counting and counted at 21 °C until a minimum of 2000 counts in the maximum channel (512 channels total) was obtained. Data were collected at less than 5% of lamp flash frequency to ensure exclusion of double photon counting. In separate runs excitation was varied over the range 250–280 nm and emission was monitored over the range 295–320 nm with an RCA 8850 photomultiplier. The decay range was independent of excitation wavelength, emission wavelength, and optical density to within 5%. The data are reported as follows: compound, average lifetime, average decay rate, number of runs, average A value.

(1) 3-Methyl-3-phenyl-1-butene, 9.18 ns, 1.09×10^8 s^{-1}, 3, 0.028.

(2) 3-Methyl-3-(*p*-methoxyphenyl)-1-butene, 4.38 ns, 2.28×10^8 s^{-1}, 3, 0.040.

(3) 3-Methyl-3-(*m*-methoxyphenyl)-1-butene, 4.60 ns, 2.18×10^8 s^{-1}, 3, 0.040.

(4) 3-Methyl-3-(*p*-cyanophenyl)-1-butene, 10.3 ns, 9.67×10^7 s^{-1}, 3, 0.027.

(5) 3-Methyl-3-(*m*-cyanophenyl)-1-butene, 4.88 ns, 2.05×10^8 s^{-1}, 2, 0.035.

Calculations. The general Pople semiempirical SCF approach[56] (ZDO) was used. A CI treatment was applied to the SCF MOs including both single and double excitations. For both single and double excitations all orbitals were included. Configurations were selected by a first-order perturbation approach.[57] Configurations were represented as a linear combination of Slater determinants such that each configuration was an eigenfunction of the spin operator S^2 as described by Murrell and McEwen.[58] Matrix elements between configurations were calculated from general formulas obtained by the standard methods for reduction of many-electron integrals.[56,58]

Valence-state ionization potentials were those described by Hinze and Jaffe.[59] Two-electron repulsion integrals were calculated by the Pariser–Parr approach.[60] Resonance integrals were calculated by the expression $\beta_{ij} = (S_{ij}/(1 + S_{ij}))(I_i + I_j)K$ where S_{ij} is the overlap integral[61] and I_i and I_j are the valence-state ionization potentials for orbitals i and j, respectively. Nearest-neighbor and selected 1,3-resonance integrals were used. The constant K was obtained by fitting β to the spectral transition of ethylene with a configuration interaction calculation that included single and double excitations.[57a]

Standard geometries were assumed, based on reported model compounds.[62] Geometries of intermediate species were assumed.

Calculations were performed with Fortran IV programs[57a] on a PDP-11/T55 computer having 32K words of memory. Direct access to and from two disks of 1.2×10^6 words per disk allowed storage and use of the large matrices encountered in configuration interaction calculations.

Acknowledgment. Support of this research by the National Science Foundation and by the National Institutes of Health Grant GM07487 is gratefully acknowledged. The synthetic portions of this research were supported by NIH while the theoretical and quantitative aspects were supported by NSF.

Registry No. **3**, 18321-36-3; **4a**, 18272-88-3; **4b**, 84565-67-3; **5a**, 90433-15-1; **5b**, 90433-16-2; **7a**, 90433-31-1; **7b**, 90433-21-9; **8a**, 90433-23-1; **8b**, 90433-24-2; **9a**, 18491-21-9; **10a**, 90433-26-4; **10b**, 90433-28-6; **11b**, 18272-91-8; **12**, 90433-29-7; **14**, 90433-30-0; **18**, 90433-20-8; **19a**, 32454-14-1; **19b**, 32454-15-2; **19c**, 32454-16-3; **19d**, 90433-17-3; **20a**, 90433-18-4; **20b**, 90433-19-5; **23**, 932-77-4; **24a**, 90433-22-0; **24b**, 90433-25-3; **25**, 3506-70-5; **26**, 90433-27-5; **27**, 104-20-1; **28**, 30780-21-3; **29**, 65292-99-1; **30**, 27200-79-9; **31**, 85964-37-0; **32**, 24964-64-5; **37**, 90460-09-6; **38**, 90460-07-4; **39**, 90433-32-2; **40**, 90433-33-3; **41**, 90460-08-5; triphenylphosphonium bromide, 1779-49-3; ethyl acetoacetate, 141-97-9; isopropyltriphenylphosphonium iodide, 1530-33-2; (2-methylpropyl)triphenylphosphonium bromide, 22884-29-3.

(56) (a) Zimmerman, H. E. "Quantum Mechanics for Organic Chemist"; Academic Press: New York, 1975. (b) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

(57) (a) Zimmerman, H. E.; Steinmetz, M. G., unpublished results. (b) Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta* **1974**, *35*, 33–58.

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(59) Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540–546.

(60) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 767–776.

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(62) Kennard, O., Ed. "Molecular Structures and Dimensions"; Unwin Brothers: Cambridge, England, 1972; Vol. A1.

