and 1.0 g. of phenyl-β-naphthylamine at 150–180° and 80 mm. pressure gave 12.3 g. (20%) of the desired styrene, b.p. 56–57° (2 mm.), n^{25}D 1.5778. A similar product was obtained in 2% yield by cracking brominated polystyrene,[10] and rectifying the product. Oxidation with potassium permanganate gave *p*-bromobenzoic acid, m.p. 250–252°.

p-**Vinylbenzoic Acid.**[4]—A mixture of 4.9 g. (0.027 mole) of *p*-bromostyrene and 2.6 g. (0.024 mole) of ethyl bromide was reacted with 1.8 g. (0.075 mole) of activated magnesium in 55 ml. of ether. The product was carbonated with dry ice and then hydrolyzed with dilute sulfuric acid to obtain 0.6 g. (15%) of *p*-vinylbenzoic acid, m.p. 139–140° (from 20% ethanol). The acid decolorized bromine and permanganate, was easily oxidized to terephthalic acid, m.p. 300°, and gave a *p*-bromophenacyl ester, m.p. 100–102°.

x-**Halogeno-α-methylstyrenes.**—The Grignard reagent from 99.5 g. (0.7 mole) of methyl iodide and 17 g. of magnesium was treated with 78 g. (0.3 mole) of methyl *p*-iodobenzoate. Hydrolysis with saturated ammonium chloride solution, isolation of the organic layer, and dehydration of the intermediate tertiary alcohol by refluxing with an excess of acetic anhydride for 20 hours gave, on distillation, 24.0 g. (33%) of the desired *p*-iodo-α-methylstyrene, b.p. 68–70° (2 mm.), m.p. 44°.

Anal. Calcd. for C_9H_9I: C, 44.3; H, 3.69. Found[11]: C, 44.7; H, 3.49.

The corresponding *m*- and *p*-bromo-α-methylstyrenes[12] were prepared by analogous methods. The *m*-bromo compound, b.p. 68–71° (2 mm.), was obtained in 49% yield from methyl *m*-bromobenzoate. The *p*-bromo compound, b.p. 95° (10 mm.), was obtained in 42% yield from ethyl *p*-bromobenzoate. It was also prepared from *p*-dibromobenzene, magnesium and acetone[12] in 51% yield.

p-**Isopropenylbenzoic Acid.**[6] (A) **From** *p*-**Iodo-α-methylstyrene and Magnesium.**—A mixture of 11.9 g. (0.05 mole) of *p*-iodo-α-methylstyrene, 5.2 g. (0.048 mole) of ethyl bromide, 3.6 g. (0.15 mole) of activated magnesium, and 60 ml. of ether was allowed to react for two hours and then carbonated. Hydrolysis with dilute sulfuric acid and purification of the product by recrystallization from water gave 0.4 g. (10%) of white crystalline acid, m.p. 156–158° (sublimes), neutral equivalent 162.5 (calcd. 162.0), *p*-bromophenacyl ester, m.p. 118–121°. Oxidation of the acid gave terephthalic acid.

(B) **From** *p*-**Bromo-α-methylstyrene and Lithium.**—A suspension of 0.7 g. (0.1 mole) of lithium in 50 ml. of ether under nitrogen was treated with a mixture of 9.85 g. (0.05 mole) of *p*-bromo-α-methylstyrene and 0.5 g. of butyl bromide in 50 ml. of ether. After two hours at reflux, the mixture was carbonated and worked up as before. The yield of recrystallized acid, m.p. 161–163°, was 31%.

p-**Triethyltin-α-methylstyrene.**—The lithium compound from 49.3 g. (0.25 mole) of *p*-bromo-α-methylstyrene and 3.47 g. (0.5 mole) of lithium in 160 ml. of ether was treated with 60.4 g. (0.25 mole) of triethyltin chloride[13] added over a period of an hour. After three hours at reflux the mixture was filtered and the liquid filtrate fractionated directly under diminished pressure. The desired product was a colorless liquid, b.p. 129–130° (2 mm.), d^{25}_{25} 1.2311, n^{25}D 1.5441, yield 12.0 g. (14.5%). The analysis of the compound for tin followed the procedure of Gilman and King.[14]

