

## Chloride Ion Exchange and $E \rightleftharpoons Z$ Isomerization of an Electrophilic Vinyl Chloride<sup>1</sup>

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Received December 30, 1988

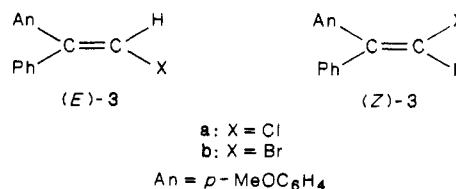
The exchange (ex) and the accompanying isomerization (isom) in the reaction of methyl ( $E$ )- and ( $Z$ )- $\beta$ -chloro- $\alpha$ -cyano- $p$ -nitrocinnamates [( $E$ )-5 and ( $Z$ )-5] with <sup>36</sup>Cl<sup>-</sup> in acetonitrile were investigated. Exchange was much faster than isomerization,  $k_{\text{ex}}/k_{\text{isom}} = 54$  [( $E$ )-5] and 123 [( $Z$ )-5]. Both exchange and isomerization were faster for ( $Z$ )-5 than for ( $E$ )-5. The exchange was a relatively fast process, and extrapolation suggested that  $k_{\text{ex}}(\text{Cl}^-)/k_{\text{substitution}}(\text{piperidine})$  of 5 is 2.7. The results are discussed in terms of formation of intermediate carbanion, which exchanged the chloride with highly preferred retention. The modes of rotations leading to inversion (isomerization) were analyzed, and it was shown that isomerizations via 120° counterclockwise rotation and 180° clockwise rotation around the C <sub>$\alpha$</sub> -C <sub>$\beta$</sub>  bond in the carbanion are distinguishable in principle, although we failed to determine the mode of rotation in our system. The relatively high nucleophilicity of Cl<sup>-</sup> was ascribed to lower hidden reversal of the nucleophilic attack by Cl<sup>-</sup> than in less activated systems. The differences in reactivity of ( $Z$ )-5 and ( $E$ )-5 were analyzed in terms of steric interactions in the transition states for the 60° and 120° internal rotations.

Recent investigations on the mechanism of bimolecular nucleophilic vinylic substitution involved the study of the substitution of strongly electrophilic chloro, bromo, and iodo olefins.<sup>2</sup> Whereas with moderately activated chloro and bromo olefins the kinetically controlled substitution proceeds with complete retention of configuration,<sup>3</sup> the highly activated systems give partial or complete stereoconvergence (i.e., formation of a mixture of the  $E$  and  $Z$  substitution products starting either from ( $E$ )- or ( $Z$ )-vinyl halide.<sup>2</sup> The interpretation of the stereochemistry is in terms of Scheme I, where the perpendicular attack on the vinyl halide ( $E$ )-1 by the nucleophile Nu<sup>-</sup> ( $k_1$ ) leads to carbanionic conformation I. Intramolecular 60° rotation ( $k_{\text{rot}}^{60}$ , clockwise in the example shown) leads to conformer II, which can expel the nucleofuge Cl<sup>-</sup> ( $k_{\text{el}}^1$ ), giving the retained product ( $E$ )-2. An initial 120° rotation ( $k_{\text{rot}}^{120}$ , counterclockwise in I) or further 180° clockwise rotation in II leads to carbanionic conformer III, which by expulsion of X<sup>-</sup> ( $k_{\text{el}}^2$ ) gives the inverted product ( $Z$ )-2. Expulsion of Nu<sup>-</sup> from conformer IV, which is obtained by 180° rotation of I, to give ( $Z$ )-1, is rare with chloro and bromo olefins, although it was found recently with Nu<sup>-</sup> = NCS<sup>-</sup>.<sup>1b,2e,4</sup>

Consequently, the stereochemistry is determined by the relative magnitude of the  $k_{\text{rot}}^{60}$ ,  $k_{\text{rot}}^{120}$ , and  $k_{\text{el}}$  terms.

It was suggested that the sum of hyperconjugative stabilizations of the carbanionic intermediate by the C-Nu, C-R, and C-X orbitals leads to preferred 60° rotation due to the higher hyperconjugative ability (HC) of the C-X orbital compared with the other terms.<sup>5</sup>  $k_{\text{el}} > k_{\text{rot}}^{60} > k_{\text{rot}}^{120}$ , and hence retention is observed when the carbanion is short-lived, i.e. when the halo olefin is only moderately activated. With long-lived carbanions, obtained when Y, Y' are strongly electron-withdrawing, the gap between the rotational barriers for 60° and 120° rotations is reduced,  $k_{\text{el}}$  decreases until it is of the same magnitude as  $k_{\text{rot}}$ , and sometimes it is even rate determining, leading to partial<sup>2b-e</sup> or even complete stereoconvergence.<sup>2a</sup>

In contrast to their appreciable nucleophilicity in aliphatic substitution, Cl<sup>-</sup> and Br<sup>-</sup> are among the weakest nucleophiles in vinylic substitution.<sup>3b</sup> Kinetic studies of the substitution of  $\beta$ -bromostyrenes by I<sup>-</sup><sup>6</sup> or of 1-anisyl-1-phenyl-2-haloethylenes [( $E$ )- and ( $Z$ )-3] by labeled



Cl<sup>-</sup> ion<sup>7</sup> required high temperatures whereas reactions with thio or oxygen nucleophiles are usually much faster.<sup>2,3</sup> Recently we showed that Cl<sup>-</sup> and Br<sup>-</sup> can catalyze the slow  $E \rightleftharpoons Z$  isomerization of several of the halo olefins which give stereoconvergence,<sup>2b-e</sup> and the mechanism suggested involves long-lived carbanions.

The kinetics of the substitution by halide ions was not investigated so far with highly electrophilic olefins. A study of labeled chloride exchange (Cl<sup>-</sup>) and an accompanying isomerization can assist in solving four different problems. (a) The relative rates of exchange and isomerization in the reaction of ( $E$ )-3 and ( $Z$ )-3 with Cl<sup>-</sup> indicated an appreciable extent of inversion, which is not expected for these low-activated systems according to the theory of nucleophilic vinylic substitution.<sup>2,3e</sup> (b) The nucleophilicity of Cl<sup>-</sup> in vinylic substitution may be higher than previously evaluated by substitution studies if exchange is extensive. (c) The number of nucleophiles known to give stereoconvergence is still small, and an additional nucleophile, much weaker than previously studied, can

(1) (a) Nucleophilic attacks on carbon-carbon double bonds. Part 38. (b) For Part 37, see: Rappoport, Z.; Avramovitch, B.; Karni, M.; Apeloig, Y. *Isr. J. Chem.*, in press.

(2) (a) Rappoport, Z.; Topol, A. *J. Am. Chem. Soc.* 1980, 102, 406. (b) Rappoport, Z.; Avramovitch, B. *J. Org. Chem.* 1982, 47, 1397. (c) Rappoport, Z.; Gazit, A. *J. Org. Chem.* 1985, 50, 3184. (d) *Ibid.* 1986, 51, 4112. (e) Rappoport, Z.; Gazit, A. *J. Am. Chem. Soc.* 1987, 109, 6698.

