[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Sulfinyl and Sulfonyl Chlorides by Chlorination[1,2]

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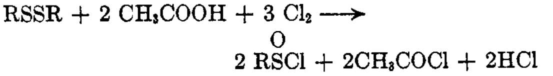
Received September 2, 1960

The critical factors in the preparation of alkanesulfinyl chlorides by the chlorination of mercaptans or disulfides in the presence of glacial acetic acid are discussed. This reaction has been extended to the preparation of alkanedisulfinyl chlorides and aromatic sulfinyl chlorides. Sulfinyl chlorides are converted to sulfonyl chlorides when treated with equimolar quantities of glacial acetic acid and chlorine.

The preparation of sulfinyl chlorides by the chlorination of disulfides or mercaptans in the presence of glacial acetic acid has been reported from this laboratory in a previous brief communication.[4] The present paper describes this reaction in greater detail and extends its application to alkanedisulfinyl chlorides, arenesulfinyl chlorides, and to the preparation of sulfinyl chlorides from alkyl thiocyanates. The observation that sulfinyl chlorides may be converted to sulfonyl chlorides when chlorinated in glacial acetic acid emphasizes the importance of stoichiometric quantities of reagents in the preparation of sulfinyl chlorides and sheds light on the mechanism of the reaction long employed for the preparation of sulfonyl chlorides.[5]

In preparing sulfinyl chlorides the mercaptan or disulfide, glacial acetic acid and chlorine should be measured as accurately as possible according to the stoichiometry of the reactions involved.

$$RSH + Cl_2 \longrightarrow RSSR + 2\,HCl \qquad (1)$$



$$RSSR + 2\,CH_3COOH + 3\,Cl_2 \longrightarrow 2\,R\overset{O}{S}Cl + 2CH_3COCl + 2HCl \qquad (2)$$

The reaction is best carried out at low temperatures (0° to −10°) to minimize the tendency for organosulfur trichlorides to decompose spontaneously with the liberation of hydrogen chloride and the introduction of a chlorine atom into the alkyl group[6] according to the equation:

$$RCH_2SCl_3 \longrightarrow RCHClSCl + HCl \qquad (3)$$

Low temperatures also decrease the escape of hydrogen chloride and the loss of reactants carried off in the gas stream.

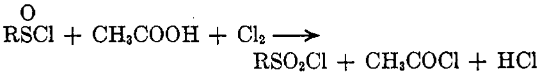
The consequences of failure to use stoichiometric quantities of reagents is apparent if one considers the stepwise nature of the reactions involved.

$$RSSR + Cl_2 \longrightarrow 2\,RSCl \qquad (4)$$

$$RSCl + Cl_2 \longrightarrow RSCl_3 \qquad (5)$$

$$RSCl_3 + CH_3COOH \longrightarrow RSOCl + CH_3COCl + HCl \qquad (6)$$

If one uses less than enough chlorine the final product will be contaminated with sulfenyl chloride and unchanged acetic acid. The use of less than the calculated amount of disulfide causes the excess chlorine and acetic acid to convert a portion of the sulfinyl chloride formed into the sulfonyl chloride according to the equation:



$$R\overset{O}{S}Cl + CH_3COOH + Cl_2 \longrightarrow RSO_2Cl + CH_3COCl + HCl \qquad (7)$$

Finally, if less than the calculated amount of acetic acid is used the cold reaction mixture will contain sulfinyl chloride, acetyl chloride, and organosulfur trichloride. As the mixture warms, the latter will decompose according to equation 3 or, if an aromatic disulfide was used, according to equation 8 and the resulting sulfinyl chloride will

$$ArSCl_3 \longrightarrow ArSCl + Cl_2 \qquad (8)$$

be contaminated with chloroalkanesulfenyl chloride or sulfenyl chloride.[6] Any liquid byproducts present in the final reaction mixture, unless their boiling points are widely separated from the desired sufinyl chloride, are difficult to remove since sulfinyl chlorides are not sufficiently stable to withstand the long-continued heating required for close fractionation.

Douglass and Poole[7] reported that 2-propanesulfinyl and 1-pentanesulfinyl chlorides, when prepared by the solvolysis of the corresponding alkylsulfur trichlorides, contained more than the theoretical amount of chlorine, probably as a result of chain substitution. This difficulty was not encountered, however, in preparing these compounds by direct chlorination of disulfides in the presence of glacial acetic acid.

