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# STEREOSELECTION IN NUCLEOPHILIC SUBSTITUTION AT AN $SP^2$ CARBON

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**Abstract**—The stereochemical possibilities of the title reaction are considered in detail, taking into account both the relative rates of rotation, inversion, formation and decomposition, and the stabilities of the species involved. Briefly, a rationale for predominant retention is outlined and a set of conditions favorable to inversion are described. First it is assumed that the exchange of X and Y in eqn (1) includes the anion 1or 2 as an intermediate. The reaction pathways can be mapped in the form of graphs: mechanisms by selected routes can now be related to the characteristics of the system or modified to accommodate special mechanistic alternatives, e.g. addition–elimination and concerted substitution. In the graph dealing with the pyramidal anion BAC̄–CXYW, the favored retention route is *anti* formation and *syn* decomposition, while the inversion route is *syn* formation and *syn* decomposition. These stereospecific models arise for different reasons: in the first, certain rotomers of 1 are favored because of the *trans* (contra-*gauche*) effect; in the second, strong ion pairing predominates over other factors. This scheme has to be altered for the "pyramidal" anion derived from the Σ isomer of AN=CXW, since the *anti–syn* sequence may give both retention and inversion. In the graph dealing with the trigonal anion BAČ–CXYW or AÑ–CXYW, retention paths are always favored. All of the stereospecific paths described hold for specified models—when constraints are removed, stereoconvergence follows.

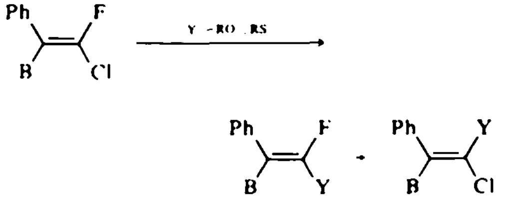
Of all unsaturated carbon sites, carbonyl, aryl, ethynyl, etc. it is only at an alkene carbon that a stereochemical choice for substitution reaction is possible.[1-3] Initially, it was thought that nucleophilic exchanges of the type in eqn (1) went with predominant or exclusive retention of

$$\begin{array}{l} AQ{=}CW{-}X \rightleftharpoons A\bar{Q}{-}CWXY \rightleftharpoons AQ{=}CW{-}Y \\ \quad +\ Y \qquad\qquad\qquad\qquad\qquad\qquad +\ X \end{array} \qquad (1)$$

**1** Q = C—B   **2** Q=N

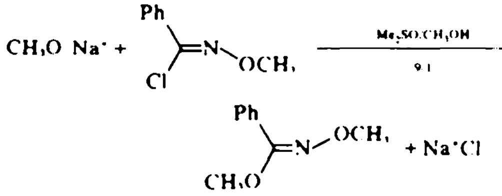
configuration. As results accumulated on diverse systems, it became clear that displacement with retention was merely the preferred end of a selectivity spectrum. Although stereoconvergent products have been obtained in some cases under equilibrium control,[1-3] exclusive inversion under kinetic control has not been observed. Because of new results in the field as well as basic deficiencies in the mechanistic descriptions of the processes involved, we re-examine this problem. It turns out that the general analysis of the several mechanisms considered for process 1 constitutes a detailed scrutiny of the fate of the model anions YWXC–CAB or YWXC-NA .

Three recent examples indicate the variations in the stereochemical results of substitution at what appears to be a similar site.



(2)

Working with similar systems ($B = CF_3$ or F), Burton and Normant provided two leaving groups in Z-PhCF=CFCl and found that substitution of either one went with virtually complete *retention* (eqn 2).[4] Johnson *et al.*, found that the reactions of sodium methoxide with Z (or Σ) hydroximoyl chlorides proceeded with predominant *inversion* (eqn 3),[5] a stereochemical



(3)

outcome which is opposite to one for eqn (4) in which substitution occurs with retention.[6] To place these stereochemical results in perspective,

$$Z\text{—}RXC{=}N\text{—}NMeAr + MeO \longrightarrow Z\text{—}R(MeO)C{=}N\text{—}NMeAr + X$$

$$X = Cl, Br;\quad R = t\text{-}Bu, Ph \qquad (4)$$

one should realize that stereoselectivity and specificity with retention are representative of numerous alkene systems, while processes 3 and 4 are still isolated examples.

Mechanistic variation in process 1 may be great; therefore, it is essential to set limits on the scope of the analysis. Solvolytic (SN1) processes, e.g. via vinyl cations, $>C{=}\dot{C}-$,[7] are excluded as is elimination–addition through an acetylene intermediate.[1,3] We propose that "normal" substitutions of the type given in eqn (1) go by way of one or more anionic intermediates and thus involve at least two elementary steps. (Attack is often by an anion; where a neutral nucleophile is involved the anionic site of the intermediate zwitterion will still be the focus of interest.) While this mechanistic proposal is not proved, a large body of diverse experimental data is consistent with it.[1-6] We regard addition–elimination, e.g. via AHQ–CWXY, as a variant of this mechanism which can be explored separately. Likewise, the proposal that the steps of process 1 may be telescoped into a single step will be examined as a limiting case.

Among several models for process 1, we consider one in which the anionic site is tetrahedral (Figs. 1 and 3) and another in which it is trigonal (Fig. 2). The reactants, products and intermediate anions are given as Newman projections at the top of the Figs. 1-3. If one considers any set of reactants, intermediates and product(s) from one of these figures, one can see that the overall stereoselectivity depends on one or more of the following factors (rate constants), (1) formation of the intermediate anion ($k_f$), (2) isomerization of the anion by rotation ($k_r$), (3) isomerization of the anion by inversion ($k_i$), and (4) dissociation of the anion to reactant or product ($k_{dr}$, $k_{dp}$). Implicit in any choice of one of the several paths to or from the anion are *possible* stereochemical or thermochemical preferences in *anti* addition or dissociation, least motion elementary steps and energetically favored conformations.

