Fluorination of the Enol Acetates 41 and 43.[19] **Method A.** After the instantaneous reactions, in both cases the crude reaction mixtures were treated with methanolic NaOH solution for 2 h. The α-fluoroketones **42** and **44** were thus obtained in 70% and 90% yields, respectively. Their physical data are in full agreement with those published in the literature.

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Registry No. **1**, 78948-09-1; **2**, 103-30-0; **3**, 78948-08-0; **4**, 78948-07-9; **5**, 645-49-8; **6**, 1694-19-5; **7**, 98014-16-5; **8**, 98014-17-6; **9**, 98014-18-7; **10**, 98014-19-8; **11**, 4180-23-8; **12**, 98014-20-1; **13**, 98014-21-2; **14**, 98014-22-3; **15**, 98014-23-4; **16**, 35897-95-1; **17**, 98014-24-5; **18**, 98014-25-6; **19**, 112-41-4; **20**, 98014-26-7; **21**, 1063-81-6; **22**, 98014-27-8; **23**, 4192-77-2; **24**, 50778-20-6; **25**, 19713-73-6; **26**, 98014-28-9; **27**, 614-47-1; **28**, 98014-29-0; **29**, 63-05-8; **30**, 98014-30-3; **31**, 98102-30-8; **32**, 91-64-5; *cis*-**33**, 98014-31-4; *trans*-**33**, 98014-32-5; **34**, 704-60-9; **35**, 25512-62-3; **36**, 1193-18-6; **37**, 10544-63-5; **38**, 501-65-5; **39**, 536-74-3; **40**, 1604-29-1; **41**, 14478-13-8; **42**, 1755-14-2; **43**, 38736-92-4; **44**, 56114-30-8; diethyl maleate, 141-05-9; diethyl fumarate, 623-91-6; cyclohexene, 110-83-8.

MO Studies on S- to N-Nitrosation Rearrangement

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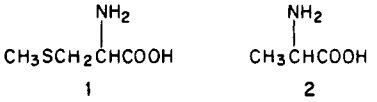
The nitrosation of sulfur–nitrogen ambident substrates has been studied by use of the frontier orbital approach. The increased diazotization rate of *S*-methyl-L-cysteine, **1**, compared with alanine, **2**, is well explained from the concept of charge and frontier controlled reactions. The nitrosyl cation prefers to attack sulfur in **1** rather than nitrogen in **1** and **2**, by an orbital controlled reaction followed by S to N rearrangement of the nitroso group. The structure of the different intermediates has been optimized by CNDO and/or INDO calculations and the electronic structure and total energy have been calculated by Gaussian 80 (4-31G). In a similar way has the nitrosation of thiourea been analyzed and the obtained results are analyzed in relation to the experimental results and a one electron-transfer mechanism.

In a recent paper[1] the diazotization of L-methionine and *S*-methyl-L-cysteine, **1**, was found to occur about 100 times faster than that of alanine, **2**.

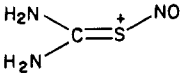


1 **2**

It was suggested that an initial S-nitrosation of L-methionine and *S*-methyl-L-cysteine was the first step, followed by an intra S to N rearrangement of the nitroso group (Scheme I).[1]

A part of the large difference in second-order rate constant for the reaction of **1** and **2** (0.109 and 0.0013 L mol^{-1} s^{-1}, respectively) can be accounted for by the difference in pK_a values of the reagents, but this effect accounts only for a factor of 7.6 relative to alanine.[1]

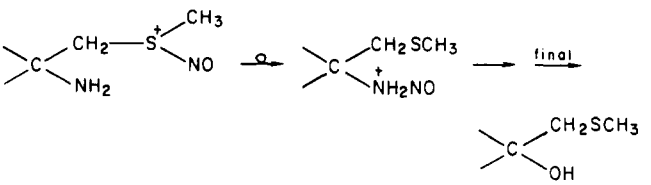
Thiourea is known to be a powerful catalyst for both nitrosation and diazotization.[2] Thiourea forms a somewhat unstable *S*-nitroso cation, **3**, which is directly observable as a yellow species.[3] Indirectly, it has also been shown that this cation can itself act as a nitrosation agent.



