Neighboring Group Participation in Organic Redox Reactions. 12. Effect of the Transannular Amide on Thioether Oxidation. Structure of the 6-Oxo-1-thionia-5-azabicyclo[4.3.0]nonane Cation

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The aqueous iodine oxidation of the nine-membered ring amide–thioether 6-oxo-1-thia-5-azacyclononane (1) is accelerated by a factor of about 100 relative to a simple thioether. The buffer-independent rate law is $d[I_3^-]/dt = -k[1][I_3^-][I^-]^{-1}[OH^-]$. The kinetics strongly suggest anchimeric assistance of the oxidation by the transannular amide group and the formation of an N-acylaza sulfonium intermediate that rapidly hydrolyzes to the sulfoxide. The proposed intermediate 6-oxo-1-thionia-5-azabicyclo[4.3.0]nonane cation (2) was prepared under anhydrous conditions and its structure was determined by X-ray analysis.

Introduction

We have shown conclusively[1] that many neighboring nucleophiles exert a profound effect on both the rate and the products obtained from the oxidation of thioethers with aqueous iodine. The neighboring nucleophiles previously examined were those found on the side chains of common amino acids with the thought that the anchimeric effect and the cyclized products we detected in the oxidation of model thioethers would also be manifest during the oxidation of a methionyl thioether in an intact protein. The amide group is one of the last functional groups that remained to be examined. Since this group occurs regularly in the backbone as well as in the side chains in proteins, it is particularly important to recognize its effectiveness as a neighboring nucleophile.

The amide group is different from the other functional groups that we have examined because it is an ambident nucleophile and either the nitrogen or the oxygen could act as the nucleophilic atom. In displacement reactions on carbon by the neutral amide group, it is the carbonyl oxygen that acts as the nucleophile.[2] Even in substituted urethanes, in which the oxygen or nitrogen is equally positioned to act as the nucleophile, oxygen acts as the nucleophile. Only after deprotonation to give the amide anion does the amide nitrogen behave as the nucleophile.

Because we anticipated that an amide would be a relatively poor nucleophile, we decided to test its involvement in thioether oxidation under the most idealized conditions. It had been shown previously by Leonard and Wilson[3] that in an amide–thioether seven-membered ring, 5-oxo-1,4-thiazepine, there was no intramolecular reaction to form a bicyclic[3.2.0] ring system on treatment with chlorine at −78 °C. For this reason we selected the larger amide–thioether nine-membered ring to optimize the interaction between the two groups during the oxidation. 6-Oxo-1-thia-5-azacyclononane (1) was prepared by a modification of the method described by Wise et al.[4] We now report that the aqueous iodine oxidation of this mesocyclic amide–thioether is accelerated by a factor of about 100 relative to a simple thioether.[5] The kinetic analysis as well as the crystal structure of the salt of the ring-fused in-

termediate, 6-oxo-1-thionia-5-azabicyclo[4.3.0]nonane (2), which was prepared by oxidation of 1 under anhydrous conditions, demonstrates that the amide nitrogen participates in electrophilic thioether oxidations.
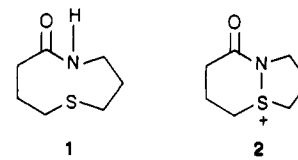
Results

Aqueous I_2 Oxidation of 1. The only product isolated from the aqueous iodine oxidation is the sulfoxide, 1,6-dioxo-1-thia-5-azacyclononane, which is obtained in 76% yield after column chromatography and was identified by its IR (1006, 910 cm^{-1} S–O).

Observed pseudo-first-order rate constants listed in Table I were obtained by monitoring the triiodide absorbance at 353 nm in the presence of excess thioether, buffer, potassium iodide, and potassium chloride. The rate law is first order in [1] as calculated by using the data from runs 1 and 7. The rate law is inverse first order in [I$^-$]; on the basis of the plots of log k_{obsd} vs. log [I$^-$] using the data from runs 2, 4, 5, and 6, the slope was −0.84, with an r value of 0.995, and using the data from runs 11–14 the slope was −0.80, with an r value of 0.998.

