

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°. 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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[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

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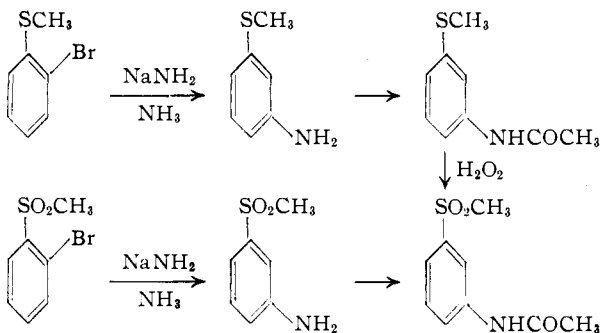
o-Chlorophenyl methyl sulfide with potassium amide and *o*-bromophenyl methyl sulfide with sodamide undergo a rearrangement amination in liquid ammonia to give *m*-aminophenyl methyl sulfide. Reaction of *o*-bromophenyl methyl sulfone with sodamide in liquid ammonia gives *m*-aminophenyl methyl sulfone.

It has been shown¹ 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 illustrations² 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

- (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**, 3338 (1949).



It is highly probable that the *p*-halogenated isomers will also rearrange to the *m*-amination products, by analogy with the reported³ 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

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

added 25 g. (0.123 mole) of *o*-bromophenyl methyl sulfide over a period of 10 minutes. After stirring for 10 minutes, 13.3 g. of powdered ammonium chloride was added, and the mixture was stirred thereafter until all of the ammonia had evaporated. The residue was treated with water; the oil that separated was extracted with ether; the ether solution was dried over sodium sulfate and then saturated with hydrogen chloride; the amine hydrochloride was separated, with ether, and treated with ammonium hydroxide to give 7.8 g. (45.5%) of *m*-aminophenyl methyl sulfide distilling at 101.5–102.5° (0.3 mm.). The acetamino derivative melted at 78–78.5° (cor.) after crystallization from dilute ethanol.⁴ In addition, there was recovered 5.29 (21%) of *o*-bromophenyl methyl sulfide, which brings the net yield of *m*-aminophenyl methyl sulfide to 57.5%.

***o*-Chlorophenyl Methyl Sulfide and Potassium Amide.**—From a corresponding reaction in liquid ammonia between 20 g. (0.126 mole) of *o*-chlorophenyl methyl sulfide and potassium amide prepared from 9.85 g. (0.252 g. atom) of potassium there was obtained 6.2 g. (35.4%) of *m*-aminophenyl methyl sulfide distilling at 144–146° (11 mm.), n_D^{20} 1.6427. The acetamino derivative melted at 77.5–78.5° (cor.) and showed no depression in a mixed m.p. determination with the derivative obtained from the rearrangement amination of *o*-bromophenyl methyl sulfide. There was recovered 6.7 g. (33.5%) of *o*-chlorophenyl methyl sulfide which brings the net yield of *m*-aminophenyl methyl sulfide up to 53%.

***o*-Bromophenyl Methyl Sulfone and Sodamide.**—To a solution of sodamide (0.106 mole) in 30 cc. of liquid ammonia was added, over a period of 10 minutes, 23.5 g. (0.1 mole) of *o*-bromophenyl methyl sulfone. The blood-red liquid ammonia solution was replenished by the addition of more liquid ammonia to replace that lost by evaporation and, after stirring for 20 minutes, 15.7 g. of ammonium chloride was added. The red color of the liquid ammonia solution persisted after the addition of the ammonium chloride. After evaporation of the ammonia, the residual solid was extracted with 250 cc. of anhydrous benzene to which was subsequently added hydrogen chloride to give 8.3 g. of the hydrochloride. From this hydrochloride, by conventional procedures, was obtained 1.7 g. (10%) of the free amine distilling over the range 165–170° (0.3 mm.). Acetylation of the amino-sulfone in chloroform by acetic anhydride gave 1.3 g. (62%) of the acetamino-sulfone which melted at 134–138°. Recrystallization from a mixture of chloroform and petroleum ether (b.p. 60–68°) gave the *m*-acetaminophenyl methyl sulfone⁵ which melted at 137.5–139°. A mixed m.p. of this acetamino-sulfone and that obtained by oxidation of the acetylation product of the *m*-aminophenyl methyl sulfide, obtained in the rearrangement amination of *o*-bromophenyl methyl sulfide, was not depressed.