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(1) Acknowledgment is made to the Petroleum Research Fund administered by the American Chemical Society and to the Office of Naval Research for support of this research.

(2) Taken in major part from a thesis submitted by Basil S. Farah in partial fulfillment of the requirements for the Ph.D. degree and in part from a Master's thesis by Evan G. Thomas.

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(4) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 330 (1958).

(5) Th. Zincke and W. Frohneberg, *Ber.*, **42**, 2721 (1909).

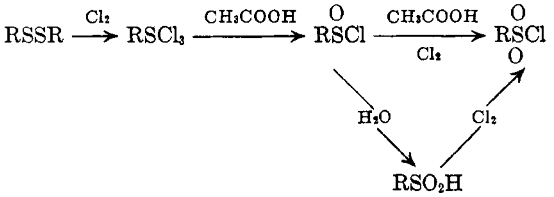
(6) I. B. Douglass, K. R. Brower, and F. T. Martin, *J. Am. Chem. Soc.*, **74**, 5770 (1952).

(7) I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).

Ethylene, trimethylene, and tetramethylene dithiols or their corresponding polydisulfides were chlorinated smoothly to give disulfinyl chlorides. Only 1,2-ethanedisulfinyl chloride could be purified sufficiently for analysis. The 1,3-propane and 1,4-butanedisulfinyl chlorides were characterized by hydrolysis in alkaline solution and conversion of the resulting sodium disulfinates into dibenzyl disulfones by reaction with benzyl chloride. In attempting to prepare 1,2-bis(benzylsulfonyl)-ethane from 1,2-ethanedisulfinyl chloride by a similar reaction, one benzylsulfonyl group was lost with the formation of 2-hydroxyethyl benzyl sulfone. This type of alkaline cleavage of certain disulfones has long been known.[8]

The observation that methanesulfinyl chloride is converted to methanesulfonyl chloride by the action of chlorine in the presence of acetic acid sheds light on the mechanism of sulfonyl chloride formation. Zincke and Frohneberg[5] converted 1,4-benzenedithiol to the disulfonyl chloride by chlorination in acetic acid and postulated the formation of the sulfur trichloride and sulfinyl chloride as intermediate stages. Although they reported carrying out the reaction in glacial acetic acid they apparently assumed that water played a role in the reaction. There seems to have been a general assumption that in sulfonyl chloride formation by this method the oxygen is furnished by water rather than acetic acid.[9]

It now seems evident that sulfonyl chlorides can be formed in one of two ways, depending on the presence or absence of water in the acetic acid. On first thought one might consider the possibility that acetic acid reacts with the sulfinyl chloride to form acetyl chloride and the sulfinic acid, followed by chlorination of the latter. Acetic acid and methanesulfinyl chloride can be recovered unchanged, however, after being mixed and allowed to stand overnight at room temperature. We have also considered the possibility that the sulfinyl chloride, by expansion of its sulfur valence shell, may form an addition complex, $\overset{\mathrm{O}}{\mathrm{RSCl_3}}$, which then undergoes solvolysis. We could find no visible evidence, however, for such a complex when chlorine was passed into methanesulfinyl chloride at low temperature.



Benzyl disulfide, as previously shown by Stirling,[10] can be chlorinated in nonhydroxylated solvent to α-toluenesulfenyl chloride and benzylsulfur trichloride. The latter compound appears to decompose spontaneously to benzyl chloride and sulfur dichloride. When benzyl disulfide is chlorinated in the presence of glacial acetic acid there is evidence for the formation of some α-toluenesulfinyl chloride and also for simultaneous formation of benzyl chloride. Similarly when glacial acetic acid was added to solid benzylsulfur trichloride both α-toluenesulfinyl chloride and benzyl chloride were formed.

The chlorination of methyl and ethyl thiocyanates in the presence of glacial acetic acid produced relatively small yields of sulfinyl chlorides.

