

Frey and Kistiakowsky<sup>16</sup> have demonstrated that methyl radicals are not responsible for the C-H substitutions of CH<sub>2</sub> by demonstrating that free

oxygen does not affect the course of this type of substitution reaction.

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

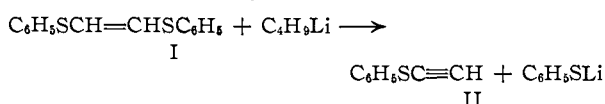
## The Reaction of Bis-(substituted-mercapto)-ethylenes with *n*-Butyllithium<sup>1</sup>

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*n*-Butyllithium reacts with bis-(substituted-mercapto)-ethylenes by elimination of mercaptide to give substituted mercaptoacetylenes:  $\text{RSCH}=\text{CHSR} + \text{C}_4\text{H}_9\text{Li} \longrightarrow \text{RSLi} + \text{HC}\equiv\text{CSR}$ . A series of symmetrical and unsymmetrical vinyl sulfides and vinyl ethers of this type has been prepared and the reaction of these compounds with *n*-butyllithium has been studied. The reaction has been found to be quite general for the synthesis of alkyl or arylmercaptoacetylenes, with little preference in elimination of normal alkyl or aromatic mercaptide. The reaction is, however, subject to steric and electrical effects, and the products of reaction are consistent with a  $\beta$ -elimination mechanism, but inconsistent with an  $\alpha$ -elimination mechanism.

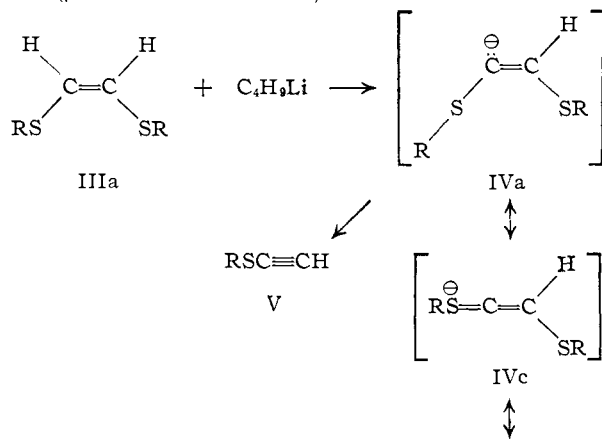
Parham and Stright<sup>3</sup> recently described a new synthesis of phenylmercaptoacetylene (II) by reaction of *cis*- or *trans*-1,2-bis-(phenylmercapto)-ethylene (I) with butyllithium.



The results described in this report summarize further studies which were designed: (a) to define the scope of the reaction, and (b) to furnish additional information concerning the reaction sequence by which the products are formed.

Elimination reactions which are formally analogous to the one described above are well known, and three general mechanisms can be formulated:  $\beta$ -elimination<sup>4</sup> (equation A), cyclic transition state<sup>5</sup> (equation B) and  $\alpha$ -elimination

A. ( $\beta$ -elimination mechanism)



(1) This work was supported by the Office of Ordnance Research, Contract No. DA-11-022-Ord-2616.

(2) From the Ph.D. thesis of Robert F. Motter, University of Minnesota, 1958.

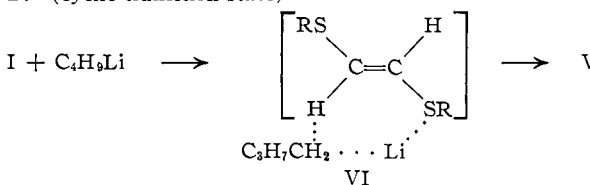
(3) W. E. Parham and P. L. Stright, *THIS JOURNAL*, **78**, 4783 (1956).

(4) Cf. (a) D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4519 (1951); (b) W. E. Truce, J. A. Simms and M. Bodakian, *ibid.*, **78**, 695 (1956).

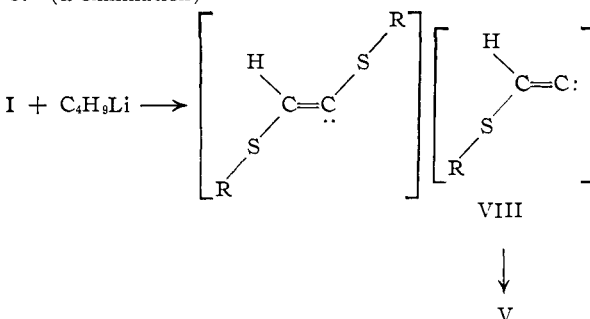
(5) Cf. (a) S. J. Cristol and R. F. Helmreich, *ibid.*, **77**, 5034 (1955); (b) A. Bothner-By, *ibid.*, **77**, 2393; (c) R. L. Letsinger and E. Bobko, *ibid.*, **75**, 2649 (1953).



B. (cyclic transition state)



C. ( $\alpha$ -elimination)



Our initial attempts to elucidate the course of this reaction by kinetic studies<sup>6</sup> were unsuccessful. *cis*- and *trans*-bis-(phenylmercapto)ethylene were prepared, and a rapid spectrophotometric method for the quantitative determination of lithium thiophenolate was developed. However, the rapid rate at which both *cis*- and *trans*-I react (reaction complete after one minute) under the conditions employed (25°, 4.9 × 10<sup>-5</sup> molar in I, 1.5 × 10<sup>-3</sup> molar in butyllithium) has precluded obtaining reliable kinetic data.

