Stereochemistry in Nucleophilic Vinylic Substitution of Activated Nitro Olefins

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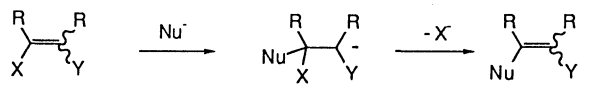
Each of *E*- and *Z*-isomers of activated α,β-dinitro olefins and α-iodo-β-nitrostilbene reacted ith several different types of nucleophiles such as amines, thiocyanate, and *p*-toluenethiolate. Only *Z*-isomers of vinylic-substituted olefins with amines and thiocyanate were observed as products due to the attractive interactions between the nitro group of substrate and the nucleophile in the intermediate state. *p*-Toluenethiolate as a nucleophile could not interact strongly enough to yield a single *Z*-product but a converged (*E*) and (*Z*) mixture of products. Still, preference is toward *Z*-configuration.

Vinylic substitution has been proved to take place through all conceivable mechanisms, namely through initial prototropy, carbene, alkyne, free radical, carbonium ion, and carbanion intermediate. Among them nucleophilic addition-elimination mechanism is the most common occurrence.[1,2]

As to mechanistic studies for nucleophilic vinylic substitution, comparison of configurations of reactants and products gives away much information. Usually it is dealt as to retention, inversion, and convergence. The last one means conversion to *E*- and *Z*-products with certain ratio starting from either *E*- or *Z*-reactant or, in extreme case, only one product(*E*- or *Z*-) irrespective of configuration of the reactant.[3] Thus, comparison of configurations of reactants and products of this reaction gives some insight into the mechanism where stereochemical information is not prevalent in spite of abundant kinetic data.[4]

Nucleophilic vinylic substitutions proceed through the addition of nucleophile(k_1) to make a carbanion intermediate followed by elimination of nucleofuge(k_2) as in Scheme 1. Usually the first step(k_1) is rate-determining and is dependent on the nature of the substrate and the nucleophile.[1d] On the other hand the configuration of product depends on the nature of nucleofuge i.e. the rate of internal rotation(k_r) and the rate of expulsion(k_2).[1d] With good nucleofuges k_2 is high and $k_r^{60}>k_r^{120}$ (60° and 120° internal rotation rate) by negative hyperconjugation[5] and the complete retention is observed.[6] Reactions with poor nucleofuges result in mostly stereoconvergence due to $k_r>k_2$.[3]

In order to probe into stereochemistry of nucleophilic vinylic substitution, we have chosen α,β-dinitro olefins(**1**,**2**, and **3**)[7] and α-iodo-β-nitro olefin(**4**)[8] without olefinic hydrogen. This will minimize complication such as involvement of base with hydrogen to lead elimination-addition route. While nitro group activates double bond toward nucleophilic addition much more efficiently than iodo group, it is a poor nucleofuge thus gives advantage toward internal rotation against its expulsion. Nucleophiles chosen are also of low basicity to reduce such complication of base with substrate. This system provides opportunity to probe into a few cases of nucleophilic vinylic substitution. We found that some of reported case[9] are in error and need to be corrected. Furthermore, we report the first observation of the interaction between the nitro group of substrate and the coming nucleophile to determine the stereochemical outcome of the nucleophilic vinylic substitution reactions.



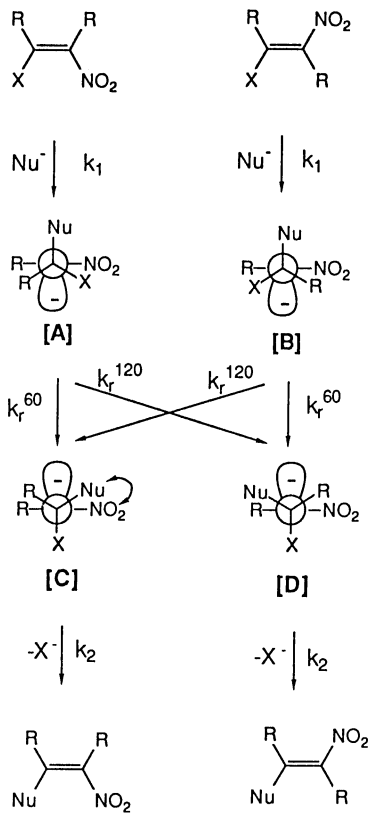
1 R = CH_3, X = Y = NO_2
2 R = C_2H_5, X = Y = NO_2
3 R = Ph, X = Y = NO_2
4 R = Ph, X = I, Y = NO_2

Nu⁻ = NH_3, CH_3NH_2, O NH
SCN^-, *p*-$MeC_6H_4S^-$

Scheme 1.

