small enough that it should not invalidate the qualitative comments above concerning the upper limit placed on the Co–H bond distance.

Acknowledgments.—We are grateful to Dr. G. F. Kokoszka for several helpful discussions This work was supported in part by the National Science Foundation, Grant GP3468.

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Donor–Acceptor Complexes of Bis(*o*-phenylenedioxy)silane and -germane

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Received May 2, 1966

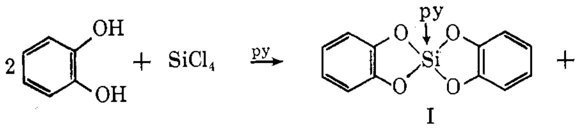
Use of bases to facilitate esterification of organosilicon, -germanium, and -tin halides is well known. While chlorosilanes react vigorously with diols to liberate hydrogen chloride, the reaction of organochlorogermanes is sluggish, requiring tertiary amines for good yields,[1] and organotin halides fail to esterify at all in the absence of base.[2] The action of base in these systems is not straightforward, however, since, apart from taking up hydrogen halide formed in the esterification reaction,[3] molecular bases may also form adducts.

This publication describes the effect of tertiary amines on the synthesis of spiro-(silicon- and germanium-) oxygen heterocycles from the tetrachlorides.

Results and Discussion

Attempts to prepare bis(*o*-phenylenedioxy)silane and -germane in the presence of tertiary amines lead to the isolation of adducts of these compounds. Addition of silicon tetrachloride to catechol in excess pyridine gives the 1:1 pyridine complex of bis(*o*-phenylenedioxy)silane (mp 265° dec). The previously elusive[4] bis(*o*-phenylenedioxy)germane forms as a 1:2 complex with pyridine (mp 215–235° dec). Both adducts sublime unchanged. Reversed addition (pyridine first mixed with the tetrachloride, followed by catechol) gives the identical 1:1 and 1:2 products

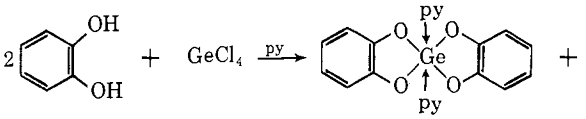
Triethylamine has larger steric requirements than pyridine, although it is a stronger base toward the proton. In our system triethylamine behaves exactly like pyridine, giving the 1:1 and 1:2 adducts independent of the order of addition. N,N-Dimethylformamide (DMF) has no observable effect. No DMF adducts of silicon[5] or germanium tetrachlorides are known.



I

4py·HCl (1)

$$SiCl_4 + 2py \longrightarrow [SiCl_4{\cdot}2py] \xrightarrow{\text{diol}} \text{I} + 4py{\cdot}HCl$$



II

4py·HCl (2)

$$GeCl_4 + 2py \longrightarrow [GeCl_4{\cdot}2py] \xrightarrow{2\text{diol}} \text{II} + 4py{\cdot}HCl$$

The complexes of tin tetrachloride with pyridine, triethylamine, and DMF are insoluble white solids impervious to further reaction with diol, in accord with reported behavior on alcoholysis.[6]

The Sn^{119m} Mössbauer spectrum of bis(N,N-dimethylformamide)tetrachlorostannane[7] contains a singlet resonance at 0.00 + 0.06 mm/sec with respect to an $Sn^{119m}O_2$ source, identical with that reported for the bis-pyridine adduct.[8]

1,8-Dihydroxynaphthalene and 2,2′-dihydroxybiphenyl give the spiro esters bis(1,8-naphthalenedioxy)silane[9] and -germane (a novel ring system[10]) and bis(2,2′-diphenylenedioxy)silane[11,12] and -germane,[4,12,13] free of associated base and independent of the order of addition. As well as failing to form adducts, these six- and seven-membered heterocycles are not so susceptible to hydrolysis or polymerization as the five-membered systems.

The thermodynamic stability of fourth-group amine adducts increases Si < Ge ≪ Sn as does the tendency for higher coordination.[14] The tetrachloride–base adducts formed as a first step in our syntheses are apparently sufficiently labile to suffer further reaction with the diol.

Heating the dipyridine complex of bis(*o*-phenylenedioxy)germane in DMF precipitates a new complex whose infrared spectrum shows the strong carbonyl and other bands characteristic of DMF.[15]

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[1] D. C. Bradley, L. Kay, and W. Wardlow, *Chem. Ind.* (London), 746 (1953).

[2] H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.* (Amsterdam), **1**, 328 (1964).

[3] Hydrogen chloride acceptors such as sodium carbonate or sodium metal which are not also molecular bases are not effective in promoting reaction of organotin chlorides with dihydric phenols.[2]

[4] J. J. Zuckerman, *J. Chem. Soc.*, 1322 (1963).

[5] T. S. Piper and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 4318 (1954).

[6] J.-Cl. Marie, *Ann. Chim.* (Paris), **6**, 969 (1961).

[7] R. C. Aggarwal and P. P. Singh, *Z. Anorg. Allgem. Chem.*, **332**, 103 (1964).

