2% ethyl acetate in hexane. The cyclobutanes eluted first and were identified by comparison with samples previously isolated (vide supra). Adduct **5** followed and was obtained as an oil. The structure assignment is based on the NMR and GC/MS data: NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.25 (s, 9 H), 3.10 (s) and 3.25, 3.38 (AB, J = 13.5 Hz, 5 H), 5.45, 5.70 (AB, J = 16 Hz, 2H), 7.10–7.50 (m, 10 H); GC/MS (15 eV) m/e (relative intensity) 206 (2, $PhCH_2CPhCN^+$), 141 (100, $MeOC(CH_3)_2CH{=}CHC(CH_3)_2^+$), 109 (90, 2^+), 92 (3, $PhCH_2^+$).

Irradiation of 1 and 2 in Ethanol. A 250-mL ethanol solution containing 5.1 g of 1 and 27.5 g of 2 was degassed by bubbling nitrogen through the solution for 15 min and irradiated 24 h through Pyrex with a Hanovia 450-W medium-pressure mercury lamp. The solvent was removed under reduced pressure. The crude product mixture was dissolved in heptane and extracted three times with acetonitrile and then three times with methanol. The methanol solutions were combined, and the solvent was removed under reduced pressure to yield **6** (R = C_2H_5) as an oil. The structure was assigned on the basis of the mass spectra and NMR data: NMR ($CDCl_3$) δ 5.6 (d, J = 16 Hz), 5.4 (d, J = 16 Hz), 3.3 (q, J = 6.8 Hz), 1.25 (s) 1.15 (t, obscured by singlets), 0.95 (s); GC/MS (15 eV) m/e (relative intensity) 155 (93, $EtOC(CH_3)_2CH{=}CHC(CH_3)_2^+$), 110 (100, 2^+), 109 (100). Cycloadducts were identified by comparison with previously isolated samples (vide supra).

Irradiation of 1 and 2 in Acetonitrile. A 200-mL acetonitrile solution containing 6.7 g of 1 and 27.5 g of 2 was degassed by bubbling nitrogen through the solution for 15 min and irradiated through Pyrex for 52 h with a Hanovia 450-W medium-pressure mercury lamp. The solvent and other volatiles were removed under reduced pressure. A 1-g sample of the crude product was chromatographed on 350 g of alumina, eluting with 2% ethyl acetate in hexane. The cycloadducts eluted first and were identified by comparison with previously isolated samples (vide supra). These were followed by **5**, which was isolated as a mixture of cycloadducts and **5**. A sample of this mixture was chromatographed successively on two preparative thick-layer plates to yield pure **5** as an oil: NMR ($CDCl_3$), δ 6.9–7.4 (m, 10 H), 5.85 (br s, 2 H), 3.2 (s, 2 H), 2.8 (s, 2 H), 1.75 (s) and 1.60 (s) and 1.55 (s) (12 H); GC/MS (15 eV): m/e (relative intensity) 315 (9, 8^+), 109 (100, 2^+), 91 (3, $PhCH_2^+$).

Irradiation of 2-Methyl-1-phenylpropene with 9-Phenanthrenecarbonitrile. A 100-mL solution of 10% methanol in acetonitrile containing 0.15 g of 9-phenanthrenecarbonitrile and 2.0 g of 2-methyl-1-phenylpropene was degassed by bubbling nitrogen through the solution for 10 min and irradiated through Pyrex for 22 h with a Hanovia 450-W medium-pressure mercury lamp. The solvent was removed under reduced pressure and the residue distilled in a Kugelrohr apparatus. The middle fractions [bp 105–118 °C (14 mm)] were combined to yield 1.67 g (65%) of 2-methoxy-2-methyl-1-phenylpropane: NMR ($CDCl_3$) δ 1.13 (s, 6 H), 2.73 (s, 2 H), 3.23 (s, 3 H), 7.20 (s, 5 H).

Acknowledgment. Support for this work was provided by the National Science Foundation (Grant No. CHE80-26020).

Registry No. *trans*-**1**, 16610-80-3; **2**, 764-13-6; **3a**, 80764-29-0; **3b**, 80795-29-5; **4a**, 80764-30-3; **4b**, 80795-30-8; **5**, 80764-31-4; **6** (R = *n*-Pr), 80764-32-5; **6** (R = C_2H_5), 80764-33-6; **7**, 2286-54-6; **8** (R = CH_3), 80764-34-7; β,β-dimethylstyrene, 768-49-0; 2-methoxy-2-methyl-1-phenylpropane, 69278-45-1; 9-cyanoanthracene, 1210-12-4; 9-cyanophenanthrene, 2510-55-6; 2-cyanonaphthalene, 613-46-7; 1-cyanonaphthalene, 86-53-3.

Nucleophilic Attacks on Carbon–Carbon Double Bonds. 28.[1,2] Complete and Partial Stereoconversion in the Substitution of Methyl (*E*)- and (*Z*)-β-Chloro-α-cyano-*p*-nitrocinnamates by Nucleophiles

Zvi Rappoport* and Bianca Avramovitch

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

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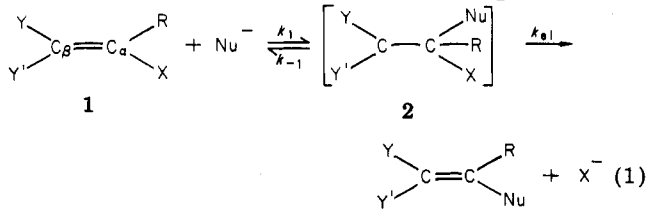
Methyl (*E*)- and (*Z*)-β-chloro-α-cyano-*p*-nitrocinnamates **5-E** and **5-Z** were prepared and separated. The stereochemistry of the substitution of the chlorine by nucleophiles was investigated in MeCN, MeOH, or their mixtures. Reaction with *p*-toluenethiolate ion gave only the *Z* substitution product **10-Z**. Reaction with MeO^- under kinetic control gave 67:33 and 33:67 mixtures of the (*E*)- to (*Z*)-methyl vinyl ethers on starting from **5-E** and **5-Z**, respectively. With excess MeO^- the MeOH adduct of the vinyl ether was obtained. Reaction with the *p*-cresolate ion gave 68:32 and 40:60 *E*/*Z* ratios of the corresponding ethers, on starting from **5-E** and **5-Z**, respectively. The thermodynamically controlled ratio of 77:23 *E*/*Z* ethers is obtained after longer reaction times. Both **5-E** and **5-Z** gave mutual isomerization to a 68:32 **5-E**/**5-Z** mixture with Et_4NCl in MeCN. $NaBH_4$ reduces both the chlorine and the double bond, N_3^- gives a nitrene-rearrangement product, and AcO^- and CF_3COO^- ions give methyl α-cyano-β-hydroxy-*p*-nitrocinnamate in their reactions with **5-E** and **5-Z**. The reactions with p-$MeC_6H_4S^-$, MeO^-, p-$MeC_6H_4O^-$, and Cl^- represent complete or partial stereoconversion in the substitution which differs from the usual stereochemical outcome of retention of configuration. This was predicted for a nucleophilic substitution of highly electrophilic olefins and indicates the intermediacy of relatively long-lived carbanionic intermediates which undergo internal rotation of 60°, 120°, and >120° before leaving-group expulsion.

An important question concerning the mechanism of nucleophilic vinylic substitution via addition–elimination[3,4] [eq 1; Y,Y′ = activating groups, X = nucleofuge (leaving group), Nu = nucleophile] is whether the reaction is a



single-step or a multistep process. In the single-step process, C_α–Nu bond formation and C_α–X bond cleavage are concerted (and these bonds in **2** are partial), the C_α–C_β bond remains mainly a double bond throughout the sub-

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(2) Preliminary report: Avramovitch, B.; Rappoport, Z. 47th Meeting of the Israel Chemical Society, Rehovot, Israel, Sept 29–30, 1980; Abstracts, p 196.

(3) (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1–114. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73–80. (c) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211–1218.

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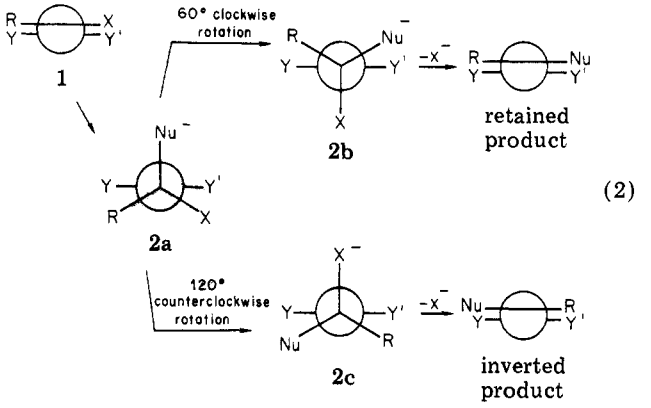
stitution, and **2** is a transition state. In the multistep process C_α–Nu bond formation precedes the C_α–X bond cleavage, and **2** is an intermediate carbanion with a single C_α–C_β bond.

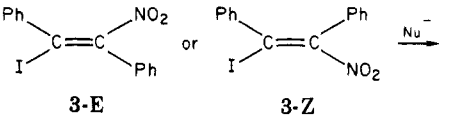
Various mechanistic tools including the stereochemistry of the substitution,[5] the observation of base catalysis,[6] the effect of the leaving group,[7] and MO calculations[1,8] were used to probe this question which was discussed in several papers and reviews.[1-10] In a recent review[4] one of us suggested that there is overwhelming evidence for a multistep route for poor nucleofuges. A hypothesis was advanced according to which **2** is a sufficiently long-lived intermediate when Y and Y′ are strongly resonative electron withdrawing and X is a good nucleofuge (e.g., Cl). When Y and Y′ become less electron withdrawing, the lifetime of **2** will become shorter until the k_1 and k_{el} steps merge into a single step, when **2** will be only a transition state. There is strong evidence for the multistep route for good nucleofuges with highly activated systems.[4]

An important tool in the mechanistic studies is the stereochemistry of the substitution. In most studies with singly activated systems (e.g., **1**; Y = CN, CO_2R, SO_2R; Y′ = R, H) and a good nucleofuge the outcome was mainly or exclusively retention of configuration regardless of whether the precursor had an *E* or a *Z* configuration.[3-5,9,10] This is a main argument for the single-step route since it involves a "least motion" process, and if the nucleophilic attack is on the π^* orbital, perpendicular to the plane of the double bond, as is usually assumed, it is difficult to visualize a concerted process with inversion.[11] In contrast, inversion or stereoconvergence,[3c] i.e., the formation of the same *E*/*Z* product ratio on starting either from the (*E*)- or the (*Z*)-vinylic system, is easily accommodated into a multistep mechanism involving an intermediate carbanion capable of internal rotation. The initially formed carbanion **2a** gives by internal rotation two conformers which can eliminate X^- with the formation of the substitution product. Conformer **2b** is obtained by 60° clockwise rotation, and elimination gives a retained product, while conformer **2c** is obtained by 120° counterclockwise rotation (or 240° clockwise rotation) and gives the inverted product (eq 2). Since **2a–c** can also be obtained from the geometrical isomer of **1**, stereoconvergence by this route is plausible. Recent calculations showed that due to hyperconjugative $2p(C^-)$–σ^*(C–X) stabilization of the carbanion, the 60° rotation will be preferred over the 120° rotation.[1] These calculations also showed that the barrier to internal rotation will decrease on increasing the negative charge dispersal ability of Y and Y′ which reduces the hyperconjugative stabilization. Consequently, the higher the electron withdrawal by Y and Y′ the lower will be the preference for 60° rotation, and since k_{el} will also become smaller, a partial or complete stereoconvergence may be obtained.[4] Such observation will strongly support the theory of a variable transition state in nucleophilic vinylic substitution and the intermediacy of carbanions, at least for activated systems.



