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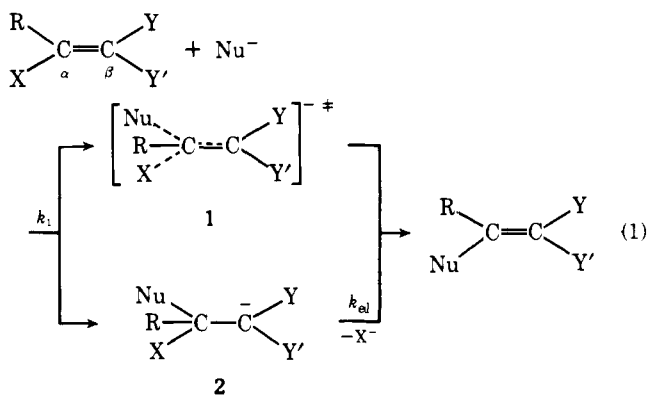
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## Nucleophilic Attacks on Carbon-Carbon Double Bonds. 26.<sup>1</sup> Stereoconvergence in Nucleophilic Vinylic Substitution of an Activated Nitro Olefin

Sir:

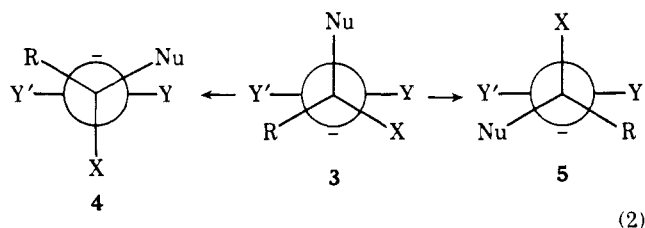
The mechanism of nucleophilic vinylic substitution via addition-elimination<sup>2</sup> continues to be of interest in recent years.<sup>3-6</sup> A main question is whether the substitution is a single-step process with concerted C-Nu bond formation and C-X bond cleavage (transition state **1**) or a multistep process via a carbanionic intermediate **2** when Nu is a negatively charged nucleophile (eq 1) or via a zwitterionic intermediate when Nu is a neutral nucleophile.



Y, Y' = activating groups; X = leaving group;  
Nu<sup>-</sup> = nucleophile

When X is a poor leaving group, e.g., F or OR, the evidence for reaction via long-lived carbanions is overwhelming. It includes the isolation of adducts in protic media,<sup>7</sup> stereoconvergence (i.e., formation of the same products from *E* and *Z* precursors),<sup>8</sup> amine catalysis in reaction with amines,<sup>1,9</sup> high  $k_F/k_{Cl}$  ratios,<sup>8,10</sup> and (*E*)-RX  $\rightleftharpoons$  (*Z*)-RX isomerization during the reaction.<sup>11</sup> When X is a good leaving group, e.g., Cl, Br, or I, some authors argue for a single-step process<sup>5,11</sup> based on the preferred or exclusive retention<sup>2-4,6,11</sup> of configuration observed for most (*E*)- and (*Z*)-chloro and bromo olefins as well as on calculations<sup>5b,c</sup> and the reactivity order  $RBr > RCl > RF$  found for a small number of unactivated systems.<sup>12</sup> In contrast, the element effects ( $k_{Br}/k_{Cl} > 1$ ,  $k_F/k_{Cl} \gg 1$ ),<sup>2,3,8,10,13</sup> the amine catalysis for activated chloro olefins,<sup>9a,13a</sup> the incomplete retention, and the recent calculations which indicate preferred retention for reaction via carbanions<sup>5c,14</sup> argue for a multistep route.

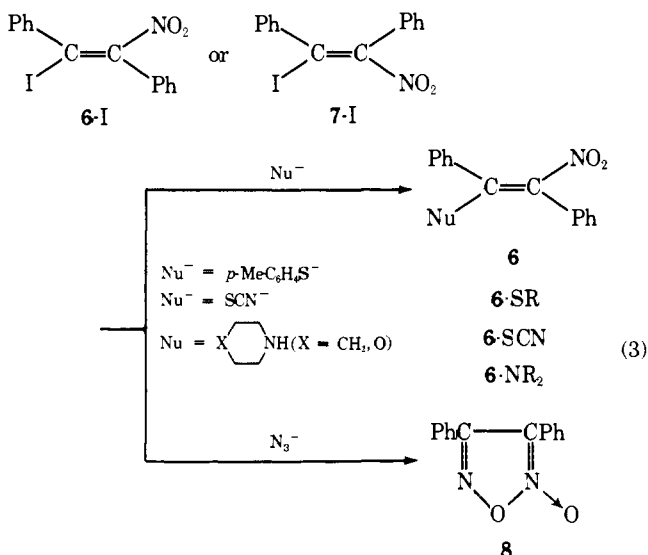
The nucleophilic attack ( $k_1$ ), the internal rotation in the intermediate or along the reaction coordinate ( $k_{rot}$ ), and leaving group expulsion ( $k_{el}$ ) are concerted in the single-step process. In the multistep process, retention will be observed only if 60° clockwise rotation of the initially formed conformer **3** to give **4** is faster than 120° anticlockwise rotation to give **5** which leads to inversion and if  $k_{el} > k_{rot}$ , i.e., when **2** is short lived (eq 2). This is likely to occur when most of the charge is