EXPERIMENTAL

The preparation of methanesulfinyl chloride. In a 500-ml., three-necked flask, fitted with an efficient sealed stirrer, a gas inlet tube extending within one inch of the reaction mixture but not below its surface, and a gas outlet tube leading through a trap cooled in a Dry Ice-acetone bath to a hydrogen chloride absorption system were placed 47.1 g. (0.5 mole) of methyl disulfide and 60.1 g. (1.0 mole) of glacial acetic acid. The reaction flask was then surrounded by a bath of acetone cooled by Dry Ice until the internal temperature has reached 0° to −10°. The temperature was maintained as closely as possible within these limits throughout the reaction except that toward the end, the temperature should be kept −10° to −15° to minimize the escape of hydrogen chloride which might carry with it unchanged chlorine. The entire reaction is best carried out in a well ventilated hood.

Chlorine (106.4 g., 1.5 mole) was condensed in a tared flask cooled by a Dry Ice-acetone bath. (The flask should be full of chlorine gas when the tare weight is taken.) This flask was then connected to the gas inlet tube of the chlorination apparatus and the cooling bath surrounding the chlorine container was removed. After 1–2 hr. the chlorine had all been absorbed by the reaction mixture with a progressive change from colorless to reddish orange to a final golden yellow or light straw color.

When the last of the chlorine had been added, any solid methylsulfur trichloride inside the flask was washed down, the cooling bath was removed, and, while continuing vigorous stirring, the reaction mixture was allowed slowly to warm to room temperature. During this period there is a vigorous evolution of hydrogen chloride. The flask was finally warmed to 35° to facilitate the escape of more hydrogen chloride.

The reaction mixture and contents of the cold trap were then transferred to a 250-ml. distilling flask attached through a short fractionating column to a water cooled condenser which, in turn, was connected in series to a receiver, a trap cooled in a Dry Ice–acetone bath, and a hydrogen chloride absorption trap which may later be attached to a water pump. The mixture was then distilled until the pot temperature reached 100° and practically all of the acetyl chloride had been driven over. The residue, consisting chiefly of methanesulfinyl chloride, was then cooled immediately to 20° or lower and transferred to a smaller flask and distilled through the same equipment under reduced pressure to remove the remaining acetyl chloride and other lower boiling impurities. As the pot temperature began to rise a yellow intermediate fraction was collected very slowly until the distillate and pot temperatures were within 3° of each other. At this point the distillation was temporarily discontinued while the accumulated acetyl chloride in the cold trap was removed and the receiver for the main product

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[8] E. Stuffer, *Ber.*, **23**, 1408 (1890).

[9] C. M. Suter, *The Organic Chemistry of Sulfur*, John Wiley & Sons, Inc., New York, N.Y., 1944, p. 461.

[10] C. J. M. Stirling, *J. Chem. Soc.*, 3597 (1957).

TABLE I

SULFINYL CHLORIDES

Sulfinyl Chloride O RSCl R—	Yield, %	B.P.	n_D^{25}	d_4^0	d_D^{25}	Neut. Equiv. Calcd.	Neut. Equiv. Found	Calcd. Cl, %	Found Cl, %
$(CH_3)_2CH$—	81	64 (17 mm.)	1.4862	1.2478	1.2198	63.3	62.4	28.03	27.79
n-C_5H_{11}	90	86 (6 mm.)	1.4822	1.1301	1.1056	77.3	75.9	22.92	23.02
C_6H_5—	90	71–72(1.5 mm.)	1.6062	1.3570	1.3469			22.08	22.22

was attached. On resuming distillation the main product should come over within a 5° boiling range[11] and the distillation and pot temperatures should remain within 2° of each other until the major part of the product has distilled. The yield was 80–88 g. (82–92%) of straw-colored or yellow product boiling 55–59° (40 mm.) and having n_D^{25} 1.500–1.501. Redistillation yielded a purified product having the properties shown in Table I. We have not found it profitable to attempt recovery of the small amount of sulfinyl chloride carried over in the acetyl chloride fraction. The yield of impure acetyl chloride is 60–80%.

This procedure, with only minor variations, was used in the preparation of several different sulfinyl chlorides. The yields and physical properties obtained for methane-, ethane-, n-propane-, and n-butanesulfinyl chlorides were practically identical with those already reported.[6] With 2-propane-, 1-pentane-, and benzenesulfinyl chlorides improved results were obtained as shown in Table I.

