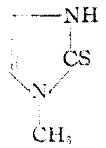
of 1-methyl-2-thioimidazolone[17] ("1-methyl-2-mercaptoimidazole") (XVI) at 2.88, 3.25, 3.40, 6.32, 6.72 and 6.86 μ can be assigned in exactly corresponding fashion, the last two to the thiourea system.

XVI



The thiothiazolone spectrum was differently interpreted by Randall, *et al.*,[4] who considered the 4,5-dimethyl derivative as a mercaptothiazole. Examination of this substance in chloroform solution during the present investigation showed that it absorbed almost indistinguishably from the 4-methyl compound between 2 and 9 μ, notably in the 3–4 μ region which suffered no interference from mineral oil. The positions of the two bands previously observed between 6.5 and 7 μ were confirmed, but instead of the reported doublet at 6.16 and 6.23 μ a single sharp peak was found at 6.12 μ. In the solid state association would be increased and the N–H stretching bands further obscured. The additional resonance caused by the double bond in the thiothiazolone ring augments the contribution of dipolar structures such as the aromatic XVII corresponding to VII and therefore promotes hydrogen bonding. Probably a great tendency to association exists in 2-thiopyridone and analogs and accounts for the failure of a recent infrared spectroscopic study[18] of certain 2- and 4-thioquinolones to reach a structural decision. The difficulty may be alleviated as present results show.

Experimental

Infrared absorption spectra were determined with a Baird Infrared Recording Spectrophotometer, Model B. Dr. E. B. Astwood generously supplied the majority of compounds examined from his collection of antithyroid drugs. 2-Thioöxazolidone was prepared by a synthesis to be described in another paper, and S,N,N,N'-tetramethylisothiourea (b. p. 62° (11 mm.)) by methylation of N,N,N'-trimethylthiourea according to a general method.[19] The solvent chloroform was anhydrous or U. S. P. Several spectra show small, spurious peaks at 4.1–4.4 μ, caused by cell impurities or imperfect compensation of the solvent absorption band in that region. The intense chloroform band at 8–8.4 μ also appears frequently.

Summary

The infrared absorption spectra of certain potentially enolic heterosubstituted thioamides have been measured and interpreted. Even if the functional group is incorporated in a five-membered aromatic ring, the substance exists solely in thione form.

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[17] Wohl and Marckwald, *Ber.*, **22**, 1353 (1889).

[18] Hannan, Lieblich and Renfrew, THIS JOURNAL, **71**, 3733 (1949).

[19] Lecher, Graf and Gnaedinger, *Ann.*, **445**, 61 (1925).

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 6, 1950

[CONTRIBUTION NO. 497 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Some Reactions of Phenylsilane

BY W. H. NEBERGALL

The use of lithium aluminum hydride[1] makes the alkyl hydrides of silicon and the other elements of the fourth group of the periodic system readily obtainable by virtue of its power to reduce the halides to the corresponding hydrides in ether solution. Accordingly, phenylsilane was prepared in this investigation by the action of lithium aluminum hydride upon phenyltrichlorosilane.

$$4C_6H_5SiCl_3 + 3LiAlH_4 \longrightarrow 4C_6H_5SiH_3 + 3LiCl + 3AlCl_3$$

The phenyltrichlorosilane was produced by the interaction of phenyllithium and an excess of tetrachlorosilane.

$$C_6H_5Li + SiCl_4 \longrightarrow C_6H_5SiCl_3 + LiCl$$

Phenylsilane, $C_6H_5SiH_3$, is a colorless, volatile liquid boiling at 120° and possessing an odor suggesting that of toluene, $C_6H_5CH_3$. This silane may be distilled at atmospheric pressure without noticeable decomposition and it was not found to be spontaneously inflammable in air at the boiling point.

