5.85; P, 12.95. Found: C, 45.47; H, 9.60; N, 6.14; P, 13.20.

Diethyl β,γ-Epoxypropylphosphonate (VII).—Triethyl phosphite (332 g., 2.0 moles) was added slowly with stirring to epibromohydrin (261 g., 2.0 mole) held at 135–145°. The addition was complete in four hours and heating and stirring was continued for two hours longer. During the reaction the ethyl bromide produced (169 g., 1.55 moles) was removed continuously by a gentle stream of nitrogen. On distillation of the reaction mixture, the main fraction (197 g., 51% yield) consisted of diethyl epoxypropylphosphonate, b.p. 68–72° (0.1 mm.); $n^{25}\text{D}$ 1.4379; reported $n^{20}\text{D}$ 1.4430,[7] 1.4405.[8]

Anal. Calcd. for $C_7H_{15}O_4P$: C, 43.30; H, 7.79; P, 16.00. Found: C, 42.59; H, 7.99; P, 15.93.

The high boiling residue from the above reaction mixture (72 g.) was molecularly distilled at about 95°. The main portion of this distillate ($n^{25}\text{D}$ 1.4549) appeared to possess approximately two phosphonate units per propane residue.

Anal. Found: C, 40.00; H, 7.18; P, 19.4.

β,γ-Dihydroxypropylphosphonic Acid (VIII).—Diethyl β,γ-epoxypropylphosphonate (VII) was placed in water and warmed on the steam-bath. The oil gradually dissolved and the solution became acidic. After heating for six days, the water was removed at reduced pressure leaving the dihydroxypropylphosphonic acid as a viscous sirup ($n^{25}\text{D}$ 1.4971) which could not be completely freed of water, but which was isolated in the form of its barium salt by the procedure of Arbuzov and Lugovkin[8] and recrystallized from water.

Anal. Calcd. for $C_6H_{16}O_{10}P_2Ba$: P, 13.85; Ba, 30.69. Found: P, 13.30, 13.10; Ba, 31.15, 31.44.

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH BRANCH, AERONAUTICAL RESEARCH LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

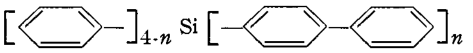
Organo-silicon Chemistry. I. The Mixed Phenyl- and p-Biphenylyl-substituted Silanes, their Physical Properties and Infrared Absorption Spectra[1]

BY LEONARD SPIALTER, DAVID C. PRIEST AND CHARLES W. HARRIS

RECEIVED APRIL 1, 1955

Triphenyl-*p*-biphenylylsilane, diphenyl-di-*p*-biphenylylsilane, phenyltri-*p*-biphenylylsilane and tetra-*p*-biphenylylsilane have been synthesized in 80–90% yields by modified Wurtz reactions between appropriate phenylchlorosilanes and *p*-bromobiphenyl with sodium in ether. Melting and boiling points and solubility data for these compounds and for tetraphenylsilane are tabulated and discussed. Infrared absorption spectra are presented and pertinent structure–spectra correlations are analyzed.

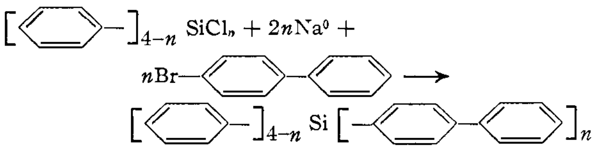
It is of interest to investigate types of organic compounds which promise unusual thermal stability coupled with low vapor pressure. One class of such compounds comprises completely arylated silicon compounds. In the present paper are described the syntheses and properties of some members of one subclass in this category, namely, the tetraarylmonosilanes wherein the aryl substituents are phenyl and *p*-biphenylyl. These compounds can be expressed by the general formula as



$n = 0,1,2,3,4$

Previously the only members of this last group which had been reported were tetraphenylsilane[2,3] and tetra-*p*-biphenylylsilane.[3,4] To help resolve the confusion which exists with respect to the simple physical properties of these compounds and to investigate the behavior of the intermediate members of this series, the entire series has been prepared and its characteristics studied.