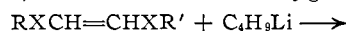
Definition of the scope of the elimination reaction, as well as further data concerning the

(6) If the  $\beta$ -elimination mechanism obtains, without rapid isomerization of the intermediate ions (IVa  $\rightleftharpoons$  IVb  $\rightleftharpoons$  IVc), then one would expect *trans* elimination from the *cis* isomer IIIa, to be more rapid than *cis* elimination from the *trans* isomer IIIb. Similarly, for the cyclic transition state mechanism (equation B) one would expect elimination from the *trans* isomer IIIb (via VI) to be more favorable than from the *cis* isomer, in view of the more favored transition state possible for the former.<sup>5b</sup>

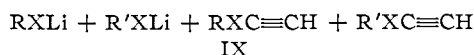
TABLE I

	Sulfide VIII	Mercaptan or alcohol eliminated	Product IX	Yield, %
VIIIa	C <sub>6</sub> H <sub>5</sub> -S-CH=CH-S-C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> SH	C <sub>6</sub> H <sub>5</sub> -S-C≡CH	IXa (90)
VIIIb	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -S-CH=CH-S-C <sub>4</sub> H <sub>9</sub> - <i>n</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -S-C≡CH	IXb (63)
VIIIc	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -S-CH=CH-S-C <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> SH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -S-C≡CH	IXc (60)
VIII d	C <sub>6</sub> H <sub>5</sub> -S-CH=CH-S-C <sub>4</sub> H <sub>9</sub> - <i>n</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> SH	C <sub>6</sub> H <sub>5</sub> -S-C≡CH	IXa (22-29)
		C <sub>6</sub> H <sub>5</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -S-C≡CH	IXb (24-33)
VIIIe	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -S-CH=CH-S-C <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -S-C≡CH	IXb (40)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> SH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -S-C≡CH	IXc (9)
VIII f	C <sub>6</sub> H <sub>5</sub> -S-CH=CH-S-C <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> SH	C <sub>6</sub> H <sub>5</sub> -S-C≡CH	IXa (56)
		C <sub>6</sub> H <sub>5</sub> -SH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -S-C≡CH	IXc (3-6)
VIII g	C <sub>6</sub> H <sub>5</sub> -S-CH=CH-OC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> -S-C≡CH	IXa (82)
VIII h	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -S-CH=CH-O-C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> OH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -S-C≡CH	IXb (69)
VIII i	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -S-CH=CH-O-C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> OH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -S-C≡CH	IXc (24) + recovd. VIIIi (37)
VIII j	C <sub>2</sub> H <sub>5</sub> -O-CH=CH-O-C <sub>2</sub> H <sub>5</sub>	.....	No reaction	.....

course of the reaction sequence, has been obtained by studies of electrical and steric effects which pertain to reactions of symmetrical and unsymmetrical ethylenic sulfides and ethers of type VIII (Table I) where X is sulfur or oxygen.



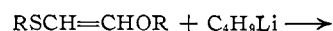
VIII



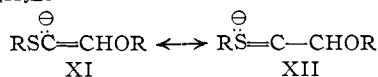
IX

From the products of the reactions shown in Table I a number of conclusions can be drawn: (1) the reaction of 1,2-substituted mercaptoethylenes with butyllithium is quite general for the synthesis of alkyl or arylmercaptoacetylenes; (2) there is little apparent difference in reactivity of between aromatic and normal alkyl substituted mercaptoethylene, and there is no significant selectivity in the elimination of aromatic or *n*-aliphatic mercaptide (VIIId→IXa + IXb); (3) the reaction is subject to steric effects as shown by the preference for the elimination of *t*-butyl mercaptan from VIIIe and VIII f; (4) the reaction is subject to electronic effects as shown by the exclusive elimination of ethanol from VIII g, and the failure of VIII j to react; and (5) the products of reaction are commensurate with the  $\beta$ -elimination mechanism (equation A), but not the  $\alpha$ -elimination mechanism (equation C).

The preferential elimination of ethanol from VIII g, VIII h and VIII i, and the failure of VIII j to react, are in accord with the previous conclusion<sup>7</sup> that bivalent sulfur increases the acidity of  $\alpha$ -hydrogen atoms to a greater extent than does

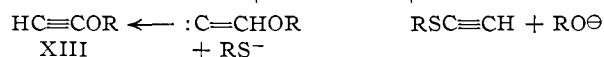
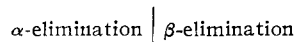


VIIIg-VIIIi



XI

XII

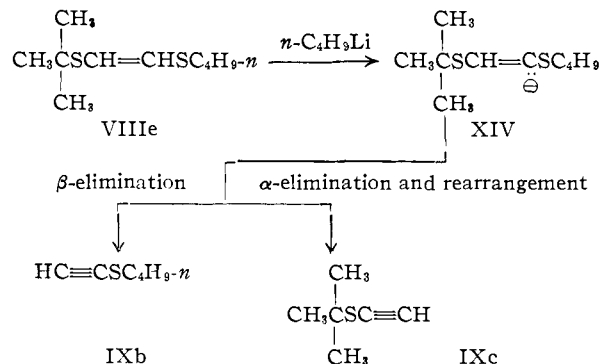


XIII

(7) (a) D. S. Tarbell and M. A. McCall, *THIS JOURNAL*, **74**, 48 (1952); (b) R. B. Woodward and R. H. Eastman, *ibid.*, **68**, 5389 (1954); (c) W. J. Brehm and T. Levenson, *ibid.*, **76**, 5389 (1954); (d) H. G. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949); (e) W. E. Parham and R. F. Motter, *ibid.*, **81**, 2146 (1959).