In its chemical reactions, phenylsilane resembles the corresponding halides, the hydrogen atoms exhibiting a negative character much like that of the halogens, but less so. Previous reports[2] have shown that the trialkylsilanes react with organolithium compounds in ether to form tetrasubstituted silanes and lithium hydride.

$$R_3SiH + R'Li \longrightarrow R_3SiR' + LiH$$

The above reaction appears to be one case of a more general reaction[3] since it was found in the present investigation that phenylsilane may be alkylated with ethyllithium to form phenyltriethylsilane and with phenyllithium to form tetraphenylsilane.

$$C_6H_5SiH_3 + 3RLi \longrightarrow C_6H_5SiR_3 + 3LiH$$

Diethyl ether was found to be a suitable reaction medium, but when low boiling petroleum

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[1] (a) Finholt, Bond, Wilzbach and Schlesinger, THIS JOURNAL, **69**, 2692 (1947); (b) Johnson and Nebergall, *ibid.*, **71**, 1720 (1949); (c) Nebergall and Johnson, *ibid.*, **71**, 4022 (1949).

[2] Gilman and Massie, *ibid.*, **68**, 1128 (1946); Meals, *ibid.*, **68**, 1880 (1946); Gilman and Melvin, *ibid.*, **71**, 4050 (1949).

[3] The reaction of diphenylsilane with organolithium compounds will be reported in a later paper.

ether was employed as the solvent, the third hydrogen atom of phenylsilane resisted replacement by an alkyl group. This observation is in

$$C_6H_5SiH_3 + 2C_2H_5Li \longrightarrow C_6H_5Si(C_2H_5)_2H + 2LiH$$

accord with that of Meals,[2] who found that low boiling petroleum ether either inhibited or failed to catalyze the reaction between trialkylsilanes and organolithium compounds.

$$(C_2H_5)_3SiH + RLi \xrightarrow{\text{petroleum ether}} \text{no reaction}$$

Phenylsilane reacts readily with lithium ethoxide in ethanol forming phenyltriethoxysilane and hydrogen.

$$C_6H_5SiH_3 + 3C_2H_5OH + (LiOC_2H_5) \longrightarrow C_6H_5Si(OC_2H_5)_3 + 3H_2 + (LiOC_2H_5)$$

The mechanism proposed by other investigators[4] for corresponding alkaline cleavage reactions of trialkylsilanes is that a hydride ion is split off the silane and that this ion combines with a proton from the hydroxyl of the solvent, thus forming the hydrogen molecule.

Phenylsilane is rapidly hydrolyzed by alkalies with the formation of hydrogen and a white gel, probably of polymeric composition. Bromination of phenylsilane produced phenyltribromosilane and hydrogen bromide.

Experimental

Synthesis of Phenyltrichlorosilane.—Phenyllithium was prepared by adding, over a period of one hour, 78.5 g. (0.50 mole) of bromobenzene to 350 ml. of absolute ether containing an excess of lithium metal shot in a 500-ml., three-necked flask fitted with a mercury-sealed, motor-driven stirrer, a reflux condenser protected by a calcium chloride tube, and a dropping funnel containing the bromobenzene. The reaction mixture was heated to the reflux temperature in order to initiate the reaction, after which the heat of reaction caused continuous refluxing for several minutes after all of the bromobenzene had been added. After filtering out the excess lithium, the solution of phenyllithium was added dropwise to a 300-ml. ether solution of 170 g. (1.0 mole) of tetrachlorosilane which was stirred and cooled in a Dry Ice–ethanol-bath. The lithium salts which had precipitated during the reaction were removed by filtration while the reaction mixture was still cold. Most of the ether and the excess tetrachlorosilane were removed by distillation and the remaining liquid was decanted from a second crop of lithium salts which had formed during the distillation. Distillation of the residual liquid under reduced pressure produced 53.8 g. (51%) of a liquid collected at 77–78°[5] (13 mm.), b. p. 200° (750 mm.). Phenyltrichlorosilane[6] boils at 201.5° (760 mm.).