One of two nitro groups in α,β-dinitro olefins is easily replaced by nucleophiles such as azide,[10] ammonia,[11] aniline,[11] thiols,[10] and SCN^-. Iodo group in α-iodo-β-nitro olefin undergoes similar reactions in much slower rate. A few α-amino-β-nitro olefins were synthesized by substitution on either (*E*)- or (*Z*)-α,β-dinitro olefins and their configurations were deduced to be those of (*Z*)-, through intramolecular hydrogen bonding in IR spectra.[11] Their configurations were confirmed by X-ray crystallography on 2-amino-3-nitro-2-butene.[12] Similarly α-thiocyanato-β-nitro olefins were prepared by substitution on a few substrate and their configurations were confirmed to be (*Z*)- by X-ray crystallography on 2-thiocyanato-3-nitro-2-butene.[13] α-Iodo-β-nitrostilbene was also substituted with a few nucleophiles such as thiocyanate and morpholine to produce exclusively *Z*- isomer as a product determined by X-ray crystallography.[14] The striking feature of this series of experiments was that from either *E*- or *Z*-starting nitro olefins all *Z*-products were formed regardless of starting configuration. On the other hand *p*-toluenethiolate as a nucleophile yielded converged products against reported exclusive *E*- products.[9a,15]

The observed phenomena could be explained using Scheme 2. At first assume that the reaction starts by



Scheme 2.

attack of nucleophiles on the carbon atoms bearing the nucleofuge. One has to also assume that since spatial and other conditions are identical, approach of the nucleophile (Nu^-) from the top on *Z*-isomer will form the intermediate with [**A**] conformation. The same intermediate will be formed by attack of nucleophile from the bottom on *E*-isomer. Likewise, the conformation [**B**] could be assumed from attack of the nucleophile from the top on *E*-isomer and from the bottom on *Z*-isomer. This line of reasoning will result in two reasonably stable intermediates [**A**] and [**B**]. Under the condition of $k_r > k_2$ free rotation around the newly formed single bond can generate intermediates with [**C**] and [**D**] conformations where the leaving nucleofuge is ready to be expelled parallel to *p*-orbital of the carbon bearing the remaining nitro group. From these intermediates only *Z*-product will be formed if the entered nucleophile must closely associate with the remaining nitro group via only [**C**] conformation.

The compounds leading to single *Z*-products, namely those of amines,[16] morpholine and a thiocyanate appear to form intermediate with [**C**] conformation due to the strongly attractive interaction between the nucleophile and the remaining nitro group: i.e., between sulfur atom of thiocyanate and the oxygen atom of nitro group and between the nitrogen atom of amines and the oxygen atom of nitro group through hydrogen bonding. With *p*-toluenethiolate partial conversion is observed due to the weaker interaction compared to thiocyanate.[18] In case of 2,3-dinitro-2-butene(**1**) and 3,4-dinitro-3-hexene(**2**) partially converged *E*- and *Z*-products were observed. Still, preference is toward *Z*-configuration even though thermodynamic stability is expected for *E*-configuration. Another supporting evidence comes from the observation of distance in (*Z*)-2-thiocyanato-3-nitro-2-butene in X-ray crystallography where distance between sulfur and oxygen of nitro group is much shorter than the sum of van der Waals radii of both atoms(2.468 Å against 3.25 Å).[13] This indicates that there is strong attraction between these two atoms since there is a way of releasing steric strain such as bending out of plain of backbone of the molecule.[14a]

In conclusion, complete conversion to *Z*-configuration in vinylic nucleophilic substitution could be observed if there is attractive interaction between the activating group of substrate and the nucleophile. A corollary of this conclusion is that if there is repulsive interaction between these two groups complete conversion to *E*-configuration will be observed.

