

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 $m\mu$, ϵ 13,720, and a strong infrared band at 6.30 μ .

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 $m\mu$, 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 $C_{12}H_{16}S_2$: 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.

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

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 $C_{12}H_{16}O_4S$: C, 49.63; H, 6.24. Found: C, 50.02; H, 5.94.

*Addition of ethanedithiol to 2-butyne-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-butyne-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^{25} 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.

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(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

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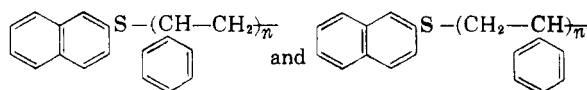
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Certain mercaptans, sulfides and disulfides of naphthalene, such as the 1- and 2-thionaphthols, their respective disulfides and mixed phenyl sulfides, as well as 2-naphthyl benzyl sulfide, 1-naphthyl allyl sulfide, the 1- and 2-naphthyl methanethiols, 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 possible: (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

forementioned 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-methylpropanethiol-2 are described in this paper.

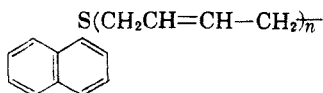
In addition, the methods of preparation and ultraviolet absorption spectra of certain model sulfides of naphthalene, which are closely related in structure to the naphthalene-containing polymer chain ends formed when the aforementioned naphthalene-containing thiols and disulfides are used in butadiene 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.*



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

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

polymerization by 1-thionaphthol or its disulfide, *i.e.*



(neglecting possible terminal groups formed as a result of 1,2 polymerization), as well as 1-naphthylmethyl benzyl sulfide, related similarly to the terminal groups formed by modification of styrene polymerization by 1-naphthyl-methanethiol, and the 1- and 2-naphthyl phenyl sulfides are so characterized herein.

The syntheses of 2-naphthylmethyl β -hydroxyethyl sulfide and 1,5-bis-(β -naphthylmethylthio)-*n*-pentane are also described.

Ultraviolet Absorption Spectra. It will be observed that two families of ultraviolet absorption curves are represented in Figs. 1 and 2. The curves shown in Fig. 1, which represent a family of sulfur derivatives of naphthalene in which the sulfur atom is separated from the naphthalene chromophore by

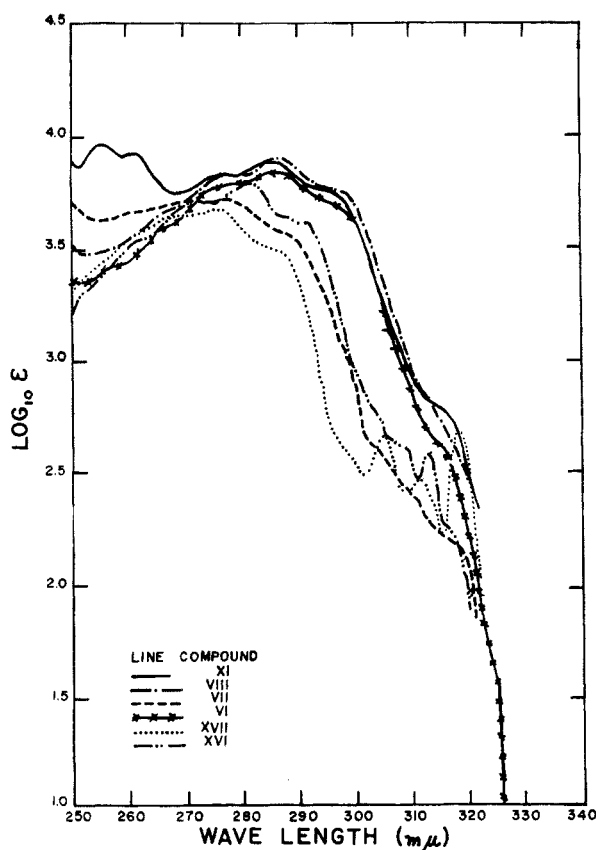


Fig. 1. Ultraviolet absorption spectra of alkylnaphthalene derivatives with sulfur-containing functions substituted on the side chain. The curves of the following compounds were obtained from chloroform solutions: 1-(α -naphthyl)-2-methyl-propanethiol-2 (XI); 1-naphthylmethyl benzyl sulfide (VIII); 2-naphthyl-methanethiol (VII); 1-naphthyl-methanethiol (VI). The curves for 1-methylnaphthalene (XVI), and 2-methylnaphthalene (XVII), which were obtained from 95% aqueous ethanol, were reproduced from the Friedel and Orchin compendium^{2a,b}

