were obtained using a Varian Aerograph Series 1200 chromatograph equipped with a flame ionization detector or a Varian Aerograph Model 90-P chromatograph equipped with a thermal conductivity detector. The mass spectra were determined by the Morgan-Schaffer Corp., Montreal, Quebec, Canada, on a Hitachi Perkin-Elmer RMU-6D spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tenn., or from Meade Microanalytical Laboratory, Amherst, Mass. The chloroform used in each experiment was distilled from barium oxide, passed through a basic alumina column, and dried over magnesium sulfate just prior to use, except as noted. Benzene and hexane were distilled from phosphorus pentoxide prior to use. Dimethylformamide (DMF) was shaken for 3 days over phosphorus pentoxide and 5 g of fresh phosphorus pentoxide was added each day. The DMF was then decanted, shaken for 5 hr over potassium hydroxide to neutralize any formic acid, decanted again, and distilled from Type 4A molecular sieves under a stream of nitrogen at reduced pressure (bp 56°). All transferring of DMF was done under a nitrogen atmosphere. Acetonitrile was distilled from phosphorus pentoxide directly into the reaction vessel.

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Addition of Nitrosyl Chloride to Trimethylsilyl Enol Ethers. A New General Method for Nitrosation of Carbonyl Compounds[1]

Jerald K. Rasmussen and Alfred Hassner*

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Received January 15, 1974

Addition of nitrosyl chloride to trimethylsilyl enol ethers **1** in dichloromethane at −10 to −15° gives good yields of α-oximinocarbonyl compounds **2**. In the case of aldehydes, these initial products are unstable, but may be trapped by hydroxylamine as the glyoximes **3**. The silyl ether of cyclohexanone **1h** yields 2,6-dioximinocyclohexanone (**4**) upon treatment with excess NOCl, whereas with 1 equiv of NOCl the unstable nitroso dimer **5** is formed. Similarly, the silyl derivatives of esters, lactones, and carboxylic acids are directly converted to α-oximino esters and acids. The results are explained by initial addition of NOCl to the silyl enol ether double bond, followed by elimination of trimethylsilyl chloride and tautomerization to the oxime.

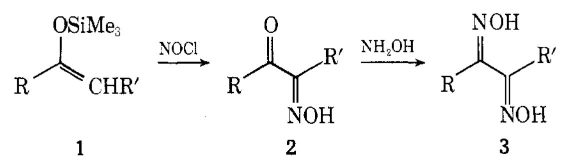
Trimethylsilyl enol ethers are now readily available from ketones or aldehydes,[2a] and their utility as synthetic equivalents of enols[3,4] has recently been demonstrated. Similar derivatives of esters[2b] and acids[2c] have also recently become available. Our interest in the regiospecific and stereospecific introduction of nitrogen functions into organic molecules by additions to double bonds[5] prompted us to study the reaction of silyl enol ethers with nitrosyl chloride. We have found that the reaction is instantaneous at −10 to −15° in dichloromethane and affords good yields of α-oximino carbonyl compounds in a high state of purity.

Results

When the ketone-derived trimethylsilyl enol ethers **1a–c** were treated with excess NOCl for <1 min, good yields of the corresponding α-oximino ketones **2a–c** were formed (Table I). The only by-products were the corresponding ketones, presumably from hydrolysis of **1**. Purification[6] of the NOCl (by removal of HCl, H_2O, and NO_2) led to no improvement in yields or reduction of hydrolysis. If the reaction time was extended to several hours, different products were formed. For instance, when the reaction mixture from **1a** was allowed to stand for 18 hr at −20°, α-oximinophenacyl chloride (**2g**, R = Ph; R′ = Cl) was obtained in 48% yield. Acetophenone (14%) and benzoic acid (21%) were identified as by-products in this reaction. The formation of **2g** is not surprising, since it can also be prepared from acetophenone and excess NOCl in 24.5% yield.[7]

