

tion C yielded 3.56 g. of α -methylbenzylaniline hydrochloride, m.p. 178–179°, neut. equiv. 233.

α -Methylbenzyl Carbanilate with Added *p*-Toluidine.—A mixture of 0.054 mole of α -methylbenzyl carbanilate and 0.27 mole of *p*-toluidine was refluxed at 215–237° for 12 hr. Products were separated by solvent treatments, fractionation and formation of hydrochlorides and picrates. Identifications were made by mixed melting points and neutral equivalents.

Benzyl Carbanilate.—The Claisen flask was replaced by a round-bottom flask with water condenser. Products were separated by use of 1:1 ether-petroleum ether to remove diphenylurea, followed by fractionation under reduced pressure and solvent treatment to separate aniline from the secondary and tertiary amines. Benzylaniline was obtained both as a solid, m.p. 37–39°, and as its hydrochloride from

benzene, m.p. 208–210°. The separation of dibenzylaniline, m.p. 67–69°, was aided by column chromatography on alumina from petroleum ether solution.

Certain other possible routes to the secondary and tertiary amines resulting from degradation of benzyl carbanilate were eliminated as major paths by control experiments. When a mixture of 0.055 mole of benzylaniline and 0.043 mole of benzyl alcohol was heated at 238–246° for 36 hr., only 3.7% of dibenzylaniline was obtained; 88% of the benzylaniline was recovered. Disproportionation among the amines was shown to be not extensive by heating a mixture of 0.0335 mole of benzylaniline and 0.0334 mole of dibenzylaniline for 23.5 hr. at 248–255°; 91% of the dibenzylaniline was recovered.

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Substituted Styrenes. IV. The Reaction of the Vinylanisoles with *p*-Nitrobenzenediazonium Chloride in Pyridine^{1,2}

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The reactions of *o*- and *p*-vinylanisole with *p*-nitrobenzenediazonium chloride in pyridine gave 4-nitrobenzyl-2'-methoxyphenylcarbinol (6.5%) and 4-nitro-4'-methoxystilbene (12%), respectively. Similar reactions could not be effected using *m*-vinylanisole. The reaction of *p*-vinylanisole with other diazonium chlorides proved to be a new and novel method for preparing substituted stilbenes which would be difficult to prepare by conventional procedures. By the method described, 4-cyano- and 4-acetyl-4'-methoxystilbene were obtained in 41 and 19% yields, respectively.

Earlier studies in this series^{3,4} have demonstrated the electrophilic character of the vinyl groups in *o*- and *p*-nitrostyrene and recent work on the syntheses and spectra of the vinylphenols⁵ included attempts to prove, by chemical means, pronounced nucleophilic character of the vinyl groups in *o*- and *p*-vinylphenol. However, the ease of polymerization of the vinylphenols hindered the initial efforts of the latter study and clear differences have yet to be demonstrated chemically for the vinyl groups in these compounds.

The vinylanisoles represent another class of styrenes with an electron-releasing nuclear substituent and, for these compounds, enhanced nucleophilic character would again be expected for the vinyl groups when situated *ortho* or *para* to the methoxy group. Pronounced reactivity for these vinylanisoles was indicated from the evidence of several earlier reports. Thus, Schmidle and Mansfield⁶ found that *p*-vinylanisole, formaldehyde and morpholine, under mild conditions, gave 4-anisyl-2-(4-morpholinyl)-ethylcarbinol and *p*-vinylanisole, formaldehyde and dimethylamine, refluxed in acetic acid, gave *N,N*-dimethyl-4-methoxycinnamylamine. Also, Shamshurin⁷ obtained 1-(acetomercurimethyl)-2,6-dimethoxyphenylcarbinol from the reaction of 2,6-dimethoxystyrene and mercuric acetate in water, and Ainley and Robin-

son⁸ prepared anisaldehyde 2,4-dinitrophenylhydrazone from *p*-vinylanisole and 2,4-dinitrobenzenediazonium sulfate in ethanol. In the latter reaction formaldehyde was eliminated. *p*-Nitrobenzenediazonium sulfate, dissolved in glacial acetic acid or suspended in alcohol, also was reported to attack the *n*-propenyl side chain of anethole, isosafrole, isoapiole and isoeugenol with the formation of the corresponding substituted benzaldehyde *p*-nitrophenylhydrazones and acet-aldehyde.^{9,10}

All these examples may be classified as electrophilic substitution or addition reactions. The influence of the *o*- or *p*-methoxy group must certainly be of importance in these reactions since styrene fails to give a sharply defined crystalline compound with 2,4-dinitrobenzenediazonium sulfate,⁹ a very powerful electrophilic reagent.