3

The nitrosation of thiourea can lead to different products depending on the acidity.[3] It was shown that reaction

Scheme I



1 was favored by high acidities, whereas reaction 2 was predominant at low acidities.[3]

$$2H^+ + 2HNO_2 + 2(H_2N)_2CS \rightarrow (NH_2)_2C^+SSC^+(NH_2)_2 + 2NO + 2H_2O \quad (1)$$

$$HNO_2 + (H_2N)_2CS \rightarrow H^+ + SCN^- + N_2 + 2H_2O \quad (2)$$

It has been suggested that N-nitrosation of thiourea which occurs at low acidity arises from an initial S attack followed by subsequent rearrangement,[3c] but ^{15}N NMR studies on the same system argue in favor of a direct attack on nitrogen.[4]

In an attempt to through light over these reactions, and as an extension of our MO studies concerning nitrosation mechanisms and ambident reactivity,[5] this paper presents a MO analysis of nitrosation *S*-methyl-L-cysteine and thiourea.

Methods, Results, and Discussion

The choice of CNDO[6] and INDO[6] as methods of calculation stems from the possibility of optimizing the geom-

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(4) Lown, J. W.; Chauhan, S. M. S. *J. Org. Chem.* **1983**, *48*, 507, 513.
(5) (a) Jørgensen, K. A.; El-Wassimy, M. T. M.; Lawesson, S.-O. *Acta Chem. Scand., Ser. B.* **1983**, *B37*, 785. (b) Jørgensen, K. A.; Lawesson, S.-O. *J. Am. Chem. Soc.* **1984**, *106*, 4687. (c) Jørgensen, K. A.; Lawesson, S.-O. *J. Chem. Soc., Perkin Trans.* **1985**, 231.
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Table I. Ab Initio[a] Calculated Atomic Net Charges, Molecular Orbital Coefficients, and HOMO Energies for 2-(Methylthio)ethylamine, 4, and Ethylamine, 5

	2-(methylthio)ethylamine		ethylamine
	HOMO	2nd HOMO	HOMO
q_N	−0.77		−0.78
q_S	0.18		
c_N	0.06	0.72	0.63
c_S	0.82	0.16	
ϵ (eV)	−8.78	−10.53	−10.19

[a] Gaussian 80, basis set 4-31G.

etry of molecular systems of the present size within reasonable efforts. These methods usually predict geometries for neutral molecules in good agreement with experimental and/or ab initio calculations. When the optimized structure obtained from CNDO and/or INDO calculations is used, the total energy and electronic structure have been calculated by using ab initio SCF-MO-LCAO 4-31G wave functions.[7]

In an attempt to describe the reactivity of the involved systems the frontier orbital approach developed by Klopman is used. For small perturbations, the total energy, ΔE, due to the formation of a bond between a nucleophile and an electrophile is

$$\Delta E = -q_n q_e \Gamma/\epsilon + \Delta \text{ solv} + \sum_{\substack{m \\ occ}} \sum_{\substack{n' \\ unocc}} \frac{2(c_n^m)^2(c_e^{n'})^2 \beta_{ne}^2}{E_n^* - E_e^*} \quad (3)$$

where q_n and q_e are the initial charge of the nucleophile and electrophile, respectively, Γ is the Coulomb repulsion term, ϵ the "micro" dielectric constant of the solvent, Δ solv is the change in solvation energy during the reaction, c_n and c_e are the molecular orbital coefficient of the nucleophile and electrophile, respectively, β_{ne} the bond integral, and E_n^* and E_e^*, the intrinsic softness of the nucleophile and electrophile, respectively. The first term in eq 3 represents the Coulomb interaction term, and the third term is the orbital interaction term. The solvent influence on the reactivity is represented in all three terms. As an approximation to eq 3 Δ solv is neglected. The influence of the solvent on the HOMO energy is relatively small compared with anionic nucleophiles,[9] as the nucleophiles in this case are neutral species. E_n^* and E_e^* are then represented by ϵ_{HOMO} and ϵ_{LUMO} for the nucleophile and electrophile, respectively. For c_n^m and $c_e^{n'}$ the molecular orbital coefficients in the HOMO and LUMO state, are used, respectively. Eq 3 is then reduced to

