

Reaction of Phenylethynylmagnesium Bromide  
or Styrylmagnesium Bromide with Thionyl  
Chloride, a Novel Coupling Reaction

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Although the formation of sulfoxides and sulfides by the reaction of alkylmagnesium halide or arylmagnesium halide with thionyl chloride has already been reported,<sup>1,2</sup> the reaction of acetylenic or olefinic Grignard reagents with thionyl chloride is unknown. In the course of our study of the syntheses of as yet unknown bis ethynyl sulfoxides or bis ethenyl sulfoxides, the reaction of phenylethynylmagnesium bromide or styrylmagnesium bromide with thionyl chloride was attempted.

When a mixture of freshly distilled thionyl chloride and 2 molar equiv of phenylethynylmagnesium bromide or styrylmagnesium bromide in tetrahydrofuran (THF) was stirred at 0° for 3.5 hr, and the product was submitted to chromatographic separation, a crystalline compound and a tarry residue were obtained. On the basis of the elementary analyses and spectroscopic data, the crystalline product was identified as 1,4-diphenylbuta-1,3-diyne or 1,4-diphenylbuta-1,3-diene. The Beilstein tests and sodium fusion tests of the tarry residue indicated the presence of halogen and sulfur, but no sulfur compounds could be isolated.

Though several coupling reactions of acetylenic compounds, such as Glaser coupling,<sup>3</sup> Grignard coupling,<sup>4,5</sup> Reformatsky reaction,<sup>6</sup> and Chodwicz-Cadiot coupling,<sup>7</sup> are known, the coupling reaction of acetylenic or vinylic compounds *via* Grignard reagents and thionyl chloride is as yet unknown.

The reaction of phenylethynylmagnesium bromide or styrylmagnesium bromide with thionyl chloride was attempted under various reaction conditions and the yields of coupling products are summarized in Table I. In expt 1-5 and 11-15, the molar ratio of Grignard reagents and thionyl chloride was varied. In the

TABLE I  
REACTION OF PHENYLETHYNYLMAGNESIUM BROMIDE OR  
STYRYLMAGNESIUM BROMIDE WITH THIONYL CHLORIDE

Expt	Temp, °C	Molar ratio, SOCl <sub>2</sub> /RMgBr	Solvent	Yield of coupling product, <sup>a</sup> %
C <sub>6</sub> H <sub>5</sub> C≡CMgBr				
1	0	0	THF	0
2	0	0.25	THF	34
3	0	0.50	THF	38
4	0	1.0	THF	61
5	0	1.5	THF	58
6	-40	1.0	THF	57
7	30	1.0	THF	55
8	0	1.0	DEE <sup>b</sup>	33
9	0	1.0	DBE <sup>c</sup>	17
10	0	1.0	DGM <sup>d</sup>	43
C <sub>6</sub> H <sub>5</sub> CH=CHMgBr				
11	0	0	THF	28
12	0	0.25	THF	35
13	0	0.50	THF	68
14	0	1.0	THF	89
15	0	1.5	THF	81
16	-40	1.0	THF	70
17	30	1.0	THF	88

<sup>a</sup> Based on the initial amounts of Grignard reagents in the reaction systems. <sup>b</sup> Diethyl ether. <sup>c</sup> Di-*n*-butyl ether. <sup>d</sup> Diethylene glycol dimethyl ether.

absence of thionyl chloride, phenylethynylmagnesium bromide gave no coupling product, and phenylacetylene was recovered quantitatively. Yet in the case of styrylmagnesium bromide, 1,4-diphenylbuta-1,3-diene was obtained in 28% yield even in the absence of thionyl chloride. This indicates the occurrence of a Wurtz type reaction during the preparation of styrylmagnesium bromide. The yields of coupling products increased with the increase of the molar ratio of reagents. Though the stoichiometric ratio of reagents for the formation of sulfoxides was 0.5, the maximum yields of coupling products were obtained at a molar ratio of 1.0. From these observations it seems reasonable to assume that thionyl chloride plays some important role in this coupling reaction.

In expt 4, 6, 7, 14, 16, and 17, the reaction temperature was varied. It is surprising that the yields of coupling products at -40° were comparatively high, and that the reaction temperature did not markedly influence the yields of coupling products.

In expt 4 and 8-10, the solvent was varied. Because of difficulty in the preparation of styrylmagnesium bromide in ethers other than THF, only the reaction of phenylethynylmagnesium bromide was investigated. The type of solvent markedly influenced the yield of diphenylbutadiyne. The maximum yield was obtained in THF, and the minimum yield in diethyl ether. The basicity of the solvent is known to influence the stability of some charged transition states and Schlenk equilibrium of Grignard reagents.<sup>8</sup> However, the Schlenk equilibrium of acetylenic Grignard reagents is unknown, and it is not possible to decide the precise effect of basicity of the solvent without more detailed experiments.

