*Anal.* Calcd. for $C_8H_{17}Cl_2N_2O_3PS$: C, 29.73; H, 5.30. Found: C, 29.50; H, 5.25.

The yellow **dipicrate** crystallized from 95% ethanol and melted at 230° (dec.) after sintering at 216–230°.

*Anal.* Calcd. for $C_{20}H_{21}N_8O_{17}PS$: N, 15.82. Found: N, 16.08.

**Diethyl 4-Methylthiazole-5-phosphonate.**—A solution of 7.8 g. (0.128 mole) of purified thioformamide[15] in 25 ml. of 95% ethanol was added dropwise to a stirred and refluxing solution of 35 g. of diethyl acetylbromomethanephosphonate in 50 ml. of 95% ethanol which was prepared as described above. After four hours stirring and refluxing another gram of thioformamide was added and refluxing was continued for 30 minutes. The mixture was worked up in a manner analogous to that described in the preceding experiment. The dark oily ester was chromatographed in benzene solution over alumina and purified by extraction into dilute acid and re-basification. Since it decomposed on distillation even under highly reduced pressure, and gave an extremely hygroscopic hydrochloride, it was characterized as the **picrate** which sintered at 173°, m.p. 178–183° (dec.).

*Anal.* Calcd. for $C_{14}H_{17}N_4O_{10}PS$: C, 36.21; H, 3.69; N, 12.07. Found: C, 36.64; H, 2.28; N, 12.31.

CHARLOTTESVILLE, VA.

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[15] We are grateful to Dr. Karl Pierson of the Stonewall Plant, Merck and Company, Inc., for the thioformamide used in this study.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

# The Reaction of Sodium with Organosilanes at Elevated Temperatures

BY ROBERT A. BENKESER AND DONALD J. FOSTER

RECEIVED APRIL 2, 1952

The reaction of sodium with phenylsilanes of the type $Ph_xSiCl_{4-x}$, $Ph_xSiH_{4-x}$ and $Ph_xMe_ySiH_{4-(x+y)}$ at elevated temperatures was investigated. These compounds appeared to disproportionate into more highly phenylated silanes and dephenylated products. This can be explained by the intermediate formation of phenylsodium arising through a cleavage of phenyl groups from the silane by the alkali metal. The phenylsodium then reacts with more silane to give the highly phenylated compounds. As a consequence of the phenylsodium formation, decalin and heptadecane are to be preferred as solvents for these reactions rather than toluene. The latter is converted to benzylsodium which reacts to form benzylsilanes and thus needlessly complicates the purification of the products. The methylphenylsilanes ($Ph_xMe_ySiH_{4-(x+y)}$) suffer loss of the phenyl groups rather than methyls, indicating the preferential cleavage by sodium of aryl, rather than alkyl groups. However, tribenzylsilane undergoes reaction with sodium despite its aliphatic characteristics. A high speed stirring apparatus was highly advantageous in increasing yields and decreasing the reaction time of these heterogeneous cleavage reactions.

In a recent publication[1] from this Laboratory, it was reported that triphenylsilane reacts with sodium–potassium alloy (1:5 by weight) in ether at room temperature to give triphenylsilylpotassium; whereas, under the same conditions, diphenylsilane and phenylsilane form tetraphenylsilane. These reactions can be summarized as

$$(C_6H_5)_3SiH + Na/K \xrightarrow{Et_2O} (C_6H_5)_3SiK + KH$$

$$(C_6H_5)_2SiH_2 + Na/K \xrightarrow[(2)\ H^+,\ H_2O]{(1)\ Et_2O} (C_6H_5)_4Si + \text{silicic material}$$

$$C_6H_5SiH_3 + Na/K \xrightarrow[(2)\ H^+,\ H_2O]{(1)\ Et_2O} (C_6H_5)_4Si + \text{silicic material}$$

The presence of triphenylsilylpotassium has been established by various coupling, reduction and hydrolysis reactions.[1-3] The formation of tetraphenylsilane from diphenylsilane or phenylsilane was visualized as follows: A primary cleavage of the silane by alloy is followed by reaction of the arylmetal compound with unreacted silane.