It was the intent in this study, therefore, to investigate differences in the reactions of isomeric vinylanisoles with a common reagent. Reaction conditions were selected to give a minimum of side reactions. *p*-Nitrobenzenediazonium chloride was chosen for the reagent because it has been demonstrated that anisole¹¹ will not react with this reagent. This would obviate the possibility of a reaction on the aromatic nucleus and restrict reactions, if any, to the side chain. Preliminary reactions of *p*-vinylanisole with *p*-nitrobenzenediazonium chloride in acetic acid gave only dark tars and pyridine was used in subsequent reactions

(1) Abstracted from a portion of a thesis submitted by H. E. H. to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the Ph.D. degree.

(2) Presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 17, 1957.

(3) W. J. Dale and C. W. Strobel, *THIS JOURNAL*, **76**, 6172 (1954).

(4) W. J. Dale and G. Buell, *J. Org. Chem.*, **21**, 45 (1956).

(5) W. J. Dale and H. E. Hennis, *THIS JOURNAL*, **80**, 3645 (1958).

(6) C. J. Schmidle and R. C. Mansfield, *ibid.*, **77**, 4636 (1955).

(7) A. A. Shamshurin, *J. Gen. Chem. (U. S. S. R.)*, **16**, 99 (1946); *C. A.*, **41**, 104 (1947).

(8) A. D. Ainley and R. Robinson, *J. Chem. Soc.*, 369 (1937).

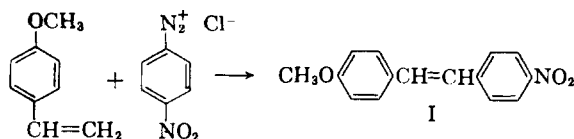
(9) A. Quilico and M. Freri, *Gazz. chim. ital.*, **58**, 380 (1928); *C. A.*, **23**, 597 (1929).

(10) A. Quilico and E. Fleischner, *Gazz. chim. ital.*, **59**, 39 (1929); *C. A.*, **23**, 3675 (1929).

(11) K. H. Meyer and S. Lenhardt, *Ann.*, **398**, 60 (1913).

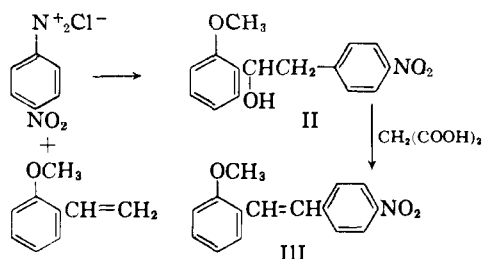
to furnish a one-phase system and to avoid acidic conditions.

The products obtained from the reactions of the vinyanisoles and *p*-nitrobenzenediazonium chloride were somewhat unexpected. 4-Nitro-4'-methoxystilbene(I) was isolated in 12% yield from the reaction of the *p*-isomer with *p*-nitrobenzenediazonium



chloride. The structure of the product was confirmed by carbon and hydrogen content and by the reduction of the stilbene to 4-amino-4'-methoxystilbene¹² followed by conversion of the amine to the benzamide.¹²

