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Notes

Synthetic Methods and Reactions. 113.[1] Reactions of Nitro- and Nitrosoalkanes with Iodotrimethylsilane

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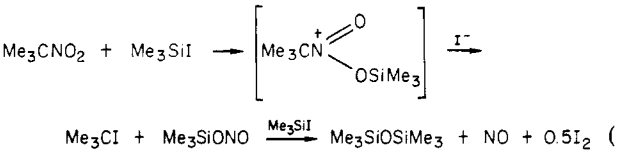
During the course of our studies on the reactions of iodotrimethylsilane with various functional groups, we and others have exploited the strong affinity of silicon for oxygen and fluoride to carry out the cleavage of esters, ethers, lactones, carbonates, fluoroalkanes, etc.[2] We have been also interested in deoxygenation reactions with iodotrimethylsilane.

In this context, we have successfully deoxygenated sulfoxides to sulfides[3] and sulfonyl halides (and sulfinic acid derivatives)[4] to the corresponding symmetrical disulfides in high yields. We now report that nitroalkanes can be deoxygenated with iodotrimethylsilane. The nature of the products formed depends on the nature of the alkyl group, i.e., whether it is primary, secondary, or tertiary (Table I).

The reactions were performed in an inert solvent (CH_2Cl_2, $CHCl_3$) under a dry nitrogen atmosphere at 25 °C for 16 h. During the course of the reaction, iodine crystallizes out of the reaction mixture with concomitant formation of hexamethyldisiloxane.

(1) Tertiary Nitroalkanes. Treatment of tertiary nitroalkanes with iodotrimethylsilane results in the formation of the corresponding tertiary iodoalkanes with cleavage of the carbon–nitrogen bond. Two equivalents of iodotrimethylsilane is consumed during the reaction. The reaction of 2-methyl-2-nitropropane can be depicted as in eq 1.

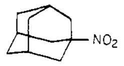
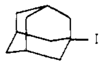
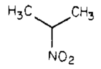
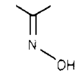
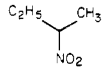
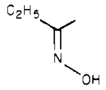
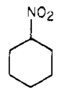
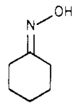
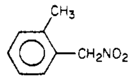
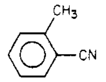
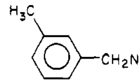
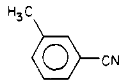


$$Me_3CNO_2 + Me_3SiI \longrightarrow \left[Me_3C\overset{+}{N}{\overset{\textstyle O}{\underset{\textstyle OSiMe_3}{\lessgtr}}} \right] \xrightarrow{I^-} Me_3CI + Me_3SiONO \xrightarrow{Me_3SiI} Me_3SiOSiMe_3 + NO + 0.5I_2 \quad (1)$$

The reaction probably proceeds via O-silylation, thereby weakening the carbon–nitrogen bond, resulting in a facile substitution by the iodide anion. Another molar equivalent of iodotrimethylsilane is consumed by converting byproduct trimethylsilyl nitrite into hexamethylsiloxane.

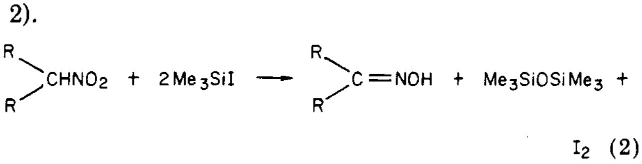
Similarly, 1-nitroadamantane was converted to 1-iodoadamantane in excellent yield.

Table I. Reaction of Nitro- and Nitrosoalkanes with Iodotrimethylsilane

substrate	product	yield,[a] %
Me_3CNO_2	Me_3CI	94[b]
		98
		89[b]
		68
		84
$PhCH_2NO_2$	$PhCN$	96
		90
		93
$CH_3(CH_2)_4CH_2NO_2$	$CH_3(CH_2)_4CN$	10
	$CH_3(CH_2)_4CH{=}NOH$	81
$PhCH{=}CHNO_2$	$PhCH_2CN$	71[c]
Me_3CNO	Me_3CI	75[b]

[a] Yield of the pure isolated product. Product characterized by IR and NMR spectroscopy. [b] NMR yield. [c] 40 mmol of iodotrimethylsilane was used.

