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METAL DERIVATIVES OF AMIDOXIMES

V. DIALKYL- OR DIPHENYL-SILYL DERIVATIVES OF AMIDOXIMES

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Summary

New monomeric dialkyl- or diphenyl-silylbisamidoximes and dialkyl(ethoxy)-silylamidoximes have been characterised. Their infrared spectra have been interpreted and diamagnetic susceptibility of some of them has been determined.

Introduction

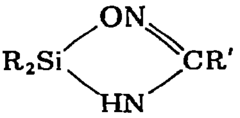
Apart from analytical applications, metal complexes of amidoximes [1] have received very little attention. Studies on metal derivatives of amidoximes, $R'(H_2N)C{=}N{-}OH$, have been initiated by us recently [2-5], and in continuation of our investigations on organosilicon derivatives, we report here the synthesis and properties of some new dialkyl- or diphenyl-silylbisamidoximes and dialkyl(ethoxy)silylamidoximes.

Results and discussion

Dialkyl- or diphenyl-diethoxysilanes were refluxed with the amidoximes in 1/2 molar ratio in benzene, in the presence of a small amount of sodium. The progress of the reaction was checked by estimating the liberated ethanol.

$$R_2Si(OEt)_2 + 2\ R'C(NH_2){=}NOH \xrightarrow[\text{Na}]{\text{Benzene}} \underset{\text{(I)}}{R_2Si[ON{=}C(R')NH_2]_2} + 2\ EtOH$$

a, R = Me, R' = Me
b, R = Me, R' = Et
c, R = Me, R' = Pr
d, R = Me, R' = Ph
e, R = Ph, R' = Et
f, R = Ph, R' = Pr
g, R = Ph, R' = Ph

Attempted preparation of mono-derivatives by carrying out the reactions in equimolar proportions invariably resulted in bis-products (I). These results are consistent with earlier findings [5, 6] that, in contrast, the dialkyldichlorosilanes reacted readily with amidoximes in equimolar ratio in the presence of triethylamine resulting in the formation of cyclic derivatives,  [4]. However, the mono-products (II) could be obtained by treating dialkyl(ethoxy)chlorosilanes, $R_2Si(OEt)Cl$, with amidoximes in the presence of triethylamine:

$$R_2Si(OEt)Cl + R'C(NH_2){=}NOH + Et_3N \xrightarrow{\text{Benzene}} \underset{\text{(II)}}{R_2Si(OEt)ON{=}C(R')NH_2} + Et_3N \cdot HCl$$

a, R = Me, R′ = Me
b, R = Me, R′ = Et
c, R = Me, R′ = Pr
d, R = Me, R′ = Ph
e, R = Et, R′ = Et
f, R = Et, R′ = Pr

All mono- (II) and bis- (I) derivatives are monomeric in refluxing benzene (Tables 1 and 2).

Infrared spectra

The ν(OH) observed at 3570-3650 cm^{-1} in the parent amidoximes [7] disappear in compounds I and II and two strong bands in the regions 3455-3475 cm^{-1} and 3320-3360 cm^{-1} due to $\nu(NH_2)$ and its deformation at 1575 ± 5 cm^{-1} are present, suggesting that the products are *O*-substituted. An intense band in the region 1640-1652 cm^{-1} can be assigned to ν(C=N) of the oxime moiety. In dialkylsilyl products, the vibrations of the R_2 group on silicon show characteristic bands [8, 9], at ca. 805 and 840-850 cm^{-1} due to ν_s(Si—C) and methyl rocking along with the δ_s(Me) at ca. 1255 cm^{-1} and δ_s(Et) at ca. 1238 cm^{-1}. Absorption bands at 1070-1110 cm^{-1} with two or three split band groups characteristic of ν_{as}(Si—O—C), (Si—O—N) and ν(C—O) frequencies have been observed in both mono- (II) and bis- (I) products. A medium to strong band at 935 ± 12 cm^{-1} is due to ν(N—O) and at 720-735 cm^{-1} is assigned to ν_s(Si—O). The positions of ν(Si—C), ν(Si—O) in comparison to dialkyldiethoxysilane [10, 11], and $\nu(NH_2)$ with respect to parent amidoxime [2] are almost unchanged, indicating the absence of any intramolecular coordination (Si←N) [12].