The basic synthetic method is essentially a modified Wurtz reaction wherein the appropriate chlorosilane and chlorobenzene or *p*-bromobiphenyl are condensed with sodium in ether. The desired product is isolated by evaporation of the reaction mixture to dryness followed by solvent extraction. Yields are of the order of 80–90%. The general preparative reaction for the biphenylylsilanes is



$n = 1,2,3,4$

Since thermal stability and low vapor pressures are important attributes in this class of compounds, a small apparatus was designed for the rough determination of boiling points at atmospheric pressure in the temperature range from about 400 to 750°.

Experimental Part[5]

Tetraphenylsilane (I).—The method of Polis[6] was used. The product, recrystallized from benzene and further purified by sublimation, consisted of long thin needles, m.p. 236.5–237° (lit. m.p. 234°[7]).

Anal. Calcd. for $C_{24}H_{20}Si$: C, 85.67; H, 5.99; Si, 8.34. Found: C, 85.20, 85.53; H, 5.90, 6.17; Si, 8.31, 8.36.

Tetra-*p*-biphenylylsilane (II).—A modification of the Polis[6] method was used. Into a 500-ml. 3-neck flask, equipped with a mercury-sealed stirrer and condenser protected by a calcium chloride tube, were placed 10.8 g. (0.046 mole) of *p*-bromobiphenyl, 1.95 g. (0.0116 mole) of silicon tetrachloride and 100 ml. of anhydrous ether. To this solution was added 2.5 g. (0.11 gram atom) of sodium ribbon. The mixture was heated to reflux temperature and stirred for about 4 hours when nearly all of the sodium had reacted. The ether was then distilled and the residue was extracted

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[1] Presented before the Division of Organic Chemistry, 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

[2] See references in H. W. Post, "Silicones and Other Organic Silicon Compounds," Reinhold Publ. Corp., New York, N. Y., 1949, p. 187.

[3] E. G. Rochow, "Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 172.

[4] Reference 2, p. 188.

[5] All melting points are corrected and were determined with a Kofler micro hot-stage with a heating rate of about 2° per minute at the melting point. Microanalyses were performed by Oakwold Laboratories, Alexandria, Va.

[6] A. Polis, *Ber.*, **18**, 1541 (1885); **19**, 1013 (1886).

[7] S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931).

with benzene in a Soxhlet apparatus. From the resulting solution was crystallized 6.7 g. of II (90%), m.p. 281–282°. Recrystallization from xylene gave small needles, m.p. 283–283.5° (lit. m.p. 274°[8]).

Anal. Calcd. for $C_{48}H_{36}Si$: C, 89.96; H, 5.66; Si, 4.38. Found: C, 89.72, 89.95; H, 5.70, 5.75; Si, 4.66, 4.50.

Triphenyl-*p*-biphenylylsilane (III).—A procedure similar to that described above for II was used. The reactants were 14.70 g. (0.05 mole) of triphenylchlorosilane, 11.65 g. (0.05 mole) of *p*-bromobiphenyl and 2.5 g. (0.11 gram atom) of sodium ribbon. However, the reaction mixture was heated at reflux temperature for 24 hours. The extracting solvent used was petroleum ether. The crude yield was 17.3 g. (84%) of product, m.p. 150–153°. Two crystallizations from *n*-hexane gave a melting point of 158.5–159.5°.

Anal. Calcd. for $C_{30}H_{24}Si$: C, 87.34; H, 5.86. Found: C, 87.18, 86.89; H, 5.75, 5.86.

Diphenyl-di-*p*-biphenylylsilane (IV).—A procedure similar to that for II was used. The reactants were 11.65 g. (0.05 mole) of *p*-bromobiphenyl, 6.23 g. (0.025 mole) of diphenyldichlorosilane and 2.5 g. (0.11 atom) of sodium ribbon. The reaction time was 14 hours. The extracting solvent used was petroleum ether. There was obtained 10.7 g. (88%) of product, m.p. 165–169°. Recrystallization from a benzene–ethanol mixture gave a melting point of 169–170°.

