Subjecting a 42-g. sample of the remaining 95% ethanol extract to basic hydrolysis (250 ml. of 5% aqueous sodium hydroxide) over a 4.5-hr. period, in refluxing ethanol (250 ml.), led to 1.9 g. of neutral material and a large quantity of dark polymer. Following acid hydrolysis of another 42-g. portion of ethanol extract, using 240 ml. of 6% hydrochloric acid and the same general procedure noted directly above, a 4.3-g. neutral fraction was isolated. Thin layer chromatograms of both neutral products on silicagel G in 9:1 benzene–ethyl acetate indicated that each was a complex mixture. Partial resolution of the neutral material from acid hydrolysis using column chromatography on activated alumina[14] substantiated this observation. However, a crude specimen (0.24 g., m.p. 162–168°) of 5α-dihydroergosterol was eventually isolated from the 1.9-g. sample of neutral product by fractional recrystallization (methanol–chloroform as solvent).

The Reaction of Vinyl Sulfides with Alkyllithium. II[1]

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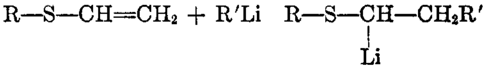
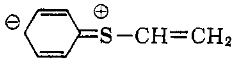
We have extended our study of the reactions of vinyl sulfides (I) with alkyllithium reagents[5] to in-



$$\underset{\text{I}}{R{-}S{-}CH{=}CH_2 + R'Li} \qquad \underset{\text{II}}{R{-}S{-}\underset{\substack{|\\ Li}}{CH}{-}CH_2R'}$$

clude cases in which R is vinyl and alkyl. The vinyl sulfides were allowed to react with an excess of alkyllithium in ether at 0°; the compounds studied and the results observed are summarized in Table I.

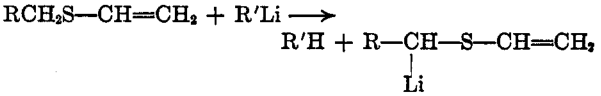
It can be seen that the addition of RLi to $RSCH{=}CH_2$ is quite sensitive to the structure of R, and proceeds to a reasonable extent, under the conditions studied, only when R is aromatic or vinyl. The facile addition of alkyllithium to phenyl vinyl sulfide, and the failure of phenyl vinyl ether to react,[5] does indeed suggest a definite sulfur 3-d-orbital effect; however, the reaction of the former may be promoted by the deshielding of the sulfur nucleus through the participation of forms such as III.[6] There is other evidence to support such an activating effect by an aromatic substituent. Con-



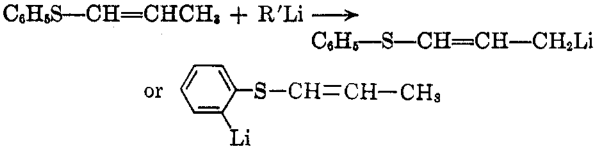
III

siderably more drastic conditions are required for the isomerization of alkyl allyl sulfides[7] than are required for aryl allyl sulfides, and no condensation occurs with benzaldehyde when phenylthioglycolic acid is replaced by alkylthioglycolic acids.[8]

Failure of R'Li to react appreciably with the aliphatic vinyl sulfides could logically be attributed to prior anion formation as shown in the accompanying equations



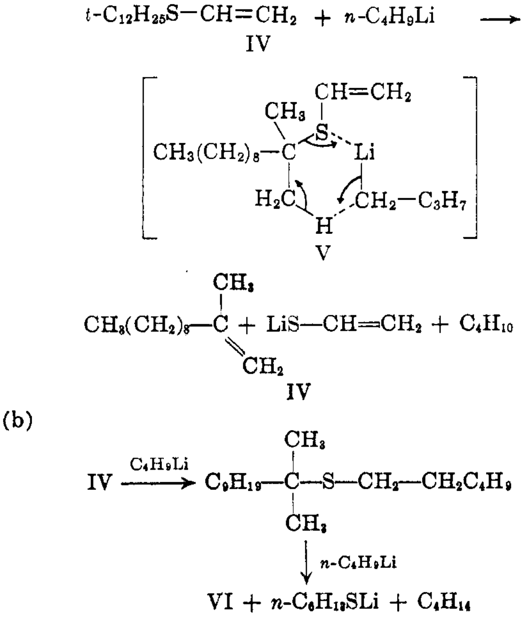
$$RCH_2S{-}CH{=}CH_2 + R'Li \longrightarrow R'H + R{-}\underset{\substack{|\\ Li}}{CH}{-}S{-}CH{=}CH_2$$