Table I
Oximes from Trimethylsilyl Enol Ethers 1 and Nitrosyl Chloride

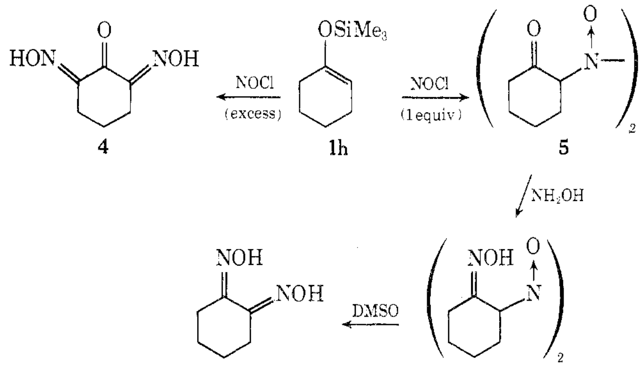
Silyl ether	R	R¹	Product	Yield, %
1a	Ph	H	**2a**	82
1b	Ph	Me	**2b**	83.5
1c	Et	Me	**2c**	72
1d	H	Et	**3d**	66
1e	H	$PhCH_2$	**3e**	77.5
1f	H	n-C_8H_{17}	**2a**	63



1 2 3

The reaction of the silyl ether of cyclohexanone (**1h**) is somewhat more complicated. With excess NOCl, 2,6-dioximinocyclohexanone (**4**)[8] was obtained in 93% yield. By contrast, treatment with 1 equiv of NOCl yielded the unstable nitroso dimer **5** in quantitative yield. Reaction of the latter with hydroxylamine afforded dimer **6**, which dissociated and tautomerized to dioxime **3h**[9] upon dissolution in dimethyl sulfoxide (DMSO). The establishment of structures **5** and **6** rests upon spectral data and upon the isolation and identification of **3h** (see Experimental Section).

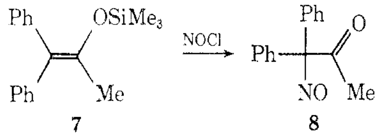
When silyl ethers of aldehydes (**1d–f**) were treated with NOCl, the initially formed α-oximino aldehydes **2d–f** were



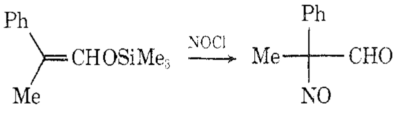
4 1h 5 3h 6

too unstable to be isolated, and polymerized upon warming to ambient temperature. However, they could be trapped in good yield (Table I) as the glyoximes **3d–f** by direct addition of a solution of hydroxylamine to the cold reaction mixture. This provides a facile two-step synthesis of this type of compound from simple aldehydes.

Reaction of NOCl with silyl ethers **7** and **9** gave the corresponding α-nitroso compounds **8** and **10**. The initial solution containing **8** was intensely green in color, and rapidly faded to pale yellow as **8** dimerized. The nmr of the crude product indicated an approximately 2:1 ratio of 1,1-diphenylacetone to nitroso dimer (See Experimental Section). No attempt was made to separate them. The low yield of **8** here may be largely due to steric problems. Compound **10** produced a deep blue solution, and was apparently quite stable at 0° or lower, slowly dimerizing at room temperature. Various attempts at purification yielded acetophenone as the only isolable compound.

