# Substitution at Saturated Carbon. Part XVI.[1] Steric Effects in the $S_E2$ Reaction

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Rate constants are reported for the substitution of tetra-alkyltins, $R_4Sn$, by mercury(II) acetate in methanol and in t-butyl alcohol. The observed steric sequence of reactivity in methanol, R = Me > Et > $Pr^n$ > $Bu^n$ > $Bu^i$ > $C_5H_{11}^{neo}$ > $Pr^i$, is suggested to be characteristic of the $S_E2$(open) mechanism with retention of configuration at the site of substitution. Since this steric sequence differs from those in the $S_N2$ reaction and from that observed by Jensen and Davis for the $S_E2$(open) mechanism, with inversion of configuration, it is now possible to distinguish between the mechanisms $S_E2$(open)Ret and $S_E2$(open)Inv by use of these different steric sequences of reactivity. On this basis, stereochemical assignments for a number of $S_E2$(open) reactions have been made. For example it is concluded that the substitution of alkylcobaloximes by mercury(II) in water proceeds by the $S_E2$(open)Ret mechanism, whereas the iodo-demetallation of tetra-alkyltins in methanol takes place by the $S_E2$(open)Inv mechanism. The substitution of tetra-alkyltins by mercury(II) acetate in t-butyl alcohol is suggested to take place through a transition state that is intermediate between an 'open' and a fully 'cyclic' one.

THERE is no unique stereochemical course of electrophilic substitution ($S_E2$) at saturated carbon. The action of halogens on acyclic organometallics can lead either to inversion [2-5] or to retention [6] of configuration at the site of substitution. In metal-for-metal exchanges with acyclic organometallics, retention of configuration seems to be the rule; [4,7,8] amongst all metal-for-metal exchanges, the only cases in which inversion of configuration has been observed are those that involve transannular rearrangement of a cyclic substrate.[9] Stereochemical studies using, for example, optically active derivatives of secondary alkyl groups are sometimes difficult to carry out, so that it is of importance to be able to deduce the stereochemical course of $S_E2$ reactions by some indirect method.

Jensen and Davis [2] have shown that reaction (1;

$$RSn(C_5H_{11}^{neo})_3 + Br_2 \xrightarrow{MeOH} RBr + (C_5H_{11}^{neo})_3SnBr \quad (1)$$

R = $Bu^s$) proceeds with inversion at the site of substitution [we denote this mechanism as $S_E2$(open)Inv] and that steric effects in reaction (1) could be correlated with steric effects in a typical $S_N2$ reaction of alkyl halides. A plot of $\log\{k[RSn(C_5H_{11}^{neo})_3]/k[MeSn(C_5H_{11}^{neo})_3]\}$ against the $S_N2$ steric quantity $\log[k(RX)/k(MeX)]$ was linear for the alkyl groups R = Me, Et, $Pr^n$, $Pr^i$, and $C_5H_{11}^{neo}$. It was then suggested [2] that the stereochemical course of an $S_E2$ reaction could be deduced from comparisons of the

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[1] Part XV, M. H. Abraham and F. J. Dorrell, *J.C.S. Perkin II*, 1973, 444.

[2] F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, 1971, **93**, 4048.

[3] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1971, **93**, 5283.

[4] G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, 1971, **93**, 1529.

[5] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1971, 571.

[6] F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *J. Amer. Chem. Soc.*, 1959, **81**, 1262; 1960, **82**, 2466; R. W. Johnson and R. G. Pearson, *Chem. Comm.*, 1970, 986; R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 1970, **92**, 5519.

[7] E. D. Hughes, C. K. Ingold, F. G. Thorpe, and H. C. Volger, *J. Chem. Soc.*, 1961, 1133.

