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ORGANOMETALLIC COMPOUNDS
2*. MECHANISMS OF ELECTROPHILIC SUBSTITUTION OF METAL ALKYLS**

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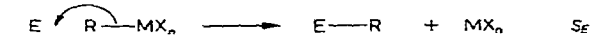
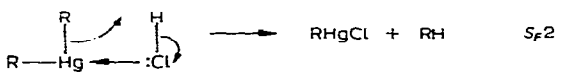
INTRODUCTION

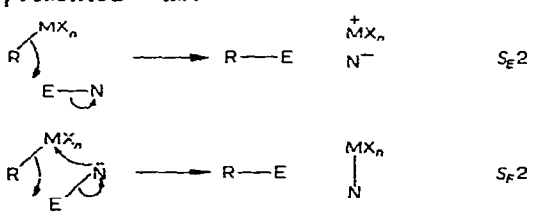
It is now widely recognised[2-5] that reactions of organometallic compounds in which an alkyl–metal bond is cleaved heterolytically may proceed by the mechanism of electrophilic substitution at saturated carbon, S_E, with a metal-containing entity as the leaving group:



Although the S_E mechanism requires, by definition, attack at the carbon atom of the C–M group by an electrophilic reagent (except for substitution with rearrangement as in the S_E2' and S_Ei' mechanisms) it leaves open the question of nucleophilic attack at the metal atom. For instance Dessy, Reynolds, and Kim[6] in a study of the cleavage of dialkylmercury compounds by hydrogen chloride in solvent dimethyl sulphoxide/dioxane showed that nucleophilic attack by the chlorine atom on mercury was an important factor, and they suggested that a four-centred cyclic mechanism, later[7] denoted as S_F2 was operating:



Gielen and Nasielski[8-12], in their brilliant studies on electrophilic substitution, have correlated a considerable number of reactions in terms of the cyclic mechanism, S_F2, and the "open" mechanism, S_E2; when the reagent can be written as E–N, where E is the electrophilic and N the nucleophilic pole, these two mechanisms may be represented[10] as:

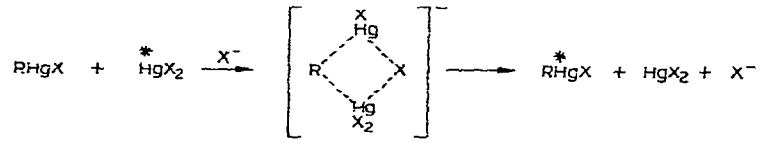


In general it is to be expected[10] that mechanism S_F2 will be favoured in non-polar

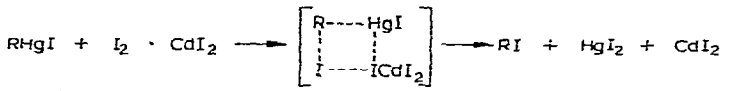
* Part 1 see ref. 1.
** A preliminary account of this work has appeared in *Chem. Ind. (London)*, (1965) 561.

solvents and mechanism S_E2 in polar solvents. Indeed Gielen and Nasielski have suggested[10] that in the relative rates of electrophilic substitution of metal alkyls of type R_nM, where R varies through R = Me, Et, Pr, and *iso*-Pr, two sequences of reactivity can be distinguished and that these two sequences are solvent-dependent. They are[10] (*a*) a steric sequence (Me > Et > Pr > *iso*-Pr) observable in polar solvents where the S_E2 mechanism is operative, and (*b*) a sequence showing an increasing contribution of polar (inductive) effects (Me < Et > Pr < *iso*-Pr) observable in non-polar solvents where the S_E2 mechanism now occurs.

