plete until room temperature was attained and then made distinctly acid with concentrated hydrochloric acid and reduced to one-half the original volume by distillation.

The reaction of p-cyanobenzencdiazonium chloride and pvinylanisole gave a brown solid which was recrystallized from aqueous ethanol to give 7.17 g. (41%) of trans-4cyano-4'-methoxystilbene, m.p. 133-141°, as red-brown plates. Neher and Miescher<sup>14</sup> report a cis-trans mixture as white plates, m.p. 149°, clearing at 162°. A sample recrystallized four times from aqueous ethanol yielded coppercolored plates, m.p. 143-143.5°. Anal. Caled. for  $C_{16}H_{13}ON$ : C, 81.68; H, 5.57. Found: C, 81.89; H, 5.54.

The reaction of p-acetylbenzenediazonium chloride and pvinylanisole gave a brown solid which was recrystallized from ethanol to give 3.55 g, (19%) of *trans*-4-acetyl-4'-methoxystilbene, m.p. 167–172°. A sample recrystallized four times from ethyl acetate gave light brown plates, m.p. 174.5– 175°.

Anal. Caled. for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>: C, 80.92; H, 6.39. Found: C, 80.96; H, 6.50. COLUMBIA, MO.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## The Reaction of Vinyl Sulfides and Alkyl Sulfides with Butyllithium<sup>1</sup>

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n-Butyllithium adds readily to the double bond of phenyl vinyl sulfide, and the lithium atom in the resulting adduct is located on the carbon atom adjacent to the sulfur atom. The driving force for this reaction is considered to be stabilization of the resulting carbanion by d-orbital interaction of sulfur. The reaction is apparently general for alkyllithium derivatives, but does not occur with phenyllithium or Grignard reagents. Vinyl ethers also do not undergo the reaction. A new synthesis of vinyl sulfides is reported which involves the elimination of phenylmercaptide from 1,2-bis-(phenylmercapto)ethane by reaction with phenyllithium.

There have been many reports of the conjugation ability of the sulfonyl<sup>3</sup> and sulfonium groups,<sup>4</sup> and it is rather generally accepted that the sulfur atom in these groups can stabilize unshared electrons on an adjacent carbon atom by using its d-orbitals. However, in systems containing bivalent sulfur, in which the sulfur exerts a smaller electrical demand, the available evidence indicates that d-orbital interaction of sulfur is small<sup>5</sup> unless there is a charge equivalent to a carbanion adjacent to sulfur. The greater acidity<sup>6-9</sup> of I relative to IV is well recognized, and this fact is best explained by assuming added stabilization of the carbanion II by d-orbital interaction of sulfur (III).

$$R-S-CH + B \xrightarrow{\ominus} R \xrightarrow{} R \xrightarrow{} S-C \xrightarrow{\ominus} \xrightarrow{} R \xrightarrow{} S-C \xrightarrow{\ominus} \xrightarrow{} R \xrightarrow{} S-C \xrightarrow{} I \xrightarrow{} I$$

Our present investigation was planned to add more information to possible d-orbital interaction of bivalent sulfur by comparing the behavior of

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(2) Procter and Gamble Research Fellow, Summer, 1958.

(3) (a) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949);
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(4) F. (2) (1950);
(b) H. P. Koch, J. Chem. Soc., 387, 394 (1949);
(c) C. C. Price and J. J. Hydock, THIS JOURNAL, **74**, 1943 (1952);
(d) F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952);
(e) F. G. Bordwell and H. M. Anderson, *ibid.*, **75**, 6019 (1953);
(f) A. Kotch, L. H. Krol, P. E. Verkade and B. M. Wepster, Rec. trav. chim., **71**, 108 (1952);
(g) H. Kloosterziel and H. J. Backer, *ibid.*, **72**, 185 (1953);
(h) **72**, 655 (1953);
(i) W. E. Doering and L. K. Levy, *ibid.*, **73**, 509 (1955).