[8] H. B. Charman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1959, 2530; H. B. Charman, E. D. Hughes, C. K. Ingold, and F. G. Thorpe, *ibid.*, 1961, 1121; H. B. Charman, E. D. Hughes, C. K. Ingold, and H. C. Volger, *ibid.*, p. 1142; O. A. Reutov and É. V. Uglova, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1959, 1691; O. A. Reutov, T. P. Karpov, É. V. Uglova, and V. A. Malyanov, *Doklady Akad. Nauk S.S.S.R.*, 1960, **134**, 360; F. R. Jensen, *J. Amer. Chem. Soc.*, 1960, **82**, 2469; D. S. Matteson and R. A. Bowie, *ibid.*, 1965, **87**, 2587.

[9] D. S. Matteson and M. L. Talbot, *J. Amer. Chem. Soc.*, 1967, **89**, 1123; E. Vedejs and M. F. Salomon, *J. Org. Chem.*, 1972, **37**, 2075.

effect of alkyl groups on the rate of substitution with alkyl group effects on the rates of substitution of other $S_E2$ reactions of known stereochemistry. Jensen and Davis[2] implied that the effects of alkyl groups on $S_E2$ reactions proceeding with retention of configuration are rather small, but, as will be shown later, this is not necessarily so.

We have previously carried out kinetic studies on reaction (2; X = Cl and I) using a number of hydroxylic solvents and have observed[10-12] a pronounced steric sequence of reactivity with respect to the alkyl group R. Unfortunately, we were unable to obtain rate constants for substrates containing highly-branched

$$R_4Sn + HgX_2 \longrightarrow RHgX + R_3SnX \qquad (2)$$

alkyl groups because of their very slow rates of reaction. Since mercury(II) acetate is *ca.* 100 times as reactive as the mercury(II) halides towards tetraethyltin in hydroxylic solvents,[13] we have now carried out a kinetic study of reaction (2; X = OAc) using the entire α- and β-methylated series of alkyl groups (except for R = $Bu^t$) in the hope that the stereochemical course of this reaction may be deduced.

TABLE 1

Second-order rate constants ($l\ mol^{-1}\ min^{-1}$) for the substitution of tetra-alkyltins by mercury(II) acetate at 30°

| Solvent | $Me_4Sn$ | $Et_4Sn$ | $Pr_4^nSn$ | $Bu_4^nSn$ |
|---|---|---|---|---|
| Methanol | 14,000 | 61·4 | 12·5 | 10·4 |
| t-Butyl alcohol | 54·4 | 0·503 | 0·114 | 0·103 |

| | $Bu_4^iSn$ | $(C_5H_{11}^{neo})_4Sn$ | $Pr_4^iSn$ |
|---|---|---|---|
| Methanol | 2·62 | 0·011 | $8·1 \times 10^{-5}$ |
| t-Butyl alcohol | 0·038 | $9·4 \times 10^{-4}$ | $6·6 \times 10^{-4}$ |

TABLE 2

Relative rates of substitution of tetra-alkyltins by mercury(II) salts

| $HgX_2$ | Solvent | *t*/°C | $Me_4Sn$ | $Et_4Sn$ | $Pr_4^nSn$ | $Bu_4^nSn$ | $Bu_4^iSn$ | $(C_5H_{11}^{neo})_4Sn$ | $Pr_4^iSn$ |
|---|---|---|---|---|---|---|---|---|---|
| $Hg(OAc)_2$ | MeOH | 30 | 100 | 0·44 | 0·089 | 0·074 | 0·019 | $7·9 \times 10^{-5}$ | $5·8 \times 10^{-7}$ |
| $Hg(OAc)_2$ | $Bu^tOH$ | 30 | 100 | 0·92 | 0·21 | 0·19 | 0·070 | $1·7 \times 10^{-3}$ | $1·2 \times 10^{-3}$ |
| $HgCl_2$ [a] | MeOH | 40 | 100 | 0·29 | 0·058 | 0·055 | $8·1 \times 10^{-3}$ | $<1·0 \times 10^{-4}$ [c] | $\leqslant 10^{-6}$ |
| $HgCl_2$ [b] | $Bu^tOH$ | 40 | 100 | 0·15 | 0·024 | 0·016 | $3·5 \times 10^{-3}$ | $<6·5 \times 10^{-5}$ [c] | $\leqslant 10^{-4}$ |

[a] Ref. 11. [b] Ref. 12. [c] This work.