Kinetic and Stereochemical Study on Bimolecular Substitution Reactions of Hydrazonates, Thiohydrazonates, and Hydrazonoyl Chlorides with Methoxide Ion

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Reaction of the (*Z*)-hydrazonoyl chlorides **2** with methoxide ion in methanol, under conditions where kinetic results show the reaction is bimolecular, leads to stereospecific formation of the (*Z*)-methyl hydrazonates, **5**. Less than 2% of the product with the "inverted" configuration at carbon (**6**) is formed. When a poorer leaving group than Cl^- is involved, then mixtures of *E* and *Z* products result. Thus the aryl thiohydrazonates (**3**) which have the *Z* configuration give 84–90% of the (*Z*)-methyl hydrazonate on reaction with methoxide ion. The (*E*)-aryl hydrazonates undergo reaction ca. 12-fold more slowly and isomer ratios of the (*Z*)- and (*E*)-methyl hydrazonates which result are closer to 1:1. The product methyl hydrazonates **5** and **6** undergo MeO^--catalyzed interconversion to an equilibrium mixture which favors **6**, but at a slower rate than the formation of either **5** or **6**. The stereochemical outcome of these displacements at the C=N bond is rationalized in terms of stereoelectronic control of the addition and elimination steps.

Introduction

Two general mechanisms for nucleophilic substitution at the carbon nitrogen doublet bond have been identified (Scheme I).

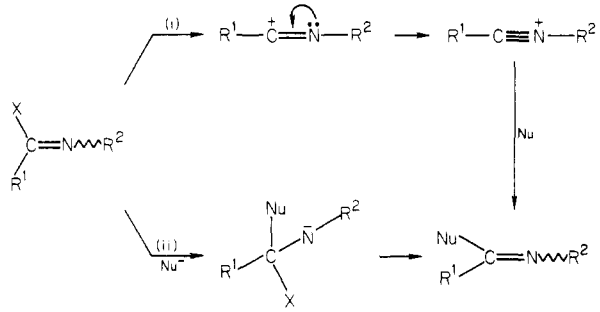
The ionization pathway (i) dominates the chemistry of imidoyl halides[2] owing to the stabilization of the nitrilium ion formed by the adjacent lone pair. We have shown previously[3] that the product is formed by this route

(1) (a) La Trobe University. (b) University College Dublin.

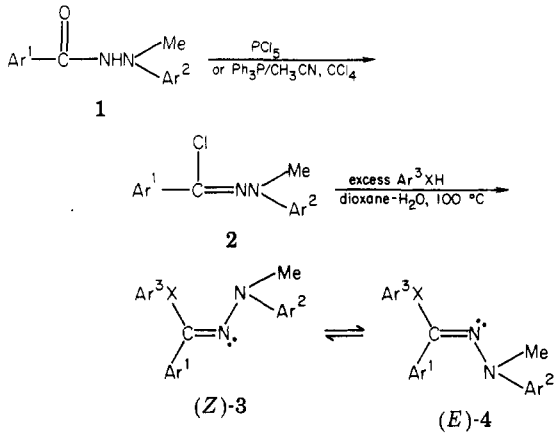
(2) Hegarty, A. F.; Cronin, J. D.; Scott, F. L. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 429.

0022-3263/84/1949-3083$01.50/0

Scheme I



Scheme II



3a, 4a, X = S; Ar^1 = 4-$MeOC_6H_4$-; Ar^2 = 2,4-$(NO_2)_2C_6H_3$-; Ar^3 = 4-$NO_2C_6H_4$-
3b, 4b, X = S; Ar^1 = 4-$NO_2C_6H_4$-; Ar^2 = 2,4-$(NO_2)_2C_6H_3$-; Ar^3 = 4-$NO_2C_6H_4$-
3c, 4c, X = S; Ar^1 = 4-ClC_6H_4-; Ar^2 = 2,4-$(NO_2)_2C_6H_3$-; Ar^3 = 4-$NO_2C_6H_4$-
3d, 4d, X = S; Ar^1 = Ph; Ar^2 = 2,4-$(NO_2)_2C_6H_3$-; Ar^3 = 4-$NO_2C_6H_4$-
3e, 4e, X = O; Ar^1 = 4-$NO_2C_6H_4$-; Ar^2 = 2,4-$(NO_2)_2C_6H_3$-; Ar^3 = 4-$NO_2C_6H_4$-

stereospecifically by addition of the nucleophile to the nitrilium ion with only the imine in which the nucleophile and the lone pair on nitrogen are trans being isolated, even though this may not be the thermodynamically more stable isomer.

