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ADDITION OF ORGANOSILICON HALIDES, PSEUDOHALIDES AND AMIDES TO ACETONITRILE OXIDE

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Summary

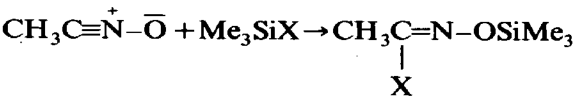
The reaction of Me_3SiX (X = Cl, I, NCS, CN, N_3, NEt_2, SMe, H (in Et_3SiH), F, OMe, NCO, O_2CMe) with acetonitrile oxide led to the formation of *O*-trimethylsilylacetohydroxamoyl adducts for the first seven members of the series. A rationale is given for the observed reactivity.

Introduction

In connection with recent studies on the utility of *O*-trimethylsilylhydroxamoyl chloride (IIa) as a shelf-stable precursor to acetonitrile oxide, we had occasion to note that while IIa is formed readily from trimethylchlorosilane and acetonitrile oxide, substitution of trimethylfluorosilane does not lead to *O*-trimethylsilylhydroxamoyl fluoride [1]. Since the only other report known to us concerning the reaction of nitrile oxides with an organosilicon reagent containing a replacable moiety also employed trimethylchlorosilane (with aromatic nitrile oxides to give, e.g., *O*-trimethylsilylbenzohydroxamoyl chloride [2]), we chose to investigate the reactivity of a range of organosilicon compounds in this regard.

Results and discussion

Acetonitrile oxide, generated from the cycloreversion of dimethylfuroxane by flash vacuum pyrolysis [3], was allowed to react at −25°C with a series of organosilicon compounds according to eq. 1. The results of these experiments are listed in Table 1.



$$CH_3C\equiv\overset{+}{N}-\bar{O} + Me_3SiX \rightarrow CH_3\underset{\substack{|\\ X}}{C}=N-OSiMe_3 \qquad (1)$$

(I) (II)

All preparations employed a 1 : 1 ratio of silane I to acetonitrile oxide, generally leading to crude product mixtures containing II and only small amounts of dimethylfuroxane (from the dimerization of acetonitrile oxide), readily removable by distillation or water-washing. An exception to this behavior was encountered in the preparation of IId, where some 60% of starting acetonitrile oxide was recovered in the form of the furoxane. Inexplicably, we were unable to increase the ratio of IId to furoxane by either longer reaction times or by using excess Id. None of the substrates Ih–Il afforded the expected adducts, as ascertained by both ^{1}H NMR and gas chromatographic analysis.

Characterization of the adducts which did form was aided by spectral data (Tables 2 and 3). Although structural assignments were relatively straightforward for the compounds IIa–IIf, some uncertainty originally centered on the structure of adduct IIb, in that Ib may have transferred the isothiocyanato group as such, or have reacted ambidently to afford the thiocyanate isomer of IIb ($-N{=}C{=}S = -SCN$). Little information is available from the literature by analogy on this point, as the initial adduct of nitrile oxides with thiocyanate ion under protic conditions rapidly undergoes subsequent transformations [4]. Clarification was, however, afforded by both the infrared and ^{13}C NMR data obtained from IIb. Contained among the former is a single, relatively weak band at 2165 cm^{-1}, characteristic of the SCN group [5], while the latter (Table 3) includes an absorption at 110 ppm which lies in the range typical of thiocyanate carbon (100–120 ppm) [6]. Isothiocyanates, in contrast, give rise to chemical shifts of between 130–190 ppm [6].