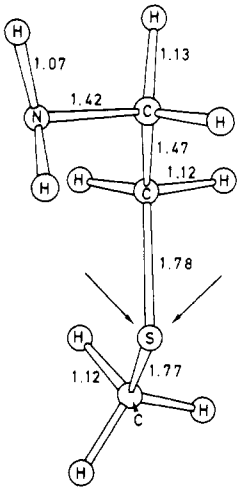
$$\Delta E = -q_n q_e \Gamma/\epsilon + \frac{2(c_n)^2(c_e)^2\beta_{ne}^2}{\epsilon_{HOMO} - \epsilon_{LUMO}} \quad (4)$$

2-(Methylthio)ethylamine, **4**, and ethylamine, **5**, have been used as model compounds for *S*-methyl-L-cysteine, **1**, and alanine, **2**, in the analysis presented here.

$CH_3SCH_2CH_2NH_2$ $CH_2CH_2NH_2$

4 **5**

The CNDO and INDO optimized structure of **4** is shown in Figure 1. Table I gives ab initio calculated atomic net charges for sulfur and nitrogen in **4**, and for nitrogen in **5**, as well as the first and second HOMO energy and the



4

Figure 1. The optimized structure of 2-(methylthio)ethylamine, **4**.

Table II. Calculated Coulomb and Orbital Interaction Energies (from Eq 4) for Interaction of the Nitrosyl Cation–Water Complex with Sulfur and Nitrogen in 4 and Nitrogen in 5

	coulomb energy,[a] eV	orbital energy, eV
S (4)	0.01	−2.05
N (4)	−0.06	∼−0.01
N (5)	−0.09	−0.10

[a] ϵ = 80 (water); $R_{S\text{-}N}$ = 1.80 Å; $R_{N\text{-}N}$ = 1.36 Å. (The distances are obtained from the optimized structures.)

molecular orbital coefficients for sulfur and nitrogen of **4**. The HOMO energy and molecular orbital coefficient for nitrogen in **5** are also given. The HOMO energy for ethylamine is in good agreement with the experimentally found ionization potential (9.50 eV).[10]

Compound **4** possesses two sites for electrophilic attack: sulfur and nitrogen. The sulfur is soft because it has a relatively large molecular orbital coefficient and a relatively high HOMO energy, whereas nitrogen is relatively hard due to its high negative charge and low energy of the frontier orbital electrons which are present there.[11] Soft electrophiles will thus prefer to attack sulfur whereas hard electrophiles will prefer to attack nitrogen.[11] The second HOMO energy, atomic net charge, and molecular orbital coefficient on nitrogen in **4** correspond to the same parameters for nitrogen in **5**.

For the nitrosyl cation which has been classified as a borderline acid with a tendency to be soft,[11] the atomic net charge and molecular orbital coefficient on nitrogen and LUMO energy have been calculated previously (0.79, 0.64, and −6.74 eV, respectively, (as a water complex)).[5c] Table II gives the calculated Coulomb and orbital interaction energies for the nitrosyl cation–water complex and sulfur and nitrogen in **4** and nitrogen in **5**. The change in frontier orbital energy for the nitrosation of sulfur and nitrogen in **4** is shown in Figure 2.

