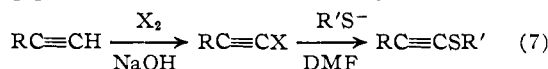


The present synthesis of acetylenic thioethers is a two-step process from an available acetylene.



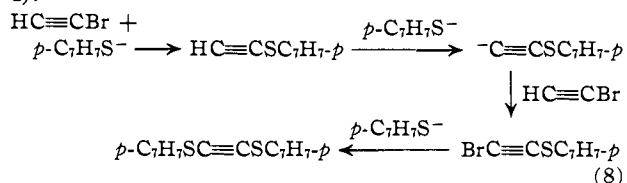
The displacement step is generally rapid even below 0° and the aprotic solvent dimethylformamide (DMF) appears to be a key factor contributing to the success of the operation. Variation in both the thiolate and the haloalkyne indicated that syntheses in alkyl and aryl series were feasible. It was found that the pentachlorophenylthiolate reacted more slowly than the other thiolates; this observation may be interpreted to mean that at least within the thiol family reactivity follows base strength. The compounds prepared are given in Table I.

TABLE I  
PRODUCTS OF THE DISPLACEMENT<sup>a</sup>  
DMF

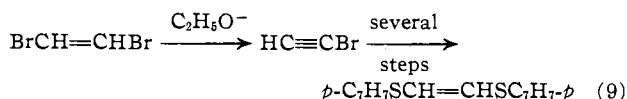
$\text{RC}\equiv\text{CX} + \text{R}'\text{S}^- \longrightarrow \text{RC}\equiv\text{CSR}' + \text{X}^-$	$\text{R}'\text{S}^- \text{Na}^+$
$\text{HC}\equiv\text{CBr}$	$p\text{-CH}_3\text{C}_6\text{H}_4^b$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$	$\text{C}_6\text{H}_5$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$	$p\text{-CH}_3\text{C}_6\text{H}_4$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$	$p\text{-}t\text{-(CH}_3)_3\text{CC}_6\text{H}_4$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$	$p\text{-ClC}_6\text{H}_4^c$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$	$\text{Cl}_5\text{C}_6$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$	$\text{C}_6\text{H}_5\text{CH}_2^c$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCl}$	$p\text{-}t\text{-(CH}_3)_3\text{CC}_6\text{H}_4$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$	$(\text{CH}_3)_2\text{CHCH}_2$
$\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$	$(\text{CH}_3)_2\text{CH}$

<sup>a</sup> Yields (30–70%) given in Experimental. <sup>b</sup> The product was ( $p\text{-C}_7\text{H}_7\text{SC}\equiv\text{C}$ )<sub>2</sub>. <sup>c</sup> Isolated as sulfones.

However, not all of the haloalkynes gave the expected products. In a few cases addition products were obtained, e.g., with thiourea. When bromoethyne was passed into a DMF solution of sodium *p*-toluene-thiolate, it gave the acetylenic dithioether, presumably according to a disproportionation mechanism (see eq. 4).



When bromoethyne was generated from dibromoethene in an ethanolic solution of the same thiolate it gave the *cis*-ethylenic dithioether, presumably following elimination-addition<sup>22</sup>



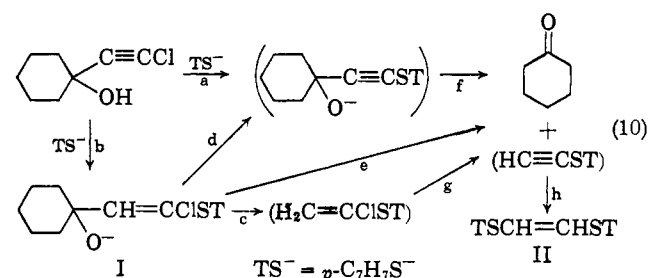
Preliminary experiments with dichloroethyne and sodium *p*-toluene-thiolate in DMF gave 1,1,2-tri-*p*-ditoluenethioethane and *p,p'*-ditoluene disulfone. Dibromoethyne and sodium thiophenolate gave phenyl disulfide. These products can be rationalized if some acetylene is produced when the thiol is oxidized by the haloalkyne.