In an earlier study,[4] bimolecular displacement of bromide ion from (*Z*)-*N*-methyl-*N*-(2,4-dinitrophenyl)pivalohydrazonoyl bromide by methoxide ion was reported. Only the *Z* isomer of the product was observed. However, since the *E* isomer of the hydrazonoyl bromide could not be isolated, a more complete investigation of the stereochemical outcome of the reaction was not possible. This difficulty is quite general for hydrazonoyl (and imidoyl halides); only one isomer, presumably the thermodynamically more stable, is available even when various synthetic routes are used.

In this paper, we report the synthyesis of several pairs of (*E*)- and (*Z*)-aryl *N*-methyl-*N*-(2,4-dinitrophenyl)-benzohydrazonates and the mechanism and stereochemistry of their bimolecular reactions with methoxide ion (path ii, Scheme I).

(3) MacCormack, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1701.
(4) Hegarty, A. F; McCormack, M. T.; Hathaway, B. J.; Hulett, L. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1136.

Scheme III

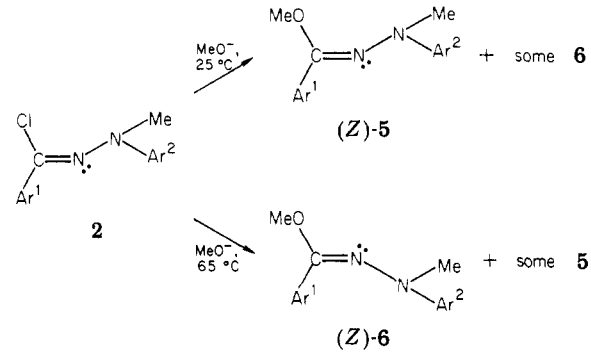


Table I. Chemical Shifts for *E* and *Z* Hydrazonates and Hydrazonoyl Chlorides, *p*-$NO_2C_6H_4C(Y)$=NNMe$C_6H_3(NO_2)_2$

	Z		*E*	
Y	OMe	NMe	OMe	NMe
Cl		3.64		
OMe	4.0	3.49	3.91	2.87
4-$NO_2C_6H_4S$		3.50		2.85
4-$NO_2C_6H_4O$		3.58		2.93

Results and Discussion

The aryl benzohydrazonates were prepared according to the sequence outlined in Scheme II. Previous work[3] has indicated that the configurational stability of these hydrazonoyl compounds increases as Ar^2 is changed from phenyl to 4-$NO_2C_6H_4$- to 2,4-$(NO_2)_2C_6H_3$- and as a result all work reported here has Ar^2 = 2,4-$(NO_2)_2C_6H_3$-.

Reaction of **2** with phenols or thiophenols under essentially thermodynamic conditions led to mixtures of **3** and **4** in which **3** (*Z*) predominated (**3** (*Z*):**4** (*E*) ~ 10 to 20:1). Thus the *Z* isomer is the thermodynamically more stable isomer from these reactions. Irradiation of the initial product mixture led to increasing amounts of the *E* isomer. The separation of the two isomers could be accomplished for most pairs by HPLC on a silica column and mixtures of ethyl acetate in hexane as the eluting solvent. The *E* and *Z* isomers of the thiohydrazonates proved to be easier to separate than the hydrazonates; thus the most extensive investigations were carried out on this series.

The (*E*)- and (*Z*)-methyl *N*-methyl-*N*-(2,4-dinitrophenyl)benzohydrazonates were prepared according to Scheme III by the reaction of methoxide ion with the hydrazonyl chlorides **2**. When the reaction was carried out at ambient temperatures, the *Z* isomer predominated (the kinetic isomer in this case) and could be obtained pure by recrystallization from the crude product. At 65 °C, the *E* isomer predominated (the thermodynamic isomer) and could similarly be obtained (Scheme III).

In spite of several attempts under different conditions, no *E* isomers of the hydrazonyl chlorides **2** could be observed on the irradiation of solutions of the *Z* isomers. Extended irradiation led to decomposition to two unidentified compounds. This is consistent with earlier studies[3] which have also reported failure to prepare the *E* isomers of **2** and related chlorides by irradiation of solutions of the *Z* isomers.

The relative chemical shifts of the NCH_3 protons in the *E* and *Z* isomers are significantly different owing to the strong shielding effect of the C-aryl ring on the NCH_3 protons in the *E* isomer.[3] The results for a series of *N*-methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazonates are given in Table I. The position of the NCH_3 resonances in these isomers shows little dependence on the substituent at the carbon–nitrogen double bond and can therefore be used in unequivocal structural assignment. Similar use