The results in Table II indicate that the nitrosyl cation prefers to attack sulfur in **4** rather than nitrogen in **4** and **5**. The difference in reactivity comes mainly from the

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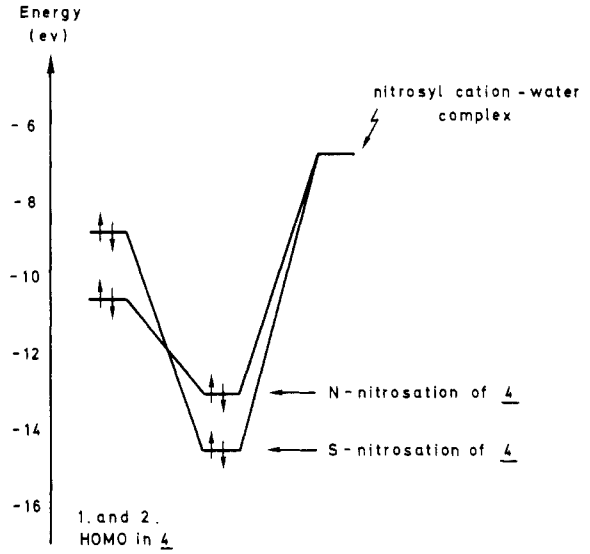
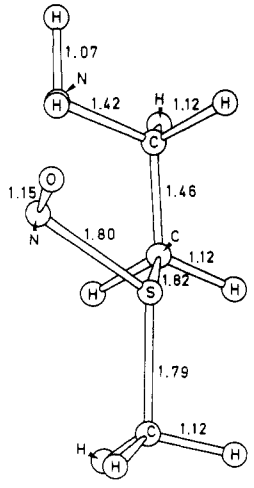


Figure 2. The change in frontier orbital energy for the nitrosation of sulfur and nitrogen in 2-(methylthio)ethylamine, 4.

small difference in the denominator of the orbital term in eq 4 between the LUMO of the nitrosyl water–cation complex and the HOMO of 4. The results in Table II also indicate that the reactivity of the nitrogen in both 4 and 5 toward nitrosation is of the same magnitude. The difference in orbital interaction energy between nitrosation of sulfur in 4 and nitrogen in 5 might then explain the experimental observed ratio between the reaction rate of 1 and 2 which has been found to be 11.[1]

Figure 2 also indicates that the S-nitrosation of 4 is favored compared with a N-nitrosation as the decrease in HOMO energy is greater for the S-nitrosated product compared with the N-nitrosated.

Nitrosation of sulfur in 4 can occur from two sites (indicated by the arrows in Figure 1), leading to two 2-(*S*-nitrosomethylthio)ethylamine cation intermediates, **6a,b**, one in which the nitroso nitrogen is "syn" to the amine nitrogen, **6a**, and one in which the nitroso group is "anti" to the amine group, **6b**. The geometry of **6a** and **6b** has been optimized by CNDO and INDO calculations. The optimized structures seem to be in agreement with the expected geometries. The total energy of **6a** is slightly lower than **6b**.



6a

By nitrosation of sulfur in 4, the HOMO which in 4 is mainly located on sulfur changes to be on the amine nitrogen in **6a** and **6b**, whereas the LUMO which is located

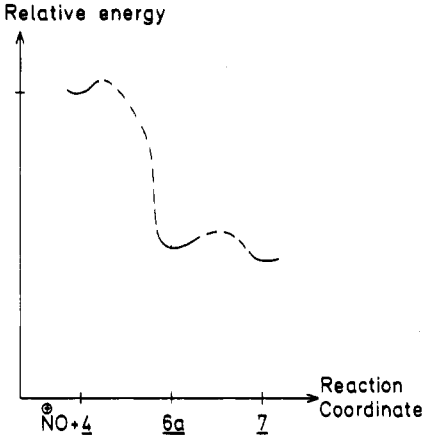
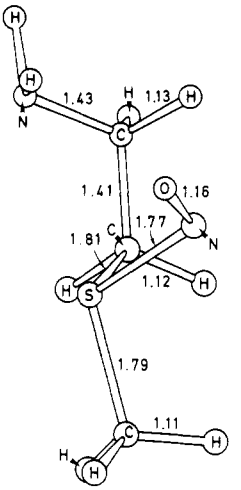


Figure 3. The change in total energy (ab initio) for the nitrosation of 2-(methylthio)ethylamine, 4, and the S- to N-nitroso rearrangement step.

on the nitroso nitrogen remains there after the nitrosation of sulfur. The HOMO energy in **6a** is −14.49 eV and the LUMO energy is −4.21 eV. The HOMO coefficient on the amine nitrogen is 0.74 and the LUMO coefficient on the nitroso nitrogen is 0.72; the atomic net charges on the two nitrogens are −0.77 and 0.03, respectively (**6a**).