Work with the 1-haloethynyl-3-ols revealed other difficulties. The hydroxyl group as a proton donor

*trav. chim.*, **80**, 244 (1961); (c) G. Pourcelot, P. Cadiot and A. Willemart, *Compt. rend.*, **262**, 1630 (1961).

(22) W. E. Truce, M. M. Boudakian, R. F. Heine and R. J. McManimie, *J. Am. Chem. Soc.*, **78**, 2743 (1956).

made a-b of eq. 1 possible and its oxide function was then properly located for the known ketonic fission.<sup>23</sup> Compound I was isolated as the sulfone and this was



shown to yield cyclohexanone under basic conditions. The ethylenic diether II, the only other compound isolated, was also formed from the reaction of *p*-toluene-thiolate and 1-bromo-3-methyl-1-butyn-3-ol. It is not clear whether the split involves the reverse of ethynylation (step f),<sup>23</sup> or vinylation (step c) of a ketone, or whether it is simply a 1,4-elimination (step e).

The most important conclusion from this work is that nucleophilic substitution at an acetylenic carbon is possible. With this new substrate in the displacement process, a host of new problems arises with regard to mechanism, reactivity of various halo-unsaturates, reactivity of various nucleophiles, solvent dependence and further synthetic applications. Some progress in this direction has already been made.<sup>3-5</sup>

### Experimental

All melting points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and by A. Bernhardt, Mülheim (Ruhr), Germany. Infrared spectra were taken on Perkin-Elmer model 21 and Infracord spectrophotometers. Nuclear magnetic resonance (n.m.r.) spectra and proton counts were measured on a Varian Associates A60 spectrophotometer; chemical shifts,  $\delta$  in p.p.m., were taken at 60 Mc. relative to tetramethylsilane.

**Materials.**—Our chief solvent was Fisher Certified Reagent *N,N*-dimethylformamide (DMF). The sodium thiolates were prepared in toluene which had been distilled from sodium. A slight excess of the thiol (*ca.* 1.05 equiv.) was refluxed with freshly cut sodium in toluene for 16–24 hours. The salt was filtered, washed with toluene, vacuum dried at *ca.* 0.1 mm. for 12–24 hr. and stored in tightly capped jars under nitrogen. The haloalkynes were generally prepared by shaking the 1-alkyne with a 10% excess of chlorine or bromine in a large excess of sodium hydroxide. The crude liquid products were vacuum distilled and stored in a refrigerator. Phenylbromoethyne had b.p. 40–41° (0.1 mm.),  $n_D^{20}$  1.6075 (lit.<sup>17</sup> 42° (0.3 mm.),  $n_D^{18}$  1.6105). Phenylchloroethyne had b.p. 26–30° (0.15 mm.),  $n_D^{19}$  1.5809 (lit.<sup>11</sup> 71° (16 mm.),  $n_D^{18}$  1.576). 1-Chloroethynylcyclohexanol was crystallized from ether and had m.p. 51–52° (lit.<sup>23</sup> 51–52°). 1-Bromo-3-methyl-1-butyn-3-ol had b.p. 68° (15 mm.),  $n_D^{20}$  1.4685 (lit.<sup>24</sup> b.p. 68° (16 mm.)).

**Acetylenic Thioethers.**—The following "usual" procedure was evolved. Solutions of the sodium thiolate and the haloalkyne were mixed and stored at *ca.* –30° in a stoppered flask which had been flushed with nitrogen. After several hours, a small aliquot was removed and the halide was estimated potentiometrically with silver nitrate. If the reaction was slow, the temperature of the solution was raised to *ca.* 25° or higher if need be. Unnecessary heating appeared to reduce the yields of products. On completion of the reaction, the solution was treated with ice and water and extracted with ether to give the impure sulfides. Sulfone derivatives were prepared by treating the sulfides with 30% hydrogen peroxide in glacial acetic acid on the steam-bath for *ca.* 1 hr.<sup>13</sup> The preparation of 1-phenyl-2-toluene-thioethyne and its sulfone has been described.<sup>3</sup>

**1-Phenyl-2-phenylthioethyne.**—In preliminary work, the reaction between sodium thiophenolate and phenylbromoethyne (6 g.) was carried out in boiling dioxane in a nitrogen atmosphere. After 20 hr., the dioxane was pumped off and the residue was distilled to give *ca.* 5.5 ml. of liquid,  $n_D^{20}$  1.6642–1.6676. By the usual procedure in DMF, sodium thiophenolate (10 g., 0.076 mole) and phenylbromoethyne (13.0 g., 0.072 mole) gave the

(23) W. Chodkiewicz, *Ann. chim.*, [13] **2**, 819 (1957); W. Chodkiewicz, P. Cadiot and A. Willemart, *Compt. rend.*, **260**, 866 (1960).