Table II. Rate and Product Data for the Reaction of Aryl Hydrazonates 3 and 4 with Methoxide Ion in Methanol

substrate	T, °C	10^3k_2 ([NaOMe], M)		10^3k_2[a]	product %E	product %Z
3a	25.0	0.605 (1.63×10^{-1})	0.606 (1.09×10^{-1})	0.605 ± 0.001		
	30.0	1.05 (2.44×10^{-1})	1.05 (1.15×10^{-1})	1.05 ± 0.01	16	84
	37.2			2.14 ± 0.01		
	43.3			4.26 ± 0.006[b]		
4a	30.0	0.06 (2.72×10^{-1})	0.077 (3.98×10^{-1})	0.068 ± 0.08	49	51
3b	30.0	44.0 (1.24×10^{-2})	42.3 (6.18×10^{-3})	43.2 ± 0.08	10	90
4b	30.0	3.15 (5.86×10^{-2})	3.13 (1.17×10^{-1})	3.14 ± 0.01	62	38
3c	30.0	6.29 (5.86×10^{-2})	6.46 (2.93×10^{-2})	6.38 ± 0.08		
3d	30.0	2.15 (5.86×10^{-2})	2.05 (8.79×10^{-2})	2.10 ± 0.05		
3e	13.5	9.39 (3.09×10^{-2})	9.71 (1.24×10^{-2})	9.54 ± 0.17		
	21.5	20.9 (2.47×10^{-2})	20.8 (1.24×10^{-2})	20.9 ± 0.1		
	30.0	48.4 (1.24×10^{-2})	49.4 (6.18×10^{-3})	48.9 ± 0.5	16	84

[a] Average values of the second order rate constants (M^{-1} s^{-1}) for the reaction with methoxide ion in methanol. [b] $\Delta H^{\ddagger}_{298}$ = 80.4 kJ mol^{-1}; $\Delta S^{\ddagger}_{298}$ = −37 J mol^{-1} K^{-1}.

Table III. Rate and Product Data for the Reaction of (Z)-Hydrazonoyl Chlorides 2 with MeO^-/MeOH

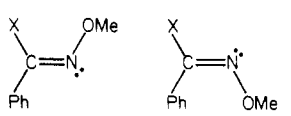
substrate	Ar^1	10^3k_2 ([NaOMe], M)		10^3k_2[b]	product %E	product %Z
2a	4-$MeOC_6H_4$				99	1
2b	4-$NO_2C_6H_4$	224 (5.86×10^{-3})	225 (2.93×10^{-3})	225 ± 1	98	2
2c	4-ClC_6H_4	22.3 (1.17 ± 10^{-2})	22.1 (2.93 ± 10^{-2})	22.2 ± 0.1		
2d	Ph	6.30 (2.93×10^{-2})	6.21 (5.81 ± 10^{-2})	6.24 ± 0.05		
2e	4-MeC_6H_4	3.52 (8.79×10^{-2})	3.70 (5.86×10^{-2})	3.61 ± 0.09		

[a] Ar^2 = 2,4-$(NO_2)_2C_6H_3$. [b] Average second-order rate constants (M^{-1} s^{-1}) measured at 30.0 °C.

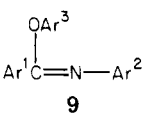
of NMR chemical shifts has been reported previously for oxime ethers[5] and other imines.[6]

The reactions with methoxide ion were followed spectrophotometrically under pseudo-first-order conditions by monitoring the appearance of the 4-nitrothiophenolate ion or the 4-nitrophenolate ion (for the aryl benzohydrazonates, compounds **3** and **4**) and by the appearance of the methyl benzohydrazonates for the benzohydrazonoyl chlorides (**2**). The second-order rate constants quoted in Tables II and III were obtained from linear $k_{obsd}/[OMe^-]$ plots.

Johnson et al.[5] have presented convincing evidence that the benzohydroximoyl chlorides **7a** undergo rate-determining attack by methoxide ion to form a tetrahedral intermediate which rapidly loses chloride ion to form the methyl benzohydroximates (**7b**). Rowe[7] has suggested the same mechanism for the methoxide substitution reactions of aryl *N*-arylbenzimidates (**9**) where the leaving group, as in this study, was the phenolate ion.



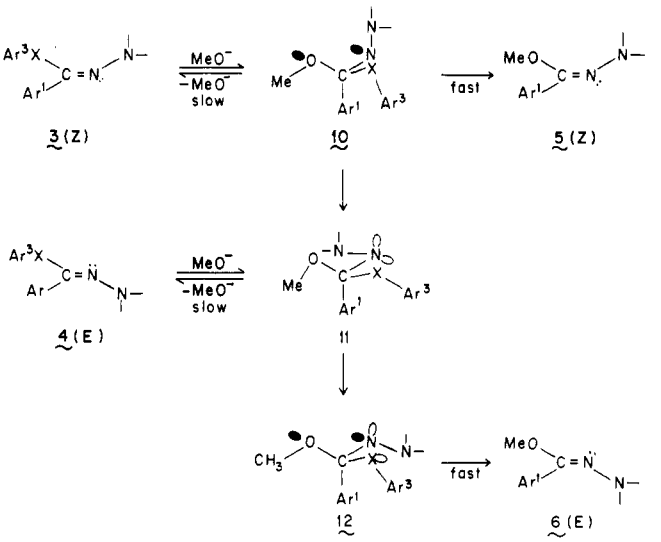
7a, X = Cl **8a**, X = Cl
7b, X = OMe **8b**, X = OMe



