[Contribution from the Purdue Research Foundation and the Department of Chemistry, Purdue University]

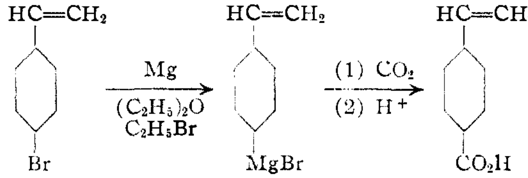
Monomers and Polymers. VII. Syntheses with the Aid of Metallostyrenes[1]

By G. Bryant Bachman, C. L. Carlson and Margaret Robinson

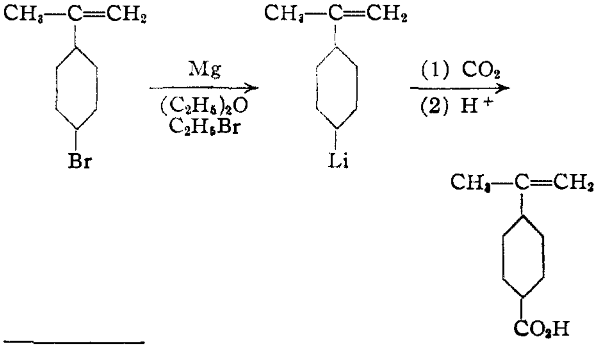
Organometallic derivatives of styrenes have been prepared by the reactions of nuclearly halogenated styrenes with magnesium or lithium. The metallation reactions require the use of cohalides and are accompanied by large amounts of polymerization. The organometallic compounds have been employed like typical Grignard reagents in the synthesis of substituted styrenes. The yields of the desired products are low because of polymer formation.

As an extension of work previously done in this Laboratory on methods of synthesizing substituted styrenes,[2] an attempt has been made to develop syntheses involving the use of organometallic derivatives of styrenes. It was expected that these metal derivatives could be prepared from nuclearly halogenated styrenes, and could be used like other typical Grignard reagents to introduce a variety of groups into the aromatic nucleus.

Halogenated styrenes were found to react extremely sluggishly with magnesium. The use of activated magnesium[3] or high boiling solvents, such as dibutyl ether did not accelerate the rate appreciably. However, the use of a cohalide such as methyl iodide or ethyl bromide caused the aromatic halogen to react rather promptly with the magnesium. Carbonation of the reaction mixture led to the formation of *p*-vinylbenzoic acid[4] in 15% yield. Large amounts of polymeric material were also obtained.



Since α-methylstyrenes have been shown to polymerize much less readily than the corresponding styrenes,[2,5] an attempt was made to prepare the organometallic compounds from nuclearly halogenated α-methylstyrenes (*p*-bromo- and *p*-iodo-α-methylstyrenes). Here again, it was found necessary to use a cohalide to obtain reaction. Furthermore, it was found that lithium reacted more satisfactorily than magnesium. Hydrolysis of the products, and titration of the resulting mixture with standard acid indicated the formation of organometallic derivatives in as high as 64% yields. However, carbonation of these derivatives gave *p*-isopropenylbenzoic acid[6] in only 10–30% yields. Again large amounts of polymeric material were formed. Reactions of the lithium derivative with acetaldehyde or benzaldehyde gave products from which polymeric materials only could be isolated. Triethyltin chloride, on the other hand, gave *p*-triethyltin-α-methylstyrene in 14.5% yield.



Efforts to decrease the amounts of polymerization occurring in these reactions were largely unsuccessful. The use of an inert atmosphere helped only a little. The addition of typical polymerization inhibitors was not practical except during isolation of the product, since these materials themselves react with organometallic compounds. It was hoped that an exchange metallation reaction could be effected between brominated styrenes and a preformed aliphatic organometallic compound. However, butyllithium and *p*-bromo-α-methylstyrene mixtures, when carbonated, gave only polymeric material and valeric acid (50% yield). It was concluded that the free radicals produced during the formation of the organometallic compounds acted as powerful activators for the polymerization. To test this an experiment was run in which methyl iodide was reacted with magnesium in the presence of an equimolar amount of unsubstituted α-methylstyrene. Hydrolysis of the reaction mixture led to the recovery of a 74% yield of the unsaturated dimer of α-methylstyrene (2,4-diphenyl-4-methyl-2-pentene)[7] and some polymeric material. A similar experiment with lithium in place of magnesium gave comparable results.

It may be concluded that the above approach to the synthesis of nuclearly substituted styrenes is not very practical. It should be noted, however, that *p*-vinylbenzoic acid is obtained in fewer steps, and in better over-all yields by this procedure than by a previously proposed one.[4]

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Experimental

***p*-Bromostyrene.**[8]—The addition of 54.2 g. (0.38 mole) of methyl iodide to 10 g. (0.4 mole) of magnesium in 400 ml. of ether, reaction of the product with 60 g. (0.33 mole) of *p*-bromobenzaldehyde,[9] and hydrolysis with 10% aqueous ammonium chloride solution gave 68 g. (66% theory) of 1-(*p*-bromophenyl)-ethanol (b.p. 105–107° at 2 mm.). Dehydration of this alcohol with 4.1 g. of potassium bisulfate

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(1) From the Ph.D. thesis of C. L. Carlson, Purdue University. Present address of C. L. C., Armstrong Cork Company, Lancaster, Pa.

(2) Bachman, *et al.*, This Journal, **70**, 622, 1772 (1948).

(3) Gilman and Kirby, *Rec. trav. chim.*, **54**, 577 (1935).

(4) Marvel, This Journal, **67**, 2250 (1945).

(5) Staudinger and Breusch, *Ber.*, **62B**, 442 (1929).

(6) Meyer and Rosicki, *Ann.*, **219**, 270 (1883).

(7) Bergmann, Taubadel and Weiss, *Ber.*, **64B**, 1493 (1931).

(8) Quelet, *Bull. soc. chim.*, **45**, 75 (1929).

(9) "Organic Syntheses," Coll. Vol. 2, p. 89.

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).

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

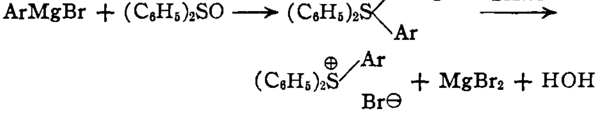
The Preparation of Triarylsulfonium Halides by the Action of Aryl Grignard Reagents on Diphenyl Sulfoxide

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).