In addition there was recovered 11.5 g. (49.5%) of crude *o*-bromophenyl methyl sulfone, which brings the net yield of *m*-aminophenyl methyl sulfone up to 15%. The net yield in another preparation was 16.5%.

***o*-Bromophenyl Methyl Sulfone.**—First, *o*-bromothiophenol was prepared⁶ from *o*-bromobenzenediazonium chloride and potassium ethyl xanthate in 61% yield (starting with 0.4 mole of *o*-bromoaniline); the product distilled at 58–60° (0.5 mm.).

Then, 0.228 mole of *o*-bromothiophenol, 0.3 mole of dimethyl sulfate and 60 cc. of 20% sodium hydroxide solution were refluxed for three hours, during which time additional small quantities of the sodium hydroxide solution and then the dimethyl sulfate (to acidity) were added. The yield of *o*-bromophenyl methyl sulfide distilling at 81–83° (0.3 mm.)⁷ was 42 g. (91%), n_D^{20} 1.6348.

To a solution of 10 g. (0.049 mole) of *o*-bromophenyl methyl sulfide in 70 cc. of warm glacial acetic acid was added 11.2 g. (0.099 mole) of 30% hydrogen peroxide in 10 cc. of glacial acetic acid. When the initial reaction had subsided, another 5 g. of the hydrogen peroxide was added

and the solution was refluxed for three hours. The yield of crystalline solid obtained when the mixture was poured into water was 10.9 g. (94%), and the compound melted at 108–108.5°.

Anal. Calcd. for C₇H₇O₂BrS: Br, 34.0. Found: Br, 33.6.

***m*-Acetaminophenyl Methyl Sulfone.**—A solution of 1 g. (0.0047 mole) of *m*-acetaminophenyl methyl sulfide, obtained by the rearrangement amination of *o*-bromophenyl methyl sulfide, in 5 cc. of glacial acetic acid was heated on a water-bath at 70° for two hours with 2 cc. (0.017 mole) of 30% hydrogen peroxide. Higher temperatures appeared to favor the formation of oily and resinous products. The acetic acid was removed under reduced pressure at a temperature below 70°. The oily residue was treated with a small amount of warm benzene, and on cooling a crystalline solid separated. Recrystallization from benzene gave 0.95 g. (80%) of *m*-acetaminophenyl methyl sulfone which melted at 136.8–137.5°.

***o*-Chlorophenyl Methyl Sulfone.**—The yield of *o*-chlorophenyl methyl sulfone, prepared from 17 g. (0.107 mole) of *o*-chlorophenyl methyl sulfide, was 18 g. (88.5%), and the compound melted at 93.5–94.2°. This sulfone was prepared by Todd and Shriner⁸ from sodium *o*-chlorobenzene-sulfinate and methyl iodide (m.p. 90°).

The *o*-chlorothiophenol⁹ (b.p. 87–88° (12 mm.)) was prepared in 51% yield by the same procedure used for the preparation of *o*-bromothiophenol.

The *o*-chlorophenyl methyl sulfide was prepared in 92.5% yield from 55.4 g. (0.383 mole) of *o*-chlorothiophenol and dimethyl sulfate: b.p. 116.5–117° (15 mm.), n_D^{20} 1.6067, d_4^{20} 1.2377.

Anal. Calcd. for C₇H₇ClS: S, 20.19; mol. ref., 44.4. Found: S, 20.11; mol. ref., 44.2.

2-Bromo-4-methylbenzene Sulfonamide.—The attempted rearrangement amination of 2-bromo- and 2-iodo-4-methyl-sulfonamide with sodamide in liquid ammonia was unsuccessful.

To 5.3 g. (0.0197 mole) of crude finely powdered 2-bromo-4-methylbenzenesulfonyl chloride in an appropriate container was added 40 cc. of concentrated ammonium hydroxide. The mixture was stirred rapidly and warmed with a free flame until the sulfonyl chloride became molten. The reaction between the base and the sulfonyl chloride set in at this time and soon the melt was replaced with a fine white solid. The mixture was cooled and filtered. The sulfonamide which was collected was washed well with water and air-dried. It amounted to 3.4 g. (70%) and melted at 150–152.5°. One recrystallization from dilute ethanol gave a product melting at 153.5–154.5°.

Anal. Calcd. for C₇H₈O₂BrNS: Br, 31.99. Found: Br, 31.72.

Yields up to 86% were observed on smaller runs.