9

A similar mechanism is consistent with the results obtained in the present study. A linear Hammett correlation was obtained with a ρ value of 1.57 (r = 0.997) for the reaction of MeO^- (variation of Ar^1) with the hydrazonates **3** and a ρ of 1.95 (r = 0.999) for the reaction with the benzohydrazonoyl chlorides **2**. These are similar to the value of 1.90 (±0.35) reported by Johnson[5] for the methoxide ion attack on *O*-methylbenzohydroximoyl chlorides (**7**). In contrast the ρ value obtained for the unimolecular reactions (path i, Scheme I) of a comparable series of hydrazonoyl halides was −2.8.[8]

Scheme IV



The activation parameters for the reaction of the aryl hydrazonates **3a** and **3e** with methoxide ion are reported in Table II. These values also parallel those reported by Johnson[5] for the reaction of *O*-methylbenzohydroximoyl chlorides with methoxide ion.

Compound **3e**, where the leaving group is the 4-nitrophenolate ion, reacts 1.13 times faster than the corresponding compound **3b**, where the leaving group is the 4-nitrothiophenolate ion. This ratio is comparable to the ratio reported by Connors and Bender[9] for the hydrolysis of ethyl 4-nitrobenzoate and ethyl 4-nitrothiobenzoate, where the ester reacted faster than the thioester by a factor of 1.21. The basic hydrolysis of esters has been shown to

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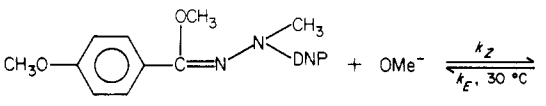
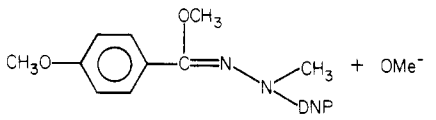
(6) For leading references see: Johnson, J. E.; Springfield, J. R.; Hwang, J. S.; Hayes, L. J.; Cunningham, W. C.; McClaugherty, D. L. *J. Org. Chem.* **1971**, *36*, 284.
(7) Rowe, J. E. *Aus. J. Chem.* **1983**, *36*, 1259.
(8) Hegarty, A. F.; Rowe, J. E., unpublished data.
(9) Connors, K. A.; Bender, M. L. *J. Org. Chem.* **1961**, *26*, 2498.

Scheme V



5a



6a

$k_Z + k_E = 1.89 \times 10^{-5}$ L mol^{-1} s^{-1}
$k_Z = 1.59 \times 10^{-5}$ L mol^{-1} s^{-1}
$k_Z/k_E = 5.30$
$k_E = 0.30 \times 10^{-5}$ L mol^{-1} s^{-1}

react via rate-determining formation of the tetrahedral intermediate.

The stereochemistry of the methoxide substitution reactions of hydrazonoyl[4] and hydroximoyl halides[5] has been rationalized in terms of Deslongchamps' theory of stereoelectronic control.[10] In Scheme IV, the tetrahedral intermediates formed from the reaction of methoxide ion with the aryl benzohydrazonates are shown.

The tetrahedral intermediate **10** formed from the *Z* starting material should, according to the theory,[8] undergo C–O bond cleavage with stereoelectronic control to give the (*Z*)-hydrazonate **5**. The tetrahedral intermediate **11** from the *E* starting material **4** cannot undergo stereoelectronically controlled C–O bond cleavage; thus the theory would predict that the rate of C–O bond cleavage would be slower than the rate of stereomutation (rotation and nitrogen inversion) to give conformations **10** and **12**, which should lead to a mixture of the *Z* and *E* isomers (**5** and **6**) in the product. Previous work with (*Z*)-hydrazonoyl halides[4] led exclusively to the (*Z*)-methyl hydrazonates as suggested by the theory.[10]

Johnson[5] has recently reported the stereochemistry of the reaction of *O*-methylbenzohydroximoyl chlorides with methoxide ion. The *Z* isomer **7a** gave 98% of **7b** and only 2% of **8b** while the *E* isomer **8a** led to 23% of **7b** and 77% of **8b**.

In the present work, the (*Z*)-benzohydrazonoyl chlorides **2** led almost exclusively to *Z* products. Compound **2a** gave 99% of **5a** and 1% of **6a**, while **2b** gave 98% of **5b** and 2% of **6b**. These product distributions are very close to those reported previously by Hegarty,[4] and by Johnson[5] for the *O*-methylbenzohydroximoyl chlorides.

The *E* isomers of the aryl benzohydrazonates (**4a** and **4b**) led to mixtures of products as predicted by the theory (Table II). However, the stereoelectronic control observed in the reactions of the (*Z*)-aryl hydrazonates (**3a**, **3b**, and **3e**) was not as tight as in the previous studies,[3,4] and more of the *E* isomer (10–16%) was observed. This suggests that stereomutation of the tetrahedral intermediates **11**, **12**, and **13** and cleavage of the C–O bond must be comparable in rate.

