tion (0.168 molal) the actual depression was found to be only 0.25°, slightly less than half the calculated value of 0.60°. In the present work, the curve for cobalt acetate was found to follow a course only slightly lower than that previously observed for the nickel salt; at 1 mole % the depression, by interpolation, is 0.35°. Although it would be unwarranted to draw any quantitative conclusion as to the molecular state of the solute from such freezing point data, they suggest the presence of dimeric species of the salts, even in these dilute solutions, thus confirming the postulate of dimerism of cobalt acetate recently pro-

posed by Benson and co-workers[12] to account for the kinetics of the Co(II)–Pb(IV) oxidation–reduction reaction in acetic acid. In this connection it appears significant also that the empirical formula of each of the solid compounds isolated in this work includes two molecules of nickel or cobalt acetate.

Alkoxychlorosilanes and Alkoxysilanes Containing Silane Hydrogen[1]

BY OLGIERD J. KLEJNOT

Syntheses and new compounds are reported for silanes $SiHCl_{3-x}(OR)_x$ and $SiH_{4-x}(OR)_x$ with $x = 1$–3, $R = CH_3$, C_2H_5. New silanes $CH_3SiHClOR$ and CH_3SiH_2OR are reported. Ligand exchanges of such silanes are described. Properties of some alkoxides of carbon and silicon are compared on the basis of new data.

Trialkoxysilanes $SiH(OR)_3$ were originally prepared from trichlorosilane and alcohols.[2-4] Recently rather low yields have been found.[5] Alkoxychlorosilanes $SiHCl_{3-x}(OR)_x$, obviously the intermediates in any direct formation of trialkoxysilanes from trichlorosilane, were obtained only indirectly.[6] Dialkoxysilanes $SiH_2(OR)_2$ and alkoxysilanes SiH_3OR were unknown at the beginning of this study. New syntheses and reactions of the simplest members of these little known classes of silanes are now reported.

Dialkyl sulfites $SO(OR)_2$[7] react with trichlorosilane in two steps, each followed by an elimination of SO_2 at higher temperature.

$$SiHCl_3 + 2SO(OR)_2 \longrightarrow 2RCl + SiHCl[O(SO)OR]_2 \longrightarrow$$
$$SiHCl(OR)_2 + 2SO_2 \quad (1)$$
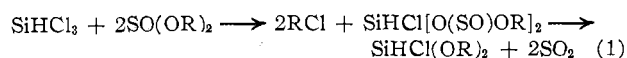
Alkyl nitrites RONO, known to alkoxylate $SiCl_4$,[8] react quantitatively with trichlorosilane

$$SiHCl_3 + xRONO \longrightarrow$$
$$SiHCl_{3-x}(OR)_x + xNOCl \quad x = 1\text{–}3 \quad (2)$$
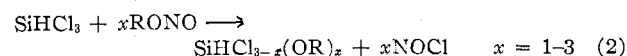
Lithium borohydride reacts with alkoxychlorosilanes to give alkoxysilanes

$$SiHCl_{3-x}(OR)_x + (3-x)LiBH_4 \longrightarrow (3-x)LiCl +$$
$$(3-x)/2B_2H_6 + SiH_{4-x}(OR)_x \quad x = 1, 2 \quad (3)$$
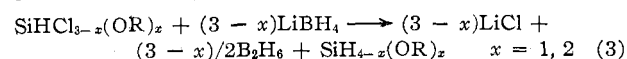
The syntheses (2 and 3) make possible the preparation of pure samples of several new silanes. Previous difficulties are explained in terms of the properties and reactions of silanes.

Results

Properties of Silanes and Methanes.—Tables I and II contain physical data obtained in this study. For the compounds I,[9] II, III, IX, X,[10] XI, XIII, XIV,[10] XV,[11] XVI, XVIII,[12] and XIX, improved and more complete data are presented. Compounds VI,[6] VIII,[13] and XII[14] are now characterized; IV, V, VII, and XVII are new. Limited data were obtained for other new compounds which disproportionate slowly at ambient temperature: $CH_3SiHClOCH_3$ (XX) with P_0 88 mm., $SiH_3OC_2H_5$ (XXI) with b.p. near 0°, $CH_3SiH_2OC_2H_5$ (XXII) with P_0 near 186 mm. The vapor pressure equations are valid up to 500 mm.

