the β isomer was 5.2 according to Accutint paper, while that of the α isomer was 5.5. This slight difference in acidity could be checked against glass–calomel electrode, but potentiometric titration showed no difference.

When equimolar solutions of the α and β chloromercurials in ethanol were treated with ethanol solutions of iodine, the disappearance of color was about 5 times faster for the α than for the β isomer.

Preparation of Inactive β-1-Bromomercuri-2-methoxycyclohexane.—A solution of 3.48 g. (0.01 mole) of β-1-chloromercuri-2-methoxycyclohexane in 4 cc. of 10% aqueous sodium hydroxide was filtered and acidified with dilute hydrobromic acid to yield 3.56 g. of bromomercurial, m. p. 115-116.1°. This would not completely redissolve in 75 cc. of 2% aqueous sodium hydroxide. It was re-acidified with hydrobromic acid and filtered, m. p. 116.1°. Two crystallizations from 11 parts of ethanol failed to raise this melting point.

Anal. Calcd. for $C_7H_{13}OHgBr$: C, 21.37; H, 3.33. Found: C, 21.24; H, 3.25.

Preparation of Inactive α-1-Bromomercuri-2-methoxycyclohexane.—Great care was necessary in acidifying the alkaline solution of α-1-chloromercuri-2-methoxycyclohexane with hydrobromic acid since over-acidification would lead to decomposition. The 3.5 g. of bromomercurial re-dissolved easily in 75 cc. of 2% alkali. Re-acidification with hydrobromic acid yielded the crude bromomercurial, m. p. 112.6°. This was twice crystallized from 11 parts of boiling ethanol to melt at 114.2°.

Anal. Calcd. for $C_7H_{13}OHgBr$: C, 21.37; H, 3.33. Found: C, 21.6; H, 3.39.

Preparation of Active β-1-Chloromercuri-2-methoxycyclohexane.—A solution of 7.6×10^{-4} mole of active α-1-chloromercuri-2-methoxycyclohexane (0.265 g.) in 5 cc. ethanol containing 1×10^{-5} mole (3 mg.) of benzoyl peroxide was refluxed for one hundred and forty-five minutes, then cooled and filtered to remove 40 mg. of mercurous salt. The filtrate was treated with 5×10^{-4} mole of mercuric chloride (0.135 g.) in 15% aqueous sodium chloride solution. The ethanol was evaporated under reduced pressure and the remaining solid filtered off. It weighed 0.18 g. and melted at 64–66°. This 68% yield was dissolved in alkali, filtered and acidified to *p*H 1 with hydrochloric acid. After two hours 0.105 g. was filtered off and crystallized from 1.2 cc. of petroleum ether (b. p. 60–70°). The 0.084 g. thus purified melted at 65.5–66°; repetition of this crystallization raised the melting point to 66.2°. Its mixed melting point with the active α diastereomer was 52–53°. The rotation of a 6% solution of this active β isomer in ethanol was $[\alpha]_D +12.82°$.

Anal. Calcd. for $C_7H_{13}OHgCl$: C, 24.05; H, 3.76. Found: C, 24.03; H, 3.82 (av.).

Summary

1. The rate of methoxymercuration decreases with time when the peroxide catalyst is present, because the peroxide is consumed by side-reaction.

2. Methoxymercuric acetate and not mercuric acetate is the substance that adds to cyclohexane during methoxymercuration, and the reaction is not reversible.

3. The labile and stable isomers of 1-chloromercuri-2-methoxycyclohexane have been redesignated α and β, respectively, and have been shown to be diastereoisomers.

4. The α diastereomer is presumed to hold its added substituents adjacent to each other, and methoxymercuration therefore occurs in the *cis* sense.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

A Method of Calculating the Boiling Points of Silicon Compounds

BY RICHARD N. LEWIS AND ARTHUR E. NEWKIRK

Several attempts have been made to find a method of correlating boiling points and molecular structure.[1] That of C. R. Kinney[2] is applicable to a wide variety of organic compounds. He developed the formula, B.p. (deg. C.) = $230.14 \sqrt[3]{\text{B.P.N.}} - 543$, where B.P.N. is "the sum of the individual atomic and group boiling point numbers expressing the structure of the molecule." The equation was derived from the known boiling points of the normal paraffin hydrocarbons. The atomic boiling point numbers for carbon and hydrogen were chosen as 0.8 and 1.0.

It is possible to extend this equation to most of the simple compounds of silicon. In applying it to the silicon hydrides it was necessary to assume that hydrogen attached to silicon had a value other than 1.0 as a constant value for silicon could not be obtained otherwise. The values which best fit the observed boiling points of the four known hydrides are 0.60 for hydrogen and 4.20 for silicon (Table IV).