This represents the first observation of an appreciable amount of inversion configuration of (*Z*)-hydrazonates. We have therefore investigated in some detail the possibility that this arises from base-catalyzed isomerization of the product methyl benzohydrazonates. The isomerization of **5a** to **6a** is indeed catalyzed by methoxide ion. The observed rate constants obtained are listed in Scheme V; the *E* isomer (**6a**) is the thermodynamically more stable isomer. The same equilibrium constant ($k_Z/k_E = 5.11$) within experimental error was obtained by heating a solution of either **5a** or **6a** in chlorobenzene. Thus the rate of isomerization of **5a** catalyzed by MeO^- is only 1/66 of the rate of displacement of PhO^- from **3a** by MeO^-. The observed ratio of **5a**:**6a** formed therefore represents the true values formed by MeO^- attack on **3a**. However, since **4a** is less reactive, the rate of reaction of **4a** with MeO^- is only 4.3-fold faster than the rate of isomerization ($k_E + k_Z$) of **5a**. Therefore the product distributions for **4a** were obtained (see Table II) by using only low percentages of conversion to products to minimize the base-catalyzed isomerisation of products.

The emerging pattern for the stereochemistry of bimolecular displacements at the carbon–nitrogen double bond is clearly more complex than the stereospecificity observed in the ionization mechanism (path i, Scheme I). The *Z* substrates give either exclusive or a high degree of retention of the *Z* configuration. The leaving group effects for the *Z* substrates are generally small, viz., the rates of reaction with MeO^- from the present study for leaving groups –Cl, –OPh, and –SPh are in the ratio 3.2:1.13:1.0. The less than complete stereospecificity observed for the thiohydrazonates and hydrazonates possibly arises from the expected more rapid stereomutation by nitrogen inversion of tetrahedral intermediates **10** relative to those formed from imidates (which have a MeO group attached to the nitrogen). The *E* isomer, reflecting the need for stereomutation of the tetrahedral intermediate before elimination, shows a variety of behavior depending on the nucleophile and leaving group present and tends toward a 1:1 ratio of *E* and *Z* products, particularly when a poor leaving group is involved.

Experimental Section

General Methods. Mass spectra were run on Jeol JMS D100 while kinetic experiments were carried out on a Varian Techtron 634 or Cary Model 210 ultraviolet spectrophotometers. Melting points are uncorrected.

Substrates. All previously unreported compounds were pure according to TLC analysis.

***N*-Methyl-*N*-(2,4-dinitrophenyl)benzohydrazides (1, Ar^2 = 2,4-$(NO_2)_2C_6H_3$-).** *N*-Methyl-*N*-(2,4-dinitrophenyl)hydrazine (1.8×10^{-2} mol) and benzoyl chloride (1.9×10^{-2} mol) were heated in dry pyridine under reflux for 2 h. On cooling the solution was poured onto ice and the precipitated hydrazide filtered off. On recrystallization from ethanol–acetone (1:1) **1** (Ar^1 = Ph, Ar^2 = 2,4-$(NO_2)_2$-C_6H_3-) was obtained (4.0 g, 87%), mp 200–201 °C (lit.[4] mp 201–201.5 °C). The following benzohydrazides were prepared by the same general procedure.

***N*-Methyl-*N*-(2,4-dinitrophenyl)-4-chlorobenzohydrazide,** mp 233–235 °C. Anal. Calcd for $C_{14}H_{11}ClN_4O_5$: C, 47.95; H, 3.16; N, 15.97. Found: C, 48.05; H, 3.30; N, 16.32.

***N*-Methyl-*N*-(2,4-dinitrophenyl)-4-methoxybenzohydrazonate,** mp 233–235 °C. Anal. Calcd for $C_{15}H_{14}N_4O_6$: C, 52.03; H, 4.07; N, 16.18. Found: C, 52.13; H, 4.19; N, 16.53.

***N*-Methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazide,** mp 245–247 °C. Anal. Calcd for $C_{14}H_{11}N_5O_7$: C, 46.29; H 3.61; N, 19.28. Found: C, 46.59; H, 3.25; N, 19.11.

***N*-Methyl-*N*-(2,4-dinitrophenyl)-4-methylbenzohydrazide,** mp 241–243 °C. Anal. Calcd for $C_{15}H_{14}N_4O_5$: C, 54.55; H, 4.27; N, 16.96. Found: C, 54.58; H, 4.05; N, 16.90.