(3) For reviews, see: (a) Patai, S.; Rappoport, Z. In *The Chemistry of Alkenes*; Patai, S., Ed.; Interscience: London, 1964; Chapter 8. (b) Rappoport, Z. *Adv. Phys. Org. Chem.* 1969, 7, 1. (c) Modena, G. *Acc. Chem. Res.* 1971, 4, 73. (d) Miller, S. I. *Tetrahedron* 1977, 33, 1211. (e) Rappoport, Z. *Acc. Chem. Res.* 1981, 14, 7. (f) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* 1985, 104, 309. (g) Shainyan, B. A. *Usp. Khim.* 1986, 55, 942.

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(5) (a) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* 1979, 101, 5095. (b) See also: Apeloig, Y.; Karni, M.; Rappoport, Z. *J. Am. Chem. Soc.* 1983, 105, 2784.

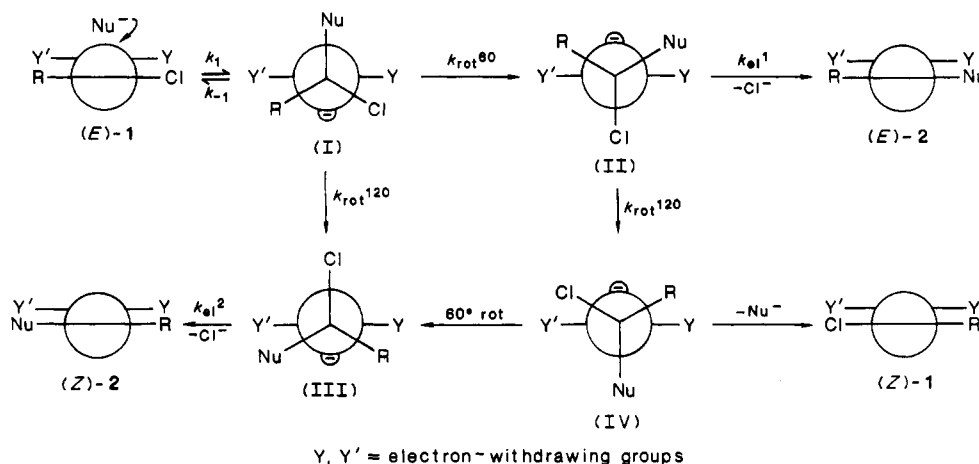
(6) Miller, S. I.; Yonan, P. *J. Am. Chem. Soc.* 1957, 79, 5391.

(7) Beltrame, P.; Bellobono, I. R.; Feré, A. *J. Chem. Soc. B* 1966, 1165.

<sup>†</sup>Leiden University.

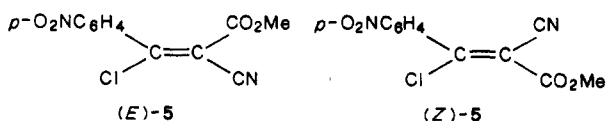
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Scheme I



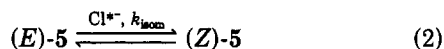
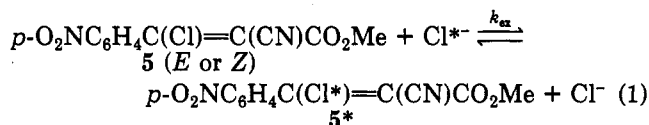
help in correlating the extent of stereoconvergence with the nucleophilicity of the nucleophile. (d) The identity of the nucleophile and the nucleofuge except for the isotopic label provides a unique opportunity to probe the detailed path of the inversion process as shown in Scheme II. Reaction of (*E*)-4 with  $\text{Cl}^{*-}$  gives carbanionic conformer V. If this is sufficiently long-lived, the two modes of rotation which may lead to inversion are distinguishable:  $120^\circ$  rotation followed by  $\text{Cl}^-$  expulsion ( $\text{V} \rightarrow \text{VI} \rightarrow (\text{Z})\text{-4}^*$ ) will lead to inverted labeled product (*Z*)-4\* whereas an overall  $180^\circ$  clockwise rotation ( $\text{V} \rightarrow \text{VII} \rightarrow (\text{Z})\text{-4}$ ) will give the nonlabeled inverted product (*Z*)-4. Hence, the operation of one of the routes or a mixture of both could in principle be probed experimentally.

For this reason we studied the  $^{36}\text{Cl}^-$  exchange and the accompanying isomerization of methyl (*E*)- and (*Z*)- $\beta$ -chloro- $\alpha$ -cyano-*p*-nitrocinnamates [(*E*)-5 and (*Z*)-5]. Cinnamates (*E*)-5 and (*Z*)-5 were shown previously to give stereoconvergence with  $\text{ArO}^{2b}$  and  $\text{ArS}^-$  nucleophiles<sup>2b,8</sup> and isomerization with  $\text{Cl}^{*-}$ <sup>2b</sup>



## Results

The preparation and separation of (*E*)-5 and (*Z*)-5 was described earlier.<sup>2b</sup> Each isomer was reacted with 15 molar excess of  $\text{Et}_4\text{NCl}[^{36}\text{Cl}]$  in acetonitrile, and two processes, (i) the exchange of labeled ( $\text{Cl}^{*-}$ ) for nonlabeled chloride (eq 1) and (ii) the simultaneous (*E*)-5  $\rightleftharpoons$  (*Z*)-5 isomerization (eq 2), were followed.



The exchange rate was much higher than the isomerization rate so that concurrent measurement of both rate constants was practically possible only at  $23^\circ\text{C}$ . In order to obtain the activation parameters the exchange was also followed at  $0^\circ\text{C}$  whereas the isomerization was also followed at  $45^\circ\text{C}$ . Three independent runs were conducted

Table I. First-Order Rate Constants for Isomerization and Exchange in the Reaction of (*E*)-5 and (*Z*)-5 with  $^{36}\text{Cl}^-$  in Acetonitrile<sup>a</sup>

| substrate      | T, °C | $10^5 k_{\text{isom}}$ , s <sup>-1</sup> | $10^4 k_{\text{ex}}$ , s <sup>-1</sup> | $k_{\text{ex}}/k_{\text{isom}}$ |
|----------------|-------|--|--|---------------------------------|
| ( <i>E</i> )-5 | 23    | 2.2 ± 0.3                                | 12.2 ± 1.2                             | 55                              |
|                |       | 1.9 ± 0.3                                | 11.5 ± 1.0                             | 61                              |
|                |       | 2.5 ± 0.3                                | 11.7 ± 1.7                             | 47                              |
| ( <i>Z</i> )-5 | 23    | 2.2 ± 0.3 <sup>b</sup>                   | 11.8 ± 0.3 <sup>b</sup>                | 54 ± 5                          |
|                |       | 4.2 ± 0.2                                | 57 ± 13                                | 136                             |
|                |       | 5.2 ± 0.2                                | 57 ± 13                                | 110                             |
|                |       | 5.0 ± 0.3                                | 62 ± 8                                 | 124                             |
| ( <i>E</i> )-5 | 0     | 4.8 ± 0.4 <sup>b</sup>                   | 59 ± 12 <sup>b</sup>                   | 123 ± 9 <sup>b</sup>            |
|                |       |  | 1.1 ± 0.1                              | 1.0 ± 0.1                       |
| ( <i>Z</i> )-5 | 0     |  | 1.2 ± 0.1                              |                                 |
|                |       |  | 1.1 ± 0.1 <sup>b</sup>                 |                                 |
|                |       |  | 5.9 ± 0.5                              |                                 |
|                |       |  | 4.7 ± 0.5                              |                                 |
| ( <i>E</i> )-5 | 45    |  | 5.5 ± 0.5                              |                                 |
|                |       |  | 5.4 ± 0.4 <sup>b</sup>                 |                                 |
| ( <i>Z</i> )-5 | 45    | 13.3 ± 1.0                               | 16.7 ± 1.7                             |                                 |
|                |       | 17.7 ± 1.3                               | 16 ± 2 <sup>b</sup>                    |                                 |
|                |       | 16 ± 2 <sup>b</sup>                      | 41.7 ± 1.7                             |                                 |
|                |       | 41.7 ± 1.7                               | 51.7 ± 1.7                             |                                 |
|                |       | 48.3 ± 1.7                               | 47 ± 4 <sup>b</sup>                    |                                 |