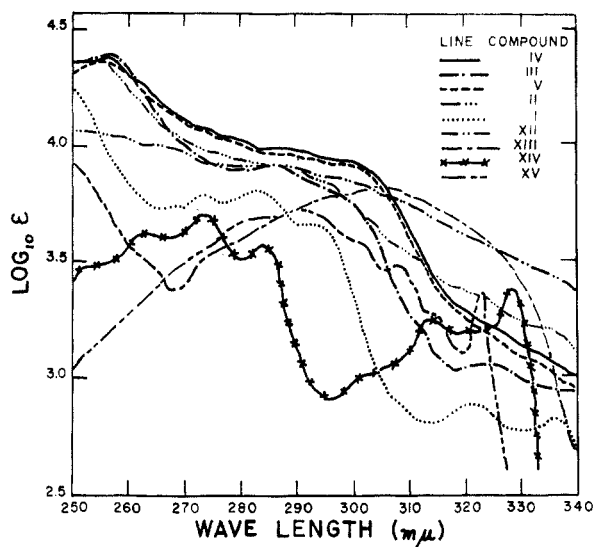


Fig. 2. Ultraviolet absorption spectra of naphthylthio-containing compounds. The curves of the following compounds were obtained from chloroform solutions: 1-naphthyl phenyl sulfide (IV); benzyl 2-naphthyl sulfide (III); 2-naphthyl phenyl sulfide (V); di-2-naphthyl disulfide (II), 2-thionaphthol (I); di-1-naphthyl disulfide (XII); 1-naphthyl allyl sulfide (XIII). The curves for 1-naphthol (XV), and 2-naphthol (XIV) which were reproduced from the compendium by Friedel and Orchin,^{2c,d} were obtained from cyclohexane solutions. The ordinate for the curves of di-1- and di-2-naphthyl disulfide is $\log_{10} (\epsilon/2)$ whereas those of all other curves is $\log_{10} \epsilon$, where ϵ is the molar extinction coefficient

at least one carbon atom, resemble the ultraviolet absorption spectra of the alkylnaphthalenes to which they are related. The curve for 2-naphthylmethane thiol (VII) bears a strong resemblance to that of 2-methylnaphthalene (XVII),^{2a} the presence of the thiol group in the former compound contributing a slight bathochromic effect and general enhancement of molar extinction with respect to the spectrum of the hydrocarbon. In the same manner, the small family of closely related curves represented by 1-naphthyl methanethiol (VI), and its carbon- and sulfur-substituted derivatives, 1-(α -naphthyl)-2-methyl-propanethiol-2 (XI), and 1-naphthylmethyl benzyl sulfide (VIII), bear the same relationship to the curve of 1-methylnaphthalene (XVI).^{2b} On the other hand, Fig. 2 represents a family of ultraviolet absorption curves containing sulfur derivatives of naphthalene in which the sulfur atom is adjacent to the naphthalene chromophore (thus containing either 1- or 2-naphthylthio- units).

It will be observed that the simplest member of this series, 2-thionaphthol (I), has a spectrum resembling that of 2-naphthol (XIV),^{2c} but with the peaks typical of the naphthalene chromophore

(2) The following ultraviolet absorption spectra are reprinted with permission from Friedel and Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, 1951: a. Spectrum No. 197; b. Spectrum No. 196; c. Spectrum No. 237; d. Spectrum No. 236; e. Spectrum No. 268.