4-Chlorobenzenesulfinyl chloride was prepared by the same procedure but the oil which remained, after removing under vacuum all products volatile at room temperature, decomposed on attempted distillation. A sample of the pale yellow oil, however, showed infrared absorption at 1155 cm.$^{-1}$[12] and upon hydrolysis was converted to 4-chlorobenzenesulfinic acid melting at 92–93°, previously reported by Krishna and Sing[13] as melting at 93–94°.

The sulfinic acid was further characterized by conversion to the benzyl sulfone by refluxing its alkaline solution with benzyl chloride. 4-Chlorophenyl benzyl sulfone, melted at 173–174°.

Anal. Calcd. for $C_{13}H_{11}ClO_2S$: C, 58.53: H, 4.16; S, 12.02; Cl, 13.29. Found: C, 58.08; H, 4.13; S, 11.90; Cl, 13.58.

1,2-Ethanedisulfinyl chloride. Fourteen grams (0.15 mole) of 1,2-ethanedithiol dissolved in 25 ml. of methylene chloride and treated with 10.6 g. (0.15 mole) of chlorine gave a white polymeric material insoluble in most organic solvents and exhibiting a wide melting point range near 125°. A suspension of 4.6 g. of the polymer, presumably $(SCH_2CH_2S)_x$, in 30 ml. of methylene chloride upon treatment with 6.0 g. of glacial acetic acid and 10.6 g. of chlorine gave a faintly yellow solution. After removal of the solvent at low temperature, there remained a white solid, 1,2-ethanedisulfinyl chloride, melting at 62.5–63.5 after recrystallization from a methylene chloride–petroleum ether (b.p. 00–00°) mixture. The compound fumed in moist air and had the odor of other sulfinyl chlorides. It showed strong infrared absorption at 1155 cm.$^{-1}$

Anal. Calcd. for $C_2H_4Cl_2O_2S_2$: Cl, 36.35; Neut. equiv.; 48.8. Found: Cl, 36.05; Neut. equiv.: 48.3.

A sample of the sulfinyl chloride was hydrolyzed and the silver salt of the resulting 1,2-ethanedisulfinic acid was warmed with methyl iodide and converted to 1,2-bis(methylsulfonyl)ethane which melted at 195–196° after recrystallization from water. The melting point was unchanged when the product was mixed with a sample prepared by the oxidation of 2,5-dithiahexane.

A 6.0-g. sample of 1,2-ethanedisulfinyl chloride was hydrolyzed in excess saturated sodium bicarbonate solution and refluxed for several hours with 8.0 g. of benzyl chloride. The only product which separated on cooling the mixture was dibenzyl sulfone. On treating the filtrate with 5.0 g. benzoyl chloride and excess sodium hydroxide 2-benzylsulfonylethyl benzoate, $C_6H_5CH_2SO_2CH_2CH_2OCOC_6H_5$ separated. Recrystallization from alcohol gave a product melting at 115–116° and unchanged when mixed with an authentic sample prepared by oxidizing 2-benzylsulfidoethyl benzoate.

1,3-Propanedisulfinyl chloride was prepared in a similar manner from 1,3-propanedithiol. The sulfinyl chloride could not be purified, however, and was characterized by conversion to 1,3-bis(benzylsulfonyl)propane by hydrolyzing in sodium bicarbonate and refluxing with benzyl chloride. The disulfone melted at 208° both alone and when mixed with an authentic sample prepared by the method of Autenrieth and Wolf.[14] The latter workers, however, reported a melting point of 189°.

Anal. Calcd. for $C_{17}H_{20}O_4S_2$: C, 57.85; H, 5.72; S, 18.19. Found: C, 58.30; H, 5.51; S, 18.10.

1,4-Butanedisulfinyl chloride. The chlorination of 1,4-butanedithiol with 1 molar equivalent of chlorine gave an oil which solidified to a solid melting at 30–32°. The latter, 6.0 g. (0.05 mole), 21.5 g. of chlorine (0.30 mole) and 6.0 g. of glacial acetic acid (0.10 mole) gave 11.0 g. of an undistillable oil. A portion of the oil upon alkaline hydrolysis and refluxing with benzyl chloride gave 1,4-bis(benzylsulfonyl)-butane melting at 198°. The melting point was not lowered when the compound was mixed with the product obtained by oxidizing 1,8-diphenyl-2,7-dithiaoctane.