$$(C_6H_5)_2SiH_2 + Na/K \xrightarrow{Et_2O} C_6H_5SiH_2K + C_6H_5K$$
$$(C_6H_5)_2SiH_2 + 2C_6H_5K \longrightarrow (C_6H_5)_4Si + 2KH$$

and

$$C_6H_6SiH_3 + Na/K \xrightarrow{Et_2O} H_3SiK + C_6H_5K$$
$$C_6H_6SiH_3 + 3C_6H_5K \longrightarrow (C_6H_5)_4Si + 3KH$$

Recently, in an attempt to prepare triphenylsilylsodium from triphenylsilane and sodium, it was found that no reaction occurred until higher temperatures were obtained and then, *only* when traces of potassium were present. When toluene was used as a solvent, the products, after acid hydrolysis, were tetraphenylsilane, triphenylbenzylsilane and a silica-like material. These products can be explained if one assumes the intermediate formation of phenylsodium, resulting from a cleavage of phenyl groups by the alkali metal.

$$(C_6H_5)_3SiH \xrightarrow{Na} (C_6H_5)_2SiHNa + C_6H_5Na \xrightarrow{Na}$$
$$C_6H_5SiHNa_2 + 2C_6H_5Na \xrightarrow{Na} SiHNa_3 + 3C_6H_5Na$$

The phenylsodium thus produced can react with both triphenylsilane[4] to form tetraphenylsilane

$$(C_6H_5)_3SiH + C_6H_5Na \longrightarrow (C_6H_5)_4Si + NaH$$

and also with toluene[5] to form benzylsodium.

$$C_6H_5Na + C_6H_5CH_3 \longrightarrow C_6H_5CH_2Na + C_6H_6$$

The benzylsodium in turn is then capable of reacting with triphenylsilane to form triphenylbenzylsilane.

$$(C_6H_5)_3SiH + C_6H_5CH_2Na \longrightarrow (C_6H_5)_3SiCH_2C_6H_5 + NaH$$

The insoluble, infusible powder obtained in this reaction could have arisen from the hydrolysis of the dephenylated silicon atoms. Undoubtedly, this material was not pure $SiO_2$ but contained some silicon atoms that carried phenyl groups. How-

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[1] R. A. Benkeser and D. J. Foster, THIS JOURNAL, **74**, 4200 (1952).

[2] R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

[3] R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952).

[4] Unpublished studies at this Laboratory have shown that compounds of type $(C_6H_5)_xSiH_y$ react with phenylsodium, quantitatively, at temperatures as low as 50°.

[5] V. L. Hansley, *Ind. Eng. Chem.*, **43**, 1759 (1951).

ever, to account for the yield of products, one must assume that practically all the phenyl groups were removed from the silane molecules undergoing cleavage. The formation of benzyltriphenylsilane was eliminated, and the yield of tetraphenylsilane correspondingly increased, when an inert solvent such as decalin or heptadecane was used.

We have prepared phenylsodium in decalin from chlorobenzene and sodium dispersion in 93% yield thus proving that this solvent did not react with the phenylsodium formed during the cleavage reactions. Phenylsodium was also prepared in pure heptadecane in good yield.

In most of the experiments described herein decalin was used as a solvent because the higher molecular weight hydrocarbons like heptadecane, which are commercially available, often contain large quantities of olefins that are difficult to remove, and which react with the phenylsodium produced in the cleavages.

The reaction described above for triphenylsilane was not limited to aryl group cleavage, however, since tribenzylsilane reacted under the same conditions to give tetrabenzylsilane.

$$(C_6H_5CH_2)_3SiH + Na \xrightarrow{\text{decalin}} (C_6H_5CH_2)_4Si$$

It can be assumed that dibenzylsilane and benzylsilane would react similarly, both by analogy with the phenylsilanes, and by comparison with results observed by Steele and Kipping.[6] These workers observed that the benzylchlorosilanes $(C_6H_5CH_2)_xSiCl_{4-x}$ react with sodium in toluene to form tetrabenzylsilane in all cases.