shifted even more bathochromically by the thiol auxochrome than the naphthalene chromophore is by a 2-hydroxy function (with a thiol peak value of λ_{\max} 283 $m\mu$, $\log \epsilon$ 3.81, as compared with λ_{\max} 273 $m\mu$, $\log \epsilon = 3.70$ for that of 2-naphthol). It will be observed that the curve of 2-thionaphthol (I), unlike that of the corresponding naphthol XIV, rises in absorbance with decreasing wave length between 265 $m\mu$ and 250 $m\mu$. In this respect the spectrogram of 2-thionaphthol resembles that of other members of the family of curves containing naphthylthio groups. The other compounds represented in Fig. 2 either have a similar rise in absorbance in this region, i.e. di-1 and di-2-naphthyl disulfides and 1-naphthyl allyl sulfide, or have peaks at $\log \epsilon$ 4.37–4.40 in the region of 255–257 $m\mu$, i.e. 1- and 2-naphthyl phenyl sulfides (IV and V), and 2-naphthyl benzyl sulfide (III). The latter series of peaks may be representative of a sulfur-benzene conjugative band which may be related to the peak found by Koch³ in cyclohexyl phenyl sulfide at λ_{\max} 257.5 $m\mu$, $\log \epsilon = 3.7$. (Note that 2-naphthyl benzyl sulfide has an insulating methylene group between the benzene ring and the sulfur atom.)

Although Koch found a similar band at λ_{\max} 250 $m\mu$, $\log \epsilon$ 4.07 in diphenyl sulfide, he did not attribute it to the same sulfur-benzene conjugative band found in this region in cyclohexyl phenyl sulfide but rather to a quasi-conjugation between aromatic rings and the $3p$ orbital of the sulfur atom. Koch did find a peak at λ_{\max} 274 $m\mu$, $\log \epsilon$ 3.76 in diphenyl sulfide which, partly on the basis of the correspondence of its peak value with that of the 257.5 $m\mu$ band of the cyclohexyl phenyl sulfide, he attributed to this sulfur-benzene conjugative band.

It will be observed that in the whole family of naphthyl thio-containing compounds, there may be found either a series of inflections followed by a shoulder, or a series of distinct peaks in the region from 270 $m\mu$ to 310 $m\mu$. These are undoubtedly related to the series of peaks found in naphthalene between 260–290 $m\mu$. The general shape of the curves for 1-naphthyl and 2-naphthyl phenyl sulfides (IV and V), 2-naphthyl benzyl sulfide (III), and di-2-naphthyl disulfide (II) is very similar to that illustrated by Koch for diphenyl disulfide which has a peak at λ_{\max} 238, $\log \epsilon$ 4.2 and inflections near 270 $m\mu$ and 300 $m\mu$. The fact that the molar extinction value of the corresponding thiol (as indicated in Fig. 2 where the absorbancy for the disulfide, whose ordinate is plotted as $\log (\epsilon/2)$ is a little greater than that of the thiol, whose ordinate is plotted as $\log \epsilon$) does tend to affirm: 1. the idea of a contribution to the resonance of the diaryl disulfide molecule through the two sulfur atoms (as proposed by Koch for the diphenyl disulfide system as caused by alternately charged resonating phenylthio chromophores) and 2. the general additive nature of the ultraviolet absorption of the

two naphthylthio chromophore units in the disulfide molecule.

The presence of a peak in 2-naphthyl benzyl sulfide (III) at λ_{\max} 286 $m\mu$, $\log \epsilon$ 3.92, bears a similar relationship to the one present in 2-naphthol (XIV) at λ_{\max} 273 $m\mu$, $\log \epsilon$ 3.70, as the peak in 1-naphthyl allyl sulfide (XIII) at λ_{\max} 303–304 $m\mu$, $\log \epsilon$ 3.82, bears to the one in 1-naphthol (XIV)^{2d} at λ_{\max} 290 $m\mu$, $\log \epsilon$ 3.71.

Syntheses. The known mixed aryl sulfides,^{4,5} 1- and 2-naphthyl phenyl sulfides (IV and V) were both obtained, surprisingly enough, from the reaction mixture of the sodium salt of 2-thionaphthol (a technical grade product) with iodobenzene in presence of copper powder, along with diphenyl disulfide and mixed di-naphthyl disulfides. Since the presence of 1-thionaphthol could not be detected in the 2-thionaphthol reagent used, it appears that presence of 1-naphthyl phenyl sulfide in the reaction product was the result of a rearrangement.⁶

The 1- and 2-naphthyl methanethiols (VI and VII) were obtained in standard fashion by treatment of 1-chloromethylnaphthalene and 2-bromomethylnaphthalene with thiourea followed by subsequent basic hydrolysis of the thiuronium salts. Compound VI, which has been prepared previously,⁷ is an oil, whereas the analogous new 2-naphthyl compound, VII, is a crystalline solid.

