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THE INSERTION OF CARBON OXYSULFIDE INTO SOME ORGANOMETALLIC AMINES

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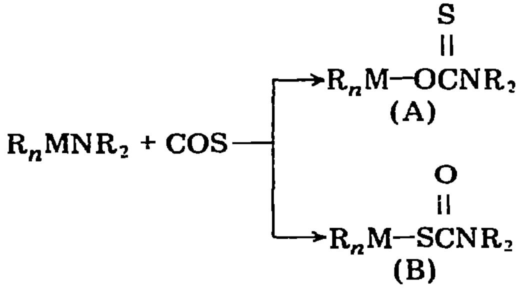
Summary

The structures of the products obtained when carbon oxysulfide is allowed to react with organometallic amines of germanium, phosphorus, and arsenic are determined and the effect of changing hardness of the organometallic center is discussed. Free energies of activation for rotation about the carbonyl—nitrogen bond in the products are determined.

The reaction of unsymmetrical unsaturated molecules with organometallic amines is of interest because of the possibility of structural isomerism. Carbon oxysulfide is particularly valuable in these reactions due to the presence of both hard and soft atoms of the same periodic group and can insert either oxygen or sulfur to metal:



$$R_nMNR_2 + COS \rightarrow R_nM{-}O\overset{S}{\overset{\|}{C}}NR_2 \quad (A)$$

$$R_nMNR_2 + COS \rightarrow R_nM{-}S\overset{O}{\overset{\|}{C}}NR_2 \quad (B)$$

The direction of insertion can be related to the hard and soft characteristics of M or, if the reaction is thermodynamically controlled, to the M—O and M—S bond energies. If bond energies are used to estimate heats of formation, the difference in the standard enthalpy changes for insertion to produce isomers A and B is:

$$\Delta H^\circ_A - \Delta H^\circ_B = E(C{=}O) - E(C{=}S) + E(C{-}S) - E(C{-}O) + E(M{-}S) - E(M{-}O)$$

TABLE 1

IR AND NMR DATA FOR INSERTION PRODUCTS

		$\nu(C{=}O)$ (cm^{-1})[a]	$\delta(M(CH_3)_n)$ (ppm)[b]	$\delta(NR_2)$ (ppm)[b]	T_c (°C)[d]	$\Delta\nu_c$ (Hz)[e]	$\Delta G^{\neq}$ (kcal/mol)[f]
IX	$(CH_3)_3GeSC(O)N(C_2H_5)_2$	1627	0.64	3.12q, 3.23q 0.90t, 1.01t	22.4	7.9(q)	15.6
X	$(CH_3)_3GeSC(S)N(C_2H_5)_2$	—	0.74	3.52q, 3.74q, 1.01t[c]	−3.4	11.7(q)	14.0
XI	$(CH_3)_3GeOC(O)N(C_2H_5)_2$	1648	0.53	3.20q[c], 0.98t[c]			
XII	$(CH_3)_2PSC(O)N(CH_3)_2$	1649	1.30 (d, J 8Hz)	2.62s, 2.67s	11.8	2.9	15.6
XIII	$(C_6H_5)_2PSC(O)N(CH_3)_2$	1648		2.58s, 2.60s	13.9	3.1	15.7
XIV	$(CH_3)_2AsSC(O)N(CH_3)_2$	1641	1.22	2.64s, 2.68s	18.8	5.1	15.7

[a] 2% in CCl_4 except for $(CH_3)_2P$ and $(C_6H_5)_2P$ derivatives which were taken neat and 2% in $CHCl_3$ respectively. [b] 5% in C_6H_5Cl at −20°C. [c] Rotational isomers not resolved. [d] Coalescence temperature. [e] Chemical shift difference (extrapolated) of rotamers (at T_c) used to calculate $\Delta G°$. [f] $\Delta G°$ of activation in C_6H_5Cl.