The task of evaluating all of the components that go into a reactivity pattern is obviously formidable. To cope with the many possibilities we find it convenient to map the problem first. Following this we examine the effect of each factor in turn and finally show how routes on the map could correspond to stereochemical results.

Network or graphic analysis, which has proved useful in other complex systems is used to advantage with processes 1.[8] The "complete" graphs for the association-dissociation are set down in Figs. 1-3. Reactants containing the group X and products containing group Y were assigned labels Z and E or Ƶ and Σ. Anionic intermediates were labeled so as to indicate a kinship with a reactant, where possible. Each species is indicated as a *vertex* or point while the transformations or elementary steps between species are given as lines or *edges* on the graphs. For reasons to be mentioned below certain lines are considered to represent steps of relatively high energy. Each reactant or product is allowed to participate only in associations, while the anions may dissociate or undergo inversions or rotations. In the course of the discussion we shall attempt to make explicit our assumptions and our models and to expand on their consequences.

*Model processes*. Inversion at the anionic center depends on the barrier ($V_i$). Since $V_i$ for an anion is unknown we can only make estimates using the amine (ABRN:) as a model for the carbanion (ABRC ). Indeed, $V_i \simeq 6$ kcal/mol, which has been calculated for $CH_3$ by some workers, is similar to $V_i$ for $NH_3$.[9,10] Theoretical calculations on pyramidal species indicate that this analogy is reasonable.[10,11] Typical low $V_i$'s (kcal/mol) are found in $PhNH_2$ ($\sim 2$), $H_2NCN$ ($\sim 1.9$), $H_2NNO_2$ (2.7), $H_3SiN(CH_3)_2$ (0.7) and $H_2NCHO$ ($\sim 1.1$) in which the lone

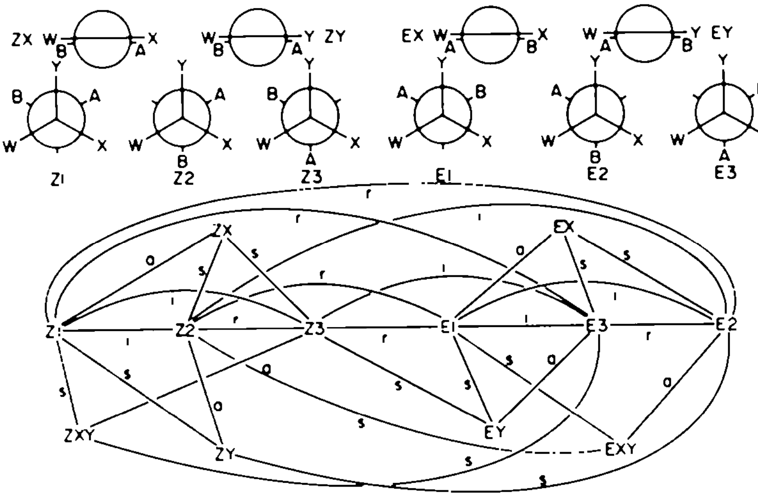


Fig. 1. A graph of the substitution reactions of E- and Z-ABC=CXW with Y$^-$ is given. The reactants are ZX and EX; one set of products is EY and ZY; the other set is EXY and ZXY for ABC=CXY. The conformations of the pyramidal anions, AB$\bar{C}$-CXYW, are indicated. The labels for the steps are anti(a), syn(s), rotation(r) and inversion(i).

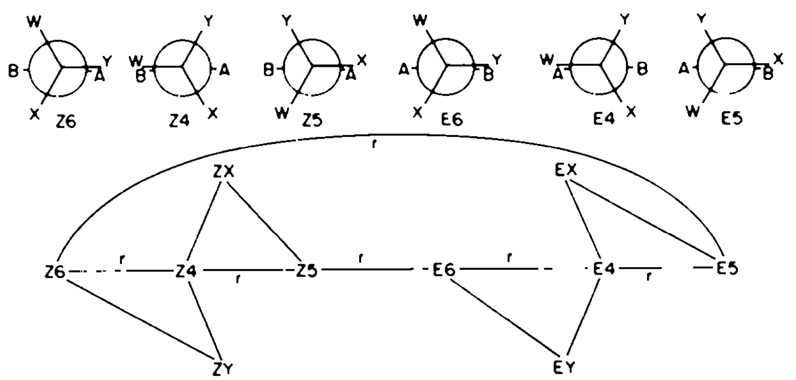


Fig. 2. A graph of the substitutions of E- and Z-ABC=CXW with Y  is given. The conformations of the trigonal anions, AB$\bar{C}$-CXYW, are indicated. See Fig. 1 for reactants and products.