**Diphenylsilane and Phenylsilane.**—Diphenylsilane and sodium when heated in decalin gave rise to triphenylsilane and tetraphenylsilane. The formation of triphenylsilane in this reaction indicated the step-wise addition of phenylsodium to diphenylsilane. This point was further brought out by the fact that it was possible to isolate diphenylsilane, triphenylsilane and tetraphenylsilane from the reaction of phenylsilane and sodium in decalin.

$$(C_6H_5)_2SiH_2 \xrightarrow[\text{decalin}]{\text{Na/K}} (C_6H_5)_3SiH + (C_6H_5)_4Si + \text{silicic material}$$

$$C_6H_5SiH_3 \xrightarrow[\text{decalin}]{\text{Na/K}} (C_6H_5)_2SiH_2 + (C_6H_5)_3SiH + (C_6H_5)_4Si + \text{silicic material}$$

**$R_xR'_{4-x}Si$ Compounds.**—Tetra-substituted silanes, such as tetraphenylsilane, triphenylmethylsilane, diphenyldimethylsilane and phenyltrimethylsilane, were found not to react with sodium in refluxing decalin or heptadecane.

**Diphenylmethylsilane and Dimethylphenylsilane.**—Diphenylmethylsilane and phenyldimethylsilane were treated with sodium to see if there was a preferential cleavage of aryl groups as compared to the alkyl groups. With diphenylmethylsilane one of the products of the reaction would have been diphenyldimethylsilane if there had been any alkyl group cleavage, whereas, if the aryl group was preferentially cleaved, the main product should be triphenylmethylsilane. An excellent yield of triphenylmethylsilane was obtained and there was no evidence for the formation of diphenyldimethylsilane. In a similar fashion, if there had been alkyl group cleavage in the case of phenyldimethylsilane, the main product of the reaction would have been phenyltrimethylsilane whereas the product was diphenyldimethylsilane, with no evidence for the formation of phenyltrimethylsilane.

$$(C_6H_5)_2Si(CH_3)H \xrightarrow[\text{decalin}]{\text{Na/K}} (C_6H_5)_3SiMe$$

$$C_6H_5Si(CH_3)_2H \xrightarrow[\text{decalin}]{\text{Na/K}} (C_6H_5)_2SiMe_2$$

**Chlorosilanes.**—Kipping and co-workers studied quite extensively the reaction of various chlorosilanes with sodium.[7] In the case of phenyltrichlorosilane, using toluene and xylene as solvents, they found < 3% of the phenyl groups in the form of tetraphenylsilane. With diphenyldichlorosilane they obtained tetraphenylsilane only after destructive distillation of one of their "glue-like" products. They thus claimed that tetraphenylsilane was not formed initially in the reaction, but was produced by the "cracking" of a more complex product during the distillation.[7d]

The choice of solvent used by these workers seemed poor to us, since phenylsodium (which they also postulated as an intermediate) reacts with toluene and xylene. In the hope of simplifying these reactions we repeated them using decalin as a solvent and obtained respectable yields of tetraphenylsilane from all the phenylchlorosilanes *without* the necessity of destructive distillation. The remainder of the amorphous product seemed to be polymeric material containing some dephenylated silicon groupings. In no case were the "glue-like" products observed which Kipping reported. Obviously one must draw conclusions from these results with caution since our reactions differ from Kipping's in *both* solvent and reaction temperature. Nonetheless it would seem that Kipping's problem of product identification was complicated by mixtures containing the benzyl and xylenyl groups.

Of further interest was our observation that in the preparation of hexaphenyldisilane from triphenylchlorosilane and sodium recently reported,[8] tetraphenylsilane was formed as a side-product. This necessitated recrystallizing the hexaphenyldisilane (a modification of the published procedure) since the polymeric silicon fragments were contaminating the final product. It is possible that it was these refractory materials which raised[8] the melting point of the disilane above the previously reported value of 354°.[9] A sample of disilane which had been first recrystallized from xylene and then sublimed we found to melt at 352° (uncor.).

**Rate of Stirring.**—A high speed stirring apparatus, consisting of a "Duplex Dispersator" head and a Morton-type flask, was found highly advantageous in increasing yields and decreasing the reaction time of these heterogeneous cleavage reactions.

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(6) A. R. Steele and F. S. Kipping, *J. Chem. Soc.*, 1431 (1928).

(7) (a) F. S. Kipping, *ibid.*, **123**, 2590 (1921); (b) F. S. Kipping and J. E. Sands, *ibid.*, **119**, 830 (1921); (c) F. S. Kipping, *ibid.*, **125**, 2291 (1924); (d) F. S. Kipping and A. G. Murray, *ibid.*, 360 (1929); (e) F. S. Kipping and J. F. Short, *ibid.*, 1029 (1930).