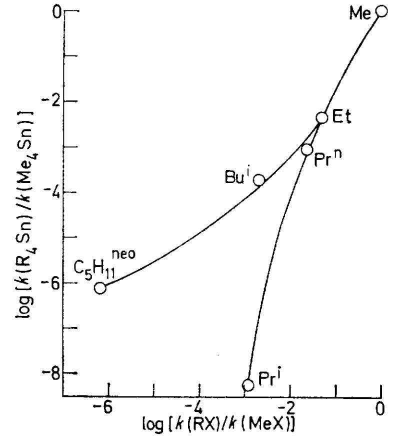

FIGURE 1 Plot of log [$k(R_4Sn)/k(Me_4Sn)$] for the reaction of tetra-alkyltins with mercury(II) acetate in methanol against log [$k(RX)/k(MeX)$] for $S_N2$ reactions

*Kinetics in Solvent Methanol.*—The methods used were essentially those described before.[11-13] Rate constants are in Table 1 and relative rate constants (taking $k = 100$ for $Me_4Sn$) in Table 2. Relative rate constants for reaction (2; X = OAc) are quite similar to those in reaction (2; X = Cl),[12] but we have now managed to obtain results for the important substrates $Pr_4^iSn$ and $(C_5H_{11}^{neo})_4Sn$. Steric effects in reaction (2; X = OAc) are extremely large; $Me_4Sn$ reacts $2 \times 10^8$ times as rapidly as $Pr_4^iSn$. In Figure 1 is plotted log [$k(R_4Sn)/k(Me_4Sn)$] for reaction (2; X = OAc) in methanol against the quantity log [$k(RX)/k(MeX)$] for typical $S_N2$ reactions of alkyl halides.[14,15] It is clear that the steric effects of α- and β-methylated alkyl groups in the $S_E2$ reaction (2; X = OAc) are not the same as in the $S_N2$ or $S_E2$(open)Inv reactions. Now since reaction (2; X = OAc) probably proceeds through an open transition state in methanol,[16] it thus remains to compare these alkyl group effects with such effects on an $S_E2$(open)Ret reaction. The only $S_E2$(open) reaction for which steric effects of alkyl groups have been obtained[17] and for which stereochemical studies (under the same conditions) demonstrate retention of configuration[7] is the metal-for-metal exchange (3; $\overset{*}{Hg}$ = radioactively labelled Hg). In Figure 2 is plotted log [$k(RHgX)/k(MeHgX)$] for reaction (3) against the $S_N2$ steric quantity; although

$$RHgX + \overset{*}{H}gX_2 \xrightarrow{EtOH} R\overset{*}{H}gX + HgX_2 \qquad (3)$$

steric effects in reaction (3) are quantitatively much less than those in reaction (2), qualitatively they follow exactly the same pattern. We have therefore shown that (i) steric effects in the $S_E2$(open) reaction (2; X = OAc) do not follow steric effects in the $S_N2$ reaction

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[10] M. H. Abraham and T. R. Spalding, *J. Chem. Soc.* (*A*), 1969, 399.

[11] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 188, 193.

[12] M. H. Abraham, F. Behbahany, and M. J. Hogarth, *J. Chem. Soc.* (*A*), 1971, 2566.

[13] M. H. Abraham and F. Behbahany, *J. Chem. Soc.* (*A*), 1971, 1469.

[14] K. Okamoto, I. Nitta, N. Imoto, and H. Shingu, *Bull. Chem. Soc. Japan*, 1967, **40**, 1905.

[15] A. Streitwieser. *Chem. Rev.*, 1956, **56**, 571.