Anal. Calcd. for $C_{36}H_{28}Si$: C, 88.48; H, 5.78; Si, 5.74. Found: C, 88.42, 88.57; H, 5.83, 5.89; Si, 5.61, 5.40.

Phenyl-tri-*p*-biphenylylsilane (V).—The above procedure was used. The reactants were 17.6 g. (0.075 mole) of *p*-bromobiphenyl, 5.28 g. (0.025 mole) of phenyltrichlorosilane and 3.6 g. (0.16 mole) of sodium ribbon. The reaction time was 6.5 hours. Extraction was performed with petroleum ether and gave 12.8 g. (92%) of material, m.p. 150–154°. Recrystallization from benzene–ethanol gave a melting point of 155.0–155.5°.

Anal. Calcd. for $C_{42}H_{32}Si$: C, 89.32; H, 5.71; Si, 4.97. Found: C, 89.76, 89.58; H, 5.59, 5.51; Si, 5.07, 5.25.

Compound V, when recrystallized twice from *n*-butyl alcohol, gave a higher-melting crystal modification, m.p. 172.5–174.0°. Further recrystallization of this latter form from methylcyclohexane produced again the original lower-melting polymorph. Infrared absorption data were identical for the two forms within the limits examined and no solvent of crystallization was found in either case.

Compounds III, IV and V gave viscous melts and readily supercooled to brittle glassy materials at room temperature. However, after standing for six months under ambient conditions, only compound V failed to crystallize. On being heated, the glassy phase in all three compounds gradually became mobile at temperatures above 200°. Although crystallization is apparently extremely slow from the glass at room temperature, it is quite readily induced by contact with common solvents such as benzene–ethanol mixtures or cyclohexane.

Boiling Point Determinations.—The apparatus consisted of an inner conical Vycor tube, 1 cm. maximum i.d. and about 9 cm. long. Around the lower half of the jacket was a heater winding, consisting of 3 feet of B & S 30 Nichrome resistance wire, with applied voltage being controlled by a variable transformer. This assembly was wrapped with asbestos paper and placed in a 250-ml. beaker packed with vermiculite, a form of expanded mica. A small sample, about 100 mg., of the desired compound was placed in the bottom of the conical tube and was then heated to reflux temperature. The temperature of the vapor was determined by means of a small stainless steel jacketed iron-constantan couple supported by a cork stopper and connected to a two channel Brown point-recording potentiometer through a voltage divider network so that full scale deflection corresponded to 750°. The apparatus was calibrated with refluxing mercury and estimated accuracy was of the order of ±3°. The vapors were observed to condense on the cool upper portion of the conical tube, so that the temperature recorded was in part the distilling temperature. The flatter the plateau on the temperature *vs.* time plot, the purer was the sample and the less the thermal decomposition which had occurred. When all of the sample had been distilled, the temperature recorded always dropped, indicating absence of superheating. The heating current, based on previous calibration, was, in general, adjusted to maintain the lower half of the conical tube at about 50° above the boiling temperature of the sample.

The experimental values for the boiling points found at atmospheric pressure (about 755 mm.) are listed in Table I.

TABLE I

	M.p., °C.	B.p., °C. Found	B.p., °C. Calcd.[b]
Tetraphenylsilane (I)	237	430	428
Triphenyl-*p*-biphenylylsilane (III)	159	512	508
Diphenyldi-*p*-biphenylylsilane (IV)	170	570	573
Phenyltri-*p*-biphenylylsilane (V)	155, 174	580[a]	628
Tetra-*p*-biphenylylsilane (II)	283 above	600 dec.[a]	678

[a] Significant decomposition occurred under conditions of the boiling point determination. [b] Boiling points calculated from Kinney formula (see text).

