output was measured by digital electronic actinometry,[9] and all runs were calibrated with ferrioxalate actinometry.[9] The photolysis solutions were purged with purified nitrogen for 1 h before and during irradiation. Workup consisted of concentration of the photolysate, addition of bibenzyl as an internal NMR integration standard, and analysis in $CDCl_3$ solution by 270-MHz proton NMR to determine the relative quantities of the photoproducts. The results are summarized in Table IV.

Single-Crystal X-ray Structure Determinations. General Procedure.[6] Crystals suitable for analysis were prepared by slow crystallization from appropriate solvents. Preliminary examinations and collection of data were carried out on a Syntex-Nicolet P_1 diffractometer, equipped with a graphite monochromated Mo Kα radiation source. The structures were solved by direct methods using the MULTAN80[6] package, employing full-matrix least-squares refinement, and hydrogen atoms were located from difference Fourier syntheses. The final cycles of the least-squares refinement assumed the non-hydrogen atoms to vibrate anisotropically and the hydrogen atoms to vibrate isotropically. Final electron density difference maps showed no significant features. All calculations were performed with a Digital Equipment VAX 11/750.

Single-Crystal X-ray Structure of (*E*)-2,5-Di(*p*-anisyl)-2,5-dimethylhexene (5a).[22] Crystals of (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene were prepared by slow crystallization from pentane. Unit cell parameters were obtained by least-squares refinement of 25 reflections ($26.6° > 2\theta > 4.31°$). Data were collected in the range $7 > h > -7$, $10 > k > 0$, $21 > l > 0$, with 4 reflections monitored every 50 with no significant intensity variation, 1372 unique data, 1172 with $F > 3\sigma(F)$. Lorentz and polarization corrections were applied and the structure was solved under $P2_1/c$ symmetry. Refinement of 165 parameters converged to $R_1(F) = 0.049$ and $R_w(F) = 0.063$. The results and structural parameters are available as supplementary material.

Single-Crystal X-ray Structure of *trans*-1-(*p*-Anisyl)-2,2-dimethyl-3-(*p*-methoxycumenyl)cyclopropane (8).[22] Crystals of *trans*-1-(*p*-anisyl)-2,2-dimethyl-3-(*p*-methoxycumenyl)cyclopropane were prepared by slow crystallization from pentane. Unit cell parameters were obtained by least-squares refinement of 25 reflections ($35.7° > 2\theta > 18.2°$). Data were collected in the range $14 > h > 0$, $14 > k > 0$, $23 > l > 0$, with 4 reflections monitored every 50 with no significant intensity variation, 2198 unique data, 1144 with $F > 3\sigma(F)$. Lorentz and polarization corrections were applied and the structure was solved under $PNA2_1$ symmetry. Refinement of 329 parameters converged to $R_1(F) = 0.043$ and $R_w(F) = 0.050$. The results and structural parameters are available as supplementary material.

Single-Crystal X-ray Structure of 4-(*p*-Anisyl)-3-(*p*-methoxybenzyl)-4-methylpentanone (23).[22] Crystals of 4-(*p*-anisyl)-3-(*p*-methoxybenzyl)-4-methylpentanone were prepared by slow crystallization from ethanol. Unit cell parameters were obtained by least-squares refinement of 25 reflections ($15.9° > 2\theta > 3.5°$). Data were collected in the range $5 > h > 0$, $15 > k > 0$, $26 > l > 0$, with 4 reflections monitored every 50 with no significant intensity variation, 1250 unique data, 768 with $F > 3\sigma(F)$. Lorentz and polarization corrections were applied and the structure was solved under PBCA symmetry. Refinement of 217 parameters converged to $R_1(F) = 0.051$ and $R_w(F) = 0.033$. The results and structural parameters are available as Supplementary Material.

Acknowledgment. Support of this research by the National Science Foundation and by NIH Grant GM07487 is gratefully acknowledged. NSF supported the mechanistic aspects while NIH support was used for the synthetic aspects.

Supplementary Material Available: Crystal data and collection parameters, positional parameters, interatomic distances, bond angles, anisotropic and isotropic temperature factors, and ORTEP drawings of **5a**, **8**, and **23** (19 pages). Ordering information is given on any current masthead page.

Stereochemistry of Substitution of Good Nucleofuges at the Stereoconvergence Region as a Tool for Investigating the Rapid Step of Nucleophilic Vinylic Substitution[1]

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Abstract: Methyl α-cyano-β-X-*p*-nitrocinnamates (**5**; X = Cl, Br, OMs, OTs, OTf) were prepared. The five (*E*) isomers and the (*Z*) isomers (X = Cl, Br, OMs) were separated and their structures assigned. Substitution of the eight substrates by p-$MeC_6H_4S^-M^+$ and p-$MeC_6H_4O^-M^+$ (M = Li, Na, K), of the (*E*) isomers by p-$O_2NC_6H_4S^-Na^+$, and of (*E*)-**5**-Cl by p-$O_2NC_6H_4O^-Na^+$ in CD_3CN always gave a mixture of the (*E*) and (*Z*) substitution products. The kinetically controlled (*E*)/(*Z*) product ratios and the equilibrium ratios derived by nucleophilic isomerization of the initially formed ratios were determined. The (*Z*) isomers gave higher extents of retention than the (*E*) isomers, and in no case was a complete stereoconvergence obtained. A relatively small dependence of the extent of the stereoconvergence on a change in the nucleofuge, the counterion, and the nucleophile characterizes the reaction. It was suggested that the reaction proceeds via the rate-determining formation of an intermediate carbanion, which then expels the nucleofuge. The order of nucleofugalities of our leaving groups and the effect of the nucleofuge on the rotational barriers were analyzed and compared with the experimental results. It is concluded that the stereochemistry of the substitution is determined in the rapid step by a rate-determining competitive intramolecular 60 and 120° rotation in the carbanion, leading to the retained and the inverted product, respectively. This is followed by a fast expulsion of the nucleofuge from the appropriate carbanionic conformers. Both hyperconjugative and steric factors affect the intramolecular rotation rates. The change in the nucleofuge does not give information on the position of the transition state along the reaction coordinate in the C-X bond cleavage step.

The stereochemistry of bimolecular nucleophilic vinylic substitution (eq 1; Nu = nucleophile, X = nucleofuge, Y, Y′ = activating groups) is one of the strongest tools for investigating the mechanism of the reaction.[2] The stereochemistry depends

$$Nu^- + \underset{\alpha}{RC(X)}=\underset{\beta}{CYY'} \rightarrow RC(Nu)=CYY' + X^- \quad (1)$$

mainly on the nature of the nucleofuge and the activating groups Y, Y′ and in special cases also on the nucleophile. With poor

(1) Nucleophilic Attacks on Carbon–Carbon Double Bonds. 36. Part 35: Rappoport, Z.; Gazit, A. *J. Am. Chem. Soc.* **1987**, *109*, 6698.

(2) (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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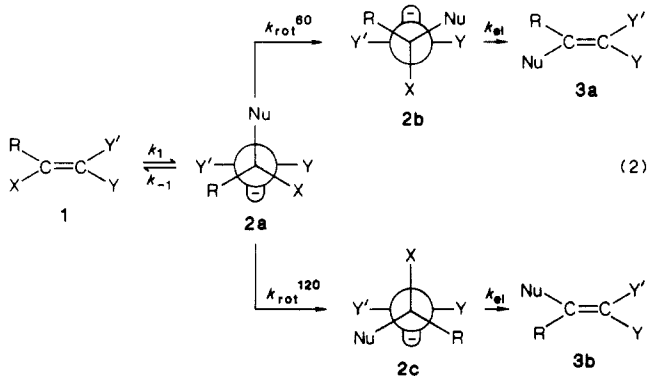
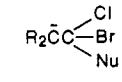
nucleofuges, such as OR and mainly F, (*E*)- or (*Z*)-vinyl precursors give mostly stereoconvergence[3] (i.e., "complete" stereoconvergence when the same (*E*)/(*Z*) product mixture (or single product) is formed from either precursor, "partial" stereoconvergence when each isomeric precursor gives nonidentical mixtures of (*E*) and (*Z*) substitution products), although retention was also observed.[4] With good nucleofuges such as Cl and Br, complete retention is observed for both (*E*) and (*Z*) precursors if Y, Y′ are moderately negative charge delocalizing substituents. However, for X = Cl, Br, and I when Y, Y′ are strongly negative charge delocalizers, e.g., NO_2, Ph;[5a] CO_2R, CN;[5b] Ph, CHO;[5c] CO_2R, CHO;[5d] and CO_2R, CO_2R',[1,5d] partial (and sometimes) complete stereoconvergence is observed. In the special case of amine nucleophiles, stereoconvergence is obtained even when Y, Y′ are not strongly activating, due to post isomerization of the product enamine, unless geometrical constraints exist in the system,[6] whereas the vinyl cation character of a thiirenium ion results in inversion of configuration in its ring-opening.[7]

The stereochemistry is consistent with the previously discussed mechanism of nucleophilic vinylic substitution.[2] The nucleophilic attack generates a carbanionic species **2a** that can undergo several processes, of which rotation around C_α–C_β and nucleofuge expulsion are relevant to the stereochemistry. As shown in eq 2,



a 60° rotation followed by nucleofuge expulsion from **2b** leads to retention, whereas rotation that leads to **2c** (e.g., k_{rot}^{120}) (and **2b**) followed by nucleofuge expulsion (k_{el}) leads to stereoconvergence. With poor nucleofuges, $k_{el} < k_{rot}$ leads to stereoconvergence. With good nucleofuges, k_{el} is high and $k_{rot}^{60} > k_{rot}^{120}$ due to negative hyperconjugation.[8] When the negative charge delocalization ability of Y, Y′ is not very high, both k_{rot}^{60} and k_{el} are enhanced, formation of **2c** from **1** is negligible, and retention is observed. When the negative charge is efficiently delocalized on Y, Y′, both k_{el} and the preference for k_{rot}^{60} over k_{rot}^{120} decrease, establishing the conditions $k_{rot} \sim k_{el}$, which leads to partial stereoconvergence, or $k_{rot} > k_{el}$, which leads to complete stereoconvergence.

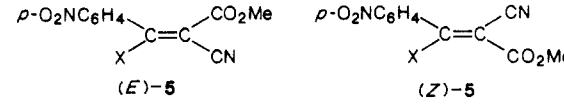
The rate-determining step for the overall substitution is the nucleophilic attack (rate constant k_1). Consequently, information concerning the k_{el} step is scarce. Information on expulsion of poor and moderate nucleofuges from carbanions (C̄—C(X) → C=C) generated in E1cB reactions or by addition of amines to electrophilic olefins has accumulated in recent years,[9] but similar data on expulsion of good nucleofuges are rare. We recently suggested that the intramolecular element effect,[10] which measures the relative expulsion rates of Br^- and Cl^- from the carbanion **4** ($k_{el}(Br)/k_{el}(Cl)$), can serve as a probe for the transition state of the elimination process. The values of 2–3 obtained in the substitution of systems where R = p-$O_2NC_6H_4$ or RR = fluorenyl suggested that the transition state for expulsion of good nucleofuges is early.[10]



4

In the present work we wanted to apply a change in the nucleofuge as a different probe to the nature of the elimination step. Choosing a system that gives stereoconvergence with the Cl nucleofuge ensures that the reaction proceeds via the multistep process depicted in eq 2. A change to a poorer nucleofuge should increase the extent of stereoconvergence as discussed above. But what would be the effect of using a better nucleofuge? The k_{el} value should increase and the extent of stereoconvergence should decrease if this is the only important factor involved in the elimination. However, k_{rot} may be as important. Data on expulsion of good nucleofuges from similarly activated systems (i.e., the same Y, Y′) are nonexistent, and in the present system we present the first such stereochemical study.

The system chosen was the (*E*)- and (*Z*)-methyl α-cyano-β-X-p-nitrocinnamates ((*E*)-**5**, (*Z*)-**5**). The system is suitable since it is known to be sufficiently activated to give partial stereoconvergence when X = Cl.[5b] On the other hand, it is not extremely



X = Cl, Br, OMs, OTs, OTf

activated so that the use of a supernucleofuge X may lead to complete retention. The compounds have an ester methyl group that is important as a stereochemical NMR probe, a very important feature in studying tetrasubstituted ethylenes. As nucleofuges we used chloride and bromide, the classical good nucleofuges of vinylic substitution,[2] mesylate and tosylate, better nucleofuges in aliphatic substitution,[11a] which are similar to or more activating than chloride in the k_1 step of eq 2,[11b] and triflate, a supernucleofuge used extensively in vinylic S_N1 reactions[12] but never investigated mechanistically in bimolecular vinylic substitution.

Results

Synthesis of Precursors and Geometrical Assignment. (a) Methyl (*E*)- and (*Z*)-β-Chloro- and -β-Bromo-α-cyano-*p*-nitrocinnamates ((*E*)- and (*Z*)-5-Cl, (*E*)- and (*Z*)-5-Br). The chloro derivatives (*E*)-**5**-Cl and (*Z*)-**5**-Cl were previously prepared[5b] from the reaction of the enol **7** (obtained from the triethylammonium enolate **6a** by acidification) and phosphorus oxychloride in the

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(4) (a) Zakharkin, L. I.; Lebedev, V. N. *Zh. Obshch. Khim.* **1972**, *42*, 558. (b) Burton, D. J.; Krutzsch, H. C. *J. Org. Chem.* **1971**, *36*, 2351. (c) Normant, J.; Sauvetre, R.; Villiers, J. *Tetrahedron* **1975**, *31*, 891.