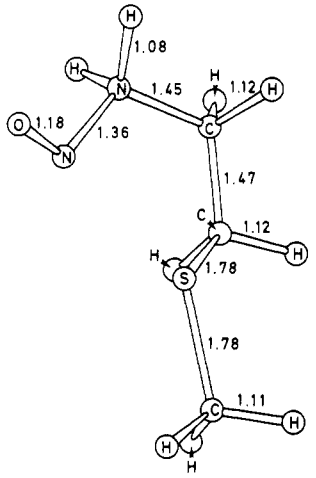
6b

The relative change in total energy (ab initio) of 4 + NO to **6a** is shown in Figure 3.

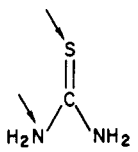
The distance between the two nitrogens is 2.44Å in **6a** and 3.74Å in **6b**, and the former should thus be most favored for an intramolecular S to N rearrangement of the nitroso group. Furthermore, the HOMO orbital on the amine nitrogen is arranged so that a favorable orbital interaction with the LUMO orbital on the nitroso nitrogen is possible.

The geometry of the optimized *N*-nitroso-2-(methylthio)ethylamine, **7**, is shown below. The change in total energy for the S- to N-nitrosation rearrangement step is shown in Figure 3. The energy difference between **6a** and **7** has been calculated to about 12 kcal mol^{-1}, a value which is reliable compared with other rearrangement reactions. The exaggerated energy difference between the starting reagents and **6a** might come from the absence of solvent.

Just as 2-(methylthio)ethylamine, 4, thiourea, **8**, possesses two sites for electrophilic attack: sulfur and nitrogen.



7



8

The geometry of 8 has also been optimized and the relevant structural and electronic data are given in Table III. The structural data are in good agreement with those found by X-ray crystallographic investigation.[12]

The electrons in the first HOMO are mainly located on sulfur (c_s = 0.74) with an energy of −8.12 eV (IP = 8.50 eV),[10] whereas the electrons in the third HOMO are located on the two nitrogens (c_N = 0.59) with an electronic energy of −11.74 eV.

The electronic results in Table III indicate that the situation here is very similar to that of 2-(methylthio)-ethylamine: soft electrophiles prefer to attack the soft sulfur and hard electrophiles prefer to attack the relatively hard nitrogen. The calculated Coulomb and orbital interaction energies for the reaction of the nitrosyl cation–water complex and 8 are given in Table IV.

The results indicate that the nitrosyl cation will prefer to attack sulfur by an orbital controlled reaction, rather than attack one of the nitrogens by a charge controlled reaction. Calculation of the orbital interaction energy for the nitrosyl cation with the nitrogen in 8 by using the molecular orbital coefficient for nitrogen in the third HOMO and the corresponding orbital energy increases this interaction by a factor of about 2.5. But this increase in orbital interaction energy does not favor a N-nitrosation of 8.

Let us return to the experimental results for the studied nitrosation reactions and try to compare these with the MO results given above.

The observed difference in reactivity between *S*-methyl-L-cysteine and alamine is well explained from the MO results; furthermore, the study of the total energy as a function of the reaction coordinate (Figure 3) accounts for the rearrangement.

With regard to the nitrosation of thiourea different experimental results depending on the acidity are obtained. It has been argued that both S- and N-protonation of thiourea are observed under acidic conditions[13] so it might

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Table III. Bond Lengths, Bond Angles, Atomic Net Charges, Molecular Orbital Coefficients, and HOMO Energy for Thiourea

	thiourea	
	structural data[a]	electronic data[b]
C=S, Å	1.71	q_S = −0.12
C–N, Å	1.35	q_C = 0.36
N–H, Å	1.07	q_N = −0.90
∢ NCS	122°	c_S = 0.74
∢ NCN	116°	c_C = 0.19
		c_N = 0.25
		ϵ_{HOMO} = −8.12

[a] CNDO/1 results. [b] Gaussian 80 results (CNDO/1 optimized structure). The HOMO of thiourea is of π symmetry.