Boiling point numbers for atoms and groups attached to silicon are obtained from the substituted monosilanes. The b.p.n. of a polysubstituted silane is in general an additive function of the group b.p.n.'s except that these must be modified according to the degree of substitution. Thus, the b. p. n. of a methyl group decreases in the series methylsilane (3.43), dimethylsilane (3.17), trimethylsilane (3.02), tetramethylsilane (2.74), and the b.p.n. of chlorine decreases in the series chlorosilane (5.05), dichlorosilane (4.17), trichlorosilane (3.59), silicon tetrachloride (3.39). However, alkyl groups and halogens in the same molecule do not seem to have much effect on each other. It is possible, therefore, to calculate the boiling points of the methylchlorosilanes (Table I).

The discrepancy in the case of trimethylchlorosilane, although small, seems large enough to warrant a special value for chlorine in the general

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[1] F. Klages, *Ber.*, **76,** 788 (1943); A. W. Francis, *Ind. Eng. Chem.*, **33,** 554 (1941); see discussion by G. Egloff, J. Sherman and R. B. Dull, *J. Phys. Chem.*, **44,** 730 (1940).

[2] C. R. Kinney, THIS JOURNAL, **60,** 3032 (1938); *Ind. Eng. Chem.*, **32,** 559 (1940); **33,** 791 (1941); *J. Org. Chem.*, **6,** 220, 224 (1941); **7,** 111 (1942).

TABLE I

BOILING POINTS OF THE METHYLCHLOROSILANES

	CH_3SiCl_3	$(CH_3)_2SiCl_2$	$(CH_3)_3SiCl$
ΣB. p. n. (CH_3)	3.43	6.34	9.06
B. p. n. Si	4.20	4.20	4.20
ΣB. p. n. Cl	10.77	8.34	5.05
B. P. N.	18.40	18.88	18.31
B. p. (calcd.)	64.6	69.8	63.6
B. p. (obs.)	66.0	70.2	57.7

case of a trialkylchlorosilane. The value derived from trimethylchlorosilane is 4.51. Likewise the b. p. n. of a tertiary bromine, based on trimethylbromosilane, is 6.58.

In the case of mixed alkyl silanes the b. p. n. of each alkyl group depends on the total number of alkyl groups in the molecule. For instance, the b. p. n.'s of methyl and ethyl groups in dimethyldiethylsilane are the same as in tetramethylsilane (2.74) and tetraethylsilane (5.89). Thus, B. P. N. = 2 × 2.74 + 2 × 5.89 + 4.20 = 21.46, and the calculated boiling point is 96.0° observed.[3]

Similarly in the chlorobromosilanes the b. p. n.'s. used for chlorine and bromine depend on the total number of halogen atoms.

The b. p. n. of a phenyl group in R_4Si (where R may be alkyl or phenyl) could have been determined from a mixed compound such as trimethylphenylsilane, but it seemed desirable to base it on tetraphenylsilane, whose boiling point, not previously published, was found to be 428°.[4]

The diminution of the b. p. n. of an organic group with increasing substitution is probably a bulk effect. The generally greater dimunition in the b. p. n. of halogens, especially in view of their small size, is probably due mainly to some other cause, possibly the action of polarity or resonance.[5]

The boiling point numbers we have calculated are given in Table II. The figures given under $\equiv SiX$ as distinct from R_3SiX are for compounds of the type $RSiH_2X$ and R_2SiHX, although only one such compound, methylchlorosilane, is known.

TABLE II

ATOMIC AND GROUP BOILING POINT NUMBERS

Si, 4.20; H, 0.60

	Type of compound (X = Cl, Br. R = Me, Et, *n*-Pr, Ph)				
	$\equiv SiX$	$=SiX_2$	$-SiX_3$	SiX_4	R_3SiX
Cl	5.05	4.17	3.59	3.39	4.51
Br	7.27	6.47	6.08	5.88	6.58
	$RSi\equiv$	$R_2Si=$	R_3Si-	R_4Si	
Me	3.43	3.17	3.02	2.74	
Et	6.83	6.17	5.91	5.89	
n-Pr	9.47	8.97	8.33	7.85	
Ph	18.87	18.76	18.41	17.73	

In Table III a summary is given of the silicon compounds containing hydrogen, chlorine, bromine, methyl, ethyl, *n*-propyl, and phenyl, their boiling points as recorded in the literature and as calculated, as well as the calculated boiling points of a few unknown compounds which have been included to complete certain series. In cases where a boiling range was given, the midpoint has been chosen; and where the recorded pressure deviated from atmospheric, an appropriate correction has been made.