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(6) For a collection of examples and discussions, see: Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1000.

(7) Cappozi, G.; Lucchini, V.; Modena, G.; Scrimin, P. *Tetrahedron Lett.* **1977**, 911.

(8) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095.

(9) (a) Albeck, M.; Hoz, S.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1248. Hoz, S.; Albeck, M.; Rappoport, Z. *Tetrahdron Lett.* **1972**, 3511. Albeck, M.; Hoz, S.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1975**, 628. (b) Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1130; (c) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *Ibid.* **1977**, 1898; (d) *Ibid.* **1977**, 1914. (e) Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *12*, 198. (f) Bernasconi, C. F.; Carrĕ, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2698. Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *Ibid.* **1980**, *102*, 2810. (g) Bernasconi, C. F.; Murray, C. J.; Fox, J. P.; Carrĕ, D. J. *Ibid.* **1983**, *105*, 4349. (h) Bernasconi, C. F.; Leonarduzzi, G. D. *Ibid.* **1982**, *104*, 5133. (i) Bernasconi, C. F.; Kanavarioti, A. *Ibid.* **1986**, *108*, 7744. (j) Grout, A.; McLennan, D. J.; Spackman, I. H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1758.

(10) Avramovitch, B.; Weyerstahl, P.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 6687.

(11) (a) For k_{OTs}/k_{Br} ratios in aliphatic systems, see: Hoffmann, H. M. R. *J. Chem. Soc.* **1965**, 6753, 6762. Cockerill, A. F. *Tetrahedron Lett.* **1969**, 4913. (b) Rappoport, Z.; Topol, A. *J. Chem. Soc., Perkin Trans. 2* (a) **1972**, 1823; (b) *Ibid.* **1975**, 863.

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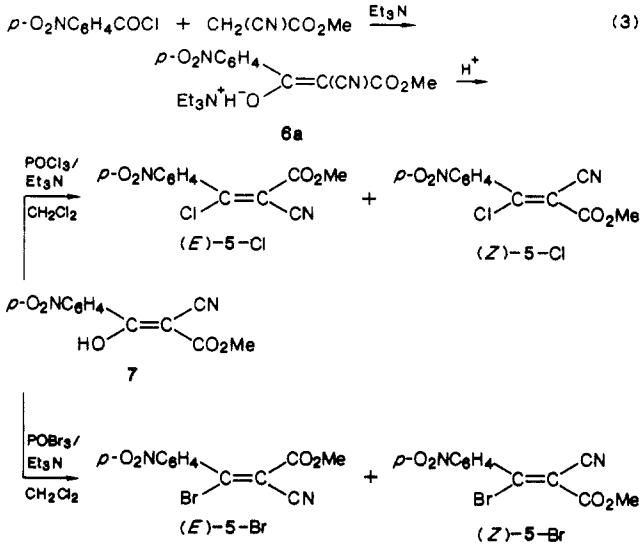
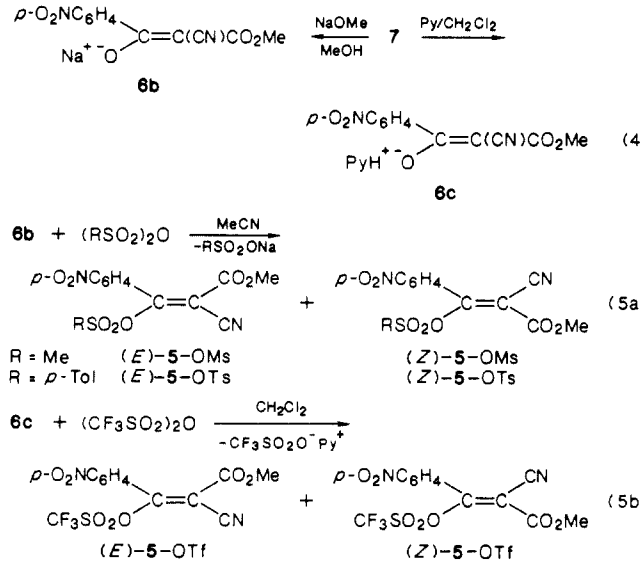
presence of Et_3N. A mixture of the bromides (*E*)-**5**-Br and (*Z*)-**5**-Br was prepared analogously in a 38:62 ratio (eq 3).



In an attempt to prepare the vinyl bromides directly from **6a** and $POBr_3$ the main product was methyl 4-nitrobenzoate together with 4-nitrobenzoic acid. On the other hand, the enol **7** was recovered unchanged from its reaction with thionyl bromide with or without pyridine.

X-ray diffraction (see below) shows that **7** has a (*Z*) configuration in the solid, and ^1H NMR shows evidence for only one species in solution. Consequently, neither of the reactions of eq 3 seems to be stereospecific.

(b) Methyl (*E*)- and (*Z*)-β-(Mesyloxy)-, β-(Tosyloxy)-, and β-[(Trifluoromesyl)oxy]-α-cyano-*p*-nitrocinnamates ((*E*)- and (*Z*)-5-OMs, (*E*)/(*Z*)-5-OTs, (*E*)-5-OTf and (*Z*)-5-OTf). The three vinyl sulfonates were prepared by converting **7** to its sodium (**6b**) or pyridinium (PyH^+) salt (**6c**), followed by reaction with the corresponding sulfonic anhydride (eq 4 and 5).



Reaction 5a gave a 55:45 mixture of (*E*)-**5**-OMs to (*Z*)-**5**-OMs and a 70:30 mixture of (*E*)-**5**-OTs to (*Z*)-**5**-OTs (as judged by NMR) and reaction 5b gave a 90:10 (*E*)-**5**-OTf to (*Z*)-**5**-OTf mixture. The (*E*)/(*Z*) ratios were dependent on the reaction conditions, especially on the reaction time. The initial (*E*)/(*Z*) sulfonate distribution in the reaction of **7** with the sulfonic anhydride in the presence of pyridine gave in $CDCl_3$ the following ratios: 61:39 (*E*)-**5**-OMs/(*Z*)-**5**-OMs at 65% reaction; 73:27 (*E*)-**5**-OTs/(*Z*)-**5**-OTs at 15% reaction; 63:37 (*E*)-**5**-OTf/(*Z*)-**5**-OTf at 50% reaction. The ratios changed slightly after 1 h.

The vinyl sulfonates underwent a relatively easy hydrolysis during the reaction or on workup. The use of the enolate salt rather than the enol gave a cleaner reaction with the sulfonic anhydrides, and extraction with ether gave the isomer mixture in the organic phase. Nevertheless, a few problems were encountered. When the MeO^- concentration used for the preparation of **6b** from **7** was higher than 1 equiv, **6b** precipitated with MeONa, and its reaction with the anhydride was accompanied by decomposition and a consequent lower yield. Since similar results were obtained when **6b** was not completely freed from MeOH, it was prepared from MeO^- with excess **7**, and the residual **7** was washed with CH_2Cl_2. (*E*)/(*Z*) mixtures of the tosylate and mesylate, but not of the triflate, were successfully prepared in this way.

Table I. Chemical Shift of the Ester Methyl Group of Methyl α-Cyano-β-X-4-nitrocinnamates

X	δ(Me), ppm *E* isomer	δ(Me), ppm *Z* isomer	X	δ(Me), ppm *E* isomer	δ(Me), ppm *Z* isomer
Cl	3.77[a]	3.96	TolO	3.73	3.83
Br	3.77	3.97	TolS	3.68	3.96[a]
TsO	3.76	3.94	*p*-$O_2NC_6H_4O$	3.79	3.88
MsO	3.82[a]	3.94	*p*-$O_2NC_6H_4S$	3.61	3.92
TfO	3.84	4.00	Me	3.68[b,c]	3.91[c,d]

[a] Structure verified by X-ray diffraction. [b] *Z* isomer. [c] Structure identical with that of the other compounds in the column. [d] *E* isomer.

In an attempt to prepare **5**-OTs from **7**, tosyl chloride, and pyridine according to Kabalka's recent method,[13] only the chlorides (*E*)-**5**-Cl and (*Z*)-**5**-Cl were obtained. When Kabalka's ratios were used, but triflic anhydride was used instead of tosyl chloride and washing with aqueous HCl, aqueous $NaHCO_3$, and water was avoided during the workup, a 78:22 mixture of the vinyl triflates (*E*)-**5**-OTf/(*Z*)-**5**-OTf was obtained.

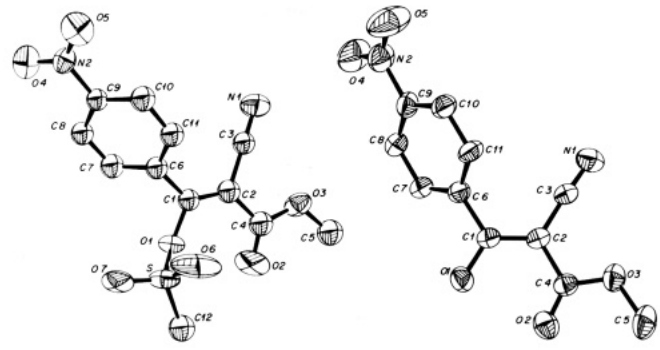
Separation of the (E) and (Z) Isomers. Separation of each (*E*)/(*Z*) mixture was attempted by either fractional crystallization or chromatography or by both methods. In the chromatography, the first fraction was usually the (Z) isomer: 100% (*Z*)-**5**-OMs and 92:8 (*Z*)-**5**-Br/(*E*)-**5**-Br were obtained from the corresponding mixtures. The following fractions were usually enriched with the (*Z*) isomer, mixed with 15–50% of the (*E*) isomer, but we were unable to obtain fractions richer in the (*E*) isomer by more than 70%. Separation of (*E*)- and (*Z*)-**5**-OTf was unsuccessful, and the fractions contained from 1:1 up to 4:6 (*E*)/(*Z*) mixtures together with an appreciable percentage of the enol **7**. Since the chromatography was accompanied by an appreciable material loss, fractional crystallization of the (*E*)/(*Z*) mixtures was preferred whenever possible. In this way, (*E*)-**5**-Cl was obtained from CCl_4 in 98% purity, and (*Z*)-**5**-Cl was obtained by crystallization of the residue from EtOAc. We were unable to obtain 100% pure (*E*)- or (*Z*)-**5**-Br, but by several repeated crystallizations from very dilute solutions in CCl_4 98% (*Z*)-**5**-Br and 97% (*E*)-**5**-Br were obtained. Pure (*Z*)-**5**-OMs could be obtained by fractional crystallization from toluene, whereas 95% (*E*)-**5**-OMs containing 5% (*Z*)-**5**-OMs was obtained from CH_2Cl_2–CCl_4. (*E*)-**5**-OTs was obtained in 95% purity from CCl_4–CH_2Cl_2.

The main difficulty was in the separation of the vinyl triflates, which were obtained as an oily mixture. Attempted crystallization from toluene, CH_2Cl_2, MeCN, CH_2Cl_2–CCl_4, EtOAc–CCl_4, or EtOAc resulted in formation of oil droplets. Chromatography of the oil on a silica column resulted in hydrolysis as shown by the increase in the concentration of the enol **7**. The fraction with the highest purity obtained contained 97% of the triflates with 3% of **7**, with a (*E*)-**5**-OTf/(*Z*)-**5**-OTf ratio of 89:11. Fractions richer in (*Z*)-**5**-OTf could not be obtained.

Geometrical Assignment. The assignment of the (*E*) and the (*Z*) configuration is based mainly on the relative positions of the ester methyl group in the ^1H NMR spectrum in $CDCl_3$. Hayashi had shown that in methyl β-cyano-α-methyl-*p*-nitrocinnamates the signal of the methyl ester at a trans position to the *p*-nitrophenyl ring (his (*E*) isomer) is at a lower field (by 0.21 ppm) than in the (*Z*) isomer where both groups are cis.[14] Table I shows

(13) Kabalka, G. W.; Varma, M.; Varma, R. S.; Srivastava, P. C.; Knapp, F. F., Jr. *J. Org. Chem.* **1986**, *51*, 2386.