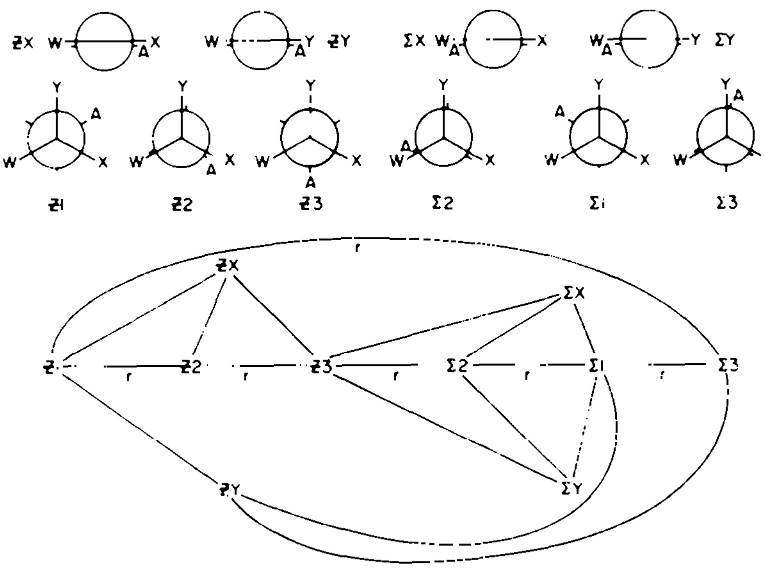


Fig. 3. A graph of the substitutions of Σ- and Z-AN=CXW with Y⁻ is given. The conformations of the pyramidal anions, A$\bar{N}$=CXYW, are indicated (labels are defined in Fig. 1).

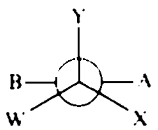
pair on nitrogen is presumably delocalized by the substituent. Higher $V_i$'s are found for $NH_3$ (5.8), $(CH_3)_2NH$ (4.4 ± 1), $(CH_2)_2NH$ or aziridine (18), $H_2NF$ (20), $H_2NNH_2$ (6.8–8.0), and $(H_3C)_2NOH$ (13).[10]

Since rotational barriers of anions are unavailable, they, too, have to be deduced from stable isoelectronic species.[12] Lower limits on $V_r$ (kcal/mol) for the carbanions ($sp^3$-$sp^3$) of Fig. 1 are approximately set by $H_3C$-$NH_2$ (1.98) or $H_3C$-$NHCH_3$) (3.2) and $H_3C$-$N(CH_3)_2$ (4.4).[13a] Bulky substituents in the amine raise $V_r$ so that it can be measured by the NMR method (see below). Since the barriers for $H_3C$-$CH_3$ (2.9), $H_3C$-$CH_2CH_3$ (3.3) and $H_3C$-$CH(CH_3)_2$ (3.9) are roughly comparable to those of the amines, we shall estimate $V_r$ for anions from the values given for ethanes, e.g. $H_3C$-$CHF_2$ (3.5), $H_3C$-$CHCl_2$ (3.5), $H_3C$-$C(CH_3)Cl_2$ (5.4).[13] The advantage of using the ethanes is that the process is unequivocal. On the other hand, the amines and the anions for which they are models may isomerize by rotation, inversion or both. Examples in which this competition is thought to occur are $(H_3C)_3C$-$N(CD_2)CH_2CD_3$ (8.5) and $(H_3C)_3C$-$N(CH_2CD_3)_2$ (~6.3).[13,14]

When $V_i = 0$, $V_r$ for the carbanion ($sp^3 - sp^2$) type pictured in Fig. 2 is required. Some low barrier models ($V_r$, kcal/mol) are $H_3C$-$CX$=$CH_2$ (X = H, F, ~2), $H_3C$-COX (X = $OCH_3$, OH, F, Cl, 0.3–1.6), $F_3C$-$COCF_3$ (~2.8).[13,16] Of the many molecules with barriers that are "high", we give two types, 2,4,6-$X_3C_6H_2$-$CHCl_2$ with $\Delta G^{\neq} = 15$–18 for X = Cl or Br, and 2,4-$(t$-$C_4H_9)_2$-6-$(H_3C)C_6H_2$-$CH_2X$ in which $E_{act} = 11$–16 kcal/mol for X = Cl, Br or I.[15]

The last $V_r$ barriers we need are those for the nitrogen anions ($sp^3 - sp^3$) of Fig. 3. Here we must use oxygen analogs, e.g. $H_3C$-OH (1.07), $H_3C$-$OCH_3$ (2.7), $H_3C$-OCOX (X = F, CN, H) (1.0–1.2), $H_3C$-OCl (3.1), $F_3C$-$OOCF_3$ (5.7). Substitutions on the carbon would normally increase $V_r$: for the anions of eqns (2) and (3), i.e. PhCl(MeO)C-NZ⁻, we estimate $V_r > 10$ kcal/mol.[15]

It will be useful to sort the possible anionic intermediates of eqn (1) according to their energies. Since the $sp^3 - sp^2$ anions ($V_i = 0$) favor the semi-eclipsed conformations of Fig. 2, others, e.g. **3**, were not included.[11,13,16] By way of contrast, only the staggered rotomers of the $sp^3 - sp^3$ species are of low energy.[11,12] We admit, however, the possibility that the three eclipsed conformations of WXYC-NA⁻ in Fig. 3 may be at or close to, energy minima. This appears to be the case for certain oximes, e.g. $R_2NOR$ (R = H, $CH_3$),[17] and is supported by an MO analysis which assigns one of the eclipsed isomers of $H_2N$-$OCH_3$, $H_2N$-OH, $H_3CNH$-OH, FHN-OH or HO-OH as the most stable form.[12] But more realistic models for the anions of Fig. 3 are available, e.g. $H_2N$-OF, hydrazines, alcohols, $H_3C$-OF and $H_3C$-$OCH_3$, and these all appear to be staggered.[12] It is for this reason that the eclipsed forms are rated as high energy and may well be deleted from Fig. 3.



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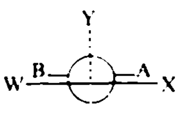
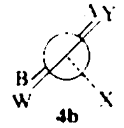
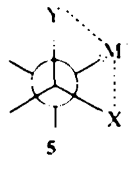


**4a**



**4b**



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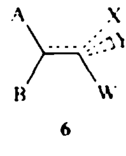


**6**

Next we consider the orientation of the reacting species in eqn (1). The low energy path for the nucleophile is presumed to lie in the plane of the π system, i.e. perpendicular to the plane of the sp² bond (**4**). This route to the anions of Figs. 1–3 is supported by quantum calculations on model systems and by natural packing arrangements in the structures of certain nucleophile-carbonyl complexes.[18,19] An entry (departure) of the nucleophile constrained in this way ensures that certain vertexes in the graph are not connected, e.g. ZX and E1 in Fig. 1 or ZX and Σ2 in Fig. 3.