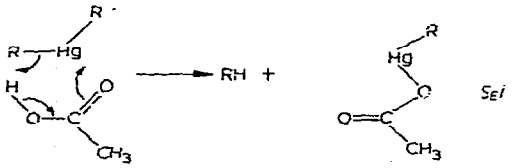
Although this suggestion of Gielen and Nasielski has served to clarify many reactions of metal alkyls, there are several anomalies to be considered. First of all, a number of reactions for which cyclic transition states have been postulated have proceeded in solvents classed by Gielen and Nasielski[10] as polar solvents. Charman, Hughes, Ingold, and Volger[13] have shown that the one-anion, and two-anion, catalysed one-alkyl mercury exchanges follow cyclic four-centred mechanisms in solvents ethanol and acetone, *e.g.*:



Change in alkyl from ethyl to neopentyl resulted in a decrease in the second-order rate constant (solvent ethanol) attributable entirely[14] to steric effects; thus this is an example of a reaction following a steric sequence in a polar solvent by a cyclic mechanism. Reutov and his co-workers[15] have also observed similar anion catalysed one-alkyl mercury exchanges in solvent dimethyl sulphoxide; in addition they suggest[16] that a number of halogenations of alkylmercury halides, for instance iodination by iodine in presence of cadmium iodide, follow cyclic mechanisms even in solvents such as dimethylformamide, methanol, ethanol, and 70% aq. dioxane:

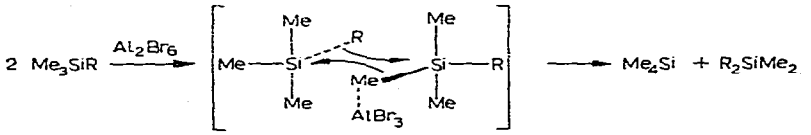


Winstein and Traylor[17] found that added sodium acetate did not accelerate the acetolysis of dialkylmercurys by an excess of acetic acid. They deduced that a cyclic transition state was formed and, following Winstein, Traylor, and Garner[18], they denoted this mechanism S_Ei and wrote:



A polar sequence of reactivity was observed[17] in that the rate constants were in the order *sec*-Bu_2Hg > Bu_2Hg. The above reactions, proceeding by cyclic mechanisms (sometimes following polar and sometimes steric sequences) in polar solvents are not accounted for on the theory of Gielen and Nasielski. Neither is the series of

disproportionations, discovered by Russell and Nagpal[19], in which steric effects (R = Et > Pr > Bu > *iso*-Bu > *iso*-Pr)* predominate even though in benzene solvent. A cyclic mechanism was[19] suggested:



Finally, a number of reactions are now known in which alkyl–metal bonds are broken electrophilically and in which enormous polar effects are observed, even though the solvents used, acetic acid[11] and water[20,21] are polar[10] solvents.

Hence although Gielen and Nasielski's division of relative rates into two solvent-dependent sequences has served to correlate many electrophilic substitutions of metal alkyls, it fails in certain specific cases and it makes no provision for mechanisms that might involve cyclic transition states other than four-centred ones. The success and failure of the Gielen and Nasielski theory can be seen from the Table, in which we have collected data on relevant electrophilic substitutions, with the various sequences arranged as far as possible in order of increasing polar effects (from 1 down to 31). Rate constants in any sequence are compared to that of the methyl compound (taken as 100); in cases where the methyl compound has not been studied, the relative rate constants have been adjusted by suitable factors so as to bring them in line, as far as can be done, with the other sequences. Only reactions proceeding in homogeneous solution, in a solvent, have been selected. Bearing in mind that the actual magnitude of steric effects depends on the nature of the reactants, and also that the various reaction sequences were not obtained at the same temperature, it can be seen that there is a gradual change on going down the Table from steric sequences of reactivity to pronounced polar sequences. And there is no rigorous correlation of these sequences with solvent; the division of Gielen and Nasielski applies in many, but not in all, cases.

In the present work, we are attempting to correlate the given reactivity sequences with the possible, and observed, mechanisms of electrophilic substitution, using the already accepted S_E2 and S_Ei mechanisms, together with a proposed new definition of electrophilic substitution by mechanism S_EC.

DISCUSSION

We first outline the possible mechanisms of electrophilic substitution of compounds of type RMX_n, where the leaving group is MX_n (and where R may be alkyl or any other group), especially with regard to steric and polar influences of the group R.

S_E1, *substitution, electrophilic, unimolecular*

This mechanism, first envisaged by Hughes and Ingold[22] in 1935, has recently been observed by Reutov and his co-workers[23,24] and by Ingold, Hughes, and Roberts[25] for the one-alkyl mercury exchange between α-carbethoxybenzylmercuric

* Sequence of relative rates.