Solubility Behavior.—Closed tubes containing solvent and excess solute were shaken at 47° for one hour to yield approximately saturated solutions. These were then placed in a thermostat at 24.0 ± 0.5°. Solubilities were calculated from the constant weight values of the solute residues. Runs were made on a microscale and duplicate determinations indicate a precision of better than 10%.

Reference solvents used were anhydrous benzene, n^{20}_{D} 1.5006) prepared from C.P. grade by repeated acid washing, drying over potassium hydroxide and fractional distillation from sodium; and ultraviolet spectroscopic grade *n*-heptane ($d^{23.2}_{4}$ 0.715, $d^{29.4}_{4}$ 0.709, n^{20}_{D} 1.3992) obtained from Phillips technical grade *n*-heptane by the method of Brunn and Hicks-Brunn.[9]

The solutes were taken from analytical samples. The solubility data are presented in Table II.

TABLE II

Solubility, mg. solute per g. solvent at 24°

Solute	*n*-Heptane	Benzene
I	<0.5	26
II	<0.5	0.6
III	2.6	210
IV	4.2	240
V	2.4	260

The solubility of II in the usual organic solvents was so low that efficient recrystallization was possible only from such solvents as boiling xylene and bromobenzene.

Infrared Absorption Spectra.—The infrared absorption spectra for the compounds discussed in this paper were determined on a Perkin–Elmer model 21 double beam infrared spectrophotometer. Samples were prepared in the form of Nujol mulls since none of the standard spectral solvents exhibited sufficient solubility for all of the compounds. The spectra are presented in Fig. 1.

Discussion

Physical Properties.—The melting point found for tetraphenylsilane (I) agrees fairly well with those previously reported which range from 230 to 234°.[2,3] For the other known compound, tetra-*p*-biphenylylsilane (II), however, the deviation is somewhat larger from the published values of 270 and 274°.[3,4] The present determinations are believed to be the more accurate since special care was taken in view of the earlier reports.

As might be expected the more symmetrically substituted compounds I and II have the higher melting points and lower solubilities. However, it remains to be established whether symmetry and

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(8) W. C. Schumb, J. Ackerman and C. M. Saffer, This Journal, **60**, 2486 (1938).

(9) J. H. Brunn and M. H. Hicks-Brunn, *J. Research Natl. Bur. Standards*, **7**, 607 (1931), R. P. 360.

close-packing (entropy) or some sort of intermolecular attraction between benzene rings (enthalpy) is the important factor in the observed order of these melting points.[10]

The only compound in the present study whose boiling point has been previously described, tetraphenylsilane, has had values reported from 360 to 530°.[2,3] The most recent determination of 428°[11] checks the value reported herein very closely. As for the other compounds in Table I, the boiling points, as expected, increase with molecular weight. Decomposition becomes marked when vapor temperatures exceed 600°. That thermal breakdown does occur under these conditions is not surprising since contact with potentially reactive or catalytically active silica walls at pot temperatures above 700° are necessary to bring about boiling.

The group boiling point number for the *p*-biphenylyl group was calculated by means of the Kinney formula[12]: b.p. (°C.) = $230.14\sqrt[3]{\text{B.P.N.}} - 543$, where B.P.N. is "the sum of the individual atomic and group boiling numbers expressing the structure of the molecule." Computation with the values for the silicon and phenyl groups in the appropriate structures, as given by Lewis and Newkirk[11] and the boiling points listed in Table I for compounds III, IV and V, gave 36.9, 35.7 and 31.6, respectively, as the boiling point number for the *p*-bi-