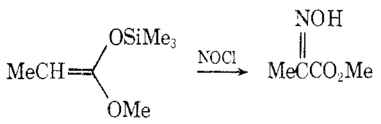


7 8

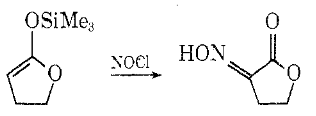


9 10

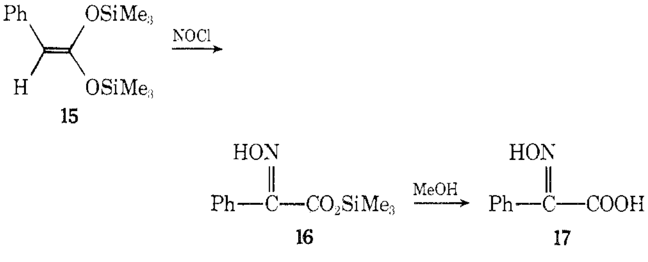
To test the generality of the reaction and its applicability to acid derivatives the nitrosation of some representative ketene alkyl trimethylsilyl[2b] and bis(trimethylsilyl) acetals[2c] was studied. The acetal **11** derived from methyl propionate produced α-oximino ester **12**[10] in 63.5% yield, while **13** derived from α-butyrolactone gave 50.5% α-oximino-γ-butyrolactone (**14**), an important intermediate in the synthesis of methionine.[11] With the bis(trimethylsilyl) acetal **15**, the initial product **16** was not isolated, but was hydrolyzed directly by treatment with methanol to α-oximinophenylacetic acid (**17**)[12] in 68.3% yield.



11 12



13 14

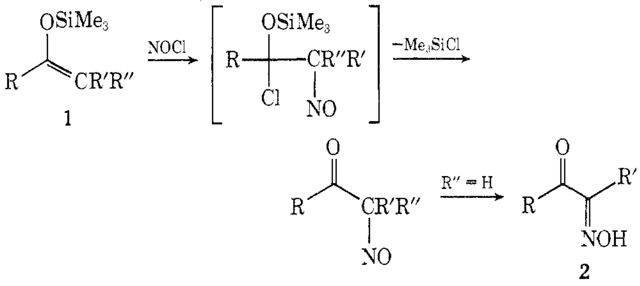


15 16 17

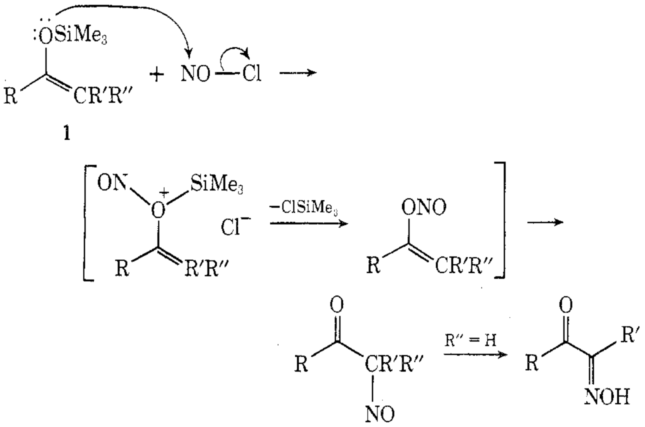
Discussion

The formation of α-oximino carbonyl products from the silyl ethers could involve initial addition of NOCl to the enol ether double bond (Scheme I). The initial adduct then rapidly eliminates trimethylsilyl chloride and tautomerization to the oxime occurs when an α hydrogen is present. An alternative explanation involves nucleophilic attack of the silyl ether oxygen on NOCl (Scheme II), followed by rearrangement of the intermediate vinyl nitrite. The fact that such a reaction might be possible was shown by reaction of the silyl ether[13] of benzyl alcohol (**18**) with nitrosyl chloride. After 3 hr at room temperature, nmr indicated a 77% conversion to benzyl nitrite (**19**).[14] However, the slower rate of this reaction as compared to that of the enol ethers, previous results on additions to silyl enol ethers,[3,4] and the known ease of addition of NOCl to double bonds,[15] make Scheme I more reasonable.