The reaction of *o*-vinyanisole with *p*-nitrobenzenediazonium chloride gave a mixture of compounds which could not be separated by crystallization and it was necessary to chromatograph the mixture to obtain a pure product. The chromatogram showed no less than seven different zones. The major zone (73% of the total crystalline product by weight) was the only product investigated. Carbon and hydrogen content, a negative bromine unsaturation test, and failure of the compound to fluoresce under ultraviolet light indicated that the compound was not a stilbene. The infrared absorption showed characteristic bands for a secondary hydroxyl function and for nitro, phenyl, phenoxy and methoxy groups. On this basis, structure II, 4-nitrobenzyl-2'-methoxyphenylcarbinol, was tentatively assigned to the product. If the proposed structure is correct, then II should undergo dehydration in the presence of a weak acid because in the condensation of *o*-methoxybenzaldehyde with *p*-nitrophenylacetic acid in the presence of a trace of piperidine, the intermediate compound decarboxylates and dehydrates to give 4-nitro-2'-methoxystilbene.¹² Similar conditions would be involved in the dehydration of II in the presence of a weak acid. Compound II did dehydrate smoothly in the presence of malonic acid to give III whose melting point was not depressed when mixed with authentic III; II was obtained in 6.5% yield.



No product or tars were obtained from the reaction of *p*-nitrobenzenediazonium chloride with *m*-vinyanisole. In an attempted reaction with anisole, however, the diazonium chloride reacted with the solvent, pyridine, to give a mixture of α -, β - and γ -(*p*-nitrophenyl)-pyridines (9.3%). This

(12) P. Pfeiffer, S. Braude, J. Kleber, G. Marcon and P. Wittkop, *Ber.*, **48**, 1777 (1915).

reaction with pyridine has been reported earlier.¹⁸ However, the reagent did not react with pyridine in the attempted reaction with *m*-vinyanisole.

The reaction of other diazonium salts with *o*-vinyanisole was not promising, but the reactions of two other diazonium chlorides with *p*-vinyanisole provided novel syntheses for other substituted stilbenes. The reaction of *p*-acetyl- and *p*-cyanobenzenediazonium chlorides with *p*-vinyanisole gave 4-acetyl-4'-methoxystilbene (19%) and 4-cyano-4'-methoxystilbene (41%), respectively. However, the physical properties of the 4-cyano-4'-methoxystilbene prepared by this method are quite different from those reported by Neher and Miescher.¹⁴ These workers prepared the compound by the dehydration of 1-(4-methoxyphenyl)-2-(4-cyanophenyl)-ethanol and also by the condensation of anisaldehyde and *p*-cyanophenylacetic acid. In both cases they obtained the compound as white plates (melting at 149° and clearing at 162°) and attributed the wide melting range to a mixture of *cis-trans* isomers. The product obtained by our method was in the form of copper-colored plates, m.p. 143-143.5°.

Infrared absorption of all the substituted stilbenes obtained in this study are completely compatible with the structures proposed and, furthermore, suggests that all these stilbenes are of the *trans* form.

The mechanism for these reactions is not obvious from our limited data. The alkaline conditions employed are certainly favorable for a Gomberg-type free radical reaction. However, the fact that *p*-nitrobenzenediazonium chloride gave insoluble products only with the *o*- and *p*-isomers and not with *m*-vinyanisole is strong evidence for an ionic mechanism. Free radical or ionic additions could occur to the ends of either the *o*- or *p*-vinyl system, followed by elimination of hydrogen as ion or radical to give stilbenes, or by addition of a hydroxy group to give a carbinol. Further studies are being conducted concerning the mechanism of this reaction.

The possibility was considered that, in the formation of the carbinol from the reaction of *p*-nitrobenzenediazonium chloride with *o*-vinyanisole, a stilbene was formed first as an intermediate. It is plausible that in an intermediate stilbene of structure III, steric requirements near the methoxy group prevent it from counteracting the electro-negative influence of the *p*-nitro group upon the double bond. However, since 4-nitro-2'-methoxystilbene failed to add water under the conditions of the coupling reactions, this stilbene cannot be considered an intermediate in the reaction.

The vinyanisoles were prepared by the decarboxylation of methoxycinnamic acids in the presence of quinoline and copper according to the method of Walling and Wolfstirn.¹⁵ The methoxycinnamic acids were prepared by the condensation of methoxybenzaldehydes with malonic acid in the presence of small amounts of pyridine and piperidine. The absence of a solvent in these conden-

(13) J. W. Haworth, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

(14) R. Neher and K. Miescher, *Helv. Chim. Acta*, **29**, 449 (1946).

(15) C. Walling and B. Wolfstirn, *THIS JOURNAL*, **69**, 852 (1947).

sations appears to have a number of distinct advantages. The yield of the cinnamic acid is high, the reaction time is short, and the procedure is appreciably simplified.