Table II. Crystallographic Data for (*E*)-**5**-OMs and **7**



(E)-5-OMs 7

bond	*d*, Å	atoms	angle, deg	atoms	angle, deg
			(*E*)-**5**-OMs[a,b]		
C(1)–C(2)	1.31 (1)	C(6)C(1)O(1)	114.2 (1)	O(3)C(4)C(2)	113 (1)
C(1)–O(1)	1.40 (1)	C(6)C(1)C(2)	128 (1)	C(1)C(6)C(11)	120 (1)
C(1)–C(6)	1.46 (1)	O(1)C(1)C(2)	117.2 (1)	C(1)C(6)C(7)	122 (2)
C(2)–C(3)	1.47 (1)	C(1)C(2)C(4)	128 (1)	C(10)C(9)N(2)	118.2 (1)
C(2)–C(4)	1.49 (1)	C(3)C(2)C(4)	114 (1)	C(8)C(9)N(2)	118.2 (7)
C(4)–O(2)	1.21 (1)	C(1)C(2)C(3)	118 (1)	AB[c,d]	169.39
C(4)–O(3)	1.31 (1)	C(4)O(3)C(5)	117 (1)	CE[c,d]	0.27
C(5)–O(3)	1.44 (1)	O(2)C(4)O(3)	124 (1)	AE[c,d]	44.70
C(3)–N(1)	1.14 (1)	O(2)C(4)C(2)	123 (1)	AF[c,d]	6.62
			7[e,f]		
C(1)–C(2)	1.361 (3)	C(6)C(1)O(1)	114.3 (2)	O(3)C(4)C(2)	112.8 (2)
C(1)–O(1)	1.330 (2)	C(6)C(1)C(2)	123.4 (2)	C(1)C(6)C(11)	118.9 (2)
C(1)–C(6)	1.479 (3)	O(1)C(1)C(2)	122.3 (2)	C(1)C(6)C(7)	121.4 (2)
C(2)–C(3)	1.430 (3)	C(1)C(2)C(4)	120.9 (2)	C(10)C(9)N(2)	118.1 (2)
C(2)–C(4)	1.463 (3)	C(3)C(2)C(4)	117.4 (2)	C(8)C(9)N(2)	119.1 (2)
C(4)–O(2)	1.213 (3)	C(1)C(2)C(3)	121.7 (2)	AB[c,d]	6.77
C(4)–O(3)	1.325 (2)	C(4)O(3)C(5)	115.9 (2)	CE[c,d]	26.75
C(5)–O(3)	1.451 (3)	O(2)C(4)O(3)	124.0 (2)	DE[c,d]	48.98
C(3)–N(1)	1.148 (3)	O(2)C(4)C(2)	123.1 (2)	DF[c,d]	4.56

[a] Aromatic bond lengths 1.378 (3)–1.395 (3) Å. [b] Aromatic bond angles 118.5–120.6° except for C(8)C(9)C(10) = 122.8°. [c] Plane A, O(1)C(1)C(6)C(2); plane B, C(3)C(2)C(4)C(1)N(1)O(2)O(3); plane C, NO_2 group; plane D, O(1)C(1)C(6)C(4)C(2)C(3); plane E, Ar group; plane F, C(2)C(4)O(2)O(3). [d] Dihedral angle. [e] Aromatic bond lengths 1.39 (1)–1.42 (1) Å except C(7)–C(8) 1.36 Å. [f] Aromatic bond angles are 118 (1)–122 (1)° except C(8)C(9)C(10) = 123 (1)°.

that for one isomer in our system δ(Me) = 3.83–4.00 and δ(Me) = 3.61–3.84 for the other isomer. The largest Δδ values are for thio-substituted systems, and the lowest values are for oxygen-substituted systems. Note that due to the priority of all the heteroatoms over carbon according to the sequence rules, our compounds with trans X and COOMe are the (*E*) isomers, in contrast to Hayashi's system.[14] Consequently, we assigned the isomer with the lower field COOMe as (*Z*) and the isomer with the higher field COOMe as (*E*).

Since polar, steric, and resonance effects may affect the relative positions of the signals, the assignment was corroborated by X-ray diffraction of (*Z*)-**5**-OMs. A similar corroboration for (*E*)-**5**-Cl (Δδ = 0.19 ppm) and the (*Z*)-*p*-toluenethiolate (Δδ = 0.28 ppm) is based on previously reported X-ray data.[5b] The generality of this method of assignment is shown by its application to the analogous $p\text{-}O_2NC_6H_4C(X)=C(CHO)CO_2Me$ system, where the magnitude of the Δδ values is similar to that in our case and X-ray data are also available.[5d] The method was recently applied also to the $ArC(Br)=C(CO_2Me)CO_2R$ (R = CD_3, *t*-Bu) system.[1,5d]

According to Table I, the single isomer of the enol **7** with δ($CDCl_3$) 4.01 has the (*Z*) configuration, and this is corroborated by X-ray diffraction. The important features of the X-ray data of (*Z*)-**5**-OMs and **7** are given in Table II. Stereoscopic views are given in Figures S1 and S2 (supplementary material), and additional crystallographic data are given in Tables S1-S8 (supplementary material).

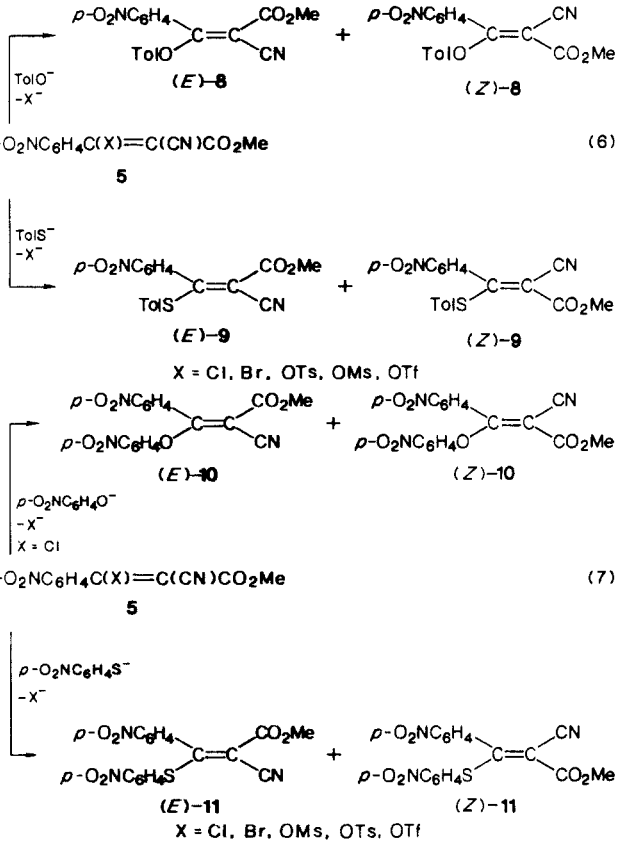
Substitution. The vinylic systems were substituted by the following anionic nucleophiles with several alkali counterions: lithium, sodium and potassium *p*-toluenethiolates ($TolS^-$) and *p*-methylphenoxides ($TolO^-$), lithium and sodium *p*-nitrophenoxides, sodium *p*-nitrothiophenolate. No substitution took place with LiH or with $NaBH_4$. The salts were mostly prepared by reacting lithium, sodium, or potassium hydride with a solution of the phenol or thiophenol in dry ether and sometimes ($TolO^-Li^+$, $p\text{-}O_2NC_6H_4O^-Na^+$) in toluene, filtering the salts, and storing them before use. In several cases traces of the metal hydride coprecipitated with the nucleophilic salt, as shown by formation of some of the reduction product $p\text{-}O_2NC_6H_4CH_2CH(CN)CO_2Me$ in addition to the main substitution product. In other cases NMR showed that traces of the phenol or the thiophenol accompanied the salt. The salts displayed an "aging" phenomenon, since after standing for some time the "effective" concentration of the nucleophile was lower than calculated from its weight, as shown by the lower than expected percentage of substitution product. The reason for this was not investigated.[15] Consequently, the nucleophile added to the solution was not weighted and the percent reaction reflects the amount of active nucleophile.

The substitution products with $TolO^-$ and $TolS^-$ ((*E*)- and (*Z*)-**8**, (*E*)- and (*Z*)-**9**) were previously isolated from the substitution of (*E*)-**5**-Cl and (*Z*)-**5**-Cl and their structures assigned.[5b] In the present work both pairs of products (*E*)- and (*Z*)-**8** and (*E*)- and (*Z*)-**9** were obtained in the substitution of the bromide, mesylate, tosylate, and triflate, and in contrast to a previous report,[5b] (*E*)-**9** was also obtained from the reaction of (*E*)- and (*Z*)-**5**-Cl (eq 6). Similar substitutions gave the *p*-nitro-substitution

(14) Hayashi, T. *J. Org. Chem.* **1966**, *31*, 3253.

(15) Hydrolysis of the salt to the free phenol or thiol or dimerization of the thiolate to a disulfide may be responsible. This was found by us earlier, as well as by others: Hoz, S., personal communication.

products (*E*)-**10** and (*Z*)-**10** from p-$O_2NC_6H_4O^-$ and (*E*)-**11** and (*Z*)-**11** from p-$O_2NC_6H_4S^-$ (eq 7).



By repeated crystallization of the substitution reaction mixtures from CCl_4 both (*E*)-**10** and (*Z*)-**11** were obtained in 100% purity and (*Z*)-**10** in 98% purity, but (*E*)-**11** was obtained in a mixture with 20% of (*Z*)-**11**. The geometrical assignments are based on the data of Table I.

The studies of the product distributions were usually conducted in an NMR tube in the probe of the spectrometer for several reasons. Due to postisomerization of the initially formed products under the reaction conditions, the observed distribution at the end of the reaction differs from the kinetically controlled distribution (see Table III). The direct follow-up avoided evaporation and contact with acidic and basic solutions, which may enhance the postisomerization. The kinetically controlled distributions were obtained by measurements at both early and late reaction percentages, thus giving the approximate kinetically controlled distribution and a measure of its change during the reaction due to the postisomerization.

Two other problems were the stability of the precursors (discussed further below) and the homogeneity of the reaction. Control experiments had shown that (*E*)- and (*Z*)-**5**-OMs hydrolyze appreciably in commercial $(CD_3)_2SO$, which contains small quantities of water. This was not the case with the vinyl bromides and chlorides. The sulfonates were therefore dissolved immediately before the substitution reaction. The mixture was heterogeneous when the nucleophile was added as a solid, but even in those experiments when it was added in solution, the reaction mixture was homogeneous up to 25% and then it became turbid due to precipitation of the salt of the nucleofuge. In these cases the solutions were filtered at this stage before further analysis, but the appearance of turbidity had no effect on the product distribution.

At our concentrations all the reactions were rapid and were nearly complete by the time that the spectra were taken. A competition experiment of p-$MeC_6H_4S^-$ with equimolar concentrations of (*E*)-**5**-OMs and (*E*)-**5**-OTf showed that the triflate reacted ca. 10 times faster.

Analysis of the Products Distribution. (a) By NMR. The (*E*)/(*Z*) product ratios and the percentages of the reactions were obtained from integration of the COOMe signals of the precursors and the products. In several cases, e.g., (*E*)-**5**-Br and (*E*)-**8**, overlap of the precursor and product signals introduced an error that was more severe when one of the signals predominated, i.e., at early and late reaction percentages. In these cases corrections based on signal heights or on integration of the aromatic protons of the (*E*) and (*Z*) species were introduced. The overlap between the COOMe signals of (*Z*)-**5**-OMs and the product (*Z*)-**9** was overcome by using the integration of the methyl of the mesylate group in (*Z*)-**5**-OMs.

The nucleophile was added portionwise to the solution of the substrate either as a solid or in solution. Parallel experiments showed that the mode of addition did not affect the product distribution, e.g., reaction of (*E*)-**5**-Cl with solid $TolS^-K^+$ or its solution in CD_3CN gave the same 34:66 (*E*)-**9**/(*Z*)-**9** ratio. The solubility of the nucleophile salt in CD_3CN is low, but unfortunately pure DMSO-d_6, a much better solvent for salts, could not be used due to hydrolysis of the mesylates and the appearance of a water signal that sometimes overlapped signals of interest. Instead, lithium or sodium 4-nitrophenoxide was dissolved in the minimum quantity of DMSO-d_6, and the solution was added to the substrate solution in CD_3CN so that the reaction mixture contained only 5% DMSO-d_6 but the solubility of the salt was sufficient to retain the homogeneity. The data are summarized in Table III.

(b) By HPLC. Use of Diol 125-4 or CN-250-4 columns enables separation of both the precursors and the (*E*) and (*Z*) substitution products, and hence a follow-up of the reaction. Unfortunately, direct injection of the reaction mixture to the column is impossible, and evaporation and filtering before the injection are necessary. Consequently, in several cases we analyzed the reaction mixture by NMR and by HPLC in parallel. The product distributions of the same sample were found always to be similar, giving credibility to both analytical methods. However, in two different experiments the results obtained by both methods differed: In the reaction of (*E*)-**5**-OMs with $TolS^-Na^+$ the HPLC gave a higher percentage of the inversion product than that obtained in another experiment analyzed by NMR, whereas in a similar reaction of (*E*)-**5**-OTs the percentage of retention product was higher when using the HPLC analysis. We note that the HPLC analysis required much longer reaction times.

The product distributions obtained by both methods are collected in Table III. They include several values, especially for the mesylates and the tosylates, which deviated from one another by several percent, and in spite of many repetitions and control experiments, we were unable to find out the reason for the discrepancies.

Stabilities and (*E*) ⇌ (*Z*) Equilibria of Reactants and Products. There are two obstacles for obtaining the (*E*)/(*Z*) equilibrium ratios of the reactants **5** in acetonitrile at room temperature: (i) The isomerization of the vinyl halides is so slow that equilibrium is not achieved after reasonable reaction times. (ii) The conversion of the vinyl sulfonates to the enol **7** is faster than the isomerization. The data are in Table IV, and the difficulties are demonstrated by the following experiments and by the footnotes to Table IV.

Starting from a 87:13 or 3:97 (*E*)-**5**-Br/(*Z*)-**5**-Br mixture no change in the composition took place after 7 days in the dark. Reaction at 70 °C for 12 days in the dark changed these initial compositions to 82:18 and 22:78, respectively. The isomerization was Br^--catalyzed, but was still very slow (see footnote *b* to Table IV). An initial 81:9:10 ratio of (*E*)-**5**-OTf/(*Z*)-**5**-OTf/**7** gave a 60:10:30 mixture of these components after reflux for 11 days in CH_3CN.