Scheme I



Scheme II



$$\underset{\mathbf{18}}{\mathrm{PhCH_2OSi(CH_3)_3}} \xrightarrow{\mathrm{NOCl}} \underset{\mathbf{19}}{\mathrm{PhCH_2ONO}}$$

α-Oximino ketones can be readily prepared from ketones under a variety of conditions.[16] The new method is superior in cases where direct nitrosation of the ketone gives (1) low yields, (2) mixtures of products, or (3) only one of two possible isomers (see ref 16 for numerous examples). The real utility of our procedure lies in the nitrosation of aldehydes, since there appears to be no report in the literature of conventional nitrosation procedures.[16] This does not seem surprising in view of the instability noted for oximino aldehydes **2d–f**. It was necessary to trap these products and it is reasonable to assume that other methods of trapping these unstable species can be developed. Since α-oximino ketones have served in the preparation of a large number of difficultly obtainable compounds,[16] the scope of these reactions can now be easily extended to aldehyde derivatives as well. Derivatives of α-keto aldehydes have been obtained previously only through multistep syntheses.[17]

α-Oximino acids and esters, which are important intermediates in the synthesis of α-amino acids and esters, have been available in the past by nitrosation of substituted β-keto esters, malonic acids, and malonic esters.[16] These oximes also provide routes to α-oxo acids and esters, to nitriles, and to hydroxamic acids.[12] The present procedure for their preparation appears to be more economical and desirable, since these α-oximino compounds are attainable directly, in two simple steps and without purification of the intermediate silyl acetals, from the corresponding acids or esters. The entire reaction sequence requires about 2-3 hr. The lower yields of oximes from ketene acetals than from enol ethers are probably a reflection of increased sensitivity of the former toward hydrolysis.

Experimental Section

Melting points (taken on a Fisher-Johns block) and boiling points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer 457 instrument. Nmr spectra were recorded on a Varian A-60A spectrometer with TMS as an internal standard. Mass spectra were taken on a Varian MAT CH-5 instrument.

Trimethylsilyl Enol Ethers. All trimethylsilyl ethers were prepared by the method of House.[2a] Ethers **1a**,[2a] **1b**,[4] **1d**,[2a] and **1h**[2a] have been described previously. The following new silyl ethers were prepared.

1c from 3-Pentanone. Nmr indicated the reaction to be complete after 11.5 hr. Normal work-up[2a] led to partial hydrolysis as evidenced by formation of starting ketone and trimethylsilyl alcohol. Purification by distillation was difficult owing to the high volatility of **1c**, which codistilled with starting ketone. Pure **1c**, along with several fractions containing **1c** and ketone, was obtained in approximately 30% yield as a mixture of *E* and *Z* isomers, bp 130–135° at atmospheric pressure. No attempt was made to improve the yield: ν (neat) 1680 cm^{-1}; nmr (CCl_4) τ 9.84 (s, 9 H), 8.98 and 9.00 (2 t, $J \cong 7$ Hz, 3 H), 8.38–8.62 (m, 3 H), 7.74–P.25 (m, 2 H), 5.30–5.77 (m, 1 H).

1e from Hydrocinnamaldehyde. The time required for complete reaction was 3 hr. **1e** was obtained as a 2:3 mixture of *E* and *Z* isomers: bp 98–102° (5.2 mm); 83.3% yield; ν (neat) 1655 cm^{-1}; nmr ($CDCl_3$) τ 9.83 (s, 9 H), 6.75 (d of d, J = 7.5 and 1.0 Hz, *E* isomer), and 6.54 (d of d, J = 7.5 and 1.50 Hz, *Z* isomer), total of 2 H, 5.27 (d of t, J = 7.5 and 6.0 Hz, *Z*) and 4.79 (d to (d of t, J = 7.5 and 12.0 Hz, *E*), total of 1 H, 3.50–3.75 (m, 1 H), 2.75 (s, 5 H).

1f from Decanal. Reaction time was 4 hr. **1f** was obtained as a 2:3 mixture of *E* and *Z* isomers: bp 115–125° (~15 mm); 64.4% yield; ν (neat) 1655 cm^{-1}; nmr ($CDCl_3$) τ 9.82 (s, 9 H), 9.12 (t, J = 4.5 Hz, 3 H), 8.69 (m, 12 H), 8.07 (m, 2 H), 5.33–5.68 (d of t, J = 7.0 and 5.5 Hz, *Z*) and 4.75–5.22 (d of t, J = 7.0 and 12.0 Hz, *E*), total of 1 H, 3.64–3.93 (m, 1 H).