<sup>a</sup> [5] =  $2.0 \times 10^{-3}$  M;  $[\text{Et}_4\text{N}^{36}\text{Cl}] = 3.0 \times 10^{-2}$  M. <sup>b</sup> Average value.

Table II. Activation Parameters for Isomerization and Exchange of (*E*)-5 and (*Z*)-5

| substrate      | process       | $E_a$ , kcal mol <sup>-1</sup> | $\Delta H^\ddagger$ , kcal mol <sup>-1</sup> | $\Delta S^\ddagger$ , eu at $23^\circ\text{C}$ |
|----------------|---------------|--------------------------------|--|--|
| ( <i>E</i> )-5 | exchange      | 16.6                           | 16.0   | -10  |
| ( <i>Z</i> )-5 | exchange      | 16.8                           | 16.2   | -6   |
| ( <i>E</i> )-5 | isomerization | 17.1                           | 16.5   | -16  |
| ( <i>Z</i> )-5 | isomerization | 19.3                           | 18.7   | -7   |

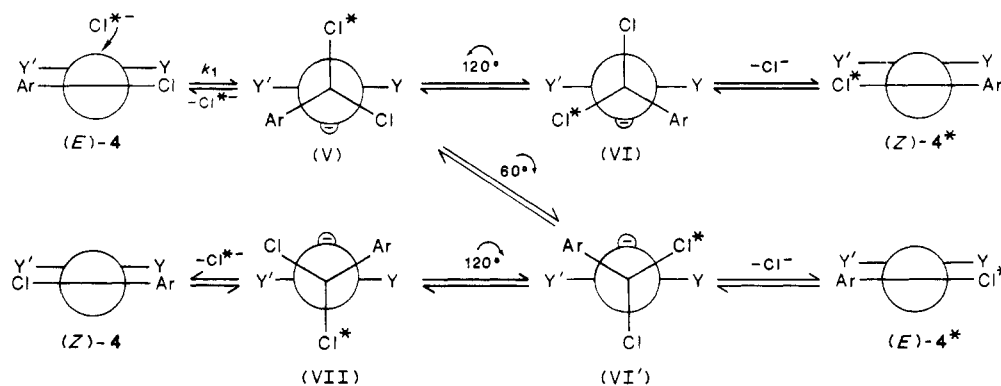
at each temperature, and the first-order rate constants for isomerization ( $k_{\text{isom}}$ ) and exchange ( $k_{\text{ex}}$ ) were calculated from the appropriate first-order plots. The agreement between the experiments, even those that were conducted one year apart, is acceptable and usually within the combined experimental errors of the individual experiments. The rate constants and the derived  $k_{\text{ex}}/k_{\text{isom}}$  ratios which are 47–136 (average: 54 [(*E*)-5]; 123 [(*Z*)-5]) at  $23^\circ\text{C}$  are given in Table I.

The exchange rate of (*Z*)-5 is ca. 5-fold faster than that of (*E*)-5 at  $23^\circ\text{C}$ , whereas the isomerization of (*Z*)-5 is ca. 2 times faster.

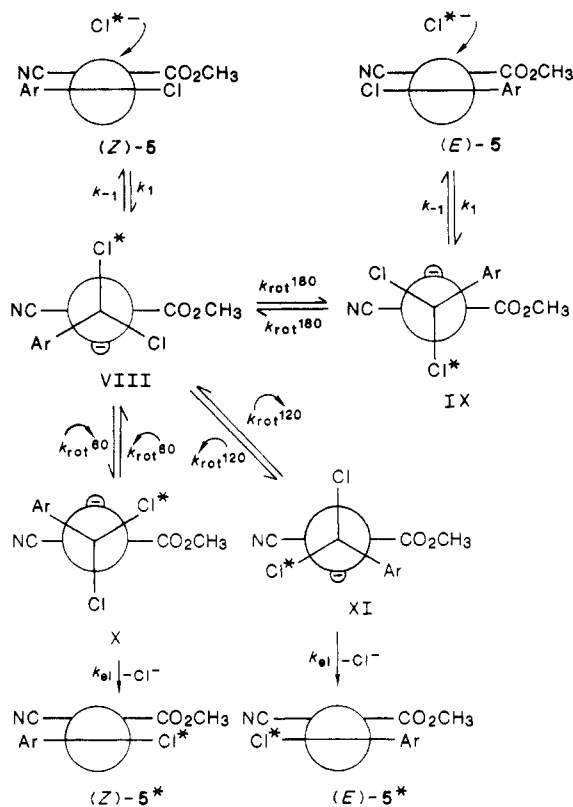
The activation parameters for the two processes are given in Table II. The values for (*E*)-5 and (*Z*)-5 are closer

(8) Avramovitch, B.; Rappoport, Z. *J. Am. Chem. Soc.* 1988, 110, 911.

Scheme II



Scheme III

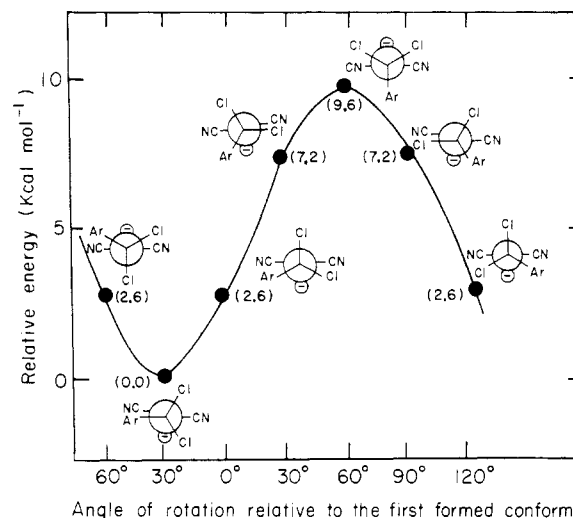


for the exchange (0.2 kcal mol<sup>-1</sup>) than for the isomerization, where they differ by 2.2 kcal mol<sup>-1</sup>.