[8] V. I. Goldanskii, E. F. Makarov, R. A. Stukan, T. N. Sumarokova, V. A. Trukhtanov, and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, **156**, 474 (1964).

[9] C. M. Silcox and J. J. Zuckerman, *J. Organometal. Chem.* (Amsterdam), **5**, 483 (1966).

[10] The Ring Index recommendation for this system is either naphtho[1,8-*de*]-2-germa-*m*-dioxin or naphtho[1,8-*de*]-1,3,2-dioxagermine. In conformity with our previous reports, we name these heterocycles as derivatives of silane and germane in this communication.

[11] R. Schwartz and W. Kuchen, *Z. Anorg. Allgem. Chem.*, **279**, 84 (1955); J. J. Zuckerman, *J. Chem. Soc.*, 873 (1962).

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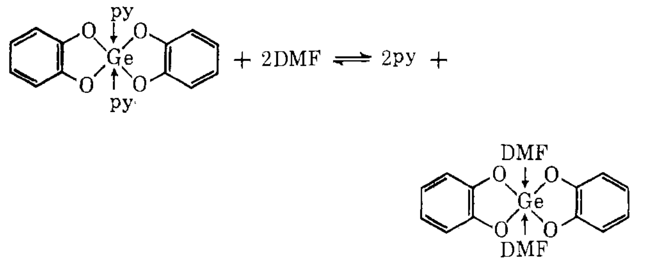
[13] R. Müller and L. Heinrich, *Chem. Ber.*, **95**, 2276 (1962).

[14] I. R. Beattie, *Quart. Rev.* (London), **17**, 383 (1963).

[15] Our study of the changes in the infrared absorption frequencies of DMF on complexation is the subject of a separate communication: E. W. Randall, C. M. S. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, **5**, 2240 (1966).



Bis(*o*-phenylenedioxy)silane–triethylamine has sufficient solubility in chloroform to record an nmr spectrum which contains the triplet and quartet of the ethyl group along with resonances due to phenyl protons. The internal chemical shift difference, Δ, between the methyl and methylene resonances in $(CH_3CH_2)_nX$ has been related to the electronegativity of X[16] and is affected by the acquisition of charge by X. In triethylamine itself, Δ is 85.2 cps, which increases to 118 cps on forming the tetraethyl quaternary salt.[17] In bis(*o*-phenylenedioxy)silane–triethylamine the methyl triplet is at τ 9.2 and the methylene quartet at τ 7.1 with Δ = 114 cps. We interpret this as confirming the donor role of triethylamine, where involving the lone pair with silicon places nitrogen in a situation which differs little from that in a quaternary salt.

Experimental Section

Our constant-acceleration, cam-drive Mössbauer spectrometer has been previously described.[18] Microanalyses were carried out by Galbraith and Schwarzkopf Microanalytical Laboratories. 1,8-Dihydroxynaphthalene was prepared by the fusion method.[9] Pyridine was dried over potassium hydroxide and triethylamine over molecular sieves. Glassware was oven dried and all operations were carried out in nitrogen.

Bis(*o*-phenylenedioxy)silane–Pyridine.—Silicon tetrachloride (0.09 mole) was added dropwise to catechol (0.18 mole) in refluxing pyridine (100 ml) with immediate formation of a white solid. Pyridine was distilled *in vacuo* and the product shaken with chloroform, collected, and sublimed *in vacuo* at 260° (dec pt 265°; some loss of C_5H_5N begins at 249°). *Anal.* Calcd for $C_{17}H_{13}NO_4Si$: C, 63.2; H, 4.06; N, 4.34; Si, 8.66. Found: C, 62.7; H, 4.58; N, 3.02; Si, 8.04. The infrared spectrum contained prominent absorptions at 1240 (s), 1000 (m), 930 (m), 920 (m), 845 (s), 740 (s), 680 (m), 620 (m), and 532 (m) cm^{-1}.

Reverse addition (half-scale in 100 ml of pyridine) gave immediate precipitation and identical product after 15-hr reflux.

Bis(*o*-phenylenedioxy)germane–Dipyridine.—Addition of germanium tetrachloride (0.045 mole) to catechol (0.09 mole) in refluxing pyridine (100 ml) gave immediate precipitation. After distillation of pyridine (36°, 36 mm) the residue was shaken with chloroform (150 ml), collected in 35% yield (dec pt 215–235°), and sublimed unchanged at 150° *in vacuo*. *Anal.* Calcd for $C_{22}H_{18}N_2O_4Ge$: C, 59.2; H, 4.03; N, 6.27; Ge, 16.25. Found: C, 58.4; H, 4.21; N, 6.33; Ge, 16.65. Prominent infrared absorptions are found at 1240 (s), 1060 (m), 1040 (m), 1030 (sh), 1020 (m), 875 (m), 790 (s), 735 (s), 692 (s), and 675 (s) cm^{-1}.

Reverse addition on the same scale gave immediate precipitation and identical product after 15-hr reflux.