(24) F. Strauss, L. Kollek and W. Heyn, *Ber.*, **63**, 1868 (1930).

liquid product in 52% yield, b.p. 142–145° (1 mm.),  $n_D^{25}$  1.6644,  $\nu_{C=C}$  4.75  $\mu$  (lit.<sup>18</sup>  $n_D^{25}$  1.664, b.p. 155–170°).

*Anal.* Calcd. for  $C_{14}H_{10}S$ : C, 79.96; H, 4.79. Found: C, 79.52; H, 4.87.

The sulfone (from Skelly B) had m.p. 73–74° (lit.<sup>13</sup> 73–74°).

**1-Phenyl-2-isopropylthioethyne.**—Phenylbromoethyne (18 g., 0.1 mole) was treated with sodium isopropyl mercaptide in the usual way. After careful distillation, a water-white fraction of the product was obtained in 33% yield,  $n_D^{25}$  1.5921.

*Anal.* Calcd. for  $C_{11}H_{12}S$ : C, 74.95; H, 6.86. Found: C, 75.33; H, 6.90.

**1-Phenyl-2-*p*-*t*-butylphenylthioethyne.**—Sodium *p*-*t*-butylthiophenolate (10 g., 0.053 mole) and phenylbromoethyne (13.03 g., 0.05 mole) gave a white solid from Skelly B in 51% yield, m.p. 49.5–51°,  $\nu_{C=C}$  4.63  $\mu$ . By the same procedure, phenylchloroethyne gave the same product.

*Anal.* Calcd. for  $C_{18}H_{18}S$ : C, 81.15; H, 6.81. Found: C, 81.16; H, 6.74.

**1-Phenyl-2-pentachlorophenylthioethyne.**—Sodium pentachlorophenylthiolate (9.3 g., 0.03 mole) and phenylbromoethyne (5.5 g., 0.034 mole) in 250 ml. of DMF gave after 2 hr. on the steam-bath white crystals (from Skelly B) in 41% yield, m.p. 110.5–111.5°,  $\nu_{C=C}$  4.61  $\mu$ .

*Anal.* Calcd. for  $C_{14}H_5$ : C, 43.96; H, 1.32. Found: C, 44.35; H, 1.36.

**1-Phenyl-2-benzylthioethyne.**—Sodium benzylthiolate (30 g., 0.206 mole) and phenylbromoethyne (36.2 g., 0.20 mole) gave 32 g. of a liquid, b.p. 170° (1 mm.),  $\nu_{C=C}$  4.73  $\mu$ . A portion of this product was converted to the sulfone, m.p. 80.5–81° (from Skelly B),  $\nu_{C=C}$  4.72  $\mu$ .

*Anal.* Calcd. for  $C_{16}H_{12}SO_2$ : C, 70.28, H, 4.71. Found: C, 70.02; H, 5.00.

The highest boiling fraction of the liquid, b.p. 123° (0.01 mm.), solidified; this proved to be dibenzyl disulfide, b.p. 69–70° (lit.<sup>25</sup> 69–72°) from ethanol.

**1-Phenyl-2-*p*-chlorophenylthioethyne.**—Sodium *p*-chlorothiophenolate (9 g., 0.054 mole) and phenylbromoethyne (9 g., 0.05 mole) gave 6 g. of a liquid, b.p. 95–125° (0.01 mm.),  $\nu_{C=C}$  4.60  $\mu$ . A portion of this product was converted to the sulfone, m.p. 101–102° (from Skelly B),  $\nu_{C=C}$  4.61  $\mu$ .

*Anal.* Calcd. for  $C_{14}H_9O_2S$ : C, 60.76; H, 3.28. Found: C, 61.15, H, 3.44.