(8) H. Gilman and G. E. Dunn, THIS JOURNAL, **73**, 5077 (1951).

(9) W. Schlenk, J. Renning and G. Rackey, *Ber.*, **44**, 1178 (1911).

A Haskins motor, rated at a top speed of 18,000 r.p.m., was used to power the dispersator head.

## Experimental

**Reaction of Triphenylsilane with** Sodium.—Thirteen grams (0.05 mole) of triphenylsilane was heated in a nitrogen atmosphere to reflux and stirred vigorously with 5.4 g. (0.23 g. atom) of sodium and 0.02 g. of potassium in 250 ml. of anhydrous toluene for a total of 24 hours. The refluxing mixture slowly acquired a dark brown color. After cooling, 6 *N* hydrochloric acid was added to destroy the excess metal and the resulting layers were separated. The organic layer was dried over anhydrous sodium sulfate and then the toluene removed. A solid was deposited on removal of the solvent which, after recrystallization from xylene, gave 3.2 g. of tetraphenylsilane (mixed m.p.).

*Anal.* Calcd. for $C_{24}H_{22}Si$: Si, 8.33. Found: Si, 8.3.

The residual oil was distilled under reduced pressure and there was obtained 8.3 g. of material boiling up to 200° (0.15 mm.). This distillate solidified on standing and after fractionation from ethanol and then petroleum ether (90–100°) there was obtained 0.3 g. of tetraphenylsilane and 7.6 g. of material melting 97.5–98°. This material did not depress the melting point of an authentic sample of benzyltriphenylsilane prepared from triphenylchlorosilane and benzylmagnesium bromide.

*Anal.* Calcd. for $C_{25}H_{22}Si$: Si, 8.0. Found: Si, 7.9.

Using heptadecane as the solvent under the same conditions, led to the formation of 9.8 g. of tetraphenylsilane and several grams of an amorphous, infusible material containing 27–28% silicon. If decalin was used as the solvent, 8.1 g. of tetraphenylsilane was obtained along with several grams of an infusible material containing 25–26% silicon. The absence of a trace of potassium led to the recovery of 85% of starting material.

**Reaction of Tribenzylsilane with** Sodium.—Tribenzylsilane was prepared by the addition of 13.6 g. (0.1 mole) of trichlorosilane in 30 ml. of anhydrous ethyl ether to an ether solution of benzylmagnesium chloride, prepared from 63 g. (0.5 mole) of benzyl chloride and 12 g. (0.5 g. atom) of magnesium in 200 ml. of anhydrous ethyl ether. After hydrolysis and isolation, the product was recrystallized from petroleum ether (60–70°). There was obtained 26.5 g. (88%) of a solid melting 91.5–92°.[10]

Fifteen and two-tenths grams (0.05 mole) of tribenzylsilane was heated under reflux and stirred at 10,000 r.p.m. for a total of 90 minutes out of a 3-hour period with 5.4 g. (0.23 g. atom) of sodium and 0.02 g. of potassium in 200 ml. of decalin in a Morton-type flask under a nitrogen atmosphere. The product was worked up in the usual manner and there was obtained 8.6 g. of tetrabenzylsilane melting 127–128°[10] along with 2 g. of an oil which resisted crystallization and identification.

**Reaction of Diphenylsilane with** Sodium.—Nine and two-tenths grams (0.05 mole) of diphenylsilane,[3] 5.4 g. (0.23 g. atom) of sodium, 0.02 g. of potassium and 200 ml. of purified decalin were heated and stirred in the previously described manner. From the acid-hydrolyzed reaction mixture there was obtained 1 g. of an infusible, amorphous powder containing 26% silicon, 2.2 g. of triphenylsilane (mixed m.p. 46°) and 2.3 g. of tetraphenylsilane (mixed m.p.).

*Anal.* Calcd. for $C_{18}H_{16}Si$: Si, 10.77. Found: Si, 10.7.