### Discussion

There are three important points of the present results. First, exchange is much faster than isomerization with both isomers. Second, both isomerization and exchange are faster with (Z)-5 than with (E)-5. Third, the exchange is a relatively rapid process at room temperature.

In terms of Schemes I and II as applied to our system (cf. Scheme III) there are two processes that lead to exchange and two that do not. Starting, for example, from (Z)-5 the initially formed carbanion VIII leads to exchange with retention by a sequence of 60° (clockwise) rotation followed by expulsion of Cl<sup>-</sup> (VIII → X → (Z)-5\*) and to exchange with inversion by 120° (counterclockwise) rotation and expulsion of Cl<sup>-</sup> (i.e., VIII → XI → (E)-5\*). The hidden reversal of the nucleophilic attack before rotation gives back the starting material with no observable change, but it may be a major route (see below). Isomerization without exchange is obtained by 180° rotation followed by expulsion of Cl<sup>-</sup> (i.e., VIII → IX → (E)-5).



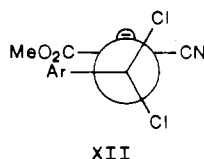
**Figure 1.** A plot of the calculated relative negative hyperconjugation energies (3-21G, kcal mol<sup>-1</sup>) for various conformations of Cl<sub>2</sub>C(Ar)-C(CN)<sub>2</sub> vs the C<sub>α</sub>-C<sub>β</sub> rotation angle. The most stable conformation is assigned an energy value of zero.

A much faster exchange than isomerization is consistent with substitution, which proceeds mainly with retention of configuration. Moreover, this means that the rate-determining steps for the retention and inversion (isomerization) pathways are the rotation processes.

The expulsion is 47–136 times faster than further clockwise rotation in conformer X if the reaction is viewed as a continuous clockwise rotation from the initially formed VIII, where expulsion of Cl<sup>-</sup> after 60° rotation gives retention, and further rotation (leakage) leads to inversion without exchange. Alternatively, if the reaction is viewed as a competition between 60° (clockwise) and 120° (counterclockwise) rotations, each followed by a complete Cl<sup>-</sup> expulsion from X and XI, then the former is preferred by 54- and 123-fold.

Three features distinguish the behavior of the present system from that of those previously studied. First, system 5 gave an appreciable stereoconvergence in the substitution by the nucleophiles *p*-toluenethiolate and *p*-cresolate anions.<sup>2b,8</sup> Consequently, Cl<sup>-</sup> gives more retention than ArO<sup>-</sup> and ArS<sup>-</sup> nucleophiles. Second, due to the presence of the two halogens with similar negative hyperconjugative abilities, the most stable conformer obtained on clockwise rotation is not X, which is stereoelectronically the favorable configuration for Cl<sup>-</sup> expulsion, but conformer XII in which the dihedral angle between the C-Cl and 2p(C<sup>-</sup>) orbital is 30°, whereas in reactions with other nucleophiles the configuration of the carbanion (e.g. II in Scheme I) is much closer to X. This is shown in Figure 1, which displays the calculated potential energy surface for rotation in the

closely related carbanion  $\text{ArC}(\text{Cl})_2\text{-}\bar{\text{C}}(\text{CN})_2$ , using a 3-21G basis set).<sup>1,9</sup> The change  $\text{CN} \rightarrow \text{CO}_2\text{Me}$  should not have a strong effect on the shape of the curve. Third, the  $k_{\text{ex}}/k_{\text{isom}}$  ratio is much higher than found previously.<sup>7</sup>



It is not clear why  $\text{Cl}^-$  gives more retention. For the model of continuous clockwise rotation (i.e., conformation X is on the potential energy surface of both the retention and inversion routes) if the expulsion of the chloride ion is assisted by both the electron pair on  $\text{C}_\beta$  and the Nu moiety on  $\text{C}_\alpha$ , the higher is the resonative electron-donating ability of the latter the less leakage (i.e., inverted product) is expected. Since  $\sigma_{\text{R}}^\circ$  values of OPh, SPh, and Cl are  $-0.34 \pm 0.02$ ,  $-0.18 \pm 0.01$ , and  $-0.27 \pm 0.06$ , respectively,<sup>10</sup> higher extent of retention for Nu = Cl compared with Nu = OPh is not expected.

The situation is different for a model of competition between  $60^\circ$  clockwise and  $120^\circ$  counterclockwise rotation. The rotational barriers and the geometry of the most stable conformer are thought to result mainly from balance of hyperconjugative interactions of the C–Nu, C–Cl, and C–Ar orbitals with the  $2p(\text{C}^-)$  orbital. The most stable conformation for each single C–X bond is a parallel one to the  $2p(\text{C}^-)$  orbital, and the rotational barriers depend on the contribution of each bond to such alignment when Nu = OR or SR. Since the hyperconjugative ability (HCA) of the Ar–C bond is low and that of the C–Cl bond exceeds that of a C–OR and a C–SH bond, the driving force for  $60^\circ$  rotation, which increases  $2p(\text{C}^-)$ –C–Cl hyperconjugation mainly at the expense of loss of C–OR (or C–SR) conjugation, is positive. Consequently, the most stable conformer on the clockwise rotation path is the one with the  $2p(\text{C}^-)$  and C–Cl orbitals nearly aligned. For  $\text{Cl}^*$  as a nucleophile, any rotation (clockwise or counterclockwise) is energetically more expensive since the C– $\text{Cl}^*$  bond of the entering chloride is already perfectly aligned with the  $2p(\text{C}^-)$  orbital in conformation I. The loss of the hyperconjugative interaction of the C– $\text{Cl}^*$  bond is, at most, only partly balanced by the gain for the C–Cl bond. Since on the first stages of either the  $60^\circ$  or the  $120^\circ$  rotation the loss of C– $\text{Cl}^*$ – $2p(\text{C}^-)$ –HC is the same, the  $60^\circ$  rotation is still preferred, but with a much lower driving force. The occurrence of both exchange and isomerization shows that rotation may take place, but these considerations do not give any clue for the higher retention with Nu = Cl.

**Comparison with Other Exchange/Isomerization Ratios.** The only additional vinylic system for which  $k_{\text{ex}}/k_{\text{isom}}$  ratios were determined is the 1,1-diaryl-2-haloethylene system, **3**. This system has lower electrophilicity than ours and shows a much lower reactivity in both the exchange and isomerization processes.