$$C_6H_5S{-}CH{=}CHCH_3 + R'Li \longrightarrow C_6H_5{-}S{-}CH{=}CH{-}CH_2Li$$

However, this does not appear to be the case. When the reaction mixture obtained from n-butyl vinyl sulfide and ethyllithium was treated directly with carbon dioxide, the olefin was recovered (81%) and there was no evidence for the formation of an organic acid other than propionic. Similarly, and more unexpected, the carbonation of the reaction product obtained from phenyl propenyl sulfide and ethyllithium afforded only recovered sulfide (94.5 %) and propionic acid.

The reaction of t-dodecyl vinyl sulfide (IV) with n-butyllithium is of interest since cleavage, rather than simple addition resulted. Failure to isolate n-hexyl mercaptan from the reaction product suggests that the reaction proceeds as shown in (a), possibly through the complex (V), rather than by path b.



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[1] This work was supported in part by the Office of Ordnance Research, U.S. Army, Contract No. DA-11-002-ORD-2616 and DA-ORD-31-124-61-G13.

[2] In part from the M.S. thesis of M. A. Kalnins, the University of Minnesota, 1959.

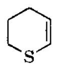
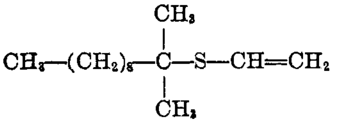
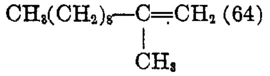
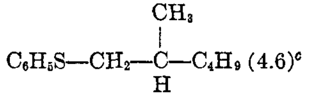
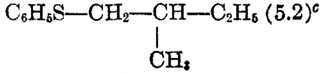
[3] In part from the Ph.D. thesis of D. R. Theissen, the University of Minnesota, 1961.

[4] Sinclair Research Fellow, 1959–1961.

[5] W. E. Parham and R. F. Motter, *J. Am. Chem. Soc.*, **81**, 2146 (1959).

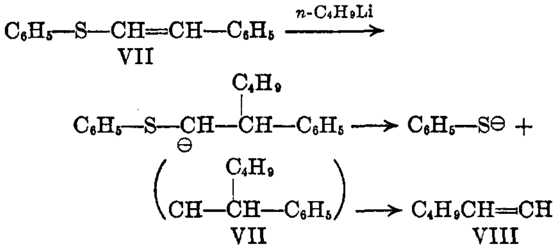
[6] The sulfur 3-d-orbital may be made more respectable by interaction with the antibonding benzene orbitals, interactions involving the 3-p-orbitals of sulfur with the benzene π system, and/or by inductive effects.

TABLE I

Vinyl sulfide	Alkyllithium	Product isolated (yield, %)
$C_6H_4SCH{=}CH_2$[a]	C_4H_9Li	$C_6H_5S{-}CH_2CH_2C_4H_9$ (51)
	C_2H_5Li	$C_6H_5SCH_2CH_2C_2H_5$ (68)
$C_2H_5S{-}CH{=}CH_2$	C_4H_9Li	Recovered olefin (high ~80)[b] $C_2H_5S({-}CH_2)_5CH_3$ (low ~5)
$C_4H_9S{-}CH{=}CH_2$	C_4H_9Li	Recovered olefin (~70) $C_4H_9S{-}CH_2CH_2C_4H_9$ (<10)
	C_2H_5Li	Recovered olefin (88) $C_4H_9S(CH_2)_3CH_3$ (not isolated)
	C_4H_9Li	Recovered olefin (81.3) Addition product (<2)
$n\text{-}C_{12}H_{25}S{-}CH{=}CH_2$	C_4H_9Li	Recovered olefin (78) $n\text{-}C_{12}H_{25}S{-}(CH_2)_5CH_3$ (4.8)
$CH_2{=}CH{-}S{-}CH{=}CH_2$	C_4H_9Li	$CH_2{=}CH{-}S{-}(CH_2)_5CH_3$ (34)
 $CH_3{-}(CH_2)_8{-}\underset{CH_3}{\overset{CH_3}{C}}{-}S{-}CH{=}CH_2$	C_4H_9Li	 $CH_3(CH_2)_8{-}\underset{CH_3}{C}{=}CH_2$ (64) Recovered olefin (some) Addition product (0) Mercaptan (0)
$C_6H_5S{-}CH{=}CH{-}CH_3$ (*trans*)	C_4H_9Li	Recovered olefin (82)  $C_6H_5S{-}CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}C_4H_9$ (4.6)[c]
	C_2H_5Li	Recovered olefin (81.8)  $C_6H_5S{-}CH_2{-}\underset{CH_3}{CH}{-}C_2H_5$ (5.2)[c]
$C_6H_5S{-}CH{=}CHC_6H_5$	C_4H_9Li	$C_6H_5CH{=}CH{-}C_4H_9$ (39) C_6H_5SH (40) Recovered olefin (~54)