(2)

This prediction was indeed fulfilled in a study of the substitution of (*E*)- and (*Z*)-α-iodo-β-nitrostilbenes (**3-E** and **3-Z**) by nucleophiles.[12] Iodine is a good nucleofuge, and although the system is singly activated by a nitro group, the activation is presumably higher than that supplied by a combination of two good activating groups such as CN and CO_2R, as judged by the lower pK_a of CH_3NO_2 compared with those of $CH_2(CN)_2$, $CH_2(CN)CO_2R$, and $CH_2(CO_2R)_2$.[13] With *p*-$MeC_6H_4S^-$ or SCN^-, both isomers gave a single substitution product and with N_3^- a single cyclization product (eq 3).[12]



$PhC(Nu)=C(NO_2)Ph$ (3)

4 (single isomer)

Consequently, both complete stereoconvergence with the highly activated system **3** and complete retention with the moderately activated systems where Y = CN, CO_2Me, and SO_2R and Y′ = H,R[3,5] have been observed with good nucleofuges. An intermediate behavior is expected when the electron-withdrawing power of Y and Y′ is intermediate between these extremes. In order to define more sharply the dividing line between the retention and the stereoconversion routes, we studied the substitution of methyl (*E*)- and (*Z*)-β-chloro-α-cyano-*p*-nitrocinnamates (**5-E** and **5-Z**), a system carrying a good nucleofuge (X = Cl) but

(5) E.g.: (a) Aguiar, A. M.; Daigle, D. *J. Am. Chem. Soc.* **1964**, *86*, 2299–2300; *J. Org. Chem.* **1965**, *30*, 2826–2828, 3527–3530. Aguiar, A. M.; Archibald, T. G. *Ibid.* **1967**, *32*, 2627–2628. (b) Dodd, D.; Johnson, M. D.; Meeks, B. S.; Titchmarsh, D. M.; Duong, K. N. V.; Gaudemer, A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1261–1267. (c) Maffeo, C. V.; Marchese, G.; Naso, F.; Ronzini, L. *J. Chem. Soc., Perkin Trans. 1* **1979**, 92–97. (d) Marchese, G.; Modena, G.; Naso, F. *Tetrahedron* **1968**, *24*, 663–674. (e) Biougne, J.; Thêron, F.; Vessière, R. *Bull. Soc. Chim. Fr.* **1975**, 2703–2706. (f) Truce, W. E.; Gorbaty, M. L. *J. Org. Chem.* **1970**, *35*, 2113–2117. (g) Montanari, F.; Negrini, A. *Gazz. Chim. Ital.* **1959**, *89*, 1543–1547. (h) Modena, G.; Todesco, P. E. *Ibid.* **1959**, *89*, 866–877. (i) Maioli, L.; Modena, G. *Ibid.* **1959**, *89*, 854–865.

(6) Rappoport, Z.; Ta-Shma, R. *J. Chem. Soc. B* **1971**, 871–881, 1461–1467. Rappoport, Z.; Ronen, N. *J. Chem. Soc., Perkin Trans. 2* **1972**, 955–961. Rappoport, Z.; Peled, P. *Ibid.* **1973**, 616–625; *J. Am. Chem. Soc.* **1979**, *101*, 2682–2693. Rappoport, Z.; Ladkani, D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1045–1052.

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(8) (a) Stohrer, W. D. *Tetrahedron Lett.* **1975**, 207–210. Stohrer, W. D.; Schmieder, K. R. *Chem. Ber.* **1976**, *109*, 285–305. (b) Texier, F.; Henri-Rousseau, O.; Bourgois, J. *Bull. Soc. Chim. Fr.* **1979**, 86–94.

(9) Klein, J.; Levene, R. *J. Am. Chem. Soc.* **1972**, *94*, 2520–2521.

(10) Chalchat, J. C.; Thêron, F.; Vessière, R. *Bull. Soc. Chim. Fr.* **1973**, 2501–2506. Chalchat, J. C.; Thêron, F. *Ibid.* **1974**, 953–957.

(11) Calculations show that in-plane attack of H^- on ethylene is energetically much more expensive than the perpendicular attack (Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1953–1961). In-plane inversion was found in the ring opening of bridged intermediates such as a trialkylthiirenium ion (Capozzi, G.; Lucchini, V.; Modena, G.; Scrimin, P. *Tetrahedron Lett.* **1977**, 911–912. Rappoport, Z. *Ibid.* **1978**, 1073–1076).

(12) Rappoport, Z.; Topol, A. *J. Am. Chem. Soc.* **1980**, *102*, 406–407.

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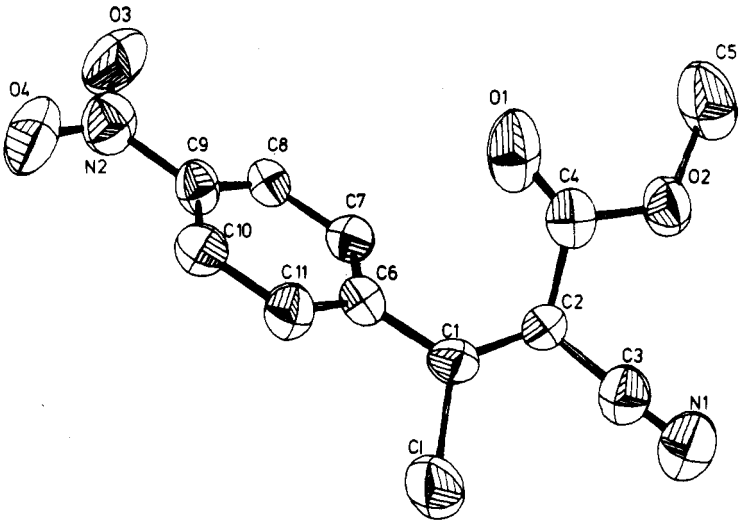
Table I. Crystallographic Data for 5-E



bond	d, Å	atoms	angle, deg	bond	d, Å	atoms	angle, deg
C_1-C_2	1.329	$C_6C_1C_2$	127.64	C_8-C_9	1.384	$C_8C_7C_6$	119.46
C_1-Cl	1.724	C_6C_1Cl	113.93	C_9-C_{10}	1.388	$C_9C_8C_7$	117.26
C_1-C_6	1.494	C_2C_1Cl	118.43	C_9-N_2	1.481	$C_8C_9C_{10}$	124.75
C_2-C_3	1.436	$C_1C_2C_3$	120.56	C_{10}-C_{11}	1.408	$C_8C_9N_2$	117.33
C_2-C_4	1.498	$C_1C_2C_4$	123.41	N_2-O_3	1.207	$C_{10}C_9N_2$	117.92
C_3-N_1	1.129	$C_3C_2C_4$	115.98	N_2-O_4	1.218	$C_9C_{10}C_{11}$	117.61
C_4-O_1	1.198	$N_1C_3C_2$	178.73			$C_6C_{11}C_{10}$	119.03
C_4-O_2	1.318	$O_1C_4C_2$	125.06			$O_3N_2O_4$	123.18
O_2-C_5	1.485	$O_1C_4O_2$	123.90			$O_3N_2C_9$	118.33
C_6-C_{11}	1.392	$O_2C_4C_2$	111.00			$O_4N_2C_9$	118.47
C_6-C_7	1.409	$C_4O_2C_5$	116.90				
C_7-C_8	1.401	$C_{11}C_6C_1$	119.75			AB[a,b]	59.82
		$C_{11}C_6C_7$	121.79			AC[a]	10.02
		$C_7C_6C_1$	118.44			BC[a]	66.51

[a] Dihedral angle: plane A, $ClC_1C_2C_3C_4C_6$; plane B, $C_6C_7C_8C_9C_{10}C_{11}N_2C_1$; plane C, $C_2C_4O_1O_2C_5$. [b] Deviations in angstroms from plane A: C_1, 0.02; C_2, 0.018; Cl, −0.0565; C_6, 0.0135; C_4, 0.1158; C_3, −0.0869.

with a degree of activation by Y, Y′ = CN, CO_2Me which is lower than that for system **3**.

For systems such as **3** or **5** the high electrophilicity may result in additional routes such as nucleophilic preisomerization and postisomerization or electron transfer, which may lead to an apparent stereoconvergence. Little is known about these routes, and we hoped to learn more about them during the study of system **5**.

Results

Synthesis and Assignment of 5-E and 5-Z. A mixture of **5-E** and **5-Z** was synthetized in a method similar to that of Saunier and co-workers[14] by a chlorination–dehydrochlorination sequence of methyl (*E*)-α-cyano-β-*p*-nitrophenylcinnamate (**6**, eq 4). The dichloride **7** was obtained

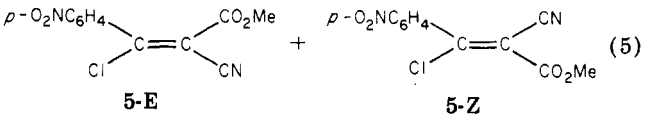
$$p\text{-}O_2NC_6H_4CH{=}C(CN)CO_2Me \xrightarrow{Cl_2} \underset{\mathbf{6}}{} p\text{-}O_2NC_6H_4CH(Cl)C(Cl)(CN)CO_2Me \xrightarrow{Dabco} \underset{\mathbf{7}}{} p\text{-}O_2NC_6H_4C(Cl){=}C(CN)CO_2Me \quad (4)$$
$$\mathbf{5\text{-}E + 5\text{-}Z}$$

by chlorination, but crystallization from methanol or pentane or purification by chromatography failed. Reaction of diazabicyclo[2.2.2]octane (Dabco) with crude **7** gave a mixture which contained **5-E** and **5-Z**, but separation was tedious, and an alternative method was applied.

Reaction of phosphorus oxychloride with methyl β-hydroxy-α-cyano-*p*-nitrocinnamate **8** in the presence of 2 molar equiv of triethylamine (eq 5) gave a 65 ± 3% to 35

$$p\text{-}O_2NC_6H_4COCl + H_2C(CN)CO_2Me \xrightarrow[C_6H_6]{Et_3N} p\text{-}O_2NC_6H_4C(OH){=}C(CN)CO_2Me \xrightarrow{POCl_3/Et_3N}$$

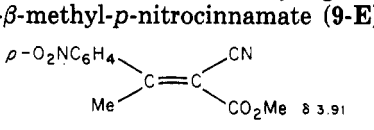
8



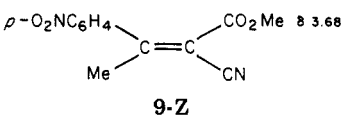
5-E **5-Z** (5)

± 4% mixture of **5-E** and **5-Z**. After various attempts at crystallization or separation it was found that **5-E** can be separated from CCl_4, while **5-Z** is crystallized from the remaining mother liquor with ethyl acetate.