**1-Phenyl-2-isobutylthioethyne.**—Sodium isobutylthiolate (11.4 g., 0.102 mole) and phenylbromoethyne (18.1 g., 0.1 mole) gave 15 g. of dark liquid. Fractionation gave a 60% yield of product: the middle cut had b.p. 65–68° (0.25 mm.),  $n_D^{25}$  1.5811,  $\nu_{C=C}$  4.6  $\mu$ .

*Anal.* Calcd. for  $C_{12}H_{14}S$ : C, 75.74; H, 7.41. Found: C, 75.63; H, 7.52.

**Di-*p*-toluenethioethyne.**—1,2-Dibromoethene was refluxed with sodium ethoxide in ethanol. A slow stream of nitrogen swept the monobromoethyne into a line containing a large calcium chloride tube, two Dry Ice traps, a reaction flask and a mineral oil bubbler. When the traps were allowed to warm up to 0–25°, the bromoethyne distilled into the flask which contained sodium *p*-toluenethiolate in DMF. When worked up, the solution gave di-*p*-toluenethioethyne, m.p. 98–99° from ethanol (lit.<sup>26</sup> 101–102°); an n.m.r. proton count indicated four phenyl protons at 6.9–7.3 p.p.m., three methyl protons at 2.3 p.p.m. and no other protons.

*Anal.* Calcd. for  $C_{16}H_{14}S_2$ : C, 71.1; H, 5.21. Found: C, 70.75; H, 5.63.

Bromine addition to the thioether was carried out in chloroform to give lemon-yellow blocks (from glacial acetic acid), m.p. 101–103° (lit.<sup>26</sup> 99–100°); this solid depressed the melting point of the acetylenic dithioether.

**1,2-Di-*p*-toluenethioethene.**—1,2-Dibromoethene (4.1 g., 0.022 mole) and sodium *p*-toluenethiolate (5.8 g., 0.04 mole) were mixed in DMF solution at –30° and allowed to come to room temperature. After 5 hr. the mixture was worked up to give a 51% yield of the dithioethene, m.p. 92–93° (lit.<sup>22,26</sup> 91–92°). A mixture melting point with an authentic sample was not depressed.

**Reaction of 1-Bromo-3-methyl-1-butyn-3-ol.**—1-Bromo-3-methyl-1-butyn-3-ol (11 g., 0.068 mole) and sodium *p*-toluenethiolate (10 g., 0.0685 mole) gave after the usual treatment 1,2-di-*p*-toluenethioethene in 17% yield,  $\nu_{C=C}$  6.0  $\mu$ , m.p. 91–92°.

*Anal.* Calcd. for  $C_{16}H_{18}S_2$ : C, 70.54; H, 5.92. Found: C, 70.34; H, 5.96.

Although this analysis is also appropriate for the not improbable acetylenic peroxide, (*p*- $C_6H_4C\equiv CC(CH_3)_2O$ )<sub>2</sub>, the product does not have peroxide properties, *e.g.*, reactions with iodide or arsenic(III) oxide. An n.m.r. proton count confirmed the di-

thioethene structure; the phenyl (*ca.* 6.9–7.3 p.p.m.), methyl (2.31 p.p.m.) and the ethylenic (6.32 p.p.m.) protons were in the proper ratio 4:3:1.

**Reaction of 1-Chloroethynylcyclohexanol.**—1-Chloroethynylcyclohexanol (7.6 g., 0.048 mole) and sodium *p*-toluenethiolate (7.3 g., 0.05 mole) were left at –30° in DMF solution for 15 hr. then allowed to reach *ca.* 25° in 2 hours. The usual work-up gave 2 g. of di-*p*-tolylthioethene, m.p. 92°. The residual oil was treated with hydrogen peroxide in the usual way to give the sulfone of 1-(1-hydroxycyclohexyl)-2-chloro-2-*p*-tolylthioethene, m.p. 128–129° (from petroleum ether). An n.m.r. proton count confirmed the cyclohexyl (*ca.* 1.65 p.p.m.), phenyl (7.2–7.92 p.p.m.), methyl (2.41 p.p.m.), alcohol (3.8 p.p.m.), and ethylenic (6.84 p.p.m.) protons in the proper ratio 10:4:3:1:1.