The disposition of the newly formed polar bond (*pb*) and lone pair (*lp*) poses a problem, that is, are they *gauche* or *trans*? If any one of the Z rotomers, say Z1, of Fig. 1 is energetically favored, it has the "new" *pb* and *lp trans*, if formed from ZX, and *gauche*, if formed from ZY. Since the energy of a given conformation is a balance between attractive and repulsive "components",[11,12] it is not surprising that the effects of interactions of vicinal *lp* and *pb* on the relative energies of rotomers could lead to apparently contradictory "rules". Contrary to the *gauche* effect,[20] what appears to prevail here is the *trans* effect in which that rotomer with *pb* and *lp gauche* is *destabilized* with respect to the rotomer in which they are *trans*.[12,20] This leads to an energy difference calculated as *ca.* 6–7 in $FCH_2$–$NH_2$, *ca.* 6 in $HOCH_2$ or $FCH_2OH$ and 2.1 kcal/mol in $(CF_3)_2CH$–$OH$;[12,22] it is found to be 1.3 – 1.5 kcal/mol for anomeric pentose (or hexose) acetates.[21] The fact that the *trans* rotomers of $XCH_2CH_2X$ or $X_2CH$–$CH_2X$ (X = F, Cl, Br) are favored over *gauche* rotomers by *ca.* 0.6 – 3.0 kcal/mol may arise from analogous causes.[11b,23] Thus, Z3 and E2 which have two *pb gauche* to a *lp* are presumed to be rotomers of high energy.

In some cases, the anionic intermediate may have three *pb* (W, X, Y) and one *lp*, as in eqn (2). *A priori* exclusion is no longer possible for the Z or E isomers of Fig. 1—the whole graph stands. Likewise, in Fig. 3, the staggered anions have two *lp* and at least two *pb* so that neglect of a given isomer is difficult to justify. If pressed, we would, however, take the following (tentative) position. Given that reaction 1 is unidirectional, i.e. the "strong" nucleophile enters and the "weak" one leaves, we postulate that the *trans* rule favors the anion in which the new *pb* and a *lp* are *trans*. Thus, for W=X, there would be a preference for ZX → Z1 in Fig. 1 and ΣX → Σ1 in Fig. 3. It is implicit that those intermediates which are thermodynamically favored will also be favored kinetically. We stress that these assumptions are only to be used in the absence of information on rotomer stabilities or the factors that influence them.

The above argument on *rate* preferences leans too heavily on uncertain *equilibrium* preferences. A pragmatic approach here is simply to admit that *anti* is usually preferred to *syn* (or *gauche*) selectivity in rate processes involving 1,2-elimination and -addition. Although *anti*-selective eliminations (E1CB) and additions which produce vinyl analogs of 1 are known,[16,24,25] analogous processes leading to 1 and 2 in eqn (1) are more difficult to identify. Certainly, many *anti*-E2 cannot be distinguished from E1CB mechanisms.[25,26] Nevertheless, a few stepwise nucleophilic additions which have been found to be kinetically controlled generally show an *anti* preference e.g. ArS or $(EtOOC)_2CH$ to substituted cyclohexenes.[27] Although *syn* additions and eliminations are known and may involve anions of the type **1** and **2** in eqn (1), the conditions and/or substrates favoring this selectivity are usually special. Weakly dissociating solvents and/or associated ionic reactants (products) appear to be most characteristic.[25,28,29] Based on this experimental background as well as on simple MO arguments,[10,25a] we favor $k_f$ and $k_d$ of *anti* over *syn* elementary steps.

Our last concern is with the decomposition rates of the anion to reactant ($k_{dr}$) and to product ($k_{dp}$). It is, in fact, easy to demonstrate that $k_{dp}$ is relatively large, particularly when X = Cl, Br, I or $ArSO_3$. Since the gas phase reaction 5 has ΔH(g) = 6 kcal/mol,[11] one can compute from the Born equation that enormous solvation energies

$$FC_2H_4 \longrightarrow C_2H_4 + F \tag{5}$$

( > 100 kcal/mol) will drive reaction (5) to the right.[12] Presumably, $k_{dp}$ for F (and Cl, Br, etc.) will also be large in solution.

On the basis of solution data it has been proposed that most E2 elimination reactions may go by E1CB mechanisms, as in eqn (6), in which

$$\mathrm{HABC{-}CWYX} \underset{k_b}{\overset{(-\mathrm{H}^+)}{\rightleftharpoons}} \underset{\mathbf{1}}{\mathrm{AB\bar{C}{-}CWYX}} \xrightarrow{k_{dp}} \mathrm{ABC{=}CWY} + \mathrm{X} \tag{6}$$

$k_{dp} \gg k_b$.[26] Another view is that whether the overall mechanism of elimination is E2 or E1CB, the overall rate is smaller than that for the $k_{dp}$ step.[26] Independent of theory or conjecture is the real difficulty in observing or validating actual examples of the E1CB mechanism in which the $k_{dp}$ step is large.[25,26]

At the other extreme are examples of isolable, detectable anions, e.g. $Ar(OR)CH\bar{C}(CN)C_6H_4NO_2$-*p*, $Ar_2C(CN)\bar{C}(NO_2)_2$ and $(CH_3O)_2CH\bar{N}C_6H_3(2\text{-}SCH_3, 4\text{-}NO_2)$.[33] These may have CN, RO, RS and F as slow leaving groups.

