Journal of Organometallic Chemistry, 72 (1974) 171—177

METAL DERIVATIVES OF AMIDOXIMES

I. MONO-, BIS- AND TRIS-(TRIMETHYLSILYL)AMIDOXIMES

A.B. GOEL and V.D. GUPTA
Chemistry Department, Rajasthan University, Jaipur - 302004 (India)
(Received December 21st, 1973)

Summary

The preparation and properties of mono-, bis- and tris-(trimethylsilyl)amidoximes are described.

Oxime and hydroxylamine derivatives of metals are of current interest [1]. Chelating oximes such as amidoximes [2], $R(H_2N)C{=}N{-}OH$, were synthesized during the end of the last century, but little attention was given to their metal derivatives apart from their analytical applications [3—5]. We report the synthesis of new mono-, bis- and tris-(trimethylsilyl)amidoximes.

Trimethylchlorosilane reacted readily at room temperature with amidoximes, $R(H_2N)C{=}N{-}OH$, (R = $ClCH_2$, Et, Pr, Ph and $PhCH_2$), in equimolar proportions, in the presence of triethylamine in solvents such as benzene, hexane or ether, giving *O*-trimethylsilylamidoximes, $R(H_2N)C{=}N{-}OSiMe_3$. In the case of acetamidoxime, however, *N,O*-bis(trimethylsilyl)amidoxime was invariably obtained, leaving half of the oxime unreacted:

$$Me_3SiCl + RC(=N{-}OH)(NH_2) + Et_3N \longrightarrow RC(=N{-}OSiMe_3)(NH_2) + Et_3N{\cdot}HCl$$

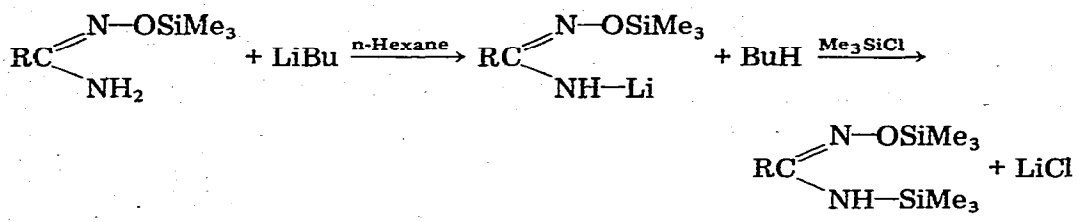
(R = $ClCH_2$, Et, Pr, Ph or $PhCH_2$)

$$2\,Me_3SiCl + 2\,MeC(=N{-}OH)(NH_2) + 2\,Et_3N \longrightarrow MeC(=N{-}OSiMe_3)(NH{-}SiMe_3) + MeC(=N{-}OH)(NH_2) + 2\,Et_3N{\cdot}HCl$$

Except in the case of acetamidoxime, the introduction of a second trimethylsilyl group in other amidoximes by the direct reaction of the chlorosilane was not achieved even after prolonged refluxing, or even by use of hexamethyldisilazane in refluxing toluene.

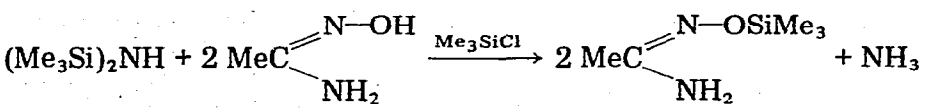
The difference in the reactivity of the amino hydrogen of acetamidoxime and that of other amidoximes towards trimethylchlorosilane is probably due to steric effects. Propionamide has also been found to react with trimethylchlorosilane to give only the mono-derivative, in contrast with acetamide, which is known to give the bis-product [6].

However, the *N,O*-bis(trimethylsilyl)amidoximes, $R[H(Me_3Si)N]C{=}N{-}OSiMe_3$, (R = Et, Pr and Ph) have been synthesized from the lithium derivatives of the mono-products:



Even *N,N,O*-tris(trimethylsilyl)amidoximes were prepared through the lithium derivatives of the bis-products.

Attempted preparation of *O*-trimethylsilylacetamidoxime, $Me(H_2N)C{=}N{-}OSiMe_3$, using different solvents under milder conditions always gave the bis-product. In absence of triethylamine, trimethylchlorosilane did not react with the amidoxime. The mono-product of acetamidoxime was prepared, however, by treating hexamethyldisilazane with acetamidoxime in the ratio 1/2, with traces of trimethylchlorosilane as catalyst:



Its lithium derivative readily reacted with trimethylchlorosilane to give *N,O*-bis(trimethylsilyl)acetamidoxime, $Me[H(Me_3Si)N]C{=}N{-}OSiMe_3$.

All these mono-, bis- and tris-(trimethylsilyl)amidoximes are distillable liquids with vapour pressures of 10 mm in the range of 65—150°, and monomeric in benzene.

