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THE CLEAVAGES OF A SERIES OF ALKYLTRIISOPROPYLTINS BY MERCURY ACETATE IN METHANOL

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Summary

Rate constants are reported for the removal by mercuric acetate in methanol at 30° of the alkyl group, R, from the compounds $RSn\text{-}i\text{-}Pr_3$ with R = Me, Et, n-Pr, i-Bu, neo-Pe and i-Pr. There are extremely large steric effects of the group R on the rate constants for substitution, $k(MeSn\text{-}i\text{-}Pr_3)/k(i\text{-}PrSn\text{-}i\text{-}Pr_3)$ being 1.1×10^8, but the pattern of reactivity as R is varied is not the same as that found in S_N2 reactions and also differs from that found for the reaction of alkyltrineopentyltins with bromine in methanol. Comparison with previous work shows that in contrast to the very large effects of the alkyl group being removed, there are only minor effects due to the alkyl groups on the leaving tin atom.

Introduction

In 1961, Gielen and Nasielski [1] suggested that the constitutional effects of alkyl groups in the halogenodemetallation of tetraalkyltins in polar solvents were steric in origin. Other workers [2] suggested that steric effects in the alkyl group undergoing substitution were more important than any constitutional effects due to the alkyl groups of the leaving SnR_3 moiety, and further studies of halogenodemetallations in polar solvents [3] confirmed this [4]. Although only one unsymmetrical tetraalkyltin was studied [5], work on the cleavage of tetraalkyltins by mercuric salts indicated that in polar solvents the effects of the alkyl groups were again steric in origin [4-6].

Jensen and Davies [7] then reported (a) that reaction 1 (R = s-Bu) took place with inversion of configuration at the carbon atom undergoing substitution, and (b) that the steric effects for R = Me, Et, i-Pr and neo-Pe paralleled the

$$RSn\text{-}neo\text{-}Pe_3 + Br_2 \xrightarrow{Br^-/MeOH} RBr + neo\text{-}Pe_3SnBr \qquad (1)$$

steric effects of alkyl groups in a typical S_N2 reaction.

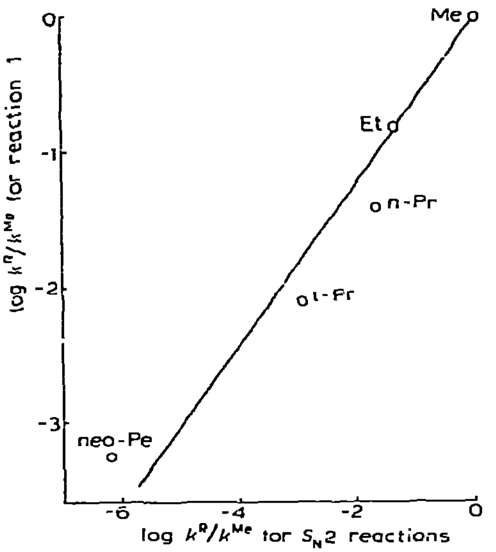

Fig. 1. Plot of log (k^R/k^{Me}) for reaction 1 against log (k^R/k^{Me}) for S_N2 reactions.

In fig. 1 log k^R/k^{Me} is plotted for reaction 1 against log k^R/k^{Me} values for S_N2 substitutions of alkyl halides [8]; a reasonably straight line is obtained (compare the corresponding Figure in ref. 7). Following Jensen and Davis's report, Abraham and Grellier [9] measured rate constants of the S_E2 (open) reaction 2 for a number of tetraalkyltins* and observed that although there were

$$R_4Sn + Hg(OAc)_2 \xrightarrow{MeOH} RHgOAc + R_3SnOAc \qquad (2)$$

exceptionally large constitutional effects of the alkyl groups, R, these effects did not parallel those observed in S_N2 reactions, or those in reaction 1. However, Abraham and Grellier's conclusions were based on rate data involving symmetrical tetraalkyltins, in which the leaving group SnR_3 changes along the series, whereas the data of Jensen and Davis (and also the data on S_N2 reactions) refer to a set of substitutions in which the leaving group remains constant. It seemed important therefore to obtain rate constants for the reaction of mercuric acetate with a series of unsymmetrical tetraalkyltins in which the leaving group remains constant. Since the isopropyl group is cleaved from tin extremely slowly by mercuric acetate (about 100 times less readily than the neopentyl group [9]), we prepared a series of compounds of type $RSn\text{-}i\text{-}Pr_3$ and studied their reactions with mercuric acetate in methanol.

Discussion

As we had expected, only the alkyl group R was removed by mercuric acetate and so the observed second-order rate constants refer only to the cleavage reaction 3. Details of the rate measurements are in the Experimental

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[*] For recent experimental evidence that reaction 2 does indeed proceed through an open transition state, see ref. 10.