[16] M. H. Abraham and D. F. Dadjour, unpublished observations.

[17] E. D. Hughes and H. C. Volger, *J. Chem. Soc.*, 1961, 2359.

or in the $S_\mathrm{E}2$(open)Inv reaction (1), and (ii) steric effects in the $S_\mathrm{E}2$(open) reaction (2; X = OAc) are qualitatively similar to steric effects in the $S_\mathrm{E}2$(open)Ret reaction (3).* We conclude that the stereochemical course of reaction (2; X = OAc) is also that of retention of configuration and denote this reaction as $S_\mathrm{E}2$(open)Ret. Since steric effects in reaction (2; X = I and Cl) parallel closely steric effects in reaction (2; X = OAc), at least where comparisons may be made, it seems reasonable to assign the $S_\mathrm{E}2$(open)Ret mechanism to these reactions as well.

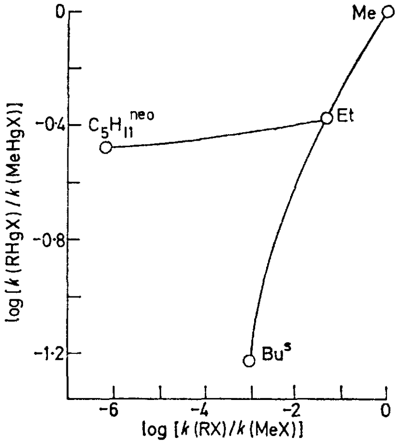

FIGURE 2 Plot of log [$k$(RHgX)/$k$(MeHgX)] for the reaction of alkylmercury(II) salts with mercury(II) salts in ethanol against log [$k$(RX)/$k$(MeX)] for $S_\mathrm{N}2$ reactions

There could be an objection to the above analysis because we have compared effects in a series of symmetrical compounds $R_4Sn$ with effects in series of compounds in which the leaving group is always constant [*e.g.* $RSN(C_5H_{11}^{neo})_3$, RHgX, and RX]. We do not think that our conclusions are affected by this factor, however, since steric effects of the leaving group are known to be much less than those of the alkyl group undergoing substitution both for halogeno-demetallation of tetra-alkyltins in polar solvents [18] and for reaction (2; X = I).[10]

*Kinetics in Solvent t-Butyl Alcohol.*—Rate constants and also relative rate constants for reaction (2; X = OAc) in t-butyl alcohol are in Tables 1 and 2. Although the steric sequence in t-butyl alcohol is not as pronounced as it is in methanol, the reactivity pattern is still quite similar to that for the $S_\mathrm{E}2$(open)Ret mechanism and does not follow that observed for the $S_\mathrm{N}2$ or $S_\mathrm{E}2$(open)Inv mechanisms (Figure 3). Now steric effects on reaction (2; X = Cl) in t-butyl alcohol are even larger than in methanol (Table 2) so that it seems as though the sequence for reaction (2; X = OAc) in t-butyl alcohol contains a ' polar ' component superimposed on a severe steric sequence. The magnitude of the polar component can be estimated either by a direct comparison of rate constants in methanol or t-butanol or by correcting the directly obtained polar component for the additional steric effect observed on reaction (2; X = Cl); results are in Table 3. Polar effects in the β-methylated series (R = Et, $Pr^n$, $Bu^i$, or $C_5H_{11}^{neo}$) are not large and cover only a 10—25 fold increase in rate along the entire series. In the α-methylated series (R = Me, Et, or $Pr^i$) the effect of a single methyl group is to produce a 2—4 fold rate increase, but two methyl groups as in R = $Pr^i$ produce an increase by a factor of $2 \times 10^3$—$2 \times 10^4$. All in all, we think that these various effects suggest that reaction (2; X = OAc) in t-butyl alcohol proceeds with retention of configuration at the site of substitution through a transition state that is intermediate between an open and a fully cyclic one.