More data are available on the equilibrium ratios of the substitution products, since longer reaction times in the presence of a slight excess of the nucleophile lead to their (*E*) ⇌ (*Z*) isomerization. Use of a large excess of nucleophile results in a partial loss of the vinylic products, presumably by a Michael-type nucleophilic addition to the double bond.

The equilibrium ratios could be obtained from experiments given in the last column of Table III or from those reported earlier,[5b] supplemented by the following new experiments.

Table III. Distribution of the Substitution Products in the Reaction of p-$O_2NC_6H_4C(X)$=$C(CN)CO_2Me$ with Nucleophiles in CD_3CN[a]

substr[b]	nucleophile	product ratio				
		$(E)/(Z)_0$[c]	$(E)/(Z)$[d]	% reactn	$(E)/(Z)$[e]	% reactn
(E)-5-Cl	$TolS^-Li^+$	45/55 ± 2	44/56	8	32/68	67
	$TolS^-Na^+$	36/64 ± 1	35/65	5	30/70	60
		34/66 ± 4[f]	34/66	6	15/85	100
	$TolS^-K^+$	33/67 ± 2	32/68	6	31/69	54
(E)-5-Br	$TolS^-Li^+$	45/55 ± 2	44/56	10	38/62	46
	$TolS^-Na^+$	37/63 ± 4[g]	33/67	5	31/68	71
			32/68[f]	18[f]		
	$TolS^-K^+$	39/61 ± 4[h]	40/60	7	35/65	54
		34/66[f,i]	28/72	17	14/86	97
(E)-5-OMs	$TolS^-Li^+$	57/43 ± 2[j]	53/47	5	41/59	52
	$TolS^-Na^+$	64/36 ± 4[h]	68/32[k]	11	58/42	77
		63/37 ± 2[l]	59/41	5	19/81	100
	$TolS^-K^+$	68/32 ± 4[i]	63/37	4	32/68	92
(E)-5-OTs	$TolS^-Na^+$	49/51 ± 2[i]	45/55	5	36/64	74
		59/41 ± 3[i]	56/44	4	17/83	100
(E)-5-OTf	$TolS^-Na^+$	45/55 ± 3[i]	42/58	5	38/62	40
	$TolS^-K^+$	41/59 ± 2[i]	39/61	4	34/66	40
(Z)-5-Cl	$TolS^-Li^+$	11/89 ± 2	10/90	7	14/86	41
	$TolS^-Na^+$	11/89 ± 3	9/91	20	15/85	49
			9/91[f]	13		
	$TolS^-K^+$	12/88 ± 3	9/91	14	15/85	85
(Z)-5-Br	$TolS^-Li^+$	12/88 ± 2	15/85	9	12/88	56
	$TolS^-Na^+$	5/95 ± 1[m]	7/93[m]	11	8/92	40
			19/81[f]	4	16/84[f]	100
	$TolS^-K^+$	10/90 ± 2	9/91	12	14/86	100
(Z)-5-OMs	$TolS^-Li^+$	12/88 ± 2	13/87	16	10/90	47
	$TolS^-Na^+$	5/95 ± 2	9/91	7	5/95	59
			20/80[l]	15	15/85	100
	$TolS^-K^+$	10/90 ± 3	8/92	13	13/87	94
			14/86[l]	27[l]		
(E)-5-Cl	p-$O_2NC_6H_4S^-Na^+$	51/49 ± 2[h]	55/45	4	43/57	48
(E)-5-Br	p-$O_2NC_6H_4S^-Na^+$	50/50 ± 1[i]	51/49	7	48/52	66
(E)-5-OMs	p-$O_2NC_6H_4S^-Na^+$	81/19 ± 3[j]	84/16	3	71/29	73
(E)-5-OTs	p-$O_2NC_6H_4S^-Na^+$	83/17 ± 1[j]	85/15	8	71/29	64
(E)-5-OTf	p-$O_2NC_6H_4S^-Na^+$	75/25 ± 2[i]	74/26	8	76/24	32
(E)-5-Cl	$TolO^-Li^+$	70/30 ± 1[h]	70/30	7	66/34	62
	$TolO^-Na^+$	68/32 ± 1	68/32	12	67/33	92
	$TolO^-K^+$	69/31 ± 3	68/32	11	72/28	100
(E)-5-Br	$TolO^-Li^+$	67/33 ± 2	70/30	7	64/36	66
	$TolO^-Na^+$	70/30 ± 2[m]	67/33	10	72/28	77
	$TolO^-K^+$	68/32 ± 3[j]	64/36	7	70/30	62
(E)-5-OMs	$TolO^-Li^+$	84/16 ± 1[j]	78/22	9	75/25	38
	$TolO^-Na^+$	83/17 ± 2[k]	80/20	7	75/25	75
	$TolO^-K^+$	84/16 ± 1[h]	80/20	4	80/20	49
(E)-5-OTs	$TolO^-Na^+$	88/12 ± 1[n,o]	79/21	3	75/25	52
(E)-5-OTf	$TolO^-Na^+$	90/10 ± 1[i,o]	85/15	6	85/15	63
(Z)-5-Cl	$TolO^-Li^+$	12/88 ± 1	13/87	11	21/79	51
	$TolO^-Na^+$	21/79 ± 3	20/80	11	26/74	57
	$TolO^-K^+$	9/91 ± 1	9/91	11	74/26	100
(Z)-5-Br	$TolO^-Li^+$	15/85 ± 1	17/83	10	73/27	100
	$TolO^-Na^+$	26/74 ± 3	29/71	12	30/70	74
	$TolO^-K^+$	11/89 ± 2	14/86	7	70/30	100
(Z)-5-OMs	$TolO^-Li^+$	8/92 ± 1	9/91	8	73/27	100
	$TolO^-Na^+$	27/73 ± 2	24/76	4	28/72	100
	$TolO^-K^+$	7/93 ± 1	8/92	8	72/28	100
(E)-5-Cl	p-$O_2NC_6H_4O^-Na^+$[p]	50/50 ± 4	48/52	15	53/47	87
(Z)-5-Cl	p-$O_2NC_6H_4O^-Na^+$	10/90 ± 3	16/84	8	35/65	41

[a] Reactions at room temperature by portionwise addition of the nucleophile. Analysis by ^1H NMR unless otherwise stated. [b] Geometrical purity ≥96% unless otherwise stated. [c] Value extrapolated to zero reaction time and corrected for the small amount of the isomeric substrate. The error given relates to each of the components in the mixture. [d] Distribution at the first reliable point measured without correction to impurity of the precursor. In the few cases where the ratio of this point is clearly either too high or too low compared with the ratios at higher reaction percentages an average value was taken for the calculation of the $(E)/(Z)$ ratios at zero reaction time. [e] Distribution at the last experimental point. [f] Analyzed by HPLC in the same experiment as above. [g] Precursor: 89% (E) isomer, containing 11% (Z) isomer. [h] Precursor: 95% (E) isomer containing 5% (Z) isomer. [i] Precursor: 90% (E) isomer containing 10% (Z) isomer. [j] Precursor: 92% (E) isomer containing 8% (Z) isomer. [k] A sample analyzed after 24% reaction by HPLC gave a 69/31 $(E)/(Z)$ ratio. [l] Experiment was analyzed by HPLC. [m] Precursor: 93% of the isomer mentioned together with 7% of the other isomer. [n] Precursor: 88% (E) isomer containing 12% of the (Z) isomer. [o] Based on the assumption that the (Z) isomer gave a 26/74 ratio of the products at the first experimental point. [p] The nucleophile was added in a DMSO-d_6 solution.

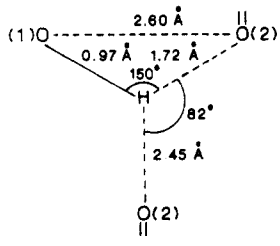
The sixth column of Table III shows that (E)- and (Z)-**5**-Cl and **5**-Br and (E)-**5**-OMs give with $TolO^-$ in CD_3CN after long reaction times nearly constant (E)-**8**/(Z)-**8** ratios of (72 (±1):28 (±1)). Likewise, constant (E)-**9**/(Z)-**9** ratios of 15:85 are obtained at the end of the reaction with $TolS^-$ starting from (E)- and (Z)-**5**-Cl, (Z)-**5**-Br, or (Z)-**5**-OMs. This corrects an erroneous report that only (Z)-**9** is formed from the vinyl chlorides.[5b]

An equilibrium ratio of 62:38 (E)-**10**/(Z)-**10** was obtained starting either from (E)-**5**-Cl or (Z)-**5**-Cl. With p-$O_2NC_6H_4S^-$ the (E)-**11**/(Z)-**11** ratios that are available at 32–73% reaction starting from all the (E) isomers increase from 43:57 starting from (E)-**5**-Cl to 76:24 starting from (E)-**5**-OTf. Reflux of a pure sample of (Z)-**11** for 200 and 320 h gave an (E)-**11**/(Z)-**11** ratio of 13:87. This is close to the equilibrium ratio at room temper-

ature, since when (*E*)-**5**-Cl and (*Z*)-**5**-Cl were reacted with slight molar excess of p-$O_2NC_6H_4S^-$ in CD_3CN until the (*E*)-**11**/(*Z*)-**11** ratio obtained remained constant, the values obtained were 12:88 and 14:86, respectively.

Crystallographic Data. Table II enables the following comparisons of the crystallographic data of the (*Z*)-enol and -mesylate as well as with that of the (Z)-tolylthio derivative that was previously determined.[5b]

(a) The C=C bond length in the mesylate is shorter (1.31 Å) and those of the enol (1.36 Å) and the STol (1.38 Å) derivatives are longer than the C=C bond in ethylene.[16a] (b) The C(1)–O(1) bond is 0.07 Å longer in the mesylate than in **7**. (c) The O(3)–C(5) bonds (1.44, 1.45 Å) are longer than the usual value of 1.43 Å for a $C(sp^3)$–O bond.[16b] (d) The deviation of the bond angles around the C=C bond from 120° is larger for the mesylate: C(6)C(1)C(2) and C(1)C(2)C(4) open to 128° and C(6)C(1)O(1) and C(2)C(3)C(4) close to 114°. (e) The CO_2Me group in both **7** and the mesylate are twisted (by 4.5° and 6.6°) from the C=C plane. (f) The torsional Ar—C=C angles are appreciable (ca. 45° and 49°). (g) The double bond is not completely planar. The torsional angles of the O(1)C(1)C(6) and the C(4)C(2)C(3) parts are 6.7 ± 0.1° for (*E*)-**5**-Cl[5b] and (*Z*)-**5**-OMs. (h) The O(1)–O(2) nonbonded distance in **7** is short (2.60 Å). The intramolecular hydrogen bond is nonlinear, with an OHO angle of 150°. The hydrogen is further bonded to the carbonyl group of a neighboring enol molecule, giving the three-center (bifurcated) hydrogen bond[17] shown below:



Discussion

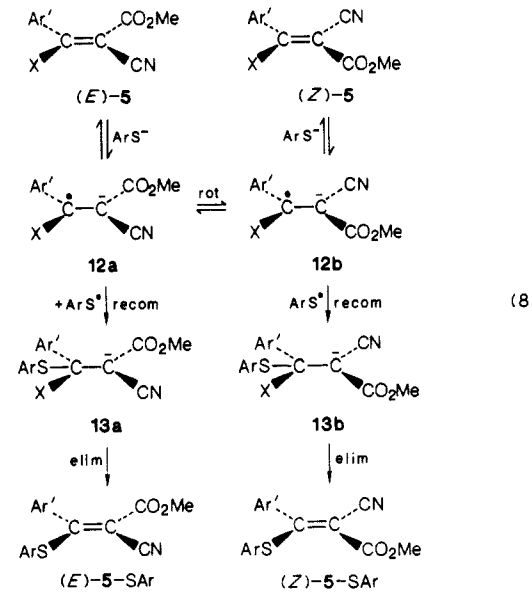
The main results of the present work are three. First, all systems gave partial stereoconvergence with all the nucleophiles studied. Second, the extent of stereoconvergence is not very strongly influenced by the nature of the nucleofuge, and the change follows only roughly the expected nucleofugality of the nucleofuges. Third, the extent of stereoconvergence is different starting from the (*E*) and the (*Z*) isomers.

Before discussing these results in terms of competing processes in the intermediate carbanion **2a** it should first be shown that alternative reaction routes are either unlikely or irrelevant and that the product distributions given in Table III are obtained under kinetic control.

Alternative Reaction Routes. The strong electron withdrawal by the β-substituents of **5** argues strongly that **5** will react via the multistep substitution route of eq 2.[5e] This is corroborated by the stereoconvergence observed with all the substrates.