The present study is being continued to investigate the use of other diazonium salts and other alkoxy-styrenes under a variety of reaction conditions.

Experimental

All melting points and boiling points are uncorrected.

Methoxycinnamic Acid Preparations.—A mixture of 100 g. (0.735 mole) of a methoxybenzaldehyde, 74.0 g. (0.711 mole) of malonic acid, 5 ml. of pyridine and 5 ml. of piperidine was heated at 120° for 0.5 hour during which time the mixture melted, vigorously evolved carbon dioxide, and solidified. The crude methoxycinnamic acids were recrystallized from ethanol to give white crystalline products in the yields: *o*-methoxycinnamic acid, 87%, m.p. 179–181° (lit.¹⁶ m.p. 182–183°); *m*-methoxycinnamic acid, 92%, m.p. 115–117° (lit.¹⁷ m.p. 115°); *p*-methoxycinnamic acid, 79%, m.p. 171–172° (lit.¹⁸ m.p. 173°).

Vinylisole Preparations.—The method described by Walling and Wolfstirn¹⁵ was adopted. A mixture of 50.0 g. (0.281 mole) of methoxycinnamic acid, 100 ml. of freshly distilled quinoline and 5 g. of finely divided copper powder was distilled at a rate such that the temperature of the distilling vapors reached 234° within 40 minutes. The distillate was dissolved in 200 ml. of ether and the ethereal solution was extracted with 6 *N* hydrochloric acid until the aqueous extracts were acid to litmus, washed once with water, and dried over anhydrous magnesium sulfate. The ether was removed by distillation and the product was purified by distillation under diminished pressure. The following yields are based on the boiling ranges indicated: *o*-vinylisole, 40%, b.p. 91–92° (16 mm.), n_D^{20} 1.5607 (lit.¹⁵ 1.5608 (20°)); *m*-vinylisole, 32%, b.p. 76–80° (3 mm.), n_D^{20} 1.5586 (lit.¹⁹ 1.5586 (23°)); *p*-vinylisole, 69%, b.p. 77–80° (3 mm.), n_D^{20} 1.5620 (lit.¹⁵ 1.5612 (20°)). Samples of the above compounds purified by fractionation through a Todd precise fractionation assembly had the values for n_D^{20} : *o*-, 1.5595; *m*-, 1.5579; *p*- 1.5609.

Reaction of *p*-Vinylisole with *p*-Nitrobenzenediazonium Chloride.—*p*-Nitrobenzenediazonium chloride (0.0747 mole) was prepared in the usual manner from a solution of 10.4 g. (0.0747 mole) of *p*-nitroaniline in 90 ml. of 5% hydrochloric acid and 220 ml. of water followed by 5.20 g. (0.0747 mole) of sodium nitrite dissolved in 25 ml. of water. This reagent was then added dropwise, with stirring, to a solution of 10.0 g. (0.0747 mole) of *p*-vinylisole in 200 ml. of pyridine; the temperature of the reaction mixture was maintained below 5° during the addition. The reaction mixture turned deep red during the addition and a black solid separated. The mixture was reduced to one-half its original volume by distillation. On cooling, a black amorphous solid and yellow plates separated. The solids were separated mechanically. The yellow plates were recrystallized from aqueous ethanol to give 0.53 g. of red-brown needles, m.p. 125–127°. The black amorphous solid was extracted 3 times with hot ethanol. The combined ethanolic extracts were diluted with water and cooled to give 1.85 g. of red-brown needles, m.p. 127–129°. This afforded a total of 2.38 g. (12%) of crude 4-nitro-4'-methoxystilbene. A sample recrystallized from aqueous ethanol and glacial acetic acid gave gold-yellow plates, m.p. 130–131° (lit.²⁰ m.p. 133°).

Anal. Calcd. for C₁₅H₁₃O₃N: C, 70.58; H, 5.13. Found: C, 70.50; H, 5.16.

