of 2.0 g. (0.288 g. atom) of lithium in 40 ml. of THF. Initially about 5 ml. of the cyclopentadiene solution was added. After 20 min. bubbles began to evolve around the pieces of lithium. The remaining cyclopentadiene solution was added, during 45 min. while cooling at 0°. The mixture was stirred at room temperature for 30 min. before filtering it into a stirred solution of 10.9 g. (0.06 mole) of benzophenone in 35 ml. of THF. The orange mixture was stirred at room temperature for 21 hr. and was poured into a mixture of ice and water. The organic layer was separated, dried, and most of the solvent was evaporated under a stream of dry air. The red residue was refluxed in petroleum ether (b.p. 28–38°) and filtered to leave a brown, gummy material. The petroleum ether was slowly evaporated under reduced pressure to leave orange crystals which were washed with 95% ethanol, filtered, and dried to give 4.88 g. (35%) of diphenylfulvene, m.p. 75–77°, identified by mixed melting point.

In another run using 8.05 g. (0.122 mole) of cyclopentadiene and 2.85 g. (0.41 g. atom) of lithium, a 45% yield of diphenylfulvene was obtained.

2-Biphenylyldiphenylcarbinol. An ethereal solution containing 0.344 mole of 2-biphenylyllithium[8] was added to a solution of 62.6 g. (0.344 mole) of benzophenone. The mixture was hydrolyzed with water and the organic layer was worked up in the usual fashion. Evaporation of the solvent under a stream of dry air left a solid which was crystallized from ethanol to give 97 g. (84%) of product, m.p. 86–88°.

2-Biphenylyldiphenylcarbinol, m.p. 87–88°, has previously been prepared in 63% yield from phenylmagnesium bromide and 2-phenylbenzophenone.[6] Refluxing the carbinol in acetic acid gave 9,9-diphenylfluorene.

Reaction of lithium with 9,9-diphenylfluorene. A mixture of 6.0 g. (0.019 mole) of 9,9-diphenylfluorene, 2.0 g. (0.29 g. atom) of lithium wire, and 50 ml. of tetrahydrofuran was stirred at room temperature for 15 hr. The organic layer was separated and dried over sodium sulfate after hydrolyzing with water. Distillation of the solvent left a material which was crystallized from a minimum of ethanol to give 3.88 g. (85%) of colorless needles, m.p. 143–144°, which showed no depression in melting point when admixed with an authentic sample of 9-phenylfluorene.

When the reaction time was limited to 1.75 hr., only a 25% yield of 9-phenylfluorene was obtained.

Acknowledgment. This research was supported in whole by the United States Air Force under contract AF 33(616)-3510 monitored by Materials Laboratory, Directive of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

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[8] H. Gilman and K. Oita, *J. Org. Chem.*, **20**, 862 (1955).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Addition of Ethyl Mercaptan to Acetylenic Compounds[1]

A. T. BLOMQUIST AND JOSEPH WOLINSKY

Received August 19, 1957

The free-radical addition of two equivalents of ethyl mercaptan to several acetylenic compounds has been studied. These comprised propargyl alcohol, propargyl acetate, 2-butyn-1,4-diol diacetate, 1-hexyne, 2-methyl-3-butyn-2-ol, propiolic acid, dimethyl acetylenedicarboxylate, and phenylacetylene. Vicininal *bis*-ethylmercapto derivatives were obtained in all but two instances. Phenylacetylene afforded phenylacetaldehyde diethyl mercaptal while from dimethyl acetylenedicarboxylate only a monoadduct was realized.

These bisethylmercapto derivatives were not active when tested *in vivo* against *M-tuberculosis* infection in mice.

Although the literature abounds with reports of studies of the addition of thiols to ethylenic substances, relatively little attention has been given to such additions involving acetylenic compounds.[2,3]

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[1] The work reported here was done as part of a general research program in organic chemistry at Cornell University, sponsored by the B. F. Goodrich Co.

[2] (a) S. Ruhemann and H. E. Stapleton, *J. Chem. Soc.*, **77**, 1179 (1900); (b) C. Finzi, *Gazz. chim. ital.*, **60**, 798 (1930); (c) K. Bowden, E. A. Braude, and E. R. H. Jones, *J. Chem. Soc.*, 945 (1946); (d) L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3109 (1949); (e) H. Behringer, *Ann.*, **564**, 219 (1949); (f) B. R. Baker and M. V. Querry, *J. Org. Chem.*, **15**, 417 (1950); (g) B. Weibull, *Arkiv Kemi*, **3**, 225 (1951); (h) C. S. Marvel and H. Wexler, *J. Am. Chem. Soc.*, **75**, 6318 (1953); (i) H. Fiesselmann and P. Schipprak, *Ber.*, **89**, 1897 (1956).