When approximate bond energies [1] for the carbon linkages are inserted this reduces to:

$$\Delta H^\circ_A - \Delta H^\circ_B = 33 + E(\text{M—S}) - E(\text{M—O})$$

Thus, if free energy changes parallel enthalpy changes, isomers A and B are equally thermodynamically favorable when the M—O bond energy is 33 kcal/mol greater than the M—S bond energy. If the difference is greater than 33 kcal/mol isomer A is favored. Of course, the reaction could also be kinetically controlled.

The direction of insertion of COS into silyl- and stannyl-amines has been reported. With the silylamine silicon bonds to oxygen, while tin behaves as a soft acid and bonds to sulfur [2,3]. While the Si—S bond energy is uncertain at best, the values [1] of 108 kcal/mol for the Si—O bond and 70 kcal/mol for the Si—S bond indicate that isomer A should be thermodynamically favored for silicon.

It was the intent of this study to determine the direction of insertion for amino derivatives of the intermediate member of Group IV (germanium) as well as several members of Group V (phosphorus and arsenic). A secondary objective was to evaluate the effect of substituents attached to the metal on the direction of insertion. Consequently, the insertion was attempted with eight compounds: $(CH_3)_3GeN(C_2H_5)_2$ (I), $Cl_3GeN(CH_3)_2$ (II), $R_2PN(CH_3)_2$ (III, R = CH_3; IV, R = Cl; V, R = C_6H_5), $(CH_3)_2PON(C_2H_5)_2$ (VI), $R_2AsN(CH_3)_2$ (VII, R = CH_3; VIII, R = Cl). The reaction proceeded exothermically with I, III, and VII, and in the presence of a small amount of dimethylamine with V. The insertion reaction did not proceed with II, IV, VI and VIII even though all but VIII were carried out in the presence of dimethyl- or diethyl-amine. The reaction with VIII was also carried out in boiling toluene for 6 hours; the reaction with IV was run at 130° for 1 hour.

The structures of the insertion products are easily determined from their infrared spectra. As discussed previously, the spectrum of isomer B contains an absorption in the carbonyl region while isomer A does not [2]. This is illustrated in Table 1 where absorptions in the carbonyl region are listed for the CO_2, CS_2, and COS insertion products of diethylaminotrimethylgermane. Also included in Table 1 are infrared and NMR data for all products. Since the COS insertion products contain an intense peak in the carbonyl region they exist as the M—S isomer B.

Like those of the silicon and tin analogs [2,3], the NMR spectra of all of the insertion products except the CO_2 germanium derivative exhibit temperature dependent N-alkyl resonances. At temperatures above room temperature the N-methyl resonances are singlets while the N-ethyl resonances are triplets and quartets. At temperatures below about 10°C the N-methyl resonances are split into two singlets and the N-ethyl resonances are two sets of triplets and quartets. These temperature dependent spectra are best explained by hindered rotation about the carbonyl—nitrogen bond which produces magnetically non-equivalent N-alkyl groups [2]. Coalescence temperatures (T_c), chemical shift differences ($\Delta\nu_c$) for the N-alkyl resonances, and the rotational free energy of activation at the coalescence temperature are listed in Table 1. The free energies of activation exhibit no significant dependence upon the nature of the organometallic group and are just slightly lower (0.8 kcal/mol) than the value for the tin analog [2,3].

Thus, of the organometallic moieties discussed here, only the trimethylsilyl group behaves as a hard acid. A similar observation has been made for addition—elimination reactions of Group IV amines [4]. Whether the lack of reaction observed when the electronegativity of the substituents at the metal atom is increased is a result of a more positive enthalpy (and free energy) change or an unfavorable rate of reaction is not clear. It appears, however, that an increase in the hardness of the organometallic group (as in the change from $(CH_3)_2P$ to $(CH_3)_2PO$ or Cl_2P) makes the production of the soft isomer B less favorable yet does not sufficiently enhance the production of isomer A to allow its isolation.

Experimental section

Because of the sensitivity of reagents and compounds to moisture most operations were performed under anhydrous conditions using oven-dried glassware with dry solvents and compounds. Carbon oxysulfide was obtained commercially and from the reaction of thioacetamide with ethyl chloroformate [5].