The 4-nitro-4'-methoxystilbene (1.00 g., 0.00393 mole) was reduced with stannous chloride in the presence of concentrated hydrochloric acid and glacial acetic acid according to the method of Pfeiffer and co-workers¹² to give 0.42 g. (47%) of 4-amino-4'-methoxystilbene as yellow-brown plates, m.p. 169–170.5° (lit.¹² 173–174°), after two recrystal-

lizations from ethanol. Further recrystallizations did not raise the melting point.

A portion of the 4-amino-4'-methoxystilbene was converted to 4-benzamido-4'-methoxystilbene by gentle heating with benzoyl chloride. The product was recrystallized from ethanol to give almost colorless shining plates, m.p. 250–252° (lit.¹² m.p. 249°).

Reaction of *o*-Vinylisole with *p*-Nitrobenzenediazonium Chloride.—*p*-Nitrobenzenediazonium chloride (0.0747 mole), prepared as previously described, was added to a solution of 10.0 g. (0.0747 mole) of *o*-vinylisole in 200 ml. of pyridine. The temperature of the reaction mixture was maintained below 5° during the addition. The solution turned a deep red and a black tarry material separated. The volume of the reaction mixture was reduced to one-third by distillation and the black tar was collected and dissolved in hot ethanol. A red tar which separated when the ethanolic solution was cooled was discarded and the ethanolic solution was heated, diluted with water, and cooled. Again a red tar separated. It was discarded and the operation was repeated. A yellow crystalline solid (1.81 g., m.p. 106–114°) separated on cooling the twice-diluted aqueous ethanolic solution. Recrystallization of a portion of the product from aqueous ethanol did not change the melting point or give a homogeneous crystalline solid. A benzene solution of the product (0.45 g.) was chromatographed through acid-washed alumina. The chromatogram showed seven colored zones. The major zone was eluted with a benzene-ether mixture (9:1 by volume). Evaporation of the solvent left a pale yellow solid residue which was recrystallized from aqueous ethanol to give 0.33 g. of 4-nitrobenzyl-2'-methoxyphenylcarbinol as fine lustrous pale yellow needles, m.p. 113–120°. This corresponds to a 6.5% yield of product from the reaction. Further recrystallizations of the compound did not change the melting point. The compound did not absorb bromine, did not dissolve in 5% hydrochloric acid, and did not fluoresce under ultraviolet light.

Anal. Calcd. for C₁₅H₁₄O₄N: C, 65.92; H, 5.53. Found: C, 65.49; H, 5.56.

A small portion of the product was mixed with an equal amount of malonic acid and the mixture was heated at 140° for 0.5 hour. The product was recrystallized from aqueous ethanol to give bright yellow needles, m.p. 119–121°. An intimate mixture (1:1) of the compound obtained in this dehydration and authentic 4-nitro-2'-methoxystilbene, m.p. 119–121°, melted at 118.5–120°. The authentic compound was prepared by the condensation of *o*-methoxybenzaldehyde and *p*-nitrophenylacetic acid in the presence of piperidine.¹² The reported¹² melting point of this compound is 122°.

Reaction of *m*-Vinylisole with *p*-Nitrobenzenediazonium Chloride.—*p*-Nitrobenzenediazonium chloride (0.0747 mole) was added to a solution of 10.0 g. (0.0747 mole) of *m*-vinylisole dissolved in 200 ml. of pyridine as previously described. A red coloration was produced; however, only 0.19 g. of brown amorphous solid separated after the reaction mixture had been reduced to 100 ml. by distillation. The solid failed to give a crystalline product when crystallization from aqueous ethanol was attempted. It burned leaving a residue and did not melt at 335°.

Reaction of Anisole with *p*-Nitrobenzenediazonium Chloride.—*p*-Nitrobenzenediazonium chloride (0.150 mole) was added as described in the previous experiments to 16.2 g. (0.150 mole) of anisole dissolved in 200 ml. of pyridine; the tar which separated was dissolved in ethanol and after 3 operations of cooling the ethanolic solution, discarding the tar which separated, diluting the ethanolic solution with water, and again cooling, a pale yellow-brown solid (2.79 g., m.p. 96–106°) separated. Two crystallizations from aqueous ethanol raised the melting point to 117–124°, but failed to give a well-defined crystalline solid. The product readily dissolved in 5% hydrochloric acid and was presumed to be a mixture of *p*-nitrophenylpyridines (9.3%). It has been reported that *p*-nitrobenzenediazonium chloride, when caused to react with pyridine at 40°, gives a mixture of *p*-nitrophenylpyridines, m.p. 105–115°.¹³