Experimental

Table 1 shows the conditions of reagents used in the

Table 1. Stereochemistry of the Substitution of Nitro Olefins

Nucleophile	Substrate	Solvent	Reaction Conditions		Yield[a]	*E*/*Z*
			°C	h	%	
NH_3	*E*-**1**, *Z*-**1**	EtOH	0	0.5	84	*Z*
CH_3NH_2	*E*-**1**, *Z*-**1**	EtOH	0	0.5	97	*Z*
	E-**2**, *Z*-**2**	EtOH	0	0.5	51	*Z*
Morpholine	*E*-**3**, *Z*-**3**	MeCN	25	16	65	*Z*[b]
	E-**4**, *Z*-**4**	MeCN	25	40	72	*Z*
NaSCN	*E*-**1**, *Z*-**1**	EtOH	0—4	0.3	80	*Z*
	E-**2**, *Z*-**2**	EtOH	25	0.6	84	*Z*
	E-**3**, *Z*-**3**	MeOH	25	0.6	80	*Z*[b]
	E-**4**, *Z*-**4**	MeCN	25	15	45	*Z*
p-MeC_6H_4SH	*E*-**1**, *Z*-**1**	EtOH	25	0.15	92	2/3
	E-**2**, *Z*-**2**	EtOH	25	0.15	95	1/3

a) Lower yield was chosen from either *E*- or *Z*-substrate. b) The configurations of products were confirmed by X-ray crystallography and were completely opposite to the Ref. 9b.

nucleophilic substitution reaction, together with the results obtained. All products were completely characterized by elemental analysis, IR and NMR spectra. Microanalyses were carried out on a Perkin-Elmer 240 DS elemental analyzer. IR spectra were recorded on a Analect FX 6160 Infrared spectrometer. ^{1}H NMR spectra were measured on either a Varian T 60 A or a Bruker AM-200 spectrometer.

2,3-Dinitro-2-butene (1): This was prepared by the reported method[7a] except for the work up procedure. The reaction mixture was washed with 30% aqueous sodium carbonate solution instead of potassium hydroxide. It was then put under vacuum and the low boiler (below 65 °C under 1 mm Hg, 1 mm Hg≈133.322 Pa) was stripped and kept in a freezer at −20 °C to give white crystalline solid which was identified to be *Z*-isomer in 46% yield. Mp 28—29 °C (lit,[7c] mp 28—28.5 °C); ^{1}H NMR (CCl_4) δ=2.47 (s); IR 2896, 1682, 1548, 1435, 1391 cm^{-1}. The blue colored distillate was chromatographed on silica gel and purified further by recrystallization from 95% ethanol in freezer to give light yellow solid melting around 5—10 °C. Bp 70—72 °C (8 mm Hg).[7c] This was found to be identical with E isomer by comparing with authentic sample prepared in different method.[10] ^{1}H NMR (CCl_4) 2.40 (s); IR 2924, 1545, 1443, 1383, 1128 cm^{-1}.

3,4-Dinitro-3-hexene (2): (*E*)- and (*Z*)-3,4-dinitro-3-hexene were prepared by the reported method[7a] except for the work up procedure. The reaction mixture was washed with 30% aqueous sodium carbonate solution instead of potassium hydroxide. It was then put under vacuum and the low boiler (below 80 °C under 1 mm Hg) was stripped and kept in a freezer at −20 °C to give light yellow needles which was identified to be *Z*-isomer in 42% yield. Mp 32—33 °C (lit,[7a] mp 31—32 °C); ^{1}H NMR (CCl_4) δ=1.24 (t, *J*=7.2 Hz, 6H), 2.66 (q, *J*=7.2 Hz, 4H); IR 2987, 1667, 1544, 1461, 1429, 1362, 1273, 1202, 1120, 1063, 967, 903, 816 cm^{-1}; MS, *m/z* (rel intensity) 174 (15, M^+), 81 (500), 79 (482), 77 (128), 67 (282), 65 (169). The blue colored distillate was chromatographed on silica gel which was found to be identical with *E* isomer by comparing with authentic sample prepared in different method.[7c] Yield 14%, bp 53—55 °C (1 mm Hg);[7c] ^{1}H NMR (CCl_4) δ=1.16 (t, *J*=7.2 Hz, 6H), 2.54 (q, *J*=7.2 Hz, 4H); IR 2986, 1545, 1461, 1438, 1352, 1273, 1119, 1062, 962, 929, 807 cm^{-1}; MS, *m/z* (rel intensity), 174 (13, M^+), 81 (241), 79 (167), 77 (78), 67 (214), 65 (112);

α,β-Dinitrostilbene (3): This was prepared by the reported method[7b] by addition of dinitrogen tetraoxide to diphenylacetylene. (*E*)-α,β-Dinitrostilbene, yield 9%, mp 186—187 °C (lit,[7b] mp 187—188 °C). (*Z*)-α,β-Dinitrostilbene, yield 15%, mp 107—108 °C (lit,[7b] mp 108—109 °C).