**Reaction of Phenylsilane and** Sodium.—Ten and eight-tenths grams of phenylsilane,[3] 16.2 g. (0.69 g. atom) of sodium and 0.02 g. of potassium in 200 ml. of purified decalin were heated and stirred in the previously described manner. Acid hydrolysis of the reaction mixture led to the isolation of 0.6 g. of phenylsilane (b.p. 117–119°, $n^{20}\mathrm{D}$ 1.5130), 1.2 g. of diphenylsilane (b.p. 76–77° (0.3 mm.), $n^{20}\mathrm{D}$ 1.5790), 0.5 g. of triphenylsilane (mixed m.p. 46°), 2.6 g. of tetraphenylsilane (mixed m.p.) and a small amount of an infusible powder containing 35–38% silicon.

**Diphenyldimethylsilane.**—Phenyllithium, prepared from 94.2 g. (0.6 mole) of bromobenzene and 8.4 g. (1.2 g. atom) of lithium in 300 ml. of anhydrous ethyl ether, was added dropwise to 36 g. (0.28 mole) of dimethyldichlorosilane dissolved in 100 ml. of anhydrous ethyl ether. After the addition was complete, the reaction mixture was heated under reflux for 3 hours and then cooled. Water was added to destroy the excess phenyllithium and dissolve the inorganic salts. The ether layer was separated and dried before the ether was removed by distillation. Distillation of the residue at reduced pressure yielded 52 g. (86%) of colorless liquid boiling 89° (0.2 mm.),[11] $n^{20}\mathrm{D}$ 1.5649, $d^{20}_4$ 0.9924; *MR* calcd. 69.92, found 69.6.

*Anal.* Calcd. for $C_{14}H_{16}Si$: Si, 13.21. Found: Si, 13.0.

The tetraalkyl or arylsilanes, tetraphenylsilane, triphenylmethylsilane,[12] diphenyldimethylsilane and phenyltrimethylsilane[13] resisted attack by sodium under the previously described conditions and were recovered in yields of 96, 88, 83 and 91%, respectively, from the reaction mixtures.

**Diphenylmethylsilane.**—Phenylmagnesium bromide prepared from 157 g. (1 mole) of bromobenzene and 26.4 g. (1.1 g. atoms) of magnesium metal in 350 ml. of anhydrous ethyl ether was added dropwise to 63 g. (0.42 mole) of methyltrichlorosilane. After the addition was complete, the reaction mixture was heated under reflux for 2 hours before the ether solution was filtered free of the magnesium salts by the use of nitrogen pressure. The ether solution of diphenylmethylchlorosilane was then added dropwise to 7.6 g. (0.21 mole) of lithium aluminum hydride partially dissolved in 200 ml. of anhydrous ethyl ether. The reaction mixture was heated to reflux for 2 hours after the addition of the chlorosilane. To the cooled reaction flask immersed in an ice-bath was added sufficient 8 *N* hydrochloric acid to completely destroy all the excess lithium aluminum hydride and dissolve the salts that were formed. The ether layer was separated and dried over anhydrous sodium sulfate before the solvent was removed by distillation. That portion of the residue (74 g.) boiling at 70–90° (0.1 mm.) was collected. Redistillation of this material gave 64.2 g. (78%) of material boiling at 82° (0.15 mm.), $n^{20}\mathrm{D}$ 1.5747, $d^{20}_4$ 0.9973; *MR* calcd. 65.55, found 65.58. This material evolved hydrogen when added to wet piperidine.

*Anal.* Calcd. for $C_{13}H_{14}Si$: Si, 14.14. Found: Si, 13.6, 14.0.

When 19.8 g. (0.1 mole) of diphenylmethylsilane, 10.8 g. (0.46 g. atom) of sodium, 0.02 g. of potassium and 200 ml. of decalin were treated under the previously described conditions and hydrolyzed with acid, there was isolated 5 g. (25%) of diphenylmethylsilane (b.p. 80–84° (0.1 mm.), $n^{20}\mathrm{D}$ 1.5743) and 10.8 g. of triphenylmethylsilane melting 67–68°. No depression of the melting point with an authentic sample of triphenylmethylsilane prepared from triphenylchlorosilane and methyllithium was observed.

*Anal.* Calcd. for $C_{19}H_{18}Si$: Si, 10.22. Found: Si, 10.2.