[a] See ref. 5. [b] Separation of *n*-butyl alcohol from the reaction products was not complete enough to give good material balance in reaction with lower boiling vinyl sulfides; the yields are estimates. [c] The products were obtained in very small amounts in an impure state; their structure is assumed and the yield would be an upper limit.

Little can be said concerning the reaction of nonterminal vinyl sulfide with alkyllithium with the data available. The cleavage of VII, by reaction with *n*-butyllithium, could proceed by addition, α-elimination of thiophenylate, and rearrangement of the intermediate carbene (VII), or conceivably, by direct cleavage.



$$\underset{\text{VII}}{C_6H_5{-}S{-}CH{=}CH{-}C_6H_5} \xrightarrow{n\text{-}C_4H_9Li}$$

$$C_6H_5{-}S{-}\underset{\ominus}{CH}{-}\overset{C_4H_9}{CH}{-}C_6H_5 \longrightarrow C_6H_5{-}S^{\ominus} +$$

$$\underset{\text{VII}}{\left(CH{-}\overset{C_4H_9}{CH}{-}C_6H_5\right)} \longrightarrow \underset{\text{VIII}}{C_4H_9CH{=}CHC_6H_5}$$

Experimental

The reactions of the vinyl sulfides with alkyllithium were carried out under comparable conditions and are illustrated by the reaction of *n*-dodecyl vinyl sulfide.

Reaction of *n*-Dodecyl Vinyl Sulfide with *n*-Butyllithium.—An ether solution of *n*-butyllithium[9] was prepared under an atmosphere of nitrogen at −10°, using lithium (2.0 g., 0.288 g.-atom) and butyl bromide (16.0 g., 0.117 mole). The solution was allowed to warm to 0° and freshly distilled *n*-dodecyl vinyl sulfide[10] (8.35 g., 0.0367 mole, b.p. 113°/0.8 mm., $n^{25}D$ 1.4707) was added slowly with stirring. Stirring was continued at 0° for 3 hr.; the solution was poured onto ice, and the hydrolysis mixture was extracted with ether which was then dried (Na_2SO_4) and distilled. There was obtained 6.5 g. (77.8% recovery) of unchanged *n*-dodecyl vinyl sulfide (identified by its physical constants and identity of infrared spectra with starting material) and a residue (1.4 g.). Distillation of the residue afforded 0.5 g. (4.8% yield) of a liquid (b.p. 150–154°/1.0 mm., $n^{25}D$ 1.4605), which was identified, as described below, as *n*-dodecyl *n*-hexyl sulfide, and 0.8 g. of polymeric, acetone-insoluble, residue.

***n*-Dodecyl *n*-Hexyl Sulfone.**—*n*-Dodecyl *n*-hexyl sulfide (250 ml., b.p. 159–161°/10.95 mm., $n^{25}D$ 1.4615) was prepared (70% yield) by the reaction of the sodium salt of *n*-dodecyl mercaptan with *n*-hexyl bromide in ethanol. The sulfide was converted to the sulfone (85% yield, m.p. 73°) by oxidation with hydrogen peroxide in acetic acid.

Anal. Calcd. for $C_{18}H_{38}O_2S$: C, 67.87; H, 12.02; S, 10.06. Found: C, 67.31; H, 11.72; S, 10.21.

This sulfone was identical (melting point and mixture melting point) to that prepared from the product described above, obtained from *n*-dodecyl vinyl sulfide and *n*-butyllithium.