Reactions of Silanes.—Silane hydrogen is surprisingly stable toward nitrosyl chloride at room temperature. On the other hand, trichlorosilane (XXIII) reacts with methyl nitrite (MN) or ethyl nitrite (EN) even at −127°. Temperatures within the liquid range of $NOCl^{15}$ are, therefore, practical for the method repre-

(1) Presented in part at the XVIIth International Congress of Pure and Applied Chemistry, Munich, Sept., 1959, as paper A220. Work done in Munich, 1955–1958, and Pasadena, 1959–1960.

(2) C. Friedel and A. Ladenburg, *Ann.*, **143**, 118 (1867).

(3) F. Taurke, *Ber.*, **38**, 1661 (1905).

(4) B. Helferich and J. Hausen, *ibid.*, **57**, 795 (1924).

(5) M. E. Havill, I. Joffe, and H. W. Post, *J. Org. Chem.*, **13**, 280 (1948).

(6) A. F. Reilly and H. W. Post, *ibid.*, **16**, 387 (1951).

(7) W. Voss and E. Blanke, *Ann.*, **485**, 272 (1931).

(8) I. G. Farbenindustrie A.G., German Patent 459,738 (1928); ref. 15, p. 325.

(9) H. J. Emeléus and M. Onyszchuk, *J. Chem. Soc.*, 604 (1958).

(10) B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **81**, 5109 (1959).

(11) M. G. Voronkov, *Zh. Obshch. Khim.*, **29**, 907 (1959); *Chem. Abstr.*, **54**, 1267h (1960).

(12) L. M. Shorr, *J. Am. Chem. Soc.*, **76**, 1390 (1954).

(13) L. W. Breed and W. J. Haggerty, Jr., *J. Org. Chem.*, **25**, 126 (1960).

(14) W. S. Miller, J. S. Peake, and W. H. Nebergall, *J. Am. Chem. Soc.*, **79**, 5604 (1957).

(15) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951).

Table I

Constants of Chlorosilanes and Alkoxychlorosilanes

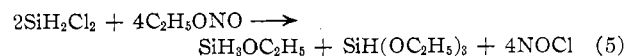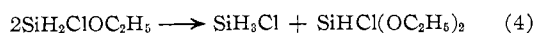| Formula	log P (mm.) = B - A/T B	A	P at 0°, mm.	d at 0°, g./ml.	M.p., °C.	B.p., °C.	B.p. calcd., °C.	H_{vap}, cal./mole	$S_{boiling}$, H/T
(CH3)2SiHCl (I)	7.6161	1458.0	189.6	0.910	-103.0	34.9	34.8	6672	21.66
CH3SiHCl2 (II)	7.6784	1506.1	146.5	1.162	-92.5	41.1	40.8	6891	21.92
CH3SiCl3 (III)	7.6160	1602.7	55.8	1.287	-77.8	65.4	65.3	7333	21.66
SiHCl2OCH3 (IV)	7.8400[a]	1600.0[a]	95.3	1.204	-105.0	50.5[a]	49.5[a]	7321[a]	22.60[a]
SiHCl(OCH3)2 (V)	8.0616	1774.0	36.9	1.078	-119.0	70.5	69.3	8117	23.62
SiHCl2OC2H5 (VI)	7.9004	1744.5	32.2	1.179	-114.0	75.7	74.4	7982	22.88
CH3SiHClOC2H5 (VII)	7.9007	1737.8	33.4	1.016	-108.0	73.6	73.0	7951	22.93
CH3SiCl2OC2H5 (VIII)	7.8500	1807.3	11.6	1.132	-91.8	100.1	99.0	8462	22.66

[a] Estimated from group data.