*Anal.* Calcd. for  $C_{15}H_{19}O_3S$ : C, 57.22; H, 6.08. Found: C, 57.13; H, 6.30.

This sulfone (1 g.) and potassium hydroxide (2 g.) in DMF (50 ml.) were allowed to stand *ca.* 15 hr. The cleavage product, cyclohexanone, was identified as its dinitrophenylhydrazone, m.p. 160–161° (lit.<sup>27</sup> 160°).

**Dihaloethyne Reactions.**—Dichloroethyne was prepared from trichloroethene by the method of Ott, *et al.*<sup>15</sup> It was swept by nitrogen through tubes containing potassium hydroxide and calcium chloride into a solution of sodium *p*-toluenethiolate at *ca.* 10°. After 16 hr., the solution was worked up to give an ether-insoluble solid, m.p. 206–207°, and a volatile ether-soluble solid, m.p. 43°. The former appears to be the di-*p*-toluene disulfone, (*p*- $C_6H_4SO_2$ )<sub>2</sub> (lit.<sup>28</sup> m.p. 210–212°) and the latter appears to be di-*p*-toluene disulfide (*p*- $C_6H_4S$ )<sub>2</sub> (lit.<sup>29</sup> m.p. 46°). In another preparation, the only product was a viscous ether-soluble oil, b.p. 226–230° (0.01 mm.). The distillate deposited white crystals which were purified by chromatography over alumina. The solid was 1,1,2-tri-*p*-toluenethioethane, m.p. 63–64° (lit.<sup>26</sup> 62–63°). Treatment of the thioether with bromine in carbon tetrachloride gave a monobromide, b.p. 127°.

*Anal.* Calcd. for  $C_{23}H_{23}BrS_3$ : C, 58.09; H, 4.89. Found: C, 57.45; H, 4.45.

Dibromoethyne was prepared from acetylene and bromine in potassium hydroxide.<sup>24</sup> The oil was treated with potassium hydroxide pellets and swept with nitrogen through one tube containing potassium hydroxide and another containing phosphorus pentoxide into an ampoule containing sodium thiophenolate in purified dioxane. The ampoule was sealed under vacuum and heated 16 hr. at 110°. The ampoule was cooled, opened and its contents washed out with water. A white solid, m.p. 60–63°, apparently the phenyl disulfide, was obtained (lit.<sup>30</sup> m.p. 60–61°).

**1-Bromo-3-methyl-3-methoxybutyne.**—3-Methyl-1-butyn-3-ol was treated with sodamide and dimethyl sulfate to give a 23% yield of crude methyl ether.<sup>31</sup> Redistilled ether (6 g.), b.p. 75–80°,  $n_D^{21}$  1.4011 (lit.<sup>31</sup> b.p. 78.5° (750 mm.),  $n_D^{20}$  1.4003) was added to an excess of bromine in cold aqueous sodium hydroxide. After 10 days on a shaker, the mixture yielded a heavy oil. On distillation, a 40% yield of the bromoalkyne was obtained, b.p. 51–53° (21 mm.),  $n_D^{24}$  1.4595,  $\nu_{C=C}$  4.63  $\mu$ .

*Anal.* Calcd. for  $C_8H_9BrO$ : C, 40.69; H, 5.12. Found: C, 40.22; H, 5.07.

When this bromoalkyne (1 g.) was treated with sodium *p*-toluenethiolate (0.8 g.) in DMF at 60°, the product obtained in 78% yield had m.p. 54° and analyzed not for the displacement product itself, but for the thiol adduct to it. The structure of this material is uncertain.

*Anal.* Calcd. for  $C_{20}H_{24}S_2O$ : C, 69.77; H, 6.98. Found: C, 69.34; H, 7.07.

**Reaction of Thiourea.**—Phenylbromoethyne (12.6 g., 0.07 mole) and thiourea (10.6 g., 0.14 mole) were refluxed in ethanol 1 hour. Treatment of the mixture with picric acid gave a low yield (< 10%) of what appears to be the picrate of the simple adduct of the reactants.