(4) Cf. (a) W. von E. Doering and K. C. Schreiber, THIS JOURNAL, 77, 514 (1955); (b) W. von E. Doering and A. K. Hoffmann, *ibid.*, 77, 521 (1955); (c) S. Oac and C. C. Price, *ibid.*, 80, 3425 (1958).

(5) Cf. F. G. Bordwell and P. J. Boutan, ibid., 78, 854 (1956)

(6) D. S. Tarbell and M. A. McCall, ibid., 74, 48 (1952).

(7) R. B. Woodward and R. H. Eastman, ibid., 68, 2229 (1954).

- (8) W. J. Brehm and T. Levenson. ibid., 76, 5389 (1954).
- (9) H. G. Gilman and F. J. Webb, ibid., 71, 4062 (1949).

vinyl sulfides and vinyl ethers in their reactions with organometallic derivatives.

Phenyl vinyl sulfide was allowed to react with n-butyllithium in ether at 0°, and the reaction product VI was treated directly with water. The

 $C_6H_5S--CH=CH_2 + n-C_4H_9Li \longrightarrow$ 

$$\begin{array}{cccc} & & & & \\ C_6H_5S-CH-C_5H_{11}--\overbrace{CO_2}^{II_2O} & & & \\ C_6H_5S-CH-C_5H_{11}--\overbrace{CO_2}^{II_2O} & & \\ C_6H_5S-CH-C_5H_{11} \\ & & \\ VI & & \\ VII & COOH \end{array}$$

product, isolated in 55% yield, was shown to be *n*-hexyl phenyl sulfide (VII) by comparison of VII, and the derived sulfilimine and palladium complex, with authentic VII and its corresponding derivatives. The yield of phenyl hexyl sulfide was 36, 55, 51, and 0% when the reaction was carried out at 25, 0, -20 and  $-40^{\circ}$ , respectively. When the reaction product VI was treated di-

When the reaction product VI was treated directly with carbon dioxide,  $\alpha$ -phenylmercaptoheptanoic acid (VIII) was formed, and was isolated in 51.7% yield. There was no evidence for the presence of isomeric acids; consequently, it was concluded that the lithium atom is located principally on the  $\alpha$ -carbon atom of the aliphatic chain, and that the reaction sequence V  $\rightarrow$  VI  $\rightarrow$ VII or VIII obtained.

The reaction of phenyl vinyl sulfide with aliphatic lithium derivatives appears to be general. *n*-Butyl phenyl sulfide was prepared in 68%yields when ethyllithium was used in place of *n*butyllithium. Phenyl vinyl sulfide does not react appreciably with phenyllithium, *n*-butylmagnesium bromide, benzylmagnesium chloride or *t*-butylmagnesium chloride.

When 1,2-bis-phenylmercapto-ethane (IX) was treated with a fourfold excess of n-butyllithium, and the resulting product treated with water,

*n*-hexyl phenyl sulfide (VII) was formed and isolated in 36% yield. This product could result by  $C_6H_5S-CH_2CH_2S-C_6H_5 + n-C_4H_9Li \longrightarrow$ 

$$\begin{array}{c} C_{6}H_{6}S - C_{6}H_{13} + C_{6}H_{6}S \Theta \\ \\ VII \end{array}$$

direct cleavage of the sulfide IX (path A), or by metalation,  $\beta$ -elimination and subsequent addition

(A) 
$$C_6H_5S-CH_2CH_2S-C_6H_5 \longrightarrow VII + C_6H_5S^{\ominus}$$

(B) IX + C<sub>4</sub>II<sub>9</sub>Li 
$$\longrightarrow$$
 C<sub>6</sub>II<sub>5</sub>SCHCII<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  $\longrightarrow$   
Li  
C<sub>6</sub>H<sub>6</sub>SCH=CII<sub>2</sub> + C<sub>6</sub>H<sub>5</sub>S $\ni$   
V  
V + C<sub>4</sub>II<sub>9</sub>Li  $\longrightarrow$  C<sub>6</sub>H<sub>6</sub>S-CH-C<sub>5</sub>H<sub>11</sub>  $\xrightarrow{\text{H}_2\text{O}}$  VII  
Li

of butyllithium to the intermediate phenyl vinyl sulfide (path B). Path B was shown to be the reaction sequence, since the intermediate phenyl vinyl sulfide was isolated in 44% yield from the reaction of bis-(phenylmercapto)-ethane (IX) and phenyllithium.