α-Iodo-β-nitrostilbene (4): This was prepared by the reported method[8] by the addition of dinitrogen tetraoxide to tolane and iodine in ether at 20 °C. (*E*)-α-Iodo-β-nitrostilbene, yield 55%, mp 177—179 °C (lit,[8] mp 175—176 °C). (*Z*)-α-Iodo-β-nitrostilbene, yield 12%, mp 115—117 °C (lit,[8] mp 113—114 °C).

General Procedure for the Substitution Reaction (Table 1): A solution of nitro olefins (10 mmol) in 10 ml of the specified solvent was stirred at a specific temperature to be dissolved. Into the solution of substrate was added dropwise the solution of nucleophile (11 mmol) in 20 ml of solvent. The reaction mixture was stirred at the specified temperature until all starting material was consumed completely. Following the standard work-up procedure the reaction product was purified by chromatography and (or) recrystallization.

(*Z*)-2-Methylamino-3-nitro-2-butene: Mp 90—91 °C; ^{1}H NMR ($CDCl_3$) δ=2.18 (s, 6H, CCH_3), 3.10 (d, *J*=5.5 Hz, 3H, NCH_3), 11.67 (s, 1H, NH); IR (KBr) 3449, 3108, 2938, 1594, 1509, 1475, 1424, 1396, 1342, 1216, 1173, 1080, 1022, 904, 820 cm^{-1}; MS *m/z* (rel intensity) 130 (100, M^+), 113 (23), 100 (11), 83 (27), 82 (70), 68 (26), 56 (33), 42 (13); Found: C, 46.2; H, 7.82; N, 21.5%. Calcd for $C_5H_{10}N_2O_2$: C, 46.1; H, 7.74; N, 21.5%.

(*Z*)-3-Methylamino-4-nitro-3-hexene: Mp 48—49 °C; ^{1}H NMR ($CDCl_3$) δ=1.07 (t, *J*=6 Hz, 3H, H-1), 1.22 (t, *J*=6 Hz, 3H, H-6), 2.48 (q, *J*=6 Hz, 2H, H-2), 2.51 (q, *J*=6 Hz, 2H, H-5), 3.15 (d, *J*=5.5 Hz, 3H, NCH_3), 11.15 (s, 1H, NH); IR (KBr) 3518, 3132, 2972, 1601, 1487, 1458, 1434, 1416, 1437, 1211, 1165, 1069, 1035, 993, 903 cm^{-1}; Found: C, 53.7; H, 8.97; N, 17.6%. Calcd for $C_5H_{10}N_2O_2$: C, 53.1; H, 8.90; N, 17.7%.

(*Z*)-α-Morphorino-β-nitrostilbene: Mp 206—207 °C; ^{1}H NMR ($CDCl_3$) δ=3.02 (t, *J*=6 Hz, 4H), 3.75 (t, *J*=6 Hz, 4H), 7.18 (bs, 5H), 7.40 (s, 5H); Found: C, 69.4; H, 5.81; N, 8.92%. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.6; H, 5.84; N, 9.02%

(*Z*)-2-Thiocyanato-3-nitro-2-butene: Mp 48—49 °C; ^{1}H NMR ($CDCl_3$) δ=2.38 (s, 3H, H-4), 2.60 (s, 3H, H-1); IR (KBr) 2936, 2163, 1602, 1493, 1440, 1391, 1365, 1299, 1096, 966, 858 cm^{-1}; MS *m/z* (rel intensity) 158 (M^+, 25), 72 (31), 69 (16), 59 (34), 58 (28), 53 (100), 51 (34), 50 (26), 43 (65), 39 (28), 30 (21); Found: C, 37.2; H, 3.73; N, 17.7%. Calcd for $C_5H_6N_2O_2S$: C, 37.9; H, 3.82; N, 17.7%.