Anal. Calcd. for $C_{15}H_{24}Sn$: Sn, 36.7. Found: Sn, 37.5.

p-Triethyltin-α-methylstyrene copolymerized normally with butadiene in a typical emulsion system to give a 100% yield of a crumbly rubber. The polymerization was rather slow.

Effect of Organometallic Compound Formation on α-Methylstyrene.—Methyl iodide, 71.0 g. (0.5 mole), in 75 ml. of ether was added to a stirred mixture of α-methylstyrene, 59 g. (0.5 mole), and magnesium, 12.0 g. (0.5 mole), in 150 ml. of ether. When the formation of the Grignard reagent was complete, hydrolysis was accomplished by the careful addition of saturated ammonium chloride solution. The ether layer was dried, and the ether removed under vacuum at room temperature. Distillation of the residual liquid yielded 43.5 g. (74% theory) of 2,4-diphenyl-4-methyl-2-pentene,[6,7] b.p. 126–129° (1–2 mm.), n^{20}D 1.5654, and some polymeric material.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.5; H, 8.50. Found[11]: C, 91.5; H, 8.77

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[10] Bachman and co-workers, *J. Org. Chem.*, **12**, 108 (1947).

[11] Carbon and hydrogen analyses by Dr. H. Galbraith, Purdue University.

[12] Seymour and Wolfstein, THIS JOURNAL, **70**, 1178 (1948).

[13] Kocheshkov, *J. Gen. Chem.* (*U. S. S. R.*), **4**, 1359 (1934), *C. A.*, **29**, 3650 (1935).

[14] Gilman and King, THIS JOURNAL, **51**, 1213 (1929).

LAFAYETTE, INDIANA RECEIVED JUNE 30, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE FLORIDA STATE UNIVERSITY, TALLAHASSEE, AND WASHINGTON UNIVERSITY, ST. LOUIS]

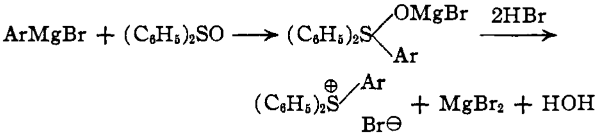
The Preparation of Triarylsulfonium Halides by the Action of Aryl Grignard Reagents on Diphenyl Sulfoxide

BY BERNARD S. WILDI, SHELDON W. TAYLOR AND H. A. POTRATZ

Aryl Grignard reagents have been successfully added to diphenyl sulfoxide and acid hydrolysis of the addition compounds has yielded the corresponding sulfonium salts. Some of the physical and chemical properties of the sulfonium salts have been determined.

All attempts in the past to add Grignard reagents to sulfoxides to form sulfonium compounds have been reported to give no reaction.[1,2] In fact Gilman and co-workers[2] have been able to obtain sulfoxides by the action of Grignard reagents on sulfones. It has also been observed in these laboratories that Grignard reagents do not add to sulfoxides in ether solution at ordinary temperatures.

The present work describes the successful addition of aryl Grignard reagents to diphenyl sulfoxide. Hydrolysis of the magnesium addition products with aqueous hydrobromic acid has yielded the sulfonium bromides.



$$\mathrm{ArMgBr} + (C_6H_5)_2SO \longrightarrow (C_6H_5)_2S\begin{matrix}\diagup \mathrm{OMgBr}\\ \diagdown \mathrm{Ar}\end{matrix} \xrightarrow{2\mathrm{HBr}}$$

$$(C_6H_5)_2\overset{\oplus}{S}\begin{matrix}\diagup \mathrm{Ar}\\ \mathrm{Br}\ominus\end{matrix} + \mathrm{MgBr_2} + \mathrm{HOH}$$