localized on C<sub>β</sub>, and we therefore predict that, for a highly activated electrophilic olefin, stereoconvergence may be obtained since, for the resulting long-lived carbanion **2**, the condition  $k_{rot} > k_{el}$  will be fulfilled.

We chose for study (*E*)- and (*Z*)- $\alpha$ -iodo- $\beta$ -nitrostilbenes **6-I** and **7-I**,<sup>15</sup> which carry the single most activating nitro group and the fast iodide leaving group but lack hydrogens which may be involved in elimination-addition routes.<sup>2,3</sup>

The reactions of **6-I** and **7-I** with five different nucleophiles are presented in eq 3. The reactions with *p*-toluenethiolate ion



in EtOH, with piperidine, morpholine, and SCN<sup>-</sup> ion in MeCN, and with N<sub>3</sub><sup>-</sup> ion in MeOH gave a single, and the same product, from both **6-I** and **7-I** in each case, as shown in Table I.<sup>16</sup> The identity of the products from **6-I** and **7-I** was established by mixture melting point, by the IR spectra, by the identical NMR spectra, and by the retention times on TLC silica plate using 10% acetone-90% petroleum ether. The possibility that the two isomers are obtained in exactly the same ratio from **6-I** and **7-I** seems remote. In all the reactions the observed optical density at infinity under kinetic conditions was identical with the calculated value,<sup>17</sup> even for the reaction of **7-I** with SCN<sup>-</sup>. The yields in the table are lower limits for the stereochemical purity since they are for the isolated material and chromatography gave no indication for the formation of the geometrical isomers. The formation of only a single isomer in each case did not enable an unequivocal structural determination and tentatively we suggest that the products in all the reactions except with N<sub>3</sub><sup>-</sup> are the (presumably) more stable *E* isomers **6**. The only product isolated from the reaction with N<sub>3</sub><sup>-</sup> is 3,4-diphenylfuroxan (**8**),<sup>18</sup> formed probably via cyclization of the initially formed vinyl azide.

The main product from the reaction of SCN<sup>-</sup> with **7-I** is the vinylic thiocyanate. A second product (mp 85-88 °C;  $\delta$  (CDCl<sub>3</sub>) 7.05-7.10 ppm;  $m/e$  282 (2%), 178 (50%), 149 (100%)) was isolated in 20% yield. Since it showed no absorption between 2800 and 1600 cm<sup>-1</sup>, it is not the isomeric **7-SCN**, but may be a cyclization product. This product was not investigated further.

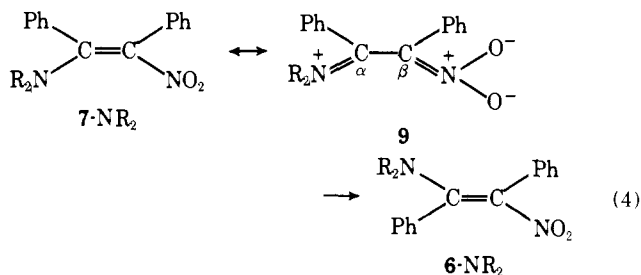
**Table I.** Stereochemistry of the Substitution of  $\text{PhC(I)=C(NO}_2\text{)Ph}$ 