TABLE 3

Polar effects of alkyl groups on the rate of substitution of tetra-alkyltins by mercury(II) acetate in t-butyl alcohol

| R | Me | Et | $Pr^n$ | $Bu^n$ | $Bu^i$ | $C_5H_{11}^{neo}$ | $Pr^i$ |
|---|---|---|---|---|---|---|---|
| Polar factor [a] | 1 | 2 | 2 | 3 | 4 | 20 | $2 \times 10^3$ |
| Corrected polar factor [b] | 1 | 4 | 5 | 9 | 9 | 100 | $2 \times 10^4$ |

[a] $k^{rel}(Bu^tOH)/k^{rel}(MeOH)$. [b] Ratios corrected by the steric factor $k^{rel}(MeOH)/k^{rel}(Bu^tOH)$ observed for reaction with $HgCl_2$ (Table 2).

*Conclusions and Applications.*—In previous work we have attempted to relate the observed constitutional effects of alkyl groups in a series of compounds $RMX_n$ (where R changes along a series and where M is a given metal atom) undergoing electrophilic substitution to the possible mechanisms of substitution.[19,20] We suggested that a steric sequence of reactivity (with respect to the alkyl group R) was characteristic of the $S_\mathrm{E}2$(open) mechanism, a polar sequence of reactivity was characteristic of the $S_\mathrm{E}2$(co-ord) mechanism and mixed steric–

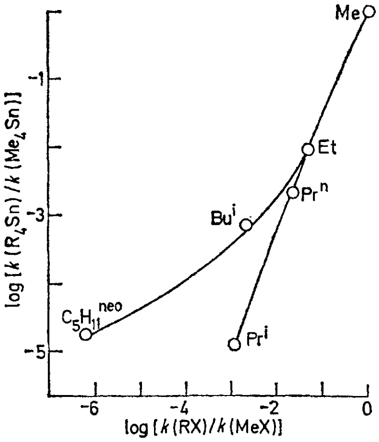

FIGURE 3 Plot of log [$k(R_4Sn)/k(Me_4Sn)$] for the reaction of tetra-alkyltins with mercury(II) acetate in t-butyl alcohol against log [$k$(RX)/$k$(MeX)] for $S_\mathrm{N}2$ reactions

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* Positive kinetic salt effects and co-solvent effects were used to demonstrate [7] that reaction (3) proceeded through an open rather than through a cyclic transition state.

[18] S. Boué, M. Gielen, and J. Nasielski, *J. Organometallic Chem.*, 1967, **9**, 443.

[19] M. H. Abraham, ' Electrophilic Substitution at Saturated Carbon,' in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, vol. 12, 1973.

[20] M. H. Abraham and J. A. Hill, *J. Organometallic Chem.*, 1967, **7**, 11.

polar sequences were characteristic of the $S_E2$(cyclic) mechanism. However, whilst we still regard a steric sequence of reactivity to be characteristic of the $S_E2$(open) mechanism, it now seems possible to be able to distinguish between the two stereochemical varients of this mechanism on the basis of different steric sequences.*

An interesting application of this method is to the reaction of alkylcobaloximes with mercury(II) acetate in aqueous solution.

Schrauzer and his co-workers [21] have suggested that this $S_E2$ reaction proceeds with inversion of configuration at the site of substitution. No supporting evidence was given, and this conclusion has been criticised by Jensen and his co-workers [3] on the grounds that the rate data for cleavage of the alkylcobaloximes was not in accord with the sequence expected for substitution with inversion. In Figure 4 is plotted log [*k*(RCo)/*k*(MeCo)] against the $S_N2$ steric quantity. It is evident that (*cf.* ref. 3) the two sets are not linearly related, but, furthermore, that the rate sequence for the alkylcobaloxime cleavage follows exactly the same pattern as observed for the $S_E2$(open)Ret reactions (2) and (3) (*cf.* Figure 4 with Figures 1 and 2). We conclude that the reaction of alkylcobaloximes with mercury(II) acetate in water thus also proceeds by the $S_E2$(open)Ret mechanism. The same conclusion may be drawn for the reactions of alkylcobaloximes with $Hg^{2+}$ studied by Adin and Espenson,[22] a similar plot to that shown in Figure 4 being obtained; Adin and Espenson [22] themselves suggested reaction took place with retention of configuration. Reactivity sequences of alkylcobalt(III) compounds in which the in-plane ligand is the corrin ring have been obtained,[21,23] but few alkyl groups have been studied and there is controversy as to the relative reactivity of the $Pr^i$ group in these compounds.[21]