[3] (a) W. H. Carothers, *J. Am. Chem. Soc.*, **55**, 2008 (1933); (b) E. P. Kohler and H. Potter, *J. Am. Chem. Soc.*, **57**, 1316 (1935); (c) S. D. Jones and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2452 (1938); (d) W. Reppe and F. Nicolai, Ger. Patent **617,543**; *Chem. Abstr.*, **30**, 733 (1936); (e) W. Reppe and F. Nicolai, Ger. Patent **625,660**; *Chem. Abstr.*, **30**, 5595 (1936); (f) W. Reppe and F. Nicolai, U. S. Patent **2,156,005**; *Chem. Abstr.*, **33**, 5874 (1939); (g) W. Reppe and A. Freytag, Ger. Patent **704,235**; *Chem. Abstr.* **36**, 1958 (1942); (h) N. V. deBataafsche Petroleum Maatschappij, Brit. Patent **532,676**; *Chem. Abstr.*, **36**, 1045 (1942); (i) M. H. M. Arnold, U. S. Patent **2,336,916**; (j) W. E. Vaughn and F. F. Rust, Brit. Patent **581,775**; *Chem. Abstr.*, **41**, 2999 (1947); (k) H. Bader, L. C. Cross, I. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 619 (1949); (l) A. Kh. Khomenko, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 280 (1951); *Chem. Abstr.*, **46**, 884 (1952); (m) L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 817 (1952); (n) W. Franke, K. Weissbach, W. Dietrich, and H. Weber, Ger. Patent **859,307**; *Chem. Abstr.*, **47**, 11220 (1953); (o) E. N. Prilezhaeva and M. F. Shostakovskii, *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik.*, **2**, 54 (1952); *Chem. Abstr.*, **48**, 731 (1954); (p) T Mo, Japan Patent **7667** (1951); *Chem. Abstr.*, **48**, 731 (1954); (q) S. J. Cristol, A. Begoon, W. P. Norr, and P. S. Ramey, *J. Am. Chem. Soc.*, **76**, 4558 (1954); (r) H. Bader, *J. Chem. Soc.*, 116 (1956); (s) M. F. Shostakovskii, E. N. Prilezhaeva, and N. I. Uvarova, *Izvest. Akad. Nauk S.S.S. Otdel. Khim. Nauk*, 906 (1955); *Chem. Abstr.*, **50**, 9278 (1956); (t) K. Yamagishi, Tanaka, and T. Hoshino, *Bull. Chem. Soc. Japan*, **29**, 447 (1956); (u) W. Reppe, *et al., Ann.*, **601**, 111 (1956); (v) W. E. Truce and J. A. Sims, *J. Am. Chem. Soc.*, **78**, 2756 (1956); (w) W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManimie, *J. Am Chem. Soc.*, **78**, 2743 (1956); (x) W. E. Truce and R. F. Heine, *J. Am. Chem. Soc.*, **79**, 1770 (1957).

Further, these additions to acetylenes have, for the most part, involved thiolacetic acid. It was of interest therefore, to study the free-radical addition of ethyl mercaptan to a representative number of acetylenic compounds. Since during the course of this study, it was announced that certain ethylmercapto compounds possessed antitubercular activity,[4] it seemed desirable also to have the ethylmercapto derivatives tested for physiological activity.

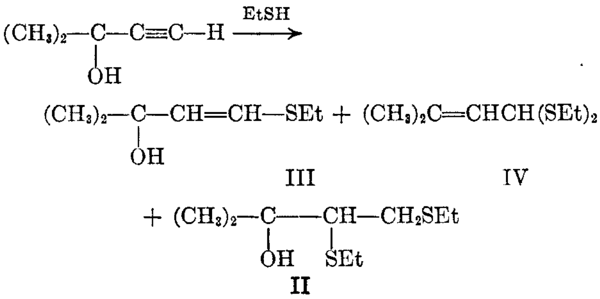
In this study all additions were carried out by irradiating with ultraviolet light for two to four weeks[5] a mixture of one molecular equivalent of the acetylene and two equivalents of ethyl mercaptan containing a catalytic amount of benzoyl peroxide. Products were isolated by direct distillation of the reaction mixtures. Structure of two of the adducts was established by conventional chemical and physical methods. In the remaining cases assignment of structure was made on the basis of analogy and qualitative tests.