The reaction of phenyl vinyl ether with organometallic intermediates is in sharp contrast to that of the analogous vinyl sulfides. Phenyl vinyl ether was recovered in 73% yield when treated with butyllithium in ether at 0°, under conditions identical to those employed for reactions with phenyl vinyl sulfide. When *n*-butyllithium in boiling ether was employed, cleavage of the vinyl ether resulted. This reaction is similar to that

$$C_6H_5O-CH=CH_2 + n - C_4H_9Li \longrightarrow C_6H_5OLi$$

previously reported for the reaction of vinyl ethers with phenyllithium<sup>10</sup> and with Grignard reagents.<sup>11</sup>

Bartlett, Friedman and Steles<sup>12</sup> have observed that secondary and tertiary alkyllithium derivatives are far more reactive toward the unsubstituted double bond than any known primary organometallic derivative, and have concluded that this high reactivity is associated with the greater stability of the primary carbanion relative to the secondary or tertiary carbanion. In reactions with vinyl sulfides the primary organolithium derivatives are converted into secondary carbanions, and it seems compelling to assume that sulfur can stabilize the resulting carbanion. The facile addition of alkyllithium derivatives to phenyl vinyl sulfide, the different behavior noted for the analogous vinyl ethers, and the other work alluded to in the introduction are all consistent with the interpretation that the driving force for the addition of alkyllithium derivatives to vinyl sulfides is the added stability of the resulting carbanion II, which is achieved by resonance involving d-orbitals of sulfur.

## Experimental

1-Phenylmercapto-2-acetoxyethane.— $\beta$ -Hydroxyethyl phenyl sulfide was prepared from thiophenol (100 g., 0.909 mole) and ethylene chlorohydrin (74.0 g., 0.92 mole) by a method previously reported.<sup>13</sup> The undistilled product was treated with acetic anhydride (130 g., 1.127 moles) and sodium acetate (3.0 g., 0.0366 mole), and the resulting solution was heated for 16 hours. The mixture was diluted with water and the organic product was dried and distilled. There was obtained 166.5 g. (93.6% yield) of 1-phenylmercapto-2-acetoxyethane<sup>14</sup> (b.p. 97-99° (0.6 mm.),  $n^{26.3}$ D 1.5443).

Phenyl Vinyl Sulfide.—1-Phenylmercapto-2-acetoxycthane (110.5 g., 0.565 mole) was added dropwise (20 drops per minute) to a glass column (50 cm., packed with glass beads) heated to 450°. The condensate was collected, washed with alkali, dried, and distilled to give phenyl vinyl sulfide<sup>15</sup> (33.1 g., 43.2%, b.p. 02-64° (5.5 mm.), n<sup>26.7</sup>D 1.5800-1.5847) and recovered acetate (46.8 g., 42.4%). Phenyl vinyl sulfide was further characterized by its conversion into the corresponding sulfone (m.p. 65-68.5°, reported<sup>15</sup> 66.5-67.5°).

The Reaction of Phenyl Vinyl Sulfide with *n*-Butyllithium. The Preparation of *n*-Hexyl Phenyl Sulfide (VII).—A solution of *n*-butyllithium (prepared<sup>16</sup> from lithium (2.0 g., 0.117 g. at.) and *n*-butyl bromide (16.0 g., 0.117 mole)) in ether (150 ml.), under an atmosphere of nitrogen, was allowed to warm to 0°, and a solution of phenyl vinyl sulfide (5.0 g., 0.036 mole) in ether (70 ml.) was added slowly. The reaction mixture rapidly became bright yellow and was stirred at 0° for 4 hours. The resulting solution was treated with water (100 ml.), and the ether layer was dried and distilled. The product, which was subsequently shown to be *n*-hexyl phenyl sulfide, was collected at 70-70° (0.3 mm.) (3.93 g., 56.4% yield,  $n^{26.7}$ p 1.5302; reported<sup>17</sup> b.p. 124.5° (2.0 mm),  $n^{20}$ p 1.5336).