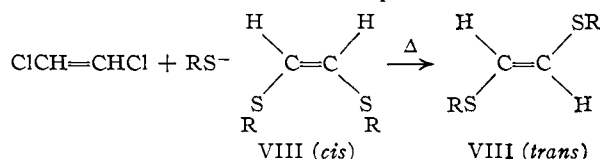
oxygen. This is explained on the basis of d-orbital interaction of the sulfur atom which can stabilize the ion XI as shown in formula XII. The preferential elimination of ethanol from XI with the formation of mercaptoacetylene is consistent with a  $\beta$ -elimination mechanism (reaction A or B); however,  $\alpha$ -elimination would result in the acetylenic ether XIII, which is not formed.

Furthermore, the steric requirements of the reaction, as noted in Table I by the preferential elimination of the *t*-butylmercapto group from VIIIe and VIII f, is consistent with the  $\beta$ -elimination mechanism (A). If it is assumed that the least



hindered hydrogen atom is removed from the ethylenic sulfide by the butyllithium (for example VIIIe → XIV); then  $\alpha$ -elimination and rearrangement is ruled out by the observed preponderant elimination of *t*-butyl mercaptide with the formation of IXb.

The symmetrical ethylenic sulfides VIIIa-VIIIc were prepared in high yield by reaction of *cis*-dichloroethylene with the corresponding mercaptide in ethanol. With the exception of VIIIa and

VIII (*cis*)VIII (*trans*)

VIIIc, all of the bis-sulfides are liquids. These products were assumed to have the *cis* configuration<sup>8,9</sup> but were partially isomerized to the *trans*

(8) Cf. W. E. Truce, M. H. Boudakian and R. J. McManis, *ibid.*, **78**, 2743 (1956).

(9) Cf. W. E. Parham and J. Heberling, *ibid.*, **77**, 1175 (1955).



sorption in the ultraviolet:  $\lambda_{\text{max}}$  257  $\mu$  ( $\epsilon$  8181),  $\lambda_{\text{max}}$  270  $\mu$  ( $\epsilon$  7710), inflection 228  $\mu$  ( $\epsilon$  4763).

A sample of the product (4.72 g., 0.0231 mole) was oxidized with hydrogen peroxide by a procedure identical to that described above. The crude product was recrystallized from ethanol which afforded white crystals melting at 148–150° (3.0 g., 48.6%).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{20}\text{S}_2\text{L}_4$ : C, 44.77; H, 7.52. Found: C, 44.54; H, 7.36.

**3. *cis*-1,2-Bis-(*t*-butylmercapto)-ethylene (VIIIc).**—The same general procedure was employed as previously described for VIIIb. A sample of the product (105 g., b.p. 70–84° (0.4 mm.), 92% yield) was recrystallized from ethanol-water, and the solid melted at 62–63° (reported<sup>12</sup> b.p. 118.5–120° (11 mm.), m.p. 58–59°); ultraviolet spectrum:  $\lambda_{\text{max}}$  250  $\mu$  ( $\epsilon$  9192), inflection 263  $\mu$  ( $\epsilon$  5377), inflection 230  $\mu$  ( $\epsilon$  5897).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{20}\text{S}_2$ : C, 58.80; H, 9.87; S, 31.39. Found (runs on same sample): C, 56.38, 59.24; H, 9.47, 9.10; S, 31.53.

**Substituted Acetylenes.** 1. *n*-Butylmercaptoacetylene (IXb).—A solution of *n*-butyllithium, prepared in the usual manner using lithium (7.0 g., 1.14 g. atoms) and *n*-butyl bromide (65.0 g., 0.407 mole), was added, in a nitrogen atmosphere, to a cold (–30°) solution of *cis*-1,2-bis-(*n*-butylmercapto)ethylene (22.75 g., 0.1115 mole) in anhydrous ether (500 ml.). The solution was allowed to warm, and was maintained at room temperature for one hour. The resulting mixture was filtered under nitrogen, and the solid was identified as lithium *n*-butylmercaptide by its conversion to *n*-butylmercaptan (b.p. 62° (140 mm.),  $n_{\text{D}}^{25}$  1.4332, 6.25 g., 62.3%). The filtrate was treated with water, and the ether extract was dried ( $\text{MgSO}_4$ ) and distilled. Most of the product was collected at: (1) 5.09 g., b.p. 68–71° (105 mm.),  $n_{\text{D}}^{25}$  1.4075–1.4258; and (2) 6.26 g., b.p. 83° (93 mm.),  $n_{\text{D}}^{25}$  1.4690.

Fraction 2 was shown to be essentially pure *n*-butylmercaptoacetylene (49.3%); infrared spectrum: absorption at 3330 and 2045  $\text{cm}^{-1}$ , typical of terminal acetylene, absence of –OH absorption.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{10}\text{S}$ : C, 63.13; H, 8.83. Found: C, 62.52; H, 9.03.