Ethyl *n*-hexyl sulfide, obtained from ethyl vinyl sulfide and *n*-butyllithium, was further characterized by conversion to, ethyl *n*-hexyl sulfone (m.p. 60–61°, from ethanol–water,

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(7) D. S. Tarbel and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

(8) V. Baliak and R. J. Varadachari, *Current Sci.* (India), **23**, 19 (1954). *Chem. Abstr.*, **49**, 3076 (1955).

(9) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

(10) Kindly supplied by the Rohm and Haas Co., Philadelphia, Pennsylvania.

identical to that prepared (60% yield) from authentic ethyl *n*-hexyl sulfide).

Anal. Calcd. for $C_8H_{18}O_2S$: C, 53.89; H, 10.18; S, 17.90. Found: C, 53.76; H, 10.30; S, 18.23.

Divinyl Sulfide.—A mixture containing β-hydroxyethyl vinyl sulfide[10] (104 g., 1.0 mole) and an equal weight of potassium hydroxide was heated carefully to 165°. The product distilled slowly, and heating was discontinued when the reaction mixture began to foam considerably. The product was trapped in a Dry Ice-cooled receiver containing sodium sulfate. Distillation of the product gave 28.2 g. (33.6%, b.p. 82–86°) of divinyl sulfide.[11]

Reaction of *t*-Dodecyl Vinyl Sulfide with *n*-Butyllithium.—The reaction of butyllithium[12] (7.49 g., 0.117 mole) in heptane and *t*-dodecylvinyl sulfide[10] (5.9 g., b.p. 86°/1.0 mm., $n^{25}\mathrm{D}$ 1.4795) in anhydrous ether was carried out by a procedure essentially identical to those described above. The dried ether extract was distilled and the following fractions were collected: 1) 2.8 g., b.p. 65–72°/8.5 mm., $n^{25}\mathrm{D}$ 1.4344–1.4352; 2) 0.3 g., b.p. 55–65°/1.3 mm., $n^{25}\mathrm{D}$ 1.4475; 3) 0.4 g., b.p. 50–61°/0.25 mm., $n^{25}\mathrm{D}$ 1.4771; 4) 1.6 g., undistilled residue.

Fraction 1 contained no sulfur, rapidly decolorized a solution of bromine and carbon tetrachloride, and the infrared spectrum showed absorption at 1640 cm.$^{-1}$ and 890 cm.$^{-1}$ consistent with a disubstituted terminal olefin structure.

Anal. Calcd. for C_nH_{2n}: C, 85.60; H, 14.40. Found: C, 83.90; H, 14.12; S, 0.00.

It was concluded that this material was principally 2-methyl-1-undecene (64.2% yield; reported,[13] b.p. 204°, $n^{25}\mathrm{D}$ 1.4339).

Fraction 3 was recovered *t*-dodecyl vinyl sulfide (b.p. 86°/1.0 mm., $n^{25}\mathrm{D}$ 1.4795) as evidenced by physical constants and identity of infrared spectra. The infrared spectrum of fraction 2 showed it to be a mixture of 2-methyl-1-undecene and *t*-dodecyl vinyl sulfide.

The aqueous layer, obtained from the original reaction mixture subsequent to the addition of water and ether extraction, was acidified (HCl), and extracted with ether. The ether layer was dried (Na_2SO_4) and the ether was removed. A vile odor, but no residue, was observed.

Reaction of Phenyl β-Styryl Sulfide with *n*-Butyllithium.—A solution of phenyl β-styryl sulfide[14] (21.0 g., 0.1 mole, b.p. 141°/0.5 mm., $n^{25}\mathrm{D}$ 1.6678) in anhydrous ether (100 ml.) was added dropwise to a solution of *n*-butyllithium (0.5 mole) in anhydrous ether (200 ml.), at 0° under an atmosphere of nitrogen. The reaction mixture was stirred for 4 hr. at 0°, water was added, and the resulting mixture was extracted with ether.

The dried ether extract was distilled and a number of fractions were combined into two principal products: (A) A sulfur-free olefin, 6.14 g., $n^{26}\mathrm{D}$ 1.5251, b.p. near 72°/1 mm., and (B) impure phenyl β-styrryl sulfide, > 9.31 g., b.p. near 114°/1 mm., $n^{26}\mathrm{D}$ 1.6000–1.6450. The recovered phenyl β-styryl sulfide amounted to about 54%. The olefin was identified, as described below, as 1-phenylhexene-1 (39% yield).