Attempts to synthesize the lithium derivative of $ClCH_2(H_2N)C{=}N{-}OSiMe_3$, in order to prepare bis- and tris-products gave a mixture of compounds which could not be separated.

It has recently been established by IR and NMR studies that amidoximes exist mainly in the amino form [7]. All the amidoximes described in this paper exhibit two bands in the regions 3650—3570 and 3220—3175 cm^{-1} due to ν(OH), which disappear in the mono-derivatives, $R(H_2N)C{=}N{-}OSiMe_3$, suggesting that the compounds are *O*-trimethylsilyl products. The pair of amino (NH_2) stretchings in the regions 3487—3450 and 3380—3305 cm^{-1} and its deformation at $\approx$ 1575 cm^{-1}, which are present in the mono-products, furthermore confirm the nature of the mono-derivatives.

An intense band in the region 1648—1630 cm^{-1} can be assigned to ν(C=N) of the oxime moiety of the mono-derivatives. A general fall of about $\approx$ 30 cm^{-1} in ν(C=N) in comparison to the parent amidoxime parallels that noted with simple oxime derivatives, and has been ascribed to be due to the mass effect of the trimethylsilyl groups [8].

In the bis-derivatives, $R[H(Me_3Si)N]C{=}N{-}OSiMe_3$, an absorption at ≈3320 cm^{-1} can be safely assigned to >NH stretching. This band is invariably absent in the tris-compounds, $R[(Me_3Si)_2N]C{=}N{-}OSiMe_3$. The bis- and tris-derivatives are characterized by the absence of any amino-deformation, and the presence of ν(C=N) in the range 1645—1625 cm^{-1} as an intense band. In the bis-derivatives derived from propanamidoxime and butanamidoxime, there is an additional strong unassigned band at ≈1620 cm^{-1}.

All the trimethylsilyl derivatives are characterized by an intense band at ≈1250 cm^{-1} due to CH_3(—Si) symmetric deformations. The strong band at ≈915 cm^{-1} is due to the N—O vibration. Two more intense absorptions at 840 ± 5 cm^{-1} due to methyl rocking and Si—C stretchings and the other at 750 ± 10 cm^{-1} due to Me_3Si group are present for all these derivatives [9]. A weak to medium band in the region 1115—1040 cm^{-1} can be tentatively attributed to the Si—O—N and CH_3 non-planar deformation. The asymmetric stretch due to Si—O probably gives rise to a band at 865—896 cm^{-1}.

A preliminary proton NMR spectrum of propanamidoxime, $CH_3CH_2(H_2N)C{=}N{-}OH$, gave the desired triplet (centred at 8.91 τ) and a quartet (centred at 7.85 τ) due to CH_3 and CH_2 protons, respectively in the ratio 3/2. The expanded spectrum of the oxime in the methyl and methylene range exhibited two sets of triplets and quartets due to *syn-* and *anti-*forms present in the amidoxime. The exact ratio of these two geometrical forms and difference in their chemical shifts could not be measured. It seems that the two geometrical forms continue to exist even in the mono-derivative of propanamidoxime, $CH_3CH_2(H_2N)C{=}N{-}OSiMe_3$, whose expanded spectrum at room temperature gave two sets of triplets (centred at 9.09 and 9.12 τ) and two sets of quartets (centred at 8.01 and 8.06 τ) respectively. Similar evidence for *syn-* and *anti-*forms was obtained from the spectra of $CH_3(H_2N)C{=}N{-}OSiMe_3$, which in a normal measurement gives only one methyl signal due to methyl protons of the amidoxime, but on 20-fold expansion this signal splits into two. The spectrum of one of the bis-derivatives, $CH_3[H(Me_3Si)N]C{=}N{-}OSiMe_3$, definitely showed two different types of trimethylsilyl protons, one probably attached to oxygen (occurring at 9.97 τ) and other to nitrogen (at 9.94 τ).

Experimental

Moisture was rigorously excluded. Freshly distilled trimethylchlorosilane (b.p. 57.7°), and hexamethyldisilazane (b.p. 126°) were used. Benzene was dried over sodium wire followed by azeotropic fractionation. Ether and hexane were dried over sodium wire. Acetonitrile was dried by storage over anhydrous K_2CO_3 followed by distillation of P_2O_5. Amidoximes were prepared by the standard methods [2,10] and analysed before use. Butyl chloride (78.5°) and triethylamine (89.4°) were dried by storage over KOH (≈24 h) followed by distillation.