There is no buffer dependence of the rate in pH 9.0 borate (runs 1–3) or in pH 8.0 phosphate (runs 8–10), when these solutions also contain 0.030M KI. There is a very slight buffer dependence of the rate in pH 7.9 phosphate with 0.0050M KI (runs 15–17) and in pH 6.9 (runs 18–20) and 5.9 (runs 21–23) phosphate buffer. While the buffer dependence is smaller than that which we have observed in other systems,[5] there are many thioethers that do not exhibit buffer assistance when they react with iodine. It was necessary to extrapolate the rates to zero concentration of buffer to determine the pH dependence of the reaction. In solutions that contain 5.03×10^{-4} M 1 and 0.0050M KI, the extrapolated values of the rate constants are as follows: pH 7.94, 73 s^{-1}; pH 6.91, 15 s^{-1}; pH 5.94, 1.24 s^{-1}. A plot of pH vs. log k_{extr} (or log k_{obsd} itself when there is no buffer

(1) For paper 11 of this series, see: Doi, J. T.; Goodrow, M. H.; Musker, W. K. *J. Org. Chem.* **1986**, *51*, 1026.

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(4) (a) Nace, H. R.; Watterson, A. C., Jr. *J. Org. Chem.* **1966**, *31*, 2109. (b) Wise, L. D.; Morrison, G. C.; Egan, K.; Kopia, G.; Lattime, E. C. *J. Med. Chem.* **1971**, *17*, 1232.

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(7) (a) Overberger, C. G.; Lusi, A. *J. Am. Chem. Soc.* **1959**, *81*, 506. (b) Leonard, N. J.; Milligan, T. W.; Brown, T. L. *J. Am. Chem. Soc.* **1960**, *82*, 4075.

Table I. Rate Constants of Aqueous Iodine Reaction of 6-Oxo-1-thia-5-azacyclononane (1)^a

run	$10^4[1]$	[KI]	buffer	pH	$10^4 k_{obsd}$, s^{-1}	k_2, M^{-1} s^{-1}
1	5.03	0.005	0.0125^b	9.0	1070 ± 30	213
2	5.03	0.005	0.025^b	9.0	1010 ± 90	201
3	5.03	0.005	0.050^b	9.0	910 ± 50	181
4	5.03	0.010	0.025^b	9.0	630 ± 30	126
5	5.03	0.020	0.025^b	9.0	345 ± 5	69
6	5.03	0.030	0.025^b	9.0	220 ± 10	44
7	10.06	0.010	0.025^b	9.0	1180 ± 60	118
8	5.03	0.030	0.050^c	8.0	24.0 ± 0.8	4.8
9	5.03	0.030	0.025^c	8.0	26.0 ± 1.4	5.2
10	5.03	0.030	0.0125^c	8.0	21 ± 4	4.2
11	5.03	0.030	0.025^c	8.0	21.6 ± 0.2	4.3
12	5.03	0.020	0.025^c	8.0	28.5 ± 0.6	5.7
13	5.03	0.010	0.025^c	8.0	51 ± 4	10
14	5.03	0.005	0.025^c	8.0	99 ± 6	20
15	5.03	0.005	0.050^c	7.94	123 ± 4	24
16	5.03	0.005	0.025^c	7.94	92 ± 7	18
17	5.03	0.005	0.0125^c	7.94	89 ± 1	18
18	5.03	0.005	0.050^c	6.91	27 ± 3	5.4
19	5.03	0.005	0.025^c	6.91	21.1 ± 0.3	4.2
20	5.03	0.005	0.0125^c	6.91	18 ± 2	3.6
21	5.03	0.005	0.050^c	5.94	6.4 ± 0.2	1.3
22	5.03	0.005	0.025^c	5.94	3.65 ± 0.05	0.72
23	5.03	0.005	0.0125^c	5.94	2.61 ± 0.04	0.52

^{a} 26.0 °C, [I$_3^-$], (3–9) × 10^{-5} M, [KI] + [KCl] = 1.00 M, all concentrations in molarity. ^{b} Borate. ^{c} Phosphate.