2-Iodo-4-methylbenzene Sulfonamide.—This compound was prepared in 69% yield in the same manner as the 2-bromo derivative. The sulfonamide after recrystallization from 95% ethanol melted at 165–166°.

Anal. Calcd. for C₇H₈O₂INS: I, 42.9. Found: I, 43.2.

Sodium Salt of 2-Bromo-4-methylbenzenesulfonic Acid.—The halogen sulfonic acid was prepared from the corresponding amino acid by diazotization and treatment of the diazonium compound with a freshly prepared hydrobromic acid-cuprous bromide solution.

A suspension of 37.4 g. (0.2 mole) of 2-amino-4-methylbenzenesulfonic acid in a mixture of 100 g. of ice, 100 g. of water and 41 g. (0.4 mole) of concentrated sulfuric acid was maintained at 0–5° and diazotized with a solution of 14.5 g. (0.2 mole) of sodium nitrite in 40 cc. of water. A flask of one-liter capacity had to be used since considerable foaming accompanied the diazotization.

Since the diazonium salt was not soluble in the reaction medium, the suspension of this compound was added portionwise to the rapidly stirred boiling HBr–CuBr solution. This mixture was refluxed for one-half hour, whereupon the green solution was cooled to 50° and then saturated with hydrogen sulfide gas. After removal of the copper sulfide by filtration, the sodium 2-bromo-4-methylbenzenesulfonate

(8) H. R. Todd and R. L. Shriner, *THIS JOURNAL*, **56**, 1382 (1934).

(4) The m.p. of *m*-acetaminophenyl methyl sulfide reported by T. Zincke and J. Muller, *Ber.*, **46**, 775 (1913), is 75°; and the b.p. of the amine observed by them is 163–165° (16 mm.).

(5) The m.p. reported by T. Zincke and J. Muller⁴ is 137°. The m.p. reported by T. Zincke and G. Seibert, *ibid.*, **48**, 1242 (1915), for *o*-acetaminophenyl methyl sulfone is 139–140°.

(6) G. Schwarzenbach and H. Egli, *Helv. Chim. Acta*, **17**, 1176 (1934).

(7) T. Van Hove, *Bull. classe sci. Acad. roy. Belg.*, **12**, 929 (1926).

(9) G. Daccamo, *Arch. Chem. Farm.*, **14**, 1 (1891) [*Chem. Zentr.*, **62**, 11, 656 (1891)].

was separated as white crystals upon concentration of the filtrate. The yield of sodium salt was 42 g. (77%).

The *p*-toluidine salt of 2-bromo-4-methylbenzenesulfonic acid after recrystallization from water melted at 216–218°.

Anal. Calcd. for $C_{14}H_{16}O_3BrNS$: S, 8.95. Found: S, 8.76.

Potassium Salt of 2-Iodo-4-methylbenzenesulfonic Acid.—

The 2-iodo compound was prepared by diazotization of the 2-amino compound and subsequent reaction with potassium iodide solution. A 94% yield of crude potassium salt was obtained by concentration of the reaction mixture.

The *p*-toluidine salt melted at 227.5–230° after recrystallization from water.

Anal. Calcd. for $C_{14}H_{16}O_3INS$: S, 7.90. Found: S, 8.00.

2-Bromo-4-methylbenzenesulfonyl Chloride.—An intimate mixture of 5 g. (0.0183 mole) of powdered sodium 2-bromo-4-methylbenzenesulfonate and 15 g. (0.072 mole) of finely divided phosphorus pentachloride was heated for 1

hour at 160°. The initial reaction began at about 130–140°. The melt was poured onto ice and a crude sulfonyl chloride (82% yield) melting at 56–62° was recovered. A sample recrystallized from petroleum ether melted at 64–65°.

Anal. Calcd. for $C_7H_6O_2BrClS$: S, 11.9. Found: S, 12.1.

The methyl and ethyl esters of the 2-bromo-4-methylbenzenesulfonic acid melted at 62–63° and 70–71°, respectively.

Anal. Calcd. for $C_8H_9O_3BrS$: S, 12.1. Found: S, 12.0. Calcd. for $C_9H_{11}O_3BrS$: S, 11.45. Found: S, 11.80.

2-Iodo-4-methylbenzenesulfonyl Chloride.—This material was prepared in the same manner as the 2-bromo compound. A crude yield of 83% was obtained, and after recrystallization from petroleum ether the pure sulfonyl chloride melted at 66–67°.