*Anal.* Calcd. for  $C_{15}H_{11}O_7N_3BrS$ : C, 37.06; H, 2.28; N, 14.41. Found: C, 37.76; H, 2.95; N, 13.68.

**Acknowledgment.**—We are greatly indebted to the National Institutes of Health for support of this work and to the National Science Foundation for Undergraduate Research Participation awards to G. R. Z., C. A. W. and C. E. O. Mr. R. Simonaitis attempted some syntheses with monochloroethyne and dibromoethyne and R. Wieleseck prepared some of the other

(27) C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2955 (1930).

(28) T. P. Hilditch, *J. Chem. Soc.*, **97**, 2579 (1910).

(29) B. Holmberg, *Ber.*, **43**, 220 (1910).

(30) K. W. Rosenmund and H. Harms, *Ber.*, **53**, 2226 (1920).

(31) R. Heilmann, R. Glenat and G. de Gaudemaris, *Bull. soc. chim France*, [5] 284 (1952).

(25) O. Hinsberg, *Ber.*, **45**, 2337 (1912).

(26) E. Fromm and E. Siebert, *ibid.*, **85**, 1014 (1922).

starting materials. Some of the thiols used in this work were gifts of the following companies: Pitt Consol

Chemical, Air Reduction Chemical, Evans Chemetics, Inc., and E. I. du Pont de Nemours.

[CONTRIBUTION FROM THE DOW CHEMICAL CO., EASTERN RESEARCH LABORATORY, FRAMINGHAM, MASS.]

## Electronic Spectra of Organolithium Compounds

BY RICHARD WAACK AND MARY A. DORAN

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The absorption maxima in the ultraviolet and visible spectra of 16 organolithium compounds in THF solution and molar absorption coefficients are reported. A convenient technique is described for measuring the spectra of these oxygen- and moisture-sensitive systems that is not restricted by vacuum operations. These data are discussed in light of the previous literature on the spectra of carbanions and with reference to the concepts expressed by molecular orbital theory.

A study of electronic absorption spectra and their interpretation in terms of the molecular orbital theory is proving a fruitful approach to an understanding of electronic structure. Of equal importance are the extremely useful analytical applications of electronic spectra. It is with these objectives that we initiated a study of the ultraviolet and visible spectra of organolithium compounds. In this first part of these studies, we report spectral data for 16 organolithium compounds.

### Experimental

The extreme sensitivity of organolithium compounds to oxygen and moisture necessitates the use of a closed absorption cell, yet it is an advantage to be able to add reagents to the cell at will without the restrictions of break seals or other vacuum operations. The absorption cell apparatus used in these studies consists of a 0.2-cm. quartz absorption cell sealed to a side arm of a round bottom flask, as shown in Fig. 1. The apparatus was connected to a high vacuum system for alternate degassing and flushing with argon. Access to the flask was through a second side arm closed by a rubber syringe cap. The organolithium compounds were handled *via* a Hamilton gas-tight syringe,<sup>1</sup> protected by an argon atmosphere. A slight positive argon pressure was maintained when piercing the rubber cap. A removable quartz spacer sealed into the side arm permitted us to decrease the cell path length to 0.015 cm. Spectra were measured with a Cary model 14 recording spectrophotometer. The extinction coefficients were determined by a difference technique, in which after a base absorption curve for the species being measured was established, an additional amount of organolithium compound was added, and the resulting difference in optical density used to calculate the extinction coefficient.<sup>2</sup> Concentrations of the organolithium compounds were determined by titration of total alkali. Each experiment was completed by the addition of a few drops of ethanol, resulting in complete loss of the long wave length absorption. In some cases the spectrum of the hydrocarbon was measurable.