The difficulties encountered in previous attempts to carry out the addition reaction were obviated by replacing the ether used in the formation of the Grignard reagent with either benzene or di-*n*-butyl ether and refluxing the Grignard–sulfoxide solution at an elevated temperature. In this manner triphenylsulfonium bromide, diphenyl-*p*-tolylsulfonium bromide, diphenyl-*m*-tolylsulfonium bromide and diphenyl-2,4-xylylsulfonium bromide have been prepared. The yields varied from 12.1% for the

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[1] R. L. Shriner, H. C. Struck and W. J. Jorison, THIS JOURNAL, **52**, 2060 (1930).

[2] H. Gilman, L. E. Smith and H. H. Parker, *ibid.*, **47**, 851 (1925).

xylyl compound to 49% for the triphenyl compound.

This method of synthesizing sulfonium compounds is advantageous since the products can be easily obtained in the crystalline state. The method has the added advantage that unsymmetrical sulfonium salts may be synthesized from the readily available unsymmetrical diaryl sulfoxides.

Several attempts were made to add phenyllithium to diphenyl sulfoxide at elevated temperatures. Hydrolysis of the reaction mixtures with aqueous mineral acids gave negligible yields of the triphenylsulfonium salt.

The triarylsulfonium compounds prepared were found to be readily crystallizable, high melting solids and were very soluble in water, pyridine, ethanol, and chloroform but practically insoluble in ether, benzene or acetone. The halide ion of the compounds was observed to be instantaneously and quantitatively precipitated in aqueous solutions with silver nitrate. Triphenylsulfonium nitrate was prepared in good yield by the reaction of triphenylsulfonium bromide with aqueous silver nitrate.

Triphenylsulfonium hydroxide was prepared in aqueous solution by the action of moist silver oxide on triphenylsulfonium bromide. All attempts to isolate the compound in pure form from its aqueous solutions resulted in decomposition.

All of the sulfonium compounds prepared gave a blue precipitate in aqueous solution when treated with the cobaltous ammonium thiocyanate complex.[3] This reaction was employed as a qualitative test for the sulfonium compounds.

Acknowledgment.—The authors are grateful to Professor D. Lipkin for his interest and valuable suggestions throughout this work.

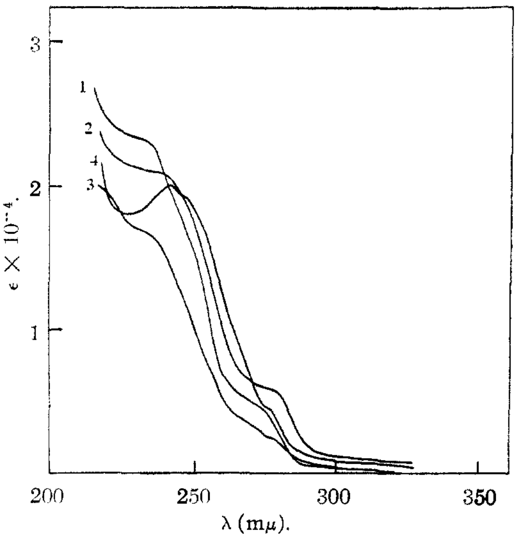

Fig. 1.—Ultraviolet absorption spectra: 1, triphenylsulfonium bromide or triphenylsulfonium nitrate; 2, diphenyl-*m*-tolylsulfonium bromide; 3, diphenyl-*p*-tolylsulfonium bromide; 4, diphenyl-2,4-xylylsulfonium bromide.