In Table II are shown the results of the reactions of

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TABLE II  
REACTION OF ACETYLENIC GRIGNARD REAGENTS  
WITH THIONYL CHLORIDE<sup>a</sup>

RMgBr, R =	Yield of coupling products, <sup>b</sup> %
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C≡C-	75
<i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> C≡C-	80
<i>p</i> - <i>i</i> -C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> C≡C-	85
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> C≡C-	33
<i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡C-	<i>c</i>

<sup>a</sup> Solvent, THF; molar ratio, 1.0; temperature, 0°. <sup>b</sup> Based on the initial amounts of Grignard reagents in the reaction systems. <sup>c</sup> Coupling product was not isolated, but detected by tlc.

para-substituted diphenylethynylmagnesium bromide and 1-hexynylmagnesium bromide. The introduction of electron-releasing groups in the para position of the phenyl group increased the yields of coupling products, and thus the electron density of the triple bond must be important at some stage in this reaction. When a similar reaction of 1-hexynylmagnesium bromide was attempted, each attempt to isolate dodeca-5,7-diyne failed, but its presence as a major component of the reaction product was confirmed by thin layer chromatography (tlc) on silica gel and activated alumina.

A mechanistic study of this coupling reaction is now in progress.

#### Experimental Section

Melting points were not corrected.

THF, diethyl ether, di-*n*-butyl ether, and diethylene glycol dimethyl ether were refluxed in the presence of sodium and then fractionated. Ethyl bromide was dried over anhydrous sodium carbonate prior to distillation. Thionyl chloride was distilled, and magnesium was used as received. Phenyl-, *p*-tolyl-, *p*-ethylphenyl-, *p*-isopropylphenyl-, and *p*-bromophenylacetylene were prepared according to the method of Campbell, *et al.*<sup>9</sup>

The nmr spectra were recorded on a JNM-3H-60 (60 MHz) nmr spectrometer; chemical shifts ( $\tau$ ) are reported in parts per million relative to tetramethylsilane (s, singlet; d, doublet; t, triplet; q, quartet; se, septuplet; m, multiplet). Mass spectra and ir spectra were measured with a Hitachi RMN-6E-type mass spectrometer and EPI-G2-type grating infrared spectrometers.

Acetylenic Grignard reagents were prepared by the reaction of acetylenic compounds with ethylmagnesium bromide in various solvents, and styrylmagnesium bromide was prepared by the reaction of *trans*- $\beta$ -bromostyrene with magnesium in THF.

A solution of 0.083 mol of Grignard reagent in 120 ml of the selected solvent was prepared under nitrogen in a 500-ml round-bottomed flask fitted with a reflux condenser, dropping funnel, gas-inlet tube, and magnetic stirrer. The flask was immersed in a Dry Ice-acetone bath or a water bath to keep the reaction temperature at -40, 0, or 30°. A solution of a predetermined amount of thionyl chloride in 80 ml of solvent was added over a period of 3 hr to the stirred solution of the Grignard reagent. An exothermic reaction took place. After the reaction mixture was stirred for an additional 0.5 hr, the solvent was removed *in vacuo*. The residue was washed with saturated aqueous ammonium chloride solution and water and then extracted with ether. The ethereal extract was dried over anhydrous magnesium sulfate. The black-brown tar which was left after removal of the ether was separated into benzene eluate and ethanol eluate by column

chromatography on activated alumina. Benzene was removed from the benzene eluate and needle crystals were obtained. Recrystallization of these crystals afforded the following coupling products.

**1,4-Diphenylbuta-1,3-diyne** (from phenylethynylmagnesium bromide) had mp 87-89° (ethanol-water); ir (KBr disk) 2140 cm<sup>-1</sup> (C≡C); nmr (CCl<sub>4</sub>)  $\tau$  2.63 (aryl H). *Anal.* Calcd for C<sub>16</sub>H<sub>10</sub>: C, 95.02; H, 4.98; mol wt, 202.24. Found: C, 95.17; H, 4.73. The mass spectrum showed *m/e* (rel intensity) 202 (100), 101 (7).

**1,4-Di-*p*-tolylbuta-1,3-diyne** (from *p*-tolylethynylmagnesium bromide) had mp 183° (ether); ir (KBr disk) 2130 cm<sup>-1</sup> (C≡C); nmr (CDCl<sub>3</sub>)  $\tau$  7.70 (s, 6 H, CH<sub>3</sub>), 2.18 (m, 8 H, aryl H). *Anal.* Calcd for C<sub>18</sub>H<sub>14</sub>: C, 93.87; H, 6.13; mol wt, 230.29. Found: C, 93.74; H, 5.99. The mass spectrum showed *m/e* (rel intensity) 230 (100), 215 (13), 115 (9).