The infrared spectrum of fraction 1 suggested that it was a mixture containing *n*-butyl alcohol (approximately 60%) and *n*-butylmercaptoacetylene (approximately 40%). The presence of *n*-butyl alcohol was confirmed by the conversion of a sample of fraction 1 into *n*-butyl 3,5-dinitrobenzoate, m.p. and mixture m.p. 64°. A minimum of 1.79 g. of *n*-butylmercaptoacetylene was shown to be present by conversion of fraction 1, by a procedure to be described, into 1-phenylmercapto-2-*n*-butylmercaptoethylene (b.p. 118° (0.2 mm.),  $n_{\text{D}}^{25}$  1.5997, 3.41 g.). Thus the yield of *n*-butylmercaptoacetylene was at least 63.5%.

This reaction was repeated several times with comparable results.

**2. *t*-Butylmercaptoacetylene (IXc).**—A. The procedure described above was used starting with 1,2-bis-(*t*-butylmercapto)-ethylene (10.0 g., 0.492 mole). The product (4.82 g., 86% calculated as pure *t*-butylmercaptoacetylene) was collected in several fractions (b.p. 40–60° (90 mm.),  $n_{\text{D}}^{25}$  1.4390–1.4473); however, infrared analysis established that each fraction was a mixture of *t*-butylmercaptoacetylene (absorption at 3300, 2035<sup>-1</sup> and 1367  $\text{cm}^{-1}$ ) and *n*-butyl alcohol (ca. 10%). The minimum yield of *t*-butylmercaptoacetylene was 61.7%. This was confirmed by conversion of the crude product into *n*-butylmercapto-*t*-butylmercaptoethylene (b.p. 65–79° (0.25 mm.),  $n_{\text{D}}^{25}$  1.5172, 6.04 g., 71.7% yield) by a procedure to be described.

B. Essentially the same procedure was employed; however, phenyllithium was employed instead of *n*-butyllithium. There was obtained 6.75 g. (48% yield) of reasonably pure *t*-butylmercaptoacetylene (b.p. 54–64° (118 mm.), mostly at 65° (118 mm.),  $n_{\text{D}}^{25}$  1.4634–1.4652), together with other fractions containing mostly benzene with some *t*-butylmercaptoacetylene.

A sample of the product ( $n_{\text{D}}^{25}$  1.4634–1.4652) was re-fractionated and 79% of it collected at 61° (109 mm.) ( $n_{\text{D}}^{25}$  1.4631) (reported<sup>12</sup> b.p. 51.2–52.5° (72 mm.),  $n_{\text{D}}^{25}$  1.4667).

The mercury derivative of *t*-butylmercaptan was prepared in 84.6% yield by the general procedure of Johnson and Mc-

Ewen.<sup>13</sup> The product was recrystallized from ethanol and melted at 145–148°.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{18}\text{S}_2\text{Hg}$ : C, 33.75; H, 4.25; Hg, 46.98. Found: C, 33.74; H, 4.17; Hg, 46.77.

**3. Phenylmercaptoacetylene** was prepared from *cis*-1,2-bis-(phenylmercapto)-ethylene by the procedure previously reported<sup>3</sup>; however, phenyllithium was used instead of *n*-butyllithium. The product (b.p. 72° (6.5 mm.),  $n_{\text{D}}^{25}$  1.5913; reported<sup>3</sup> b.p. 78–79° (7 mm.),  $n_{\text{D}}^{25}$  1.5938) was obtained in yields varying from 73 to 90%.

**Preparation of the Unsymmetrical Sulfides (VIII).** 1. **1-Phenylmercapto-2-*n*-butylmercaptoethylene (VIIIa).** (a) **From *n*-Butylmercaptoacetylene.**—*n*-Butylmercaptoacetylene (1.70 g., 0.149 mole) was added to a solution prepared from sodium (0.27 g., 0.017 g. atom), thiophenol (1.90 g., 0.01725 mole) and absolute ethanol (60 ml.), and the resulting solution was heated at the reflux temperature for 40 hours. The ethanol was then removed under reduced pressure (140 mm.); the residue was diluted with water and extracted with ether. The combined extracts were dried ( $\text{MgSO}_4$ ) and distilled. The product was collected at 118–119° (0.2 mm.) (2.80 g., 84% yield,  $n_{\text{D}}^{25}$  1.6010); ultraviolet spectrum:  $\lambda_{\text{max}}$  271  $\mu$  ( $\epsilon$  12991), inflection 217 ( $\epsilon$  9924).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{S}_2$ : C, 64.27; H, 7.19. Found: C, 64.04; H, 7.41.

**1-Phenylsulfonyl-2-*n*-butylsulfonylethylene** was prepared in the usual manner by oxidation of VIIIa with hydrogen peroxide; m.p. 81.5–82.5° (from petroleum ether (60–68°) containing ethanol), 75% yield; ultraviolet spectrum:  $\lambda_{\text{max}}$  237  $\mu$  ( $\epsilon$  9887),  $\lambda_{\text{max}}$  206  $\mu$  ( $\epsilon$  14070),  $\lambda_{\text{inf}}$  270  $\mu$  ( $\epsilon$  1773).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{S}_2\text{O}_4$ : C, 50.00; H, 5.60. Found: C, 49.72; H, 5.66.