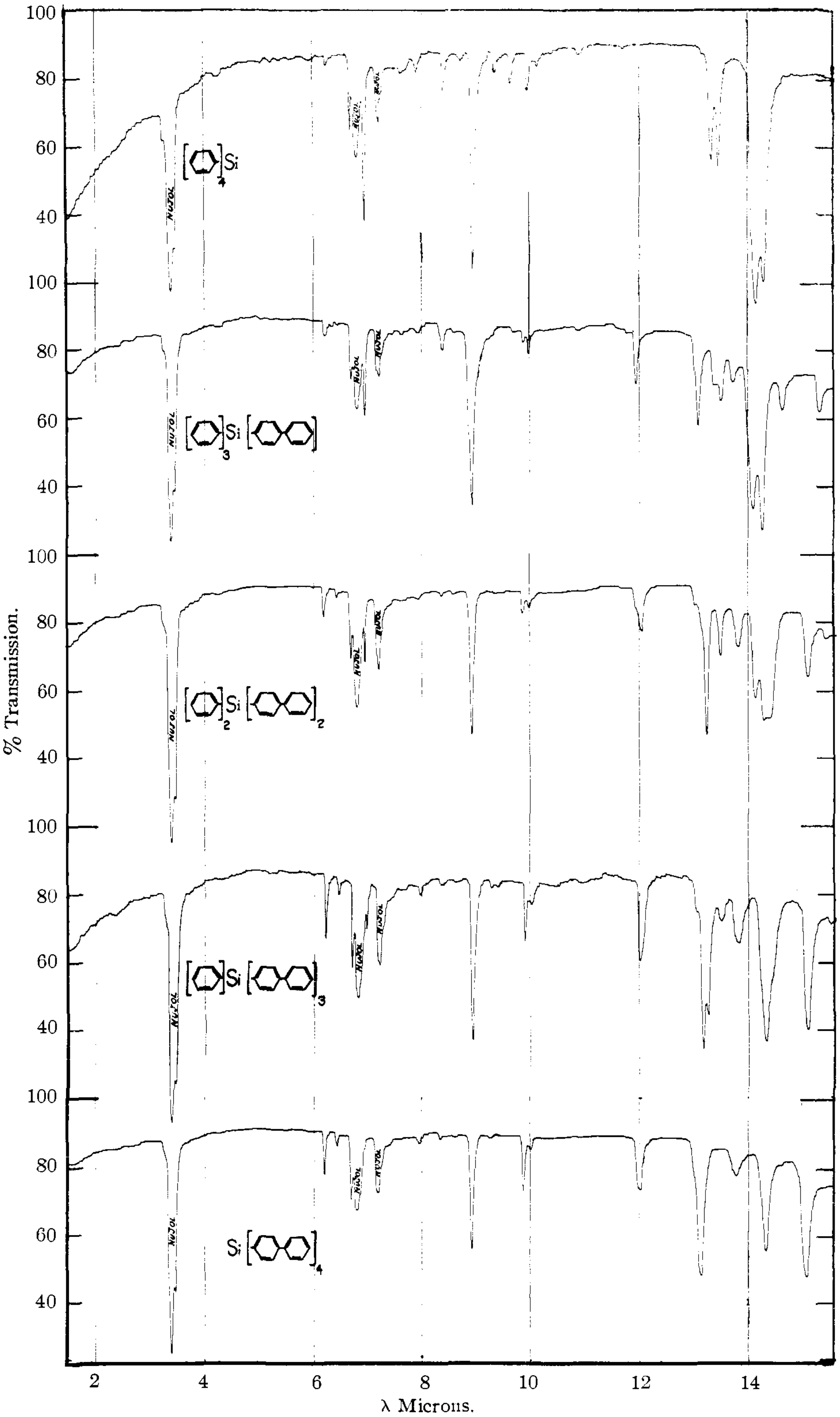

Fig. 1.—Infrared absorption spectra of mixed phenyl-*p*-biphenylylsilanes in Nujol mulls.

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[10] The danger in using intuitive reasoning in such matters for aromatic compounds has been pointed out by L. Ebert, *Monatsh.*, **77**, 398 (1947).

[11] R. N. Lewis and A. E. Newkirk, THIS JOURNAL, **69**, 702 (1947).

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

phenyl group. In view of the observable decomposition which occurred in the case of V, it is felt that the mean of the two former values (36.3) probably represents a better value for the *p*-biphenylyl group. This number is almost exactly twice those suggested for the phenyl group.[11] The predicted boiling points calculated with this value are given in Table I. No correction has been applied for the number of biphenyl substituents on the silicon, as was done by Lewis and Newkirk for the phenyl group boiling point number.