The new compounds 1-naphthyl allyl sulfide (XIII), 1-naphthylmethyl benzyl sulfide (VII), and 2-naphthylmethyl β -hydroxyethyl sulfide (IX) were prepared by treatment of the alkali metal salts of the respective thionaphthol and naphthylmethanethiols with suitable alkyl, aralkyl or hydroxyalkyl halides in a manner similar to that used for the preparation of 2-naphthyl benzyl sulfide (III), a known compound,^{8a,b} from 2-thionaphthol.

The bismonosulfide, 1,5-bis(β -naphthylmethylthio)-*n*-pentane (X), was synthesized by treatment

(4) E. Bourgeois, *Ber.*, **28**, 2327 (1895).

(5) F. Krafft and E. Bourgeois, *Ber.*, **23**, 3045 (1890).

(6) It is possible that both β -naphthyl and β -naphthylmercaptyl radicals, as well as phenyl and phenylmercaptyl radicals were formed in the reaction mixture by thermal cleavage at 220°. Under such circumstances α -naphthyl phenyl sulfide could be formed by recombination of either a β -naphthyl or β -naphthylmercaptyl radical which had rearranged to the α -form, with the appropriate benzenoid radical. This explanation would account for the presence of diphenyl disulfide as well as a mixture of di-naphthyl sulfides in the reaction product. It is to be noted that lead aryl mercaptides are known to decompose when heated to form lead sulfide and di-aryl sulfides.

(7) This mercaptan has been prepared previously by W. Windus and H. G. Turley, *J. Am. Leather Chem. Assn.*, **33**, 246 (1938), *cf. Chem. Abstr.*, **32**, 8821 (1938), as an oil, b.p. 165–175°/16 mm., by treating the corresponding carbinol with potassium hydrosulfide.

(8) a. H. Rheinboldt, F. Berti, M. Perrier, W. Pregnolato, G. Cilento, and G. Nazario, *Univ. São Paulo, Fac. filosof., ciênc. e letras, Quim. No. 3 Bol. No. 129*, **8** (1951); *cf. Chem. Abstr.*, **46**, 7554 (1952); b. D. S. Tarbell and D. P. Harnish, *J. Am. Chem. Soc.*, **74**, 1862 (1952).

(3) H. P. Koch, *J. Chem. Soc.*, 387, 394 (1949).

of disodium pentamethylene dimercaptide with 2-bromomethyl-naphthalene.

The tertiary mercaptan 1-(α -naphthyl) 2-methyl-propanethiol-2 (XI) was prepared by hydrosulfurating 1-methallyl-naphthalene.

EXPERIMENTAL⁹

Absorption Spectra. The ultraviolet absorption spectra of di-1-naphthyl disulfide, 1-naphthyl allyl sulfide, and 1-(α -naphthyl)-2-methyl-propanethiol-2 were determined with a Cary Recording Spectrophotometer, Model 11. All other ultraviolet absorption spectra shown, other than those reproduced from Friedel and Orchin's compendium,² were determined with a Model DU Beckman quartz spectrophotometer. The solvent used for all samples and blanks was chloroform (Baker and Adamson tech. grade).

2-Thionaphthol (I). Du Pont's commercial product, pre-extracted with hot methanol, was treated with aqueous potassium hydroxide. By adding mineral acid to the alkaline extract, the thiol was reprecipitated. The collected, washed, dried precipitate was recrystallized twice from absolute ethanol to m.p. 81.8–82.4° (reported m.p. 81°¹⁰). The ultraviolet absorption spectrum obtained from this sample was very similar to that published for this compound by Friedel and Orchin.^{2e}

Di-2-naphthyl disulfide (II). A solution of 64.0 g. of I (E. I. du Pont commercial grade β -thionaphthol) in 260 ml. of hot ethanol was filtered through a medium porosity sintered glass funnel and the residue discarded. To the filtrate, in a 3 neck 3 l. flask equipped with heating mantle, mechanical stirrer, and reflux condenser, was added 50.4 g. of iodine, in a slurry in 800 ml. methanol with stirring. The mixture was refluxed for 1 hr., and the disulfide precipitate was washed with 3 portions of 95% aqueous alcohol, then with water, and oven dried. The crude white disulfide product, weighing 51.5 g. (80.5%) having m.p. 140.5–141.5°, was recrystallized twice from benzene and once from chloroform to form yellow-white flakes of m.p. 141.8–142.6° (reported m.p. is 139°¹¹).