Anal.[7] Calcd. for $C_6H_5SiCl_3$: Si, 13.24. Found: Si, 13.3.

A second fraction of liquid, 16 g., distilling at 154–155° (9 mm.) was collected and analyzed. Diphenyldichlorosilane[8] boils at 160° (10 mm.).

Anal. Calcd. for $C_{12}H_{10}SiCl_2$: Si, 11.09. Found: Si, 10.9.

Reduction of Phenyltrichlorosilane by Lithium Aluminum Hydride.—A solution of 42 g. (0.20 mole) of phenyltrichlorosilane in 50 ml. of absolute ether was added dropwise to an excess of lithium aluminum hydride in 150 ml. of ether contained in an apparatus adapted for refluxing and excluding moisture. The reaction mixture was refluxed for one hour after all of the phenyltrichlorosilane had been added and then most of the ether was removed by distillation. The remaining ether and the product of the reaction were removed from the lithium chloride, aluminum chloride and excess lithium aluminum hydride under reduced pressure, the receiver being cooled in a bath of Dry Ice and ethanol. Distillation was stopped when the temperature of the distilling vapor reached 48° at a pressure of 75 mm. The ether was removed from the distillate and the product was purified by distillation at atmospheric pressure; yield 18.5 g. (86%), b. p. 119.5–120° (757 mm.), $n^{25}\text{D}$ 1.5112. The calculated boiling point for phenylsilane[1a] is 120° (760 mm.), $n^{20}\text{D}$ 1.5125.

Anal. Calcd. for C_6H_8Si: Si, 26.06. Found: Si, 25.9.

Phenylsilane and Phenyllithium.—Phenyllithium was prepared from 10.0 g. (0.064 mole) of bromobenzene in 100 ml. of ether solution in the manner described above. To this solution was added dropwise 1.7 g. (0.0080 mole) of phenylsilane in 10 ml. of ether with the immediate formation of a white precipitate and sufficient heat was evolved to cause refluxing of the solvent. The reaction mixture was stirred for one hour and then the lithium hydride and the excess phenyllithium were hydrolyzed by pouring the mixture into cracked ice and dilute sulfuric acid. The product, tetraphenylsilane, was removed by filtration and recrystallized from benzene; yield 4.5 g. (85%), m. p. 233–234°.

Anal. Calcd. for $C_{24}H_{20}Si$: Si, 8.33. Found: Si, 8.4.

No evidence of a reaction was observed when phenylsilane was treated with a large excess of phenylmagnesium bromide and the mixture worked up in the usual manner. There may not be a reaction here analogous to that with phenyllithium because magnesium hydride[9] is apparently formed only at high temperatures and is unstable at low temperatures.

Phenylsilane and Ethyllithium in Ethyl Ether.—Phenylsilane (0.02 mole) and ethyllithium (0.30 mole) were interacted in ethyl ether in the manner described above with the immediate formation of a white precipitate, presumably lithium hydride. The heat of reaction was great enough to bring about refluxing of the solvent and the refluxing continued several minutes after all of the phenylsilane had been added to the solution of ethyllithium. The reaction mixture was allowed to stand for 24 hours after which the lithium hydride and the excess ethyllithium were destroyed by pouring the reaction mixture into cracked ice and dilute sulfuric acid. After drying the ether layer over calcium chloride, the ether was removed and the product was distilled at 122–125° (20 mm.); yield 3.0 g. (78%), b. p. 235.5° (748 mm.), $n^{25}\text{D}$ 1.4927. Phenyltriethylsilane[2] boils at 238.4° (760 mm.).

Anal. Calcd. for $C_{12}H_{20}Si$: Si, 14.55. Found: Si, 14.4.