Experimental

Triphenylsulfonium Bromide.—A phenylmagnesium bromide solution was prepared under an atmosphere of nitrogen in a one-liter, three-necked flask fitted with a stirrer, dropping funnel, guarded reflux condenser and gaseous inlet tube, from 41.8 g. of freshly distilled bromobenzene, 300 ml. of dry ether and 6.0 g. of magnesium turnings. Three hundred ml. of benzene was introduced into the flask and the ether was removed by distillation until the temperature of the distillate vapors had reached 70°. Ten grams (10 g.) of diphenyl sulfoxide dissolved in 100 ml. of benzene was added to the Grignard solution and the mixture was refluxed under nitrogen for 23 hours. The Grignard solution was cooled to 0° and hydrolyzed with a solution consisting of 21 ml. of hydrobromic acid (sp. gr. 1.38) and 21 ml. of water. The benzene layer was separated and extracted with four 80-ml. portions of aqueous 5% hydrobromic acid. The aqueous acid extracts and the aqueous layer from the hydrolysis were combined and extracted with six 100-ml. portions of chloroform. The combined chloroform extracts were evaporated to dryness to yield 8.40 g. (49.4% yield) of colorless crystals of triphenylsulfonium bromide, m.p. 277–279°. Two recrystallizations from a mixture of chloroform and acetone (1:5 by volume) by the addition of ether yielded 7.29 g. of pure material, m.p. 285–286°. The melting point was unchanged on further recrystallizations from either water or water and pyridine.

Anal. Calcd. for $C_{18}H_{25}SBr$: C, 62.97; H, 4.41; Br, 23.28. Found: C, 63.00, 62.81; H, 4.38, 4.26; Br, 23.21, 23.30.

The substance was readily soluble in water, chloroform, ethanol and pyridine but insoluble in ether, acetone or benzene. The material gave a blue precipitate with the cobaltous ammonium thiocyanate complex in aqueous solution.[3] Silver bromide was formed instantaneously on treatment of an aqueous solution of the salt with silver nitrate.

The benzene solution obtained from the hydrolysis of the Grignard solution was dried with anhydrous sodium sulfate. Evaporation of the benzene yielded an amber colored liquid which on vacuum distillation yielded 8.00 g. of bromobenzene, b.p. 54° (25 mm.). A fraction, b.p. 108–148° (3 mm.) was obtained which crystallized partially on standing at 0° to yield 1.18 g. of diphenyl sulfoxide, m.p. 67°. Further recrystallizations from petroleum ether yielded pure material, m.p. 70°. The melting point was unaltered on admixture with an authentic sample of diphenyl sulfoxide.

Several preliminary attempts to prepare triphenylsulfonium bromide by using a two-mole excess of phenylmagnesium bromide per mole of sulfoxide under the conditions given above resulted in yields of 12.2–36.3%. No triphenylsulfonium bromide was obtained on refluxing two moles of phenylmagnesium bromide with one of sulfoxide in ether solution for 24 hours.

One run in which the Grignard solution obtained from 14.29 g. of magnesium and 126 g. of bromobenzene was refluxed for 12 hours at 129° with 50 g. of diphenyl sulfoxide in a solution of 200 ml. of benzene and 600 ml. of di-*n*-butyl ether, yielded 12.1 g. (14.4% yield) of triphenylsulfonium bromide, m.p. 279–81°. Pure material, m.p. 284–285°, was obtained on further recrystallizations from acetone and chloroform (5:1 by volume) on the addition of ether.

Triphenylsulfonium Nitrate.—To 1.725 g. of triphenylsulfonium bromide dissolved in 25 ml. of water was added 25 ml. of a solution of 0.845 g. of silver nitrate in water. The precipitated silver bromide was removed by filtration and the filtrate was evaporated to dryness to yield colorless crystals of the nitrate. The compound was recrystallized from acetone and chloroform (5:1 by volume) to yield 0.268 g. of elongated prisms, m.p. 227–227.5°.

Anal. Calcd. for $C_{18}H_{15}O_3SN$: C, 66.44; H, 4.68; N, 4.39. Found: C, 66.69; H, 4.75; N, 4.39.