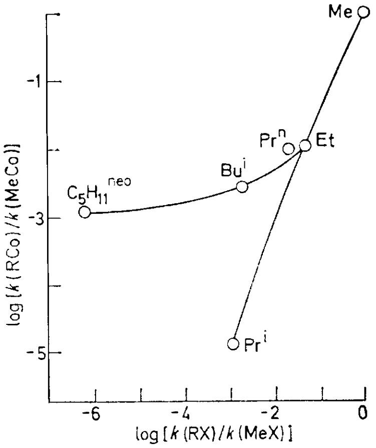
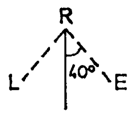
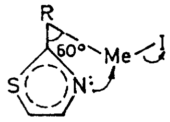


FIGURE 4 Plot of log [*k*(RCo)/*k*(MeCo)] for the reaction of alkylcobaloximes with mercury(II) acetate in water against log [*k*(RX)/*k*(MeX)] for $S_N2$ reactions

We have assumed that the observed effects of alkyl groups in the $S_E2$(open)Ret reaction arise mainly through steric interaction between the alkyl group undergoing substitution and (i) the incoming electrophile, E, and (ii) the leaving group, L. Now in the quaternisation of 2-alkylthiazoles (II) by methyl iodide,[24] a very similar steric arrangement prevails. Hence steric effects of the group R in (II) should parallel, at least qualitatively, steric effects of the group R in the $S_E2$(open)Ret transition state (I). In Figure 5 is plotted log [*k*(2-alkyl)/*k*(2-methyl)] for the quaternisation [24] against the usual $S_N2$ steric quantity. Comparison of Figure 5 with Figures 1—4 suggests that indeed the $S_E2$(open)Ret reactivity sequence arises from the steric effect of the group R in (I).



(I)



(II)

We can now use the results on the various $S_E2$(open)Ret reactions in metal-for-metal exchanges examined in this and in previous work [11,12,17,21,22] to assign tentatively steric substituent constants, σ, through equation (4). We have not tied the parameter ρ to any particular

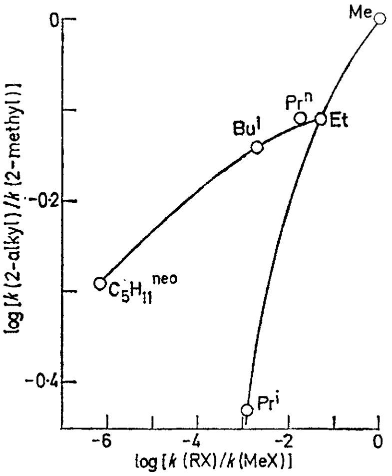


FIGURE 5 Plot of log [*k*(2-alkyl)/*k*(2-methyl)] for the quaternisation of 2-alkylthiazoles with methyl iodide against log [*k*(RX)/*k*(MeX)] for $S_N2$ reactions

$$-\log [k(\mathrm{R})/k(\mathrm{Me})] = \sigma\rho \qquad (4)$$

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* Examination of Figures 1 and 2 reveals a possible anomaly. Should the polar component of reaction increase considerably, as is likely in the $S_E2$(cyclic) mechanism, the point for R = $Pr^i$ will approach the line for the β-methylated alkyl groups, and points for the α- and β-methylated series might appear to be scattered about the same straight line. Thus a linear plot can be obtained, not only for a reaction proceeding by the $S_E2$(open)Inv mechanism but also, in some circumstances, for an $S_E2$(cyclic) reaction.

