of separate samples was employed.

In this case, 0.5 ml samples of a methanol solution of *o*-carboranyltrimethylstannane (0.05 *M*) were placed in a thermostat bath and the samples were maintained at the required temperature following the addition of 0.056 ml of a methanol solution of sodium hydroxide (0.5 *M*). At various time intervals 1 ml of *M* HCl was added to the samples and the cleavage products isolated by the method mentioned above.

The cleavage reactions with KOD in CD_3OD were carried out in a similar manner.

GLC analysis for *m*- and *p*-carboranes was effected using *o*-carborane as an internal standard and for *o*-carborane the internal standard used was *m*-carborane. Each analysis was repeated 2–3 times.

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