Infrared Spectra.—The infrared absorption spectra for the present series of compounds, Fig. 1, show a high degree of similarity of bond positions to about 13 μ where skeletal vibrations become important. No marked shifts or degeneracy splittings occur below this value. Instead most of the bands either increase or decrease progressively in intensity down the series. This suggests that there is negligible additional simple vibrational coupling transmitted through either the central silicon or space as *para*-phenyl substitution occurs in these tetraarylsilanes. (This comment does not pertain to the new biphenylyl bands which arise due to direct phenyl–phenylene interaction.)

A preliminary scanning of the infrared absorption spectra in Fig. 1 shows that the extreme members, tetraphenylsilane and tetra-*p*-biphenylylsilane, have the fewest absorption bands, particularly in the region of skeletal vibrations above 13 μ. This is to be expected since these possess the greatest symmetry in the series. In general, the more symmetric the molecule, the fewer the infrared-active fundamentals which occur.[13]

The spectrum for tetraphenylsilane is remarkably similar to that found for tetraphenylmethane.[14] These two spectra have at least 14 bands in common appearing at wave lengths within 0.1 μ of each other throughout the sodium chloride region. The significant difference appears in the band intensities which do not have the same relative values in each curve. The infrared absorption curve reported for tetraphenylstannane possesses only ten obvious bands in the 2 to 16 μ region[15] and all of these are also present in the spectrum of tetraphenylsilane although, again, with differing intensities. For these related symmetrical compounds, the main effect of the central atom is to change transition probabilities for the characteristic phenyl vibrations such as the various C=C and C–H modes and ring deformations. Whether this fact is attributable to steric factors or crystal forces, since the data on these compounds came from Nujol mulls,[16] is uncertain. Vibrations involving bonds to the central Si atom appear to contribute little in the rock salt region.

Owing to the poor solubility characteristics of the end members of the present phenyl- and *p*-biphenylyl substituted silanes, the infrared absorption spectra were uniformly obtained for suspensions in mineral oil (Nujol). Unfortunately, the usual mull technique did not lend itself to quantitative intensity analysis because of uncertainties in sample thickness and concentration so only relative comparisons can be made.[17]

The bands at 3.43–3.50 (doublet), 6.86 and 7.26 μ are those of Nujol,[18] the mulling and suspending agent, and are so marked in the spectra of Fig. 1. It is convenient to use the band at 6.73 μ as a fiducial intensity since it appears to remain practically constant in intensity as one progresses through the series of compounds whose spectra are presented. This is only a rough approximation but appears to be a useful one in view of the absorption trends observed. Inspection of the curves shows that as one increases the number of biphenylyl substituents (and correspondingly decreases the number of phenyl groups on silicon) the following occur[19]: 1. New bands appear and increase in intensity at 6.48, 7.40, 9.91 and 12.00 μ (characteristic of vibrations in *p*-biphenylyl group). 2. Bands, already present in tetraphenylsilane and which either increase in intensity or remain relatively constant, are at 3.35, 6.25, 6.73, 7.66, 7.97, 8.95 and 10.02 μ (characteristic of C–H and C=C vibrations and ring deformations). 3. Bands gradually decrease in intensity at 7.00, 9.68 and 13.50 μ (characteristic of phenyl on silicon). 4. Bands gradually decrease in intensity at 8.40, 8.98, 9.30 and 14.34 μ (characteristic of specialized phenyl group vibrations).

More exact assignments are available or deducible from the literature for certain of the above bands. These include: 3.35 μ (which appears as a shoulder on the short wave length side of the first Nujol band) arises from aromatic C–H stretching.[20] 6.25 and 6.73 μ[21] represent conjugated C=C stretching in the phenyl rings, generally monosubstituted with the intensity at the former wave length being determined by the nature of the substituent. Evidently, the phenylene group intensifies the 6.25 μ band more than does silicon. No absorption is observed in the 6.33–6.37 μ region which appears for most biphenyl derivatives[22] and has been ascribed to conjugated ring systems.[23] Absence of this band has also been observed by Clark, *et al.*,[24]

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[13] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 239, 362.