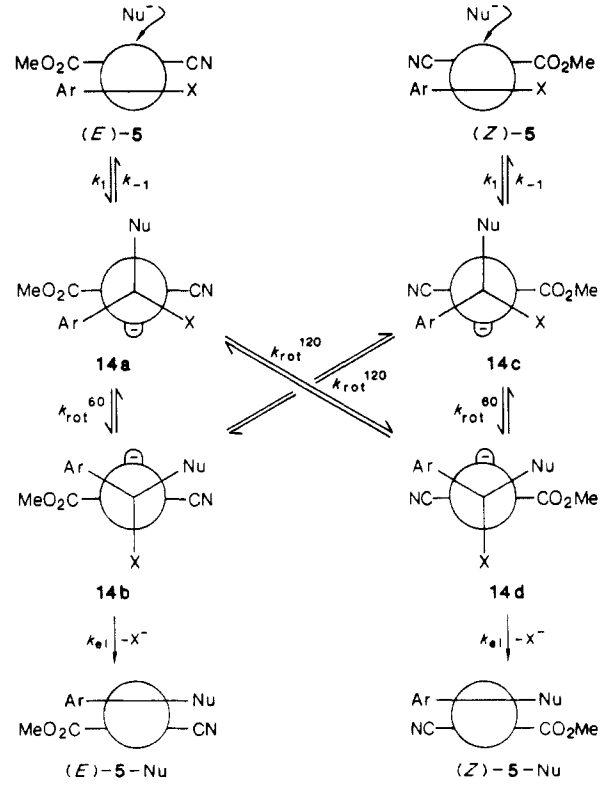
A mechanism involving an initial single-electron transfer (SET) from the nucleophile to **5** is an alternative to eq 2, but we found no evidence for the intermediacy of radical anions. Neither a CIDNP phenomenon nor an (*E*)-**5** ⇌ (*Z*)-**5** isomerization was observed in these reactions. Such an isomerization is expected if an initial SET to (*E*)-**5** forms the radical anion **12a**, which undergoes a faster rotation around C_α–C_β to give **12b** and reversal of the electron transfer to form (*Z*)-**5** than other reactions, e.g., recombination of **12a** or **12b** with ArS• (eq 8).

A rate-determining expulsion of X^- from **12a** (leading to the $S_{RN}1$ route) is expected to be much faster for a better nucleofuge[18]



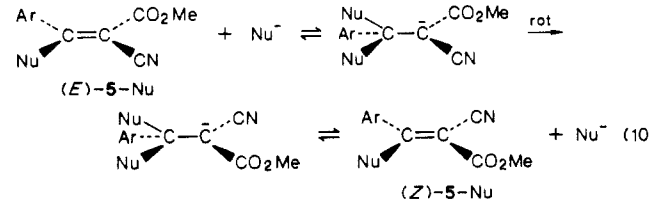
(8)

and is excluded since (*E*)-**5**-OTf is substituted only ca. 10 times faster than (*E*)-**5**-OMs. On the other hand, if recombination of **12a** with ArS• (formed by the electron transfer) to give **13a** is faster than rotation in **12a**, the rotation and elimination steps (eq 9) leading to the substitution product are identical with those of eq 2 when **13a** (=**2a**) is formed by a nucleophilic attack of ArS^- on (*E*)-**5**. The substitution will be therefore discussed in terms of eq 9.



(9)

The kinetically controlled product ratios changes with the progress of the reaction in the direction of the thermodynamic ratios. We ascribe this change to a nucleophile-promoted isomerization (eq 10), and indeed the extent of isomerization was



(10)

(16) (a) Costain, C. C.; Stoicheff, B. P. *J. Chem. Phys.* **1959**, *30*, 777. (b) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1962; Vol. 3, p 276.

(17) See: Jeffrey, G. A.; Mitra, J. *J. Am. Chem. Soc.* **1984**, *106*, 5546. Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320.

(18) Bunnett, J. F. *Acc. Chem. Res.* **1977**, *11*, 413. Parker, V. D. *Adv. Phys. Org. Chem.* **1983**, *19*, 131.

Table IV. Equilibrium Distributions of Reactants and Products for the p-$O_2N_6H_4C(X)$=$C(CN)CO_2Me$ System in Acetonitrile

X	T, °C	(E)/(Z)	X	T, °C	(E)/(Z)
Cl	room temp	68/32[a]	TolO	room temp	72/28
Br	room temp	83/17	p-$O_2NC_6H_4O$	room temp	62/38
		72/28[b]	TolS	room temp	15/85
		49/51[c]	p-$O_2NC_6H_4S$	room temp	13/87
OMs	70	54/46[d,e]			
OTs	reflux	61/39[d,f]			

[a] From isomerization of both isomers with or without added Cl^-.[5b] [b] From Br^--catalyzed isomerization in the dark, after 31 days, starting from (E)-**5**-Br and (Z)-**5**-Br, respectively ([**5**]/[Bu_4NBr] = 0.005 M/0.05 M). [c] Value obtained from both isomers after standing for 90 days in acetonitrile at room temperature, without protection from daylight. [d] Equilibrium was not achieved. The percentage of the (E) isomer at equilibrium may be lower. [e] Value obtained after 32 days in the dark. Starting from (E)-**5**-OMs, but the enol content is 72% (after 5 days (E)-**5**-OMs 69/31, **7** = 33%). Starting from (Z)-**5**-OMs; after 32 days **7** = 70%, and (E)-**5**-OMs/(Z)-**5**-OMs 1/3. [f] Starting from (E)-**5**-OTs; after 5 days **7** consists 19% of the mixture.

reduced by keeping the relative concentration of the nucleophile low throughout the reaction by its portionwise addition. The extrapolated ratios to zero reaction time gave a distribution (Table III) that we estimate to be within ±1–3% of the kinetically controlled ratio.

Rotation in and Nucleofuge Expulsion from the Intermediate Carbanion. Eq 9 shows the steps involved in the substitution of (E)-**5** and (Z)-**5** by a nucleophile. Nucleophilic attack on (E)-**5** gives the carbanion conformer **14a**, which by 60° rotation gives conformer **14b** and by 120° (or 240°) rotation gives conformer **14d**. For stereoelectronic reasons the expulsion of X^- is possible only when the carbanionic orbital and the C–X orbital are parallel, and expulsion of X^- from **14b** and **14d** give the retained (E)-**5**-Nu and the inverted (Z)-**5**-Nu product, respectively. A similar scheme involving initial formation of **14c** applies for the reaction of (Z)-**5**.

Consequently, both rotation and expulsion of X^- are essential steps on the way to the substitution product, and a priori either step may be rate determining. Three situations can be envisioned: (a) Rotation is rate determining, i.e., once **14b** and **14d** are formed they expel X^- before further rotation takes place. The ratio of the retained to the inverted product is then determined by the [**14b**]/[**14d**] ratios, i.e., by the relative rates of 60 and 120° rotation (k_{rot}^{60}, k_{rot}^{120}). When $k_{rot}^{60} \gg k_{rot}^{120}$, only a retained product is observed, whereas the variant $k_{rot}^{120} \gg k_{rot}^{60}$, which gives exclusive inversion for both isomers, is unknown. (b) Rotation is much faster than the rate-determining elimination, i.e., k_{rot}^{60}, $k_{rot}^{120} \gg k_{el}$. According to the Curtin–Hammett principle,[19] both precursors will then give the same ratio of products (or a single product), i.e., complete stereoconvergence. (c) $k_{rot} \sim k_{el}$, and both rotational barriers and elimination rates will determine the product ratios.

Since neither complete retention nor complete stereoconvergence was observed in any of our reactions, either situation (c) or situation (a) when k_{rot}^{60} and k_{rot}^{120} differ by less than 1 order of magnitude is applicable. Whether these situations are distinguishable experimentally depends on the expected effect of the nucleofuge on k_{el}, k_{rot}^{60} and k_{rot}^{120}.

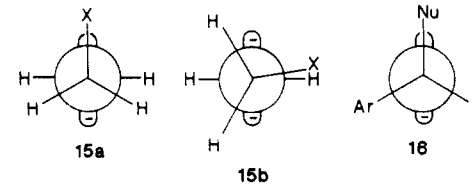
Dependence of the Nucleofugality on the Nucleofuge. Qualitative orders of nucleofugality for our nucleofuges are available for saturated[11,20,21] and vinylic[12,21] S_N1 reactions and for S_N2 reactions.[20,22] Expulsion of nucleofuges X from carbanions $\bar{C}CX$ had received considerable attention in recent years,[9] and a quantitative scale was established.[9e] However, all the nucleofuges investigated were poorer than those studied now by us, and the scale could not be extended to them.

The nucleofuge expulsion step most closely resembles an E1 process from a carbanionic species. In the endothermic R–X bond cleavage step of S_N1 or E1 reactions the reactivity span of good nucleofuges is large. k_{Br}/K_{Cl} ratios of $10–10^3$,[20,21] k_{OTs}/k_{Br} ratios of $10^2–10^3$,[11,12,23] and k_{OTf}/k_{OTs} ratios of $10^4–10^5$[12,24] are common, so that the k_{OTf}/k_{Cl} ratio can be $\leq 10^{10}$. The expulsion of X^- from the carbanion should be much less endothermic (and may even be exothermic) so that a much earlier transition state and consequently much smaller differences between the k_{el} values of the good nucleophiles are expected. The k_{Br}/k_{Cl} ratios obtained recently in vinylic substitution from a study of the "intramolecular element effect" were indeed ascribed to an early transition state for the C–X bond cleavage.[10] Nevertheless, the expected qualitative order of the C–X bond cleavage from the intermediate carbanion is Cl < Br < OTs ~ OMs ≪ OTf.

Dependence of the Rotational Barriers on the Nucleofuge. Useful data for evaluation of the effect of nucleofuge on the rotational barrier are almost nonexistent. The competition between 60 and 120° rotations in carbanions **14a** and **14c** could be discussed in terms of two components of the rotational barrier: steric and hyperconjugative.

In the 60° rotation there is only a single eclipsing interaction of vicinal substituents: Ar/CO_2Me for the **14a** → **14b** rotation and Ar/CN for the **14c** → **14d** rotation. Hence, to a good approximation the steric barrier to this rotation is independent of X. Two eclipsing interactions occur along the 120° rotation: X/CO_2Me and Nu/CN for the **14c** → **14b** rotation and X/CN and Nu/CO_2Me for the **14a** → **14d** rotation. Since they occur at a 60° phase difference, the largest of them will determine the barrier. The steric bulks are CN ≪ CO_2Me, X > Nu = OAr, X ≤ Nu = ArS, provided that the Ar groups are arranged in the less sterically demanding conformations. The qualitative conclusion is that the steric barrier could be different starting from (E)-**5** or from (Z)-**5** and that it may also be nucleophile dependent (see below).

The hyperconjugative barrier arises from anionic hyperconjugation, which is the net difference between the stabilizing two-electron interaction between the doubly occupied donor carbanionic 2p orbital and the acceptor π^*_{C-X} orbital and the destabilizing four-electron interaction between the π_{C-X} and the 2p(C^-) orbitals.[25] We previously calculated the hyperconjugative stabilization energies (HSE) (at the STO-3G level) from the energy difference between conformers **15a** (maximum overlap and stabilization) and **15b** (orthogonal orbitals, no stabilization) for various groups X.[8,26] By using the angle dependence of the



15a 15b 16

hyperconjugative interaction[8,25] and assuming additivity of the substituent effects at C_α the rotational barrier in carbanion **16** could be calculated. It was shown that for X = Cl the 60° rotation is so much preferred that the stereochemistry will be retention of configuration.[8] When the two α-hydrogens on **15** ($\bar{C}H_2CH_2X$) are replaced by the electron-withdrawing CN groups to give $(NC)_2\bar{C}CH_2X$, these calculated rotational barriers are strongly reduced, e.g., from 10.1 to 5.5 and from 29.4 to 6.3 kcal mol^{-1}

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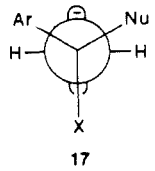
for X = F and OCl, respectively.[8,26] Three points are important in this connection: (a) The gas-phase barriers for good nucleofuges such as Cl are high, so that even after their appreciable reduction by the β-substituents and the solvent the rotation processes can still be rate determining. (b) The reduction of the barriers by two β-CN groups that serve as an adequate model for the β-CO_2Me and β-CN of **5** is extensive, but is higher for better hyperconjugative groups X. (c) The barriers should be further reduced by the solvent. We conclude that the calculated gas-phase HSEs should give a reliable but only a qualitative order of the effect of the X groups on the rotational barrier.

Of our five nucleofuges, HSE was available only for X = Cl at the STO-3G level. The value for X = Br cannot be calculated as yet, but we suggested previously[10] that HSE(Cl) ~ HSE(Br). New HSE values were calculated now at the higher 3-21G level.[27] Conformer **15b** has been fully optimized except for the dihedral angles, and conformer **15a** was fully optimized except for the C–X bond length, which was kept as in **15b**. The carbanionic centers of both **15a** and **15b** were held planar. The HSEs (in kcal mol^{-1}) were 12.5 for X = OH, 21.1 for X = SH, 27.5 for X = OSO_2H, and 36.2 for X = Cl. A change from OSO_2H to OSO_2CH_3 and OSO_2Tol-*p* is not expected to change appreciably the HSE as judged by the HSE changes (STO-3G) OH (11.5) → OMe (12.6),[8] OOH (16.4) → OOMe (17.1).[26] However, the change of OSO_2H → electron-withdrawing OSO_2CF_3 should increase the HSE appreciably, as found for the change OH → OSO_2H (above) or OH (12.4) → OCl (29.4) (STO-3G).[26] The HSE value for X = OTf is therefore likely to be ≥ than for X = Cl. Hence, the gas-phase HSEs will follow the order OTf ≥ Cl ~ Br > OMs, OTs. The β-substituents and the solvent are expected to reduce the values drastically (see below) and to bring them much closer to one another.