TABLE III

COMPOUNDS USED TO DERIVE BOILING POINT NUMBERS

Cpd.	B. p., °C.	Ref.	Cpd.	B. p., °C.	Ref.
SiH_3Cl	−30.4	*a*	Me_3SiBr	80.1	*g*
SiH_2Cl_2	8.3	*a*	$EtSiCl_3$	100	*h*
$SiHCl_3$	31.8	*a*	Et_2SiCl_2	129	*h*
$SiCl_4$	57.6	*b*	Et_3SiH	107	*h*
SiH_3Br	1.9	*a*	Et_4Si	153.7	*i*
SiH_2Br_2	64.0	*c*	$PrSiCl_3$	125	*i*
$SiHBr_3$	111.8	*c*	Pr_2SiCl_2	176	*i*
$SiBr_4$	153.4	*c*	Pr_3SiH	170.5	*j*
$MeSiH_3$	−56.8	*a*	Pr_4Si	214	*k*
Me_2SiH_2	−20.1	*a*	$PhSiCl_3$	201.5	*l*
Me_3SiH	10	*d*	Ph_2SiCl_2	305.2	*l*
Me_4Si	26.64	*e*	Ph_3SiCl	378.0	*l*
Me_3SiCl	57.7	*f*	Ph_4Si	428	*m*

[a] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, 1933. [b] "International Critical Tables." [c] W. C. Schumb and R. C. Young, THIS JOURNAL, **52**, 1464 (1930). [d] A. G. Taylor and B. V. deG. Walden, *ibid.*, **66**, 842 (1944). [e] J. G. Aston, R. M. Kennedy and G. H. Messerly, *ibid.*, **63**, 2343 (1941). [f] W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944). [g] W. F. Gilliam, R. O. Sauer and R. N. Meals, *ibid.*, **68**, 1161 (1946). [h] A. Ladenburg, *Ann.*, **164**, 300 (1872). [i] Ref. 3. [j] C. Pape, *Ber.*, **14**, 1872 (1881). [k] S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931). [l] E. G. Rochow and W. F. Gilliam, THIS JOURNAL, **67**, 1772 (1945). [m] See text.

The case of diethyldiphenylsilane served as a test of the reliability of the method. Two boiling points are recorded in the literature, 295–298° (cor.),[6] and 305–315°.[7] The calculated value is 312.9°. A redetermination of the boiling point gave 310°,[8] which is a satisfactory check.

The method in its present form does not give good results with oxygen and fluorine compounds of silicon or with derivatives of disilane, but in all probability additional corrections for certain structural arrangements can be found which will extend it to these systems.

This method of calculating boiling points, which consists essentially of assigning b. p. n.'s to groups according to the total number of groups attached to a central atom, might be considered less convenient than Kinney's. We have found, however, that it can be applied to aliphatic hydrocarbons with exceptionally good results, even in cases of highly branched compounds.

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(3) A. Bygdén, Inaug. Diss., Uppsala, 1916.

(4) The boiling point was measured with a thermometer which had been calibrated with boiling sulfur. The tetraphenylsilane was prepared from triphenylchlorosilane, chlorobenzene, and sodium, and had a melting point of 232.5–234.5° (cor.); A. Polis, *Ber.*, **19**, 1012 (1886), reported 233°.

(5) J. M. Stevels, *Chem. Weekblad*, **34**, 334 (1937).

(6) F. S. Kipping and N. W. Cusa, *J. Chem. Soc.*, 1088 (1935).

(7) A. Ladenburg, *Ann.*, **173**, 143 (1874).

(8) The sample for this determination was made from ethylmagnesium bromide and diphenyldichlorosilane. It boiled at 309–310.5° (cor.) and was analyzed as follows: calcd. for $C_{16}H_{20}Si$: C, 79.94; H, 8.39; Si, 11.68. Found: C, 80.6; H, 8.5; Si, 11.0.