7 from 1,1-Diphenylacetone. Reaction time was 18 hr. **7** was obtained in 70% yield: bp 115–120° (0.5 mm); ν (neat) 1660 and 1625 cm^{-1}; nmr ($CDCl_3$) τ 9.85 (s, 9), 7.99 (s, 3), 2.64 (m, 5), 2.25–2.50 (m, 3), 1.97–2.18 (m, 2).

9 from 2-Phenylpropionaldehyde. Reaction time was 1.5 hr. **9** was obtained in 91% yield as a 3:1 mixture of *E* and *Z* isomers: bp 100–105° (7.5 mm); ν (neat) 1645 cm^{-1}; nmr ($CDCl_3$) τ 9.84 and 9.79 (2 s, 9 H), 8.12 and 8.02 (2 d, J = 1.5 Hz, *Z* and *E* 3 H), 3.58 and 3.28 (2 q, J = 1.5 Hz, *Z* and *E*, 1 H), 2.50–2.87 (m) and 2.20–2.42 (m, *Z* isomer), total of 5 H.

Ketene Alkyl Trimethylsilyl and Bis(trimethylsilyl) Acetals. The silyl acetals were prepared according to literature procedures[2b,c] and were used without purification for the subsequent reaction. Acetals **11**[2b] and **15**[2c] were previously described, while **13** was obtained from γ-butyrolactone in 90.6% yield: ν (neat) 1685 cm^{-1}; nmr ($CDCl_3$) τ 9.73 (s, 9 H), 7.38 (d of t, J = 2.0 and 9.0 Hz, 2 H), 6.30 (t, J = 2.0 Hz, 1 H), 5.68 (t, J = 9.0 Hz, 2 H).

General Procedure for Reaction of Silyl Ethers with NOCl. Dichloromethane solutions (10-15 ml) of nitrosyl chloride were prepared at −10 to −15° (Dry Ice-carbon tetrachloride bath) according to the procedure of Hassner and Heathcock.[18] A dichloromethane solution of the silyl ether was added, and the mixture was stirred for *ca.* 30 sec. Slow concentration of solvent *in vacuo* at ~0° often led to crystallization of relatively pure oxime **2**. In the case of aldehydes, a slight excess of hydroxylamine solution[9] was added directly to the cold reaction mixture. The mixture was then allowed to warm to room temperature, stirred for about 1 hr, washed with water, and dried (Na_2SO_4), and the solvent was removed to give crude dioxime **3**. Variations in the procedure and identification of products are described below.

α-Oximinoacetophenone (2a). Silyl ether **1a** (5 mmol) gave 608 mg (82%) of **2a** as pale yellow crystals, displaying infrared, nmr, and melting point properties identical with those published in Sadtler.

α-Oximinopropiophenone (2b). Silyl ether **1b** (10 mmol) produced 1.28 g of **2b** as colorless crystals: mp 112–113° (lit.[19] mp 111–113°); ν (KBr) 3240, 1660, 1650, 1190, 1020, 1005, 905 cm^{-1}; nmr (acetone-d_6) τ 7.85 (s, 3 H), 2.32–2.64 (m, 3 H), 1.88–2.11 (m, 2 H), −1.29 (br s, 1 H); mass spectrum *m/e* (rel abundance) 163 (41.2), 118 (7.6), 105 (100). Chromatography of the filtrate on alumina gave 126 mg of propiophenone (9.5%) and an additional 80 mg of **2b** (total yield 83.5%)

2-Oximino-3-pentanone (2c). Silyl ether **1c** (9.4 mmol) gave 775 mg (72%) of **2c** as colorless crystals: mp 70–71° (lit.[20] mp 69–72°); ν (KBr) 3300, 1665, 1020 cm^{-1}; nmr ($CDCl_3$) τ 8.87 (t, J = 7 Hz, 3 H), 7.94 (s, 3 H), 7.12 (q, J = 7 Hz, 2 H), 0.23 (br s, 1 H); mass spectrum *m/e* (rel abundance) 115 (9.1), 98 (10.3), 87 (10.7), 58 (14.7), 57 (100), 42 (34.9).