A rate scheme of intermediate complexity will suffice to define some of these questions. Assume that eqn (7) represents such a system in which $A_i$ are isomers of RXY formed by inversion or rotation ($k_i$). If

$$\begin{tikzcd}
Y^- + RX \arrow[r, shift left, "k_f"] & RXY^- \arrow[l, shift left, "k_{dr}"] \arrow[r, shift left, "k_i"] \arrow[d, "k_{dp}"] & A_i^- \arrow[l, shift left, "k_{-i}"] \\
 & RY + X^- &
\end{tikzcd} \tag{7}$$

the steady state condition applies to $RXY^-$, the expression (8) follows. Several limiting cases are of special interest: if $k_{dp} \gg k_{dr} > k_i$,

$$\frac{d[RY]}{dt} = k_{dp}\frac{(k_f[RX][Y^-] + k_{-i}[A_i^-])}{(k_{dr} + k_{dp} + k_i)} \tag{8}$$

then the observed rate constant reduces to $k_f$ and the effect of the leaving group is small; if $k_{dp} \ll k_{dr}$ or $k_i$, the observed rate constant remains complex but the effect of the leaving group is fully reflected in the contribution of $k_{dp}$. Other restrictions which lead to

$$k_{obs} \simeq k_{dp}k_f/(k_{dr} + k_{dp}) \tag{9}$$

and

$$k_{obs} = k_{dp}k_f/k_{dr} \tag{10}$$

are easily included.

*Retention models*. Retention appears to be consistent with a few relatively simple paths in the graphs of Figs. 1–3. That of Fig. 1 depicts the possible paths through tetrahedral carbanions connecting reactants and products. Surprisingly, perhaps, it is possible to lift out stereospecific paths in defined systems. We shall examine only a few of them here.

In the typical examples there is only one leaving group (X) in 1. Therefore, ZXY and EXY and edges to them need not be included. If $k_d \gg k_r$, $k_i$, then the retention paths are

$$\begin{tikzcd} ZX \arrow[r, "\cdot"] \arrow[dr, "\cdot"'] & Z1 \arrow[r, "\cdot"] & ZY \\ & Z2 \arrow[ur, "\cdot"'] & \end{tikzcd} \qquad (11)$$

$$\begin{tikzcd} EX \arrow[r, "\cdot"] \arrow[dr, "\cdot"'] & E1 \arrow[r, "\cdot"] & EY \\ & E3 \arrow[ur, "\cdot"'] & \end{tikzcd} \qquad (12)$$

and the inversion paths are

$$ZX \xrightarrow{\cdot} Z3 \xrightarrow{\cdot} EY \qquad (13)$$

$$EX \xrightarrow{\cdot} E2 \xrightarrow{\cdot} ZY. \qquad (14)$$

As pointed out in the previous section the anions Z3 and E2 are probably of high energy because of the *trans* effect—two *pb gauche* to a *lp*. This would be the *primary* reason for favoring retention eqns (11) and (12) over inversion routes (13) and (14).

We regard the preference for *anti* (a) over *syn* (s) steps as a second and supporting explanation of retention. Moreover, there is a bias for the upper a–s over the lower s–a routes of eqns (11) and (12). Consider the reaction coordinates for the retention path (Fig. 4). When X = Y and ZX = ZY, the s–a and a–s routes are energetically equivalent overall even if the individual steps $k_f(a) > k_f(s)$ and $k_{dp}(a) > k_{dp}(s)$. When X ≠ Y and ZX ≠ ZY, the reaction proceeds to the right. It is probable that the relative energies of some species will be lowered as indicated. This is the energy pattern that favors the a–s path of eqn (11). If, in fact, the relative energies of the activated complexes on the left hand side of Fig. 4 were lowered, the s–a path of eqn (11) will be favored. In either case retention would be preferred to an inversion (s–s) sequence.

In the less typical alkenes in which there are two leaving groups (X, W), we must consider the whole of the graph in Fig. 1. Retention is again preferred for the reasons discussed above.

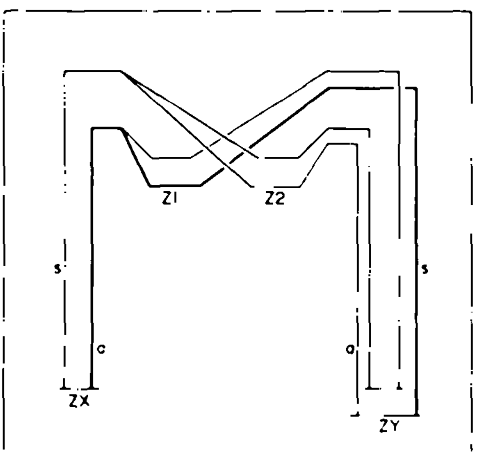


Fig. 4. Exchange of ABC=CXW or ZX with Y according to eqn 11. Symmetrical energy profile, sa or as, for Y=X. Unsymmetrical profile for Y ≠ X follows the as path (thick line).

In the second graph (Fig. 2) we deal with the formation of trigonal carbanion intermediates or with tetrahedral anions whose inversion barrier ($V_i$) is so low ($k_i \gg k_d$, $k_r$) that two of them are effectively equivalent to one trigonal anion, e.g. Z1, Z2 → Z4, E1, E3 → E4, etc. In addition to the restriction that X is the leaving group, the special features of Fig. 2, i.e. the favored rotomers, the implicit 6-fold rotational barrier and the absence of certain edges have been discussed previously. Provided that $k_d \gg k_r$, the implications of this graph are simple. Substitution occurs with retention in two steps as in eqns (15) and (16). If W were also a leaving group, analogous retention processes would

$$ZX \to Z4 \to ZY \qquad (15)$$

$$EX \to E4 \to EY \qquad (16)$$

prevail.