Hayashi showed that the methoxy signal of methyl (*E*)-α-cyano-β-methyl-*p*-nitrocinnamate (**9-E**) in $CDCl_3$



9-E



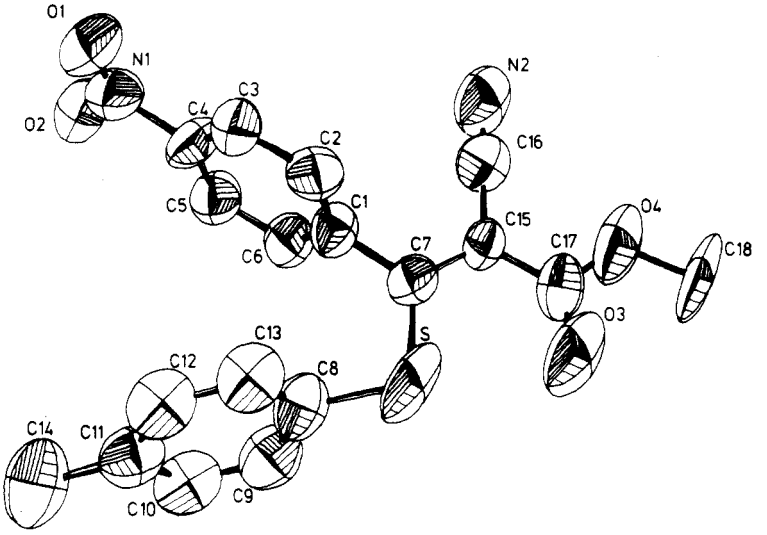
9-Z

appears at a higher field than in the *Z* isomer (**9-Z**).[15]

(14) Saunier, Y. M.; Danion-Bougot, R.; Danion, D.; Carrié, R. *Bull. Soc. Chim. Fr.* **1976**, 1963–1966.

(15) Hayashi, T. *J. Org. Chem.* **1966**, *31*, 3253–3258.

Table II. Crystallographic Data for 10-Z



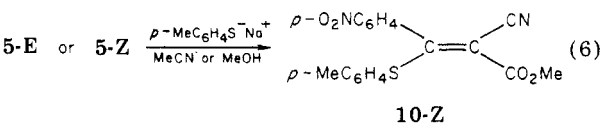
bond	d, Å	atoms	angle, deg	bond	d, Å	atoms	angle, deg	atoms	angle, deg
C_1-C_2	1.41	$C_6C_1C_2$	124.3	C_9-C_{10}	1.41	$C_{15}C_7S$	121.7	$O_3C_{17}C_{15}$	126.4
C_1-C_6	1.38	$C_7C_1C_2$	116.7	C_{10}-C_{11}	1.40	C_8SC_7	103.8	$O_4C_{17}C_{15}$	111.5
C_1-C_7	1.52	$C_7C_1C_6$	119.0	C_{11}-C_{12}	1.42	C_9C_8S	116.7	$O_4C_{17}O_3$	122.0
C_2-C_3	1.42	$C_3C_2C_1$	117.0	C_{11}-C_{14}	1.56	$C_{13}C_8C_9$	123.6	$C_{18}O_4C_{17}$	115.8
C_3-C_4	1.37	$C_4C_3C_2$	117.5	C_{12}-C_{13}	1.41	$C_{10}C_9C_8$	119.4		
C_4-C_5	1.40	$C_5C_4C_3$	125.9	C_{15}-C_{16}	1.43	$C_{11}C_{10}C_9$	119.1	AB[a]	85.45
C_4-N_1	1.50	$N_1C_4C_3$	116.3	C_{15}-C_{17}	1.45	$C_{12}C_{11}C_{10}$	120.5	AC[a]	74.76
C_5-C_6	1.41	$N_1C_4C_5$	117.8	N_2-C_{16}	1.12	$C_{14}C_{11}C_{10}$	119.4	AD[a]	8.12
O_1-N_1	1.17	$C_6C_5C_4$	116.5	O_3-C_{17}	1.18	$C_{14}C_{11}C_{12}$	120.1	BC[a]	43.03
O_2-N_1	1.21	$C_5C_6C_1$	118.7	O_4-C_{17}	1.32	$C_{13}C_{12}C_{11}$	121.5	BD[a]	90.16
S-C_7	1.73	$O_1N_1C_4$	117.7	O_4-C_{18}	1.46	$C_{12}C_{13}C_8$	115.8	CD[a]	82.69
C_{15}-C_7	1.38	$O_2N_1C_4$	116.0	S···O_3	2.74	$C_{16}C_{15}C_{17}$	118.4		
C_8-S	1.79	$O_2N_1O_1$	126.2			$C_{16}C_{15}C_7$	120.2		
C_8-C_9	1.39	SC_7C_1	119.2			$C_{17}C_{15}C_7$	121.2		
C_{13}-C_8	1.41	$C_{15}C_7C_1$	119.1			$NC_{16}C_{15}$	177.0		

[a] Dihedral angle: plane A, $C_7C_{15}C_1SC_{16}C_{17}N_2$; plane B, $C_1C_2C_3C_4C_5C_6N_1$; plane C, $C_8C_9C_{10}C_{11}C_{12}C_{13}SC_{14}$; plane D, $C_{17}C_{18}O_3O_4$.

Since the methoxy signal of the low-melting isomer of **5** is at δ 3.78 and that of the high melting isomer is at δ 3.97, analogy suggests that the former is **5-E** and the latter is **5-Z**. This assignment neglects the difference in the inductive, resonative, and field effects of methyl and chlorine. Corroboration was achieved when the structure of the low-melting isomer was determined by X-ray crystallography[16] and found to be **5-E**. The structural parameters are given in Table I. Noteworthy features are that the aromatic ring is twisted by 60° from the plane of the double bond whereas the deviations of the cyano and carbomethoxy groups from this plane are small. The double bond (1.33 Å) is slightly shorter than that in ethylene (1.34 Å).

The two isomers are relatively stable to isomerization. Both were recovered unchanged after being stirred for 115 h in acetonitrile at room temperature.

Reaction with *p*-Toluenethiolate Ion. The reaction of either **5-E** or **5-Z** with sodium *p*-toluenethiolate in acetonitrile or methanol gave a quantitative yield of only a single isomer of methyl α-cyano-β-*p*-nitrophenyl-β-(*p*-tolylthio)acrylate. This isomer was identified unequivocally as the *Z* isomer **10-Z** isomer **10-Z** (eq 6) by X-ray



(6)

10-Z

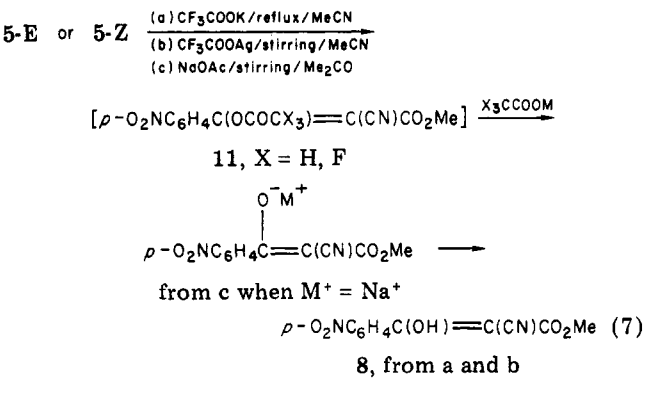
crystallography. The structural data are given in Table II. A 1:1 molar ratio of the two reagents was used in order to avoid postisomerization by the excess *p*-toluenethiolate ion. The reaction was rapid. At a 0.005 M concentration of the reagents in methanol it was complete in ≤45 min. When the reaction of **5-E** in acetonitrile was interrupted after 15 min, 32% of **10-Z** and 68% of **5-E** were observed, whereas interruption of the reaction of **5-Z** after 15 min gave 75% of **10-Z** and 25% of **5-Z**. In either case no trace of the isomeric vinyl halide or the (*E*)-vinyl *p*-toluenethiolate (**10-E**) was observed. Consequently, the stereochemical outcome is complete stereoconvergence.

Reactions with Oxygen Nucleophiles. (a) Reaction with Trifluoroacetate and Acetate Ions. Reflux of a heterogeneous mixture of equimolar amounts of **5-E** or **5-Z** with potassium trifluoroacetate in MeCN for 3 h or stirring equimolar mixtures of **5-E** with silver trifluoroacetate in MeCN at room temperature gave only the enol **8** together with the unreacted chloride. No evidence for the formation of the vinyl trifluoroacetate **11** (X = F) was observed either by NMR or by TLC.

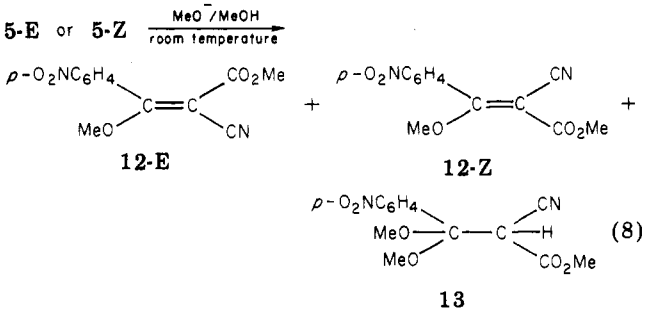
Stirring of either **5-E** or **5-Z** with sodium acetate in acetone at room temperature gave a salt with an approximate analysis for the sodium enolate of **8** and which showed an aromatic quartet and a methoxy singlet in a 4:3 ratio. Acidification with dilute HCl gave the enol **8** which was identified by its infrared spectrum. No vinyl acetate **11** (X = H) was obtained (eq 7).

(b) Reaction with Methoxide Ion. The solubility of **5-E** and **5-Z** in methanol is low, and the reaction with

(16) We are indebted to Dr. S. Cohen for the X-ray data.



NaOMe is partially heterogeneous unless large volumes of the solvent are used. The reaction is rapid, and at equimolar concentrations of ca. 0.0005 M of **5** and MeO^-, ca. 75% reaction is observed after 3 min. The NMR shows the unreacted starting material, the enol **8**, the vinyl ether **12-E**, and another compound with $\delta(CDCl_3)$ 4.29 (1 H), 3.61, 3.41, and 3.36 (3 H each) in the aliphatic region. The latter compound consists of ca. 15% of the product at early reaction times, but it is ca. 50% at the end of the reaction. We ascribe these signals to the formation of **13**, the dimethyl acetal of **8**, by methoxide-catalyzed addition of methanol to the double bond of **12-E** (eq 8). Precedents



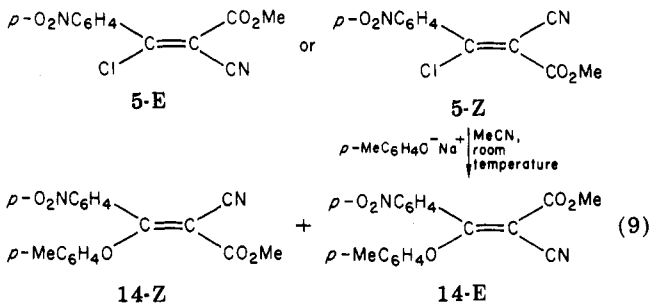
for similar formation of acetals during vinylic substitution by alkoxide ions are available.[17] Attempts to isolate **13** were unsuccessful. Crystallization of the reaction product from methanol gave only the ether **12-E**. When pure **12-E** was reacted with 0.5 M NaOMe/MeOH to give **13** (according to the NMR), the ether **12-E** was recovered on crystallization, and the mother liquor contained the enol **8** and signals which are presumably due to decomposition products. The difficulty in isolating **13** probably reflects the **13** + $MeO^- \rightleftharpoons$ **12-E** equilibrium, and similar difficulties were encountered earlier in attempts to isolate acetals from similar reactions.[17a]

In order to establish the stereochemistry of the substitution under homogeneous conditions, we conducted the reaction in a 4:1 mixture of CD_3CN and CD_3OD (where both reactants are soluble) in an NMR tube. Formation of **13** at early reaction times was avoided by gradual addition of small quantities of NaOMe to a solution of the vinyl chloride so that **5** was always in excess, except when the last portion of the base was added. The NMR spectrum shows the absence of transesterification of the methoxy group of **5** with CD_3OD and the formation of the two vinyl ethers **12-E** and **12-Z** and the acetal **13**. The percentage of **13** is low (1–8%) at short reaction times on starting from either **5-E** or **5-Z**, but it increases up to 99% with the progress of the reaction when the NaOMe concentration exceeds that of the vinyl chloride. The **12-E/12-Z** distribution remains nearly constant during the reaction: 30–35% **12-E** to 65–70% **12-Z** on starting from **5-Z** and 65–68% **12-E** to 32–35% **12-Z** on starting from **5-E**. This is a kinetically controlled product distribution, and it shows that the stereochemical outcome of the substitution is partial stereoconversion.