Anal. Calcd. for $C_{18}H_{22}O_4S_2$: C, 58.99; H, 6.05; S, 17.50. Found: C, 58.70; H, 5.94; S, 17.50.

Sulfinyl chlorides from alkyl thiocyanates. Chlorination of 21.75 g. (0.25 mole) of freshly prepared ethyl thiocyanate in 15.0 g. (0.25 mole) of glacial acetic acid yielded 11.4. g. (41%) of ethanesulfinyl chloride. Similar treatment of 15 g. methyl thiocyanate gave only 7.0 g. (35% yield) of methane sulfinyl chloride.

Methanesulfonyl chloride from methyl disulfide. A solution of 49.0 g. (0.5 mole) of methyl disulfide in 120 g. (2.0 moles) of glacial acetic acid was treated with 185 g. (2.6 moles) of chlorine in the manner described for preparing methanesulfinyl chloride. As the reaction progressed the temperature was lowered until the last of the chlorine was added at −40°. The reaction mixture was then allowed to stir while bath and reaction flask slowly came to room temperature. After standing overnight the mixture was distilled and yielded 71 g. (45% yield) of acetyl chloride and 94 g. (82% yield)

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[11] The lower boiling impurities are believed to be methanesulfenyl chloride, chloromethanesulfenyl chloride, and acetic acid. Those boiling higher than the principal product are methanesulfonyl chloride (b.p. 63°/20 mm., 72°/31 mm., 82°/48 mm.) and methyl methanethiolsulfonate (b.p. 115°/15 mm.) Unless these impurities are kept to a minimum through the use of stoichiometric quantities of reactants, the close boiling ranges described cannot be attained.

[12] S. Detoni and D. Hadzi, *J. Chem. Soc.*, 1955, 3163.

[13] S. Krishna and H. Sing, *J. Am. Chem. Soc.*, **50**, 792 (1928).

[14] W. Autenrieth and K. Wolf, *Ber.*, **32**, 1368 (1899).

of methanesulfonyl chloride boiling at 56° (12 mm.) and having n^{20}_{D} 1.4458. The product formed an anilide melting at 98–99° both alone and when mixed with an authentic sample.

Other sulfonyl chlorides from disulfides. In a similar manner 30.0 g. (0.25 mole) of ethyl disulfide upon treatment with 60.0 g. (1.0 mole) of glacial acetic acid and 92.5 g. (1.3 moles) of chlorine yielded 52.6 g. (82% yield) of ethanesulfonyl chloride boiling at 63–65° (14–15 mm.) and having n^{25}_{D} 1.4518. It formed a *p*-toluidide melting at 80–81° and at the same temperature when mixed with a known sample.

Likewise 10.9 g. (0.05 mole) of phenyl disulfide was dissolved in 30 ml. of methylene chloride and 12.2 g. (0.2 mole) of glacial acetic acid and treated with 19.0 g. (0.27 mole) of chlorine. After standing overnight the mixture was distilled and yielded 14.4 g. of colorless benzenesulfonyl chloride boiling at 115–116° (10 mm.). The product formed an anilide melting at 110° and unchanged when mixed with a pure sample of pure benzenesulfonanilide.

Sulfonyl chlorides from sulfinyl chlorides. A mixture of 29.6 g. (0.3 mole) of methanesulfinyl chloride and 20 g. (0.33 mole) of glacial acetic acid was treated with 22 g. (0.31 mole) of anhydrous chlorine at about −30° in the manner described. On distilling the mixture there was obtained 10.7 g. (47% yield) of acetyl chloride and 26.7 g. (78% yield) of methanesulfonyl chloride boiling at 52–55° (14 mm.) and having n^{25}_{D} 1.4450. The latter formed a *p*-toluidide melting at 103–104° and unchanged when mixed with a pure sample.

In the same way, ethanesulfinyl chloride (11.2 g., 0.1 mole) was treated with 0.1 mole of acetic acid and 0.1 mole of chlorine and yielded 10.4 g. (81% yield), of ethanesulfonyl chloride boiling at 80–81° (28 mm.) and having n^{25}_{D} 1.4514. Its *p*-toluidide was identical with that obtained from other preparations.