TABLE 1

RELATIVE RATES OF ELECTROPHILIC SUBSTITUTIONS

No.	R = Me	Et	Pr	Bu	iso-Pr	sec-Bu	tert-Bu	Temp.(°C)	Reactants	Solvent	Ref.	No.
1	100	4.3	—	—	—	—	—	25	R_4Sn+I_2	DMSO	12	1
2	100	11	4	3	—	—	—	25	$R_4Pb+HClO_4$	AcOH	47	2
3	100	12	1.5	0.6	—	—	—	20	R_4Sn+I_2	MeOH	8	3
4	100	25	—	—	—	—	—	25	R_4Pb+I_2	DMSO	12	4
5	100	36	—	—	—	—	—	25	R_4Pb+I_2	MeOH	12	5
6	100	41	4.4	3.7	0.04	—	—	20	R_4Sn+I_2	AcOH	9	6
7	100	40	22	—	13	—	0.81	110	$RHgI+HClO_4$	H_2O	38	7
8	—	40	—	18	—	—	—	70	$R_2Hg+HCl$	90% aq. dioxane	48	8
9	100	42	—	—	—	6	—	60–100	$RHgX+HgX_2$	EtOH	14	9
10	—	45	27	7	0.2	—	—	40	$2\,Me_3SiR+AlBr_3$	Benzene	19	10
11	100	46	6.1	—	—	—	—	20	R_4Sn+Br_2	DMF	9	11
12	100	57	—	—	—	—	—	25	R_4Pb+I_2	AcOH	12	12
13	100	68	20	26	—	—	—	60	$R_4Pb+AcOH$	AcOH	47	13
14	100	79	19	27	—	—	—	25	$R_4Pb+AcOH$	AcOH	47	14
15	100	83	12	10.4	2.6	—	—	20	R_4Sn+Br_2	AcOH	9	15
16	100	85	—	—	—	—	—	25	R_4Pb+Br_2	MeOH	12	16
17	100	146	18	—	—	—	—	20	$R_3SnBr+Br_2$	AcOH	12	17
18	100	244	102	—	149	—	—	35	R_2Zn+p-toluidine	Ether	49	18
19	—	244	81	—	163	—	—	68	R_2Zn+p-toluidine	iso-Pr_2O	49	19
20	100	600	78	60	560	—	—	20	R_4Sn+I_2	PhCl	10	20
21	100	630	390	—	430	—	—	50	$R_2Hg+HCl$	DMSO/ dioxane	6	21
22	100	750	300	—	300	—	—	—	$R_4Sn+HCl$	Benzene	50	22
23	100	1200	450	425	1300	—	—	20	R_4Sn+Br_2	PhCl	10	23
24	100	1670	980	—	3500	—	—	35	"RMgBr"+1-hexyne	Ether	51	24
25	—	1670	980	—	3000	—	—	35	R_2Mg+1-hexyne	Ether	52	25
26	100	2080	2260	—	1920	—	—	35	$R_2Hg+HgI_2$	Dioxane	53	26
27	100	9300	4500	5300	80000	—	—	20	R_4Sn+Br_2	CCl_4	10	27
28	100	13500	9000	7000	20200	—	—	20	$R_4Sn+CrO_3$	AcOH	11	28
29[a]	100	—	—	3020	—	—	39200	25	$RB(OH)_2+H_2O_2$	H_2O	20	29
30[a]	100	—	—	3800	—	18300	56500	25	$RB(OH)_2+HOO^-$	H_2O	20	30
31[a]	100	3×10^5	—	—	—	—	3×10^7	30	$RB(OH)_2+HCrO_4^-$	H_2O	21	31

[a] Overall relative rate constants.

bromide and mercuric bromide in dimethyl sulphoxide[23,25] and between *p*-nitrobenzylmercuric bromide and mercuric bromide in the same solvent[24]. The only cases in which simple alkyl groups are involved are those, studied by Hart and Ingold[26], in which a sec-butyl group was transferred from Hg to Tl and from Tl to Hg, and an ethyl group from Tl to Tl all with dimethylformamide as solvent. They may be represented as:

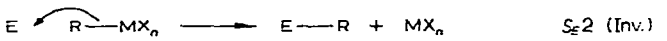
$$R\text{–}MX_n \xrightarrow{\text{slow}} R^- + \overset{+}{M}X_n \qquad S_E1$$

$$R^- + E \xrightarrow{\text{fast}} R\text{–}E$$

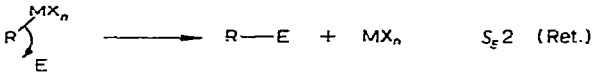
In view of this limited number of S_E1 mechanisms amongst compounds of type RMX_n we merely add that constitutional influences in the alkyl group undergoing substitution will be such that groups able to support a carbanion will aid the (slow) ionisation and hence the reactivity sequence (in R) will be Me > Et ~ Pr > *iso*-Pr > *tert*-Bu.

S_E2, substitution, electrophilic, bimolecular

When Hughes and Ingold[22] first suggested this as a possible mechanism, they considered that it would proceed with inversion of configuration at the centre of substitution:

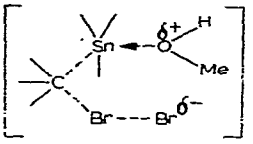


Later, it was recognised[18,27] that the S_E2 mechanism might involve retention of configuration:



Alkylmercury exchanges[13,28–33] and the bromination of sec-butylmercuric bromide[34] (by Br_2/pyridine) have been shown to proceed with retention of configuration and optical activity, and the bromination of sec-butylmercuric bromide[35] (by Br_2/CCl_4/MeOH), the acidolysis of di-sec-butylmercury[36], and the cleavage[37] of dibutyl 1-phenylethaneboronate by $HgCl_2$ all proceed with predominant retention of configuration. Several of the above substitutions may involve the S_Ei, rather than the S_E2, mechanism but the stereochemical course of both of these mechanisms is apparently retention of configuration of the substituted alkyl group. We shall thus drop the qualification (Ret.) and refer simply to mechanism S_E2. The most documented studies of the S_E2 mechanism are those by Ingold and his co-workers on alkyl mercury exchanges. For instance they showed[30] that the one-alkyl exchange between methyl- and sec-butyl-mercuric salts with mercuric salts in ethanol proceeded with retention of configuration (in the sec-butyl group) in a single bimolecular step. Added salts increased the second order rate constants and it was concluded[30] that the transition states involved were "open" ones, apart from solvation. In these one-alkyl exchanges the major influence of the alkyl group appears[14] to be a steric effect. Gielen and Nasielski have also observed steric effects of alkyl groups in several halogenations of tetraalkyltins proceeding (as deduced from positive salt effects) via open transition (S_E2) states, *e.g.*, iodination[8] in methanol solvent, and bromination[9]

in dimethylformamide solvent. In a later paper[12] they suggest that the solvent, functioning as a Lewis base, might be explicitly involved in the transition state, as shown for bromodemetallation of tetraalkyltins in solvent methanol:



(I)

In the cleavage of alkylmercury iodides by aq. perchloric acid, steric effects are again dominant[38], and again the proposed mechanism was[38] S_E2*.

We suggest that these above reactions are examples of a general rule that reactions proceeding by the S_E2 mechanism [S_E2 (Ret.)] follow a steric pattern of reactivity with respect to the alkyl group undergoing substitution, and thus the observed sequence of relative rates is Me > Et > Pr > iso-Pr > tert-Bu. Clearly in an alkyl of type R_nM, this steric pattern may well be enhanced by the effect of the leaving group MR_{n-1}.

It would be expected that polar solvents might solvate to advantage the S_E2 transition state, as the latter normally involves a separation of charge, either generally or by some specific interaction [*cf.* (I)].

S_Ei, substitution, electrophilic, internal

In a bimolecular electrophilic substitution, in which an alkyl–metal bond is broken, it is possible for some nucleophilic part of the reagent to co-ordinate with the metal atom as electrophilic cleavage takes place. This leads to an internal, cyclic mechanism first described[18] and observed[17] by Winstein and his co-workers, who noticed that in the S_Ei acetolysis of dialkylmercurys by an excess of acetic acid, polar effects in the dialkyls were of some consequence, the relative rates of acetolysis being[17] sec-Bu_2Hg (640) to Bu_2Hg (65). Charman, Hughes, Ingold, and Volger[13] have observed the S_Ei mechanism in the anion-catalysed one-alkyl mercury exchanges, but these exchanges follow[14] a steric pattern of reactivity with regard to the alkyl group. We defer discussion of these polar and steric sequences in S_Ei reactions until we have dealt with the S_EC mechanism.