The substitution and exchange of (*E*)-**3** and (*Z*)-**3** with 2 molar equiv of  $\text{Li}^{36}\text{Cl}$  were studied in DMF.<sup>7</sup> Substitution was followed by radiochlorine count and the isomerization by IR spectroscopy, and initial rates were used for calculating the rate constants. Both processes were very

Table III. Temperature Dependence of the  $k_{\text{ex}}/k_{\text{isom}}$  Ratios

| substrate      | $T, ^\circ\text{C}$ | $10^5 k_{\text{isom}}, \text{s}^{-1}$ | $10^4 k_{\text{ex}}, \text{s}^{-1}$ | $k_{\text{ex}}/k_{\text{isom}}$ |
|----------------|---------------------|---------------------------------------|-------------------------------------|---------------------------------|
| ( <i>E</i> )-5 | 0                   | 0.18 <sup>a</sup>                     | 1.1                                 | 61                              |
|                | 23                  | 2.2                                   | 11.8                                | 54                              |
|                | 45                  | 16                                    | 82 <sup>a</sup>                     | 51                              |
|                | 170                 | $31 \times 10^3$ <sup>a</sup>         | $12.7 \times 10^4$ <sup>a</sup>     | 41                              |
| ( <i>Z</i> )-5 | 0                   | 0.30 <sup>a</sup>                     | 5.3                                 | 177                             |
|                | 23                  | 4.8                                   | 59                                  | 123                             |
|                | 45                  | 47                                    | 413 <sup>a</sup>                    | 88                              |
|                | 170                 | $24 \times 10^4$ <sup>a</sup>         | $71 \times 10^4$ <sup>a</sup>       | 30                              |

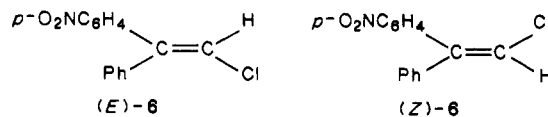
<sup>a</sup> Calculated value.

slow and required high temperature. The most pronounced feature is the formation of a considerable amount of the inverted isomer, which increased with the progress of the reaction. Control studies showed lack of isomerization in the absence of  $\text{Cl}^-$  or in the presence of  $\text{LiNO}_3$  after 312 h at  $186^\circ\text{C}$  in DMF. At  $170^\circ\text{C}$   $k_{\text{ex}} = 3.1 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}$  and  $k_{\text{isom}} = 2.5 \times 10^{-6}$  for (*Z*)-**3**, and  $k_{\text{ex}} = 5.4 \times 10^{-6}$ ,  $k_{\text{isom}} = 2.4 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}$  for (*E*)-**3**. For the exchange  $\Delta E^\ddagger = 36.2 \text{ kcal mol}^{-1}$ ;  $\Delta S^\ddagger = -4.8 \text{ eu}$  for (*Z*)-**3** and  $33.5 \text{ kcal mol}^{-1}$  and  $-10 \text{ eu}$  for (*E*)-**3**.

It was concluded that isomerization is part of the exchange process, where the reaction of (*Z*)-**3** proceeds with prevalent inversion, while inversion and retention have similar importance for (*E*)-**3**. The formation of a carbanionic intermediate that loses  $\text{Cl}^-$  and  $\text{Cl}^*$  with equal rates and forms equal fraction of labeled retained (inverted) product and nonlabeled retained (inverted) products was assumed. This led to an equation  $k_{\text{ex}} = 0.5k_1$ , where  $k_1$  is the rate constant for formation of the intermediate. This analysis suggested that retention is the main pathway for both isomers, that inversion is an important component of the reaction, and that the barrier for  $\text{Cl}^-$  expulsion is lower or of the same order of magnitude as that for internal rotation.

The  $k_{\text{ex}}/k_{\text{isom}}$  values of 1.25 and 1.14 for (*Z*)-**3** at  $170^\circ\text{C}$  and  $186^\circ\text{C}$  and of 2.25 and 1.8 for (*E*)-**3** at  $170^\circ\text{C}$  and  $186^\circ\text{C}$  are in contrast to our much higher ratios and to the predicted higher retention for the less reactive system. These data suggest the existence of relatively long-lived carbanions for one of the least activated systems studied so far.

A study of the *p*-nitro analogues (*E*)-**6** and (*Z*)-**6** showed that these more activated systems required a lower temperature ( $110$ – $140^\circ\text{C}$ ) for the observation of exchange in DMF. More important is that (*E*)-**6**  $\rightleftharpoons$  (*Z*)-**6** isomerization was not observed within the sensitivity of the IR detection method,<sup>11</sup> i.e.  $k_{\text{ex}}/k_{\text{isom}} = \infty$ .



Reservations concerning the assumptions used for the calculations of the rate constants for system **3** can be raised. However, they will not be discussed since, in a later experiment in which analysis of the reactions of (*E*)-**3** and (*Z*)-**3** with  $\text{LiCl}$  involved titration of  $\text{Cl}^-$ , a significant loss of  $\text{Cl}^-$  was observed, indicating that DMF reacts with  $\text{LiCl}$  in parallel to the vinylic exchange. By applying this conclusion to the previous analysis it was concluded that "It seems probable that isomerization and exchange are separate processes and do not have a common intermediate, as had been assumed for the interpretation of the results".<sup>11</sup>

(9) These values were calculated by Dr. M. Karni and Prof. Y. Apeig. Curves with similar shapes were obtained either when the energy of the conformers was calculated directly or when additivity of single interactions was assumed. For details of such calculations in related system, see ref 1b and 5.

(10) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1986; Chapter 10, p 439.

(11) Beltrame, P.; Beltrame, P. L.; Carboni, G.; Cereda, M. L. *J. Chem. Soc. B* 1970, 730.

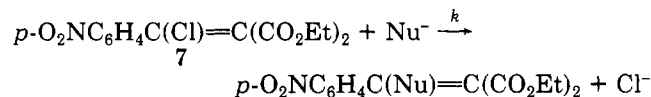
Regardless of these reservations, it was of interest to see whether the large difference in the reaction temperature between Beltrame's work and ours may lead to the large difference in  $k_{\text{ex}}/k_{\text{isom}}$  ratios. Extrapolation of Beltrame's data<sup>7</sup> to 23 °C gave  $k_{\text{ex}} = 5.8 \times 10^{-16} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{isom}} = 3.5 \times 10^{-14} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{ex}}/k_{\text{isom}} = 60$  for (*E*)-3, and  $k_{\text{isom}} = 8.4 \times 10^{-16} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{ex}} = 4.2 \times 10^{-15} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{ex}}/k_{\text{isom}} = 5$  for (*Z*)-3. Consequently, the  $k_{\text{ex}}/k_{\text{isom}}$  value for (*E*)-3 at 23 °C is of the order of magnitude of our values, and the values for both isomers indicate predominant retention. Table III shows that extrapolation of our data to 170 °C has a smaller effect on the  $k_{\text{ex}}/k_{\text{isom}}$  values and that exchange with retention still predominates. In view of Beltrame's own reservation<sup>11</sup> we regard our values as the first reliable data for Cl<sup>-</sup> promoted concurrent exchange and isomerization in vinylic systems.