Table II

Constants of Alkoxymethanes and Alkoxysilanes

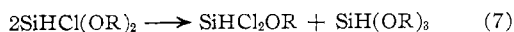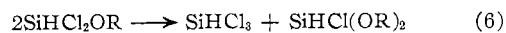| Formula	log P (mm.) = B - A/T B	A	P at 0°, mm.	d at 0°, g./ml.	M.p., °C.	B.p., °C.	B.p. calcd., °C.	H_{vap}, cal./ mole	$S_{boiling}$, H/T	$n^{25}D$
CH2(OCH3)2 (IX)	7.8444	1562.2	133.4	0.888	-104.8	41.6	41.6	7148	22.71	1.3515
SiH2(OCH3)2 (X)	7.8897	1558.6	156.2	.857	-98.0	38.3[a]	38.1	7133	22.90	
CH2(OC2H5)2 (XI)	8.0433	1857.2	17.5	.864	-66.5	88.0	86.6	8498	23.53	1.3706
SiH2(OC2H5)2 (XII)	8.0006	1810.0	23.5	.864	-123.0	81.0	80.4	8282	23.40	
CH(OCH3)3 (XIII)	8.3885	2039.0	8.5	.974	-55.38	100.7	97.0	9330	24.96	1.3765
SiH(OCH3)3 (XIV)	8.3100	1929.0	17.7	.932	-113.5	83.9	82.1	8827	24.73	
Si(OCH3)4 (XV)	8.2770	2128.2	2.5	1.040[b]	5.35	123.0[a]	121.2	9738	24.58	1.3662
CH3CH(OCH3)2 (XVI)	7.9287	1696.2	50.5	0.880	Glassy	63.3	62.9	7762	23.06	1.3638
CH3SiH(OCH3)2 (XVII)	8.0139	1712.5	55.7	.896	ca. -136	61.1	60.5	7836	23.44	1.3574
CH3SiH(OC2H5)2 (XVIII)	8.0628	1922.8	9.6	.875	Glassy	99.4	97.9	8799	23.62	
(CH3)3SiOSi(CH3)3 (XIX)	7.9875	1898.9	10.0	.794	-69.8	100.5	98.7	8689	23.25	1.3745

[a] Extrapolated above 400 mm. [b] Density at melting point.

sented by eq. 2. Dichlorosilane (XXIV) reacts with EN to give products of a disproportionation of ethoxychlorosilane SiH2ClOC2H5

$$2SiH_2ClOC_2H_5 \longrightarrow SiH_3Cl + SiHCl(OC_2H_5)_2 \quad (4)$$

$$2SiH_2Cl_2 + 4C_2H_5ONO \longrightarrow$$
$$SiH_3OC_2H_5 + SiH(OC_2H_5)_3 + 4NOCl \quad (5)$$

Results of adding XXIV to an excess of EN are represented by eq. 5; here a limited side reaction of silane hydrogen and nitrosyl chloride was observed. The reaction of XX and EN gave two dialkoxy compounds instead of CH3SiHOCH3OC2H5. In partial substitutions of III and XXIII the selectivity was poor with MN, but pronounced with EN; e.g., the formation of CH3Si(OC2H5)3 could be suppressed and a separation of products was possible in contrast to earlier attempts.[13] Silicon tetrafluoride is inert toward EN.

Some stored samples of alkoxychlorosilanes lost their crystallizability and their P_0 increased. The purity criteria were reattained by distilling and the products of ligand exchange were identified.
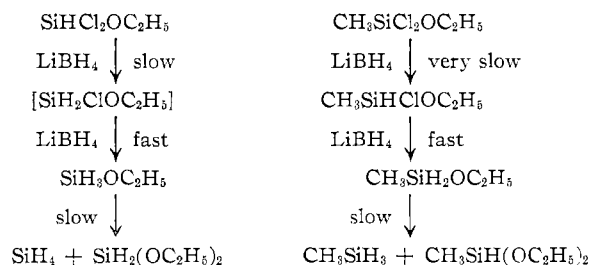
$$2SiHCl_2OR \longrightarrow SiHCl_3 + SiHCl(OR)_2 \quad (6)$$
$$2SiHCl(OR)_2 \longrightarrow SiHCl_2OR + SiH(OR)_3 \quad (7)$$
$$2CH_3SiHClOR \longrightarrow CH_3SiHCl_2 + CH_3SiH(OR)_2 \quad (8)$$

The reaction was prevented by treating the glass apparatus with the vapor of chlorosilanes (e.g., 10 mm. of SiHCl3, 10 min.) and fractionating the substance for removal of all traces of HCl. Silanes IV and XX, however, could not be stabilized at room temperature. Silane V forms highly concentrated solutions with polyborane (BH)$_x$. Silane VII reacts with red HgO to form HgCl2 and a liquid siloxane.