Although *E/Z* stereochemistries of the adducts IIa–IIf could not be assigned from the available data, it was noticed that IIg displayed a change in spectral parameters with time. It became clear that the material initially obtained (IIg$_K$)

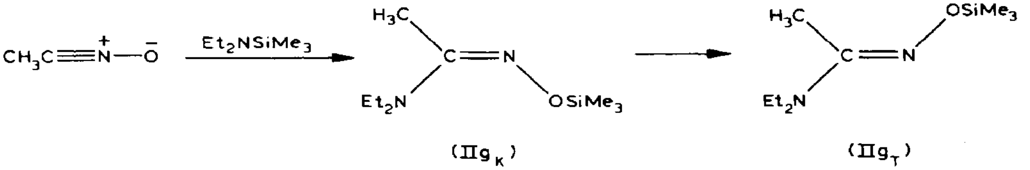
TABLE 1

ADDUCTS OBTAINED FROM ACETONITRILE OXIDE AND VARIOUS Me_3SiX

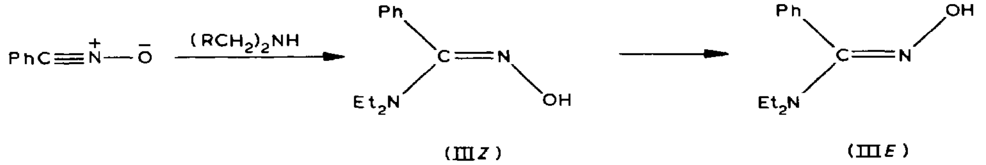
Me_3SiX	Adduct (% yield) [a]	Analyses (%) [b]		
		C	H	N
Me_3SiCl (Ia)	IIa (77)		[c]	
Me_3SiNCS (Ib)	IIb (68) [d]	38.18	6.37	15.04
		(38.27)	(6.42)	(14.88)
Me_3SiCN (Ic)	IIc (56)	46.25	7.73	17.93
		(46.12)	(7.74)	(17.93)
Me_3SiSMe (Id)	IId (22) [d]	40.87	8.61	8.07
		(40.64)	(8.53)	(7.90)
Me_3SiN_3 (Ie)	IIe (83)	34.82	6.95	32.48
		(34.86)	(7.02)	(32.52)
Me_3SiI (If)	IIf (68)	23.24	4.73	5.56
		(23.35)	(4.70)	(5.45)
Me_3SiNEt_2 (Ig)	IIg (80)	53.50	11.01	13.90
		(53.42)	(10.96)	(13.84)
Me_3SiF (Ih)	IIh (0)			
Me_3SiOMe (Ii)	IIi (0)			
Me_3SiNCO (Ij)	IIj (0)			
Me_3SiO_2CMe (Ik)	IIk (0)			
Et_3SiH (Il)	IIl (0)			

[a] Isolated (distilled) yield unless stated otherwise. [b] Calculated values in parentheses. [c] Ref. 1. [d] Calculated yield from ^{1}H NMR data.

isomerized upon standing at 25°C to a new species (IIg_T) over a period of several days (eq. 2).



(2)



(3)

This behavior parallels that reported for the initial adducts of dialkylamines to aromatic nitrile oxides, where the kinetic product has been identified as the *Z*-amidoxime III*Z* (eq. 3) [7]. Similarities also exist between ^1H and ^{13}C NMR data of III*Z*/III*E* pairs and corresponding data of the initial (IIg_K) and isomerized (IIg_T) *O*-trimethylsilyl amidoxime isomers obtained here. In point, both the ^1H and ^{13}C NMR absorptions of the NCH_2 groups in III*Z* are downfield of these same resonances in III*E* [7]. This pattern is repeated in the ^1H NMR data (Table 2, the X entries in italics) and the ^{13}C NMR data (Table 3, the X entries in italics) for IIg_K and IIg_T. While structural differences obviously exist between these two systems which may influence the NMR data, the close correspondence in both spectral and chemical behavior lead us to tentatively assign IIg_K as *Z*-*O*-trimethylsilyldiethylaminoacetamidoxime and IIg_T as the *E*-isomer. We also note significant differences in both ^{13}C NMR and IR adsorptions of the C=N functionality of these species which, if proved general, may serve as additional indicators of stereochemistry for amidoximes.