The addition of ethyl mercaptan to propargyl alcohol afforded 2,3-bis(ethylmercapto)-1-propanol (I) in 95% yield.[6] This I was identical with I prepared by ethylation of 2,3-dimercapto-1-propanol (BAL). This BAL was prepared by hydrolysis of the mixture of acetates which resulted from the addition of thiolacetic acid to propargyl alcohol. The BAL obtained showed b.p. 86–90° (1 mm.), n_D^{22} 1.5690 and gave a benzylidene derivative which had m.p. 75–77°.

Free-radical addition of ethyl mercaptan to propargyl acetate, 2-butyn-1,4-diol diacetate, and 1-hexyne proceeded smoothly and essentially quantitatively. By analogy to propargyl alcohol the products obtained were 2,3-bis(ethylmercapto)-1-propyl acetate, 2,3-bis(ethylmercapto)-1,4-butanediol diacetate, and 1,2-bis(ethylmercapto)hexane, respectively. All three products were inert toward Brady's reagent.[10] Attempts to oxidize these bissulfides to sulfones gave water soluble products only.

Similarly, ethanedithiol and 2-butyn-1,4-diol diacetate afforded 1,2-bis(acetoxymethyl)1,4-dithiane (43%) and viscous, insoluble polymeric products which were not investigated.

The addition of ethyl mercaptan to 2-methyl-3-butyn-2-ol gave two colorless liquid organic products and water. The higher boiling product failed to respond to Brady's reagent and hence is considered to be 3,4-bis(ethylmercapto-)2-methyl-2-butanol (II). The lower boiling product developed a pinkish color rapidly on standing. It reacted immediately with Brady's reagent to give a red crystalline solid of m.p. 182–183° which proved to be identical with the 2,4-dinitrophenylhydrazone of β-methylcrotonaldehyde. The lower-boiling product thus appeared to be III and/or IV.



$$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}—C{\equiv}C—H \xrightarrow{EtSH}$$

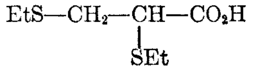
$$\underset{III}{(CH_3)_2—\underset{\displaystyle OH}{\underset{|}{C}}—CH{=}CH—SEt} + \underset{IV}{(CH_3)_2C{=}CHCH(SEt)_2}$$

$$+ \underset{II}{(CH_3)_2—\underset{\displaystyle OH}{\underset{|}{C}}—\underset{\displaystyle SEt}{\underset{|}{CH}}—CH_2SEt}$$

From the addition of ethyl mercaptan to propiolic acid two products were realized: β-ethylmercaptoacrylic acid (V), m.p. 74–75°, and α,β-bis(ethylmercapto)propionic acid (VI), b.p. 128–131° (0.5 mm.). The product V gave the 2,4-dinitrophenylhydrazone of acetaldehyde when treated with Brady's reagent. Its infrared spectrum showed strong absorption at 6.36μ and its ultraviolet spectrum showed λ_{max} 276 mμ, ϵ 6,000. The elemental analysis of VI was not satisfactory. This was probably due to the fact that it was very hygroscopic. VI gave no reaction with Brady's reagent, showed no maximum in the ultraviolet, and its infrared spectrum was void of absorption maxima in the region 6.0–6.7μ.

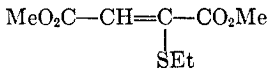
$EtS—CH{=}CH—CO_2H$

V



$$EtS—CH_2—\underset{\displaystyle SEt}{\underset{|}{CH}}—CO_2H$$

VI



$$MeO_2C—CH{=}\underset{\displaystyle SEt}{\underset{|}{C}}—CO_2Me$$

VII

The monoadduct VII was the only product isolated from the addition of ethyl mercaptan to dimethyl acetylenedicarboxylate. Small amounts of higher boiling substances were obtained, but in quantity too small to characterize. VII displayed a strong maximum at 6.30μ in its infrared spectrum and possessed an ultraviolet maximum at λ_{max} 283 mμ, ϵ, 13,720. VII gave a 2,4-dinitrophenylhydrazone derivative, m.p. 173–180°. This derivative was not examined further.