**Relative Nucleophilicity of Cl<sup>-</sup> in Vinylic Substitution.** Chloride, bromide, and iodide ions are much weaker nucleophiles compared with thio nucleophiles, N<sub>3</sub><sup>-</sup>, and even alkoxides in vinylic substitution.<sup>3b,12</sup> They are also notably less reactive compared with their reaction at a saturated carbon.<sup>3b</sup> This conclusion is based on several sources: For the substitution of  $\beta$ -bromo-*p*-nitrostyrene with iodide in butyl cellosolve<sup>6</sup> vs thiophenoxide ion in methanol,<sup>13</sup> the  $k_{\text{PhS}^-}/k_{\text{I}^-} \approx 10^9$ ; likewise *p*-MeC<sub>6</sub>H<sub>4</sub>S<sup>-</sup> is 9 orders of magnitude more reactive than Cl<sup>-</sup> toward 2-chloro-1,1-diarylethylenes in DMF.<sup>7,14</sup> Also, Cl<sup>-</sup> is  $\geq 10^6$  times slower than EtS<sup>-</sup> in substitution of ethyl  $\beta$ -chloroacetate.<sup>15</sup> Halide ion catalyzed *E*  $\rightleftharpoons$  *Z* isomerizations of electrophilic halo olefins<sup>2b-e</sup> are slow and take days at room temperature, whereas the substitutions of the same substrates by ArS<sup>-</sup> and ArO<sup>-</sup> ions are rapid.

Three interconnected questions arise: (a) What is the reason for the low nucleophilicity? (b) Is the relative reactivity substrate-dependent? (c) Does a "hidden" reversal of the nucleophilic attack contribute to the low nucleophilicity?

The orbital attacked in nucleophilic substitution is the LUMO  $\pi^*$  orbital which is higher in energy than the  $\sigma^*$  orbital attacked in reaction at an sp<sup>3</sup> hybridized carbon. The HOMO orbital of the attacking Cl<sup>-</sup> is lower than both and consequently the interaction between the reacting orbitals, and hence the reactivity, will be lower in the vinylic case. This means that the relative nucleophilicity will increase the lower is the  $\pi^*$  orbital, as a result of electron-withdrawal by the  $\beta$ -substituents. Hence, it is expected that both the overall reactivity and the relative reactivity compared with, e.g., ArO<sup>-</sup> will increase with the increased electrophilicity of the halo olefin.

Comparative data of the nucleophilicity of Cl<sup>-</sup> vs other nucleophiles toward 7 are unavailable, but indirect comparison leads to a surprising result. For the substitution of 7 by morpholine and piperidine in acetonitrile at 30 °C  $k = 7.1 \times 10^{-4}$  and  $1.19 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ , respectively.<sup>16</sup> The

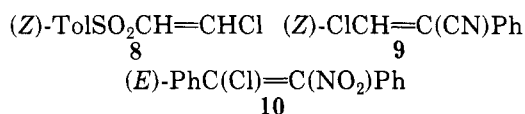


corresponding value for Cl<sup>-</sup> exchange for (*Z*)-5 at 23 °C (calculated from the observed first-order constant on the assumption that the reaction is overall second order) is  $0.19 \text{ M}^{-1} \text{ s}^{-1}$ . If a factor of 8 favoring the reaction of a cyano

ester over the diester is applied<sup>17</sup> and the difference in the temperatures is taken to reduce this ratio to 6 at 23 °C, then  $k_{\text{ex}}(\text{Cl}^-)/k(\text{piperidine}) = 2.7$ , i.e., Cl<sup>-</sup> is a better nucleophile than piperidine, morpholine, N<sub>3</sub><sup>-</sup>, RO<sup>-</sup>,<sup>12</sup> and of the order of reactivity of ArO<sup>-</sup> ions.

The generalization that "The halide ions Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> should be added at the bottom of any nucleophilicity scale"<sup>12</sup> which was based on the data available before our exchange experiments is therefore invalidated.

Inspection of the literature data suggests that this is part of a trend when the more activated (softer) is the electrophilic olefin due to electron withdrawal by the  $\beta$ -substituent, the higher is the soft nucleophile/hard nucleophile relative nucleophilicity. This is shown by the change in the  $k_{p\text{-TolS}^-}/k_{\text{piperidine}}$  ratios from 1.1 for 8, via 191 for 9 to 13625 for 10.<sup>12</sup> The soft Cl<sup>-</sup> resembles the soft ArS<sup>-</sup> in this respect, and although it is presumably much less reactive than ArS<sup>-</sup> toward 5, it still has an appreciable nucleophilicity.



Comparison of the nucleophilicities of various nucleophiles in vinylic substitution is based on the rate constants for the substitution, assuming that the nucleophilic attack is rate determining. Consequently, any "hidden return", i.e., reversal of the nucleophilic attack before any chemical change (substitution, isomerization) takes place, is not taken into account. It should be at least recognized that this return step may be of importance in determining nucleophilicity scales. The initially formed carbanion (or zwitterion in reactions with amines) is at the proper conformation for intramolecular expulsion of the entering nucleophile ( $k_{-1}$ ) and its expulsion may be faster than the bimolecular addition of proton (if nucleophilic addition is used for building the nucleophilicity scale) or from the rotation required in the intermediate for substitution.

Indeed, the low activation energies obtained in substitution of systems carrying poor nucleofuges by amines were ascribed to a faster reversal of the nucleophilic attack than are further reactions of the intermediate zwitterion.<sup>18</sup> In expulsion of nucleofuges X<sup>-</sup> from  $\bar{\text{C}}\text{-C-X}$  systems,<sup>19</sup> chloride is a better nucleofuge than R<sub>3</sub>N<sup>+</sup>,<sup>20</sup> and this process should therefore be considered.

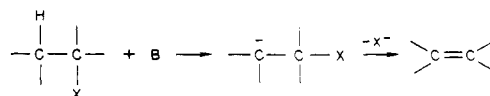
In vinylic substitution increase in the electrophilicity of the system decreases the negative hyperconjugative stabilization of the C-X and C-Nu with the 2p(C<sup>-</sup>) orbitals and hence reduces the elimination rate of X<sup>-</sup>. On the other hand, it reduces the rotational barrier when the HCA of C-Cl is higher than that of the C-Nu bond. Consequently, it is difficult to predict whether rotation will be so fast compared to C-Nu bond cleavage as to make the reverse reaction unimportant. However, recent data collected by

(17) Judged by the ratio of 8 for the base catalyzed hydrolysis of *p*-MeOC<sub>6</sub>H<sub>4</sub>C=C(CN)Y, Y = CN vs Y = CO<sub>2</sub>Et in 95% EtOH (Patai, S.; Rappoport, Z. *J. Chem. Soc.* 1962, 392).

(18) E.g., Rappoport, Z.; Greenzeld, P.; Horowitz, A. *J. Chem. Soc.* 1964, 1334. Grunbaum, Z.; Patai, S.; Rappoport, Z. *J. Chem. Soc. B* 1966, 1133.

(19) Stirling, C. J. M. *Acc. Chem. Res.* 1979, 12, 198.

(20) The model reaction for determining nucleofugality,<sup>19</sup> i.e.,



proceeds via the carbanion for X = N<sup>+</sup>R<sub>3</sub> and for weaker nucleofuges but is converted to an E2 reaction with stronger nucleofuges, e.g. X = Cl.

(12) Rappoport, Z. In *Nucleophilicity*, Adv. Chem. Ser. 1987, 215, 399.

(13) Marchese, G.; Modena, G.; Naso, F. *Tetrahedron* 1968, 24, 663.

(14) Beltrame, P.; Pitea, D.; Simonetta, M. *J. Chem. Soc.* 1967, 1108.

(15) Jones, D. E.; Morris, R. O.; Vernon, C. A.; White, R. F. M. *J. Chem. Soc.* 1960, 2349.