Reactions of *p*-Cyano- and *p*-Acetylbenzenediazonium Chlorides with *p*-Vinylisole.—The diazonium chlorides (0.0747 mole) were prepared in the manner previously described for the preparation of *p*-nitrobenzenediazonium chloride and added in the same manner to 10.0 g. (0.0747 mole) of *p*-vinylisole dissolved in 200 ml. of pyridine. The reaction mixtures were stirred after the addition was com-

(16) W. H. Perkin, *J. Chem. Soc.*, **31**, 414 (1877).

(17) F. Tiemann and R. Ludwig, *Ber.*, **15**, 2043 (1882).

(18) R. Robinson and J. Shinoda, *J. Chem. Soc.*, **127**, 1973 (1925).

(19) E. Matsui, *J. Soc. Chem. Ind., Japan*, **46**, 171 (1943); *C. A.*, **44**, 9188 (1950).

(20) R. von Waltherr and A. Wetzlich, *J. prakt. Chem.*, **61**, 169 (1900).

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*-cyanobenzenediazonium chloride and *p*-vinylanisole gave a brown solid which was recrystallized from aqueous ethanol to give 7.17 g. (41%) of *trans*-4'-cyano-4'-methoxystilbene, m.p. 133–141°, as red-brown plates. Neher and Miescher¹⁴ report a *cis-trans* mixture as white plates, m.p. 149°, clearing at 162°. A sample recrystallized four times from aqueous ethanol yielded copper-colored plates, m.p. 143–143.5°.

Anal. Calcd. for C₁₆H₁₃ON: C, 81.68; H, 5.57. Found: C, 81.89; H, 5.54.

The reaction of *p*-acetylbenzenediazonium chloride and *p*-vinylanisole 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. Calcd. for C₁₇H₁₅O₂: C, 80.92; H, 6.39. Found: C, 80.96; H, 6.50.

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

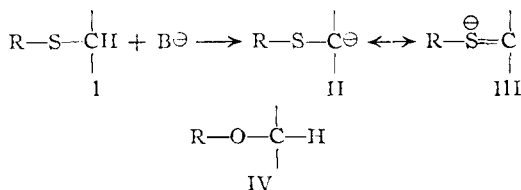
The Reaction of Vinyl Sulfides and Alkyl Sulfides with Butyllithium¹

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RECEIVED SEPTEMBER 20, 1958

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 alkyl lithium 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.

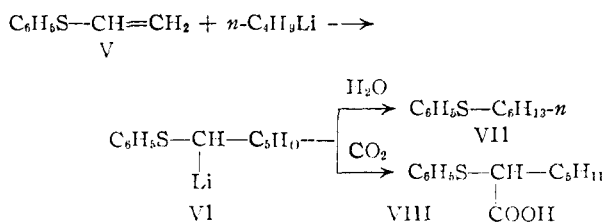
There have been many reports of the conjugation ability of the sulfonyl³ and sulfonium groups,⁴ and it is rather generally accepted that the sulfur atom in these groups can stabilize unshared electrons on an adjacent carbon atom by using its d-orbitals. However, in systems containing bivalent sulfur, in which the sulfur exerts a smaller electrical demand, the available evidence indicates that d-orbital interaction of sulfur is small⁵ unless there is a charge equivalent to a carbanion adjacent to sulfur. The greater acidity^{6–9} 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).



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

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



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°, respectively.

When the reaction product VI was treated directly with carbon dioxide, *α*-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 *α*-carbon atom of the aliphatic chain, and that the reaction sequence V → VI → 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,

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

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

(3) (a) E. A. Fehnel and M. Carmack, *THIS JOURNAL*, **71**, 231 (1949), **72**, 1292 (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. F. 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. Oae and C. C. Price, *ibid.*, **80**, 3425 (1958).

(5) Cf. F. G. Bordwell and P. J. Bortan, *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. Breitm and T. Levenson, *ibid.*, **76**, 5389 (1954).

(9) H. G. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949).