When **5-E** was reacted with 0.5 M NaOMe in CD_3CN–CD_3OD, **13** was obtained nearly exclusively together with 1% of the enol **8**. The isomer **12-Z** was not formed. This isomer is probably less stable than **12-E**, and when different mixtures of **12-E** and **12-Z** are reacted with 0.1–0.2 M of NaOMe either in MeOH or in CD_3CN-CD_3OD, a mixture containing 93 ± 3% of **12-E** and 7 ± 3% of **12-Z** is obtained. **12-E** was isolated from such a reaction, and its structure was determined by X-ray crystallography.

(c) Reaction with *p*-Cresolate Ion. In order to overcome the problems encountered with the methoxide ion, we conducted the substitution with the *p*-cresolate (*p*-methylphenolate) ion. It is a weaker and a bulkier base than MeO^-, and it was expected to show better solubility properties and slower side reactions.

Reaction of equimolar amounts of sodium *p*-cresolate with **5-E** or **5-Z** in acetonitrile with stirring at room temperature was followed by NMR. The products were the two vinyl ethers **14-E** and **14-Z**, but the isomeric chloride was not formed in either of the reactions (eq 9). At the



concentration range of 0.025 M the reaction is rapid, and 60–90% of the products are formed within 2 min. When the reaction mixture stands for a longer reaction time (e.g., 1–2 h), the initial product distribution slowly changes and the percentage of **14-E** increases at the expense of **14-Z**. The assignments are based on the MeO positions in the NMR.[15]

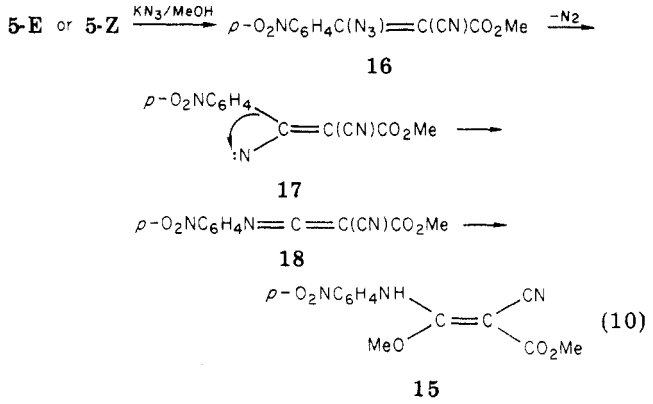
In order to obtain the kinetically controlled product distributions, we followed the reaction in an NMR tube with CD_3CN as the solvent. The sodium *p*-cresolate was added portionwise until an equimolar amount was added, but the concentration of unreacted **5** always exceeded the concentration of the added nucleophile. Under these conditions the product distributions changed only slightly during the first 4 half-lives of the reaction. The extrapolated product distributions were 68 ± 1% of **14-E** to 32 ± 1% of **14-Z** on starting from **5-E** and 40 ± 2% **14-E** to 60 ± 2% of **14-Z** on starting from **5-Z**. Again, a partial stereoconversion is evident.

When the reaction mixtures were left for longer reaction times, the product distributions were changed to 75:25 and 79:21 of **14-E** to **14-Z**, starting from **5-E** and **5-Z**, respectively.

Reaction with Azide Ion. The reaction of either **5-E** or **5-Z** with potassium azide in methanol proceeds rapidly at room temperature with evolution of nitrogen. The isolated product was identified as methyl α-cyano-β-methoxy-β-(*p*-nitrophenyl)acrylate (**15**), and the NMR suggests that it is a single isomer, probably with a *Z* configuration. Its formation is ascribed to a series of reactions involving vinylic substitution to form the vinyl azide **16**,

(17) van der Sluijs, M. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1268–1274.

from which the nitrene **17** is formed by loss of nitrogen. Rearrangement of the *p*-nitrophenyl group to the nitrogen gives the ketenimine **18** which adds methanol across the carbon–nitrogen double bond to form the enamine **15** (eq 10).

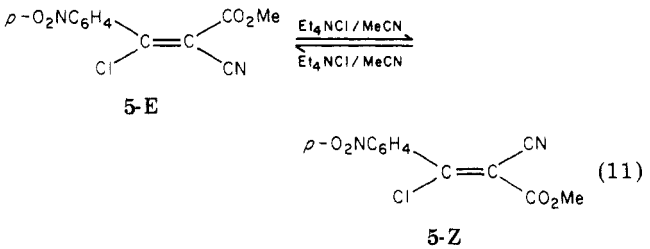


(10)

There are precedents for each step of eq 10. Vinyl azides activated by electron-withdrawing groups lose nitrogen readily, and nitrene rearrangements followed by addition of nucleophiles to the resulting ketenimines are well-known.[18] The stereochemistry is lost in the formation of **18**, but since **15** is a push–pull enamine, it should be configurationally unstable anyway.

When the reaction of **5-E** with KN_3 was repeated in acetonitrile, no product was obtained after 48 h at 0–5 °C. After few hours at room temperature a complex mixture of products, whose composition was a function of the reaction time, was detected by NMR and by TLC. This is presumably due to nitrene reactions and was not investigated further.

Reaction with Halide Ions. (a) With Cl^-. While **5-E** and **5-Z** are stable to mutual isomerization in the absence of catalysts at room temperature in the dark, when either isomer was stirred with Et_4NCl in MeCN, slow isomerization took place (eq 11). When a 0.25 M solution of each

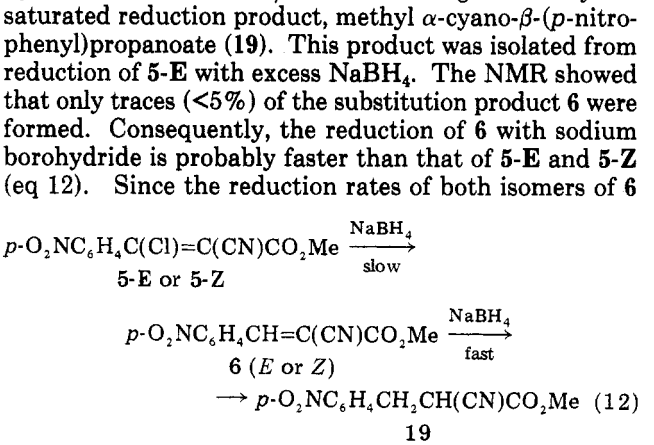


(11)

reactant was used, **5-E** gave 22% of **5-Z** after 20 h, whereas a 68:32 ratio of **5-E** to **5-Z** was observed between 40 and 450 h. Likewise, a 60:40 ratio of **5-E** to **5-Z** was obtained after 40 h on starting from **5-Z**, and a 68:32 ratio was obtained after 150 h. This is apparently the thermodynamic distribution which is also close to that obtained during the preparation of the chlorides. A stereoconversion is therefore evident.

(b) With F^-. The reaction of ethyl β-chloro-α-cyanocinnamate with KF/MeCN in the presence of dibenzo-18-crown-6 gave 65% of fluoride–chloride exchange after 18 h.[14] Suprisingly, although **5** should be more reactive, a similar reaction of equimolar concentrations of **5-E** or **5-Z** with dried KF in the presence of 0.1 molar equiv of dibenzo-18-crown-6 ether in acetonitrile for 4 days gave no reaction. The vinylic chloride started to disappear after 12 h of reflux with the formation of several products, including the potassium enolate of **8**. When tetraethylammonium fluoride dihydrate was used instead of KF, a compound with spectra similar to those of the sodium salt of **8** was isolated.

Reaction with Sodium Borohydride. The reaction of **5-E** or **5-Z** with a 0.25 molar equiv of sodium borohydride in 85:15 MeCN/MeOH for 3 h gave mainly the saturated reduction product, methyl α-cyano-β-(*p*-nitrophenyl)propanoate (**19**). This product was isolated from reduction of **5-E** with excess $NaBH_4$. The NMR showed that only traces (<5%) of the substitution product **6** were formed. Consequently, the reduction of **6** with sodium borohydride is probably faster than that of **5-E** and **5-Z** (eq 12). Since the reduction rates of both isomers of **6**



(12)

will be probably different, no attempt was made to determine the stereochemistry of the small percentage of **6** formed during the reduction.

Reaction with Cyanide Anion. Reaction of dry KCN with **5-E** and **5-Z** in the presence of dibenzo-18-crown-6 ether (in a 1:1:0.1 ratio) is slow at room temperature. On reflux for several hours, the potassium enolate of **8** and several decomposition products, which were not identified further, were formed.

Discussion

The nucleophiles studied belong to two categories: (a) nucleophiles which gave substitution products from which the stereochemical outcome could be delineated (*p*-$MeC_6H_4S^-$, MeO^-, *p*-$MeC_6H_4O^-$, Cl^-); (b) nucleophiles whose reactions give products where the stereochemistry is lost due to further reactions of the initially formed substitution products (N_3^-, AcO^-, CF_3COO^-, BH_4^-, F^-, and probably CN^-). We will mainly discuss the reactions of nucleophiles of the first category and comment briefly on some reactions of nucleophiles of the second group.

The stereochemical outcome in the reactions of the first group is summarized in Table III, which gives both the kinetically controlled and the thermodynamically controlled *E*/*Z* ratios. It will be analyzed in terms of the two-step mechanism (eq 2). The possibility that the stereochemistry is determined by competing routes will be discussed afterward.

Complete and Partial Stereoconvergence. Kinetic Control of the Stereochemistry. On the assumption that the substitution proceeds via a perpendicular nucleophilic attack and an intermediate carbanion, the competition between the rates of internal rotation (k_{rot}) and elimination of X^- (k_{el}) will determine the stereochemistry. If rotation around the C_α–C_β bond is free in the sense that the two conformers formed by attack on the *E* precursor and on the *Z* precursor completely equilibrate by rotation before leaving group expulsion, the product compositions will be determined by the energy difference between the two transition states leading to the *E* and the *Z* products. The steric interactions in the transition states reflect part of the similar, but larger, interactions in the two products, but the products in this case are still those of kinetic control.

The previously studied reactions of **3-E** and **3-Z**[12] and the reactions of **5-E** or **5-Z** with the *p*-toluenethiolate ion

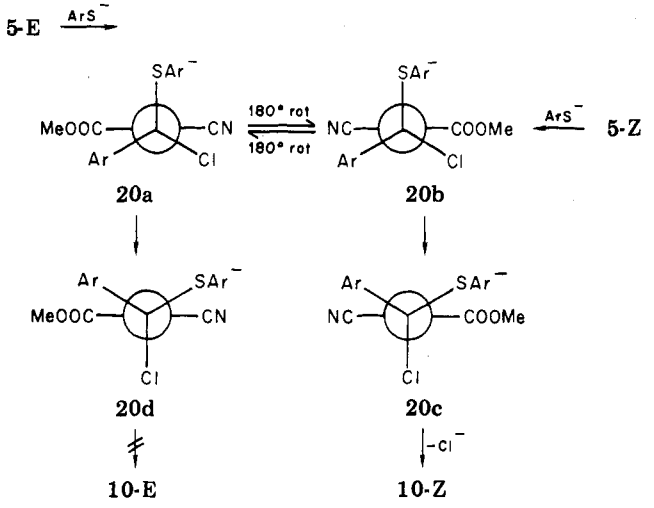
(18) Smolinsky, G.; Pryde, C. A. In "The Chemistry of the Azido Group"; Patai, S., Ed.; Wiley-Interscience: London, 1971; Chapter 10.