(16) Rappoport, Z.; Topol, A. *J. Chem. Soc., Perkin Trans. 2* 1975, 863.

Bernasconi's group for expulsion of leaving groups from carbanions similar to ours<sup>21</sup> suggest that the  $k_{-1}$  values will be appreciable but much lower than the expulsion rate of  $\text{Cl}^-$ .

Chloride as a nucleophile holds a special position in this respect. For example, if isomerization is used as the process defining the nucleophilicity, the choice of exchange rather than of isomerization as the probe process for  $\text{Cl}^-$  "increases" the nucleophilicity by 2 orders of magnitude. Moreover, the HCA of the entering and leaving groups are identical and  $\text{Cl}^-$  is the best nucleofuge of those investigated so far, and the more stable conformer on the surface (XII) is less prone to expulsion of the  $\text{Cl}^-$  than the initially formed one (VIII). Consequently, hidden expulsion of the entering chloride is a priori more important than expulsion of any other entering nucleophile. We believe that such return is indeed an important part of the overall reaction and that it reduces appreciably the relative "measured" nucleophilicity of  $\text{Cl}^-$  compared with those of other nucleophiles. The effect becomes smaller the more electrophilic is the halo-olefin, and hence in our system the "apparent" nucleophilicity of the  $\text{Cl}^-$  is higher than in the less activated systems. However, evidence for corroborating this speculation or a method for measuring the magnitude of the effect is not available. The normal activation energies do not indicate such behavior.

**Configuration Dependence of the  $k_{\text{ex}}$  and  $k_{\text{isom}}$  Values.** Both the exchange and the isomerization processes are faster for (*Z*)-5 than for (*E*)-5 by ca. 5- and 2-fold, respectively, at 23 °C. Consequently, the  $k_{\text{ex}}/k_{\text{isom}}$  values are also higher for (*Z*)-5. Since the exchange process is degenerate in terms of the products, these differences should reflect different steric interactions in the transition states for the exchange. In carbanion VIII, formed from (*Z*)-5, the only eclipsing interaction in the 60° rotation required for the exchange is Ar/CN, whereas in carbanion IX formed by attack on (*E*)-5 (from "below") it is an Ar/ $\text{CO}_2\text{Me}$  interaction.<sup>22</sup> Since the Ar/CN interaction is sterically less demanding than the Ar/ $\text{CO}_2\text{Me}$  interaction, (*Z*)-5 is more reactive in the exchange.

In the 120° counterclockwise rotation required for the isomerization, both Cl/ $\text{CO}_2\text{Me}$  and Cl/CN interactions are encountered in different order in carbanions VIII and IX. Since the highest of them will determine the steric contribution to the rotational barrier, the barriers for both rotations will be identical. However, here the stabilities of the products are different. The equilibrium (*E*)-5/(*Z*)-5 ratio is 2.1,<sup>8</sup> almost identical with the (*Z*)-5/(*E*)-5 rate ratio, suggesting that the thermodynamic driving force is reflected also in the kinetics, i.e., that the steric effects favoring the products are also reflected in the transition states for the elimination.

The isomerization rates of (*E*)-3 and (*Z*)-3 are almost the same, as expected from the above considerations, since anisyl and phenyl display the same steric bulk in the rotational transition state. However, the exchange rates differ [ $k(\text{Z})\text{-3}/k(\text{E})\text{-3} = 0.65$  at 186 °C].<sup>7</sup> In view of the discussion above it is not clear if this difference is meaningful.

**The Possibility To Distinguish between the Directions of Intramolecular Rotation in the Carbanion.** Here and earlier<sup>2,3</sup> we presented the inversion (or isomerization) route as proceeding via 120° counterclockwise rotation in the carbanionic intermediate (V). We men-

tioned above the alternative pathway for inversion (or isomerization when Nu = Cl) via 180° clockwise rotation in V (Scheme II, V → (VI') → VII). This route could be regarded as a leakage from the retention route if the VI' → VII step precedes nucleofuge expulsion.

It is impossible to distinguish between these two inherently different routes when Nu = Cl, but they are distinguishable in principle when Nu =  $\text{Cl}^*$  as shown in Scheme II: an isomerized labeled product [(*Z*)-4\*] is obtained in the former and an isomerized nonlabeled product [(*Z*)-4] is obtained in the latter route.

Unfortunately, when we tried to use this approach we found that it is experimentally unfeasible in our system. Due to the reversibility of the reaction, meaningful results could be obtained only if the inverted isomer is isolated at very early stages of the exchange. However, due to the higher preference for exchange with retention, the amount of inverted product before reversibility plays a role is too small (<0.01%) to enable isolation. In spite of our failure, we believe that this approach is sufficiently important to deserve mentioning. A system where  $k_{\text{ex}}/k_{\text{isom}} \approx 1$  is apparently required to make the use of this mechanistic tool feasible, and we are searching now for such a system.

### Experimental Section

The synthesis and separation of (*E*)-5 and (*Z*)-5 have been described.<sup>2b</sup>  $\text{Et}_4\text{NCl}$  (<sup>36</sup>Cl) was prepared according to Hayami et al.<sup>23</sup> The (*E*)-5/(*Z*)-5 equilibrium ratio obtained by HPLC is (70±2):(30±2) at both 23 and 45 °C, quite similar to that (68:32) obtained by NMR.<sup>3</sup> The latter ratio was used to obtain the rate constant for isomerization reported in Table I. Acetonitrile was spectroscopic grade; hexane (technical quality) and THF (from  $\text{CaH}_2$ ) were distilled before use.

The exchange/isomerization experiments were conducted in a 100-mL two-neck round-bottomed flask thermostated at 0, 23, and 45 °C, respectively. The reaction mixtures were magnetically stirred. The reactions were started by mixing equal volumes of prethermostated stock solutions of double concentrations of the respective reactants. The resulting concentrations in the reaction mixture were  $2.0 \times 10^{-3}$  M of substrate and  $3.0 \times 10^{-2}$  M of  $\text{Et}_4\text{N}^{36}\text{Cl}$ .

The reactions were followed by removing 0.50-mL samples with a syringe at appropriate time intervals. The samples were added to 10.0 mL of hexane in 50-mL separation funnels. The mixtures were subsequently washed twice with water; 4.0 mL of the hexane solutions was used for the radioactivity incorporation measurements; 20 μL was injected on the HPLC column. The total amount of radioactivity added was determined by measuring unwashed samples.

The <sup>36</sup>Cl incorporation was followed on a Packard 4640 liquid scintillation counter using 10.0 mL (LKB Optiphase MP) scintillator cocktail per 4.0-mL sample. Quenching corrections were obtained with the external standard method. The isomerization was followed on a HPLC system consisting of a (Kipp 9208) pump, a (Kipp 9202) UV detector (254 nm), and a (Chrompack) Si 60.5 4.6 mm × 25 cm column. The eluent used was 5% THF in hexane. The response of the system was calibrated using standard solutions of the starting materials.