Infrared spectra were recorded as neat or in $CHCl_3$ using KBr optics (Perkin Elmer 337) in the range 4000—400 cm^{-1}. An ebulliometer (Gallenkamp) and Mechrolab osmometer (abbreviated below as E and O respectively) were used for molecular weight determinations. Refractive indices were determined with an Abbé refractometer. PMR spectra were recorded in $CDCl_3$, CCl_4 and in deuterated acetone on HA 60 and HA 100 machines.

TABLE 1

O-TRIMETHYLSILYLAMIDOXIMES[a]

Reactants (g)			Reaction time (h)	B.p. of product (°C/mm)	Yield (%)	Product $RC(=N-OSiMe_3)NH_2$ R =	Analysis found (calcd.) (%)		Mol. wt, found (calcd.)	$n_D^{31°}$
Me_3SiCl	Amidoxime	Et_3N					Si	N		
1.66	Chloroethenylamidoxime 1.66	1.56	Stirred for 5 min	38/0.05	75	$ClCH_2$	15.40 (15.54)	15.58 (15.50)	182.4(O), 180.2(E) (180.7)	1.4650
1.76	Propanamidoxime 1.43	1.64	3	79/10.0	90	Et	17.20 (17.50)	17.42 (17.47)	173.4(O), 162.1(E) (160.3)	1.4370
1.14	Butanamidoxime 1.07	1.07	3	93/10.0	87	Pr	15.80 (16.11)	15.92 (16.06)	173.7(O), 173.8(E) (174.3)	1.4365
1.48	Benzamidoxime 1.85	1.39	1	84/0.1	76	Ph	13.20 (13.49)	13.48 (13.45)	212.2(O), 209.5(E) (208.2)	1.5215
1.56	Benzylamidoxime 2.14	1.44	2	140—142/10.0	90	$PhCH_2$[b]	12.52 (12.64)	12.54 (12.61)	225.4(O), 224.6(E) (222.2)	

[a] Reactions have been carried at room temperature in benzene. All the products are colourless liquids except the compound ([b]) which is a low melting solid. (O) = Osmometry, (E) = Ebulliometry.

Silicon was estimated as silica, and nitrogen by the Kjeldahl method.

O-trimethylsilylamidoximes

To a cooled solution of amidoxime in benzene (≈40 ml) and triethylamine, trimethylchlorosilane was added dropwise. The mixture was stirred at room temperature and filtered, the solvent removed, the residue distilled in vacuo to give a colourless liquid. The reactions are summarized in Table 1.

O-trimethylsilylacetamidoxime

To a suspension of acetamidoxime (1.235 g) in benzene (≈40 ml), hexamethyldisilazane (1.34 g) (molar ratio 2/1) was added, with a drop of trimethylchlorosilane as catalyst. The mixture was refluxed for ≈10h, then the solvent was removed and the product distilled at 68°/10.0 mm to yield a colourless liquid (88%). (Found: Si, 18.85; N, 18.80. Mol. wt., 155.5(O), 150.1(E). $C_5H_{14}N_2OSi$ calcd.: Si, 1919; N, 19.15%. Mol. wt., 146.3.) $n_D^{31°}$ 1.4455.

Reaction of trimethylchlorosilane with acetamidoxime in the presence of triethylamine (molar ratio 1/1/1)

To acetamidoxime (1.639 g) in benzene (≈50 ml), triethylamine (2.246 g) and trimethylchlorosilane (2.404 g) were added. The mixture was stirred at 35° for ≈6 h, and filtered (Found: 3.85; calcd.: 3.05); after removal of the solvent, the residue was distilled under reduced pressure to yield a colourless liquid, b.p. 80°/10.0 mm (60%). (Found: Si, 25.25; N, 12.81. Mol wt., 202.4. $C_8H_{22}N_2OSi_2$ calcd.: Si, 25.70; N, 12.82%. Mol. wt., 218.5.) $n_D^{31°}$: 1.4405. When the above reaction was performed in acetonitrile or with a 2/1/2 reactant ratio, the same product was formed.

Reaction of trimethylchlorosilane with acetamidoxime in the absence of triethylamine (molar ratio 1/1/1)

To acetamidoxime (0.83 g) in benzene (≈40 ml), trimethylchlorosilane (1.21 g) was added. Dry air was bubbled through for ≈10 h to facilitate the removal of hydrogen chloride. Excess of solvent was removed under vacuo, and the product on drying at 30°/0.5 mm was the amidoxime. (Found: N, 37.5. $C_2H_6ON_2$ calcd.: N, 37.8%.) M.p.: 135° (Lit. 136°).

Trimethylsilylpropionamide

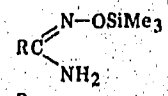
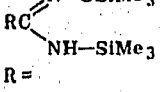
Trimethylchlorosilane (3.276 g) was added dropwise to propionamide (2.204 g) and triethylamine (3.02 g) in benzene (≈60 ml). This was stirred for ≈2 h, then filtered, and removal of volatile material left a crystalline solid at 89—90°/9.0 mm. (Found: Si, 19.24; N, 9.54. $C_6H_{15}NOSi$ calcd.: Si, 19.32; N, 9.63%.) This mono-product did not react further with trimethylchlorosilane in the presence of excess triethylamine even on 6 h refluxing.