Table IV. Calculated Coulomb and Orbital Interaction Energies (Eq 4) for the Nitrosyl Cation–Water Complex and Thiourea

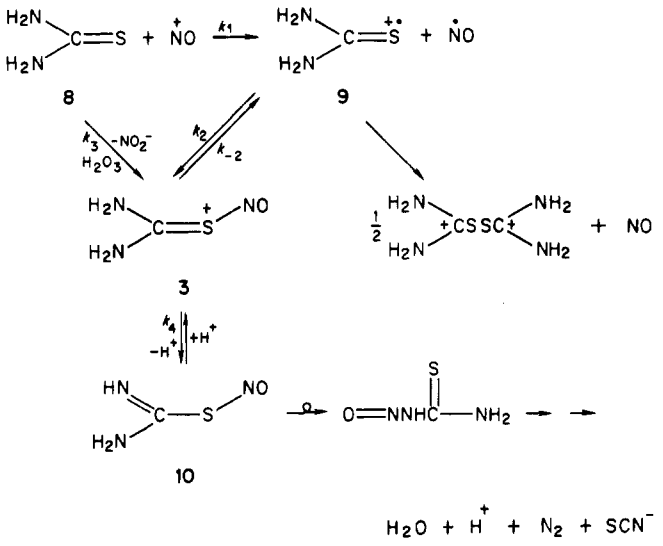
	coulomb energy,[a] eV	orbital energy, eV
S	−0.01	−2.71
N	−0.07	−0.14

[a] ϵ = 80 (water); R_{S-N} = 1.74 Å; R_{N-N} = 1.33 Å (from CNDO/1 optimized structures).

Table V. The Distribution of NO and N_2 Obtained from Nitrosation of Thiourea with Sodium Nitrite in Different Acids.[3b]

acid	NO, %	N_2, %
hydrochloric acid	95.95	4.05
oxalic acid	88.66	11.34
tartaric acid	58.01	41.99
malonic acid	51.88	48.12
malic acid	39.68	60.32
lactic acid	35.91	64.09
glycollic acid	32.51	67.49
succinic acid	19.37	80.63
acetic acid	12.55	87.45
propionic acid	11.60	89.40

Scheme II

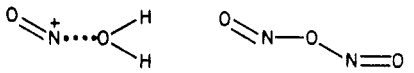


be expected that N-protonation will favor S-nitrosation and the reverse. It has experimentally been shown that α,α-dithiobis(formamidinium) and nitrogen oxide are formed at high acidities (reaction 1) and thiocyanate and nitrogen at low acidities (reaction 2).[3]

Werner and Coade have studied[3b] the distribution of NO (from eq 1) and N_2 (from eq 2) with different acids, Table V. Inspection of these results indicates that two reactions take place simultaneously. To account for the different

products, two different reaction mechanisms which occur simultaneously are suggested: At high acidity a one electron transfer is predominant (Scheme II, k_1), whereas an electrophilic attack of the nitrosyl cation (from dinitrogen oxide, Scheme II, k_3) on the sulfur atom and loss of a proton followed by a S- to N-nitroso rearrangement, dominate at low acidity.

The advantage of introducing the two different reaction paths for the nitrosation of thiourea is that it explains the different products formed. To account for the difference in reaction mechanism it might be useful to draw the attention to the nitrosation reagents. At high acidity it is a nitrosyl cation–water complex, **11**, which is the effective nitrosation reagent, whereas at low acidity it is dinitrogen trioxide, **12**.[2] The two nitrosation species, **11** and **12** have different reduction potential, 1.46 V and 0.984 V,[14] respectively (different LUMO energy[5c]), whereas the oxidation peak potential for thiourea remains constant at about 1.5 V in the pH interval 0–7.[15]



11 **12**

When the nitrosation of thiourea takes place at high acidity the redox potentials indicate that the first step is a one electron transfer from thiourea to the nitrosyl cation (k_1) with formation of a thiourea cation radical, **9**, and nitrogen oxide. From **9** there might be two possibilities, dimerization to give the α,α-dithiobis(formamidinium) or a reaction between **9** and nitrogen oxide to give **3** (k_2).