Ethyl Glyoxime (3d). Silyl ether **1d** (3.47 mmol) gave 267 mg (66%) of **3d** as a colorless solid: mp 127–128° (lit.[17a] mp 129°); ν (KBr) 3240 with tailing to about 2500, 1425, 955, 825 cm^{-1}; nmr (DMSO-d_6) τ 8.96 (t, J = 7 Hz, 3 H), 7.47 (q, J = 7 Hz, 2 H), 2.36 (s, 1 H), −1.43 (br s, 2 H); mass spectrum *m/e* (rel abundance) 116 (28.5), 99 (100), 71 (28.8), 55 (29.7), 54 (46.4), 44 (73.3).

Benzyl Glyoxime (3e). Silyl ether **1e** (5 mmol) gave 690 mg (77.5%) of **3e** as a colorless solid: mp 160–161.5° (lit.[17b] mp 163°); ν (KBr) 3290, 3050, 2930, 1430, 970, 940, 875, 755, 710 cm^{-1}; nmr (DMSO-d_6) τ 6.03 (s, 2 H), 2.75 (br s, 5 H), 2.20 (s, 1 H), −1.08 (br s, 1 H), −1.32 (br s, 1 H); mass spectrum *m/e* (rel abundance) 178 (68.8), 161 (11.4), 144 (31.1), 143 (18.2), 117 (71.8), 91 (100).

***n*-Octyl Glyoxime (3f).** Silyl ether **1f** (10 mmol) gave 1.26 g (63.0%) of **3f** as a colorless solid (from acetone-hexane): mp 117–118°; ν (KBr) 3280, 3100, 1465, 1430, 965 cm^{-1}; nmr (DMSO-d_6) τ 9.13 (t, J = 4.5 Hz, 3 H), 8.72 (m, 12 H), 7.50 (m, 2 H), 2.35 (s, 1 H), −1.45 (br s, 2 H); mass spectrum *m/e* (rel abundance) 200 (9.7), 183 (100), 169 (21.3), 112 (35.0), 102 (71.9), 99 (12.2), 98 (73.3), 85 (16.1), 71 (16.7), 69 (25.6), 57 (22.3), 55 (75.2), 43 (59.7).

Reaction of Silyl Ether 1h with NOCl. A. Silyl ether **1h** (10 mmol) under the general reaction conditions gave 1.45 g (93%) of **4** as an unstable pale yellow solid which displayed properties identical with those reported:[8] ν (KBr) 3160, 3070, 1700, 1570, 1435, 1415, 1105, 900 cm^{-1}; nmr (DMSO-d_6) τ 8.23 (p, J = 6.5 Hz, 2 H), 7.25 (t, J = 6.5 Hz, 4 H), 0.92 (br s, 2 H); mass spectrum *m/e* (rel abundance) 156 (100), 139 (17.8), 127 (11.3), 126 (6.5), 111 (37.1), 82 (13.7), 80 (12.1).