When the above reaction was carried out at 25, -20 and  $-40^{\circ}$ , the yields of *n*-hexyl phenyl sulfide were, 36, 51 and 0%, respectively.

0%, respectively. The structure of the product was established by comparing its infrared spectrum with that of authentic *n*-hexyl phenyl sulfide, and by its conversion into the sulfilimine derivative (m.p. and mixture m.p. 82-83°), and the palladous chloride complex (m.p. and mixture m.p. 92.5-93.5°) of *n*-hexyl phenyl sulfide.

Authentic *n*-hexyl phenyl sulfide<sup>17</sup> ( $n^{26.5}$ <sub>D</sub> 1.5305, reported  $n^{20}$ <sub>D</sub> 1.5336) was prepared in 71% yield from thisphenol and *n*-hexyl bromide by a procedure essentially identical to that previously reported.

The sulfilimine (m.p. 82-83°) was prepared in acctone in the usual way, and was recrystallized from methanol.

Anal. Caled. for  $C_{19}H_{25}NO_5S_2$ : C, 62.77; H, 6.93; N, 3.85. Found: C, 62.94; H, 6.90; N, 3.74.

The Reaction of Phenyl Vinyl Sulfide with *n*-Butyllithium. The Preparation of  $\alpha$ -Phenylmercaptoheptanoic Acid (VIII). —The reaction of phenyl vinyl sulfide (5.0 g., 0.0368 mole) and *n*-butyllithium (from 2.0 g., 0.289 g. at., of lithium) was carried out as described above. The product was not treated with water, but instead was poured onto powdered Dry Ice. The resulting mixture was diluted with water, acidified with hydrochloric acid, and extracted with ether. The combined ether extract was dried and distilled through a short path column. There was obtained, in addition to valeric acid, a high boiling acid (b.p. 140–145° (0.20 mm.),  $n^{26.3}$ p. 1.5382, 4.53 g., 51.7% yield) and undistilled residue (2.56 g.).

column. There was obtained, in addition to valeric acid, a high boiling acid (b.p. 140–145° (0.20 mm.),  $n^{26.3}$ D 1.5382, 4.53 g., 51.7% yield) and undistilled residue (2.56 g.). The acid was converted into the amide, m.p. 105–106°, and the anilide, m.p. 86–87°. These derivatives caused no depression in melting points when admixed with the corresponding amide and anilide of  $\alpha$ -phenylmercaptoheptanoic acid.

The Amide and Anilide of  $\alpha$ -Phenylmercaptoheptanoic Acid.— $\alpha$ -Bromoheptanoic acid<sup>18</sup> (10.5 g., 0.0502 mole) was added to a solution prepared from sodium (2.3 g., 0.10

(14) Werner Zerweck and Walter Brunner, German Patent 887,504, Aug. 24, 1953, C. A., 48, 12166c (1954).

<sup>(10)</sup> G. Wittig and G. Harborth, Ber., 77B, 306 (1944).

<sup>(11)</sup> C. M. Hill, R. M. Prigmore and G. J. Moore, This JOURNAL, 77, 352 (1955).

<sup>(12)</sup> P. D. Bartlett, S. Friedman and M. Steles, *ibid.*, 75, 1771 (1953).

<sup>(13)</sup> W. R. Kirner and G. H. Richter, ibid., 51, 3409 (1929).

<sup>(15)</sup> C. C. Price and H. Morita, THIS JOURNAL, 75, 4747 (1953).
(16) R. G. Jones and H. Gilman, "Organic Reactions," Vol. 6, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339 ff.