Table III. Stereochemistry of the Substitution of 5-E and 5-Z

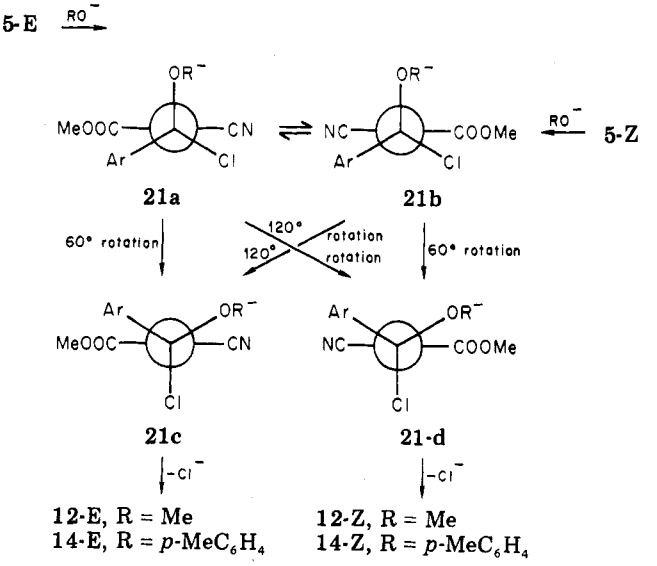
substrate	nucleophile	solvent	E/Z product ratio: kinetically controlled	E/Z product ratio: thermodynamically controlled
5-E	p-$MeC_6H_4S^-$	MeCN or MeOH	0:100[a]	0:100[a]
5-Z	p-$MeC_6H_4S^-$	MeCN or MeOH	0:100[a]	0:100[a]
5-E	MeO^-	CD_3CN-CD_3OD (4:1)	67 ± 2:33 ± 2	93 ± 3:7 ± 3
5-Z	MeO^-	CD_3CN-CD_3OD (4:1)	33 ± 3:67 ± 3	93 ± 3:7 ± 3
5-E	p-$MeC_6H_4O^-$	CD_3CN	68 ± 1:32 ± 1	75:25
5-Z	p-$MeC_6H_4O^-$	CD_3CN	40 ± 2:60 ± 2	79:21
5-E	Cl^-	CH_3CN		68:32
5-Z	Cl^-	CH_3CN		68:32

[a] Within the detection limit of the NMR.

Scheme I



Scheme II



belong to this class. Attack on **5-E** and **5-Z** gives the carbanionic conformers **20a** and **20b** (or their enantiomers), respectively. They are transformed to one another by a 180° rotation (Scheme I). The barriers to internal rotation due to the hyperconjugative stabilization[1] are sufficiently lowered by the β-CN and the β-COOMe substituents so that 60° clockwise rotation followed by elimination of X^- is no more the preferred route for both isomers. The different steric interactions encountered in the rotations in **20a** and **20b** have no influence on the stereochemistry. Elimination of X^- could take place either from conformer **20c** or **20d**. In spite of the apparent larger steric interactions in **20c** (SAr, COOMe; Ar, CN) compared with those in **20d** (SAr, CN; Ar, COOMe), elimination is exclusive via **20c**, leading to **10-Z**. Since **10-Z** is the more stable isomer in spite of the larger steric interactions between cis substituents than in **10-E**, an additional factor which stabilizes both **10-Z** and the transition state leading to it should be operating. We believe that this is a dipole–dipole interaction between the partially positively charged sulfur and the negatively charged oxygen of the *cis*-carbomethoxy group. Evidence for such interaction is discussed in the next section.

The situation is different with MeO^- and p-$MeC_6H_4O^-$ ions. Both isomeric vinyl ethers are obtained from either **5-E** or **5-Z**. The kinetically controlled ratio differs from the thermodynamically controlled one. The extent of stereoconvergence can be given as the sum of the percentages of the retention and the inversion routes. For example, with the p-cresolate ion, **5-E** gives 68% retention and 32% inversion whereas **5-Z** gives 60% retention and 40% inversion.

Since the extents of stereoconvergence are different for **5-E** and **5-Z** and the product distribution from either of them differs from the thermodynamically controlled ratio, the products are due to kinetic control. We will discuss the stereochemistry in terms of competition between the retention and the inversion routes.

When the barrier to rotation is lowered due to the β-CN and β-COOMe groups, the steric effect in the clockwise 60° vs. counterclockwise 120° rotations should be important. The initially formed carbanions from **5-E** and **5-Z** are **21a** and **21b**, respectively (Scheme II). In hyperconjugative stabilization of **21c** and **21d**, the precursor conformers of the elimination products are the same. Consequently, the **12-E**/**12-Z** and the **14-E**/**14-Z** ratios are determined by the relative rates of formation of **21c** and **21d** if it assumed that the elimination of X^- takes place when these conformers are formed. The steric interaction in the transition state of 60° rotation leading to **21c** involves Ar,CO_2Me interactions on starting from **5-E** and **21a**, whereas formation of **21d** by 120° rotation involves Cl,CN and OAr,CO_2Me interactions and loss of hyperconjugative stabilization at the first stages of the rotation. The retention route via **21d** involves an Ar,CN interaction on starting from **5-Z** and **21b**, whereas the inversion route via **21c** involves Cl,CO_2Me and OAr,CN interactions.

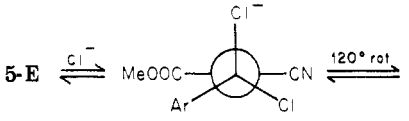
It is therefore not surprising that both **5-E** and **5-Z** show preferential retention, and **12-E** and **14-E** are formed in excess on starting from **5-E**, whereas the opposite is true on starting from **5-Z**. Moreover, the higher percentage of inversion for **5-E** than for **5-Z** is consistent with the larger steric interactions (Cl,CO_2Me) on 120° counterclockwise rotation of **21b** compared with those for the OAr,CO_2Me interaction on 120° rotation of **21a**. In conclusion, the stereochemistry of the substitution with the oxygen nucleophiles is consistent with formation of intermediate carbanions which are long-lived enough to give some in-

version but not sufficiently long-lived to give stereoconversion. The extent of inversion depends on the steric interactions in the transition states leading to the product-forming conformers.

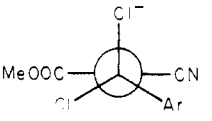
The thermodynamic preference for the *E* isomers is reminiscent of the higher stability of the corresponding chlorides and suggests that the p-$O_2NC_6H_4$,CO_2Me interaction is smaller than the OR,CO_2Me interaction.

An interesting question is the reason for the difference between the analogous sulfur and oxygen nucleophiles p-$MeC_6H_4G^-$ (G = O or S); i.e., why for G = S is $k_{rot} > k_{el}$ while for G = O $k_{el} > k_{rot}$? The MO calculations show that the hyperconjugative barrier to rotation by an SH substituent is 2.3 kcal mol^{-1} lower than that for an OH group in the gas phase,[1] thus increasing k_{rot} for the sulfur-containing carbanion. The dipole–dipole interaction discussed below will operate in the same direction, but steric effects should favor rotation in the (smaller) oxygen-containing carbanion. The main problem is that our understanding of the factors which control elimination of nucleofuges from carbanions is meager, although there has been progress in this field in recent years.[19] A tentative model for the effect of G on k_{el} is given by the relative solvolysis rates of GCH_2Cl (G = O, S). Although the k_O/k_S value of 115[20a] is consistent with our result, extreme caution should be exercised when comparing the k_O/k_S ratios in carbonium ion forming reactions. Values between 20 000 and 0.08 were reported,[20a,b] and it is clear that the ratio is strongly dependent on the system studied.[20] If one excepts Modena's view that the values are higher when the formation of the carbonium ion is less advanced, it is not surprising that in our system $k_{el(O)} > k_{el(S)}$ since positive charge is not developed at all in the transition state for our "solvolysis" step.

The observation of the Et_4NCl-promoted **5-E** ⇌ **5-Z** isomerization is again consistent with the formation of a relatively long-lived intermediate carbanion, **22a** (from **5-E**), which can sometimes undergo 120° or 180° rotation to **22b** before expulsion of the Cl^- (eq 13). Since exchange



22a



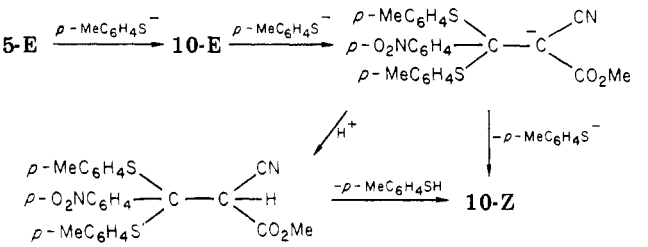
Cl⁻ ⇌ 5-Z (13)

22b

with retention is a degenerate rearrangement, giving back the starting material, it is impossible to determine the retention to inversion ratio from our data. However, this ratio can be evaluated by using a labeled Cl^- as a nucleophile and determining the extent of incorporation in the retained and in the inverted product.[21]

It should be noted that iodide-catalyzed isomerization of β-bromo-*p*-nitrostyrenes[22] and chloride ion catalyzed isomerization of 1-(*p*-anisyl)-1-phenyl-2-chloroethylenes[23]

Scheme III



were observed previously. However, high temperatures were required, and in the latter case the amount of exchange in the inverted product alone was not determined.[23] It is not impossible that the isomerization in both cases may be due to alternative routes.[24] The present case is the first one where isomerization is observed under mild conditions.

Possibility of Stereoconversion via Competing Routes. Although a consistent explanation for the stereoconversion is given above in terms of substitution via long-lived carbanions, it should be realized that the substrates for which the stereoconversion test is applied (systems **3** and **5**) are highly electrophilic olefins, and stereoconversion may result from several other routes. Four of them are discussed for the highly polarizable (soft) *p*-toluenethiolate ion, with comments concerning their feasibility for the other nucleophiles.

(a) A rapid preisomerization of the starting chloride, e.g., **5-E**, to its isomer **5-Z** will give apparent stereoconversion even if the actual substitution step proceeds with retention. This route can be excluded for both the thio and the oxygen nucleophiles for two reasons. First, no isomeric chloride was observed when the reaction was interrupted before completion or when a 2:1 ratio of **5-E** to p-$MeC_6H_4S^-$ was used. Second, it is highly unlikely that the intermediate carbanions will lose (before or after rotation) the poor nucleofuges ArS^-, ArO^-, or RO^- in preference to the much better nucleofuge Cl^-; only in this case a **5-E** ⇌ **5-Z** isomerization will be observed.

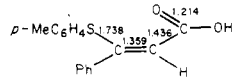
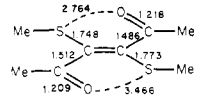
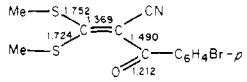
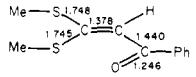
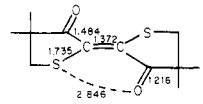
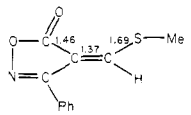
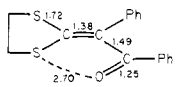
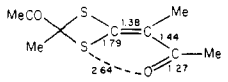
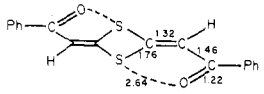
(b) Isomerization of an initially formed substitution product can take place by addition–elimination of the nucleophile as demonstrated in Scheme III. The addition can give only a carbanion from which the elimination can take place or the saturated adduct. In both cases rotation around the C_α–C_β bond will be faster than leaving-group expulsion since now the leaving group is a poor nucleofuge.