TABLE IV

COMPOUNDS USED TO CHECK BOILING POINT NUMBERS

Cpd.	B. p., °C.	Δ[a]	Ref.	Cpd.	B. p., °C.	Δ	Ref.
SiH_4	−111.9	+0.6	*b*	$MeEtSiCl_2$	100.5	−0.3	*j*
Si_2H_6	− 14.5	−1.6	*b*	$Me_2EtSiCl$	89.2	−0.7	*k*
Si_3H_8	52.9	+0.4	*b*	$Me_2EtSiBr$	110.2	−1.3	*k*
Si_4H_{10}	109	+0.6	*b*	Pr_3SiCl	200.4	(Calcd.)	
$SiCl_3Br$	80.3	+4.1	*c*	Pr_3SiBr	213	+2.4	*l*
$SiCl_2Br_2$	104.4	+4.6	*c*	Me_3PrSi	89.7	−5.2	*h*
$SiClBr_3$	128.0	+4.0	*c*	Me_2Pr_2Si	141.5	−8.2	*h*
$MeSiCl_3$	66.0	−1.4	*d*	$MePr_3Si$	176.0	(Calcd.)	
Me_2SiCl_2	70.2	−0.4	*d*	Et_3PrSi	172.6	−2.7	*h*
$MeSiH_2Cl$	7	+3.1	*b*	$Me_2EtPrSi$	121.4	−5.9	*h*
$MeSiHCl_2$	41.5	+2.4	*e*	$EtPrSiCl_2$	154	−0.7	*h*
Me_2SiHCl	39.1	(Calcd.)		$PhSiHCl_2$	184	+3.8	*k*
$MeSiBr_3$	133.5	+4.1	*f*	Me_3PhSi	171.2	+2.4	*h*
Me_2SiBr_2	112.3	+3.7	*f*	Me_2Ph_2Si	276.4	(Calcd.)	
$MeSiCl_2Br$	90.8	(Calcd.)		Et_3PhSi	238.4	+3.1	*h*
$MeSiClBr_2$	115.1	(Calcd.)		Et_2Ph_2Si	310	+2.9	*m*
$Me_2SiClBr$	93.7	(Calcd.)		$Me_2EtPhSi$	198	−0.6	*h*
Et_3SiCl	143.5	−0.9	*g*	$MeEtPrPhSi$	229	+4.5	*n*
Et_3SiBr	161	− .9	*g*	$MePhSiCl_2$	204	+2.1	*o*
Me_3EtSi	63	+ .6	*h*	$Me_2PhSiCl$	195	+1.4	*p*
Me_2Et_2Si	96.0	−0.6	*h*	$EtPhSiCl_2$	229.5	−2.3	*n*
$MeEt_3Si$	127	−0.6	*i*	$EtPrPhSiCl$	255	−2.1	*n*

[a] Δ = b. p. (calcd.) − b. p. (obs.). [b] Ref. *a*, Table III. [c] H. H. Anderson, THIS JOURNAL, **67**, 859 (1945). [d] The b. p. of methyltrichlorosilane was redetermined by Mr. W. J. Scheiber and that of dimethyldichlorosilane by Dr. R. O. Sauer; see W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, *ibid.*, **63**, 798 (1941). [e] R. O. Sauer, W. J. Scheiber and S. D. Brewer, *ibid.*, **68**, 962 (1946). [f] Ref. *g*, Table III. [g] Ref. *h*, Table III. [h] Ref. 3. [i] Ref. 9. [j] Private communication from Drs. J. Marsden and D. W. Scott. [k] R. N. Lewis, THIS JOURNAL, **69**, 717 (1947). [l] Ref. *j*, Table III. [m] See text. [n] F. S. Kipping, *J. Chem. Soc.*, **91**, 209 (1907). [o] Private communication from Mr. C. P. Haber. [p] Private communication from Dr. S. D. Brewer.

Silicon compounds containing more complex groups than those discussed in this paper can probably be included by combining our data with Kinney's, as the influence of the silicon undoubtedly falls off rapidly with distance. Thus, a B. P. N. for trimethyl-*n*-butylsilane can be obtained by adding 2.8, the value for CH_2, to that calculated for trimethyl-*n*-propylsilane. The calculated boiling point is then 112.2°, while the observed value is 115.4°.[3] In a similar manner we have checked the boiling points of the series of tetraalkylsilanes reported by Whitmore.[9]

Summary

The equation of C. R. Kinney for calculating the boiling points of organic compounds has been found applicable to silicon compounds. Boiling point numbers are given for silicon and the following atoms and groups attached to silicon: hydrogen, chlorine, bromine, methyl, ethyl, *n*-propyl, and phenyl.

The constants were derived from the boiling points of 30 compounds and checked on 33 others. Boiling points of seven unknown compounds have been calculated.

SCHENECTADY, N. Y. RECEIVED OCTOBER 11, 1946

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(9) F. C. Whitmore, *et al.*, THIS JOURNAL, **68**, 475 (1946).