N,O-bis(trimethylsilyl)amidoximes

A solution of butyllithium in hexane (≈ 40 ml) was prepared from lithium and butyl chloride in molar ratio 2/1. *O*-Trimethylsilylamidoxime was added, and the mixture stirred for ≈3 h. Trimethylchlorosilane was then added dropwise, and the mixture stirred for ≈1 h, then filtered. Removal of the solvent and distillation in vacuo gave a colourless liquid. Results are tabulated in Table 2.

TABLE 2

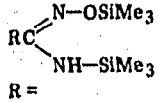
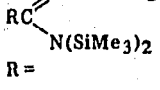
N,O-BIS(TRIMETHYLSILYL)AMIDOXIMES[a]

Reactants (g)			BuLi	Reaction time (h)	B.p. of product (°C/mm)	Yield (%)	Product	Analysis found (calcd.) (%)		Mol. wt. found. (calcd.)	n_D^{31}
Me_3SiCl	 R =						 R =	Si	N		
1.18	Me	1.58	0.69	14	80/10.0	89	Me	25.50 (25.70)	12.67 (12.82)	206.5(E) (218.5)	1.4405
1.18	Et	1.73	0.69	15	95/11.0	84	Et	23.95 (24.15)	11.91 (12.05)	225.7(E) (232.5)	1.4350
1.18	Pr	1.88	0.69	14	98–100/10.0	87	Pr	22.10 (22.79)	11.23 (11.37)	229.8(E) (246.5)	1.4335
1.18	Ph	2.25	0.69	12	108/0.5	90	Ph	19.82 (20.02)	10.10 (10.00)	263.6(E) (280.4)	1.5000

[a] Footnote as in Table 1.

TABLE 3

N,N,O-TRIS(TRIMETHYLSILYL)AMIDOXIMES[a]

Reactants (g)			BuLi	Reaction time (h)	B.p. of product (°C/mm)	Yield (%)	Product	Analysis found (calcd.) (%)		Mol. wt. found (calcd.)	$n_D^{31°}$
Me_3SiCl	 R =						 R =	Si	N		
0.88	Me	1.78	0.53	Stirred for 16	96–97/10.0	72	Me	28.50 (28.98)	9.47 (9.64)	269.9(E) (290.6)	1.4375
1.18	Et	2.51	0.69	17	106–108/10.0	80	Et	27.20 (27.65)	8.97 (9.19)	283.7(E) (304.7)	1.4220
1.18	Pr	2.66	0.69	18	105–108/5.0	67	Pr	26.19 (26.44)	8.79 (8.79)	294.5(E) (318.7)	1.4200
1.18	Ph	3.03	0.69	18	108/0.2	76	Ph	23.63 (23.90)	7.85 (7.94)	342.6(E) (352.6)	1.4880

[a] Footnote as in Table 1.

N,N,O-tris(trimethylsilyl)amidoximes

The lithium derivative of the bis-product was treated with trimethylchlorosilane in n-hexane. After the usual treatment a colourless liquid was obtained (Table 3).

Acknowledgement

Thanks are due to Professor R.C. Mehrotra for his keen interest and suggestions, and for providing laboratory facilities during the work. Financial assistance extended by The C.S.I.R., New Delhi is gratefully acknowledged.

References

1 A. Singh, V.D. Gupta, G. Srivastava and R.C. Mehrotra, J. Organometal. Chem., 64 (1974) 145.
2 F. Elog and R. Lenaers, Chem. Rev., 62 (1962) 155.
3 G.A. Pearse Jr. and R.T. Pflaun, J. Amer. Chem. Soc., 81 (1959) 6505.
4 V. Stuzka, J. Kvapil and M. Kuras, Z. Anal. Chem., 179 (1961) 401.
5 A.I. Busev, T.N. Zholondkovskaya, L.S. Krysing and L.I. Korobkina, Sovrem Metody Anal. Mater., (1969) 153.
6 L. Birkofer, A. Ritter and W. Giessler, Angew. Chem., 75 (1963) 93; J. Pump and E.G. Rochow, Chem. Ber., 97 (1964) 627.
7 L. Brandt, Meded. Vlaam. Chem. Ver., 29 (1967) 57.
8 P.G. Harrison and J.J. Zuckerman, Inorg. Chem., 9 (1970) 175.
9 N.B. Colthup, L.H. Daly and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, London, 1964.
10 J. Barrans, R. Mathis-Noel and F. Mathis, C.R. Acad. Sci., 245 (1957) 419.