B. Alternatively, **1h** (5 mmol) was dissolved in 10 ml of CH_2Cl_2 and placed in a Dry Ice-CCl_4 bath, and 3.5 ml of a NOCl solution[18] was added and stirred for 10 min. Removal of solvent *in vacuo* gave 634 mg (100%) of **5** as a colorless solid, ν (KBr) 1725, 1240, 1210, 1195, 850 cm^{-1}. Since dimer **5** turned yellow and decomposed fairly rapidly on standing, it was treated with 1 equiv of a hydroxylamine solution at room temperature overnight, then placed in the refrigerator for 2 hr. Filtration gave 256 mg (35.6%) of **6** as a colorless solid: ν (KBr) 3280, 1140, 1385, 1330, 1195, 980, 955, 870 cm^{-1}; nmr (DMSOd_6) τ 8.70–6.90 (series of m, >18 H), 4.20–4.58 (m, 2 H), −0.90 (br s, 2 H), integration of the upfield multiplet was not accurate owing to partial dissociation (see below); mass spectrum *m/e* (rel abundance) no M$^+$, 224 (5.4), 207 (2.2), 204 (2.2), 187 (4.0), 142 (21.3), 125 (5.3), 112 (56.7), 94 (34.7), 81 (26.7), 79 (21.3), 67 (100). The filtrate from **6** yielded only polymer on evaporation. Monitoring of the nmr sample of **6** showed complete conversion to 1,2-dioximinocyclohexane (**3h**) after 3 days. The nmr pattern was identical with Sadtler's but shifted somewhat owing to the different solvent: nmr (DMSO-d_6) τ 8.44 (m, 4 H), 7.48 (m, 4 Hz, −1.12 (br s, 2 H). The sample was poured into water, and precipitated **3h** was filtered and identified by comparison of its ir spectrum with Sadtler's. Mass spectrum: *m/e* (rel abundance) 142 (74.2), 125 (15.6), 107 (23.3), 95 (19.0), 94 (16.4), 80 (22.4), 68 (24.2), 67 (70.8), 66 (23.3), 55 (50.0), 41 (100).

Reaction of Silyl Ether 7 with NOCl. Silyl ether 7 (5 mmol) was treated with excess NOCl according to the general procedure to give a deep green solution. While excess NOCl was removed *in vacuo* at 0°, the solution faded to light yellow. Removal of solvent *in vacuo* gave a yellow oil, ν (neat) 1720, 1660, 1285 cm^{-1}. Nmr indicated this to be a 2:1 mixture of 1,1-diphenylacetone and the nitroso dimer [τ 7.62 (s)].

Reaction of Silyl Ether 9 with NOCl. A. Silyl ether **9** (5 mmol) was treated with excess NOCl according to the general procedure for ketones and the solvent was removed *in vacuo* to give 0.83 g of **10** as an intensely blue oil which, upon standing for 30 sec, underwent an exothermic reaction to give the dimer as an orange oil: ν (neat) 1735, 1550, 1495, 1450, 1290, 770, 705 cm^{-1}; nmr ($CDCl_3$) τ 8.02 (s, 3), 2.52 (br s, 5), 0.50 (s, 1). No purification was achieved by chromatography on silica gel–ether, while treatment with 1 equiv of hydroxylamine for 1 hr led to a polymer.

B. The reaction was repeated according to the general procedure for silyl ethers **1d–f**, to yield a yellow oil (largely acetophenone by nmr). Chromatography on alumina–ether gave 365 mg (54.5%) of acetophenone as the only identifiable product.

C. The reaction was repeated as in A, except that the excess NOCl was removed *in vacuo* at 0° to give a deep blue solution, ν (CH_2Cl_2) 1720 and 1570 cm^{-1}. Upon warming to room temperature, the solution slowly turned yellow. Removal of solvent *in vacuo* gave a yellow oil, the nmr of which indicated the presence of the dimer (as in A) as the major product, along with acetophenone and polymer.

Reaction of Acetal 11 with NOCl. Acetal **11** (8.33 mmol), under the general reaction conditions, gave 620 mg (63.5%) of methyl α-oximinopropionate (**12**) as colorless crystals: mp 69° (lit.[10] mp 68–69°); ν (KBr) 3200, 1725, 1440, 1315, 1200, 1160, 1035, 1000, 845, 770, and 750 cm^{-1}; nmr ($CDCl_3$) τ 7.86 (s, 3 H), 6.10 (s, 3 H), −0.20 (br s, 1 H); mass spectrum *m/e* (rel abundance) 117 (71.3), 86 (33.4), 85 (100), 59 (77.3), 58 (95.5), 57 (50.0).