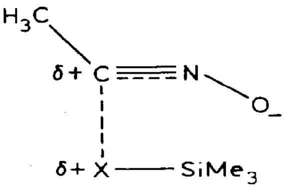
TABLE 2

^1H NMR AND IR DATA FOR THE ADDUCTS $CH_3C(X)=N-OSiMe_3$

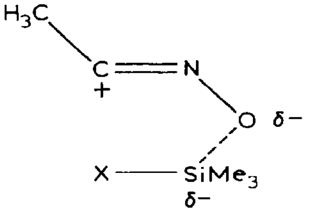
Adduct	X	^1H NMR (ppm) [a]			IR (cm^{-1}) [b]		
		$SiMe_3$	CH_3	X	$SiMe_3$	C=N	X
IIa	Cl	0.23	2.25		1255	1618	
IIb	SCN	0.22	2.43		1254	1605	2165
IIc	CN	0.25	2.20		1254	1589	2280, 2230
IId	SMe	0.25	2.21	2.37 s	1248	1582	
IIe	N_3	0.18	1.79		1255	1614	2120, 2170
IIf	I	0.23	2.59		1252	1608	
IIg_K	NEt_2	0.16	1.88	1.13 t *3.30 q*	1246	1609	
IIg_T	NEt_2	0.14	1.82	1.08 t *3.21 q*	1248	1594	

[a] In $CDCl_3$ with TMS as internal reference. [b] Film.

In a series of papers [7b–d,8a], Hegarty and co-workers have addressed details of the mechanism whereby HX species ($X = OH$, OAc, NR_2, N_3) add to aromatic nitrile oxides in aqueous solutions. In each instance, the process appears to be initiated by nucleophilic (X^-) attack at the carbon of the nitrile oxide to form an early transition state with little C–X bond formation. Simultaneously, the initially linear C–N–O grouping bends to position the oxygen *syn* to the incoming nucleophile. Subsequent protonation completes the formation of the adduct isomer with kinetically determined *Z* (X and OH *cis*) configuration. Thus nucleophiles derived from "weak" conjugate acids (N_3^-, CN^-, F^-, RO^-, RS^-) react very slowly with nitrile oxides at low pH, where they exist almost totally in protonated form. Preliminary evidence also exists, however, for a change in mechanism at even lower pH values ($= 0$–1) for the most weakly basic nucleophiles (e.g., HOH) which may involve initial formation of the protonated species $RC{\equiv}\overset{+}{N}{-}OH$ [8]. By analogy *, one could consider two limiting views (IV, V) of an early transition state for the reaction of compounds I with acetonitrile oxide.



(IV)



(V)

TABLE 3

^{13}C NMR DATA FOR THE ADDUCTS $CH_3C(X){=}N{-}OSiMe_3$

Adduct	X	^{13}C NMR (ppm) [a]			
		$SiMe_3$	CH_3	C=N	X
IIa	Cl	−1.18	22.85	139.77	
IIb	SCN	−1.12	19.30	146.81	109.60
IIc	CN	−1.15	17.76	133.21	110.93
IId	SMe	−0.91	18.27	158.07	12.66
IIe	N_3	−1.70	16.27	145.68	
IIf	I	−0.73	30.05	117.97	
IIg_K	NEt_2	−1.55	17.79 or [b] 14.14	152.00	14.14, *44.49* or [b] 17.79
IIg_T	NEt_2	−1.46	12.60 or 9.99	158.46	9.99, *41.85* or 12.60

[a] In $CDCl_3$ taken as 77.000 ppm. [b] $(CH_3CH_2)_2N$– vs. CH_3–C=N unassigned.

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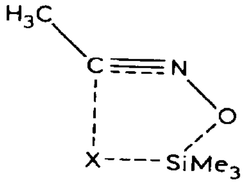
* Our system is of course non-aqueous. However, cycloadditions to nitrile oxides are noted for their insensitivity to solvent effects. See ref. 8a for a comparison of aqueous and diethyl ether systems.

The observed reactivity distribution shown in Table 1, however, does not correlate completely with either the pentacoordination ability of silicon bonded to the ligands in question [9] (V), nor to the carbon nucleophilicities ascribed to the heteroatom present in I (as extrapolated from the all-carbon onium salt formation series: $R_3N > R_2S > R_2O > RCl$ [10]) *. Nevertheless, a unifying working concept is arrived at if one assumes that an arrangement such as IV is necessary to initiate bond reorganization, but that Si–X bond cleavage is significant in the transition state. Species with either the highest bond strengths (Si–F, Si–O) ** or lowest X nucleophilicities (H < F < O) would then require the highest activation energies ***. This concept of course corresponds to a more, but not necessarily completely, synchronous picture of bond reorganization (VI).