Indeed, this route is probably responsible for the slow change in the kinetically controlled ratio to the thermodynamically controlled ratio in the reactions with the oxygen nucleophiles. The acetal **13** was indeed detected in the reaction mixtures, and it may be the main product in the presence of excess nucleophile. The portionwise addition of the nucleophile reduced the contribution of this route to a minimum and gave the kinetically controlled distribution with the oxygen nucleophiles. The absence of the corresponding thioacetal in the reaction of p-$MeC_6H_4S^-$ suggests that under our reaction conditions this route has no importance.

It is noteworthy that with $NaBH_4$ as the nucelophile, the addition of the nucleophile to the substitution product is fast and irreversible so that **19** is the main product and the stereochemical information is lost.

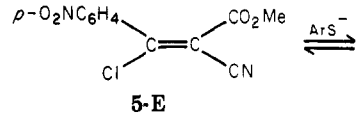
(19) Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *12*, 198–203.
(20) (a) Modena, G.; Scorrano, G.; Venturello, P. *J. Chem. Soc., Perkin Trans, 2* **1979**, 1–6. (b) Chwang, W. K.; Kresge, A. J.; Wiseman, J. R. *J. Am. Chem. Soc.* **1980**, *101*, 6972–6975. (c) Taft, R. W., Jr.; Martin, R. H.; Lampe, F. W. *Ibid.* **1965**, *87*, 2490–2492. (d) Saeva, F.; Olin, G. R. *Ibid.* **1980**, *102*, 299–303.
(21) This experiment is now is progress in Professor J.-I. Hayami's laboratory in Kyoto University, Japan.
(22) Miller, S. I.; Yonan, P. K. *J. Am. Chem. Soc.* **1957**, *79*, 5931–5937.
(23) Beltrame, P.; Bellobono, I. R.; Ferē, A. *J. Chem. Soc. B* **1966**, 1165–1169.
(24) E.g., a reaction which takes place by electron transfer from the I^- to the nitrostyrene is a mechanistic possibility.

Table IV. Structural Data for Some Compounds with the S—C=C—C=O Subunit[a]

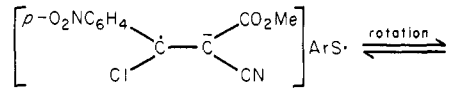
no.	compd	ref
1		b
2		c
3		d
4		e
5		c
6		f
7		g
8		h
9		i

[a] Bond lengths in angstroms. [b] Stephens, F. S. *J. Chem. Soc. A* **1970**, 1843–1846. [c] Ammon, H. L.; Hermann, H. *J. Org. Chem.* **1978**, *43*, 4581–4586. [d] Abrahamsson, S.; Rehnberg, G.; Liljefors, T.; Sandström, J. *Acta Chem. Scand., Ser. B* **1974**, *28*, 1109–1120. [e] Mellor, I. P.; Nyburg, S. C. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1954–1958. [f] van Meerssche, M.; Verdonq, B.; Germain, G.; Declercq, J. P. *Bull. Soc. Chim. Belg.* **1977**, *86*, 97–107. [g] Schmidt, W. H.; Tulinsky, A. *Tetrahedron Lett.* **1967**, 5311–5313. [h] Kapecki, J. A.; Baldwin, J. E.; Paul, I. C. *J. Am. Chem. Soc.* **1968**, *90*, 5800–5805. [i] Lynch, T. R.; Mellor, I. P.; Nyburg, S. C.; Yates, P. *Tetrahedron Lett.* **1967**, 373–377.

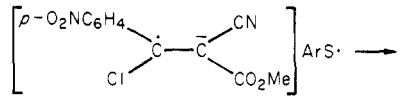
(c) A reversible one-electron transfer from the thiolate ion to the chloro olefin, e.g., **5-E**, will give initially the radical–anion pair **23-E**. This can rapidly convert to the isomeric radical anion pair **23-Z** by rotation. Recombination of the two radicals within **23-Z** will give the anion **20c**, which by Cl^- expulsion will give **10-Z** (eq 14). This is not an unlikely possibility in view of the high electrophilicity of **5-E**, the presence of the *p*-nitrophenyl group, and the ability of the thio nucleophile to be involved in an electron transfer process.[25] Some features of this process can be excluded. Since no **5-E** ⇌ **5-Z** isomerization was observed during the reaction, the steps leading from **23-Z** to **5-E** should be slower than the forward steps leading to **10-Z**. Addition of hydroquinone had no effect either on the reaction rate or on its stereochemistry, indicating that if process 14 is occurring, it is not a chain process. At present we do not have any other evidence to exclude this route with *p*-$MeC_6H_4S^-$. However, for this



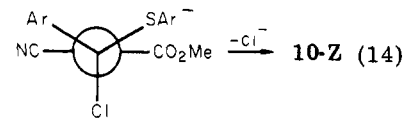
5-E



23-E



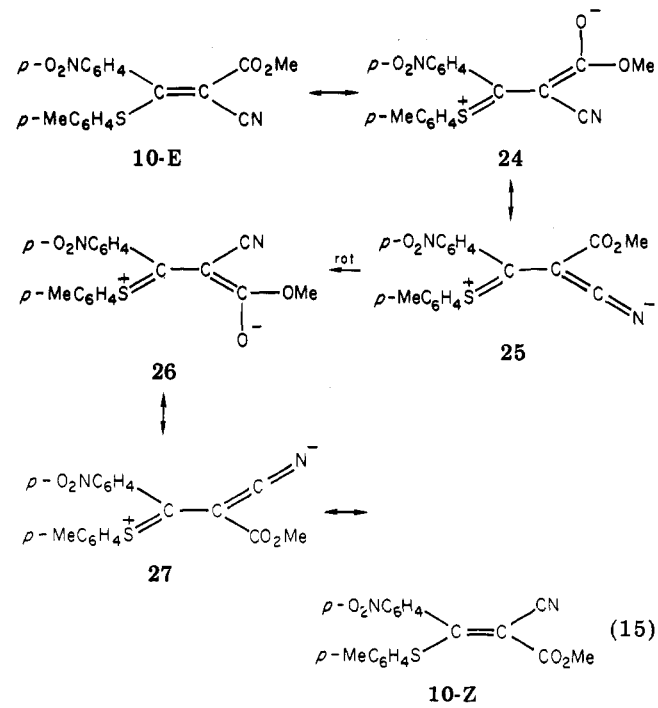
23-Z



20c

reason the reaction with the oxygen nucleophile was performed, since these nucleophiles are much less prone to be involved in an electron transfer process due to the much higher ionization potentials. The fact that a partial stereoconversion was observed with these nucleophiles suggests that the reaction of *p*-$MeC_6H_4S^-$ will be a "normal" nucleophilic substitution via a simultaneous two-electron transfer, rather than substitution via two consecutive one-electron transfers.

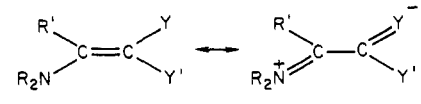
(d) Since the products are push–pull ethylenes, it is possible that there will be a rapid dynamic equilibrium between the *E* and the *Z* isomers at room temperature due to a partial single bond between C_α and C_β (cf. structures **24–27** in eq 15). Contributions of structures such as **29**



10-E **24** **26** **25** **27**

10-Z

(eq 16; similar to **24–27**) to the overall structure of acti-



28 **29**

vated enamines **28** are responsible for the configurational

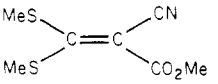
(25) For related reactions see: (a) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734–745. (b) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59–67.

instability of the enamines.[26] If the same phenomenon is applicable for **10-E**/**10-Z**, **10-Z** should be the thermodynamically more stable isomer, as is indeed the case.

The contributions of structures **26** and **27** (and by analogy of **24** and **25**) to the ground-state structure of **10-Z** is corroborated by the X-ray data (Table II) for this compound. The following features are relevant. (a) The C_α–C_β bond length is 1.38 Å, which is longer than the double bond (1.34 Å) in ethylene[27] or in **5-E** (1.33 Å, Table I). (b) The C_α–S bond length is 1.73 Å, which is shorter than the usual value of 1.75 Å for an C(sp^2)–S bond.[27] (c) The C_β—C=O bond length of 1.44 Å is shorter than the value of 1.48 Å found in many esters.[27] (d) The two substituents on C_β and the sulfur on C_α are in the plane of the double bond. (e) The dihedral angles between the aromatic rings and the plane of the double bond are large, being 85° with the *p*-$O_2NC_6H_4$ ring and 75° with the *p*-MeC_6H_4S ring. (f) The sulfur is 0.085 Å out of the plane of its substituent aromatic ring. (g) The C≡N and the C—CN bond lengths of 1.125 and 1.434 Å, respectively, are similar to the corresponding values for **5-E** (1.129 and 1.435 Å, (Table I). The C≡N bond length is shorter than in HCN (1.16 Å),[27] whereas the C—CN bond is similar to that in acrylonitrile (1.43 Å).[27]

Consequently, the double bond is longer and the C_β–CO_2Me and C_α-SAr bonds are shorter than in compounds where the interaction between the substituents on C_α and C_β does not exist. However, a longer C_α–C_β bond does not necessarily mean that the **10-E** ⇌ **10-Z** interconversion is fast under the reaction conditions. In order to probe this question, we searched the literature for a correlation between the C_α–C_β bond length and the ability to separate stable isomers in structurally related compounds. The Cambridge data file[28] gave 72 compounds with the S—C=C—C=O subunit whose structures were determined by X-ray crystallography. However, most of these include thiophenes and related compounds which are irrelevant to our problem. The few compounds which give relevant data are given together with some structural parameters in Table IV. The following conclusions are pertinent. (i) In all cases where C_β is substituted by electron-withdrawing groups and C_α by electron-donating groups the double bond is longer than in ethylene. We did not find any literature reference to a relation between this phenomenon and the free-energy barrier to rotation around the double bond. (ii) The interaction between the opposite charges on sulfur and on the carbonyl oxygen when the two groups are in a cis relationship stablizes the dipole and decreases the distance between sulfur and oxygen at the expense of other distances in the molecule. This is especially surprising in the case of (*E*)-3,4-bis(methylthio)-2,5-pentanedione, where one S–O bond distance is shortened at the expense of the other, although the molecule is symmetrical. The sum of the van der Walls radii of sulfur (1.85 Å) and oxygen (1.4 Å) is 3.25 Å, and in several systems the S–O bonds are shorter than this value. Although crystal packing effects may be important in this respect, it is noteworthy that the S–O bond distance in **10-Z** is one of the shortest found so far,[29] and it may reflect a dipole–dipole stabilization (cf. structure **26**) of the close charges which is absent in **24**. Consequently, this dipole–dipole interaction may be responsible for the higher stability of **10-Z** than of **10-E**. (iii) Only in two cases, compounds **1** and **5** in Table IV,[30,31] were the two geometrical isomers isolated and separated. In both cases the carbon–carbon double bond is shorter and the carbon–sulfur bond longer than those in **10-Z**. However, the difference in the relevant bond lengths between **10-Z** and these compounds is small, indicating that fast rotation as described in eq 15 is unlikely.

This conclusion is corroborated by NMR data on internal rotation in compounds **30** and **31** which contain the



30

31

same structural moieties as **10-Z**. Compound **30** differs from **10-Z** in having a MeS group on C_α instead of a *p*-$O_2NC_6H_4$ group. The free energy of activation for the rotation around the C_α–C_β bond of **30** at 25 °C is 24.6 kcal mol^{-1}.[32] It can be expected that since C_α in **10-Z** is substituted by an electron-withdrawing substituent, the $\Delta G^\ddagger$ value for the rotation will be much higher. The $\Delta G^\ddagger$ value at 25 °C for **31** is >27.5 kcal mol^{-1},[33] and since Me is more electron-donating than *p*-$O_2NC_6H_4$, whereas CN is resonatively less electron withdrawing than CO_2Me, the same conclusion is obtained: the formation of **10-Z** in the substitution is not due to free rotation around the C_α–C_β bond.