dependence of the rate) has a slope of 0.92, r = 0.997. Therefore, the rate law is first order in [OH$^-$].
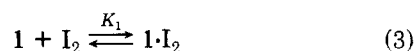
Therefore, the rate law of the reaction of I$_3^-$ with 1 in the absence of buffer effects is
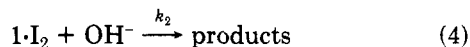
$$d[I_3^-]/dt = -k[1][I_3^-][I^-]^{-1}[OH^-] \qquad (1)$$

Possible mechanisms consistent with the buffer-free rate law involve the initial formation of I$_2$ (eq 2) followed by

$$I_3^- \underset{}{\overset{K_{I_3^-}}{\rightleftharpoons}} I_2 + I^- \qquad (2)$$

the formation of an iodine complex (eq 3). The rate-de-

$$1 + I_2 \underset{}{\overset{K_1}{\rightleftharpoons}} 1{\cdot}I_2 \qquad (3)$$

termining step is reaction of the complex with hydroxide (eq 4). Since 1 is only weakly acidic, involvement of

$$1{\cdot}I_2 + OH^- \overset{k_2}{\longrightarrow} products \qquad (4)$$

hydroxide in an acid–base reaction is unlikely to occur before the formation of the iodine complex.

Experimental Section

Equipment. The ^{1}H NMR were obtained by using a Varian EM-390 and the IR were obtained on an IBM IR32 FTIR spectrometer.

Kinetics. The kinetic procedure has been described previously.[5]

Synthesis. 6-Oxo-1-thia-5-azacyclononane (1) was prepared from 5-thiacyclooctane[8] by Beckmann rearrangement[4a] of 5-thiacyclooctanone oxime *p*-toluenesulfonate[4b] on alumina. It was purified by recrystallization from toluene, mp 86–7 °C. A single crystal was analyzed by X-ray diffraction:[8] ^{1}H NMR (CDCl$_3$) 5.8 (br, 1), 3.65 (m, 2), 2.65 (m, 6), 1.8 (overlapping m, 4); IR (KBr) 1642, 3400 cm^{-1}.

Product Run. Amide 1 (0.094 g, 5.8 × 10^{-4} mol) was dissolved in 0.6 mL of water. A solution of 0.5 g of I$_2$ and 0.5 g of KI (5.9 × 10^{-4} mol of I$_3^-$) was added in portions alternately with solid K$_2$CO$_3$ over 2.5 h to maintain the pH at about 8. The water was removed under vacuum and the residue was extracted into CHCl$_3$ for flash chromatog. on a 17-mm o.d. column containing 4.5 g of

silica gel (EM 0.040–0.063 mm) by using 20% ethanol/CHCl$_3$ and pressure. The product (0.078 g, 4.4 × 10^{-4} mol) was found in the fractions that composed eluent volumes 30–36 mL: ^{1}H NMR (CDCl$_3$) 7.1 (br s, 1), 3.4 (m, 4), 1.7–2.9 (m, 8); IR (film) 3285 (N—H), 1656 (C=O), 1006, 910 (S—O) cm^{-1}.

6-Oxo-1-thionia-5-azabicyclo[4.3.0]nonane Hexafluorophosphate (2·PF$_6$). Under nitrogen, amide 1 (0.0973 g, 6.0 × 10^{-4} mol) in 1 mL of dry CH$_3$CN was cooled with stirring at –40 °C. A solution of chlorobenzotriazole[8] (0.0901 g, 6.1 × 10^{-4} mol) in 1 mL of dry CH$_3$CN was added dropwise and the mixture was stirred for 1.5 h during which time the bath temperature rose to 25 °C. By syringe, a solution of AgPF$_6$ (0.153 g, 6.0 × 10^{-4} mol) in 2 mL of CH$_3$CN was added. The mixture was transferred to a covered centrifuge tube under N$_2$ and after centrifugation the supernatant was transferred to a clean, dry flask. The CH$_3$CN was evaporated off under a stream of N$_2$ overnight. The solid was divided between two 6 mm × 150 mm tubes. In one tube dry CH$_3$CN was used to redissolve the solid. In the other, dry CH$_3$NO$_2$ was used as solvent. The solvents were allowed to evaporate slowly in an N$_2$ atmosphere. After 3–4 weeks, crystals had grown in both tubes. X-ray analysis was done on the crystals grown in CH$_3$NO$_2$: IR (KBr) 1680 cm^{-1} (C=O).