The 60 vs 120° rotational barriers are mainly dependent on the HSE(X) value. Carbon substituents have low HSEs (CH_3, 2.1 at STO-3G),[8] and the loss or gain of HSE(Ar) on 60 and 120° rotation in **14a** and **14c** will be relatively small compared with those due to HSE(X) and HSE(Nu). The rotation results in an appreciable loss of HSE(Nu), which is identical for 60 and 120° rotation. The 60° clockwise rotation in **14a** and **14c** leads to a very high gain in HSE. Assuming that eq 11 applies for each

$$E(\theta) = 0.5V_x(1 + \cos 2\theta) \qquad (11)$$

substituent X, where $E(\theta)$ is the hyperconjugation stabilization energy at a dihedral angle θ between the C–X and the 2p(C^-) orbitals and V_x is the value at $\theta = 0$, the 60° clockwise rotation should have no barrier, whereas the 120° rotation should have a high barrier. E.g., by applying eq 11 for the three substituents and the assumptions HSE(ArO) = HSE(HO), HSE(ArS) = HSE(HS), HSE(OSO_2H) = HSE(OMs), and HSE(Ar) = 2.1 kcal mol^{-1}, the conformers obtained by 30 and 60° clockwise and 30 and 60° anticlockwise rotations in **16** differ in energy in kcal mol^{-1} from **16** by 14.5, 17.7, −11.2, −7.8 (Nu = OH, X = Cl); 12.3, 11.3, −13.4, −16.2 (Nu = SH, X = Cl); 10.1, 11.2, −9.0, −7.8 (Nu = OH, X = OMs); and 7.9, 5.2, −11.2, −16.2 (Nu = SH, X = OMs), respectively. The $k_{rot}^{60}/k_{rot}^{120}$ ratio arising from energy differences of 19–17.5 kcal mol^{-1} would lead to complete retention if k_{rot} is rate determining. That this is not the case (Table III) demonstrates clearly the large effect of the β-substituents and the solvent on the barrier. An interesting outcome of the calculations is that the rotamer of lowest energy is not necessarily **17**.



17

The closer the V_x values of Nu and X the higher is the dihedral angle of the C–X and the 2p(C^-) orbitals. E.g., when Nu = SH, X = OMs, the rotamer formed by 30° clockwise rotation in **16** is more stable than **17** by 2.7 kcal mol^{-1}.

Precursor Configuration and Nucleofuge and Cation Effects on the Extent of Stereoconvergence. The only qualitative predicted orders of k_{el} and k_{rot} as a function of X make it difficult to predict the order of the k_{rot}/k_{el} values as a function of X. Nevertheless, comparison with the data of Table III leads to several important conclusions.

First, all the systems are in the stereoconvergence region. Consequently, the 120° rotation competes with the 60° rotation. Second, none of the systems give the same products ratio from both the (*E*) and the (*Z*) isomer, i.e., complete stereoconvergence. Hence, carbanions **14b** and **14d** do not equilibrate completely before nucleofuge expulsion, and expulsion of X^- is not ultimately rate determining. Third, the extent of stereoconvergence depends on the geometry of the precursor, the nucleofuge, and in some cases the counterion of the anionic nucleophile. For comparison of these effects two approaches for presenting the results seem conceivable. The first one is the "percent retention" in each reaction, obtained from the experimental values of Table III. It has the mechanistic advantage that "complete retention" is the usual outcome for most moderately and slightly activated electrophilic chloro- and bromoalkenes,[2] so that lower extents of retention reflect the deviation from this extreme. A disadvantage is that the thermodynamic equilibrium ratio of the substitution products is not reflected by this presentation. E.g., both high extents of retention and stereoconvergence are observed if the retained isomer is highly dominant in the product mixture. The second approach is the "percent of stereoconvergence". The equilibrium ratio of the products is the standard of comparison, and the difference of the observed products distribution from this value reflects how far the system is from being under thermodynamic control. The advantage is that since the equilibrium product ratios nearly always differ from unity this approach apparently reflects more truly the difficulty of a system to deviate from complete retention. It also resembles the use of the term "enantiomeric excess" in substitution at a saturated carbon. A practical difficulty of this approach is the necessity to know the equilibrium product ratio under the reaction conditions. A disadvantage is that for a certain isomer the deviation from complete stereoconvergence may be in either the retention or the inversion direction and these two types of behavior may have different mechanistic explanations.

Both approaches are presented in Table V. Since the average error in the percentage of each product is ≥±2%, the estimated errors in the percent retention and precent of stereoconvergence are ±2%, and ±4–8%, respectively.

The percent retention column of Table V indicates that the effect of changing either the cation or the nucleofuge on the stereochemistry is relatively small. The effect of the change in the cation is unsystematic. Li^+, Na^+, and K^+ salts give the same extent of retention in the reaction of $TolO^-$ with (*E*)-**5**-Cl, (*E*)-**5**-Br, and (*E*)-**5**-OMs and show small differences in the reactions of the corresponding (*Z*) isomers with $TolS^-$. Li^+TolS^- gives somewhat more retention with (*E*)-**5**-Cl and (*E*)-**5**-Br, but the trend is reversed with (*E*)-**5**-OMs. $TolO^-Na^+$ gives less retention than the other salts in the reaction with the (*Z*) isomers. The small effect of the counterion was previously observed for a closely related system,[1] and it seems to be more consistent with minor effects, if at all, on k_{rot} and k_{el} rather than with a cancellation of larger effects on two competing processes, e.g., k_{rot}^{60} and k_{rot}^{120}.

The large changes associated with either the nucleofugalities or the calculated gas-phase rotational barriers for the model conformers **15a** and **15b** are not reflected in the percent retention values for our nucleofuges. For X = Cl or Br the extents of retention are nearly always similar; somewhat higher values were observed for X = OMs in the (*E*) series, whereas the changes in the (*Z*) series are relatively smaller. A critical evaluation of the nucleofuge effect involves comparison of the stereochemistry for the vinyl chloride and triflate. Rather surprisingly, these changes

(27) Calculations by Dr. M. Karni and Prof. Y. Apeloig. The details will be published elsewhere.

Table V. Stereochemistry of the Substitution of Compounds 5-X with p-$RC_6H_4G^-M^+$ in CD_3CN[a]

			(E)-5-Cl		(E)-5-Br		(E)-5-OMs		(E)-5-OTs		(E)-5-OTf		(Z)-5-Cl		(Z)-5-Br		(Z)-5-OMs	
R	G	M	R	SC	R	SC	R	SC	R	SC	R	SC	R	SC	R	SC	R	SC
Me	S	Li	45	65	45	65	57	51					89	73	88	80	88	80
Me	S	Na	36	75	37	79	63	42	59	48	45	65	89	73	95	33	95	33
Me	S	K	33	79	34	78	68	38			41	69	88	80	90	67	90	67
NO_2	S	Na	51	56	50	57	81	20	83	22	75	29						
Me	O	Li	70	100[b]	67	100[b]	84	57					88	17	85	21	92	11
Me	O	Na	68	100[b]	70	100[b]	83	61	88	43	90	36	79	29	74	36	73	38
Me	O	K	69	100[b]	68	100[b]	84	57					91	13	89	15	93	10
NO_2	O	Na	50	81									90	26				

[a] R = percent retention; SC = percent stereoconvergence, based on the equilibrium values of Table IV. [b] The small excess inversion that can be deduced from the data is within the combined experimental errors of the product distribution in the reaction and at equilibrium.

are small, the larger ones being from 51% retention for (*E*)-**5**-Cl to 75% retention for (*E*)-**5**-OMs with p-$O_2NC_6H_4S^-Na^+$ or from 68% to 90% retention for the corresponding reactions with $TolO^-Na^+$. These minor changes are incompatible with a mechanism involving a rate determining C–X bond cleavage or a competition between C–X bond cleavage and internal rotation.

The stereochemical outcomes differ appreciably on starting from an (*E*) or the corresponding (*Z*) isomer; the (*Z*) isomer almost always gives a higher percent retention. However, (*Z*)-**5**-Cl gives higher percent stereoconvergence (as well as higher percent retention!)[28] than (*E*)-**5**-Cl on reaction with $TolS^-$, and the same is true for the reaction of (*Z*)-**5**-OMs (compared with (*E*)-**5**-OMs) with $TolS^-K^+(Li^+)$. In contrast, except in one case, with all the $TolO^-$ salts and p-$O_2NC_6H_4O^-Na^+$ the (*E*) isomers usually give less retention but always more stereoconvergence. Indeed, within the experimental error, the reactions of (*E*)-**5**-Cl and (*E*)-**5**-Br with $TolO^-$ give the equilibrium (*E*)-**8**/(*Z*)-**8** distribution.

The discussion above on the calculated rotational barriers suggest that the hyperconjugative contribution to the $k_{rot}^{60}/k_{rot}^{120}$ ratio should be independent of the nucleophile. It should be the same for **14a** and **14c**, i.e., there should be no difference in the stereochemistry starting from (*E*)-**5**-X and (*Z*)-**5**-X due to hyperconjugation. The observed differences therefore arise from steric contribution to the $k_{rot}^{60}/k_{rot}^{120}$ ratio, which is dependent both on the structure of the vinylic precursor and on the nucleophile.

An estimate of the relevant eclipsing interactions could be obtained from the equilibrium data for (*E*)/(*Z*) isomeric pairs. Table IV shows that the (*E*) isomers of the substituted alkenes **5**-X are more stable than the (*Z*) isomers when X = OAr, but the order is reversed when X = SAr. This is surprising, since it implies that the two bulky substituents prefer to be in syn positions in our system. Although explanations for this preference could be raised,[29] our interest is to apply this conclusion to our stereochemical data.

Since the Ar/CN steric interaction on the reaction coordinate for 60° rotation in **14c** is smaller than the X/CO_2Me interaction on the reaction coordinate for 120° rotation in **14c**, both steric and hyperconjugative factors will lead to preferred retention in the (*Z*) isomer. In contrast, the 60° rotation in **14a** involves the unfavorable Ar/CO_2Me interaction, compared with the more favorable X/CN and Nu/CO_2Me interactions in the 120° rotation. Consequently, the steric contribution to the rotational barrier operates against the hyperconjugative one, which prefers 60° rotation, and the (*E*) isomers show less retention than the (*Z*) isomers. Although the lower extent of retention for the ArS^- than for ArO^- nucleophile is consistent with the stabilities of (*E*)-**8**/(*Z*)-**8** and (*E*)-**9**/(*Z*)-**9** discussed above, it is not clear if data related to a pair of syn interactions in the alkenes are applicable for a single eclipsing interaction in the carbanion.

Electronic effects in the nucleophile are also important. More retention was obtained in the reaction of all the (*E*) isomers with p-$O_2NC_6H_4S^-Na^+$ than with $TolS^-Na^+$, but the reverse is true for the single reaction of (*E*)-**5**-Cl with p-$O_2NC_6H_4O^-Na^+$ and $TolO^-Na^+$. The data are too limited to justify speculations concerning the reason for this.

Details of the Rapid Step of Nucleophilic Vinylic Substitution. The above considerations suggest the following detailed mechanism for the substitution of good nucleofuges from highly electrophilic alkenes. A rate-determining nucleophilic attack leads to a carbanion (e.g., **14a**) where the C–X and the 2p(C^-) orbitals are at a 60° dihedral angle. Competition between intramolecular 60 and 120° rotations then gives two conformers (e.g., **14b** and **14d**, respectively) where the 2p(C^-) and the C–X orbitals are at a dihedral angle of 0°. The relative rotation rates are determined by a hyperconjugative factor that normally favors the 60 over 120° rotation and a steric factor that favors the rotation leading to the lower steric interaction between eclipsing vicinal substituents. Once these conformers are formed, expulsion of X^- is faster than further rotation; i.e., the product ratios are controlled by the $k_{rot}^{60}/k_{rot}^{120}$ ratios. Consequently, a study of the effect of a change in the nucleofuge on the stereochemistry of the substitution does not give information on the transition state in the expulsion step of the nucleofuge. This conclusion is applicable to system **5** but not necessarily to others,[10] since the complete stereoconvergence in the reaction of PhC(I)=C(Ph)NO_2 with $TolS^-$[5a] is consistent with a faster internal rotation compared with nucleofuge expulsion.

It is interesting that in a substitutiong involving a C–X bond cleavage, a change of X does not give information on the extent of the C–X bond cleavage in either the rate-determining nucleophilic addition step[2] or the product-determining elimination step.

Experimental Section

General Methods. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Ultraviolet and visible spectra were measured with Varian Techtron 635 and UV1KON 820 spectrophotometers. IR spectra were taken with a Perkin-Elmer 157 G spectrometer. Mass spectra were determined with a MAT 311 instrument. ^1H NMR spectra were recorded with Bruker WH-300 and Bruker WP200 SV pulsed FT spectrometers operating at 300.133 and 200.133 MHz, respectively. Tetramethylsilane was usually used as a reference except in CD_3CN, where the quintet of the partially deuteriated acetonitrile was used. HPLC separations were conducted with a Tracor 970 A instrument with a UV detector attached to a Merck Hitachi D-2000 Chromato integrator with Diol (125-4) and CN (250-4) columns (Merck).

X-ray Crystal Structure Analysis. Data were measured on a Philips four-circle computer-controlled diffractometer. The method is identical with that described previously,[5b,d] except that the unit-cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $10 \leq \theta \leq 15°$. Intensity data were collected by the ω–2θ technique to a maximum 2θ of 45°. The scan width $\Delta\omega$ for each reflection was $(1.00 + 0.35 \tan \theta)°$ with a scan speed of 3°/min.[30]

Crystallographic Data. **7**: $C_{11}H_8N_2O_5$; space group $P2_1/c$; a = 4.042 (1) Å, b = 11.696 (3) Å, c = 23.485 (5) Å; β = 91.19 (4)°; V = 1110.0 (5) Å^3; Z = 4; ρ_{calcd} = 1.49 g cm^{-3}; μ(Mo K_α) = 0.77 cm^{-1}; unique

(28) This is a result of the much higher percentage of (*Z*)-**9** compared with (*E*)-**9** at their equilibrium mixture (see Table IV).