Phenylsilane and Ethyllithium in Low Boiling Petroleum Ether.—Phenylsilane (0.02 mole) and ethyllithium (0.30 mole) interacted in the manner described above except that the ethyl ether was replaced by petroleum ether (20–40°) as the reaction medium. A white precipitate formed immediately and the heat of reaction caused refluxing of the solvent as in the above experiment, but the refluxing continued for a considerably longer period of time than when ethyl ether was employed as the solvent. The reaction mixture was permitted to stand for 24 hours and then it was worked up as described above. The product distilled at 97–100° (25 mm.); yield 2.5 g. (77%), b. p. 204.5° (748 mm.), $n^{25}\text{D}$ 1.4908. The product appeared to be phenyldiethylsilane, $C_6H_5Si(C_2H_5)_2H$, which evolved hydrogen when dissolved in ethanol and treated with aqueous sodium hydroxide.

Anal. Calcd. for $C_{10}H_{16}Si$: Si, 17.09. Found: Si, 17.1.

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(4) Price, THIS JOURNAL, **69**, 2600 (1947); Gilman, *ibid.*, **68**, 1128 (1946); Kraus and Nelson, *ibid.*, **56**, 195 (1934).

(5) All boiling and melting points are uncorrected.

(6) Rochow and Gilliam, THIS JOURNAL, **67**, 1772 (1945).

(7) Johnson and Nebergall, *ibid.*, **70**, 1706 (1948).

(8) Hyde and DeLong, *ibid.*, **63**, 1194 (1941).

(9) Private communication from John S. Peake of this Laboratory.

Phenylsilane and Lithium Ethoxide in Ethanol.—An ethanol solution of lithium ethoxide was prepared from 0.58 g. (0.084 mole) of lithium metal shot and 50 ml. of absolute ethanol. A 20-ml. ethanol solution of 3.0 g. (0.028 mole) of phenylsilane was added to the solution of lithium ethoxide. The resulting reaction was sufficiently exothermic to bring about refluxing of the solvent and hydrogen was rapidly evolved. After distilling off the ethanol, the product of the reaction was removed from the lithium ethoxide by distillation under reduced pressure; yield 3.5 g. (54%), b. p. 108.5° (4 mm.). Phenyltriethoxysilane[10] boils at 120° (15 mm.).

Anal. Calcd. for $C_{12}H_{20}SiO_3$: Si, 11.68. Found: Si, 11.7.

Phenylsilane and Bromine.—A solution of 2.5 g. (0.023 mole) of phenylsilane in 20 ml. of carbon tetrachloride was treated with a slight excess of bromine in carbon tetrachloride solution. The heat of the reaction caused the solution to rise to the reflux temperature as the bromine solution was added dropwise to the phenylsilane, and hydrogen bromide was evolved. After the reaction was complete, the excess bromine and the solvent were removed by distillation at atmospheric pressure. The product distilled at 160° (82 mm.) but decomposed when an attempt was made to obtain its boiling point at atmospheric pressure. The yield of phenyltribromosilane was 6.5 g. (82%).

Anal. Calcd. for $C_6H_5SiBr_3$: Si, 8.14. Found: Si, 8.2.

Hydrolysis of Phenylsilane.—When pure, phenylsilane may be stored in glass vials for long periods of time without apparent decomposition but becomes cloudy in the presence of moisture and alkali. When phenylsilane is dissolved in ethanol and shaken with aqueous alkali, hydrogen is evolved rapidly and a white gel separates from the reaction mixture.

Summary

1. The synthesis of phenyltrichlorosilane by the action of phenyllithium upon an excess of tetrachlorosilane and the reduction of phenyltrichlorosilane to phenylsilane by lithium aluminum hydride have been described.

2. It has been found that phenylsilane in ethyl ether reacts with phenyllithium and ethyllithium to form tetraphenylsilane and phenyltriethylsilane, respectively. Ethyllithium in low boiling petroleum ether replaces only two of the three hydrogens attached to silicon in phenylsilane to form phenyldiethylsilane, a new compound.

3. When phenylsilane is interacting with the lithium ethoxide in ethanol solution, phenyltriethoxysilane is formed and hydrogen is evolved.