The problem does not exist with the oxygen analogues where the two isomers are stable at room temperature.

Side Reactions. Two side reactions deserve comment. The faster reaction of **6** than of **5-E** or **5-Z** with $NaBH_4$ indicates that at least with this nucleophile the inductive electron-withdrawing effect of the chlorine is more than offset by its steric bulk compared with hydrogen when a perpendicular attack by the bulky nucleophile takes place. It is interesting to note that since the rates of reduction of **6-E** and **6-Z** are probably different, even if the reductions of **6** and **5** proceed with similar rates the stereochemical information will be lost, unless extrapolation of the product distribution to very low reaction percentages will be made.

The formation of the enol **8** from the reactions of **5** with acetate and trifluoroacetate ions have many precedents in vinylic solvolysis in AcOH.[34] However, the reaction here proceeds under much milder conditions and is probably due to increased electrophilicity of the carbonyl oxygen of the ester by the three electron-withdrawing α and β substituents and the CF_3 group when X = F. The formation of the enol probably follows the sequence of eq 17 (X = H, F).

Conclusions. The observation of complete or partial stereoconversion in the reaction of **5** with several nucleophiles supports the variable-transition-state theory for nucleophilic vinylic substitution[4] and suggests that stereoconversion or even retention (depending on the bulk of the substituents and the relative stabilities of the sub-

(26) E.g.: Shvo, Y.; Shanan-Atidi, H. *J. Am. Chem. Soc.* **1969**, *91*, 6683–6689, 6689–6696. Kalinowski, H. O.; Kessler, H. *Top. Stereochem.* **1973**, *7*, 295–383. Jackman, L. M. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 7.

(27) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 23.

(28) The Cambridge data base which is published by the Cambridge crystallographic data center comprises files of bibliographic data for organic and organometallic compounds studied by X-ray and neutron diffraction methods.

(29) Very short S–O distances (2.04–2.41 Å) were found in substituted dithiapentalenes: Hordvik, A.; Sletten, E.; Sletten, J. *Acta Chem. Scand.* **1969**, *23*, 1377–1388. Mammi, M.; Bardi, R.; Troverso, G.; Bezzi, S. *Nature (London)* **1961**, *150*, 1282.

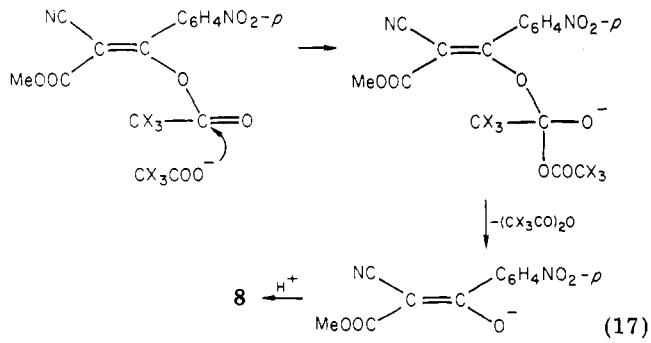
(30) Stephens, F. S. *J. Chem. Soc. A* **1970**, 1843–1846.

(31) Ammon, H. L.; Hermann, H. *J. Org. Chem.* **1978**, *43*, 4581–4586.

(32) Isaksson, G.; Sandström, J. *Acta Chem. Scand.* **1967**, *21*, 1605–1611.

(33) Shvo, Y.; Belsky, I. *Tetrahedron* **1969**, *25*, 4649–4665.

(34) For a review see: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.



(17)

stitution products) will be observed for systems with similar or higher activation than **5**, such as **3**.[12] Other systems which were previously studied and showed retention[5] were usually much less activated, usually only by a single (although not NO_2) group. The observation of a partial stereoconversion with the oxygen nucleophiles suggests therefore that the border region between stereoconversion and retention is closer to the diactivated system **5** than to the monoactivated systems RC(Cl)=CR'Y (Y = CN, CO_2Me, SO_2R, etc.). Consequently, we predict that systems with a degree of activation between the latter ones and **5** will show exclusive or nearly exclusive retention of configuration in substitution via addition–elimination.

Experimental Section

Melting points were measured with a Thomas-Hoover instrument and are uncorrected. Ultraviolet spectra were recorded with a Varian Techtron 635 instrument and infrared spectra with a Perkin-Elmer 157G instrument. NMR spectra were measured with Varian H-100 and T-60 instruments or with a Brucker Spectrospin 300-MHz instrument, and the chemical shifts are given in parts per million downfield from internal tetramethylsilane. Mass spectra were recorded with an MAT 311 instrument and are given in terms of m/e (relative intensity) values compared with the base peak and possible assignments.

Methyl β-Hydroxy-α-cyano-*p*-nitrocinnamate (8). To a mixture of *p*-nitrobenzoyl chloride (93 g, 0.5 mol) and methyl cyanoacetate (49.5 g, 0.5 mol) in dry benzene (500 mL) was added triethylamine (101 g, 1 mol) dropwise with stirring at 0–5 °C. Triethylammonium chloride precipitated immediately, and the solution turned red. The stirring was continued for 3 h, the salt was filtered, the solvent was evaporated, and the red oil obtained was dissolved in methanol (100 mL). Addition of HCl (10 mL) gave methyl β-hydroxy-α-cyano-*p*-nitrocinnamate (115.5 g, 90%) which was filtered and crystallized from methanol, giving yellow prisms of pure **8**: mp 158 °C (lit.[35] mp 159–160 °C); UV (MeCN) λ_{max} 302 nm (log ε 4.00); IR (KBr) ν_{max} 3420(OH), 2220 (s, CN), 1670 cm^{-1} (s, COOMe); NMR ($CDCl_3$) δ 4.01 (3 H, s, MeO), 8.2 (4 H, AA'BB' q, Ar), 12.04 (1 H, br s, OH); mass spectrum, m/e (relative intensity) 248 (50, M), 150 (100, p-$O_2NC_6H_4CO$), 104 (18, C_6H_4CO). Anal. Calcd for $C_{11}H_8N_2O_5$: C, 53.22; H, 3.22; N, 11.30. Found: C, 52.97; H, 3.48; N, 11.65.

Methyl (*E*)- and (*Z*)-β-Chloro-α-cyano-*p*-nitrocinnamates (5-E and 5-Z). To a mixture of the enol **8** (5 g, 0.02 mol) in dry methylene chloride (100 mL) was added phosphorus oxychloride (3 g, 0.02 mol). Triethylamine (4.04 g, 0.04 mol) was added dropwise with stirring, and the mixture was refluxed for 5 h. The triethylammonium chloride was filtered, the solvent was evaporated, and the remainder was extracted 10–20 times with dry ether (50-mL portions). On evaporation of the solvent a 65:35 mixture of **5-E** to **5-Z** was obtained. Repeated recrystallization from carbon tetrachloride gave methyl (*E*)-β-chloro-α-cyano-*p*-nitrocinnamate (**5-*E***), mp 149 °C. The mother liquor, which is enriched with the *Z* isomer, was evaporated, and the residue was crystallized from ethyl acetate, giving the pure *Z* isomer, mp 162 °C.

5-E: UV (MeCN) λ_{max} 283 nm (log ε 3.97); IR (KBr) ν_{max} 2220 (s, CN), 1740 cm^{-1} (vs, COOMe); NMR ($CDCl_3$) δ 3.78 (3 H, s, MeO), 8.00 (4 H, AA'BB' q, Ar); mass spectrum, m/e (relative intensity) 266 (100, M), 235 (63, M – MeO), 231 (81, M – Cl). Anal. Calcd. for $C_{11}H_7ClN_2O_4$: C, 49.53; H, 2.63; N, 10.50; Cl, 13.32. Found: C, 49.34; H, 2.50; N, 10.18; Cl, 13.05.

5-Z: UV (MeCN) λ_{max} 285 nm (log ε 4.25); IR (Nujol) ν_{max} 2215 (m, CN), 1730 cm^{-1} (vs, COOMe); NMR ($CDCl_3$) δ 3.97 (3 H, s, COOMe), 8.12 (4 H, AA'BB' q, Ar); mass spectrum, m/e (relative intensity) 266 (90, M), 235 (83, M – MeO), 231 (100, M – Cl). Anal. Calcd for $C_{11}H_7ClN_2O_4$: C, 49.35; H, 2.63; N, 10.50; Cl, 13.32. Found: C, 49.66; H, 2.71; N, 10.07; Cl, 13.42.

Methyl (Z)-α-Cyano-*p*-nitro-β-(*p*-tolylthio)cinnamate (10-Z). To *p*-toluenethiol (62 mg, 0.5 mmol) in methanol (10 mL) was added sodium hydroxide (20 mg, 0.5 mmol) with stirring. When the solution became homogeneous, the chloride **5-E** (133.2 mg, 0.5 mmol) was added, and sodium chloride started to precipitate immediately. The mixture was stirred for an additional 1 h, the salt was filtered, and the solvent was evaporated. The yield of the product (by NMR) was 99%. Crystallization from methanol gave yellow-green crystals of methyl (*Z*)-α-cyano-*p*-nitro-β-(*p*-tolylthio)cinnamate; mp 187 °C; UV (MeCN) λ_{max} 295 nm (log ε 4.00); IR (KBr) ν_{max} 2200 (s, CN), 1720 cm^{-1} (s, COOMe); NMR ($CDCl_3$) δ 2.23 (3 H, s, MeC_6H_4S), 3.97 (3 H, s, COOMe), 6.98 (4 H, AA'BB' q, ArS), 7.65 (4 H, AA'BB' q, $ArNO_2$); mass spectrum, m/e (relative intensity) m/e 354 (70, M), 295 (100, M – COOMe), 166 (53, p-$O_2NC_6H_4CS$). Anal. Calcd for $C_{18}H_{14}N_2SO_4$: C, 61.00; H, 3.95; N, 7.91; S, 9.04. Found: C, 61.38; H, 4.22; N, 7.52; S, 8.58.

Methyl (*E*)-α-Cyano-β-methoxy-*p*-nitrocinnamate (12-E). To a solution of **5-E** (400 mg, 1.5 mmol) in methanol (10 mL) was added a solution of 0.1 M NaOMe in methanol (14 mL). Sodium chloride started to precipitate immediately. After 1 h the yield of the crude reaction product was 97%. The salt was filtered, the solvent was evaporated, and the remainder was crystallized from methanol, giving yellow crystals of methyl (*E*)-α-cyano-β-methoxy-*p*-nitrocinnamate (**12-E**): mp 196–197 °C; UV (MeCN) λ_{max} 261 nm (log ε 4.28); IR (Nujol) ν_{max} 2210 (m, CN), 1725 cm^{-1} (s, COOMe); NMR ($CDCl_3$) δ 3.67 (3 H, s, C=COMe), 3.74 (3 H, s, COOMe), 7.98 (4 H, AA'BB' q, Ar); mass spectrum, m/e (relative intensity) 262 (57, M), 231 (100, M – MeO). Anal. Calcd for $C_{12}H_{10}N_2O_5$: C, 54.96; H, 3.81; N, 10.68. Found: C, 55.18; H, 3.65; N, 10.69.