X-ray Data Collection and Structure Solution. Colorless plates of salt **2** were grown by slow evaporation of a nitromethane solution at room temperature in an inert atmosphere. The compound [C$_7$H$_{12}$ONS]$^+$PF$_6^-$ crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with cell dimensions (at 130 K) of a = 6.482 (3), b = 10.640 (4), and c = 16.261 (7) Å with Z = 4. A crystal of dimensions 0.25 × 0.30 × 0.12 mm was used. All diffraction measurements were made at 130 K with a Syntex P2$_1$ diffractometer and graphite-monochromated Mo K$_\alpha$ radiation. Intensity data were collected by ω-scan techniques to a $2\theta_{max}$ of 45° and corrected for decay, absorption[9] and Lp effects. A total of 894 unique reflections were collected, of which 693 with $F > 2 \sigma(F)$ were retained for solution and refinement of the structure. The structure was solved by direct method and refined on F by full-matrix least-squares techniques using SHELXTL (version 5.1) program package.[10] Hydrogen atoms were not included. Anisotropic refinements of S, N, O, and P atoms and isotropic refinement of all atoms led to the convergence with R_f = 0.1204, R_{wf} = 0.1181 and the conventional goodness-of-fit value of 1.928. Maximum and minimum peaks of 0.83 and 0.76 e Å^{-3} were found on a final difference Fourier map, which were near the F atoms.

(8) (a) Rees, C. W.; Storr, R. C. *J. Chem. Soc. C* **1969**, 1474. (b) Johnson, C. R.; Bacon, C. C.; Kingsbury, W. D. *Tetrahedron Lett.* **1972**, 501.

(9) Program XABS. H. Hope and B. Moezzi; the program obtains an absorption tensor from $F_o - F_c$ differences.

(10) Crystallographic programs used were those of SHELXTL, version 5.1, installed on a Data General Eclipse Computer.
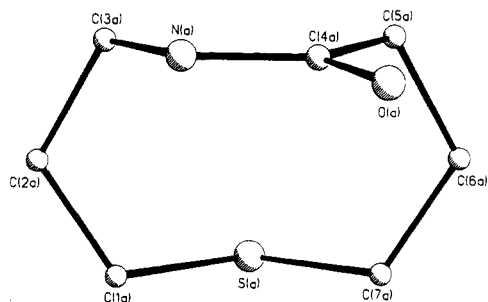
Figure 1. Perspective drawing of 6-oxo-1-thia-5-azacyclononane (1) showing the crystallographic atom numbering. The drawing shows one unit of the hydrogen-bonded dimer. Bond lengths and angles show normal values throughout. Some important distances and angles are as follows: S(1a)–C(1a), 1.836 (4) Å; O(a)–C(4a), 1.246 (5) Å; N(a)–C(4a), 1.323 (5) Å; S(a)–C(7a), 1.830 (4) Å; N(a)–C(3a), 1.484 (5) Å; S(a)···N(a), 3.62 Å; S(a)···C(4a), 3.66 (1) Å; O(a)···S(a), 4.554 Å; C(1a)–S(a)–C(7a), 103.1 (2)°; O(a)–C-(4a)–N(a), 120.0 (4)°; dihedral angle between C(3a)–N(a)–C(4a) and N(a)–C(4a)–O(a), 176 (1)°. The sulfur atom is approximately equidistant from the transannular N and C(O) atoms, outside the plane of the amide atoms, and oriented such that the S···C–O angle is 129.6°.