Hydrogenation of alkoxychlorosilanes with lithium borohydride, following eq. 3, occurs at room temperature and is accelerated by diethyl ether. Unknown liquids of lower volatility are formed in side reactions. Conversions observed in the investigated two-step hydrogenation reactions are listed in Chart I. The reactions were observed independently by starting with isolated compounds. A synthesis for SiH2ClOC2H5, however, is presently not available.

The alkoxysilanes hydrolyze without gas evolution in water, with which XII gives a hydrophobic prototype of the silicone oils. Hydrogen evolution which follows in aqueous solutions of acid or base is slow for the type CH3SiH(OR)2. Dimethoxysilane (X) has a faint ethereal odor, fumes in air, and disproportionates slowly

Chart I

SiHCl2OC2H5	CH3SiCl2OC2H5
LiBH4 ↓ slow	LiBH4 ↓ very slow
[SiH2ClOC2H5]	CH3SiHClOC2H5
LiBH4 ↓ fast	LiBH4 ↓ fast
SiH3OC2H5	CH3SiH2OC2H5
slow ↓	slow ↓
SiH4 + SiH2(OC2H5)2	CH3SiH3 + CH3SiH(OC2H5)2

at room temperature, whereas diethoxysilane (XII) has an ester-like odor and is thermally stable up to the boiling point. Also, methoxysilane (SiH3OCH3[16]) seems to be stable, whereas XXI and XXII disproportionate easily.

(16) B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **83**, 3384 (1961).

TABLE III

REACTIONS AND PRODUCTS[a]

Run	Reactants, moles	Time, hr.	Temp., °C.	Silane products (pure fractions, ml. at 0°) and remarks
1	$SiHCl_3$ 0.10, $SO(OR)_2$ 0.30	1	50–100[ob]	Some $SiHCl_2OR$, much $SiHCl(OR)_2$; R = C_2H_5, C_4H_9
2	SiF_4 1.0, EN 4.0	4	15°	No reaction
3	$SiHCl_3$ 0.50, MN 1.00	1	−50°	IV 7, V 20, XIV 2.6, XV 0.6[c]
4	$SiHCl_3$ 0.10, EN 0.10	1	−100°	VI and XXV; high total yield
5	$SiHCl_3$ 0.35, EN 0.80[d]	2	−60°	XXV 50, yield 94%
6	$SiHCl_3$ 0.26, EN 0.93	0.5	−20°	XXVI; 37g., yield 87%; crude EN added as liquid
7	SiH_2Cl_2 0.118, EN 0.137	1.5	−80°	XXV 8, 50 mole %; the other half quite volatile
8	SiH_2Cl_2 0.0577, EN 0.132	1.5	−80°	XXVI 4.475 g., 47 mole %, and 1.0 ml. of less volatile liquid[e]
9	CH_3SiHCl_2 0.50, MN 0.50	2	−65°	XX 20, XVII 15, II 5; 90 mole % of MN
10	CH_3SiHCl_2 0.39, EN 0.47	2	−60°	50 ml. fully separated, VII, XVIII; yield 95%
11	$CH_3SiHClOCH_3$ 0.10, EN 0.10	0.5	−78°	XVII, XVIII, total yield 99%
12	CH_3SiCl_3 0.395, EN 0.342	1	−60°	III 5, VIII 24, VIII + XXVII 16[f]
13	$SiHCl(OCH_3)_2$ 0.0588, LB 0.080	3	25°	X 4, yield 63%, disprop. at room temp. slow
14	$SiHCl(OC_2H_5)_2$ 0.045, LB 0.050[g]	0.1	20°	XII 1.4, yield 22%; 4.0 ml. of liquid of P_0 2–6 mm.
15	$SiHCl_2OC_2H_5$ 0.019, LB 0.046	1	20°	XXI 1.1, yield 40%, P_{-79} 13 mm.[h]
16	CH_3SiCl_3 0.05, LB 0.10	4	25°	No reaction
17	$CH_3SiCl_2OC_2H_5$ 0.10, LB 0.10	5[i]	20°	XXII 1.6,[j] yield about 99%, gave CH_3SiH_3 and XVIII
18	$CH_3SiHClOC_2H_5$ 0.027, LB 0.030	0.1	25°	XXII, yield high. Unstable at room temperature.