[14] C. G. Cannon and G. B. B. M. Sutherland, *Spectrochim. Acta*, **4**, 373 (1951). The absorption data for tetraphenylmethane were interpolated from the spectrum on p. 387.

[15] C. R. Dillard, E. E. Holmes, T. R. Lawson, D. E. Simmons and J. B. Yeldell, ONR Contract N9Onr-95700 at Tennessee Agricultural and Industrial State University, Final Report, August 31, 1952.

[16] F. A. Miller in "Organic Chemistry," Vol. III, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 138.

[17] L. E. Kuentzel, *Anal. Chem.*, **27**, 301 (1955), has recently described the use of an internal standard for mull samples which overcomes most of the quantitative problems.

[18] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Substances," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 93.

[19] M. Margoshes and V. A. Fassel, *Anal. Chem.*, **27**, 351 (1955), have recently made a novel and useful analytical application of analogous absorption trends in the infrared spectra of the mixed phenyl- and *p*-tolyl-substituted silanes.

[20] Reference 16, p. 143.

[21] C. W. Young, P. C. Servais, C. C. Currie and N. J. Hunter, THIS JOURNAL, **70**, 3758 (1948). These workers list bands at 6.29, 6.71, 6.99, 8.40, 8.93, 9.71 and 10.05 μ as all being characteristic of the phenyl group on a silicon atom, at least in siloxane-type molecules. Of these, all are visible in each of the present spectra but not in the same relative intensities as in this reference.

[22] Reference **14**, p. **378**.

[23] Reference 19, p. 20.

[24] H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, THIS JOURNAL, **73**, 3798 (1951).

in the case of the trimethylbiphenylylsilanes. As in this paper, these workers observed absorption at 6.47 μ resulting probably from *para*-substitution in unhindered biphenyls. This conclusion is supported by the data of Cannon and Sutherland[14] and others.[25]

Although Young and co-workers[21] noted a symmetrical splitting of the 8.95 μ band upon diphenyl substitution in polysiloxane chains, there is no such comparable branching in the spectra of diphenylsilanes of the present paper or in 1,1-diphenylalkanes.[26]

Absorption at 9.91 μ is characteristic of certain biphenyl compounds and seems to be due to stretching vibration in the ring-to-ring C–C bond. It appears at this wave length in *ortho*- or *para*-substituted biphenyl.[14,24]

The characteristic 10.05 μ band probably arises from benzene ring C–C stretching, although this mode is infrared inactive in more symmetrical compounds such as benzene itself. The same band has been reported as a characteristic phenyl frequency in trimethylphenylsilane.[27]

The bands at about 13.5–13.6 and 14.3 μ appear to be due to C–H out-of-plane deformations associated with monosubstituted benzenes, whereas such vibrations cause absorption at 12.0 μ in *p*-disubstituted benzenes.[14,28,29]

WRIGHT PATTERSON AIR FORCE BASE, OHIO

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(25) R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

(26) K. T. Serijan, I. A. Goodman and W. J. Yankauskas, National Advisory Committee for Aeronautics, Technical Note 2557, November, 1951.

(27) C. C. Cerato, J. L. Lauer and H. C. Beachell, *J. Chem. Phys.*, **22**, 5 (1954).

(28) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 268 (1945).

(29) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION OF LEVER BROTHERS CO.]