Scheme I. Mechanism for the Buffer-Independent Aqueous
I$_2$ Oxidation of 1
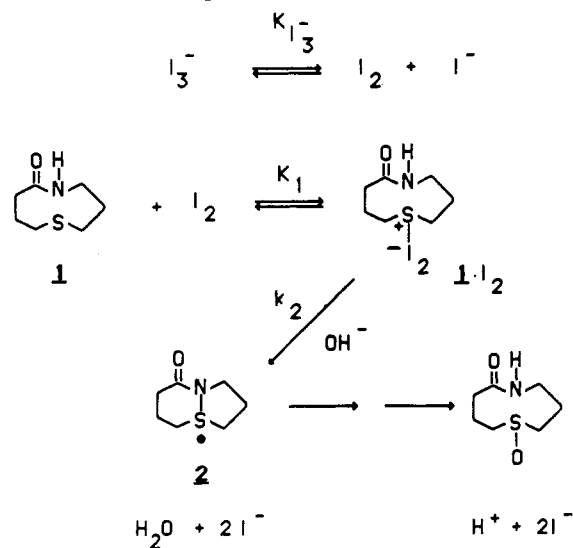
The PF$_6^-$ anion was disordered and was refined by giving fractional occupancy to several F atoms. The conventional R factor was higher when it is compared with most modern structures. This may be attributed to the disordering of the PF$_6^-$ anion, which led to the mosaic nature of the crystals (as evidenced from ~2° width of reflections). These crystals also did not show any intense reflections beyond 45° in 2θ. See the paragraph at the end of the paper about supplementary material.

Discussion

Aqueous I$_2$ Oxidation of 1. The oxidation of 1 is 100 times faster than the oxidation of thiacyclooctane (after necessary corrections are made for any buffer assistance at pH 8.0). The rate laws of the two compounds differ in that the iodide dependence of thiacyclooctane is inverse second order while that observed for 1 is inverse first order. The inverse first-order dependence has been observed before in oxidations that are anchimerically assisted by neighboring amino[11] or hydroxyl[5] groups and that have

(11) deLeeuw, D. L.; Goodrow, M. H.; Olmstead, M. M.; Musker, W. K.; Doi, J. T. *J. Org. Chem.* **1983**, *48*, 2371.
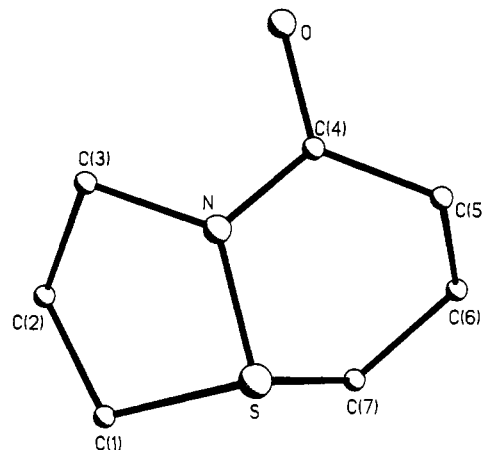

Figure 2. Perspective drawings of the 6-oxo-1-thionia-5-azabicyclo[4.3.0]nonane cation (2), showing the crystallographic atom numbering scheme. Some important distances and angles are as follows: S–N, 1.76 (2) Å; N–C(4), 1.33 (3) Å; N–C(3), 1.52 (3) Å; S–C(1), 1.79 (2) Å; S–C(7), 1.78 (2) Å; O–C(4), 1.33 (3) Å; C-(1)–S–C(7), 109 (1)°; C(1)–S–N, 91 (1)°; C(3)–N–C(4), 121 (2)°; C(3)–N–S, 120 (1)°; C(4)–N–S, 118 (2)°; C(5)–C(4)–N, 117 (2)°; C(7)–S–N, 103 (1)°; O–C(4)–N, 118 (2)°; dihedral angle C(3)–N–C(4), N–C(4)–O, 164°.

formed their respective aza sulfonium and alkoxy sulfonium salts. While nucleophilic buffers increase the rate of reaction of simple thioethers such as thiacyclooctane, they increase the rate of oxidation of 1 only very slightly. The buffer effect is much like the complete lack of buffer effects in the oxidations of amine thioethers.