sub- strate	nucleophile <sup>a</sup>	solvent	reaction conditions h/°C	% product <sup>b</sup>	mp of product °C
6-I	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> S <sup>-</sup>	EtOH	1/25	93 6-SR	125–127
7-I	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> S <sup>-</sup>	EtOH	1/25	91 6-SR	125–127
6-I	SCN <sup>-</sup>	MeCN	96/25	89 6-SCN	196
7-I	SCN <sup>-</sup>	MeCN	168/25	41 6-SCN	196
6-I	N <sub>3</sub> <sup>-</sup>	MeOH	24/0	78 8	118 <sup>c</sup>
7-I	N <sub>3</sub> <sup>-</sup>	MeOH	24/0	75 8	118 <sup>c</sup>
6-I	piperidine	MeCN	2/25	90 6-NR <sub>2</sub>	172–173
7-I	piperidine	MeCN	2/25	90 6-NR <sub>2</sub>	172–173
6-I	morpholine	MeCN	12/25	90 6-NR <sub>2</sub>	213–214
7-I	morpholine	MeCN	12/25	90 6-NR <sub>2</sub>	213–214

<sup>a</sup> [Nucleophile]/[substrate] = 10 except for the reactions of *p*-MeC<sub>6</sub>H<sub>4</sub>S<sup>-</sup> when the ratios were 1. <sup>b</sup> Yield of the isolated product. <sup>c</sup> Lit.<sup>18</sup> 117 °C.

The kinetics gave excellent first-order rate coefficients and, since 6-I and 7-I react with different rates,<sup>17</sup> a 6-I  $\rightleftharpoons$  7-I isomerization did not take place during the reaction. 7-I is less stable than 6-I as shown by the conversion of 7-I into 100% 6-I in the presence of one crystal of iodine in EtOH for 1 week at room temperature. When 1 equiv of 6-I was reacted with 0.5 equiv of *p*-MeC<sub>6</sub>H<sub>4</sub>S<sup>-</sup> in ethanol, the NMR after normal workup was consistent with that of a mixture of 6-I and 6-SR with no evidence for 7-I. A 6-I  $\rightleftharpoons$  7-I isomerization under these conditions is therefore excluded.

The stereoconvergence with morpholine and piperidine probably has no relevance to our mechanistic problem since the (*Z*)-nitroenamines 7-NR<sub>2</sub> are expected to be configurationally unstable owing to a low rotational barrier around the C<sub>α</sub>-C<sub>β</sub> bond in the dipolar structure 9 (eq 4).<sup>2,19</sup> Stereocon-



vergence is generally found for this reason for substitution by amines<sup>2,20</sup> (except for ethylenimine).<sup>21</sup> The possibility that similar low rotational barriers may be responsible for the stereoconvergence for the thionucleophiles cannot be ruled out unequivocally. However, the thio substitution products of less activated electrophilic olefins are usually configurationally stable.

An initial electron transfer from the thio nucleophile, followed by combination of the formed radical anion with the thio radical to give 2, is another possibility for our  $\alpha$ -nitrobenzyl system.<sup>22</sup> Stereoconvergence is then expected at the radical-anion stage,<sup>22b</sup> but, since this step is assumed to be reversible and 6-I  $\rightleftharpoons$  7-I isomerization during the reaction was not observed, this route is unlikely. The use of less ambiguous, but slower nucleophiles, such as CF<sub>3</sub>COO<sup>-</sup> is currently under study.

In conclusion, the present first example of stereoconvergence under kinetic control<sup>23</sup> in substitution of an activated halo olefin (X  $\neq$  F) by nonamine nucleophiles strongly supports other evidence for the multistep substitution route, at least for highly activated systems.

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## An Experimental Study of Nucleophilic Addition to Formaldehyde in the Gas Phase

Sir:

The addition of nucleophiles to carbonyl compounds has long played a vital role in organic chemistry.<sup>1</sup> The adducts themselves have rarely been sufficiently stable to be observed or isolated but are commonly invoked as "tetrahedral intermediates" in the mechanisms of important transformations in solution.<sup>2,3</sup> More recently several attempts have been reported to identify and assess the role of such intermediates in analogous gas-phase anion-molecule reactions. These attempts were carried out at low pressures (<10<sup>-4</sup> Torr) and for adducts which again almost invariably acted as transient species.<sup>4</sup> Here we report results of gas-phase measurements of reactions of several simple nucleophiles with the simplest carbonyl system, formaldehyde, at higher pressures (~0.5 Torr).<sup>5</sup> They provide the first direct observation of stabilized nucleophile-formaldehyde adducts including the simplest adduct with H<sup>-</sup> whose formation has recently been supported theoretically.<sup>6</sup> Furthermore, they provide examples of carbonyl additions which yield intermediates that undergo further transformation. The intrinsic behavior of these addition reactions, which are so fundamental to solution chemistry, has been fully characterized through the identification of products and the measurement of reaction kinetics.