To shed light on the mechanism of the above reactions 29.3 g. (0.3 mole) of methanesulfinyl chloride and 20.0 g. (0.31 mole) of glacial acetic acid were mixed and allowed to stand overnight. Distillation of the mixture at reduced pressure gave 14.6 g. (73% recovery) of acetic acid and 26.8 g. (91% recovery) of methanesulfinyl chloride indicating that no appreciable chlorine interchange had occurred. A similar experiment with acetic acid and ethanesulfinyl chloride resulted in the recovery of 83 and 89%, respectively, of the starting materials.

To determine whether a chlorine-sulfinyl chloride complex might be formed as an intermediate, 10 g. of methanesulfinyl chloride in 25 ml. of methylene chloride was cooled to −70° in a Dry Ice–ether bath and treated with anhydrous chlorine for 30 min. When no change other than the condensation of liquid chlorine appeared to take place, the chlorination was discontinued and the reaction mixture was allowed to warm to room temperature under continuous observation. No change was observed and distillation of the mixture gave a nearly quantitative recovery of the methanesulfinyl chloride.

The chlorination of benzyl disulfide. Benzyl disulfide was chlorinated in methylene chloride to form α-toluenesulfenyl chloride which reacted with ethylene to form an 80% yield of 2-chloroethyl benzyl sulfide (b.p. 137–140° at 6–7 mm.). The sulfide was oxidized by 30% hydrogen peroxide to the sulfone (m.p. 94–95°) and treated with aqueous Chloramine-T to form the sulfilimine (m.p. 133–134°), thus confirming the observations of Stirling.[9]

On treating a solution of 6.2 g. (0.025 mole) of benzyl disulfide in 25 ml. of methylene chloride at −70° with 5.5 g. (0.075 mole) of chlorine a white crystalline product, presumably benzylsulfur trichloride, precipitated. This product decomposed at too low a temperature to permit analysis. Benzyl chloride and sulfur dichloride were found in the decomposition products.

The white solid obtained as described above from 6.2 g. of benzyl disulfide was treated with 3.0 g. of glacial acetic acid. The resulting orange solution was treated with 10% sodium bicarbonate and extracted with ether. From the ether solution 3.0 g. of benzyl chloride was isolated. The alkaline aqueous layer was refluxed with benzyl chloride and yielded dibenzyl sulfone suggesting that α-toluenesulfinyl chloride had also been formed in the acetolysis.

A solution of 12.3 g. (0.05 mole) of benzyl disulfide in 6.0 g. of acetic acid and 25 ml. of methylene chloride was treated with 11.0 g. (0.15 mole) of chlorine at −40°. After warming to room temperature dry nitrogen was passed through the mixture for several hours. The resulting liquid showed strong infrared absorption at 1158 cm.$^{-1}$ indicating the presence of a sulfinyl chloride. Treatment of the liquid with 10% sodium bicarbonate led to the isolation of benzyl chloride and refluxing of the alkaline solution with benzyl chloride produced a 52% yield of dibenzyl sulfone.

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The Reactions of Two Homocyclic Organosilicon Compounds with Organometallic and Organosilylmetallic Reagents

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Received August 31, 1960

Octaphenylcyclotetrasilane and dodecaphenylcyclohexasilane were treated with phenyllithium, phenylmagnesium bromide, and triphenylsilyllithium. It was found that dodecaphenylcyclohexasilane was more resistant to the silicon-silicon cleavage attack by these reagents than was octaphenylcyclotetrasilane.

A considerable amount of work has been done on the cleavage by organometallic reagents of the silicon-silicon bond in open-chain polysilanes. The first reported study is that of Friedel and Ladenburg[1–3] who found that the reaction of diethylzinc with hexaiododisilane gave tetraethylsilane in addition to the expected hexaethyldisilane. Later, Schumb, *et. al.* showed[4] that hexasubstituted disilanes could not be prepared by

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[1] C. Friedel and A. Ladenburg, *Compt. rend.*, **68**, 923 (1869).

[2] C. Friedel and A. Ladenburg, *Ann.*, **203**, 251 (1880).

[3] C. Friedel and A. Ladenburg, *Ann. Chim. Phys.* [5], 19, 401 (1880).

[4] W. C. Schumb, J. Ackerman, and C. M. Saffer, *J. Am. Chem. Soc.*, **60**, 2486 (1938).