Since the neutral amide group is far less nucleophilic than the amine group, it is not surprising that under comparable conditions (pH 6, 0.015 M KI) the exocyclic amine group in 5-amino-1-thiacyclooctane is about 10^3 times more reactive than the transannular amide group in 1. The transannular tertiary amine, 5-methyl-1-thia-5-azacyclooctane,[12] reacts about 10^6 times faster and has the same rate law as 1.

A mechanism for the reaction of 1 with aqueous I$_2$ that is consistent with the rate law in eq 1, was outlined briefly in eq 2–4 in the Results section. A more explicit mechanism is proposed in Scheme I. There is no N–S interaction in the starting amide. The crystal structure of 1[6] is shown in Figure 1. Only normal bond lengths and angles are observed. The S atom is equidistant from the carbonyl carbon and the nitrogen atoms. It is also out of the amide plane. In the thioether·I$_2$ complex, 1·I$_2$, the positively charged sulfur atom is attacked by the amide nitrogen at the same time that the N–H proton is removed to give the bicyclic N–S-bonded ring system. No iodide ions can be lost from the intermediates until after the rate-determining step. Thus, the rate law for the mechanism proposed in Scheme I would be as follows:

$$d[I_3^-]/dt = -\{K_{I_3^-}[I_3^-]/[I^-]\}\{[1]K_1\}[OH^-]k_2 \qquad (5)$$

Equation 5 is consistent with the observed rate law given in eq 1.

The buffer dependence of the rates in the more acidic solutions suggests that in these solutions, the buffer competes with the hydroxide ion in the deprotonation reaction.

6-Oxo-1-thionia-5-azabicyclo[4.3.0]nonane Hexafluorophosphate (2·PF$_6$). In order to support the kinetic evidence for a transannular reaction in the aqueous I$_2$ oxidation of 1, we decided to oxidize 1 in a nonaqueous solvent so that we could isolate the intermediate before

(12) Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1981**, *103*, 1159.

it hydrolyzed to the sulfoxide. Therefore 1 was treated with N-chlorobenzotriazole[8] in acetonitrile, and the chloride salt was metathesized using $AgPF_6$. Swern and co-workers[13a,b] have isolated and characterized acyclic N-acetylaza sulfonium salts and Gassman and co-workers[13c] have generated acyclic N-acetyl-N-arylaza sulfonium intermediates at 0 °C in dichloromethane and used these in situ. We could find no literature reports on any crystal structures of N-acylaza sulfonium salts. The X-ray structure of the acylazasulfonium salt of 2, as shown in Figure 2, indicates that it has a bicyclic [4.3.0] ring system with an N–S bond distance of 1.76 (2) Å. The N–S bond is a single bond since the sum of the covalent radii of S and N is 1.74 Å.[14] The dihedral angle between C(3)–N–C(4) and N–C(4)–O is 164°, showing a distortion of the amide planarity by the formation of the bicyclic system. The sum of the angles about the nitrogen is 359°, which indicates that it is sp[2] hybridized. We can compare these

parameters to those of trans-4-tert-butyl-1-[ethyl(p-tolylsulfonyl)amino]-1-thioniacyclohexane ion, 3.[15] The

3
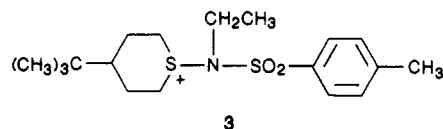
nitrogen atom in 3 is also sp[2] hybridized, but the S–N bond distance of 1.644 Å is considerably shorter than the predicted single-bond distance of 1.74 Å. In ion 3 the shortened S–N bond has been attributed to p(N)–d(S) π bonding.[15]

The preparation and characterization of 2·PF_6 strengthens our proposal that the reaction of 1 proceeds with neighboring amide participation via an acylaza sulfonium intermediate.

Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters, bond distances and angles for 2·PF_6 (4 pages). Ordering information is given on any current masthead page.

(13) (a) Kise, H.; Whitfield, G. F.; Swern, D. *Tetrahedron Lett.* 1971, 1761. (b) Dawson, A. D.; Swern, D. *J. Org. Chem.* 1977, *42*, 592. (c) Gassman, P. G.; Parton, R. L. *Tetrahedron Lett.* 1977, 2055.
(14) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 224.