At low acidity a direct overlap between the HOMO of thiourea and the LUMO of the nitrogen in the nitrosyl group of **12** is necessary for a reaction to take place; the *S*-nitrosothiourea cation, **3**, is then formed.

From **3** there might be two possibilities. A homolytic fission (k_{-2}) or loss of a proton to give **10** (k_4). At high acidity it might be expected that $k_{-2} > k_4$, whereas at low acidity $k_4 > k_{-2}$.

If a one electron-transfer reaction is occurring at high acidity one should also, according to the Marcus theory,[16] expect to find a very fast reaction compared with the reaction which takes place at low acidity. Stedman et al. have shown that the nitrosation at high acidity occurs much faster than at low acidity,[3c] which supports the mechanism.

Formulation of electrophile attack on a nucleophile as a one electron-transfer mechanism has been suggested by Perrin in 1977.[17] He suggested that the nitronium cation mediated nitration of all aromatic compounds with an oxidation potential lower than that of toluene should follow a one electron-transfer mechanism.[17] Gas-phase ion molecule and ^{15}N nuclear polarization nitration studies reveal that an electron-transfer process takes place.[18] A similar result is observed in nitrosation reactions.[18a] For the reaction studied here this idea is supported by the ionization potential of thiourea which is 8.50 eV,[10] whereas it is 8.93 eV for toluene. It should thus be easier to transfer an electron from thiourea compared with toluene to an acceptor.

It is concluded that the difference in reactivity of *S*-methyl-L-cysteine and alanine toward nitrosation can be accounted for by the frontier orbital method. Studies of the total energy functional of the nitrosation of *S*-methyl-L-cysteine followed by the S to N rearrangement of the nitroso group explain and support[1] the experimental results. Similarly the S-nitrosation of thiourea can also be described by the frontier orbital approach, and the difference in products at different acidity can be accounted for by assuming that a one electron-transfer process takes place.

Acknowledgment. Thanks are expressed to Dr. Henning Lund for fruitful discussions and help and to the Danish Natural Research Council for financial support.

Registry No. 1, 1187-84-4; 2, 56-41-7; 4, 18542-42-2; 5, 75-04-7; thiourea, 62-56-6.

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A Selective Synthesis of a Mixture of 15-Epimers of (±)-11-Deoxyprostaglandin E_2 Methyl Ester[1]

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A highly regio- and stereoselective procedure for allylation of 3-alkenyl-substituted 1-cyclopentenolates involving the use of readily obtainable and thermally stable allylic acetates, BEt_3 (2 equiv), and $Pd(PPh_3)_4$ (2 mol %) was applied to the synthesis of a ca. 50:50 diastereomeric mixture of 11-deoxyprostaglandin E_2 methyl ester (**1a**) and its 15-epimer (**1b**) as well as [2α(2′*Z*),3β]-2-(6′-methoxycarbonyl-2′-hexenyl)-3-ethenylcyclopentanone (**5**). The isolation yield of the allylated intermediate **8** for **1** was 74%, and that of **5** was 66%. Conversion of **8** into **1** was achieved in 89% yield. Apart from the fact that **8** was a ca. 50:50 diastereomeric mixture, the overall purities of the crude products, i.e., **5** and **8**, were ca. 85–90%. The major byproducts, which presumably were the products of γ-allylation, accounted for 5–10% of the entire products. The regioselectivity with respect to cyclopentenone in each case was estimated to be nearly 100%, and the overall stereoselectivity in each case was estimated to be ca. 95%.

Although conjugate addition to cyclopentenones followed by allylation of the resulting enolates with (*Z*)-allylic electrophiles is a conceptually attractive route to 5-unsaturated prostanoids,[2,3] this approach has been plagued

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