[a] Symbols and numerals of Table I and II; others used here: $SiHCl(OC_2H_5)_2$ XXV, $SiH(OC_2H_5)_3$ XXVI, $CH_3SiCl(OC_2H_5)_2$ XXVII, $LiBH_4$ LB. [b] Evolution of RCl, followed at 130° by the evolution of SO_2. [c] Total yield 48 mole % based on OCH_3, capable of much improvement by column fractionation of NOCl. Formation of XV occurs only upon standing of reaction mixture at room temperature. [d] A reflux column was used as dispenser of EN. [e] Analytical data indicate the presence of disilanes in this fraction. [f] Yield of mole % of EN: VIII 50.3, mixed fraction contained 8.7 as VIII and 20.3 as XXVII; total 99.6% based on OC_2H_5. The mixed fraction upon distilling once gave half fractions with 63 and 76 mole % of XXVII. [g] In ether solution. [h] Disproportionation at 0° slow, gave SiH_4 and XII. [i] With 5 ml. of ether. [j] The ether was complexed at room temperature with $LiBH_4$ and the silanes stripped at −40° *in vacuo*.

Experimental

Materials.—Methyl nitrite (MN) was made by: (a) heating a 1:2 mixture of isoamyl nitrite (Eastman) and methanol to 60°; (b) adding concentrated HCl to an ice-cooled solution of $NaNO_2$ in water and methanol; (c) adding NOCl gas as in (b). MN was purified by trap fractionation. Ethyl nitrite (EN) was made analogously, as in (b) and (c), and distilled repeatedly *in vacuo* to a P_0 of 373 mm. (pure).[17] EN is markedly decomposed after 1 day at room temperature but the bulk stays intact in sealed ampoules. Trichlorosilane of P_0 218 mm. (pure) was prepared from Si + HCl, distilled using a 1-m. column, and passed into a trap *in vacuo* for removal of HCl. Dichlorosilane, kindly supplied by Dr. O. Stecher, was pure (P_0 551 mm.). Samples of I, XIX (Dow Chemical), II (Union Carbide), III (Th. Goldschmidt), IX, XI, XIII, XVI (Eastman), and XV (Anderson) were purified by repeated column distillation *in vacuo*.

Procedures. (a) General.—The silanes were handled using vacuum techniques.[18] Isothermal distillation in a vacuum reflux column (30 cm., glass helices, mercury-frit valve after Stecher,[18,19] tap-water cooled head), with stirring of still-pot contents and temperature-controlled bath, was applied throughout for separating silane mixtures. A 60-cm. column with a membrane valve[20] made of chromed brass and Teflon was used for distilling EN. Vapor pressure equations were determined from numerous points between 3 and 770 mm. (immersible tensimeter, 8-mm. wide mercury manometers with a glass mirror scale). Precision thermometers were corrected for emergent stem by comparison with an Anschuetz thermometer. Active hydrogen was determined by hydrolysis with NaOH solution[2] *in vacuo* (6 N for alkyl, 2 N for alkoxy, and 0.1 N for alkoxychloro compounds) and volumetric measurement of the evolved hydrogen gas. The solution (5–10 ml.) was dropped onto the sample (2–5

(17) J. W. Goodeve, *Trans. Faraday Soc.*, **30**, 501 (1934), whose equation gives 363 mm.

(18) H. Lux, "Anorganisch-Chemische Experimentierkunst," 2nd Ed., J. A. Barth, Leipzig, 1959, pp. 411–551.

(19) E. Wiberg, Th. Johannsen, and O. Stecher, *Z. anorg. Chem.*, **251**, 114, 120 (1943).

(20) O. J. Klejnot, ref. 18, p. 445.

mmoles), which was cooled with liquid nitrogen and then warmed. Some unreacted silane was trapped by freezing before the Toepler pump, then returned to the reaction vessel to complete the hydrolysis. Chloride was titrated in the reaction solution (Mohr).

(b) Alkoxylation.—Alkyl nitrite is added as a gas stream of about 10 mm. pressure to a flask containing the liquid chlorosilane, stirred at −60°. Condensation of the gas is rapid. For alkoxychlorosilanes the addition is stopped at the desired molar ratio; for alkoxysilanes the liquid reactants may be poured together in optional order at −20°, with cooling. The silanes are separated from the nitrosyl chloride[15] *in vacuo* by lower temperature evaporation or trap fractionation at −65 to −68°- Traces of NOCl (yellow) can be removed by refluxing and flushing the condenser with nitrogen or by shaking with Hg in the absence of air.