In the third graph (Fig. 3), we come to exchanges involving tetrahedral nitrogen anions. Again we assume $k_d \gg k_r$, $k_i$. The retention path (a–a) of

$$ZX \xrightarrow{\cdot} Z1 \xrightarrow{\cdot} ZY \qquad (17)$$

eqn (17) will always hold when the leaving group is *cis* to the substituent on nitrogen. An unlikely path (eqn 18) from the other isomer also proceeds with retention, but here *syn* steps and the eclipsed intermediate appear to

$$\Sigma X \xrightarrow{\cdot} \Sigma 2 \xrightarrow{\cdot} \Sigma Y \qquad (18)$$

be unfavorable (see previous section). A more acceptable path is eqn (19),

$$\Sigma X \xrightarrow{\cdot} Z3 \xrightarrow{\cdot\cdot} \Sigma Y \qquad (19)$$

which gives exclusive retention. This would be plausible, except that $k_i$ is *syn* in eqn (19) and *anti* in the competing eqn (20). In the latter, partitioning of Σ1 could yield both the product of retention and of inversion. Apart from particular molecules in which there may be special constraints, ***we know of no way to require stereospecific reaction paths from ΣX at the present time.***

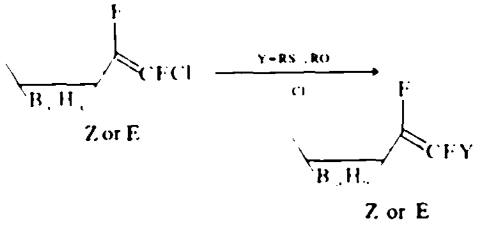
$$\begin{tikzcd} & & \Sigma Y \\ \Sigma X \arrow[r, "\cdot"] & \Sigma 1 \arrow[ur, "\cdot"] \arrow[dr, "\cdot"'] & \\ & & ZY \end{tikzcd} \qquad (20)$$

Trigonal nitrogen anions are, of course, possible in eqn (1), but the graph of Fig. 2 is completely adequate to cover this case, as long as group B is understood to be *lp*. Subject to the condition that $V_i \approx 0$ and $k_d \gg k_r$, substitution of ZX and ΣX by Y always goes with retention.

A large majority (>90%) of the collected examples of eqn (1) involving *ca.* 60 pairs of isomers going to products under kinetic control fit the category of exchange with retention.[1] Slightly more than half of these are stereospecific and the rest are stereoselective with retention. In applying the retention mechanisms we shall draw mainly on examples that have appeared after Rappoport's comprehensive review.[1]

In order that process 1 occur, the alkene must be activated. Electron-withdrawing substituents which facilitate nucleophilic attack usually fall very clearly into the σ vs π types and will be illustrated presently. Moreover, it is convenient that these two groups also correspond to high vs low $V_r$ which we associate with Figs. 1 and 3 vs 2.

Paths from the graph of Fig. 1 correspond to retention when $k_d \gg k_s, k_r$. $V_r$ (and $V_s$) will tend to be high when electronegative groups, e.g. F, $CF_3$, Cl, RO, $R_2N$, etc. are substituents at the carbanion site. A perfluoro example of high retention selectivity is the system $RO^- + CF_3CCl{=}CCF_2Cl$.[34] Reactions (2) and (21)[35] are stereospecific examples close to 100% retention in which the leaving group effect shows remarkable variation. The case of $k_d(Cl)/k_d(F) \simeq 1$ for n-BuONa in eqn (2) (B=F), presumably corresponds to $k_{obs} \simeq k_f$.[4b] $k(Cl)/k(F) \simeq 9$ for n-BuSNa (B=F)[4] and $\simeq 25$ for $CH_3ONa$(B=$CF_3$) in eqn (2) and > 100 for eqn (21)[35] appear to conform more to rate laws 9 and 10. Completely analogous findings for $k(Br)/k(Cl)$ ratios have been compiled by Rappoport.[1]



(21)

The graph of Fig. 2 corresponds to the case of $V_r \simeq 0$. Substituents which are likely to lead to planarity in the anionic site of 1 or 2 in eqn (1) are CN, COR, $C_6H_5$, p-$O_2NC_6H_4$, $SO_2R$, and c-$C_5H_4$. Now, subject to $k_d > k_r$, the retention paths are eqns (15) and (16). Probable examples of this type are the group summarized by c-$C_2H_4NH$ + ClRC=CHR′ (R=$CH_3$, H; R′ = $COOC_2H_5$, CN, Ts, COPh).[36] XCH=C($CH_3$)CN + $Y^-$ ($Y^-$ = $CH_3O^-$, $C_2H_5S^-$, $(CH_3)_2NH$, $(C_2H_5)_2NH$; X = Cl, Br),[37] PhCH=CHX + n-BuLi (X = F, Cl),[38] RCH=CBrR′ + $LiCuMe_2$ (R=Ph, Me; R′ = COOH, COOMe)[39a] and PhCH=CHBr + $Pt(Ph)_3$.[39b] Several excellent rate comparisons are available from the work of Chalchat *et al.*, for the system $Y^- + H_3CCX{=}CHR'$ ($Y^-$ = $C_2H_5O^-$, $C_2H_5S^-$; R′ = CN, $COOC_2H_5$; X = F, Cl, Br, I).[40] Where process 1 has been identified and $C_2H_5S^-$ is the nucleophile, stereoselectivity is high (> 95%), $k(Z)/k(E) = 0.26-3.2$ and $k(F)/k(Cl) \simeq 1-13$.[40] Incidentally, none of these rate effects seem to be strongly dependent on the relative stabilities of the starting alkene since $[Z]/[E] \sim 1-1.5$ for $CH_3CX{=}CHCN$ (X = Br, Cl).[41] At the same time, corresponding "clean" eliminations between $C_2H_5O^-$ and $H_3CCX{=}CHR'$ show large rate factors favoring Z over E-isomers and X = Br or I over Cl.[40]

*Inversion models.* Were it not for Johnson's interesting examples (eqn 3),[5] there would perhaps be no need for this section. Although their rationale may be difficult to contrive, there is no difficulty in formulating inversion paths (see also eqns 13, 14). It is now largely a matter of finding real systems which might conform to these models.