***N*-Methyl-*N*-(2,4-dinitrophenyl)benzohydrazonoyl Chlorides (2, Ar^2 = 2,4-$(NO_2)_2C_6H_3$-).** *N*-Methyl-*N*-(2,4-dinitrophenyl)-4-chlorobenzohydrazide (2×10^{-3} mol), triphenylphosphine (2.5×10^{-3} mol), and carbon tetrachloride (0.2 mL) in dry acetonitrile (40 mL) were heated under reflux for 4 h.[11] After removal of the solvent, the crude product was purified by dry column chromatography on silica with chloroform as eluant.

(10) Deslongchamps, P. *Tetrahedron* **1975**, *3* 2463.

(11) Wolkoff, P. *Can. J. Chem.* **1975**, *53*, 1333.

N-Methyl-*N*-(2,4-dinitrophenyl)-4-chlorobenzohydrazonoyl chloride was obtained (50% yield) as a yellow crystalline solid from chloroform-pentane and had mp 121–122 °C (M^+, $C_{14}H_{10}Cl_2N_4O_4$ requires 368.008, found 368.009). The following benzohydrazonoyl chlorides were prepared by the same general procedure.

***N*-Methyl-*N*-(2,4-dinitrophenyl)benzohydrazonoyl chloride (2d)**: mp 125.5–126.5 °C (lit. mp 116–117 °C).

***N*-Methyl-*N*-(2,4-dinitrophenyl)-4-methoxybenzohydrazonoyl chloride (2a)**: mp 170–172 °C (M^+, $C_{15}H_{13}ClN_4O_5$ requires 364.057, found 364.056).

***N*-Methyl-*N*-(2,4-dinitrophenyl)-4-methylbenzohydrazonoyl chloride (2e)**: mp 121–122 °C. Anal. Calcd for $C_{15}H_{13}ClN_4O_4$: C, 51.66; H, 3.76; N, 16.07. Found: C, 51.81; H, 3.91; N, 16.54.

***N*-Methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazonoyl chloride (2b)**: mp 144–145 °C (M^+, $C_{14}H_{10}ClN_5O_6$ requires 379.032, found 379.033). Compound **2b** was also prepared by the following method. The *N*-methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazide (5.5×10^{-3} mol) and phosphorus pentachloride (1.04×10^{-3} mol) were well mixed and heated on an oil bath at 120 °C for 1 h. On cooling the yellow solid was dissolved in chloroform (40 mL) and the chloroform solution was washed with water. Removal of the solvent gave the crude product which was recrystallized from chloroform–cyclohexane to give the desired product in 67% yield, mp 144–145 °C.

(*Z*)-Methyl *N*-Methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazonate (5b). *N*-Methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazonyl chloride (2.6×10^{-4} mol) in 0.3 M sodium methoxide (20 mL) and methanol (20 mL) was stirred at room temperature for 1 h. Water was added and the hydrazonate extracted into chloroform. Removal of the solvent gave the crude product as a 6:1 ratio of *Z*:*E* (by NMR). Pure (*Z*)-methyl *N*-methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazonate was obtained as yellow crystals (55% yield) from dichloromethane–cyclohexane, mp 135–136 °C (M^+, $C_{15}H_{13}N_5O_7$ requires 375.082, found 375.082).

(*Z*)-Methyl *N*-methyl-*N*-(2,4-dinitrophenyl)-4-methoxybenzohydrazonate (5a), mp 118–118.5 °C, was similarly prepared. (M^+, $C_{16}H_{16}N_4O_6$ requires 360.107, found 360.106.)

(*E*)-Methyl *N*-methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazonate (6b) was prepared under similar conditions except that the sodium methoxide solution was heated under reflux for 4 h. **(*E*)-Methyl *N*-methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazonate (6b)** (the thermodynamic product) was obtained from chloroform–cyclohexane, mp 171–172 °C. Anal. Calcd for $C_{15}H_{13}N_5O_7$: C, 48.01; H, 3.49; N, 18.66. Found: C, 47.99; H, 3.65; N, 18.35.

(*E*)-Methyl *N*-methyl-*N*-(2,4-dinitrophenyl)-4-methoxybenzohydrazonate (6a), mp 119–120 °C, was similarly prepared. (M^+, $C_{16}H_{16}N_4O_6$ requires 360.107, found 360.107.)

(*Z*)-4-Nitrophenyl *N*-Methyl-*N*-(2,4-dinitrophenyl)-4-methoxythiobenzohydrazonate (3a). 4-Methyl-*N*-(2,4-dinitrophenyl)-4-methoxybenzohydrazonyl chloride (6.4×10^{-4} mol), 4-nitrothiophenol (8.5×10^{-4} mol), and triethylamine (0.15 mL) in dioxan (5 mL) and water (1 mL) were heated under reflux for 90 min. On cooling, dichloromethane (50 mL) was added and the organic solution was washed with dilute base and with water. Removal of the solvent gave the crude product which was purified by dry column chromatography on silica with chloroform as the eluting solvent. Orange-yellow crystals (0.16 g 50%), mp 164–165 °C. Anal. Calcd for $C_{21}H_{17}N_5O_7S$: C, 52.17; H, 3.54; N, 14.49. Found: C, 52.25; H, 3.54; N, 14.44.