The addition of ethyl mercaptan to phenylacet-

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(4) H. D. Brown, *et al.*, *J. Am. Chem. Soc.*, **76**, 3860 (1954); S. Kushner, *et al.*, *J. Am. Chem. Soc.*, **77**, 1152 (1955).

(5) The volume of the reactants generally became constant after 3 to 6 days which suggested that reaction was complete. As a matter of convenience and in order to insure complete addition, the reactants were irradiated for the periods specified.

(6) Yamagishi[3f] reported that irradiation of a mixture of propargyl alcohol and methyl mercaptan gave 2,3-bis-(methylmercapto)-1-propanol. However, this structural assignment to the product was based on its similarity to a compound prepared by Barbieri[7] which recently has been best described as 1,3-bis(methylmercapto)-2-propanol.[8,9]

(7) A. De Barbieri and S. Tricerri, *Boll. soc. ital. biol. sper.*, **25**, 522 (1949); *Chem. Abstr.*, **44**, 8862 (1950).

(8) F. D. Doyle and J. H. C. Naylor, *Chemistry & Industry*, 714 (1955).

(9) N. S. Johary and L. N. Owen, *J. Chem. Soc.*, 1302 (1955).

(10) O. L. Brady, *J. Chem. Soc.*, 756 (1931).

ylene proved to be different from the other additions studied since phenylacetaldehyde diethyl mercaptal (VIII) was obtained. VIII was identified by its conversion to the 2,4-dinitrophenylhydrazone of phenylacetaldehyde, by oxidation to a sulfone derivative and finally by comparison with an authentic sample of VIII prepared directly from phenylacetaldehyde and ethyl mercaptan. The formation of a stable benzyl free radical intermediate, as pictured below, apparently controls the path of addition in this instance.[11]

$$C_6H_5—C\equiv C—H \longrightarrow C_6H_5—CH{=}CH—SEt \longrightarrow C_6H_5—\dot{C}H—CH(SEt)$$

$$\longrightarrow \underset{\text{VIII}}{C_6H_5—CH_2—CH(SEt)_2}$$

Several of these compounds were tested *in vivo* against experimental *M-tuberculosis* (My 5) infection in mice. None of the compounds prolonged significantly the survival time of the treated mice.[12]

EXPERIMENTAL[13]

2,3-Dimercapto-1-propanol (*BAL*). A solution of 20 g. (0.357 mole) of propargyl alcohol, 60 g. (0.789 mole) of thiolacetic acid, and 0.1 g. of benzoyl peroxide was irradiated in a sealed Pyrex tube for one month. The reaction mixture was dissolved in ether and washed with aqueous sodium carbonate solution. Distillation afforded 30.5 g. of an orange liquid; b.p. 102–117° (0.6 mm), n_D^{25} 1.5147–1.5161, λ_{max} 230–233 mμ, ϵ, 6,100 [reported for the diacetate of BAL;[14] b.p. 60° (0.1 mm.), n_D^{20} 1.5198, λ_{max} 230 mμ, ϵ, 7,800]. The infrared spectrum of this product showed weak hydroxyl and mercaptan absorption which suggested that it comprised a mixture of diacetates and possibly triacetate.

Hydrolysis of 25 g. of the above acetate mixture with 2.5 ml. of concentrated hydrochloric acid in 150 ml. of methanol gave 9.2 g. of colorless BAL; b.p. 86–90° (1.0 mm., nitrogen atmosphere), n_D^{22} 1.5690. Lit. b.p. 71–75° (1 mm.), n_D^{15} 1.5733;[13] b.p. 60° (0.1 mm.), n_D^{23} 1.5735.[15]

Heating a mixture of 0.5 g. of BAL, 0.45 g. of benzaldehyde, and 2 drops of concentrated hydrochloric acid in benzene gave 0.45 g. (53%) of a white crystalline benzylidene derivative, m.p. 75–77° from hexane (lit. m.p. 79°[15]).

2,3-Bis(ethylmercapto)-1-propanol. (I). (*A*) A solution of 20 g. (0.357 mole) of propargyl alcohol, 53 g. (0.855 mole) of ethyl mercaptan, and 0.1 g. of benzoyl peroxide was irradiated in a Pyrex bomb for two weeks. Distillation afforded 61.6 g. (95%) of a colorless liquid; b.p. 118–120° (3.4 mm.), n_D^{25} 1.5248, d_4^{25} 1.0658.