**Phenyldimethylsilane.**—To 84 g. (0.65 mole) of dimethyldichlorosilane was added phenylmagnesium bromide prepared from 18 g. (0.75 g. atom) of magnesium and 113 g. (0.72 mole) of bromobenzene. After two hours stirring the chlorosilane was filtered by nitrogen pressure and added dropwise to an ether suspension of 15 g. (0.4 mole) of lithium aluminum hydride. The reaction mixture was refluxed for 6 hours and then hydrolyzed with acid. Distillation of the residue after removal of the solvent gave 51.7 g. (59%) of phenyldimethylsilane, b.p. 157° (744 mm.),[14] $n^{20}\mathrm{D}$ 1.4995, $d^{20}_1$ 0.8891; *MR* calcd. 45.8, found 45.0. This material evolved hydrogen when added to wet piperidine.

*Anal.* Calcd. for $C_8H_{12}Si$: Si, 20.6. Found: Si, 20.8.

Eighteen and five-tenths grams (0.136 mole) of phenyldimethylsilane, 13.8 g. (0.6 g. atom) of sodium, 0.02 g. of potassium and 150 ml. of decalin were heated and stirred as previously described. After acid hydrolysis there was obtained 5.6 g. (30%) of starting material (b.p. 155–157°, $n^{20}\mathrm{D}$ 1.4992) as well as 3.1 g. of diphenyldimethylsilane (b.p. 90° (0.25 mm.), $n^{20}\mathrm{D}$ 1.5644). This latter material did not evolve hydrogen when added to wet piperidine. There was no evidence of the formation of phenyltrimethylsilane.

*Anal.* Calcd. for $C_{14}H_{16}Si$: Si, 13.21. Found: Si, 13.1.

**Reaction of Triphenylchlorosilane with Sodium.**—A mixture of 45 g. (0.153 mole) of triphenylchlorosilane, 6.3 g. (0.274 g. atom) of sodium and 225 ml. of xylene was heated

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[10] A. Polis, *Ber.*, **18**, 1540 (1885).

[11] F. S. Kipping, *J. Chem. Soc.*, 104 (1927).

[12] H. Marsden and F. S. Kipping, *ibid.*, **93**, 198 (1908).

[13] A. Bygden, *Ber.*, **45B**, 707 (1912).

[14] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 146.

and stirred for 3 hours. The solid was filtered off and washed with ethanol to remove excess metal. The solid, 34 g., was recrystallized from xylene and there was obtained 30.4 g. (77%) of hexaphenyldisilane melting at 352–354°. A small sample was sublimed at atmospheric pressure and the sublimate melted at 352°.[9] The filtrate from the reaction mixture was concentrated and the solid thus obtained was washed with cold xylene. This was then dissolved in the least amount of hot xylene and the first crop of crystals discarded. The remainder of the mother liquor was evaporated to dryness and the solid sublimed (*ca.* 190°) at atmospheric pressure. There was obtained 2.9 g. of pure tetraphenylsilane (mixed m.p.).

*Anal.* Calcd. for $C_{24}H_{20}Si$: Si, 8.33. Found: Si, 8.3.

Higher yields of tetraphenylsilane would be expected using an inert solvent such as decalin or heptadecane. Although the trace of potassium is not necessary for reaction to occur in the case of the chlorosilanes, in contrast to Si–H compounds such as triphenylsilane, the trace of potassium decreases the reaction time.

**Reaction of Diphenyldichlorosilane with Sodium.**—A typical reaction involving 12.7 g. (0.05 mole) of diphenyldichlorosilane, 11.6 g. (0.5 g. atom) of sodium, 0.02 g. of potassium and 200 ml. of decalin over a three-day reaction period gave rise to 4.5 g. of tetraphenylsilane and an amorphous material containing 14–15% silicon. This probably contained a mixture of products containing the $(C_6H_5)_2Si<$ group. The last traces of tetraphenylsilane were easily removed by sublimation at atmospheric pressure.

**Reaction of Phenyltrichlorosilane and Sodium.**—From a reaction mixture which contained 10.4 g. (0.05 mole) of phenyltrichlorosilane, 16.2 g. (0.69 g. atom) of sodium and 0.02 g. of potassium in 200 ml. of decalin there was obtained 1.1 g. of tetraphenylsilane (mixed m.p.) and a xylene-insoluble material containing 22–26% silicon.