The following aryl benzothiohydrazonates were prepared by the same general procedure.

(*Z*)-4-Nitrophenyl *N*-methyl-*N*-(2,4-dinitrophenyl)-4-nitrothiobenzohydrazonate (3b), mp 212–213 °C. Anal. Calcd for $C_{20}H_{14}N_6O_8S$: C, 48.20; H, 2.83; N, 16.86. Found: C, 48.37; H, 2.88; N, 16.81.

(*Z*)-4-Nitrophenyl *N*-methyl-*N*-(2,4-dinitrophenyl)-4-chlorothiobenzohydrazonate (3c), mp 142–143 °C; M^+ calcd for $C_{20}H_{14}ClN_5O_6S$ 487.035, found 487.035.

(*Z*)-4-Nitrophenyl 4-methyl-*N*-(2,4-dinitrophenyl)thiobenzohydrazonate (3d), mp 160–161 °C; M^+ calcd for $C_{20}H_{15}N_5O_6S$ 453.074, found 453.075.

(*Z*)-4-Nitrophenyl *N*-methyl-*N*-(2,4-dinitrophenyl)-4-nitrobenzohydrazonate (3e), mp 181–182 °C. Anal. Calcd for $C_{20}H_{14}N_6O_9$: C, 49.80; H, 2.93; N, 17.42. Found: C, 50.15; H, 3.02; N, 17.68.

(*E*)-4-Nitrophenyl *N*-Methyl-*N*-(2,4-dinitrophenyl)-4-methoxythiobenzohydrazonate (4a). Irradiation of solutions of the *Z* isomer led to mixtures of the two isomers (*Z*:*E* 2:1). Pure *E* isomer was obtained by using HPLC on a silica column with ethyl acetate/hexane as eluting solvent. The **(*E*)-thiohydrazonate** had mp 149–150 °C; M^+ calcd for $C_{21}H_{17}N_5O_7S$ 483.085, found 483.082.

Kinetics. Sodium methoxide solutions were prepared by dissolving clean dry sodium metal in dry methanol. The solutions were standardized by titration against hydrochloric acid with bromocresol as indicator.

Rate measurements were carried out in dry methanol (NaOMe = 0.006–0.4 M) under pseudo-first-order conditions. All compounds were studied at more than one base concentration within the above limits. For compounds **3** and **4** the production of the 4-nitrophenolate or the 4-nitrothiophenolate ion was monitored at 390 and 410 nm, respectively. In the reactions of the benzohydrazonyl chlorides **2**, the formation of the methyl benzohydrazonates was monitored at 390 nm.

The isomerization of **5a** to **6a** could not be monitored by UV, due to the small spectral change. Aliquots of the reacting mixtures were taken after appropriate time intervals and the reaction was quenched with water. The organic products were extracted with dichloromethane and analyzed by HPLC on a silica column with 40% ethyl acetate in hexane as the eluting solvent.

Product Analysis. The reactions were carried out at the same concentrations and under the same conditions as the kinetic experiments. The reactions were quenched by pouring the methanol solutions into water. The products were extracted from the aqueous solution and dried over anhydrous sodium sulfate before the solvent was removed by evaporation. The residue was dissolved in a little ethyl acetate and the solution analyzed by HPLC on a silica column with mixtures of ethyl acetate in hexane as the eluant.

Registry No. 1 (Ar^1 = 4-$MeOC_6H_4$, Ar^2 = 2,4-$(NO_2)_2C_6H_3$), 90913-79-4; 1 (Ar^1 = 4-$NO_2C_6H_4$, Ar^2 = 2,4-$(NO_2)_2C_6H_3$), 90913-80-7; 1 (Ar^1 = 4-ClC_6H_4, Ar^2 = 2,4-$(NO_2)_2C_6H_3$), 90913-81-8; 1 (Ar^1 = Ph, Ar^2 = 2,4-$(NO_2)_2C_6H_3$), 62055-72-5; 1 (Ar^1 = 4-MeC_6H_4, Ar^2 = 2,4-$(NO_2)_2C_6H_3$), 90913-82-9; 1 (Ar^1 = 4-MeC_6H_4, Ar^2 = 2,4-$(NO_2)_2C_6H_3$), 90913-83-0; **2b**, 90913-84-1; **2c**, 90913-85-2; **2d**, 59259-45-9; **2e**, 90913-86-3; **3a**, 90913-87-4; **3b**, 90913-88-5; **3c**, 90913-89-6; **3d**, 90913-90-9; **3e**, 90913-91-0; **4a**, 90913-92-1; **4b**, 90913-93-2; **5a**, 90913-94-3; **5b**, 90913-95-4; **6a**, 90913-96-5; **6b**, 90913-97-6.