4. Phenylsilane reacts vigorously with bromine to form phenyltribromosilane and hydrogen bromide.

BLOOMINGTON, IND. RECEIVED MARCH 15, 1950

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[10] Corning Glass Works, U. S. Patent 2,386,452 (1945).

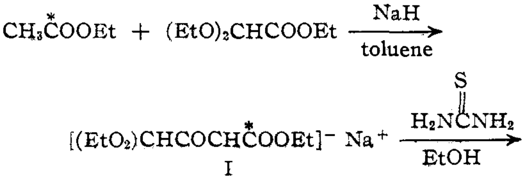
[CONTRIBUTION FROM THE McARDLE MEMORIAL LABORATORY, MEDICAL SCHOOL, UNIVERSITY OF WISCONSIN]

The Synthesis of Oxalacetic Acid-1-C^{14} and Orotic Acid-6-C^{14} [1]

BY CHARLES HEIDELBERGER AND ROBERT B. HURLBERT

Owing to the current interest in oxalacetic and orotic (uracil-4-carboxylic) acids in many biochemical problems, it appeared desirable to develop new methods for the synthesis of these compounds labeled with C^{14}. The synthesis of ethyl oxalacetate has been known for many years,[2] but the hydrolysis to oxalacetic acid results in extensive decarboxylation, and the yield obtained by the method now in common use[3] is only 9%. A new method of hydrolysis, described below, has been developed which gives consistent yields of 30–35%, and this is now the method of choice for the preparation of oxalacetic acid for enzyme studies. However, this yield was not considered high enough for use with isotopic materials, so a new synthesis based on the pyrolysis of a *t*-butyl ester[4] has been developed. Tertiary butyl acetate was prepared from sodium acetate[5] and condensed with di-*t*-butyl oxalate in the presence of potassium *t*-butoxide to give a 79% yield of di-*t*-butyl oxalacetate. This ester, when heated in benzene solution with a trace of *p*-toluenesulfonic acid, evolved isobutene and gave a 90% yield of oxalacetic acid. It is of interest to note that the oxalacetic acid obtained by this method is actually hydroxyfumaric acid, first characterized by Wohl,[6] whereas the compound obtained by the aqueous hydrolysis of the ethyl ester is in the *cis*-enol form, hydroxymaleic acid.

For the preparation of orotic acid-6-C^{14} (4-carboxyuracil-6-C^{14}), the general reaction scheme of Johnson and Schroeder[7] was adopted, but the experimental conditions were greatly modified. The reactions are



$$CH_3\overset{*}{C}OOEt + (EtO)_2CHCOOEt \xrightarrow[\text{toluene}]{\text{NaH}}$$

$$\underset{\text{I}}{[(EtO_2)CHCOCH\overset{*}{C}OOEt]^-}\ Na^+ \xrightarrow[\text{EtOH}]{H_2N\overset{\overset{\textstyle S}{\|}}{C}NH_2}$$

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[1] This work was supported in part by a grant from the Wisconsin Section of the American Cancer Society, recommended by the Committee on Growth of the National Research Council, and in part by a grant-in-aid of the National Cancer Institute.

[2] W. Wislicenus, *Ann.*, **246**, 306 (1888).

[3] R. H. Burris, in W. W. Umbreit, R. H. Burris and J. F. Stauffer, "Manometric Techniques and Tissue Metabolism," Burgess Publishing Co., Minneapolis, 1949, p. 210.

[4] D. S. Breslow, E. Baumgarten and C. R. Hauser, THIS JOURNAL, **66**, 1286 (1944).

[5] A. C. Cope, T. R. Clark and R. Conner, *Org. Syn.*, **19**, 38 (1939).

[6] A. Wohl, *Ber.*, **40**, 2282 (1907).

[7] T. B. Johnson and E. F. Schroeder, THIS JOURNAL, **53**, 1989 (1931).