Unlike the S_E2 mechanism, the S_Ei mechanism in which but little charge separation occurs in the transition state might generally be expected[10,27,39] to be favoured by non-polar solvents. Also, solvents which are strong Lewis bases (as are many polar solvents) may co-ordinate with the metal atom and thus force an "open", S_E2, transition state [*cf.* (I)] but in solvents with poor donor properties, the nucleophilic part of the electrophile can now compete more effectively with the solvent for the metal atom and so complete the closed cycle.

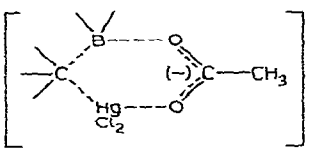
Dessy and his co-workers[7], and later Gielen and Nasielski[10], use the symbol S_F2, substitution four-centred bimolecular, to indicate mechanisms in which a cyclic four-centred transition state is formed. We prefer to retain the nomenclature of Winstein[17,18], Ingold[2], and Reutov[3] and to use the symbol S_Ei to denote mechanisms in which cyclic transition states (which may be four-, five-, or six-centred etc.) are involved.

* The mechanism given was not stated[38] to be S_E2, but as portrayed falls under this definition.

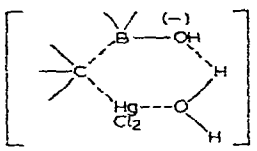
$S_E2 \sim S_Ei$ boundary

Very recently, Kitching and Wells[40] and Matteson and Bowie[37] have opined that there are actually very few examples of S_E2 mechanisms, and that reactions claimed to be S_E2 do, in fact, proceed via cyclic transition states. The former workers offer no evidence for this view, but Matteson and Bowie criticise the assignment of mechanism S_E2 to the two-alkyl mercury exchange in solvent ethanol on the grounds that the leaving group is unlikely to be the unsolvated RHg^+ cation and that the electrophile is probably an ion-pair in ethanol. Neither point is relevent, as the S_E2 mechanism does not preclude either the leaving group acquiring a solvent molecule or the electrophile existing as an ion-pair, provided that there is no covalent interaction between the entering and leaving groups. No explanation of the positive salt effects found[3,9,30] in many reactions labelled S_E2 was offered by Kitching and Wells[40] or by Matteson and Bowie[37], and we conclude that experimental observations to date can be accounted for satisfactorily only by use of both the open S_E2 and cyclic S_Ei mechanisms.

Matteson and Bowie[37] also suggested that one or more solvent molecules could bridge the entering and leaving groups and so produce a cyclic transition state as in (II), with a bridging acetate ion derived from solvent, or (III), with a bridging water molecule. Both Reutov[39] and Ingold[28] have suggested that the S_E2 and S_Ei



(II)

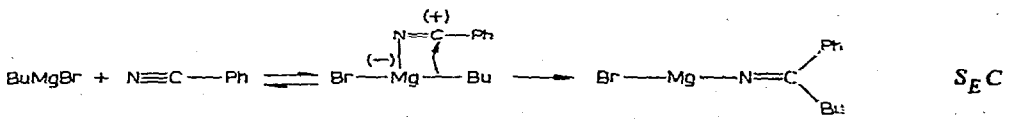


(III)

mechanisms may shade into each other. One view of (II) and (III) might be that these represent cases of the $S_E2 \sim S_Ei$ borderline; another view would be that unless there is some direct covalent interaction between the entering and leaving groups, the mechanism still remains S_E2, and Charman, Hughes, Ingold, and Thorpe[29] have implicitly accepted this when they remark on an S_E2 transition state that it is an open one "apart from solvation". We incline, at the moment, to this latter view.