(b) **From Phenylmercaptoacetylene.**—Phenylmercaptoacetylene (3.0 g., 0.024 mole) was treated with sodium *n*-butylmercaptide (0.028 mole) by a procedure essentially identical to that described in (a) above. The infrared spectrum of the product (4.0 g., 86%, b.p. 118° (0.3 mm.),  $n_{\text{D}}^{25}$  1.5975) was identical to that of the product described above.

(c) 1-Phenylmercapto-2-*n*-butylmercaptoethylene was isolated in 60% yield when an ethereal solution of phenylmercaptoacetylene was shaken for five minutes with an aqueous alkaline solution of *n*-butylmercaptan.

**2. 1-Phenylmercapto-2-*t*-butylmercaptoethylene (VIIIf).**—The same general procedures were employed as described above for VIIIa.

(a) Compound VIIIf was obtained in 70% yield (b.p. 95–110° (0.2 mm.),  $n_{\text{D}}^{25}$  1.5915) from phenylmercaptoacetylene and *t*-butylmercaptan. This material was refractionated with little loss (b.p. 112° (0.25 mm.),  $n_{\text{D}}^{25}$  1.5983); ultraviolet spectrum:  $\lambda_{\text{max}}$  273  $\mu$  ( $\epsilon$  14100),  $\lambda_{\text{inf}}$  217  $\mu$  ( $\epsilon$  11.043).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{S}_2$ : C, 64.27; H, 7.19; S, 28.54. Found: C, 64.12; H, 6.78; S, 28.71.

**1-Phenylsulfonyl-2-*t*-butylsulfonylethylene** was prepared in the usual way by oxidation of VIIIf with hydrogen peroxide; m.p. 151.5–152° (from petroleum ether (b.p. 60–68°)-acetone); 44% yield of pure product.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{S}_2\text{O}_4$ : C, 50.00; H, 5.60. Found: C, 49.85; H, 5.69.

(b) Compound VIIIf was obtained in 70% yield from *t*-butylmercaptoacetylene and thiophenol; b.p. 95–110° (0.2 mm.),  $n_{\text{D}}^{25}$  1.5960.

**3. 1-*n*-Butylmercapto-2-*t*-butylmercaptoethylene (VIIIe).**—The same general procedure described above for VIIIa was employed.

(a) Compound VIIIe was prepared in 75% yield from *n*-butylmercaptoacetylene and *t*-butylmercaptan; b.p. 65–74° (0.2 mm.),  $n_{\text{D}}^{25}$  1.5183. The material was redistilled (b.p. 78° (0.2 mm.),  $n_{\text{D}}^{25}$  1.5187) for analysis; ultraviolet spectrum;  $\lambda_{\text{max}}$  251  $\mu$  ( $\epsilon$  11,348),  $\lambda_{\text{inf}}$  268  $\mu$  ( $\epsilon$  6560).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{20}\text{S}_2$ : C, 58.76; H, 9.86; S, 31.33. Found: C, 59.27; H, 9.42; S, 31.60.

**1-*n*-Butylsulfonyl-2-*t*-butylsulfonylethylene** was prepared by oxidation of VIIIe with hydrogen peroxide in acetic acid.

(13) J. R. Johnson and W. L. McEwen, *THIS JOURNAL*, **48**, 469 (1926).

(12) J. F. Arens and T. Doornbos, *Roc. trav. chim.*, **76**, 481 (1956).

No precipitate formed when the reaction mixture was added to water; the product was extracted from the aqueous acetic acid with methylene chloride, and was recrystallized from methylene chloride-petroleum ether (b.p. 60–68°). The white sulfone (m.p. 98°) was obtained in 63% yield, and was dried in vacuum (48 hours at 78°) for analysis.

*Anal.* Calcd. for  $C_{10}H_{12}S_2O_4$ : C, 44.77; H, 7.52. Found: C, 43.98; H, 7.12.

(b) Compound VIIIe was prepared in 65% yield from *t*-butylmercaptoacetylene and *n*-butylmercaptan; b.p. 65–75° (0.25 mm.),  $n_D^{25}$  1.5112–1.5117. This material was redistilled with little loss (b.p. 78° (0.2 mm.),  $n_D^{25}$  1.5187) and was identical to VIIIe, prepared in a above.

4. 1-*n*-Butylmercapto-2-methylmercaptoethylene was prepared, as described above for VIIIId, from *n*-butylmercaptoacetylene and methyl mercaptan; b.p. 56–58° (0.2 mm.),  $n_D^{25}$  1.5398; ultraviolet spectrum:  $\lambda_{max}$  252 m $\mu$  ( $\epsilon$  9717),  $\lambda_{max}$  226 m $\mu$  ( $\epsilon$  5392),  $\lambda_{inf}$  275 m $\mu$  ( $\epsilon$  3749). The exact yield, comparable to those described above, was not determined.

*Anal.* Calcd. for  $C_7H_{14}S_2$ : C, 51.84; H, 8.70. Found: C, 51.92; H, 8.74.

1-Mercapto-2-Ethoxyethylenes (VIIIg–VIIIi). 1. 1-Phenylmercapto-2-ethoxyethylene (VIIIg).—Phenylmercaptoacetylene (11.24 g., 0.084 mole) was added to a solution prepared from sodium (1.71 g., 0.0745 mole) and absolute ethanol (70 ml.). The resulting solution was heated at the reflux temperature for three days, and the ethanol was then removed by distillation (140 mm.). Water was then added and the mixture was extracted with ether. The ether extract was dried ( $MgSO_4$ ) and distilled, affording 12.66 g. (84% yield) of VIIIg ( $n_D^{25}$  1.5790) boiling at 82° (0.2 mm.).