The tetrahydrofuran (THF) solvent was purified by distillation from lithium aluminum hydride under an argon atmosphere. So treated, it was optically transparent to  $\sim 215 \mu$ . The organolithium compounds were obtained as follows: *n*-Butyllithium was obtained from Foote Mineral Corp. and Lithium Corp. of America in hydrocarbon solution. *sec*-Butyllithium and *t*-butyllithium in hydrocarbon solution were obtained from Lithium Corp. of America. Ethyllithium in benzene solution was supplied by Orgmet, Hampstead, N. H. Phenyllithium which we prepared<sup>3</sup> from lithium metal and bromobenzene in ether, from chlorobenzene in THF,<sup>4</sup> from diphenylmercury in THF or in ether<sup>5</sup> gave identical results to phenyllithium in ether solution obtained from Anderson Chemical Co. and Lithium Corp. of America. Vinylithium and allyllithium were prepared

in *n*-hexane from the corresponding tetrasubstituted tin compounds *via* transmetalation with *n*-butyllithium.<sup>6</sup> The insoluble organolithium was twice washed with hexane before dissolving it in THF. Benzyllithium was prepared from tribenzyltin chloride and phenyllithium in ether,<sup>3,7</sup> chilling the reaction after 2 hours to precipitate the tetraphenyltin and filtering, and from dibenzylmercury and lithium metal<sup>8</sup> in THF, shaking for 3–4 hours.  $\alpha$ -Methylbenzylithium and methylallyllithium were prepared from the corresponding triphenyltin compounds<sup>8</sup> *via* transmetalation with phenyllithium in ether in the previous manner.<sup>3</sup> 1-Phenyl-2-propenyllithium was prepared by metalating allylbenzene with *n*-butyllithium in THF solution. The spectrum of terminated [EtOH] 1-phenyl-2-propenyl-lithium solution shows >85% conversion of the allylbenzene to  $\beta$ -methylstyrene, in agreement with previous findings.<sup>9</sup> Triphenylmethylithium was prepared in THF from freshly recrystallized<sup>10</sup> triphenylmethyl chloride and metallic lithium at 0°, filtering after stirring for 4 hours. The two substituted diphenylmethylithium species were produced *via* the reaction of the appropriate organolithium compound and 1,1-diphenylethylene. Polystyryllithium and poly- $\alpha$ -methylstyryllithium were formed by adding *n*-butyllithium to the respective monomer in THF solution. The concentration of the latter monomer was well below its equilibrium value.<sup>11</sup> Thus, the initiation product 1-methyl-1-phenyl-*n*-hexyllithium should predominate. The olefins were vacuum distilled from CaH<sub>2</sub>.

Several of the organolithium compounds were carbonated to the corresponding acids or ketones. Phenyllithium gave benzoic acid in 87% yield; benzyllithium gave phenylacetic acid in 65% yield; vinylithium gave only a poor yield of acrylic acid, but on carbonation of its reaction product with 1,1-diphenylethylene a 68% yield of 2,2-diphenyl-4-pentenoic acid was recovered; hydrolysis of vinylithium gave ethylene quantitatively, identified by mass spectroscopy.

Allyllithium was characterized by its reaction with styrene and near infrared analysis of the polymer showing a single vinyl group per polymer chain. The recovery of tetraphenyltin was 95–100% in the preparations of benzyllithium,  $\alpha$ -methylbenzylithium and methylallyllithium. The recovery of mercury was 95–100% in the preparation of phenyllithium and benzyllithium from the corresponding mercury compounds.

### Results

The wave lengths of the absorption maxima of the major bands we observe in the spectrum of each organolithium compound and the molar extinction coefficients are reported in Table I. Prior literature data are summarized in the right-hand column of Table I.

Some of the organolithium compounds were prepared in solvents other than THF. In such cases the other solvents were present in 5–10% concentration. We feel these solvent mixtures do not differ appreciably from THF in their ability to solvate the carbanions.<sup>11a</sup> This is

(1) Obtained from Hamilton Co., Inc., Whittier, Calif. These were found to be much more effective for handling the organolithium compounds than the usual ground glass syringes, which were used in the early phase of this work.

(2) The extinction coefficients given in Table I are reproducible within the limits  $\pm 10\%$  from one experiment to the next or between different preparations of organolithium compounds. However, in view of the sensitivity of these compounds to impurities, we feel it is better to consider these extinction coefficients as "best estimates" (minimum values) and not as final values.

(3) These preparations will be described in detail in a subsequent publication.

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(11a) For convenience we use the term carbanion or anion in referring to organolithium compounds. This is not meant to imply that the organolithium compounds are completely ionized. Although the true nature of organolithium compounds is not known, they are believed to exist as ion pairs or aggregates of ion pairs.