(2) Secondary Nitroalkanes. In contrast to tertiary nitroalkanes, iodoalkanes are not formed on reaction of secondary nitroalkanes with iodotrimethylsilane. Instead, the corresponding oxime trimethylsilyl ethers were obtained. Nitrocyclohexane yielded cyclohexanone oxime in excellent yield, when the reaction mixture was subjected to an aqueous workup. The deoxygenation probably proceeds via O-silylation followed by deoxygenation (eq 2).



$$\begin{matrix} R \\ R \end{matrix}\!\!>CHNO_2 + 2Me_3SiI \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>C{=}NOH + Me_3SiOSiMe_3 + I_2 \quad (2)$$

Absence of any iodoalkanes in the products indicates that tautomerization to the oxime is extremely rapid, thus preventing further deoxygenation. The oxime is silylated under the reaction conditions. The formation of cyclohexanone oxime silyl ether in the reaction of nitrocyclohexane with iodotrimethylsilane was confirmed by ^{29}Si NMR studies before aqueous workup to the free oxime.

The reaction of secondary nitroalkanes with iodotrimethylsilane provides a new method for the selective reduction of nitroalkanes to the corresponding oximes. Previous literature methods for this reduction include the use of cuprous acetate/carbon monoxide,[5] iron–acetic acid,[6]

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[1] For part 112, see: Olah, G. A.; Husain, A.; Singh, B. P.; Mehrotra, A. K. *J. Org. Chem.*, accepted for publication.

[2] For a comprehensive review on the reactions of iodotrimethylsilane, see: Olah, G. A.; Narang, S. C. *Tetrahedron Rep.* **1982**, *38*, 2225.

[3] Olah, G. A.; Gupta, B. G. B.; Narang, S. C. *Synthesis* **1977**, 583.

[4] Olah, G. A.; Narang, S. C.; Field, L. D.; Salem, G. F. *J. Org. Chem.* **1980**, *45*, 4792.

[5] Knifton, J. F. *J. Org. Chem.* **1973**, *38*, 3296.

[6] Wehrli, P. A.; Schaer, B. *Synthesis* **1977**, 649.

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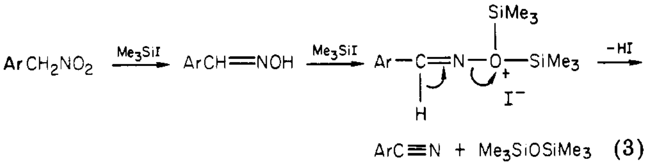
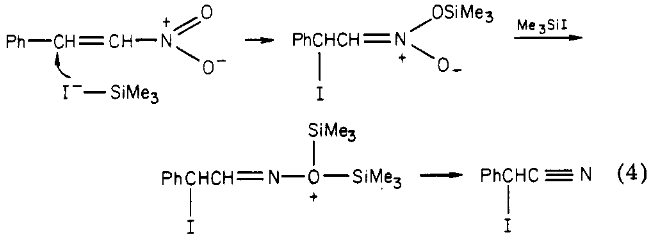
zinc–acetic acid,[7] photolysis,[8] etc. However, these methods either require the use of hazardous gases or acidic and harsh reaction conditions or are limited to special cases and therefore are not general in nature. Use of iodotrimethylsilane permits the reduction to occur under extremely mild and neutral conditions. The reaction stops at the oxime stage, and further reduction to the imine is not observed.

(3) Primary Nitroalkanes. The reaction of iodotrimethylsilane with primary nitroarylalkanes results in the formation of corresponding nitriles via deoxygenation followed by in situ dehydration of the resulting oximes (eq 3).



When α-nitrotoluene was treated with iodotrimethylsilane, benzonitrile was obtained in 98% yield. Due to the high acidity of benzylic hydrogens, the transformation of oxime to the nitrile via the oxime is very facile. 1-Nitrohexane yielded only a small amount of the nitrile, the main product being the oxime.

(4) ω-Nitrostyrene. The reaction of ω-nitrostyrene with iodotrimethylsilane provides an interesting combination of reactions. The final product, phenylacetonitrile, is obtained in 71% yield. The mechanism probably involves Michael addition, followed by deoxygenation, dehydration, and finally dehalogenation of the α-halonitrile (eq 4).



All these reactions have precedence in the literature. The Michael addition of iodotrimethylsilane to various Michael acceptors, the dehalogenation of α-halo ketones, and the reaction of acetonitrile with this reagent are well documented.[2]

The reaction of 1-nitrocyclohexene yielded a complex mixture of products even at low temperatures.

(5) Tertiary Nitrosoalkanes. 2-Methyl-2-nitrosopropane yielded 2-methyl-2-iodopropane in high yield in a reaction analogous to the reaction of 2-methyl-2-nitropropane (eq 5).

$$(Me)_3CNO \xrightarrow{2Me_3SiI} Me_3CI + Me_3SiOSiMe_3 \qquad (5)$$

Conclusions

We have demonstrated the facile reaction of nitro- and nitrosoalkanes with iodotrimethylsilane, where the reaction is initiated by the formation of a strong bond between silicon and oxygen. The deoxygenation reactions occur due to the excellent reducing power of iodide. The strong affinity of silicon for oxygen and the reducing power of iodide has allowed us to develop a mild, neutral method to convert secondary nitroalkanes to oximes, which can be regarded as masked ketones.