PMR spectra

The PMR spectra of IIb gave two multiplets due to methylene protons of ethoxy and ethyl groups each of which splits into two sets of quartets at τ 6.14, 6.20 and τ 7.79, 7.84 respectively, suggesting the presence of some isomeric forms. Methyl protons could be distinguished at τ 8.82 (ethoxy) and 8.97 (ethyl). The presence of isomers is also indicated by three closely spaced signals (τ 9.80, 9.91 and 9.97) due to Me_2Si protons. Methylene (two multiplets), methyl and Me_2Si protons are observed in the ratio 1/1/3/3. The most likely

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TABLE 1

PREPARATION AND ANALYSES OF DIMETHYL- AND DIPHENYL-SILYLBISAMIDOXIMES

Reactants (g)		Product	Reaction time (h)	B.p. (°C/mm)	Nature and yield (%)	Analysis found (calcd.)			Mol. wt. found (calcd.)	n_D^{35}
$R_2Si(OEt)_2$ R	$R'(H_2N)C{=}N{-}OH$ R'					Ethanol in azeotrope (g)	Si (%)	N (%)		
Me 2.07	Me 2.06	Ia	42	128/0.1	White crystn. solid (85)	1.22 (1.28)	13.72 (13.75)	29.20 (29.39)	254 (204.3)	
Me 1.53	Et 1.92	Ib	39	68/0.1	Colourless liquid (84)	0.95 (1.00)	12.04 (12.09)	24.06 (24.12)	248 (232.3)	1.4495
Me 1.29	Pr 1.77	Ic	40	79/0.1	Colourless liquid (80)	0.76 (0.80)	10.68 (10.78)	21.50 (21.51)	275 (260.4)	1.4630
Me 1.27	Ph 2.33	Id	38	Crystd. from hot benzene	White solid (92)	0.75 (0.79)	8.45 (8.55)	17.01 (17.06)	327 (328.5)	
Ph 1.46	Et 0.95	Ie	37	—	Viscous liquid (98)	0.46 (0.49)	7.81 (7.88)	15.60 (15.71)	367 (356.5)	
Ph 0.99	Pr 0.74	If	38	Crystd. from hot benzene	White solid (88)	0.30 (0.33)	7.24 (7.30)	14.50 (14.57)	389 (384.5)	
Ph 1.27	Ph 1.27	Ig	35	Crystd. from hot benzene	White solid (94)	0.40 (0.44)	6.12 (6.20)	12.30 (12.38)	450 (452.6)	

TABLE 2

PREPARATION AND ANALYSES OF DIALKYL(ETHOXY)SILYLAMIDOXIMES[a]

Reactants (g)			Product	Reaction time	B.p. (°C/mm)	Yield (%)	Analysis found (calcd.)(%)		Mol. wt. found (calcd.)	n_D^{35}
$R_2Si(OEt)Cl$ R	$R'(H_2N)C=N-OH$ R'	Et_3N					Si	N		
Me	Me		IIa	1 h	57/0.2	90	15.86	15.81	189	1.4475
1.13	0.60	0.84					(15.92)	(15.89)	(176.3)	
Me	Et		IIb	30 min	73/1.0	88	14.65	14.70	197	1.4465
1.17	0.74	0.86					(14.75)	(14.72)	(190.3)	
Me	Pr		IIc	25 min	74/0.7	86	13.64	13.71	211	1.4465
1.18	0.87	0.87					(13.75)	(13.72)	(204.3)	
Me	Ph		IId	25 min	140/0.2	78	11.70	11.72	233	—
1.19	1.17	0.90					(11.70)	(11.76)	(238.4)	
Et	Et		IIe	30 min	85/0.1	85	12.77	12.78	237	1.4515
1.10	0.58	0.72					(12.86)	(12.82)	(218.4)	
Et	Pr		IIf	30 min	87/0.1	86	12.01	12.02	239	1.4515
1.08	0.66	0.66					(12.08)	(12.05)	(232.5)	

[a] All the products are colourless liquids prepared at room temperature.

TABLE 3

DIAMAGNETIC SUSCEPTIBILITY DATA FOR DIMETHYLSILYLBISAMIDOXIMES AND DIMETHYL(ETHOXY)SILYLAMIDOXIMES[a]

Compound (R')	χ_M observed	% Difference between observed and calculated χ_M
Ia (Me)	124.4	−4.8
Ib (Et)	146.9	−4.4
Ic (Pr)	169.4	−3.7
IIa (Me)	113.4	−3.6
IIb (Et)	124.5	−3.5
IIc (Pr)	135.8	−3.2

[a] 10^{-6} c.g.s. units.

isomers are *syn* and *anti* forms for which evidence has been gathered in the PMR data of trimethylsilylamidoxime [2].

Diamagnetic susceptibility

A wave-mechanical method using the concept of bond susceptibility has been used [13, 14]. The experimentally determined values and the percentage difference between observed and calculated diamagnetic susceptibilities of the compounds have been summarised in Table 3.

The values reported (Table 3) have been treated graphically for each individual series by plotting molar susceptibility against the length of the alkyl chains in the homologous compounds. Both plots were linear and the information obtained from them for each series is given in Table 4. χ_{Si} have been calculated using the standard χ values of different groups [14-16].