*Anal.* Calcd. for  $C_{10}H_{12}SO$ : C, 66.65; H, 6.71. Found: C, 66.23; H, 6.77.

Reaction of this product with 2,4-dinitrophenylhydrazine gave glyoxal-2,4-dinitrophenylosazone<sup>14</sup> (m.p. 325°; mixture melting point with authentic osazone, m.p. 328°, was 325–328°).

2. 1-*t*-Butylmercapto-2-ethoxyethylene (VIIIi) was prepared from *t*-butylmercaptoacetylene (13.0 g. containing 30% *n*-butyl alcohol) and sodium ethoxide (0.10 mole) in absolute ethanol (300 ml.), as described above for VIIIg. The product (12.00 g., 65.8% yield,  $n_D^{25}$  1.4730) was collected at 60–63° (4.0 mm.). The infrared spectrum of this product showed the presence of small amount of carbonyl impurity (olefin absorption at 1617  $cm^{-1}$ , carbonyl absorption at 1720  $cm^{-1}$ ) which was not completely removed by repeated distillation.<sup>15</sup>

A sample collected at 77° (7 mm.),  $n_D^{25}$  1.4747, was analyzed; ultraviolet spectrum:  $\lambda_{max}$  215 m $\mu$  ( $\epsilon$  8534),  $\lambda_{max}$  248 m $\mu$  ( $\epsilon$  3928).

*Anal.* Calcd. for  $C_8H_{16}SO$ : C, 59.94; H, 10.06. Found: C, 59.71; H, 9.47.

3. 1-*n*-Butylmercapto-2-ethoxyethylene (VIIIh) was prepared in 84% yield from *n*-butylmercaptoacetylene (6.26 g., 0.055 mole) and sodium ethoxide, as described above for VIIIg; 7.39 g., b.p. 43–51° (0.3 mm.),  $n_D^{25}$  1.4804. The infrared spectrum of this material showed olefin absorption at 1615  $cm^{-1}$  and weak carbonyl absorption at 1725  $cm^{-1}$ . The small amount of carbonyl impurity was still present after the product was redistilled (b.p. 72° (2.5 mm.),  $n_D^{25}$  1.4765); ultraviolet absorption  $\lambda_{max}$  215 m $\mu$  ( $\epsilon$  8534),  $\lambda_{max}$  248 m $\mu$  ( $\epsilon$  3928).

*Anal.* Calcd. for  $C_8H_{16}SO$ : C, 59.94; H, 10.06. Found: C, 57.48, 61.27; H, 9.74, 10.06.

1-*n*-Butylmercapto-2-ethoxyethylene was further characterized by its conversion in glyoxal 2,4-dinitrophenylosazone, by reaction with 2,4-dinitrophenylhydrazine as described above for VIIIg, and by its conversion, by oxidation with hydrogen peroxide, to *n*-butylsulfonylacetic acid (27% yield of pure product, m.p. and mixture melting point with authentic 70–71°).

Authentic *n*-Butylsulfonylacetic Acid.—A mixture prepared from potassium hydroxide (3.0 g., 0.0536 mole), water (50 ml.),  $\alpha$ -chloroacetic acid (2.0 g., 0.0212 mole) and

*n*-butylmercaptan (2.0 g., 0.0222 mole) was allowed to stand for 16 hours. The solution was then acidified (hydrochloric acid), and extracted with methylene chloride. The oil, obtained from the methylene chloride extract, was dissolved in glacial acetic acid (15 ml.) and oxidized with hydrogen peroxide in the usual way at steam-bath temperature. The mixture was poured onto ice, and the resulting aqueous solution was extracted with methylene chloride. Evaporation of the methylene chloride afforded a white solid which was purified by recrystallization from methylene chloride-petroleum ether (b.p. 60–68°). The transparent plates melted at 70° (0.65 g., 17%).

*Anal.* Calcd. for  $C_8H_{16}SO_4$ : C, 40.00; H, 6.71. Found: C, 40.47; H, 6.90.

Reaction of Unsymmetrical Sulfides VIII with *n*-Butyllithium.—The reactions of the sulfides (10.0 g.) with *n*-butyllithium were carried out, and the products processed, by a procedure essentially identical to that described earlier in this report, for the symmetrical sulfides VIII. In all cases the insoluble mercaptides formed were filtered under nitrogen.

1. Reaction of 1-Phenylmercapto-2-*n*-butylmercaptoethylene (VIIId) with *n*-Butyllithium.—Three essentially identical runs gave *n*-butylmercaptoacetylene in yields of 33.7, 32.8 and 23.8%, and phenylmercaptoacetylene in yields of 22.9, 29.5 and 24.0%, respectively. Phenylmercaptoacetylene was obtained essentially pure by distillation. Certain fractions of the *n*-butylmercaptoacetylene were contaminated with *n*-butyl alcohol, formed by air oxidation of excess *n*-butyllithium. The percentage of *n*-butylacetylene present was estimated by spectral analysis, and by conversion to derivatives as previously described.