Anal. Calcd. for $C_7H_6O_2ClIS$: S, 10.10. Found: S, 9.85.

AMES, IOWA

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

An "Isoaromatic" Product from 2-Methyl-3-benzofurymethylmagnesium Chloride

BY RUSSELL GAERTNER¹

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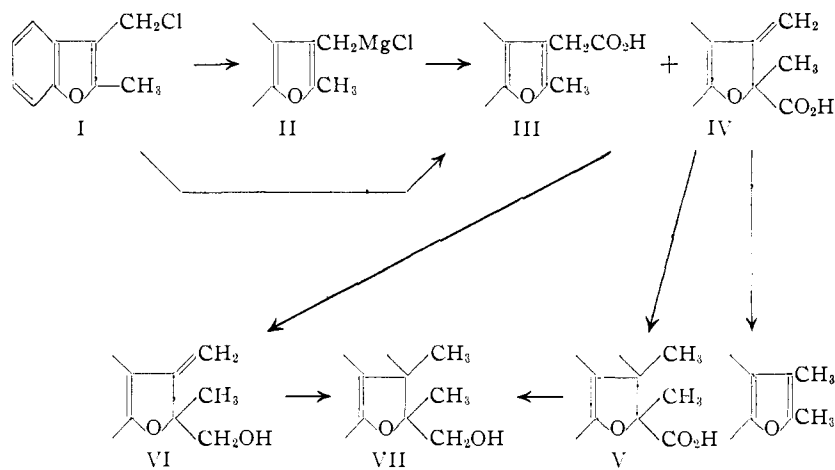
A Grignard reagent has been prepared from 3-(chloromethyl)-2-methylbenzofuran and allowed to react with carbon dioxide and ethyl chlorocarbonate. A trace of the normal product was isolated only with carbon dioxide. In both reactions, the major product, after hydrolysis, was the "isoaromatic" 2-methyl-3-methylene-2,3-dihydro-2-benzofuroic acid, the result of a novel "abnormal" reaction. This β , γ -unsaturated acid decarboxylated at its melting point (110°) to give 2,3-dimethylbenzofuran, a reaction analogous to the similar behavior of β -keto acids.

Two previous attempts to obtain "isoaromatic"² products in abnormal reactions of heteroaryl-methyl Grignard reagents have been reported. The first, involving 3-methyl-2-thianaphthenylmethylmagnesium chloride, resulted mainly in cleavage of the C_2 -S bond,³ while the second, using 2-bromo-3-(bromomethyl)-thianaphthene, gave only polymers.⁴ Since benzofuran is less aromatic than thianaphthene its arylmethyl Grignard reagents should react abnormally even more readily; to avoid cleavage of the furan moiety,⁵ a 3-chloromethyl derivative was indicated.

3-Chloromethyl-2-methylbenzofuran (I) was obtained by chloromethylation of 2-methylbenzofuran. It was converted normally in the cyclic reactor and the reagent II was obtained in yields of about 80%. The presence of a coupling product, probably 1,2-bis-(2-methyl-3-benzofuryl)-ethane, was demonstrated by isolation of the picrate. Small amounts of 2,3-dimethylbenzofuran were also present in all re-

actions, resulting from unavoidable hydrolysis of the reagent.

When the reagent II was carbonated, only a trace of the normal product, 2-methyl-3-benzofuryl-



acetic acid (III), could be isolated; III was also prepared for comparison from I *via* the nitrile. The main product of carbonation, and the sole acid product isolated from the reaction of I with ethyl chlorocarbonate followed by alkaline hydrolysis, was 2-methyl-3-methylene-2,3-dihydro-2-benzofuroic acid IV. The structure of this compound has not been unequivocally established but any other appears to be inconceivable in view of the mode of its formation and its reactions.

The acid, IV, or its ethyl ester, absorbed very nearly one mole of hydrogen over platinum oxide,

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(2) "Isoaromatic" is used to refer to a structure with adjacent quaternary and doubly bonded carbon atoms in an otherwise aromatic nucleus. Application of this usage here presupposes agreement that benzofuran is "aromatic," although it must be granted that this nucleus undergoes many reactions typical of arylethylenes.

(3) R. Gaertner, *THIS JOURNAL*, **74**, 2991 (1952).

(4) R. Gaertner, *ibid.*, **74**, 4950 (1952).

(5) R. Gaertner, *ibid.*, **73**, 4400 (1951).