[21] G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Letters*, 1971, 275.

[22] A. Adin and J. H. Espenson, *Chem. Comm.*, 1971, 653.

[23] H. A. O. Hill, J. M. Pratt, S. Ridsdale, F. R. Williams, and R. J. P. Williams, *Chem. Comm.*, 1970, 341.

[24] R. Gallo, M. Chanon, H. Lund, and J. Metzger, *Tetrahedron Letters*, 1972, 3857.

reaction but have scaled the σ values so that ρ varies from 0·16 in reaction (3) to 2·4 in reaction (2; X = Cl, solvent = t-butyl alcohol). In Table 4 are the calculated σ values together with those [14] for the $S_N2$ reaction. The value of σ for the $Bu^t$ group in $S_E2$(open)Ret reactions has very roughly been estimated. It is clear from the data in Table 4 that a choice between $S_E2$(open)Ret and $S_E2$(open)Inv mechanisms on the basis of substituent effects can only be made if the branched alkyl groups are used. The σ values for the n-alkyl groups in each series lie so close that there is little distinction between the sets in these cases.

TABLE 4

Comparison of steric substituent constants, σ, in the $S_E2$(open)Ret and $S_N2$ reactions

| | σ | |
|---|---|---|
| R | $S_E2$(open)Ret | $S_N2$ [a] |
| Me | 0 | 0 |
| Et | 1·3 | 1·31 |
| $Pr^n$ | 1·5 | 1·67 |
| $Bu^n$ | 1·55 | 1·68 |
| $Bu^i$ | 1·8 | 2·70 |
| $C_5H_{11}^{neo}$ | *ca.* 2·6 | 6·18 |
| $Pr^i$ | *ca.* 4 | 2·92 |
| $Bu^t$ | *ca.* 9 [b] | 4·4 [c] |

[a] Ref. 14. [b] Estimated value. [c] D. Cook and A. J. Parker, *J. Chem. Soc.* (*B*), 1968, 142.

TABLE 5

Steric effects, $-\log [k(R)/k(Me)]$, in $S_N2$ and $S_E2$(open) reactions

| | R | | | | | |
|---|---|---|---|---|---|---|
| Reaction | Me | Et | $Pr^n$ | $Bu^n$ | $Pr^i$ | $Bu^t$ |
| $S_E2$(open)Ret [a] | 0 | 1·3 | 1·5 | 1·6 | *ca.* 4 | *ca.* 9 |
| $S_E2$(open)Inv [b] | 0 | 0·8 | 1·4 | | 2·1 | |
| $S_N2$ [a] | 0 | 1·3 | 1·7 | 1·7 | 2·9 | 4·4 |
| $RSnMe_3 + I_2$ in MeOH [c] | 0 | 0·8 | 1·5 | 1·3 | *ca.* 2·2 | |
| $RSnEt_3 + I_2$ in MeOH [c] | 0 | 1·2 | 1·7 | 1·8 | 3·0 | |
| $R_4Sn + I_2$ in MeOH [d] | 0 | 0·9 | 1·8 | 2·2 | 3·2 | |
| $RHgI + H_3O^+$ in $H_2O$ [e] | 0 | 0·40 | 0·66 | | 0·89 | *ca.* 2·1 |

[a] Values of σ from Table 4. [b] Reaction (1), ref. 2. [c] Ref. 18. [d] Refs. 18 and 26. [e] M. M. Kreevoy and R. L. Hansen, *J. Amer. Chem. Soc.*, 1961, **83**, 626.