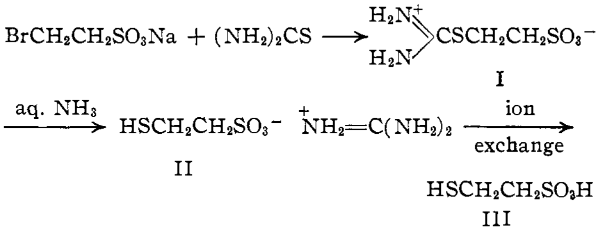
The Synthesis of Mercaptoalkanesulfonic Acids

BY CHARLES H. SCHRAMM, HENRY LEMAIRE AND R. H. KARLSON

RECEIVED OCTOBER 18, 1954

2-Mercaptoethane-, 3-mercaptopropane- and 4-mercaptobutanesulfonic acids and several salts of these acids have been synthesized. A series of new betaine-type compounds has been prepared and these products have been found to undergo a novel cleavage reaction with ammonium hydroxide.

The chemical literature describes the preparation of the gold–sodium salt,[1] $\mathrm{Au(SCH_2CH_2SO_3Na)_2}$, of 2-mercaptoethanesulfonic acid and an impure sample of the sodium salt,[2] $\mathrm{HSCH_2CH_2SO_3Na}$. The use of the sodium salt as a chemical intermediate has been mentioned in two patents.[3] However, there are no published data relative to the preparation of pure ω-mercaptoalkanesulfonic acids or their salts. This paper describes the first practical synthesis[4] of these compounds which were prepared by the following reactions, using the ethane derivative as an example

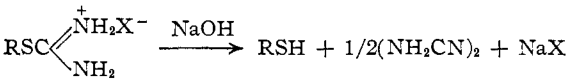


$$\mathrm{BrCH_2CH_2SO_3Na + (NH_2)_2CS} \longrightarrow \underset{\text{I}}{\begin{array}{l}\mathrm{H_2N^+}\\ \quad\rangle\mathrm{CSCH_2CH_2SO_3^-}\\ \mathrm{H_2N}\end{array}}$$

$$\xrightarrow{\text{aq. NH}_3} \underset{\text{II}}{\mathrm{HSCH_2CH_2SO_3^-\quad \overset{+}{N}H_2{=}C(NH_2)_2}} \xrightarrow[\text{exchange}]{\text{ion}} \underset{\text{III}}{\mathrm{HSCH_2CH_2SO_3H}}$$

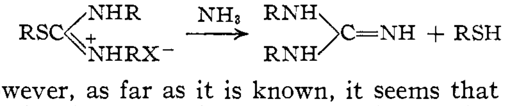
Sodium 2-bromoethanesulfonate[5] was allowed to react under carefully controlled conditions with thiourea to yield the internal salt, 2-S-thiuronium ethanesulfonate (I). The thiuronium compound was recrystallized from water from which it was obtained as a hard, white crystalline solid. It was insoluble in organic solvents and did not possess a sharp melting point but decomposed slowly upon heating to 265°. These characteristically ionic features helped to verify the above assigned structure of this compound. It appears that this is the first time that compounds of this type have been prepared.

Thiuronium compounds are readily converted into mercaptans by treatment with sodium hydroxide.[6]



$$\mathrm{RSC}\begin{array}{l}\diagup\overset{+}{\mathrm{N}}\mathrm{H_2X^-}\\ \diagdown\mathrm{NH_2}\end{array} \xrightarrow{\text{NaOH}} \mathrm{RSH + 1/2(NH_2CN)_2 + NaX}$$

Although the betaine-type compounds, the thiuronium alkanesulfonates, can be cleaved readily by this method, a pure product is not obtained since the dicyandiamide (or a product derived therefrom) cannot be removed readily from the reaction mixture. Substituted guanidine compounds have been prepared by the reaction of N-alkyl isothioureas with ammonia,[7] *i.e.*



$$\mathrm{RSC}\begin{array}{l}\diagup\mathrm{NHR}\\ \diagdown\overset{+}{\mathrm{N}}\mathrm{HRX^-}\end{array} \xrightarrow{\mathrm{NH_3}} \begin{array}{l}\mathrm{RNH}\diagdown\\ \mathrm{RNH}\diagup\end{array}\mathrm{C{=}NH + RSH}$$

However, as far as it is known, it seems that this reaction has never been used in the synthesis of mercaptans, nor is there any published record of re-

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