(*Z*)-3-Thiocyanato-4-nitro-3-hexene: Mp 23.5—24 °C; ^{1}H NMR ($CDCl_3$) 1.20 (t, *J*=8 Hz, 3H, H-6), 1.38 (t, *J*=8 Hz, 3H, H-1), 2.76 (q, *J*=8 Hz, 2H, H-5), 2.88 (q, *J*=8 Hz, 2H, H-2); IR (KBr) 2982, 2158, 1597, 1504, 1476, 1463, 1456, 1382, 1312, 1272, 1116, 1106, 1067, 1052, 1018, 929, 864, 813 cm^{-1}; Found: C, 45.2; H, 5.41; N, 15.0%. Calcd for $C_7H_{10}N_2O_2S$: C, 45.1; H, 5.41; H, 15.0%

(*Z*)-α-Thiocyanato-β-nitrostilbene: Mp 188—189 °C; ^{1}H NMR ($CDCl_3$) δ=7.15—7.30 (m); ^{13}C NMR ($CDCl_3$) 108.9, 128.3, 128.7, 128.8, 129.5, 130.0, 130.3, 130.9, 134.1 144. 2, 147.7; IR (KBr) 2075, 1490, 1295 cm^{-1}; Found: C, 61.4; H, 3.56; N, 9.95; S, 11.1%. Calcd for $C_{15}H_{10}N_2O_2S$: C, 63.8; H, 3.57; N, 9.92; S, 11.35%.

(*E*)-2-(*p*-Tolylthio)-3-nitro-2-butene: ^{1}H NMR ($CDCl_3$) δ=2.04 (s, 3H, methyl), 2.30 (s, 3H, methyl), 2.39 (s, 3H, methyl), 7.20 (d, *J*=8 Hz, 2H), 7.36 (d, *J*=8 Hz, 2H); Found: C, 58.9; H, 5.92; N, 5.9I%. Calcd for $C_{11}H_{13}NO_2S$: C, 59.1; H, 5.86: N, 6.27%.

(*Z*)-2-(*p*-Tolylthio)-3-nitro-2-butene: ^{1}H NMR ($CDCl_3$) δ=1.91 (s, 3H, methyl), 2.32 (s, 3H, methyl), 2.39 (s, 3H, methyl), 7.18 (d, *J*=8 Hz, 2H), 7.42 (d, *J*=8 Hz, 2H); Found: C, 59.2; H, 5.88; N, 6.19%. Calcd for $C_{11}H_{13}NO_2S$: C, 59.1; H, 5.86; N, 6.27%.

(*E*)-3-(*p*-Tolylthio)-4-nitro-3-hexene: ^{1}H NMR ($CDCl_3$) δ=1.04 (t, *J*=7.3 Hz, 3H, H-1), 1.15 (t, *J*=7.3 Hz, 3H, H-6), 2.24 (q, *J*=7.3 Hz, 2H, H-5), 2.36 (s, 3H, methyl), 2.89 (q, *J*=7.3 Hz, 2H, H-2), 7.15 (d, *J*=7.8 Hz, 2H), 7.26 (d, *J*=7.8 Hz, 2H); IR (neat) 1501, 1313 cm^{-1}; MS *m/z* (rel intensity), 251 (84, M^+), 221 (80), 177 (35), 163 (100), 123 (32), 119 (43), 79 (64); Found: C, 62.1; H, 6.88; N, 5.61%. Calcd for $C_{11}H_{17}NO_2S$: C, 62.1; H, 6.81: N, 5.57%.

(*Z*)-3-(*p*-Tolylthio)-4-nitro-3-hexene: Mp 56—58 °C; ^{1}H NMR ($CDCl_3$); δ=0.97 (t, *J*=7.3 Hz, 3H, H-1), 1.15 (t, *J*=7.3 Hz, 3H, H-6), 2.24 (q, *J*=7.3 Hz, 2H, H-5), 2.40 (s, 3H, methyl), 2.72 (q, *J*=7.3 Hz, 2H, H-2), 7.27 (d, *J*=7.8 Hz, 2H), 7.41 (d, *J*=7.8 Hz, 2H); IR (KBr) 1561, 1294 cm^{-1}; MS *m/z* (rel

intensity) 251 (60, M^+), 221 (67), 177 (31), 163 (100), 123 (31), 119 (50), 79 (93); Found: C, 62.2; H, 6.94; N, 5.82%. Calcd for $C_{11}H_{17}NO_2S$: C, 62.1; H, 6.81: N, 5.57%.

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