Ether was added to the water layer, obtained from the original reaction mixture, and the resulting mixture was made acidic by the addition of hydrochloric acid. Distillation of the dried, water-washed, ether extract gave phenyl mercaptan (4.3 g., 40% yield, b.p. 164°, $n^{23}\mathrm{D}$ 1.5837).

Identification of 1-Phenylhexene-1.—The oil, described above, was redistilled (b.p. 74°/2 mm., $n^{23.5}\mathrm{D}$ 1.5243).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.22; H, 10.12; S, 0.00.

Ozonolysis of this olefin gave benzaldehyde and *n*-valeraldehyde, identified by comparison of the corresponding 2,4-dinitrophenylhydrazones with those prepared from authentic samples.

1-Phenylhexene-1, prepared from *n*-butyllithium and ω-bromostyrene has $n^{25}\mathrm{D}$ 1.5377.[15] A sample of 1-phenylhexene-1, prepared (24% over-all yield) from benzaldehyde and 1-bromopentane, through the intermediate Grignard reagent with subsequent dehydration of the derived alcohol with phosphoric acid, boiled at 97–100°/8 mm. and had $n^{25}\mathrm{D}$ 1.5528. The infrared and ultraviolet spectra of this sample of 1-phenylhexene-1 were identical to the corresponding spectra derived from the olefin described in the preceding section, and were consistent with the *trans* substituted ethylene structure.

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[11] W. E. Lawson and E. M. Reid, *J. Am. Chem. Soc.*, **47**, 2821 (1925).

[12] Obtained from Lithium Corp. of America.

[13] B. T. Brooks and J. Humphrey, *J. Am. Chem. Soc.*, **40**, 839 (1918).

[14] H. R. Davis, Ph.D. thesis, University of Minnesota, p. 42 (1949).

[15] C. S. Marvel, F. D. Hager, and D. D. Coffman, *J. Am. Chem. Soc.*, **49**, 2327 (1927).

Reactions of Triisopropyl Phosphite with Diphenyldiazomethane

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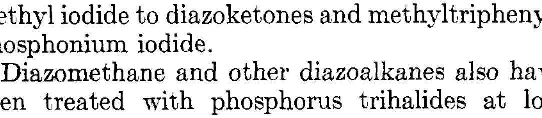
Staudinger and his co-workers[1] prepared phosphazines from tertiary phosphines and substituted diazomethanes. The phosphazines reported were basic, moderately stable, highly reactive com-

$$R_3P + R'_2C{=}N_2 \longrightarrow R_3P{=}N{-}N{=}CR_2'$$

pounds; upon heating they decomposed to give nitrogen and other products. An ylide was identified among the decomposition products from fluorenone triphenylphosphazine.[1b]



$$Ph_3P{=}N{-}N{=}C\begin{matrix}C_6H_4\\C_6H_4\end{matrix} \longrightarrow Ph_3P{=}C\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix} + N_2$$

Recently Bestmann and Buckschewski[2] treated triphenylphosphine with α-ketodiazomethanes. The resulting α-oxotriphenylphosphazines in 80% ethanol were hydrolyzed to the corresponding α-oxoaldehyde al-hydrazones and converted by methyl iodide to diazoketones and methyltriphenylphosphonium iodide.

Diazomethane and other diazoalkanes also have been treated with phosphorus trihalides at low temperatures.[3] Phosphazines, however, were not isolated and, if formed, were unstable; nitrogen was evolved and moisture-sensitive products were obtained. Furthermore, no phosphazine was isolated when benzene phosphorus tetrachloride

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[1] (a) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 619 (1919). (b) H. Staudinger and W. Braunholtz, *ibid.*, **4**, 897 (1921). (c) H. Staudinger and G. Lüscher, *ibid.*, **5**, 75 (1922).

[2] H. Bestmann, H. Buckschewski, and H. Leube, *Ber.*, **92**, 1345 (1959).

[3] A. Ya. Yakubovich and V. A. Ginsburg, *Zh. Obshch. Khim.*, **22**, 1534 (1952).