Anal. Calcd. for $C_7H_{16}OS_2$: C, 46.62; H, 8.94; S, 35.57. Found: C, 46.44; H, 8.89; S, 35.30.

The *α-naphthylurethan* derivative of this alcohol melted at 49.5-51° from benzene-hexane. This melting point was not depressed on admixture with the α-naphthylurethan derivative of authentic 2,3-bis(ethylmercapto)-1-propanol.

Anal. Calcd. for $C_{18}H_{23}O_2NS_2$: C, 61.85; H, 6.63. Found: C, 61.83, 61.90; H, 6.50, 6.62.

(*B*)[16] Ethyl iodide (25 g., 0.22 mole) was added to a well stirred solution of 8.5 g. (0.082 mole) of BAL and 6.0 g. (0.22 mole) of sodium hydroxide in 50 ml. of water. The stirred mixture was heated for one hour and extracted with ether. Distillation of the washed and dried ether extract gave 8.7 g. of colorless liquid I; b.p. 100–103.5° (1 mm.), n_D^{22} 1.5263. The α-naphthylurethan derivative of this I had m.p. 49–51° from ethanol.

Addition of ethyl mercaptan to other acetylenic compounds. The procedure used was similar to that described above for the addition of ethyl mercaptan to propargyl alcohol. (1) *To propargyl acetate.* From 15 g. (0.153 mole) of propargyl acetate, b.p. 121–122.8°, n_D^{20} 1.4169, there was obtained 31.7 g. (93%) of a colorless 2,3-bis(ethylmercapto)-1-propyl acetate; b.p. 100–102° (0.8 mm.), n_D^{25} 1.4978, d_4^{25} 1.0639.

Anal. Calcd. for $C_9H_{18}O_2S_2$: S, 28.84. Found: S, 28.95.

(2) *To 2-butyn-1,4-diol diacetate.* From 42 g. (0.247 mole) of 2-butyn-1,4-diol diacetate there was obtained 67.6 g. (93%) of 2,3-bis(ethylmercapto)-1,4-butanediol diacetate; b.p. 145–146° (1.4 mm.), n_D^{20} 1.4932, d_4^{20} 1.1100.

Anal. Calcd. for $C_{12}H_{22}O_4S_2$: C, 48.96; H, 7.53; S, 21.79. Found: C, 48.57, 48.61; H, 7.50, 7.30; S, 21.90, 21.75.

(3) *To 1-hexyne.* 1-Hexyne (20 g., 0.244 mole) afforded 47.0 g. (94%) of 1,2-bis(ethylmercapto)hexane; b.p. 72–75.5° (0.2 mm.), n_D^{25} 1.4934, d_4^{25} 0.9339.

Anal. Calcd. for $C_{10}H_{22}S_2$: C, 58.18; H, 10.75. Found: C, 57.97, 58.12; H, 10.84, 10.68.

(4) *To 2-methyl-3-butyn-2-ol.* Irradiation of a solution of 32 g. (0.516 mole) of ethyl mercaptan, 20 g. (0.238 mole) of 2-methyl-3-butyn-2-ol, and 0.15 g. of benzoyl peroxide gave 1.3 g. of an aqueous layer. Distillation of the organic layer gave two fractions: (*a*) 21.10 g. of a colorless liquid which rapidly turned pink on standing, b.p. 66–87° (0.3 mm.), n_D^{25} 1.5146–1.5115; and (*b*) 17.8 g. of colorless II, b.p. 87–89° (0.3 mm.), n_D^{25} 1.5080, d_4^{25} 1.0196. Fraction (*b*), the alcohol II, was analyzed.

Anal. Calcd. for $C_9H_{20}OS_2$: C, 51.87; H, 9.57. Found: C, 51.57; H, 9.92.

Fraction (*a*) gave an immediate precipitate with Brady's reagent. Recrystallized from ethanol–ethyl acetate the resulting red solid showed m.p. 182–183° (reported[17] for the 2,4-dinitrophenylhydrazone derivative of β-methylcrotonaldehyde, m.p. 182–183°). A precipitate was not obtained from fraction (*b*) after 24 hr. of heating with Brady's reagent.