Triphenylsulfonium nitrate gave a blue precipitate with the cobaltous ammonium thiocyanate complex in aqueous solution.[3]

Reaction of Diphenyl Sulfoxide and Phenyllithium.—In a solution consisting of 50 ml. of benzene and 50 ml. of ether was prepared a solution of phenyllithium from 1.94 g. of lithium and 22.2 g. of bromobenzene. The apparatus used was similar to that described above for the preparation of triphenylsulfonium bromide. Fifteen grams (15 g.) of diphenyl sulfoxide dissolved in 50 ml. of benzene was added dropwise to the phenyllithium solution over a period of 3 hours. The solution was refluxed for 24 hours then decomposed with dilute hydrobromic acid solution as described above for the preparation of triphenylsulfonium bromide.

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(3) H. Potratz and J. Rosen, *Anal. Chem.*, **21**, 1276 (1949).

Evaporation of the chloroform extracts yielded a small quantity of residue which on recrystallization from acetone and chloroform (5:1 by volume) by the addition of ether yielded 0.050 g. of triphenylsulfonium bromide, m.p. 284–285°. The melting point was unchanged on admixture with an authentic sample of triphenylsulfonium bromide.

Triphenylsulfonium Hydroxide.—One gram (1.00 g.) of triphenylsulfonium bromide was dissolved in 100 ml. of water and treated with a gram equivalent of moist silver oxide. The solution was stirred for 3 days at room temperature in the dark. The mixture was filtered and the filtrate was observed to be strongly basic to litmus. Evaporation of the aqueous solution yielded a strongly basic oil which could not be induced to crystallize. On standing at room temperature the material lost its basicity and yielded a brown amorphous gum from which nothing could be identified.

Diphenyl-*p*-tolylsulfonium Bromide.—Diphenyl-*p*-tolylsulfonium bromide was prepared in the same manner as described above for the preparation of triphenylsulfonium bromide by the Grignard reaction. The Grignard reagent prepared from 77.8 g. of *p*-tolyl bromide and 7.74 g. of magnesium was refluxed with 10 g. of diphenyl sulfoxide at 70° for 24 hours. Hydrolysis of the reaction mixture with dilute aqueous hydrobromic acid yielded 6.01 g. (34.1% yield) of the sulfonium bromide, m.p. 214.5–217°. Pure material was obtained on further recrystallization from acetone and chloroform (5:1 by volume) by the addition of ether. Pure material melted at 224–225°.

Anal. Calcd. for $C_{19}H_{17}SBr$: C, 63.87; H, 4.79. Found: C, 64.29; H, 5.03.

The compound was readily soluble in chloroform, water, ethanol and pyridine but insoluble in acetone, benzene and ether. The compound gave a blue precipitate with the cobaltous ammonium thiocyanate complex.[3]

Diphenyl-*m*-tolylsulfonium Bromide.—Diphenyl-*m*-tolylsulfonium bromide was prepared by a procedure similar to the one described above for the preparation of triphenylsulfonium bromide. The Grignard reagent was prepared from 77.8 g. of *m*-tolyl bromide and 7.74 g. of magnesium and treated with 10.0 g. of diphenyl sulfoxide at 70° for 48 hours. The yield of the sulfonium bromide after one recrystallization from acetone and chloroform (5:1 by volume) by the addition of ether was 4.12 g. (23.4% yield), m.p. 209–223°. Pure material was obtained on further recrystallizations from the same solvent system.

Anal. Calcd. for $C_{19}H_{17}SBr$: C, 63.87; H, 4.79. Found: C, 63.99; H, 5.09.

The compound was soluble in water, chloroform, ethanol and pyridine but insoluble in ether, benzene or acetone. It gave a blue precipitate with the cobaltous ammonium thiocyanate complex.[3]

Diphenyl-2,4-xylylsulfonium Bromide.—The procedure was similar to the one employed in the preparation of triphenylsulfonium bromide given above. The Grignard reagent was prepared from 44.0 g. of 2,5-dimethylbromobenzene and 6.10 g. of magnesium and treated with 7.20 g. of diphenyl sulfoxide for 75 hours at 70°. The crude material, 1.60 g. (12.1% yield), m.p. 225–230°, was recrystallized from acetone and chloroform (5:1 by volume) by the addition of ether to yield pure material, m.p. 239–239.5° dec.