At the outset we need not refer to Fig. 2, since the inversion paths on the graph are less plausible energetically than the retention paths. As applied to the carbanions of Fig. 1 but not Fig. 3, certain conditions can be specified. The inversion paths, eqns (22) and (23), for example, are subject to the conditions, $k_r, k_a \gg k_s$, i.e. only rotations and *anti* processes

$$\begin{tikzcd}
ZX \arrow[r, dashed, "a"] & Z1 \arrow[r, "r"] \arrow[dr, "r"'] & E3 \arrow[r, "a"] & EY \\
& & E2 \arrow[u, "r"'] &
\end{tikzcd} \qquad (22)$$

$$\begin{tikzcd}
EX \arrow[r, "a"] & E1 \arrow[r, "r"] \arrow[dr, "r"'] & Z2 \arrow[r, "a"] & ZY \\
& & Z3 \arrow[u, dashed, "r"'] &
\end{tikzcd} \qquad (23)$$

are permitted. There are, in fact, examples in which a sequence such as eqn (22) was applied *selectively* to rationalize the formation of a stable product, e.g. Z-Ar($CH_3S$)C=$CHSO_2CH_3$ + $CH_3S^-$ → E-Ar($CH_3S$)C=$CHSCH_3$.[42] We do not, however, know of paired examples in which inversions via eqn (22) and (23) have been found.

In a rather different mode, consider eqns (24) and (25) from Fig. 1 and eqns (26) and (27) from Fig. 3 subject to $k_d \gg k_r, k_a$; only *syn* processes are

$$ZX \xrightarrow{s} Z3 \xrightarrow{s} EY \qquad (24)$$

$$EX \xrightarrow{s} E2 \xrightarrow{s} ZY \qquad (25)$$

$$ZX \xrightarrow{s} Z3 \xrightarrow{s} \Sigma Y \qquad (26)$$

$$\Sigma X \xrightarrow{s} \Sigma 1 \xrightarrow{s} ZY \qquad (27)$$

allowed. We believe that the *syn* constraint to $k_f$(s) and $k_d$(s) may well hold in a system reacting by associated ion pairs. Since ion pairing is thought to favor *syn* additions and eliminations,[25,28,29] the formation of the "unfavorable" Z3 and E2 conformers could perhaps be induced in the presence of a counterion (5). Such an ion pair is somewhat special, of course, in that the cation faces two *pb* as well as the *lp*. For a neutral nucleophile such as $R_3N$ or $R_3P$, the "internal" ion pairs $Z_3$ and $E_2$ could be favored in a nonpolar solvent.

We have no firm evidence that the ion pairing just described leads to the inversion selectivity of eqn (3). It is known, however, that $CH_3O^-M^+$ is tightly associated in $(CH_3)_2SO$ containing small amounts of $CH_3OH$.[43] As a result, the proton rearrangement in a triene is at least partly intramolecular (47%) in $CH_3OD + CH_3ONa$ and slightly less so (40%) in $(CD_3)_2SO$–10%$CH_3OD + CH_3OK$.[44] Stepwise reactions promoted by amines (rather than $RO^-$) produce ion pairs, $R_3NH^+X^-$, without the intervention of a solvent molecule. These are closer models to the ion pairs that might be generated in eqn (1). Amine promoted eliminations and additions are, in fact, often *syn*, e.g. PhSCHF–$CHDSO_2Ph$ + $Et_3N$ and $PhSO_2CH{=}CHSPh$ + $Et_3NH^+$ $^-SPh$.[28,29] In this regard, the *syn* eliminations from onium salts are apropos.[28]

In the absence of more detailed information, we believe that eqns (26) and (27) could provide a rationale for the inversion selectivity summarized in eqn (3).[5] Certainly, the ion pairing notion is susceptible to test.

In this section two new mechanisms have been described. For the first the challenge is mainly to devise reactants and for the second to arrange favorable conditions to elicit these paths.

*Stereoconvergence.* We regard isomerization of the reactants or post-isomerization of the products as irrelevant; fortunately, they can usually be investigated independently and taken into account.

By now it should be apparent that the magnitudes of $k_s$, $k_r$ and $k_a$ may be permuted in ways other than those given. Clearly, this may give rise to various stereochemical selectivities. Therefore, $k_r$ might exceed $k_a$ in one isomer and the reverse might be true in the other, e.g. eqn (28).[41] We shall, in fact, take it as understood that deviations from stereospecificity usually arise by such "leakage", although necessary partitioning, as in eqn (20), should be kept in mind.

$$\begin{tikzcd} Z\text{—}PhSO_2CH{=}CHF \arrow[r, "MeO^-"] \arrow[dr] & Z\text{—}PhSO_2CH{=}CHOCH_3 \\ E\text{—}PhSO_2CH{=}CHF \arrow[r, "MeO^-"] & E\text{—}PhSO_2CH{=}CHOCH_3 \end{tikzcd} \tag{28}$$