2. Reaction of 1-Phenylmercapto-2-*t*-butylmercaptoethylene (VIIIf) with *n*-Butyllithium.—Yields of products: phenylmercaptoacetylene, obtained essentially pure by distillation 35–56.6%; *t*-butylmercaptoacetylene 3–6%, estimated as described above for *n*-butylmercaptoacetylene; thiophenol (one run only) 6%, which corresponded well with the 6% yield of *t*-butylmercaptoacetylene.

3. Reaction of 1-*n*-Butylmercapto-2-*t*-butylmercaptoethylene (VIIIe) with *n*-Butyllithium.—*t*-Butylmercaptoacetylene boils at 61° (109 mm.) and *n*-butylmercaptoacetylene boils at 82° (105 mm.). In this experiment the product was first distilled at 108 mm. The lower boiling *t*-butylmercaptoacetylene distilled first, contaminated with *n*-butyl alcohol. The *n*-butylmercaptoacetylene was obtained essentially pure by distillation. The yield of *n*-butylmercaptoacetylene was 40%; the yield of *t*-butylmercaptoacetylene was estimated (infrared spectrum, and conversion to derivatives) to be 9%.

4. Reaction of 1-Phenylmercapto-2-ethoxyethylene (VIIIg) with *n*-Butyllithium.—No evidence for the presence of ethoxyacetylene in the product was obtained. *n*-Butylmercaptoacetylene was isolated in 60 and 68% yields in two runs.

5. Reaction of 1-*t*-Butylmercapto-2-ethoxyethylene (VIIIi) with *n*-Butyllithium.—Yields of products: *t*-butylmercaptoacetylene, 24.1 and 23.9, respectively; recovered starting sulfide, VIIIi, 24.9 and 37%, respectively.

6. Reaction of 1,2-Diethoxyethylene (VIIIj) with *n*-Butyllithium.—The product obtained from the reaction of VIIIj<sup>16</sup> with *n*-butyllithium contained no terminal acetylene. Distillation gave two fractions: (1) b.p. 100–125°, 5.70 g.,  $n_D^{25}$  1.4120; and (2) b.p. 125–133°,  $n_D^{25}$  1.4093. Infrared analysis of these products indicated that fraction 2 was principally recovered VIIIj (47.2%) and fraction 1 was a mixture of recovered VIIIj (80%) and *n*-butyl bromide (20%). Fraction 1 gave a positive Beilstein test; it was concluded that little, if any, reaction occurred between VIIIj and butyllithium.

Kinetic Studies. 1. Determination of Thiophenol.—Lithium thiophenolate in water has strong absorption in the ultraviolet at 262 m $\mu$ . Known concentrations of lithium thiophenolate (from thiophenol and butyllithium) were used to prepare the calibration curves. The absorbance,  $A$ , was found to be a linear function of concentration,  $C$ ;  $A = 1.5 \times 10^4 C - 0.08$  in a 1-cm. cell, where  $C$  is concentration in moles/liter.

A 25-ml. solution of ether, containing lithium thiophenolate, was shaken for two minutes with 10 ml. of distilled

(14) W. E. Parham and I. D. Jones, *THIS JOURNAL*, **76**, 1068 (1954).

(15) Vinyl ethers of this type are known to be extremely sensitive to water, in the presence of a trace of acid, and are hydrolyzed to aldehydes of the type  $RSCH_2CHO$ .

(16) S. M. McElvain and C. H. Stammer, *ibid.*, **73**, 915 (1951).

water. The ether layer was extracted two additional times with water. The combined water extract was extracted for two minutes with fresh ether, and the fresh ether was washed two additional times with water. The combined water extract was diluted to 25 ml. and analyzed spectrophotometrically for lithium thiophenolate.

2. Reaction of *cis*- and *trans*-Bis-(phenylmercapto)-ethylene (I) with *n*-Butyllithium at Room Temperature.—Anhydrous ether (950 ml.) was added to a dry 1-liter volu-

metric flask previously filled with nitrogen. A solution of *cis*- or *trans*-I ( $4.9 \times 10^{-3}$  mole) in ether, and *n*-butyllithium ( $1.5 \times 10^{-3}$  mole) in ether was added, and the total volume was made up to 1 liter. It was found that the reaction was complete (90% yield of lithium thiophenolate) by the time the first sample could be taken (one minute).

Attempts to obtain reliable kinetic data at 0° have not yet been successful.

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[CONTRIBUTION FROM FULMER LABORATORY, DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

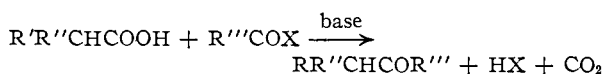
## The Mechanism of Base-catalyzed Acylative Decarboxylation<sup>1,2</sup>

BY GRANT GILL SMITH AND DENNIS M. FAHEY<sup>3</sup>

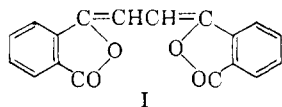
RECEIVED MARCH 3, 1958

Examination of the reaction of *o*-chlorophenylacetic acid with acetic anhydride in the presence of pyridine reveals: first-order kinetics with respect to the acid in the presence of excess anhydride and base, the importance of anhydrous reaction conditions, and an isotope effect of 1.13 with acetic-1-C<sup>14</sup> anhydride, but no isotope effect with *o*-chlorophenylacetic-1-C<sup>14</sup> acid. The mechanism of base-catalyzed acylative decarboxylation is discussed.