**Kinetics.** The experimental conditions have been chosen so that  $[\text{Et}_4\text{NCl}] \gg [5]$  and pseudo-first-order kinetics apply. The rate constants for isomerization ( $k_{\text{isom}}$ ) and exchange ( $k_{\text{ex}}$ ) were obtained from the data obtained as described above by using the following equations after least-squares treatment:

$$tk_{\text{isom}} = \ln \frac{\%E_o - \%E_\infty}{\%E_t - \%E_\infty} \quad \text{and} \quad tk_{\text{isom}} = \ln \frac{\%Z_o - \%Z_\infty}{\%Z_t - \%Z_\infty} \quad (\text{ref 24a})$$

$$\text{and} \quad tk_{\text{ex}} = \ln \frac{n_\infty}{n_\infty - n_t} \quad (\text{ref 24b})$$

(21) Bernasconi, C. F. *Tetrahedron*, in press.

(22) It is interesting that for the substitution by  $\text{Cl}^-$  the eclipsing is almost maximal at the "stable" conformation XII on the potential energy surface.

(23) Hayami, J.; Tanaka, N.; Kurabayashi, S.; Kotani, Y.; Kaji, A. *Bull. Chem. Soc. Jpn.* 1971, 44, 3091.

where  $%E_0$ ,  $%E_t$ , and  $%E_\infty$  represent  $[5E]/([5E] + [5Z])$  at times  $t = 0$ ,  $t = t$ , and  $t = \infty$ ; and  $%Z_0$ ,  $%Z_t$ , and  $%Z_\infty$  represent  $[5Z]/([5E] + [5Z])$  at times  $t = 0$ ,  $t = t$ , and  $t = \infty$ ;  $n_t$  = radioactivity incorporated in **5** at time  $t = t$ ; and  $n_\infty$  = radioactivity

in **5** at time  $t = \infty$ .

**Acknowledgment.** We are indebted to Prof. C. F. Bernasconi for sending us ref 21 and to Prof. Y. Apeloig and Dr. M. Karni for discussions and calculations. This paper was supported by a grant from the United States-Israel Binational Science Foundation (BSF), Jerusalem, Israel, to whom we are grateful.

(24) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; (a) p 304, (b) p 311.

## Methyltriarylphosphonium Arenesulfonates. Preparation and Characterization by $^1\text{H}$ , $^{31}\text{P}$ , and $^{17}\text{O}$ FTNMR, Cyclic Voltammetry, and Molecular Orbital Calculations

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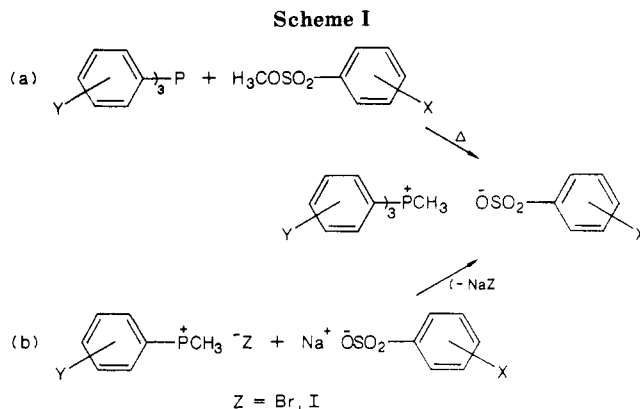
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Received September 12, 1988

Two series of methyltriarylphosphonium arenesulfonates (**1a-i**, **2a-g**) were prepared in which either the anion or the cation is systematically varied. The frontier molecular orbitals of these salts were evaluated by a combination of spectroscopic, electrochemical, and theoretical techniques. For the cation variations, irreversible reductions are observed by cyclic voltammetry, which correlate well with substituent electronegativities.  $^1\text{H}$  NMR (for the *P*-methyl group) and  $^{31}\text{P}$  NMR (for the phosphorus itself) data also correlate well with substituent constants. For the anion variations, irreversible oxidations are observed which correlate better with  $\sigma^\circ$  than with  $\sigma$ , implying that the aromatic  $\pi$ -system is involved in the oxidation.  $^{17}\text{O}$  NMR chemical shifts for the sulfonate group, on the other hand, yield a better correlation with  $\sigma^\circ$ , as would be expected for a purely inductive effect. Semiempirical molecular orbital calculations at the AM1 level were also performed on both series of ions. The calculations are consistent with the expectation that, for a given phosphonium sulfonate salt, the LUMO is on the cation and the HOMO is on the anion. Both HOMO and LUMO energies exhibit very good linear correlations with substituent constants. While the LUMO energies also correlate well with the cathodic peak potentials, the HOMO energies give a substantially poorer correlation with the anodic peak potentials. However, by using the energies calculated for the highest occupied  $\pi$ -orbitals (HOPO's) for the anions, a much improved correlation is observed. This is also consistent with the removal of an electron from the aromatic  $\pi$ -system rather than the charge-bearing sulfonate group.

### Introduction

The phenomenon of triboelectrification plays a critical role in the electrostatic charging of dry electrophotographic developers of the type commonly used in office copying machines.<sup>1-3</sup> A two-component developer consists of toner and carrier. The toner is comprised of a thermoplastic binder, a colorant, and a charge-control agent (charge-agent).<sup>3</sup> The toner becomes triboelectrically charged (tribocharged) through frictional contact with the carrier. The charged toner particles are then used to develop the electrostatic latent image on the photoconductor. The carrier consists of polymer-coated magnetic particles, which attain an electrostatic charge opposite that of the toner. Carrier is retained in the machine by virtue of its magnetism. The charge-agent is used to control the magnitude and polarity of the electrostatic charge on the toner.<sup>3</sup> Quaternary ammonium and phosphonium salts are commonly used for positively charging toners.<sup>4</sup> These salts can be envisioned to function as electron donors (via the highest occupied molecular orbital (HOMO) of the anion)



and/or electron acceptors (via the lowest unoccupied molecular orbital (LUMO) of the cation).<sup>1,5</sup> To test this model we have subtly and systematically perturbed the HOMO and LUMO energies by preparing a series of methyltriarylphosphonium arenesulfonates (**1a-i**, **2a-g**) in which the electronegativities of the substituents on either the cation or the anion are varied over a wide range. By keeping either the anion or cation constant and varying the respective counterion, we can independently adjust either the HOMO or LUMO energies of the salts.

In this paper we describe the preparation and characterization of the phosphonium sulfonates listed in Table

(1) Portions of this work have been previously communicated: (a) Anderson, J. H.; Bugner, D. E. 17th Northeast Regional Meeting of the American Chemical Society; Rochester, NY, November 8-11, 1987. (b) Anderson, J. H.; Bugner, D. E. 4th International Congress on Non-Impact Printing Technologies; New Orleans, LA, March 20-25, 1988.

(2) Jewett, W. S. IAS '77 Annual, 557 (1977).

(3) Schaffert, R. M. In *Electrophotography*; John Wiley and Sons: New York, 1975; p 71.

(4) (a) Jadwin, T. A.; Mutz, A. N.; Rubin, B. J. USP no. 3,893,935, July 8, 1975. (b) Wilson, J. C.; DeMejo, L. P.; Jadwin, T. A.; Merrill, S. H. USP no. 4,496,643, January 29, 1985.

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