Anal. Calcd. for $C_{20}H_{19}SBr$: C, 64.69; H, 5.16. Found: C, 64.44; H, 5.35.

The compound was soluble in water, chloroform, ethanol and pyridine but insoluble in acetone, benzene or ether. The substance gave a blue precipitate with the cobaltous ammonium thiocyanate complex in aqueous solution.[3]

Absorption Spectra.—Measurements were made in 95% ethanol solution with a Beckman spectrophotometer, model DU. Since the data for triphenylsulfonium bromide and triphenylsulfonium nitrate were practically identical within experimental error only one curve for these two substances is shown.

DAYTON, OHIO RECEIVED OCTOBER 31, 1950

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

N-(β-Aminoethyl)-morpholine as a Reagent for the Characterization of Esters

BY R. W. BOST AND LEO V. MULLEN, JR.

The suitability of N-(β-aminoethyl)-morpholine as a reagent for esters was investigated. It was found to be an excellent reagent for esters of aromatic acids and aliphatic dicarboxylic acids.

The structure of N-(β-aminoethyl)-morpholine suggested that it might be an excellent reagent for the characterization of esters. It possesses an amino group located at a favorable position to give added basicity to the morpholine molecule. The compound also contains a tertiary nitrogen atom which should enable the molecule to undergo quaternization with ease, thus affording a second derivative of the ester in doubtful cases, or where the N-(β-aminoethyl)-morpholide is an oil. In addition, N-(β-aminoethyl)-morpholine is inexpensive, stable, and a good solvent (b.p. 202°) for esters.

In this work thirty nine esters representing the aliphatic and aromatic monocarboxylic acids and the aliphatic dicarboxylic acids were studied. It was found to be an excellent reagent for the characterization of aromatic esters and aliphatic dicarboxylic esters, giving rise to good yields of pure, crystalline, stable derivatives whose melting point spread was wide enough to insure complete identification. Although the melting point spread of the derivatives of the aliphatic monocarboxylic esters was not as great as desired, with the exception of ethyl caprate, pelargonate, and caprylate, identification is afforded by the reagent. Where the N-(β-aminoethyl)-morpholide was an oil, it was converted to the quaternary salt with methyl iodide. All melting points are corrected. The N-(β-aminoethyl)-morpholine used in this work was obtained from the Carbide and Carbon Chemicals Corporation, Charleston, W. Va. It was redistilled and the portion boiling at 202° was used.

Experimental

Preparation of N-(β-Aminoethyl)-morpholides. (A) From Aliphatic Esters.—To 0.02 mole of N-(β-aminoethyl)-morpholine was added 0.02 mole of ester and the reaction refluxed 3 hours. Upon cooling (ice-bath) the resulting solution, the N-(β-aminoethyl)-morpholide precipitated. Precipitation is facilitated by addition of 5 ml. of ligroin to the cold reaction mixture of those aliphatic esters containing less than eleven carbon atoms. The derivatives of esters containing more than eleven carbon atoms were easily recrystallized from ethanol, while those of eleven or fewer carbon atoms were best purified from hot ligroin.

The derivatives of low boiling esters of formic, acetic, and propionic acids were best prepared by refluxing the reagent and ester with 5 ml. of ethylene glycol for 3 hours, followed by removal of the glycol under reduced pressure.

(B) From Aromatic Esters.—To 0.02 mole of reagent was added 0.02 mole of ester and refluxed 2 hours. Upon cooling the resulting solution (ice-bath), the product precipitated. Addition of 5 ml. of ether to cold mixture aids