**1,4-Di-*p*-ethylphenylbuta-1,3-diyne** (from *p*-ethylphenylethynylmagnesium bromide) had mp 98-99° (ethanol); ir (KBr disk) 2140 cm<sup>-1</sup> (C≡C); nmr (CCl<sub>4</sub>)  $\tau$  8.74 (t, 6 H, CH<sub>3</sub>, *J* = 7.0 Hz), 7.37 (q, 4 H, CH<sub>2</sub>, *J* = 7.0 Hz), 2.77 (m, 8 H, aryl H). *Anal.* Calcd for C<sub>20</sub>H<sub>18</sub>: C, 92.98; H, 7.02; mol wt, 258.34. Found: C, 93.01; H, 7.03. The mass spectrum showed *m/e* (rel intensity) 258 (100), 243 (67), 229 (28), 129 (8).

**1,4-Di-*p*-isopropylphenylbuta-1,3-diyne** (from *p*-isopropylphenylethynylmagnesium bromide) had mp 131-132° (ethanol); ir (KBr disk) 2140 cm<sup>-1</sup> (C≡C); nmr (CCl<sub>4</sub>)  $\tau$  8.75 (d, 12 H, CH<sub>3</sub>, *J* = 7.0 Hz), 7.17 (se, 2 H, CH, *J* = 7.0 Hz), 2.77 (q, 8 H, aryl H). *Anal.* Calcd for C<sub>22</sub>H<sub>22</sub>: C, 92.26; H, 7.75; mol wt, 286.40. Found: C, 92.22; H, 7.44. The mass spectrum showed *m/e* (rel intensity) 286 (100), 256 (12), 143 (6), 128 (27).

**1,4-Di-*p*-bromophenylbuta-1,3-diyne** (from *p*-bromophenylethynylmagnesium bromide) had mp 260° (benzene); ir (KBr disk) 2150 cm<sup>-1</sup> (C≡C); very insoluble in common organic solvents. *Anal.* Calcd for C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub>: C, 53.39; H, 2.24; mol wt, 360.05. Found: C, 53.37; H, 2.18. The mass spectrum showed *m/e* (rel intensity) 362 (52), 360 (100), 358 (52), 200 (30).

***trans,trans*-1,4-Diphenylbuta-1,3-diene** (from *trans*-styrylmagnesium bromide) had mp 152-153° (ether); ir (KBr disk) 994, 986 cm<sup>-1</sup> (*trans* CH=CH); nmr (CCl<sub>4</sub>)  $\tau$  2.72 (m, 4 H, CH=CH), 3.27 (m, 10 H, aryl H). *Anal.* Calcd for C<sub>16</sub>H<sub>14</sub>: C, 93.16; H, 6.58; mol wt, 206.29. Found: C, 93.10; H, 6.58. The mass spectrum showed *m/e* (rel intensity) 206 (100), 191 (38), 128 (33).

After ethanol was removed from ethanol eluates, black-brown colored tarry materials were obtained. Beilstein tests and sodium fusion tests indicated the existence of halogen and sulfur in these substances. However, each attempt to separate compounds containing sulfur by distillation or recrystallization failed.

When the reaction of 1-hexynylmagnesium bromide with thionyl chloride was attempted under the condition described previously, separation of reaction products by distillation or recrystallization was impossible. However, dodeca-5,7-diyne was detected in the reaction product by tlc on silica gel and activated alumina. Two spots appeared on the plates after development with benzene. The larger spot (*R<sub>f</sub>* 0.60 on silica gel and 0.78 on activated alumina) corresponded to an authentic sample of dodeca-5,7-diyne prepared by the method described by Cameron, *et al.*<sup>10</sup>

**Registry No.**—Phenylethynylmagnesium bromide, 6738-06-3; *trans*-styrylmagnesium bromide, 35672-47-0; thionyl chloride, 7719-09-7; 1,4-diphenyl-1,3-butadiyne, 886-66-8; 1,4-di-*p*-tolylbuta-1,3-diyne, 22666-07-5; 1,4-di-*p*-ethylphenylbuta-1,3-diyne, 35672-48-1; 1,4-di-*p*-isopropylphenylbuta-1,3-diyne, 35672-49-2; 1,4-di-*p*-bromophenylbuta-1,3-diyne, 959-88-6; *trans,trans*-1,4-diphenylbuta-1,3-diene, 538-81-8.

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