TABLE I

RATE CONSTANTS ($l\ mol^{-1}\ min^{-1}$) FOR THE CLEAVAGE OF TETRAALKYLTINS BY MERCURIC SALTS IN METHANOL

Reactants	T(°C)		R					
			Me	Et	n-Pr	i-Bu	neo-Pe	i-Pr
$RSn\text{-}i\text{-}Pr_3 + Hg(OAc)_2$[a]	30	k_2:	2190	4.97	0.952	0.514	5.27×10^{-3}	2.02×10^{-5}
$RSnR_3 + Hg(OAc)_2$[b]	30	k_2:	3500	15.3	3.13	0.665	2.85×10^{-3}	2.02×10^{-5}
$RSn\text{-}i\text{-}Pr_3 + Hg(OAc)_2$	30	Rel. k_2:	100	0.23	0.044	0.024	2.4×10^{-4}	9.2×10^{-7}
$RSnR_3 + Hg(OAc)_2$	30	Rel. k_2:	100	0.44	0.089	0.019	8.1×10^{-5}	5.8×10^{-7}
$RSnR_3 + HgCl_2$[c]	40	Rel. k_2:	100	0.29	0.058	8.1×10^{-3}	6.6×10^{-5}	$<4.0 \times 10^{-7}$

[a] This work. [b] Statistically corrected rate constants from ref. 9. [c] Refs. 6 and 9; the value for R = neo-Pe is a more recent one.

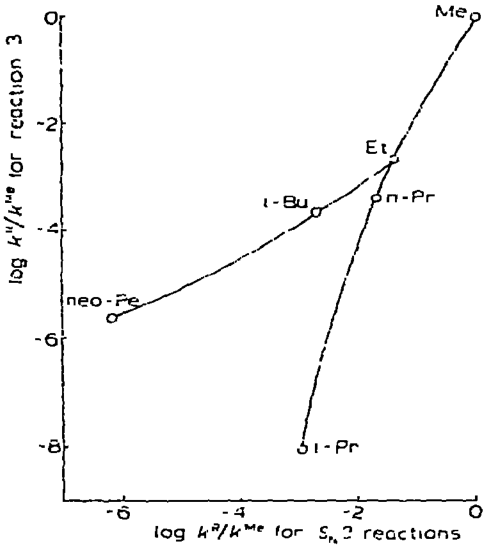

Fig. 2. Plot of log (k^R/k^{Me}) for reaction 3 against log (k^R/k^{Me}) for S_N2 reactions.

Section, and Table 1 lists rate constants for reaction 3 as well as those for the related reaction 2. The two sets of rate constants are closely related, as can be seen from the relative rate constants for reactions 2, 3, and the $R_4Sn/HgCl_2$ reaction [6], also in Table 1. The steric effects of the alkyl groups in the three reactions are very similar; values of log k^R/k^{Me} are linearly related, and when plotted against log k^R/k^{Me} values for S_N2 reactions, all three sets of data yield almost identical curves (see Fig. 2). Abraham and Grellier's conclusions are thus not changed by the new results, and it is clear that the steric effects of

$$\mathrm{RSn\text{-}i\text{-}Pr_3 + Hg(OAc)_2 \xrightarrow{MeOH} RHgOAc + i\text{-}Pr_3SnOAc} \tag{3}$$

the alkyl group R in reaction 1 are not similar to those in reaction 3, especially when branched-chain alkyl groups (R = i-Pr, i-Bu, neo-Pe) are involved. In reaction 1 the isopropyl group is removed about 12 times as rapidly as the neopentyl group, but in reaction 3 the neopentyl group is removed 260 times as rapidly as the isopropyl group.

The present work together with previous results [6, 9] shows that in methanol, (a) the electrophiles $Hg(OAc)_2$ and $HgCl_2$ react with tetraalkyltins giving rise to rate sequences that are almost identical, and (b) with the electrophile $Hg(OAc)_2$ the effect of the leaving group SnR_3 on the rate constant is very small. In Table 2 are shown values of $k(RSnR_3)/k(RSn\text{-}i\text{-}Pr_3)$; these values cover a range of only 0.54 to 3.29, whereas variation of the displaced alkyl group leads to factors of up to 1.1×10^8. The leaving group effects for reaction with different electrophiles in methanol [3, 11] are as follows:

$k(MeSnMe_3)/k(MeSn\text{-}i\text{-}Pr_3)$ for $Hg(OAc)_2$ 1.60, for Me_2Sn^{2+} 1.56 and for I_2 10.0.

It is surprising that the effects of the leaving R_3Sn groups in reactions 2 and 3

TABLE 2

LEAVING-GROUP EFFECTS IN THE CLEAVAGE OF TETRAALKYLTINS BY MERCURIC ACETATE IN METHANOL AT 30°

Substrates		Ratio of rate constants[a]
$MeSnMe_3$	$MeSn\text{-}i\text{-}Pr_3$	1.60
$EtSnEt_3$	$EtSn\text{-}i\text{-}Pr_3$	3.08
$n\text{-}PrSn\text{-}n\text{-}Pr_3$	$n\text{-}PrSn\text{-}i\text{-}Pr_3$	3.29
$i\text{-}BuSn\text{-}i\text{-}Bu_3$	$i\text{-}BuSn\text{-}i\text{-}Pr_3$	1.27
$neo\text{-}PeSn\text{-}neo\text{-}Pe_3$	$neo\text{-}PeSn\text{-}i\text{-}Pr_3$	0.54

[a] $k(R\text{-}SnR_3)/k(R\text{-}Sn\text{-}i\text{-}Pr_3)$

are so small if these reactions do indeed proceed with retention of configuration at the carbon atom undergoing substitution. With such a stereochemistry, there must be considerable steric congestion at the front of the carbon atom under attack.