(29) For example, the longer C–S bond compared with the C–O bond will reduce the interactions involving the ArS group compared with the ArO group. Steric attraction can also be invoked. The preferred interaction of the apparently bulker cis substituents is reminiscent of the higher stability of (*Z*)-MeCH=CHR, R = OMe, Cl, compared with the (*E*) isomer: Epiotis, N. D.; Bjorkquist, D.; Bjorkquist, L.; Sarkanen, S. *J. Am. Chem. Soc.* **1973**, *95*, 7558.

(30) All crystallographic computing was done on a Cyber 74 computer at the Hebrew University of Jerusalem, by using the SHELX 1977 structure determination package.

reflections, 2489, reflections with $I \geq 2\sigma(I)$, 1794; $R = 0.054$; $R_w = 0.081$; $w = (\sigma_F^2 + 0.001509F^2)^{-1}$.

(*Z*)-5-OMs: $C_{12}H_{10}N_2O_7S$; space group P_n; $a = 9.742$ (2) Å, $b = 8.416$ (1) Å, $c = 8.702$ (2) Å; $\beta = 96.59$ (4)°; $V = 708.8$ (3) Å^3; $Z = 2$; $\rho_{calcd} = 1.68$ g cm^{-3}, μ(Mo K$_\alpha$) = 2.15 cm^{-1}; unique reflections, 983; reflections with $I \geq 2\sigma(I)$, 898; $R = 0.098$; $R_w = 0.123$; $w = (\sigma_F^2 + 0.017015F^2)^{-1}$.

Methyl (*E*)- and (*Z*)-β-Chloro-α-cyano-*p*-nitrocinnamates ((*E*)-5-Cl, (*Z*)-5-Cl). The two isomeric compounds were prepared by a modification of the previously reported procedure.[5b] To a solution of the enol **7** (5 g, 0.02 mol), in dry methylene chloride (200 mL), was added phosphorus oxychloride (3 g, 0.02 mol). Triethylamine (4.04 g, 0.04 mol) was added dropwise with vigorous stirring, and the mixture was refluxed for 5 h. The triethylammonium chloride was filtered, and the organic phase was extracted with water (3 × 150 mL), dried ($MgSO_4$), and evaporated. The solid obtained (4.6 g, 87%), was a 1:1 (*E*)/(*Z*) mixture according to ^{1}H NMR. The (*E*) isomer, mp 149 °C (2.0 g, 38%), was obtained by repeated crystallization from CCl_4, and the (*Z*) isomer, mp 162 °C (1.3 g, 25%), was obtained by crystallization of the remainder from ethyl acetate. The analytical and spectral properties were previously described.[5b]

Methyl (*E*)- and (*Z*)-β-Bromo-α-cyano-*p*-nitrocinnamates ((*E*)-5-Br, (*Z*)-5-Br). (a) To a solution of the enol **7** (5 g, 0.02 mol) in dry CH_2Cl_2 (200 mL) was added phosphorus oxybromide (5.74 g, 0.02 mol). Triethylamine (4.04 g, 0.04 mol) was added dropwise with vigorous stirring, and after the addition, the mixture was refluxed for 5 h. The triethylammonium chloride was filtered, the solvent was evaporated, and the residue was extracted with ether (10 × 50 mL), dried ($MgSO_4$), filtered, and evaporated. From the solid obtained (4.0 g, 65%) the (*E*) isomer, mp 149–150 °C, was obtained by repeated crystallization from CCl_4 (1.2 g, 30%). The (*Z*) isomer, mp 152 °C (0.75 g, 18%), was obtained from the enriched CCl_4 solution by further crystallization from CCl_4. The geometrical assignments are based on the relative positions of the methyl ester signal in the ^{1}H NMR according to Hayashi.[14]

(*E*)-5-Br: UV (MeCN) λ_{max} 280 nm (log ϵ 4.10); IR (Nujol) ν_{max} 2210 (s, CN), 1725 cm^{-1} (vs, COOMe); ^{1}H NMR ($CDCl_3$) δ 3.77 (3 H, s, COOMe), 7.51, 8.30 (4 H, AA′BB′, q, J = 9 Hz, Ar); mass spectra, m/z (relative abundance, assignment) 310, 312 (10, M), 279, 281 (10, M − OMe), 231 (44, M−Br), 59 (B, COOMe). Anal. Calcd for $C_{11}H_7BrN_2O_4$: C, 42.44; H, 2.25; N, 9.00. Found: C, 42.38; H, 2.37; N, 8.78.

(*Z*)-5-Br: UV (MeCN) λ_{max} 280 nm (log ϵ = 4.10); IR (Nujol) ν_{max} 2210 (s, CN), 1725 cm^{-1} (vs, COOMe); ^{1}H NMR ($CDCl_3$) δ 3.97 (3 H, s, COOMe), 7.77, 8.35 (4 H, AA′BB′ q, J = 9 Hz, Ar); mass spectra, m/z (relative abundance, assignment) 312, 310 (51, M), 281, 279 (27, M − MeO), 231 (B, M − Br), 59 (58, COOMe). Anal. Calcd for $C_{11}H_7BrN_2O_4$: C, 42.44; H, 2.25; N, 9.00. Found: C, 42.60; H, 2.48; N, 8.78.

(b) A yellow color was developed when pyridine (0.05 mL) was added to a solution of **7** (0.25 g, 1 mmol) in CH_2Cl_2 (25 mL). Thionyl bromide (0.25 g, 1.2 mmol) was added to the solution, and the mixture was stirred for 72 h. After being washed successively with water, aqueous $NaHCO_3$, and water, the organic phase was separated, dried ($MgSO_4$), and evaporated. ^{1}H NMR spectrum of the remainder showed the presence of only **7**.

(c) To a mixture of *p*-nitrobenzoyl chloride (1.86 g, 0.01 mol) and methyl cyanoacetate (0.99 g, 0.01 mol) was added triethylamine (2.02 g, 0.02 mol) with stirring. After the resultant mixture was stirred for 3 h, phosphorus oxybromide (2.87 g, 0.01 mol) was added, and the mixture was refluxed for 3 h. After filtering and evaporation of the solvent, the remainder was extracted with ether (3 × 150 mL), and the organic phase was dried, filtered, and evaporated. ^{1}H NMR spectrum of the residue shows the formation of a mixture of methyl *p*-nitrobenzoate and *p*-nitrobenzoic acid. The ester was separated by dissolution in chloroform, filtering, and evaporation and was identified by ^{1}H NMR, IR, mass spectra, elemental analysis, and mp: 93 °C (lit.[31] mp 96 °C); mass spectra, m/z (relative abundance, assignment) 181 (14, M), 180 (85, M − H), 149 (B, M − MeOH). The *p*-nitrobenzoic acid remaining from the chloroform extract has mp 236–237 °C (lit.[32] mp 239–241 °C).

Methyl (*E*)- and (*Z*)-α-Cyano-β-(mesyloxy)-*p*-nitrocinnamates ((*E*)-5-OMs, (*Z*)-5-OMs). To a reaction mixture containing sodium enolate **6b** (2.7 g, 10 mmol) in dry acetonitrile (150 mL) was added with stirring in the dark methanesulfonic anhydride (1.01 g, 11 mmol). The mixture was refluxed for 2 h and then cooled with ice. The sodium mesylate was filtered, the solvent was evaporated, and ^{1}H NMR showed the presence of 10% **7**, 40% (*Z*)-**5**-OMs, and 50% (*E*)-**5**-OMs. In attempted crystallization from CCl_4 or warm toluene partial decomposition of the vinyl mesylate took place, giving gray-yellow oily droplets. Separation was therefore achieved on a silica column, using a petroleum ether–chloroform gradient. Pure (*Z*)-**5**-OMs (0.5 g, 15%) was obtained by using 25% $CHCl_3$–75% petroleum ether. The following fraction (1.2 g, 37%) was an (*E*)-**5**-OMs/(*Z*)-**5**-OMs mixture from which (*E*)-**5**-OMs, mp 104 °C, was obtained, and crystallization from toluene gave pure (*Z*)-**5**-OMs, mp 129 °C. In each case a partial decomposition with formation of oil droplets was observed. The geometrical assignment is based on the X-ray diffraction of (*Z*)-**5**-OMs. The positions of the methyl ester groups are consistent with Hayashi's generalization.[14]

(*E*)-5-OMs: UV (MeCN) λ_{max} 289 nm (log ϵ 4.16); IR (Nujol) ν_{max} 2220 (s, CN), 1740 cm^{-1} (s, CO_2Me); ^{1}H NMR ($CDCl_3$) δ 3.42 (3 H, s, CH_3SO_2), 3.82 (3 H, s, COOMe), 7.76, 8.33 (4 H, AA′BB′ q, J = 9 Hz, *p*-$O_2NC_6H_4$); mass spectra, m/z (relative abundance, assignment) 326 (15, M), 248 (30, M − SO_2CH_3 − H), 150 (96, *p*-$O_2NC_6H_4CO$), 79 (B, CH_3SO_2). Anal. Calcd for $C_{12}H_{10}N_2SO$: C, 44.17; H, 3.07; N, 8.59; S, 9.82. Found: C, 44.04; H, 3.12; N, 8.77; S, 10.04.

(*Z*)-5-OMs: UV (MeCN) λ_{max} 290 nm (log ϵ 4.18); IR (Nujol) ν_{max} 2220 (s, CN), 1740 cm^{-1} (vs, COOMe); ^{1}H NMR ($CDCl_3$) δ 3.47 (3 H, s, CH_3SO_2), 3.94 (3 H, s, COOMe), 8.04, 8.38 (4 H, AA′BB′ q, J = 9 Hz, *p*-$O_2NC_6H_4$); mass spectra, m/z (relative abundance, assignment) 326 (5, Me), 248 (10, M − SO_2CH_3 − H), 150 (40, *p*-$O_2NC_6H_4CO$), 79 (B, CH_3SO_2). Anal. Calcd for $C_{12}H_{10}N_2SO_7$: C, 44.17; H, 3.07; N, 8.59; S, 9.82. Found: C, 44.04; H, 3.12; N, 8.77; S, 10.04.

Methyl (*E*)- and (*Z*)-α-Cyano-*p*-nitro-β-(tosyloxy)cinnamates ((*E*)-5-OTs, (*Z*)-5-OTs). (a) To a solution of the sodium enolate **6b** (2.7 g, 0.01 mol) in acetonitrile (100 mL) was added with stirring in the dark tosylic anhydride (3.4 g, 0.01 mmol). The yellow color was immediately discharged, and sodium tosylate started to precipitate. After being stirred for 24 h, the solution was filtered, the acetonitrile was evaporated, and the remainder was chromatographed on silica column with a petroleum ether–chloroform gradient. According to NMR the fraction obtained with 1:4 $CHCl_3$–petroleum ether was rich in (*Z*)-**5**-OTs (20:80 (*E*)/(*Z*); 0.84 g, 21%). The fraction eluted with 1:3 $CHCl_3$–petroleum ether (1.1 g, 28%) consisted of 1:1 (*E*)-**5**-OTs/(*Z*)-**5**-OTs from which (*E*)-**5**-OTs (containing 5% (*Z*)-**5**-OTs) was obtained by crystallization from CCl_4 as a white solid, mp 88–89 °C (0.48 g, 12%). Assignment of the geometry was based on the relative position of the ester methyl group.

(*E*)-5-OTs: UV (CH_3CN) λ_{max} 280 nm (log ϵ 4.06); IR (Nujol) ν_{max} 2225 (s, CN), 1745 cm^{-1} (vs, COOMe); ^{1}H NMR ($CDCl_3$) δ 2.47 (3 H, s, *p*-$MeC_6H_4SO_2$), 3.76 (3 H, s, COOMe), 7.35, 7.65 (4 H, AA′BB′ q, J = 9 Hz, *p*-$MeC_6H_4SO_2$), 7.71, 8.24 (4 H, AA′BB′ q, J = 9 Hz, *p*-$O_2NC_6H_4$); mass spectra, m/z (relative abundance, assignment) 402 (13, M), 248 (24, M − *p*-$MeC_6H_4SO_2$ − H), 155 (B, *p*-$MeC_6H_4SO_2$), 150 (20, *p*-$O_2NC_6H_4CO$). Anal. Calcd for $C_{18}H_{14}N_2O_7S$: C, 53.73; H, 3.48; N, 6.97. Found: C, 54.17; H, 3.55; N, 6.75.

(*Z*)-5-OTs: ^{1}H NMR ($CDCl_3$) δ 2.47 (3 H, s, *p*-$MeC_6H_4SO_2$), 3.84 (3 H, s, COOMe), 7.33, 7.66 (4 H, AA′BB′ q, J = 9 Hz, *p*-$MeC_6H_4SO_2$), 7.72, 8.23 (4 H, AA′BB′ q, J = 9 Hz, *p*-$O_2NC_6H_4$).