Experimental Section

To a stirred solution of the 1-nitroadamantane (10 mmol) in dichloromethane (50 mL) was added iodotrimethylsilane (20 mmol) under a dry nitrogen atmosphere. The reaction mixture was allowed to stirr at 25 °C for 16 h. The reaction mixture was quenched with aqueous sodium bicarbonate solution (50 mL) and washed with aqueous sodium thiosulfate solution (2 × 25 mL) and NaCl solution (50 mL). The organic extract was dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure to give 1-iodoadamantane: 98% yield; mp 74 °C.

Acknowledgment. Support of our work by the U.S. Army Office of Research, Durham, NC, is gratefully acknowledged.

Registry No. Me_3CNO_2, 594-70-7; $CH_3CH(NO_2)CH_3$, 79-46-9; $C_2H_5CH(NO_2)CH_3$, 600-24-8; $PhCH_2NO_2$, 622-42-4; CH_3-*o*-$C_6H_4CH_2NO_2$, 38362-89-9; CH_3-*m*-$C_6H_4CH_2NO_2$, 38362-90-2; $CH_3(CH_2)_4CH_2NO_2$, 646-14-0; $PhCH{=}CHNO_2$, 102-96-5; Me_3CNO, 917-95-3; Me_3SiI, 16029-98-4; Me_3CI, 558-17-8; $(CH_3)_2C{=}NOH$, 127-06-0; $C_2H_5C(CH_3){=}NOH$, 96-29-7; PhCN, 100-47-0; CH_3-*o*-C_6H_4CN, 529-19-1; CH_3-*m*-C_6H_4CN, 620-22-4; $CH_3(CH_2)_4CN$, 628-73-9; $CH_3(CH_2)_4CH{=}NOH$, 6033-61-0; $PhCH_2CN$, 140-29-4; 1-nitroadamantane, 7575-82-8; nitrocyclohexane, 1122-60-7; 1-iodoadamantane, 768-93-4; cyclohexanone oxime, 100-64-1.

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[7] Baer, H. H.; Ramk, W. *Can. J. Chem.* **1972**, *50*, 1292.

[8] Saito, I.; Takami, M.; Matsuura, T. *Tetrahedron Lett.* **1975**, 3155.

Synthesis of Enantiomerically Pure (*S*)-(+)-3-Hydroxytetrahydrofuran and Its *R* Enantiomer from Malic or Tartaric Acid

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In connection with the development of chiral analogues of tosylmethyl isocyanide (TosMIC),[1] a simple, enantiomerically pure, low molecular weight, secondary alcohol was need in quantity. The likeliest candidate, 2-butanol, is expensive,[2] probably because resolution of racemic 2-butanol is tedious.[3]

(−)-Menthol, a popular[4] and relatively cheap optically pure secondary alcohol, has certain disadvantages: (1) the molecular weight is twice that of 2-butanol; (2) in displacement reactions (for example, of menthyl tosylate), eliminations to menthenes sometimes are observed;[5] (3) only one enantiomer is normally available.

Our attention was drawn to 3-hydroxytetrahydrofuran (4), which is readily available by acid-catalyzed cyclodehydration of 1,2,4-butanetriol (**3**).[6] To our surprise, 3-hydroxytetrahydrofuran (4) had not been reported in optically active form. It seemed to us that both (*S*)-3-hydroxytetrahydrofuran (**4a**) and the *R* enantiomer (**4b**) ought to be accessible by using the enantiomers (**3a** or **3b**) of 1,2,4-butanetriol, *provided that cyclodehydration could be carried out without racemization of the secondary*

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[1] Cf.: Van Leusen, D.; Rouwette, P. H. F. M.; van Leusen, A. M. *J. Org. Chem.* **1981**, *46*, 5159.

[2] Both enantiomers are commercially available. Prices for research quantities of (+)- and (−)-2-butanol of various degrees of purity range from 25 to 40 U.S. dollars per gram. The price tends to decrease for the higher homologues to $3–4 for (−)-2-octanol.

[3] Kantor, S. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1953**, *75*, 1744.

[4] Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall: Englewood Cliffs, NJ, 1971. Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908.

[5] Hückel, W.; Maucher, D.; Fechtig, O.; Kurz, J.; Heinzel, M.; Hubele, A. *Justus Liebigs Ann. Chem.* **1961**, *645*, 115.

[6] Wynberg, H.; Bantjes, A. *Org. Synth.* **1958**, *38*, 37; "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 534.

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