**Phenylsodium in Decalin.**—Sodium metal, 9.2 g. (0.4 g. atom) was dispersed in 150 ml. of purified decalin in a Morton type flask by heating to 110° and stirring at 10,000 r.p.m. until the desired particle size was obtained. After the sodium dispersion had cooled to 30°, 19.2 g. (0.17 mole) of chlorobenzene was added slowly while stirring was continued at 2,000 r.p.m. The formation of the black phenylsodium was slow and the temperature remained between 35–40° for several hours. After the reaction was essentially complete, as evidenced by the drop in temperature, the mixture was heated slowly to 150° over a period of three hours and allowed to remain there for one hour. The reaction mixture was then cooled and carbonated with gaseous carbon dioxide at 10–20°. The yield of benzoic acid (mixed m.p.) after one recrystallization from water amounted to 19.3 g. or 93% of the theoretical.

If the temperature at the beginning of the reaction is greater than 40°, the yield of phenylsodium is materially reduced. However, the temperature does not have to be raised at the end of the reaction to give good yields of product.

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LAFAYETTE, INDIANA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# Rearrangement Amination of *o*-Chloro- and *o*-Bromophenyl Methyl Sulfides and *o*-Bromophenyl Methyl Sulfone in Liquid Ammonia

BY HENRY GILMAN AND GEORGE A. MARTIN

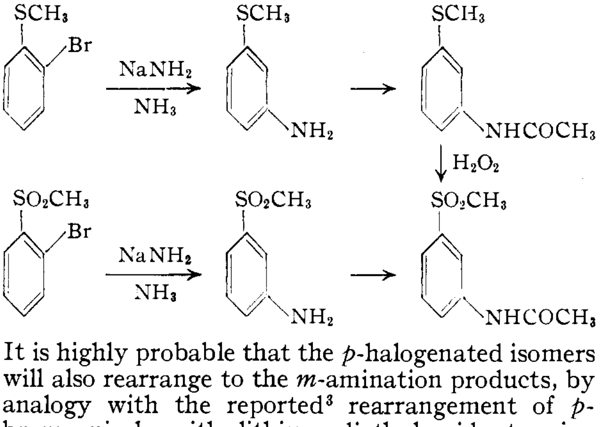
RECEIVED JUNE 5, 1952

*o*-Chlorophenyl methyl sulfide with potassium amide and *o*-bromophenyl methyl sulfide with sodamide undergo a rearrangement amination in liquid ammonia to give *m*-aminophenyl methyl sulfide. Reaction of *o*-bromophenyl methyl sulfone with sodamide in liquid ammonia gives *m*-aminophenyl methyl sulfone.

It has been shown[1] that 4-iododibenzothiophene undergoes a rearrangement amination with sodamide in liquid ammonia to give 3-aminodibenzothiophene. This rearrangement appears to be general with *o*-halogenoaryl sulfides, as well as with *o*-halogenoaryl ethers,[2] for *o*-chlorophenyl methyl sulfide with potassium amide and *o*-bromophenyl methyl sulfide with sodamide rearrange to give *m*-aminophenyl methyl sulfide in liquid ammonia.

Of greater interest is the rearrangement amination reported below, of *o*-bromophenyl methyl sulfone with sodamide in liquid ammonia to give *m*-aminophenyl methyl sulfone, for earlier illustrations[2] of this rearrangement have been confined generally to aryl halides having so-called positive groups in the nucleus.

The following is a sequence of the reactions



It is highly probable that the *p*-halogenated isomers will also rearrange to the *m*-amination products, by analogy with the reported[3] rearrangement of *p*-bromoanisole with lithium diethylamide to give *m*-diethylaminoanisole.

## Experimental

***o*-Bromophenyl Methyl Sulfide and Sodamide.**—To a solution of sodamide (0.24 mole) in liquid ammonia, was

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(1) H. Gilman and J. F. Nobis, THIS JOURNAL, **67**, 1479 (1945).

(2) See H. Gilman and R. H. Kyle, *ibid.*, **74**, 3027 (1952), for general references to rearrangement aminations by alkali amides in liquid ammonia, and by lithium dialkylamides in ether. See, particularly, R. A. Benkeser and R. G. Severson, *ibid.*, **71**, 3838 (1949).

(3) H. Gilman and R. H. Kyle, *ibid.*, **70**, 3945 (1948).