Finally, it should be pointed out that the rate differences in reaction 3 arise merely through replacement of one alkyl group in the substrate by another, and as such represent one of the largest steric effects ever reported. The ratio $k(MeSn\text{-}i\text{-}Pr_3)/k(neo\text{-}PeSn\text{-}i\text{-}Pr_3)$ is 4.1×10^5 and the ratio $k(MeSn\text{-}i\text{-}Pr_3)/k(i\text{-}PrSn\text{-}i\text{-}Pr_3)$ no less than 1.1×10^8. For comparison, the largest rate factor in S_N2 reactions [8] is one of about 1×10^6 for the ratio $k(MeX)/k(neo\text{-}PeX)$.

Experimental

Methanol was distilled under nitrogen; a large fraction was rejected and the middle fraction retained. Mercuric acetate was recrystallised from glacial acetic acid.

All the compounds were made by standard procedures [12] involving the reaction of a Grignard compound on triisopropyltin bromide, which was made as described in ref. 13. They were purified by column chromatography on SiO_2 on elution with petroleum ether. The methyl, ethyl and propyl compounds were more than 99% pure, as shown by GLC. The purity of the isobutyl compound was better than 93%. The neopentyl derivative contained hexaneopentylditin. After treatment with iodine in chloroform until the solution remained coloured the compound was purified again by chromatography, to give a very pure compound.

Kinetic measurements were carried out as described previously [9, 10]. All runs were in the presence of acetic acid (4.0×10^{-2} mol l^{-1}) in order to inhibit solvolysis of the mercuric acetate. Runs were carried out at 30.00 ± 0.01°C, and reactant solutions were made up at 30°C so that no corrections for solvent expansion were necessary. Runs were followed for > 75% reaction, and application of the usual second-order rate equation yielded excellent straight lines. Details of the kinetic experiments are listed in Table 3. The compound $MeSn\text{-}i\text{-}Pr_3$ reacted too rapidly to be followed by our usual method and so we set up a series of "one-point" kinetic runs in which solutions of the reactants were syringed simultaneously into the reaction vessel. The reacting solution was quenched by the rapid addition of methanolic potassium iodide from a syringe,

TABLE 3

RATE CONSTANTS (l mol^{-1} min^{-1}) FOR THE CLEAVAGE OF COMPOUNDS RSn-i-Pr$_3$ BY MERCURIC ACETATE IN METHANOL AT 30°

R	Initial concentration, mol l^{-1}		
	RSn-i-Pr$_3$	Hg(OAc)$_2$	k_2
Me	1.12×10^{-3}	7.22×10^{-4}	$(2.19 \pm 0.04) \times 10^{3}$ [a]
Et	1.68×10^{-2}	5.93×10^{-3}	5.04
	1.69×10^{-2}	6.72×10^{-3}	4.91
	1.69×10^{-2}	5.45×10^{-3}	4.96
n-Pr	1.51×10^{-2}	1.01×10^{-3}	0.954
	1.51×10^{-2}	1.03×10^{-3}	0.952
	1.51×10^{-2}	1.06×10^{-3}	0.953
neo-Pe	1.15×10^{-2}	7.29×10^{-3}	$(5.28 \pm 0.05) \times 10^{-3}$ [c]
i-Bu	1.42×10^{-2}	9.70×10^{-3}	0.521 [b]
	1.42×10^{-2}	1.03×10^{-2}	0.507 [b]
i-Pr	3.75×10^{-2}	1.94×10^{-2}	$(2.02 \pm 0.08) \times 10^{-5}$ [d]

[a] Value calculated from 25 "one-point" determinations. [b] Another sample of i-BuSn-i-Pr$_3$, judged by GLC to be rather less pure, gave values for k_2 of 0.445, 0.476, and 0.480. [c] Value calculated from 32 "one-point" determinations. [d] Statistically corrected value calculated from 50 "one-point" determinations (ref. 9 and 14).

and reaction times as short as 5 sec were thereby attained. A series of "one-point" determinations had also to be made in the case of neo-PeSn-i-Pr$_3$ because of the very slow rate of reaction of this compound with mercuric acetate. Portions of the reaction mixture were sealed in glass ampoules under nitrogen and the contents of the ampoules analysed during 20 days, by which time about 75% reaction had taken place.

The value of the rate constant for the reaction of i-Pr$_4$Sn with mercuric acetate was taken from previous work [9].

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