Bis(*o*-phenylenedioxy)silane–Triethylamine.—Triethylamine (175 ml) and catechol (0.09 mole) gave a chloroform-soluble white complex (mp 69.5–70.5°). Silicon tetrachloride (0.045 mole) addition resulted in exothermic reaction and another precipitate, which after three recrystallizations from chloroform produced white crystals (212–230° dec) in 8% yield, slightly soluble in chloroform and DMF and insoluble in benzene and ether. The product was found to cause slight pruritus on handling. *Anal.* Calcd for $C_{18}H_{23}NO_4Si$: C, 62.61; H, 6.66; N, 4.06; Si, 8.12. Found: C, 62.94; H, 7.92; N, 5.70; Si, 7.75. The infrared spectrum contained prominent absorptions at 1240 (s), 1090 (m), 1010 (m), 810 (s), 735 (s), 683 (s), and 523 (s) cm^{-1}.

Reverse addition on the same scale in 50 ml of triethylamine gave the identical product after Soxhlet extraction with chloroform.

Bis(*o*-phenylenedioxy)germane–Bis(triethylamine).—To catechol (0.09 mole) and triethylamine (100 ml) germanium tetrachloride (0.045 mole) was added producing an exothermic reaction and a voluminous amount of light-weight, white solid. The product crystallized from chloroform after Soxhlet extraction and sublimed unchanged *in vacuo*. Like its silicon analog, it causes some slight pruritus on handling. *Anal.* Calcd for $C_{24}H_{38}N_2O_4Ge$: C, 58.4; H, 7.71; N, 5.68; Ge, 14.81. Found: C, 57.64; H, 7.47; N, 4.89; Ge, 13.30. The infrared spectrum contained prominent absorptions at 1240 (s), 1090 (m), 1012 (m), 795 (m), 735 (m), and 650 (s) cm^{-1}.

Reverse addition on the same scale in 50 ml of triethylamine gave identical product after Soxhlet extraction with chloroform.

Bis(dimethylformamide)-Tetrachlorostannane.[7]—To catechol (0.15 mole) in DMF (100 ml) at 50° stannic chloride (0.075 mole) was added with precipitation and fuming. During vacuum distillation, the stillpot contents turned black, but sublimation of the black residue at 185° *in vacuo* gave white crystals, mp 232–233°. *Anal.* Calcd for $C_6H_{14}Cl_4N_2O_2Sn$: C, 17.7, H, 3.44. Found: C, 17.67; H, 3.44. The infrared spectrum contained prominent absorptions at 1235 (m), 1120 (m), 1090 (m), 750 (m), and 695 (s) cm^{-1}.

Bis(*o*-phenylenedioxy)germane–Bis(dimethylformamide).—Heating this compound in excess DMF at 85° for 11 hr precipitated a tan solid (dec pt 222°). *Anal.* Calcd for $C_{18}H_{22}N_2O_6Be$: C, 49.6; H, 5.06; N, 6.45; Ge, 16.8. Found: C, 47.11; H, 4.83; N, 6.58; Ge, 17.95. The infrared spectrum contained prominent absorptions at 1640 (s), 1580 (sh), 1230 (s), 1210 (sh), 1125 (m), 1100 (m), 1025 (m), 915 (m), 878 (m), 795 (s), 745 (sh), 735 (s), 680 (s), and 695 (sh) cm^{-1}.[15]

Bis(1,8-naphthalenedioxy)germane.—Germanium tetrachloride (0.021 mole) was added to a red solution (54°) of the diol (0.043 mole) in pyridine (100 ml) with slight precipitation. Pyridine hydrochloride sublimed first with the desired product subliming at 288° *in vacuo* as white, needlelike crystals (mp 335–337°), insoluble in pyridine, acetonitrile, or common organic solvents. Unlike its seven-membered spiro analog, bis(1,8-naphthalenedioxy)germane is very sensitive to atmospheric moisture. *Anal.* Calcd for $C_{20}H_{12}O_4Ge$: C, 61.7; H, 3.09; Ge, 18.7. Found: C, 61.64; H, 3.20; Ge, 18.80. The infrared spectrum contained prominent absorptions at 1255 (s), 1170 (m), 1155 (m), 1025 (s), 828 (s), 815 (s), 752 (s), 618 (m), 595 (m), and 565 (m) cm^{-1}. Identical results were obtained from a dilute pyridine–acetone solution.

Similarly silicon tetrachloride (0.016 mole) was added to a red solution of 1,8-dihydroxynaphthalene in refluxing pyridine (150 ml). No precipitation occurred. Pyridine was distilled *in vacuo* and the residue was shaken with chloroform, collected, and sublimed at 350° *in vacuo* to give bis(1,8-naphthalenedioxy)silane.[9]

Bis(2,2-diphenylenedioxy)silane[11,12] and -germane[4,12,13] were obtained in analogous fashion from pyridine solutions of the diol on the tetrachloride.

Acknowledgment.—This investigation was supported by Public Health Service Research Grant CA-07064-03 from the National Cancer Institute and the Advanced Research Projects Agency. We are indebted to Texas Instruments, Inc., and the Germanium Information Center for gifts of germanium and to C. H. Yoder and J. G. Zavistoski for helpful discussions.

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[18] A. J. Bearden, H. S. Marsh, and J. J. Zuckerman, *Inorg. Chem.*, **5**, 1260 (1966).