(5) *To propiolic acid.* Irradiation of 10 g. (0.143 mole) of propiolic acid with ethyl mercaptan gave the following two fractions on distillation: (*a*) 5.7 g., b.p. 107–125° (0.5 mm.), n_D^{25} 1.5208 and (*b*) 12.04 g., b.p. 128–131° (0.5 mm.), n_D^{25} 1.5222–1.5229.

A pentane solution of fraction (*a*) deposited solid V which after several recrystallizations from pentane had m.p. 74–75°.

Anal. Calcd. for $C_5H_8O_2S$: C, 45.43; H, 6.10. Found: C, 45.92; H, 6.10.

On warming V overnight with Brady's reagent a yellow solid of m.p. 140.5–144° was obtained. Recrystallization from ethanol raised the m.p. to 145–147°. No depression in melting point was observed on admixture of this derivative with an authentic sample of the 2,4-dinitrophenylhydrazone derivative of acetaldehyde.

Anal. Calcd. for $C_8H_8N_4O_4$: C, 42.86; H, 3.60. Found: C, 42.84, 43.11; H, 3.60, 3.71.

Careful distillation of fraction (*b*) gave a sample of VI uncontaminated with V as shown by the absence of an ultraviolet maximum and the absence of a peak at 6.36μ in its infrared spectrum. VI showed b.p. 133–134° (0.65 mm.), n_D^{25} 1.5217, d_4^{25} 1.1356. No reaction was noted when VI was treated with Brady's reagent.

(6) *To dimethyl acetylenedicarboxylate.* From 20 g. (0.14 mole) of dimethyl acetylenedicarboxylate there was obtained 26.4 g. of a yellow liquid, b.p. 96–120° (1.0–2.0 mm.), n_D^{20} 1.5097–1.5038. A similar result was observed when dimethyl acetylenedicarboxylate was heated at 140° with

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(11) F. G. Bordwell, R. D. Chapman, and W. H. McKellin, *J. Am. Chem. Soc.*, **76** 3637 (1954).

(12) The tests were made at the laboratories of the Wm. S. Merrell Co.

(13) All melting points and boiling points are uncorrected.

(14) H. R. Ing, *J. Chem. Soc.*, 1393 (1948).

(15) L. A. Stocken, *J. Chem. Soc.*, 592 (1947).

(16) For related alkylations of BAL see refs. 8 and 9.

(17) M. Julia, *Ann. chim.* (*Paris*), **5**, 618 (1950)

ethyl mercaptan and benzoyl peroxide. A redistilled sample of this adduct (VII) showed b.p. 107–109° (1.0 mm.) n_D^{25} 1.5132, d_4^{25} 1.1747, λ_{max} 283 mμ, ε 13,720, and a strong infrared band at 6.30μ.

Anal. Calcd. for $C_{18}H_{12}O_4S$: C, 47.04; H, 5.92; S, 15.70. Found: C, 46.67; H, 6.08; S, 16.12.

On standing with Brady's reagent VII gave a crystalline derivative which had m.p. 173–180°.

(7) *To phenylacetylene.* From 20 g. (0.484 mole) of phenylacetylene there was obtained 39.3 g. (93%) of colorless VIII; b.p. 114–116° (0.75 mm.), n_D^{25} 1.5604, d_4^{25} 1.0419. The ultraviolet spectrum showed only shoulders at λ 260, 268, and 269.5 mμ, ε, 380, 238, and 230, respectively. The infrared spectrum of this VIII was identical with that of an authentic sample of phenylacetaldehyde diethyl mercaptal;[18] b.p. 124–126° (1.0 mm.), n_D^{25} 1.5601.

Anal. Calcd. for $C_{12}H_{18}S_2$: S, 28.33. Found: S, 28.09.

Heating the above adduct VIII for an hour with Brady's reagent afforded a yellow solid, m.p. 117–119°, which did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of phenylacetaldehyde.

Oxidation of 1 g. of the adduct VIII with 2 ml. of 30% hydrogen peroxide in 7 ml. of glacial acetic acid gave 1.1 g. of a crystalline sulfone which melted at 133–134° after recrystallization from benzene. Lit. m.p. 133–135°.[19]

Anal. Calcd. for $C_{12}H_{18}O_4S$: C, 49.63; H. 6.24. Found: C, 50.02; H, 5.94.