(15) Cook, R. E.; Glick, M. D.; Rigau, J. J.; Johnson, C. R. *J. Am. Chem. Soc.* 1971, *93*, 924.

Notes

Reaction of Ethyl Azidoformate with Ketene Silyl Acetals[1]

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The thermolysis of ethyl azidoformate ($EtOCON_3$) in enol trimethylsilyl ethers gave N-(ethoxycarbonyl)-α-amino ketones.[2] Our interest has been directed, in general, to the reactivity of other electron-rich alkenes toward ethyl azidoformate and particularly toward (ethoxycarbonyl)-nitrene (EtOCON).[3,4] In this paper we describe the results obtained in the reactions of ketene silyl acetals[5] with ethyl azidoformate.

Results and Discussion

The ketene silyl acetals 1[6] were reacted with ethyl azidoformate either at room temperature or at 110 °C. GC

(1) Taken in part from the thesis of R. Maestro, 1985. Part of this paper has been presented at the First Belgian Organic Synthesis Symposium (BOSS-1), Namur, May 19–23, 1986, Abstract P1B14.
(2) Lociuro, S.; Pellacani, L.; Tardella, P. A. *Tetrahedron Lett.* 1983, *24*, 593.
(3) Fioravanti, S.; Loreto, M. A.; Pellacani, L.; Tardella, P. A. *J. Org. Chem.* 1985, *50*, 5365.
(4) Pellacani, L.; Persia, F.; Tardella, P. A. *Tetrahedron Lett.* 1980, *21*, 4967.
(5) Among very recent examples of ketene silyl acetal reactions, see: (a) Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* 1985, 1309. (b) Colvin, E. W.; McGarry, D. G. *J. Chem. Soc., Chem. Commun.* 1985, 539. (c) Slougui, N.; Rousseau, G. *Tetrahedron* 1985, *41*, 2643. (d) Gennari, C.; Bernardi, A.; Scolastico, C.; Potenza, D. *Tetrahedron Lett.* 1985, *26*, 4129. (e) Oppolzer, W.; Pedrosa, R.; Moretti, R. *Tetrahedron Lett.* 1986, *27*, 831.
(6) Slougui, N.; Rousseau, G.; Conia, J. M. *Synthesis* 1982, 58.

Table I. Reaction of $EtOCON_3$ with Ketene Alkyl Silyl Acetals 1

entry[a]	condts	reactn time, h	products,[b] % 2	3	4
a	110 °C	0.5	12 (1)	65 (42)	18 (4)
	rt[c]	24	14	53	32
	hν, 0 °C	5	44 (21)	1	20 (4)
b	110 °C	0.5	6 (4)	68 (42)	14 (13)
	rt	24	10	79	10
	hν, 0 °C	5	70 (38)	2 (2)	8 (4)
c	110 °C	0.5	19 (7)	16 (9)	61 (35)
	rt	120	34	11	53
	hν, 25 °C	5	48 (30)	2 (1)	8 (7)

[a] See Scheme I. [b] GC percentages; absolute yields are given in parentheses. [c] rt = room temperature.

analysis of the crude reaction mixtures showed only insignificant differences in product ratio (see Table I) and silica gel chromatography allowed isolation of the three main products detected by GC analysis.

Reaction of $EtOCON_3$ at 110 °C with the monosubstituted ketene silyl acetal 1a (see Scheme I) gave a compound retaining the trimethylsilyl group as the main product (42%), which was identified by analytical and spectral data (IR, ^{1}H NMR, ^{13}C NMR, MS) as the carbonimidate 3a. Two other minor products were separated by column chromatography: the first (4%) was identified as the alkoxyacylurethane 4a and the second (1%) as the N-(ethoxycarbonyl)-α-amino ester 2a. The other monosubstituted ketene silyl acetal 1b gave similar results: the silylated carbonimidate 3b was the main product (42%) accompanied by 4b (13%) and 2b (4%) as minor products.

The ratio of products from the disubstituted ketene silyl acetal 1c was different. In this case the alkoxyacylurethane 4c was isolated as the principal compound (35%) with 3c (9%) and 2c (7%) as minor products. The structure of