The lower values of χ_{Si} (17.90 and 17.85) for both series (Table 4) in comparison with χ_{Si} for the Si—C system (reported to be 21.00 for tetra-compounds [17]) are explainable by "back-bonding" to the silicon atom from the oxygen lone-pair. These observations are consistent with the data of Abel et al. [17].

TABLE 4

VALUES OF THE DIAMAGNETIC SUSCEPTIBILITIES OF THE METHYLENE GROUPS AND THE CENTRAL METAL ATOM IN THE SERIES STUDIED

Series	Gradient of plot χ_M against *n*	χ_{CH_2}	Axial intercept	χ_{Si}
I	11.25	11.25	100.4	17.90
II	11.20	11.20	101.7	17.85

Experimental

Experimental details and analytical methods are as described in an earlier report [5]. Freshly distilled dimethyldiethoxysilane (113.8°) and diphenyldiethoxysilane (151-153°/6.0 mm) were used. Dimethyl(ethoxy)chlorosilane (95-96°) and diethyl(ethoxy)chlorosilane (146-147°) were prepared [18] and distilled before use. Amidoximes were synthesized by the standard methods [1, 19].

Infrared spectra were recorded on neat samples or on nujol mulls, using KBr optics (Perkin—Elmer 337) in the range 4000-400 cm^{-1}. Molecular weights were determined in refluxing benzene in a semi-micro (Gallenkamp) ebulliometer. Refractive indices were determined with an Abbé refractometer. The PMR spectrum was run on a Varian A-60 in CCl_4 using TMS as internal standard.

All diamagnetic susceptibility measurements have been carried out at room temperature (26°) by the Gouy method. Benzene was used as a reference liquid having specific susceptibility -0.702×10^{-6} c.g.s. units. The accuracy of the determination of the Gouy force was of the order of ± 0.05 mg.

Reaction between dimethyl- or diphenyl-diethoxysilane and amidoxime (molar ratio 1/2)

Dimethyl- or diphenyl-diethoxysilane and the appropriate amidoxime were added to anhydrous benzene (ca. 50 ml). A small piece of metallic sodium was added and the reaction mixture was refluxed and the ethanol liberated was fractionated azeotropically with benzene for ca. 30-40 h. Solvent was removed under reduced pressure and the residue was distilled in vacuo or crystallized to give the product. The details are given in Table 1.

Reactions of dialkylchloroethoxysilanes with amidoximes in the presence of triethylamine (molar ratio 1/1/1)

To the amidoxime in benzene (ca. 40 ml), triethylamine and dialkylchloroethoxysilane were added. The mixture was stirred at room temperature for ca. 1/2 h and filtered. The solvent was removed and the residue on distillation in vacuo gave the product. Results are collected in Table 2.

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References

1 F. Elog and R. Lenaers, Chem. Rev., 62 (1962) 155.
2 A.B. Goel and V.D. Gupta, J. Organometal. Chem., 72 (1974) 171.
3 A.B. Goel and V.D. Gupta, J. Organometal. Chem., 77 (1974) 183.
4 A.B. Goel and V.D. Gupta, Aust. J. Chem., (1974) in press.
5 A.B. Goel and V.D. Gupta, Indian J. Chem., (1974) in press.
6 E. Larsson, Acta Chem. Scand., 8 (1954) 898.
7 L. Brandt, Meded. Vlaam. Chem. Ver., 29 (1967) 57.

8 E.W. Abel and R.P. Bush, J. Organometal. Chem., 3 (1965) 245.
9 N.B. Colthup, L.H. Daly and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, London, 1964.
10 R. Forneris and E. Funk, Z. Electrochem., 62 (1958) 1130.
11 T. Tanaka, Bull. Chem. Soc. Jap., 33 (1960) 446.
12 R.C. Mehrotra and P. Bajaj, J. Organometal. Chem., 24 (1970) 611.
13 J. Baudet, J. Chim. Phys., 58 (1961) 228.
14 A. Pacault, J. Hoarau and A. Marchand, Advances in Chemical Physics, Interscience, New York, 1961, p. 171.
15 Ya.G. Dorfman, Diamagnetism and Chemical bond, Elsevier, New York, 1965, p. 24.
16 W.R. Angus, G.I.W. Llewelyn and G. Scott, Trans. Faraday Soc., 55 (1959) 887.
17 E.W. Abel, R.P. Bush, C.R. Jenkins and T. Zobel, Trans. Faraday Soc., 60 (1964) 1214.
18 L.W. Breed, J.W. Haggerty Jr. and F. Baiocchi, J. Org. Chem., 25 (1960) 1633.
19 J. Barrans, R. Mathis-Noel and F. Mathis, C.R. Acad. Sci. Paris, 245 (1957) 419.