Experimental

Literature procedures were used to synthesize 3,4-dimethylfuroxane [13] and acetoxytrimethylsilane [14]. Other silanes were obtained from Petrarch Systems, Inc. and, after spectral confirmation of purity, used as received. Methylthiotrimethylsilane was determined to be free of methanethiol by ^1H NMR analysis. Infrared spectra were obtained from neat films using a Sargent-Welch 3-200 spectrophotometer. The ^1H NMR data were recorded with a Varian A60A spectrometer, and the ^{13}C NMR spectra taken with an IBM NR-80 spectrometer. GLPC was used for product analysis and to obtain analytical samples for the indicated adducts: IIa, 10 ft., 20% PMPE; IIb, 5 ft., 20% SE-30; IIc, IId, 5 ft., 15% FFAP; IIg, 5 ft., 3% FFAP.

General procedure for addition of silanes to acetonitrile oxide

A horizontally-mounted Lindberg tube furnace (12 inch hot zone) at 630°C was used in a flash vacuum pyrolysis system. The pot was charged with 0.50 g (4.38 mmol) of 3,4-dimethylfuroxane and any volatiles removed under 10 mmHg vacuum for 10 min (trap heated). The trap was then cooled to −78°C and the furoxane slowly evaporated through the hot zone at 0.05 mmHg. The trapped acetonitrile oxide, while still in the −78°C bath, was placed under positive nitrogen pressure, and 15 ml of anhydrous ethyl ether slowly added by syringe through a septum, followed by addition of 8.76 mmol of the silane in an identical manner. After warming to −25°C, the trap was sealed (Parafilm) and held at −25°C overnight.

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* Actual heteroatom nucleophilicities in I are expected to be lower but in like order.

** Si–X bond strengths in Me_3SiX species [11]: Si–S, 99; Si–N, 100; Si–Cl, 113; Si–O, 128 and (calculated here) Si–F, 144 kcal mol^{-1}.

*** Although the nucleophilicity of nitriles is low, trimethylsilyl cyanide is known to be in equilibrium with the much more nucleophilic isocyanide [12].

After warming to 25°C, the reaction mixture was concentrated under reduced pressure and the residue Kugelrohr distilled (IIa–IIf, b.p. 25°C/0.05 mmHg; IIg, b.p. 55°C/0.4 mmHg).

The preparation of IId gave virtually identical results, regardless of whether (a) the general procedure was followed (b) a 1/1 mixture of nitrile oxide and Id was held at −25°C for 72 h or (c) a 1/3 mixture of nitrile oxide and Id was held at −25°C for 72 h.

When Ih–Il were employed in the general procedure, only starting silane and 3,4-dimethylfuroxane were obtained.

Abstracted IR data for IIa–IIg are contained in Table 2. More complete IR data for the initial (IIg_K) and isomerized (IIg_T) amidoximes are given below.

Z-O-Trimethylsilyldiethylaminoacetamidoxime (*IIg_K*). IR: 2961s, 2930m, 2900m, 2870w, 1609s, 1450w, 1434m, 1405m, 1377m, 1345w, 1308w, 1275m, 1246s, 1209m, 1160w, 1091w, 1080w, 1065w, 1040m, 1021m, 953m, 922m, 890s, 840s, 787w, 749m, 689w cm^{-1}.

E-O-Trimethylsilyldiethylaminoacetamidoxime (*IIg_T*). IR: 2969s, 2935m, 2900m, 2875w, 1594m, 1477w, 1460m, 1448m, 1420m, 1376m, 1365w, 1347w, 1309w, 1285m, 1248s, 1213w, 1174w, 1091w, 1070w, 1034w, 1004w, 950m, 919s, 903s, 870m, 840s, 802w, 787w, 749m, 730m, 690w cm^{-1}.

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