(b) To a cooled solution of **7** (2.5 g, 0.01 mmol) in chloroform (50 mL) was added pyridine (1.62 mL, 0.02 mmol) with stirring. The yellow pyridinium enolate **6c** immediately started to precipitate. After 15 min, *p*-toluenesulfonic anhydride (2.85 g, 0.015 mol) was added portionwise to the mixture, and stirring continued for 24 h. The mixture was extracted with ether (3 × 30 mL), and the organic phase was washed successively with water (3 × 10 mL), 1 N HCl (25 mL), 5% aqueous $NaHCO_3$ (50 mL), and water (50 mL), dried ($MgSO_4$), filtered, and evaporated. The resulting oil was crystallized from CCl_4, giving needles, mp 140–148 °C (30 mg) and square crystals, mp 143–145 °C (60 mg). A later fraction gave 0.5 g, mp 120–125 °C. The ^{1}H NMR and IR spectra and microanalyses are consistent with formation of a mixture of (*E*)-**5**-Cl and (*Z*)-**5**-Cl. The ^{1}H NMR spectra of the needles and the square crystals are identical with that of (*Z*)-**5**-Cl and (*E*)-**5**-Cl, respectively: mass spectra, m/z (relative abundance, assignment) 268, 266 (29, 82, M), 231 (B, M − Cl). Anal. Calcd for $C_{11}H_7ClN_2O_4$: C, 49.53; H, 2.63; N, 10.50. Found: C, 49.24; H, 2.59; N, 10.35.

Methyl (*E*)- and (*Z*)-α-Cyano-*p*-nitro-β-[(trifluoromesyl)oxy]-cinnamates ((*E*)-5-OTf, (*Z*)-5-OTf). To a solution of **7** (2.85 g, 11.5 mmol) in dry methylene chloride (100 mL) was added with stirring pyridine (1.83 mL, 22 mmol), and **6c** started to precipiate immediately. After 15 min of additional stirring, triflic anhydride (5 g, 17 mmol) was added, the mixture was cooled, and colorless sodium triflate precipitated from the pink solution. Samples that were taken after 2 and 48 h of stirring in the dark had the same compositions. After the mixture was filtered and the solvent evaporated, the remaining oil was extracted with ether (3 × 50 mL) and water (20 mL), and the organic phase was dried ($MgSO_4$), filtered, and evaporated. ^{1}H NMR of a sample showed traces of **7**, 90% (*E*)-**5**-OTf, and 10% (*Z*)-**5**-OTf. Attempted fractional crystallizations of the triflates from CCl_4, $CHCl_3$, CH_2Cl_2, MeCN, EtOAc, toluene, hexane, ether, petroleum ether, or several of their mixtures or

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chromatography on a silica column using CCl_4, petroleum ether–$CHCl_3$–EtOAc or toluene–CH_2Cl_2 gradients resulted in increased percentage of the enol **7** in the mixture, presumably due to decomposition of the vinyl triflates.

The geometrical assignment is based on the position of the signal of the methyl ester in the NMR. 9:1 (*E*)-**5**-OTf/(*Z*)-**5**-OTf mixture: IR ($CDCl_3$) ν_{max} 2225 (s, CN), 1745 cm^{-1} (vs, COOMe); mass spectra, *m/z* (relative abundance, assignment) 380 (6, M), 285 (10, M – CN – CF_3), 150 (B, CF_3SO_2OH and/or *p*-$O_2NC_6H_4CO$), 69 (54, CF_3). ^1H NMR ($CDCl_3$) (*E*)-**5**-OTf δ 3.84 (3 H, s, COOMe), 7.75, 8.37 (4 H, AA′BB′ q, J = 9 Hz, *p*-$O_2NC_6H_4$); (*Z*)-**5**-OTf δ 4.00 (3 H, s, COOMe), 7.95, 8.41 (4 H, AA′BB′ q, J = 9 Hz, *p*-$O_2NC_6H_4$). 1:1 (*E*)-**5**-OTf/(*Z*)-**5**-OTf mixture Anal. Calcd for $C_{12}H_7N_2F_3SO_7$: C, 37.89; H, 1.84; N, 7.37. Found: C, 37.55; H, 1.95; N, 6.97.

Methyl (*E*)- and (*Z*)-α-Cyano-β-(*p*-nitrophenoxy)-*p*-nitrocinnamates ((*E*)-10, (*Z*)-10). To a solution of (*E*)-**5**-Cl (2.5 g, 9.5 mmol), which is kept in the dark in acetonitrile (50 mL), was added with stirring sodium *p*-nitrophenoxide (1.9 g, 12 mmol). The mixture was filtered after 24 h, the acetonitrile was evaporated, and the remaining solid, which according to the NMR was a 63:37 (*E*)-**10**/(*Z*)-**10** mixture, was crystallized from toluene giving crystals (2 g, 60%), mp 179–180 °C, of (*E*)-**10**. Crystallization of the remainder from CCl_4 gave (*Z*)-**10** (0.5 g, 14%), mp 184 °C. The geometrical assignment is based on the position of the ester methyl signals.

(*E*)-**10**: UV (CH_3CN) λ_{max} 288 nm (log ϵ 4.39); IR (Nujol) ν_{max} 2220 (s, CN), 1730 cm^{-1} (vs, COOMe); ^1H NMR (CD_3CN) δ 3.72 (3 H, s, COOMe), 7.25, 7.70, 8.12, 8.15 (8 H, 2 AA′BB′ q, J = 9 Hz, Ar, ArO); mass spectra, *m/z* (relative abundance, assignment) 369 (11, M), 310 (44, M – COOMe), 150 (B, *p*-$O_2NC_6H_4CO$). Anal. Calcd for $C_{17}H_{11}N_3O_7$: C, 55.28; H, 2.98; N, 11.38. Found: C, 55.50; H, 3.17; N, 11.60.

(*Z*)-**10**: ^1H NMR (CD_3CN) δ 3.84 (3 H, s, COOMe), 7.16, 7.26, 7.97, 8.24 (8 H, 2 AA′BB′ q, J = 9 Hz, Ar, ArO); mass spectra, *m/z* (relative abundance, assignment) 369 (33, M), 310 (91, M – COOMe), 277 (49), 150 (B, *p*-$O_2NC_6H_4CO$). Anal. Calcd for $C_{17}H_{11}N_3O_7$: C, 55.28; H, 2.98; N, 11.38. Found: C, 54.40; H, 3.04; N, 11.15.

Methyl (*E*)- and (*Z*)-α-Cyano-β-[(*p*-nitrophenyl)thio]-*p*-nitrocinnamates ((*E*)-11, (*Z*)-11). To a solution of (*E*)-**5**-Cl (2.5 g, 9.5 mmol) in acetonitrile (50 mL) was added sodium 4-nitrothiophenoxide (2.1 g, 12 mmol) in the dark. The mixture was stirred for 24 h and filtered, the acetonitrile was evaporated, CH_2Cl_2 (100 mL) was added, and the solution was filtered from the unreacted *p*-nitrothiophenoxide. The CH_2Cl_2 was evaporated, and NMR of the residue in $CDCl_3$ showed 67% (*Z*)-**11**, 25% (*E*)-**11**, and 8% **7**. Recrystallization from CH_2Cl_2 gave a solid, mp 172–174 °C, which is a 1:2 (*E*)-**11**/(*Z*)-**11** mixture by NMR. (*Z*)-**11**, mp 194–195 °C, was obtained by crystallization from CCl_4. The geometrical assignment is based on the positions of the methyl ester signals in the NMR.

(*Z*)-**11**: UV (CH_3CN) λ_{max} 267 nm (log ϵ 4.16), 310 nm (log ϵ 4.12); IR (Nujol) ν_{max} 2210 (s, CN), 1735 cm^{-1} (vs, COOMe); ^1H NMR (CD_3CN) δ 3.12 (3 H, s, COOMe), 7.41, 7.48, 7.92, 8.02 (8 H, 2AA′BB′ q, J = 9 Hz, Ar, ArS); mass spectra, *m/z* (relative abundance, assignment) 385 (98, M), 326 (B, M – COOMe), 280 (32, M – COOMe – NO_2), 166 (42, *p*-$O_2NC_6H_4CS$). Anal. Calcd for $C_{17}H_{11}N_3O_6S$: C, 52.99; H, 2.86; N, 10.91. Found: C, 52.69; H, 2.88; N, 10.57.

(*E*)-**11**: ^1H NMR (CD_3CN) δ 3.61 (3 H, s, COOMe), 7.34, 7.52, 7.95, 7.98 (8 H, 2 AA′BB′ q, J = 9 Hz, Ar, ArS). Anal. Calcd for $C_{17}H_{11}N_3O_6S$: C, 52.99; H, 2.86; N, 10.91. Found: C, 51.23; H, 2.80; N, 10.30.

Relative Reactivities of (*E*)-5-OMs and (*E*)-5-OTf. To a 1:1 mixture of (*E*)-**5**-OMs and (*E*)-**5**-OTf (0.12 mmol each) in CD_3CN (1 mL) was added portionwise $TolO^-Na^+$. The relative disappearance rate of the vinyl sulfonates was calculated from the decrease in the integrals of their CO_2Me groups relative to the hydrogen signal of the residual CHD_2CN in the solvent. (*E*)-**5**-OTf disappeared ca. 10 times faster than (*E*)-**5**-OMs when the reaction was followed up to 80%.

Attempted Substitution of (*E*)-5-Cl with LiH and $NaBH_4$. (a) To a solution of (*E*)-**5**-Cl (13.3 mg, 0.05 mmol) in a CD_3CN (0.5 mL) or DMSO-d_6 (0.5 mL) was added solid LiH with vigorous shaking for 5 min. NMR after 10 min or 24 h (in CD_3CN) or after 5 h (in DMSO-d_6) showed no reaction. (b) To a solution of (*E*)-**5**-Cl (26.6 mg, 0.1 mmol) in CD_3CN (0.5 mL) was added solid $NaBH_4$ in small portions with shaking for 2–3 min, and the NMR spectrum was immediately recorded. The only product observed was methyl α-cyano-*p*-nitrophenylpropanoate, and even when (*E*)-**5**-Cl was in large excess, α-cyano-*p*-nitrobenzylidene acetate was not observed.

Equilibration of the Vinyl-X Derivatives. (a) Solutions of the (*E*) and (*Z*) isomers of the five vinylic systems (*E*)-**5**-X, X = Cl, Br, OMs, OTs, or OTf, (or (*E*)/(*Z*) mixtures when the pure isomers were not available, 0.05 mmol) in CD_3CN (0.5 mL) were kept for 48 h in the dark at room temperature. NMR analysis showed that no (*E*) ⇌ (*Z*) isomerization took place.

(b) Solutions of the (*E*) or (*Z*) isomers (1.5 mmol) in CH_3CN (25 mL) were refluxed for 10 h, and the compositions were analyzed by ^1H NMR in CD_3CN or $CDCl_3$ after evaporation of the solvent. The following ratios were observed: (*E*)-**5**-Br/(*Z*)-**5**-Br 47:53; (*E*)-**5**-OMe/(*Z*)-**5**-OMs 27:73; (*E*)-**10**/(*Z*)-**10** 82:18; (*E*)-**11**/(*Z*)-**11** 2:98.

Determination of the Product Distributions. (a) By NMR. To a solution of the vinylic compound (0.01 mmol) in CD_3CN or in DMSO-d_6 (0.5 mL) was added with stirring the solid nucleophile, in portions that were much less than equivalent. The solution was usually homogeneous up to 25% reaction, although occasionally turbidity was observed. At higher reaction percentages the sample was filtered before the measurement. Occasionally the nucleophile was added in CD_3CN or in DMSO-d_6 solution, but the product distribution was unaffected. The product ratios and the percentage of reaction were determined from the integrals of the COOMe signals of the reactants and products and sometimes from integration of other signals.

(b) By HPLC. The solid nucleophile was added portionwise to solutions of the vinylic compound (0.1 mmol) in dry acetonitrile (10 mL). Samples were rapidly evaporated in a nitrogen stream, and the remainder was dissolved in CH_2Cl_2 (1 mL)–hexane (9 mL). After being filtered, samples were injected onto a LiChrosorb Diol (125-4) glass column or a CN (250-4) column attached to a UV detector (254 nm). Chromatographies took ca. 40 min, and signals were identified by peak enhancements with the isolated samples. Correction for the different absorption of the products at 254 nm was introduced. The reaction conditions (which were found to be the optimal) and the corresponding retention times (min) were as follows. Diol column: (*Z*)-**5**-Cl (13.5), (*E*)-**5**-Cl (15), (*E*)-**9** (24), (*Z*)-**9** (27), (*Z*)-**5**-Br (12.5), (*E*)-**5**-Br (13.5) with 1:9 CH_2Cl_2–hexane, 0.4 mL/min; (*E*)-**5**-OMs (26), (*Z*)-**5**-OMs (34), (*E*)-**9** (13), (*Z*)-**9** (14) with 15:85 CH_2Cl_2–hexane, 0.4 mL/min. CN column: (*E*)-**9** (14), (*Z*)-**9** (15), (*Z*)-**5**-OTs (18), (*E*)-**5**-OTs (19), (*Z*)-**5**-OMs (20), (*E*)-**5**-OMs (25) with 30:70 CH_2Cl_2–heptane, 0.5 mL/min.

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Supplementary Material Available: Figures S1 and S2 giving stereoscopic views of (*Z*)-**5**-OMs and **7** and Tables S1–S8 giving their bond lengths and angles and position and thermal parameters (8 pages). Ordering information is given on any current masthead page.