S_EC, substitution, electrophilic, via co-ordination

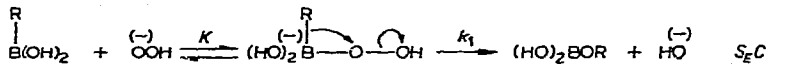
The alkyl–metal bond is usually polarised in the sense $R^{\delta-}$–$M^{\delta+}$, thus not only rendering the alkyl group susceptible to electrophilic attack, but also the metal atom susceptible to nucleophilic attack; in the S_Ei mechanism these two processes are concurrent. It is possible, however, for a nucleophilic centre in the reagent to co-ordinate to the metal in an initial step, and then to be followed by a shift (1,2 or 1,3 etc.) of the alkyl to an electrophilic centre in the reagent. We suggest that this mechanism be named the S_EC mechanism. Such a mechanism was first used by Swain[41] who wrote (omitting solvent molecules):



S_EC

There are several variants of this mechanism, depending on the rate constants of

the three elementary reactions involved, a number of which have been discussed[42] in connection with electrophilic substitutions of metal alkyls. Minato, Ware, and Traylor[20] have established such a mechanism for the cleavage of alkylboronic acids by aq. hydrogen peroxide and its corresponding anion:



It was shown[20] that changes in the alkyl group R, led to very great changes in the overall rate constants Kk_1 and in the rate constants for the electrophilic step, k_1, whilst producing little change in K, as shown in the relative rate constants:

R^{20} =	Me	Bu	sec-Bu	tert-Bu
Kk_1 =	1	38	183	565
k_1 =	1	52	185	330

Rather unfortunately, Minato, Ware, and Traylor[20] referred to their mechanism as an S_E2 mechanism, although it is clearly quite a distinct mechanism to the S_E2 and has a unimolecular electrophilic cleavage step (in complete contrast to the bimolecular electrophilic step in an S_E2 mechanism). Nevertheless, these authors have shown that polar effects in the substituted alkyl can be very large in the S_EC mechanism (which we shall refer to Traylor's mechanism as). Complementary to our hypothesis that steric effects dominate S_E2 mechanisms, we now also put forward the hypothesis that polar effects dominate S_EC mechanisms and that the sequence of reactivity in the substituted group will normally be Me < Et ≃ Pr < iso-Pr < tert-Bu. Should the metal alkyl be of type R_nM, then the leaving group, MR_{n-1}, might contribute a steric effect, in opposition to the polar one, to the overall total. The S_EC mechanism would be expected to be observed in cases where the metal atom in the organometallic compound shows a strong tendency to increase its covalency, and it is noteworthy that boron alkyls seem particularly prone to react[43] by this mechanism.

S_E(Alkyl bridge)

A number of alkyl exchanges, superficially resembling the S_Ei mechanism, proceed by cyclic, usually four-centred, intermediates. These exchanges are inhibited[44] by solvents which are Lewis bases, and are considerably reduced in rate along such a series of reactants (R = Me, Et) as[45] $R_3Al/R_3Al > R_3Al/R_2AlCl > R_3Al/R\ AlCl_2 > R_2AlCl/R_2AlCl$. Apparently if metal–alkyl–metal bridges are prevented, either by solvent co-ordination or by chlorine bridges, exchange ceases. This effect of chlorine is quite different to that expected for an S_Ei mechanism, where R_3Al/R_3Al would be the slowest pair of reactants in the series, and suggests that this substitution via bridging alkyl must proceed by a different mechanism. Perhaps the distinguishing feature is that the four-centred system in an S_Ei mechanism is a transition state, but in an S_E(alkyl bridge) mechanism it is a chemical intermediate, and the transition state in this latter mechanism occurs between the reactants and the four-centred intermediate (*cf.* ref. 46). The ease of transfer of alkyl should correspond to its ability to stabilise the bridged intermediate, *i.e.*, Me > n-alkyl > sec-alkyl > tert-alkyl, but we refer to this mechanism only for the sake of completeness as our interpretation of the Table does not depend on this mechanism.

CONCLUSIONS

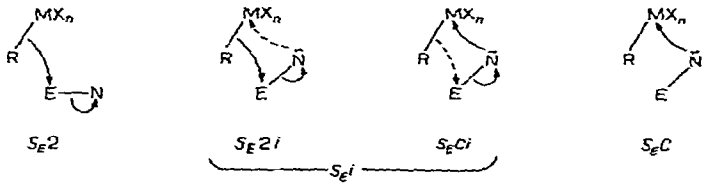
Our conclusions are derived from the following assumptions, based on the evidence we have discussed above.