Methyl (E)-α-Cyano-β-(*p*-methylphenoxy)-*p*-nitrocinnamate (14-E). To *p*-cresol (1.08 g, 10 mmol) in a mixture of dichloromethane (15 mL) and water (5 mL) was added sodium hydroxide (0.4 g, 10 mmol). The mixture was shaken for few minutes, and the solvents were evaporated. The remaining sodium *p*-cresolate was dried overnight. The salt (325 mg, 2.5 mmol) was added with stirring to a solution of the chloride **5-E** (667 mg, 2.5 mmol) in acetonitrile (10 mL) at room temperature. Sodium chloride started to precipitate immediately, and after the mixture was stirred for 1 h, it was filtered, and the solvent was evaporated at room temperature at reduced pressure. The NMR of the remainder showed that 99% of methyl (*E*)- and (*Z*)-α-cyano-β-(*p*-methylphenoxy)-*p*-nitrocinnamates (**14-E** and **14-Z**) were formed in a ratio of 75:25, respectively. Crystallization of the mixture from carbon tetrachloride gave pure **14-E**: mp 165 °C; UV (MeCN) λ_{max} 254 nm (log ε 4.33); IR (Nujol) λ_{max} 2220 (s, CN), 1725 cm^{-1} (s, COOMe); NMR ($CDCl_3$) δ 2.21 (3 H, s, MeC_6H_4O), 3.73 (3 H, s, COOMe), 6.86 (4 H, AA'BB' q, ArO), 7.79 (4 H, AA'BB' q, $ArNO_2$); mass spectrum, m/e (relative intensity) 338 (19, M), 279 (22, M – COOMe), 150 (100, p-$O_2NC_6H_4CO$). Anal. Calcd for $C_{18}H_{14}N_2O_5$: C, 69.90; H, 4.14; N, 8.28. Found: C, 63.93; H, 3.91; N, 8.15.

Attempts to crystallize the *Z* isomer [**14-Z**: NMR ($CDCl_3$) δ 2.21 (3 H, s, MeAr), 3.83 (3 H, s, COOMe), 6.88 (4 H, AA'BB' q, ArO), 8.02 (4 H, AA'BB' q, $ArNO_2$)] from the remaining mother liquor were failed.

Methyl α-Cyano-*p*-nitrocinnamate (6). To a mixture of *p*-nitrobenzaldehyde (756 mg, 5 mmol) and methyl cyanoacetate (495 mg, 5 mmol) in methanol (10 mL) was added sodium methoxide (13.5 mg, 2.5 mmol), and the mixture was stirred for 5 h. The solvent was evaporated, warm carbon tetrachloride was added, and the solution was filtered. Methyl α-cyano-*p*-nitrocinnamate (mp 173–174 °C) crystallized on standing: UV (MeCN) λ_{max} 306 nm (log ε 4.38); IR (Nujol) ν_{max} 2220 (w, CN), 1720 cm^{-1} (m, COOMe); NMR ($CDCl_3$) δ 3.98 (3 H, s, COOMe), 8.30 (4 H,

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AA'BB' q, $ArNO_2$), 8.39 (1 H, s, =CH); mass spectrum, *m/e* (relative intensity) 232 (100, M), 201 (35, M - OMe). Anal. Calcd for $C_{11}H_8N_2O_4$: C, 56.89; H, 3.45; N, 12.07. Found: C, 56.98; H, 3.45; N, 11.81.

Methyl α-Cyano-β-(*p*-nitrophenyl)propanoate (19). To a solution of methyl α-cyano-*p*-nitrocinnamate (232 mg, 1 mmol) in a mixture of acetonitrile (5 mL) and methanol (5 mL) was added sodium borohydride (18.9 mg, 0.5 mmol). Hydrogen was evolved, the solution was stirred for 1 h and filtered, and the solvent was evaporated. The remainder was extracted with chloroform and crystallized from carbon tetrachloride, giving yellow crystals of methyl α-cyano-β-(*p*-nitrophenyl)propanoate (**19**): mp 100 °C; UV (MeCN) λ_{max} 267 nm (log ε 4.00); IR (Nujol) ν_{max} 2250 (w, CN), 1725 cm^{-1} (m, COOMe); NMR ($CDCl_3$) δ 3.37 (2 H, 2 q, CH_2), 3.83 (1 H, q, COOMe), 3.84 (3 H, s, $CH(CN)CO_2Me$), 7.85 (4 H, AA'BB' q, Ar); mass spectrum, *m/e* (relative intensity) 234 (20, M), 175 (32, M - COOMe), 136 (100, M - CH(CN)COOMe). Anal. Calcd for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.27; N, 11.96. Found: C, 56.50; H, 4.46; N, 11.54.

Methyl α-Cyano-β-methoxy-β-(*p*-nitroanilino)acrylate (15). To a solution of **5-E** (200 mg, 0.75 mmol) in methanol (10 mL) was added potassium azide (61 mg, 0.75 mmol) with stirring. Potassium chloride started to precipitate immediately. After the mixture was stirred for 1 h, the salt was filtered, and the solvent was evaporated. The yield (as calculated from the NMR) is 100%. Crystallization from methanol gave yellow crystals of methyl α-cyano-β-methoxy-β-(*p*-nitroanilino)acrylate (**15**): mp 188 °C; UV (MeCN) λ_{max} 338 nm (log ε 4.32); IR (Nujol) ν_{max} 2200 (s, CN), 1685 cm^{-1} (m, COOMe); NMR ($CDCl_3$) δ 3.87 (3 H, s, COOMe), 4.38 (3 H, s, C=COMe), 7.40 (4 H, AA'BB' q, Ar), 8.26 (1 H, br s, NH); mass spectrum, *m/e* (relative intensity) 277 (42, M), 245 (75, M - MeOH), 28 (100, CO). Anal. Calcd for $C_{12}H_{11}N_3O_5$: C, 51.98; H, 3.97; N, 15.16. Found C, 51.70; H, 3.87; N, 14.76.

Reaction of 5-E with Sodium Acetate. To a solution of **5-E** (266 mg, 1 mmol) in acetonitrile (10 mL) was added sodium acetate (82 mg, 1 mmol), and the mixture was stirred at room temperature for 135 h. The solvent was evaporated, and the remainder was dissolved in warm chloroform (200 mL). Only part of the solid was soluble. The chloroform solution was concentrated, and when the mixture was allowed to stand, the sodium salt of the enolate of methyl α-cyano-β-(*p*-nitrobenzoyl)acetate crystallized, mp ≥240 °C dec. The salt is soluble in water, and on addition of dilute HCl the enol **8** precipitated. Atomic absorption shows one atom of sodium for each molecule: UV (MeCN) λ_{max} 268 nm (log ε 4.17); IR (Nujol) ν_{max} 2190 (s, CN), 1650 cm^{-1} (s, COOMe); NMR (CD_3COCD_3) δ 3.56 (3 H, s, COOMe), 7.98 (4H, AA'BB' q, Ar). The mass spectra did not show a molecular peak but only small fragments including *m/e* 150 (10%, $p\text{-}O_2NC_6H_4CO$) and 28 (100%, CO). Anal. Calcd for $C_{11}H_7N_2O_5Na$: C, 48.89; H, 2.59; N, 10.37. Found: C, 48.94; H, 2.71; N, 9.87.

Reaction with Trifluoroacetate Ion. (a) To a solution of either **5-E** or **5-Z** (267 mg, 1 mmol) in acetone (10 mL) was added sodium trifluoroacetate (136 mg, 1 mmol), and the mixture was stirred for 24 h at room temperature. TLC and NMR analysis showed the presence of the unreacted vinyl chloride and the enol **8**.

(b) To a solution of **5** (267 mg, I mmol) in acetonitrile (10 mL) was added potassium trifluoroacetate (152 mg, 1 mmol), and the mixture was refluxed for 3 h. TLC and NMR analyses showed only the presence of **5** and **8**.

(c) To a similar mixture of **5** in acetonitrile was added silver trifluoroacetate (221 mg, 1 mmol), and the mixture was stirred for 24 h at room temperature. After evaporation of the solvent only **5** and **8** were detected by NMR.

Reaction of 5-E and 5-Z with Sodium Methoxide. To a solution of **5-E** or **5-Z** (13.3 mg, 0.05 mmol) in a mixture of CD_3CN (0.5 mL) and CD_3OD (0.5 mL) was added sodium methoxide gradually until 0.05 mmol was added. The NMR showed the formation of **12-E**, **12-Z** [NMR ($CDCl_3$) δ 3.82 (3 H, s, =COMe), 3.85 (3 H, s, COOMe), 8.18 (4 H, AA'BB' q, Ar)], and **13**. The concentration of the latter increased with the progress of the reaction and on addition of more NaOMe.

Reaction of 12-E with Sodium Methoxide. To a solution of **12-E** (65.5 mg, 0.5 mmol) in a mixture of CD_3CN (0.5 mL)–CD_3OD (0.5 mL) in an NMR tube was added sodium methoxide in small portions, and the reaction was followed by NMR. When the reaction was completed as judged by the complete disappearance of the signal at δ 3.55 (**12-E**) and the appearance of a signal at δ 3.31 (**13**), the solvents were evaporated. Attempts to crystallize the acetal **13** from CH_2Cl_2, CCl_4, MeOH, or their mixtures were unsuccessful, and the NMR of the mixtures after the attempted crystallization showed the presence of **12-E**, **13** [NMR ($CDCl_3$) δ 3.36 (3 H, s, MeO), 3.41 (3 H, s, MeO), 3.61 (3 H, s, MeO), 4.29 (1 H, s, CH), 8.00 (4 H, AA'BB' q, Ar)], and the enol **8**.

Reaction of 5-E and 5-Z with Sodium *p*-Cresolate. To a solution of **5-E** or **5-Z** (13.3 mg, 0.05 mmol) in CD_3CN (1 mL) was added sodium *p*-cresolate gradually until a concentration equimolar to that of **5** was added. The NMR showed the formation of a 68:32 mixture of **14-E** to **14-Z** on starting from **5-E** or of a 40:60 mixture of **14-E** to **14-Z** on starting from **5-Z**. When the mixture was allowed to stand, a 75:25 mixture of the two isomers was obtained. The NMR ($CDCl_3$) spectrum of **14-Z** which remained after crystallization of **14-E** is as follows: δ 2.21 (3 H, s, $p\text{-}MeC_6H_4$), 3.83 (3 H, s, COOMe), 6.88 (4 H, AA'BB' q, ArO), 8.02 (4 H, AA'BB' q, $ArNO_2$).

Reactions of 5-E and 5-Z with Tetraethylammonium Chloride. (a) A solution of **5-E** or **5-Z** (400 mg, 1.5 mmol) in acetonitrile (20 mL) was left for 115 h in the dark. NMR analysis showed that isomerization of either vinyl chloride did not take place.

(b) To a similar solution of **5-E** or **5-Z** was added Et_4NCl (250 mg, 1.5 mmol). The mixture was stirred, and samples were taken at time intervals starting after 20 h and ending after 450 h. NMR analysis showed that a **5-E** ⇌ **5-Z** isomerization took place and gave the isomer ratio, which at long reaction times was 68% **5-E** to 32% **5-Z**.

Reaction of 5-E and 5-Z with $Et_4NF \cdot 2H_2O$. To a solution of **5-E** or **5-Z** (267 mg, 1 mmol) in acetonitrile (10 mL) was added tetraethylammonium fluoride dihydrate (185.3 mg, 1 mmol). The mixture was stirred for 135 h and filtered, and the solvent was evaporated. The remaining oil was chromatographed over silica column by using acetone–CH_2Cl_2 mixtures as the eluant. The solid obtained from 25% acetone–75% CH_2Cl_2 decomposes above 300 °C. The IR spectrum shows very strong CN absorption at 2200 cm^{-1} and a carbonyl absorption at 1655 cm^{-1}. The NMR spectrum (in CD_3COCD_3) and the mass spectrum are similar to those of the enolate of **8** obtained in the reaction with sodium acetate.

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