Addition of ethanedithiol to 2-butyn-1,4-diol diacetate.[20] An exothermic reaction occurred on adding 0.25 g. of benzoyl peroxide to a solution of 50 g. (0.294 mole) of 2-butyn-1,4-diol diacetate and 28 g. (0.298 mole) of ethanedithiol. The reactants were then irradiated for 4 days. Distillation gave 21.2 g. of unreacted diacetate, b.p. 91–94° (1.2 mm.), and 20.0 g. of 1,2-bis(acetoxymethyl)-1,4-dithiane, b.p. 156–161° (1.0 mm.). The still residue was an extremely viscous oil and proved to be insoluble in benzene and in ethanol.

A redistilled portion of the dithiane showed b.p. 156° (1.0 mm.), n_D^{20} 1.5252.

Anal. Calcd. for $C_{10}H_{16}O_4S_2$: C, 45.34; H, 6.10; S, 24.26. Found: C, 45.15; H, 6.00; S, 23.97.

ITHACA, N. Y.

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[18] M. L. Wolfrom and J. V. Karabinos, *J. Am. Chem. Soc.*, 66, 909 (1944).

[19] M. W. Cronyn, *J. Am. Chem. Soc.*, 74, 1225 (1952).

[20] A quartz flask was used in this experiment.

[CONTRIBUTION NO. 229 FROM THE GOODYEAR TIRE AND RUBBER RESEARCH LABORATORY]

Syntheses and Ultraviolet Absorption Spectra of Certain Sulfur-Containing Derivatives of Naphthalene

ARTHUR H. WEINSTEIN AND ROBERT M. PIERSON

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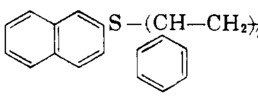
Certain mercaptans, sulfides and disulfides of naphthalene, such as the 1- and 2-thionaphthols, their respective disulfides and mixed phenyl sulfides, as well as 2-naphthyl benzyl sulfide, 1-naphthyl allyl sulfide, the 1- and 2-naphthyl methanethiols, 2-naphthylmethyl benzyl sulfide, and 1-(α-naphthyl)-2-methylpropanethiol-2 were either synthesized or purified, and their ultraviolet absorption spectra recorded and correlated. Syntheses for 2-naphthylmethyl β-hydroxyethyl sulfide, and 1,5-bis(β-naphthylmethylthio)pentane are also described.

The ultraviolet absorption spectra of various sulfur-containing naphthalene derivatives were required for a study of the number and type of sulfur linkages to be obtained from polybutadiene and polystyrene polymers prepared in polymerization systems containing either a naphthalene-substituted mercaptan or a dinaphthyl disulfide as a polymerization modifier. The use of such modifiers in these polymerization systems would provide these polymers with naphthalene-chromophore-tagged chain ends, making possile: (*1*) corroboration of the theory of the mode of interaction of polymerization systems with mercaptans and disulfides, and (*2*) a correlation of polymer molecular weight with macrostructure for polymers so prepared. Earlier work on this subject, dealing with the determination of the number of naphthalene-containing chain ends incorporated into bulk polymerized polystyrenes, has involved systems containing either 1-naphthyl methanethiol or di-2-naphthyl disulfide.[1] The syntheses, methods of purification, and ultraviolet absorption spectra of the aforementioned mercaptan and disulfide as well as a similar characterization of such other naphthalene-containing mercaptans and disulfides as 2-thionaphthol, 2-naphthyl methanethiol, di-1-naphthyl disulfide, and 1-(α-naphthyl) 2-methyl-propanethiol-2 are described in this paper.

In addition, the methods of preparation and ultraviolet absorption spectra of certain model sulfides of naphthalene, which are closely related in structure to the naphthalene-containing polymer chain ends formed when the aforementioned naphthalene-containing thiols and disulfides are used in butadiene or styrene polymerization systems, are also reported. For example, 2-naphthyl benzyl sulfide, structurally related to the terminal groups formed by modification of a styrene polymerization system by 2-thionaphthol or its disulfide, *i.e.*



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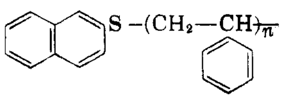

1-naphthyl allyl sulfide, related to a possible terminal group formed by modification of butadiene

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[1] R. M. Pierson, A. J. Costanza, and A. H. Weinstein, *J. Polymer Sci.*, 17, 221 (1955).