(1) In mechanism S_E2, steric effects in the alkyl group undergoing substitution are dominant, and in alkyls of type R_nM these effects are reinforced by the steric effect of the leaving group MR_{n-1}. Hence the normal sequence of rate constants in a series R_nM will be R = Me > Et > Pr > iso-Pr > tert-Bu.

(2) In mechanism S_EC, polar effects in the alkyl group undergoing substitution are dominant and lead to a reactivity sequence R = Me < Et ~ Pr < iso-Pr < tert-Bu; this sequence might be somewhat moderated by the steric effect of a leaving group MR_{n-1}.

(3) Intermediate between mechanisms S_E2 and S_EC are those involving cyclic transition states, S_Ei. We envisage that these might include cases where electrophilic attack at the α-carbon is dominant, and those in which nucleophilic attack at the metal is the predominant feature. The former are more close to the S_E2 mechanism and might be referred to as S_E2i, whereas the latter are nearer to the S_EC mechanism and might be referred to as S_ECi. Through the series S_E2, S_E2i, S_ECi and S_EC there is a gradual change from dominant electrophilic attack to dominant nucleophilic attack, and we expect a corresponding gradual change in the effect of the alkyl group undergoing substitution from a steric to a polar one. Hence the observed S_Ei reactivity sequences can stretch from the extreme steric sequence (1) to the extreme polar sequence (2), and include any combination or "mixture" of the two extreme sequences.

We can illustrate the change from S_E2 to S_EC quite simply for the case where the reagent may be denoted[10] E–N:



Of the reactions shown in the Table, Nos. 3, 6, 7 and 9 have been identified as examples of the S_E2 mechanism by the investigators concerned* (see refs. in Table). These four sequences are all steric sequences, and we may expect all of the examples Nos. 1 to 9, following steric sequences, to proceed by the S_E2 mechanism, especially in view of the polar nature of the solvents used.

The majority of the tabulated reactions, Nos. 10 to 28, illustrate the progression from steric to polar sequences that we expect for S_Ei reactions, covering the spread from close to S_E2 to close to S_EC. Several of these reactions, 10 to 28, have been suggested to proceed via cyclic transition states, and we cautiously identify 10 to 28 as examples of reactions proceeding by the S_Ei mechanism. As predicted by the "solvent rule" of Gielen and Nasielski, there is some correlation of reactivity sequence with solvent—the less polar the solvent, the more pronounced the polar sequence—

* Thus excluding mechanisms S_E1 and S_E(alkyl bridge) which might also be expected to give rise to similar sequences of relative rate constants.

but there are notable exceptions, Nos. 10 and 28 especially.

The last three cases, Nos. 29 to 31, illustrate the very powerful polar effects in reactions following the S_EC mechanism. The gradual enhancement of these polar effects going down from No. 10 to No. 31 is noteworthy, especially over the last six or so cases, where the solvent changes from non-polar (dioxane, CCl_4) to polar (H_2O). Now the "solvent rule" fails completely here, but our hypotheses accomodate these cases without difficulty.

We have thus correlated and interpreted the sequences of relative rate constants, shown in the Table, not as solvent effects, but in terms of the possible mechanisms of electrophilic substitution of metal alkyls.

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SUMMARY

The relative rates of electrophilic substitution of a number of series of metal alkyls of type RMX_n (where X may = R), in which the alkyl group R varies along the series, have been interpreted in terms of the following mechanisms of substitution: (*a*) mechanism S_E2, which results in a steric sequence of relative rate constants (R = Me > Et > Pr > iso-Pr > tert-Bu), (*b*) a newly-defined mechanism S_EC, which results in a polar sequence of relative rate constants (R = Me < Et ~ Pr < iso-Pr < tert-Bu), and (*c*) mechanism S_Ei which can lead to either of the above sequences or to a combination of them. Thirty such series of substitutions, by a variety of electrophilic reagents, have been satisfactorily interpreted in this way.

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