Besides the metal-for-metal exchanges discussed above, there are a few other $S_E2$(open) reactions for which substituent effects are known but for which stereochemical assignments have not been carried out; details are in Table 5. By comparison with the σ values for the $S_E2$(open) reactions and for the $S_N2$ reaction, the substituent effects in the iodo-demetallations indicate that these three reactions proceed by the $S_E2$(open)Inv mechanism, just as in the related bromo-demetallation (1). Substituent effects in the acidolysis reaction are not well correlated with any of the sets of σ values and in order to achieve a definite stereochemical assignment, data on the β-methylated groups $Bu^i$ and $C_5H_{11}^{neo}$ are needed. This is also true for the iodo-demetallation of tetra-alkyl-leads in polar solvents; although the observed steric sequences ($Me_4Pb > Et_4Pb > Pr_4^nPb$) [25] are quite well correlated with that [18,26] for the iodo-demetallation of symmetrical tetra-alkyltins in methanol, more extensive data are needed to confirm our provisional assignment of the $S_E2$(open)Inv mechanism to these iodo-deplumbylations.

It should be stressed that in order to deduce the stereochemical course of $S_E2$(open) reactions on the basis of steric effects, it is desirable to have rate constants for both the α- and the β-methylated series. Our assignments for the halogenations in Table 5 are therefore not as definite as those for the metal-for-metal exchanges discussed above.

## EXPERIMENTAL

The materials used have been described before,[10-13] except for tetraneopentyltin which was a gift. Kinetics were followed by our usual methods and computed exactly as previously described.[11,13] In methanol, initial concentrations of reactants were $2 \times 10^{-4}$M-mercury(II) acetate and $1 \times 10^{-3}$M-tetra-alkyltin.

These concentrations were increased to $2 \times 10^{-3}$ and $4 \times 10^{-3}$M respectively for reactions of tetraneopentyltin and to $2 \times 10^{-2}$ and $4 \times 10^{-2}$M respectively for reactions of tetraisopropyltin. In the case of tetramethyltin, reaction in methanol was so fast that initial concentrations were reduced to $3 \times 10^{-5}$M-mercury(II) acetate and $6 \times 10^{-5}$M-tetramethyltin; even then, we had to reduce reaction times to <*ca.* 30 s, as follows. Solutions of the reactants were syringed simultaneously into a small reaction vessel, and the reaction mixture was subsequently quenched by the rapid addition of methanolic potassium iodide from a syringe. Reaction times of between 2 and 30 s were timed using a stopwatch. In t-butyl alcohol, initial concentrations of reactants were $5 \times 10^{-3}$M-mercury(II) acetate and $2 \times 10^{-2}$M-tetra-alkyltin. Again, concentrations were increased somewhat for reactions of $(C_5H_{11}^{neo})_4Sn$ and $Pr_4^iSn$. For tetramethyltin, concentrations were $4 \times 10^{-4}$M-mercury(II) acetate and $1 \times 10^{-3}$M-tetramethyltin, but the reactions were slow enough to follow normally.

All reactions involving mercury(II) acetate were carried out in presence of 0·04M-acetic acid. Good second-order kinetics were found, although the rate constants in methanol did vary slightly with the initial concentration of mercury(II) acetate. The rate constants obtained are in Table 1,

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[25] L. Riccoboni, G. Pilloni, G. Plazzogna, and G. Tagliavini, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1966, **11**, 340.

[26] M. Gielen and J. Nasielski, *Bull. Soc. chim. belges*, 1962, **71**, 32.

and are averages from 8—12 separate kinetic runs in each case.

Reactions of tetraneopentyltin with mercury(II) chloride were followed for periods of up to 6 months using methanol and t-butyl alcohol as solvents, but < 10% reaction occurred during this time. We were able to obtain only maximum values for the second-order rate constants at 40°, *viz.* $1 \cdot 5 \times 10^{-4}$ l mol$^{-1}$ min$^{-1}$ (methanol as solvent) and $1 \cdot 2 \times 10^{-5}$ l mol$^{-1}$ min$^{-1}$ (t-butyl alcohol as solvent). The maximum relative rate constants are in Table 2.

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