Only one model, that of $k_c$, $k_t > k_d$, will be taken up. Here the anions are *equilibrated* and a stereoconvergent result is obtained. That is, products are formed with $[ZY]/[EY]$ or $[ZY]/[\Sigma Y]$ = constant. Such a result is more likely to be found in eqn (1), when the entering group is neutral ($R_3N$, $R_3P$), the leaving group is $F^-$, $RO^-$ or $CN^-$, or **1** and **2** are highly stablized anions.[1,2] These characteristics are illustrated by apparent stereoconvergence in the products of $n\text{-}BuNH_2 + CH_3CF=CHCN$ (95%E),[40] $(C_2H_5)_2NH + CH_3CF=CHCOOC_2H_5$ (95%E),[40] $(C_2H_5)_2NH + PhCOCH=CHCl$ (100%E)[36] and $R_3P + XCR'=CR''COOH$ (100%E: R = n-Bu, Ph, EtO; R' − R'' = H, $CH_3$; X = Cl, Br).[46] A related phenomenon is found in systems of the type $RNH_2 + ArCX=C(CN)_2$ which are often second order in amine: the first intermediate (**1**) is so stable that it requires a second amine molecule for deprotonation and ejection of $CN^-$.[47] It seems likely that analogous reactions in which a stereochemical choice is possible would be stereoconvergent.

*Other substitution models*. Consider the addition–elimination mechanism involving protonation ($k_h$) of **1** or **2**. Of necessity this implies that $k_h > k_d$. Note that extremely rapid proton transfer to remove ($k_h$) or form ($k_{-h}$) **1** or **2** leaves us with the cases described in the previous sections, at least for Figs. 1 and 2. Therefore, new situations allow sufficient time for rotations of AHQ-CWXY. Now, one or more of E1CB and *syn* and *anti* E2 processes could follow. Unless *syn or anti* prevails (see below), the very multiplicity of routes to products renders stereospecificity improbable and stereoconvergence plausible. Where the addition–elimination route for eqn (1) has been established, this outcome has been found, e.g. Z- or $E\text{-}ArSO_2CH=CHOPh \rightarrow E\text{-}ArSO_2CH=CHOR$,[48a] Z- or $E\text{–}CF_3CF=CFH \rightarrow$ Z- and $E\text{–}CF_3CF=CHOR$[48b] and perhaps eqn (28).

With respect to eqn (3) and Fig. 3, Johnson *et al.* has suggested that *anti* addition of $CH_3OH$ followed by rotation and *anti* elimination of HX provides a rationale for predominant inversion.[5] Provided that the proton is identified with the *lp* in eqns (24) or (23), this mechanism is essentially that of eqns (22) or (23). To be stereospecific, this mechanism requires the *immobility* of a proton attached to neutral nitrogen. The difficulty is that protonation and deprotonation of such a nitrogen in $CH_3OH\text{–}CH_3O^-Na^+$ is likely to take place at or close to the encounter rate.[49] Effectively, this would lead to *syn* and *anti* addition of $CH_3OH$ in eqn (3) *before* rotation could occur. Clearly, there are a number of tests that have to be applied to distinguish the Johnson proposal for inversion from that we gave previously in eqns (26) or (27).

In the last model we consider the concerted mechanism for substitution at an sp² site: the several steps of eqn (1) are telescoped into one. For 10–15 years the early arguments against the one-step process were essentially unquestioned.[2,3] Recently, several groups have suggested—some tentatively, others forcefully—that the concerted process could account for substitution with retention.[19a,40,50] Stohrer formulates the one-step mechanism essentially in the form of eqn (15), provided that Z4 is identified with activated complex **6** lying between **4a** and **4b**.[50] He also gives an orbital correlation diagram which indicates that the process is allowed.

In our view, the concerted mechanism is unlikely. As for orbital correlation, this can be constructed both for the implausible SN2 inversion as well as for the stepwise processes (11) or (12); all are *allowed*! Indeed, the basis of our arguments against the one step process is that it usually will be of higher energy than that given by eqn (1). Although the isolation of anionic intermediates formed by addition of nucleophiles to sp² sites does not ensure their intermediacy in all substitution reactions at carbonyl, aryl, alkenyl, etc. centers, their detection is certainly suggestive and supportive. Likewise in theoretical studies, anions have usually been assumed or found to inhabit energy minima in potential energy space.[18,19,51] If this is granted, then the alleged activated complex **6** is merely a vibrationally excited state of **1**.

At the present time, the concerted retention mechanism cannot be validated or rejected on the basis of known experimental results. Surely it does not—nor does it claim to—account for substitution with varied selectivities, for second and third order kinetics, for both "normal" and inverted element effects, for Hammet $\rho$ values,[52] etc. Nor does it bring substitutions (eqn 1) into close relation with eliminations, additions, rearrangements, etc. in which dissociated or associated anions are often common intermediates. According to his calculations (EH, CNDO *ab initio*), Strohrer finds that the key factor which determines whether **6** is to be an activated complex or an intermediate depends on how strongly the leaving group X is solvated. This same factor came up in the discussion of eqn (5) in the context of the stepwise mechanism. In any case, a single-factor explanation is arguable here, if only on the basis that leaving group ratios $k(F)/k(Cl) \gtrless 1$ are variable.

We would prefer to discuss the changeover of concerted to stepwise mechanism in terms of the magnitude of $k_d \lessgtr 10^{13}\ sec^{-1}$. That is, the aggregate which does not exist for more than one (or perhaps a few) vibrations is not an intermediate. In certain carbonyl[53] and elimination reactions[25,26] the existence of an intermediate is either doubtful or unnecessary. Until similar evidence for concerted substitution in eqn (1) is forthcoming,[3b] even selective use of this mechanism remains questionable.

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