<sup>(17)</sup> A. I. Vogel, J. Chem. Soc., 1820 (1948).

<sup>(18)</sup> V. B. Abderhalden and S. Glaubach, Fermentf., 6, 348 (1923).

mole), thiophenol (6.0 g., 0.0546 mole) and ethanol (50 ml.). A rapid reaction occurred and sodium bromide precipitated immediately. The solution was heated at the reflux temperature for 12 hours, then ethanol was removed (140 mm.), and the resulting mixture was diluted with water. The aqueous solution was acidified with hydrochloric acid and extracted with ether. The ether extract was dried and distilled. The product,  $\alpha$ -phenylmercaptoheptanoic acid, was collected at 140–150° (0.25 mm.) (10.0 g., 84% yield,  $n^{19.3}$  1.5378).

 $\alpha$ -Phenylmercaptoheptanoic acid was converted to its amide in the usual manner by reaction first with thionyl chloride, and then subsequent reaction of the intermediate acid chloride with ammonium hydroxide. The product was recrystallized from petroleum ether (b.p. 60–68°) and melted at 105–106°.

Anal. Caled. for  $C_{13}H_{19}NO_3$ : C, 65.78; H, 8.07; N, 5.90. Found: C, 66.05; H, 8.11; N, 5.88.

 $\alpha$ -Phenylmercaptoheptanoic acid was converted to its anilide in the usual way by treating the intermediate acid chloride (prepared by reaction with thionyl chloride) with aniline. The product was recrystallized from ethanolwater, and melted at 87–87.5°.

Anal. Caled. for  $C_{19}H_{23}NSO$ : C, 72.80; H, 7.39; N, 4.47. Found: C, 73.12; H, 7.50; N, 4.47.

Reaction of Phenyl Vinyl Sulfide with Ethyllithium. The Preparation of *n*-Butyl Phenyl Sulfide.—A solution of phenyl vinyl sulfide (5.0 g., 0.0368 mole) in anhydrous ether (70 ml.) was added to a solution of ethyllithium<sup>19</sup> (0.119 mole) in anhydrous ether (150 ml.), precooled to  $-15^{\circ}$ . The resulting solution was maintained at  $-15^{\circ}$  for 4 hours and then processed as described for the reaction using *n*butyllithium. There was obtained 4.04 g. (68.2% yield) of *n*-butyl phenyl sulfide (b.p. 78–83° (2.3 mm.),  $n^{28}_{D}$  1.5463). The infrared spectrum of this product was identical to that of an authentic sample of *n*-butyl phenyl sulfide ( $n^{28.7}_{D}$ 1.542), prepared (75% yield), as previously described,<sup>20</sup> from thiophenol and *n*-butyl bromide.

Anal. Caled. for C<sub>10</sub>H<sub>14</sub>S: C, 72.26; H, 8.49. Found: C, 72.55; H, 8.77.

The palladous chloride complex prepared from authentic *n*-butyl phenyl sulfide melted at 109–110° (reported<sup>20</sup> m.p. 106–106.5°), and that prepared from the product of reaction of phenyl vinyl sulfide and ethyllithium melted at 109–110°. A mixture melting point of these materials was 108–110°.

Attempted Reaction of Phenyl Vinyl Sulfide with Other Organometallic Derivatives.—The same general procedure was employed in these reactions as described above with *n*-butyllithium and ethyllithium.

When phenyl vinyl sulfide was allowed to react with phenyllithium for 6 hours at 0°, only starting material (65% recovery) and small amounts of biphenyl were obtained. Similar results were obtained with *n*-butylmagnesium bromide ( $25^{\circ}$ , 4 hours, 76% recovery of V), benzylmagnesium chloride ( $25^{\circ}$ , 4 hours, 89% recovery of V), *t*-butylmagne-

(19) W. H. Nebergall, THIS JOURNAL, 72, 4702 (1950).