Compound I was prepared from the reaction of the lithium salt of diethylamine with trimethylbromogermane in ether—hexane, b.p., 142-142.5°, yield 80% (Lit. [6] 138-139°). II was obtained by amination of $GeCl_4$ (0.069 mol) with dimethylamine (0.138 mol) in ether; b.p. 55°/42 mmHg, yield 15% (Lit. [7] b.p. 57.5°/42 mmHg). III and IV were secured by the procedure of Slota and Burg [8]; III (best procedure used methylmagnesium bromide in ether) b.p. 97°, yield 40% (Lit. [8], b.p. 99.4°); IV, b.p. 151-152°, yield 80% (Lit. [8] b.p. 150°). V was obtained by amination of diphenylchlorophosphine with dimethylamine in petroleum ether, b.p. 111-112°/1.4 mmHg, yield 55% (Lit. [9] 112°/2 mmHg). VI was prepared by amination of $(CH_3)_2POCl$ (from the procedure of Pollart and Harwood [10] with diethylamine in benzene, b.p. 117-118°/15 mmHg, yield 60% (Lit. [11] b.p. 131-142°/26 mmHg.) VII was obtained by the procedure of Modritzer [12], b.p. 110-110.5° (Lit. [12] b.p. 108°). VIII was obtained by amination of $AsCl_3$ with dimethylamine, b.p. 71-72°/22 mmHg, yield 76% (Lit. [13], 73-75°/25 mmHg).

With the exceptions noted earlier concerning solvents, catalysts and temperatures, all COS insertion products were obtained by bubbling COS into the neat liquid at room temperature. The CO_2 and CS_2 products were prepared by the addition of freshly powdered dry ice and dry CS_2, respectively, to the neat liquid at room temperature. Products were isolated by fractional distillation of the product mixtures. IX, b.p. 61-62°/0.64 mmHg, n_D^{25} 1.4897, yield 15%. (Found: C, 38.21; H, 8.15; N, 5.83. $C_8H_{19}GeNOS$ calcd.: C, 38.45; H, 7.66; N, 5.60%.) X, b.p. 98.5-99°/0.65 mmHg, n_D^{25} 1.5628, yield 69%. (Found: C, 36.01; H, 7.20; N, 5.05. $C_8H_{19}GeNS_2$ calcd.: C, 36.13; H, 7.20; N, 5.27%.) XI, b.p. 43°/0.48 mmHg, n_D^{25} 1.4355, yield 66%. (Found: C, 40.91; H, 8.36; N, 6.00. $C_8H_{19}GeNO_2$ calcd.: C, 41.09; H, 8.19; N, 5.99%.) XII, b.p. (decomp.), 73°/0.66 mmHg, n_D^{25} 1.5387. (Found C, 36.87; H, 7.65. $C_5H_{12}NOPS$ calcd.:

C, 36.35; H, 7.32%.) XIII, m.p. 50-55°, yield 95%; (Found: C, 62.49; H, 5.75. $C_{15}H_{16}NOPS$ calcd.: C, 62.27; H, 5.58%.) XIV, b.p. 98°/0.017 mmHg, n_D^{25} 1.5678, yield 84%; (Found: C, 29.08; H, 5.85. $C_5H_{12}AsNOS$ calcd.: C, 28.71; H, 5.78%.)

Infrared spectra were run on a Perkin—Elmer 621 spectrophotometer. NMR spectra were obtained on a Varian A-60D spectrometer. Free energies of activation were obtained from 30% solutions in ClC_6H_5 by taking 3 to 5 tracings of the N-alkyl region at 4 temperatures 25-45° below coalescence. The chemical shift difference for the rotamers, $\Delta\nu$, was then extrapolated to coalescence temperature and $\Delta G^{\neq}$ obtained by the approximate method (which gives values in good agreement with total line shape values when $\Delta\nu > 3$Hz [14].

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