(c) Hydrogenation.—Ether-free lithium borohydride is obtained *in vacuo* by evaporating an ether solution of $LiBH_4$. A stoichiometric amount of alkoxychlorosilane is condensed into the vessel and upon warming to room temperature an endothermic reaction occurs, the voluminous $LiBH_4$ shrinking to a small volume of white LiCl. Gas is slowly evolved into a gas bulb; repeated recondensing ensures full conversion. The silanes are separated from diborane by a trap at −150°.

Experimental Data.—Tables III and IV contain experimental data other than the physical data of Tables I and II.

Discussion

Early workers found that in the synthesis of trialkoxysilanes, adding trichlorosilane to an alcohol gives better results than the reverse procedure.[3,4] A method has been, nevertheless, recommended[5] in which an alcohol ROH is added to a heptane solution of trichlorosilane at 0°. The yields increase with the size of R, beginning with 0% for trimethoxysilane and 45% for triethoxysilane. In such procedures large quantities of unreacted $SiHCl_3$ (40%) and some volatile products

TABLE IV

ANALYSES OF SILANES

Silane	Calcd. Mol. wt.	Calcd. Active H	Calcd. Cl	Found Mol. wt.	Found Active H	Found Cl
IV	131.0	0.769	54.12	131.3	0.822	53.86
V	126.6	.796	28.01	127.2	.812	28.46
VI	145.0	.695	48.89	144.3	.700	48.53
VII	124.6	.809	28.45	123.7	.801	28.53
VIII	159.1		44.58			44.76
X	92.14	2.19		91.45		
XII	120.2	1.68		121.2	1.50[a]	
XIV	122.2	0.825		120.8	0.780[a]	
XV	152.1			154.6		
XVII	106.2	.950		104.5	.903[b]	
XVIII	134.2	.752		135.5	.739	

[a] Low value due to incomplete trapping. [b] Reacts incompletely.

are lost with the escaping gas stream. Gas evolution occurs similarly in the orthoformate method[12] and in our dialkyl sulfite method. The alkyl nitrite method, without gas evolution, gives quantitative yields in partial and total alkoxylation of chlorosilanes. Moreover, its by-product nitrosyl chloride can be easily condensed, separated, and used again by conversion to alkyl nitrite.

Alkoxychlorosilanes which simultaneously contain H–, Cl–, and OR– ligands are more reactive than silanes containing only a combination of two such ligands (Table III, runs 13–18 in Table IV). The hydrogenation using lithium borohydride represents a new reaction of unknown scope. It is noteworthy that CH_3SiCl_3 is inert toward $LiBH_4$ (run 16), whereas SiF_4, $SiCl_4$, and $SiHCl_3$ react in various ways,[21] the latter being only converted to SiH_2Cl_2. The high, sometimes atypi-

cal and unique reactivity of alkoxychlorosilanes containing silane hydrogen has been a source of difficulties. A convenient synthesis of hydrogen-rich silanes is now based on this reactivity, which suggests novel syntheses, mechanistic studies, etc.

New physical data, listed in Tables I and II, confirm similarities between alkoxymethanes and alkoxysilanes,[2] especially for thermodynamic constants. In several series of alkoxides of Ti, Zr, and Hf, the compounds of the heavier elements are found to have the higher volatility.[22] Likewise, alkoxysilanes have lower boiling points than alkoxymethanes (Table II). Thus the alkoxides differ sharply from the chlorides and alkyls of these quadrivalent elements. On the other hand, while chlorosilanes have Trouton constants of non-associated liquids (about 21.7), we observe that mono- and dialkoxy compounds have values of 22.6 to 23.6, with or without the presence of chloro ligands. Trimethoxycompounds and tetramethoxysilane are close together with higher values of 24.6 to 25.0. The alkoxides and chloroalkoxides thus apparently form associated liquids. Accordingly, their vapor pressure curves deviate typically from the straight plot, $\log P$ vs. $1/T$, as reflected by the listed boiling point data, observed and calculated.

(21) E. Wiberg and G. Hoeckele, unpublished work (1960), quoted by H. Noeth, *Angew. Chem.*, **73**, 371 (1960).

(22) D. C. Bradley, *Rec. Chem. Progr.*, **21**, 179 (1960).