(20) V. N. Ipatieff, H. Pines and B. S. Friedman, *ibid.*, **60**, 2731 (1938).

sium chloride (0°, 3 hours, 54.8% recovery of V). Only small amounts, if indeed any, addition products were formed.

Reaction of 1,2-Bis-(phenyImercapto)-ethane (IX) with *n*-Butyllithium.—A solution of *n*-butyllithium (0.226 mole) in anhydrous ether (200 ml.) was added to a solution of bis-(phenyImercapto)-ethane<sup>21</sup> (10 g., 0.0464 mole) in anhydrous ether (400 ml.). The solution was stirred at 25° for 5 hours. Water (200 ml.) was added to the reaction mixture, and the ether layer was separated, dried (MgSO<sub>4</sub>), and distilled. There was obtained 3.04 g. (b.p. 60–75° (0.3 mm.),  $n^{26.6}$ D 1.5240–1.5309, 36.8% yield) of *n*-hexyl phenyl sulfide, and 47.2% recovery of unchanged IX. There was a trace of material collected at 55–60° (2.5 mm.),  $n^{26}$ D 1.5705. The infrared spectrum of this material was essentially identical to that of phenyl vinyl sulfide.

The *n*-hexyl phenyl sulfide was characterized by comparison of its infrared spectrum with authentic VII, and by its conversion into the corresponding sulfilimine (m.p. and mixture m.p.  $82-83^{\circ}$ ).

Reaction of 1,2-Bis-(phenylmercapto)-ethane (IX) with Phenyllithium.—A solution of phenyllithium<sup>16</sup> (0.266 mole) in anhydrous ether (200 ml.) was added (under nitrogen) to a solution of 1,2-bis-(phenylmercapto)-ethane (10.0 g., 0.0408 mole) in anhydrous ether (400 ml.). The solution was stirred for 10 hours in refluxing ether, and then was hydrolyzed with water (200 ml.); the resulting mixture was extracted with ether. The combined ether extract was dried (MgSO<sub>4</sub>) and distilled. There was obtained 2.45 g. (44% yield) of phenyl vinyl sulfide (b.p. 65-70° (6.8 mm.),  $n^{30}$ D 1.5762) and 4.17 g. (41.7% recovery) of unchanged IX (m.p. 70-71.5°).

The phenyl vinyl sulfide was further characterized by comparing its infrared spectrum with that of authentic phenyl vinyl sulfide, and by its conversion into *n*-hexyl phenyl sulfide by reaction with *n*-butyllithium.

Reaction of Phenyl Vinyl Ether with *n*-Butyllithium.—A cold  $(0^{\circ})$  solution of *n*-butyllithium (0.117 mole) in anhydrous ether (150 ml.) was added to a solution of phenyl vinyl ether<sup>22</sup> (5.0 g., 0.041 mole) in anhydrous ether (70 ml.). The solution was stirred at  $-10^{\circ}$  for one hour, and then was heated at the reflux temperature for 6 hours. Water (100 ml.) was added to the reaction mixture, and the ether layer was dried and distilled. There was obtained 0.33 g. (6.6%) of recovered phenyl vinyl ether.

The aqueous layer was acidified with hydrochloric acid, extracted with ether, and the ether layer was dried and distilled. There was obtained 1.95 g. (50.7%) of phenol (b.p. 88-94° (22 mm.). The phenol solidified and was shown to be identical to authentic phenol (infrared spectra).

be identical to authentic phenol (infrared spectra). When the above reaction was carried out for four hours at  $0^{\circ}$ , there was obtained a 73.4% recovery of phenyl vinyl ether.

When phenyl vinyl ether was treated under similar conditions with phenylmagnesium bromide (4 hours at  $25^{\circ}$ ), there was obtained at 95.4% recovery of unchanged phenyl vinyl ether.

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<sup>(21)</sup> J. Hine and W. H. Broder, Jr., ibid., 75, 3964 (1953).

<sup>(22)</sup> W. M. Lauer and M. A. Spielman, ibid., 55, 1572 (1933).