Many acids with at least one  $\alpha$ -hydrogen atom condense with acylating agents in the presence of a basic catalyst to yield ketones and carbon dioxide.



Although it has been indicated recently<sup>4</sup> that the first described base-catalyzed acylative decarboxylation was in the late twenties,<sup>5</sup> as early as 1877 Gabriel and Michael<sup>6</sup> reported the isolation of I



from the reaction of succinic acid with phthalic anhydride in the presence of sodium acetate. The product I is the result of two acylations and decarboxylations, the diketone having been isolated as the double enol ester. Enol ester formation is common under such acylative conditions.<sup>7</sup>

Numerous studies of acylative decarboxylation of arylacetic acids have been made and several widely differing mechanisms have been proposed. In spite of the information accumulated, many critical facts concerning the mechanisms have not been reported. The purpose of this investigation was to better define the nature of the reaction with reaction kinetics, to investigate the effect of moisture and to determine the atoms involved in the rate-determining steps with the use of carbon-14.

(1) Presented before the Division of Organic Chemistry, 131st Meeting of American Chemical Society, Miami, Fla., April 8, 1957, p. 88-O.

(2) Abstracted from a thesis presented to the Graduate School of the State College of Washington by Dennis M. Fahey in partial fulfillment of the requirements for the Ph.D. degree, January, 1957.

(3) Research Corporation research assistant 1953-1954 and National Science Foundation Fellow 1954-1956.

(4) (a) G. H. Cleland and C. Nieman, *THIS JOURNAL*, **71**, 841 (1949); (b) S. Searles and C. J. Cvejanovich, *ibid.*, **72**, 3200 (1950); (c) C. S. Rondvested, Jr., E. Manning and S. Tabibian, *ibid.*, **72**, 3183 (1950); (d) J. A. King and F. H. McMillan, *ibid.*, **77**, 2814 (1955).

(5) (a) P. A. Levene and R. E. Steiger, *J. Biol. Chem.*, **74**, 689 (1927); (b) H. D. Dakin and R. West, *ibid.*, **78**, 91 (1928).

(6) S. Gabriel and M. Michael, *Ber.*, **10**, 1551 (1877).

(7) G. G. Smith, *THIS JOURNAL*, **76**, 1134 (1953).

### Experimental<sup>8</sup>

**Effect of Moisture on Acylative Decarboxylation. Reagents.**—Acetic anhydride and pyridine were dried with phosphorus pentoxide and barium oxide, respectively, and freshly distilled in oven-dried (110°) glassware.

*o*-Chlorophenylacetic acid was prepared according to the method described by Smith and Ott. Crystallization from 30% ethanol gave 63.8 g. (74.8%), m.p. 94.5-95.5°. The *o*-chlorophenylacetic acid was stored in a vacuum desiccator.

**Condensation Apparatus.**—A 100-ml. three-necked flask was fitted with a Metroware spiral condenser as a nitrogen inlet, a thermometer adapted to the center neck, a Liebig condenser as a nitrogen outlet, and a glass-covered magnet for a stirrer. Only ground glass was used for the reaction vessel connections. The Liebig condenser was attached to a Dry Ice cold trap, a concentrated sulfuric acid wash bottle, a three-way stopcock, and weighed Ascarite tubes in series. The heat source was a Powerstat-regulated mantle.

**Condensation of *o*-Chlorophenylacetic Acid.**—In each run, 6.82 g. (40 mmoles) of the acid, 19 ml. (200 mmoles) of acetic anhydride and 29 ml. (360 mmoles) of pyridine were heated for four hours at 100°. This temperature was attained 20 minutes after heating was begun. The evolved carbon dioxide was swept into the weighed Ascarite tubes with nitrogen. The reaction was stopped by immersion of the reaction vessel in an ice-bath followed by the addition of approximately 45 ml. of ice-water. The decomposed mixture was poured into a solution of 4 g. of sodium hydroxide dissolved in 13 ml. of water in a separatory funnel, and the alkaline mixture was treated with a 50-ml. portion and two 25-ml. portions of ether. The ether extracts were combined, shaken for five minutes with a solution of 6 g. of sodium hydroxide dissolved in 54 ml. of water, washed with three 10-ml. portions of water, dried with anhydrous magnesium sulfate, and evaporated to a volume of about 25 ml. The solution was diluted to 50 ml. with absolute methanol in a volumetric flask, and 10-ml. aliquots were used for ketone analyses. The results are reported in Table I.

The remaining solutions not used for analysis were combined and evaporated. Evaporative distillation of part of this yielded *o*-chlorophenyl-2-propanone,  $n_D^{20}$  1.5385, b.p. 100° (0.05 mm.).<sup>10</sup>

**Anal.** Calcd. for C<sub>9</sub>H<sub>9</sub>ClO: C, 63.8; H, 5.35. Found: C, 64.0; H, 5.4.

(8) All melting points are corrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., or by Weiler and Strauss Laboratories, Oxford, England. All ketone derivatives were prepared by the methods of R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 170, 202.

(9) G. G. Smith and D. G. Ott, *THIS JOURNAL*, **77**, 2342 (1955), reported m.p. 94.5-95.5°.

(10) The value from evaporative distillation was difficult to compare with the values for distillation; R. T. Gilsdorf and F. F. Nord, *ibid.*, **74**, 1837 (1952), reported 103° (6 mm.).