Reaction of Acetal 13 with NOCl. Acetal **13** (20 mmol) gave 1.16 g (50.5%) of α-oximino-γ-butyrolactone (**14**) as a pale yellow solid: mp 184–186° (lit.[11] mp 183–185°); ν (KBr) 3250, 1745, 1660, 1390, 1295, 1265, 1000 cm^{-1}; nmr ($CDCl_3$) τ 7.00 (t, J = 7.0 Hz, 2 H), 5.52 (t, J = 7.0 Hz, 2 H), −0.25 (br s, 1 H); mass spectrum *m/e* (rel abundance) 115 (100), 114 (41.3), 97 (54.4), 85 (59.8), 83 (15.2), 70 (13.6), 57 (68.5), 54 (76.1). The filtrate from **14** was a deep green in color. Upon standing overnight, the color had changed to yellow-orange. Removal of the solvent *in vacuo* gave 1.0 g of orange oil. Nmr indicated that this oil contained γ-butyrolactone, polymer, and perhaps a small amount of nitroso dimer.

Reaction of Acetal 15 with NOCl. Acetal **15** (20 mmol) gave a red-orange oil. This was dissolved in chloroform, excess methanol was added, and after 15 min the solvent was removed *in vacuo* to give 3.65 g of red oil. Repeated fractional crystallization from chloroform gave 2.25 g (68.3%) of α-oximinophenylacetic acid (**17**) as colorless needles, mp 147° dec (lit.[12] mp 144–145° dec). The residue from the recrystallizations was dissolved in ether and extracted twice with 5% aqueous sodium bicarbonate. The ether layer yielded 638 mg of a red polymeric oil. Acidification and reextraction of the bicarbonate layer gave 445 mg (16.3%) of phenylacetic acid.

Reaction of Benzyloxytrimethysilane (18) with NOCl. A solution of **18** (5 mmol) and NOCl was stirred at room temperature and monitored by nmr. After 3 hr, the solvent was removed *in vacuo* to give a pale greenish oil which displayed infrared absorptions identical with those reported[14] for benzyl nitrite. Nmr indicated benzyl nitrite (77%), **18** (10%), and benzyl alcohol (13.2%). A similar reaction with benzyl alcohol (3 hr at room temperature) led to a 60% conversion to benzaldehyde.

Registry No.—**1a,** 13735-81-4; **1b,** 37471-46-8; (*E*)-**1c,** 51425-53-7; (*Z*)-**1c,** 51425-54-8; **1d,** 6651-33-8; (*E*)-**1e,** 51425-55-9; (*Z*)-**1e,** 51425-56-0; (*E*)-**1f,** 51425-57-1; (*Z*)-**1f,** 51425-58-2; **2b,** 119-51-7; **2c,** 32818-79-4; **3d,** 51425-59-3; **3e,** 4732-56-3; **3f,** 51425-60-6; **5,** 51425-61-7; **6,** 51425-62-8; **7,** 51425-63-9; (*E*)-**9,** 51425-64-0; (*Z*)-**9,** 51425-65-1; **11,** 34880-70-1; **12,** 5634-53-7; **13,** 51425-66-2; **14,** 5400-68-0; **15,** 31491-21-1; **18,** 14642-79-6; 3-pentanone, 96-22-0; hydrocinnamaldehyde, 104-53-0; decanal, 112-31-2; 1,1-diphenylacetone, 781-35-1; 2-phenylpropionaldehyde, 93-53-8; γ-butyrolactone, 96-48-0; nitrosyl chloride, 2696-92-6.

References and Notes

(1) Synthetic Methods. VI. For paper V see ref 4.

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(13) The authors thank Dr. A. H. Andrist for a sample of this compound.

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