2-Naphthyl benzyl sulfide (III). Although this compound was prepared twice in recent years^{8a,b} by treatment of an alkaline solution of I with benzyl chloride, details of these preparations were not given. Therefore, our preparation of III is described as follows: To a refluxing solution of potassium 2-naphthyl mercaptide (0.086 mole) in aqueous ethanol (prepared from 13.9 g. I, 5.8 g. potassium hydroxide pellets, 400 ml. abs. ethanol, and 20 ml. water), was added, dropwise, a solution of 12.7 g. benzyl chloride (0.10 mole) in 50 ml. ethanol. After 2 hr. at reflux, the system was cooled and diluted with several volumes of water, thus precipitating the crude sulfide product. Unreacted thiol was removed from the product by extracting with hot 10% aqueous potassium hydroxide. The residual sulfide, an oil which solidified upon cooling to 0°, was washed with water and recrystallized from abs. ethanol, forming 10.6 g. of fine white crystals, m.p. 87.4–89.9 (49%), which melted at 89.8–90.5° when recrystallized again from this solvent. Analytical data for this compound are to be found in Table I.

Compounds 1-naphthylmethyl benzyl sulfide (VI), 2-naphthylmethyl β -hydroxyethyl sulfide (IX), 1,5-bis-(β -naphthylmethylthio)-n-pentane (X), and 1-naphthyl allyl sulfide (XIII) were prepared by the same general procedure as that used to prepare III. Pertinent data relating to these preparations may be found in Table I.

(9) All melting points are corrected. Element analyses were done by Messrs. William C. Hukari and Wellman W. Dietz of this laboratory.

(10) F. Krafft and R. Schönherr, *Ber.*, **22**, 824 (1889).

(11) P. T. Cleve., *Ber.*, **21**, 1100 (1888).

1- and 2-Naphthyl phenyl sulfides (IV and V). To 25.0 g. (0.137 mole) of sodium 2-naphthyl mercaptide (prepared by concentrating an alkaline extract obtained from Du Pont commercial grade β -thionaphthol) was added 8.4 g. of iodobenzene, and 1.0 g. of copper powder. After refluxing the system at 188° for 3 hr., the mixture was cooled, diluted with benzene, and filtered. After distilling benzene and iodobenzene from the filtrate *in vacuo*, the residual 24.7 g. of semisolid sulfides was fractionally distilled. The following fractions were obtained:

1. 0.5 g. orange oil, b.p. 125–137°/0.25 mm. (diphenyl disulfide).

2. 12.4 g. yellow oil, b.p. 144–156°/0.25 mm., m.p. 47.5–50°.

3. 5.0 g. yellow oil, b.p. 154–165°/0.25 mm., m.p. 38–41°.

4. 3.6 g. amber oil, b.p. 170–223°/0.25 mm. (dinaphthyl sulfides).

5. 2.0 g. black, greasy, solid residue.

By recrystallizing fraction 2 twice from absolute ethanol, 5.7 g. of 2-naphthyl phenyl sulfide (V), m.p. 50.7–51.7°, (17.6%) was obtained. The product melted at 51.2–52.2° (reported m.p. 51.8°⁴) after a third recrystallization. Recrystallization of fraction 3 from 93% aqueous ethanol yielded 3.3 g. of 1-naphthyl phenyl sulfide (IV), m.p. 39.0–40.5° (11.7%). The product melted at 40.0–41.0° (reported m.p. 41.8°⁵) after another recrystallization.

Analysis of crude β -thionaphthol. By extracting 10.0 g. of crude β -thionaphthol with several 100 ml.-portions of chloroform, and removing solvent from the extract, 7.4 g. of thiol, m.p. 73–77° (compared with m.p. 81.8–82.4° for pure II) was obtained. The chloroform insoluble residue was primarily a metallic powder which could be decomposed with mineral acid.

By treating 4.00 g. (0.0250 mole) of the extracted thiol in alcohol solution containing an equivalent of aqueous sodium hydroxide with an alcohol solution of 5.06 g. (0.0250 mole) of 2,4-dinitrochlorobenzene by the method of Bost *et al.*,¹² 6.57 g. (80%) of crude dinitrophenyl sulfide, m.p. 120–130°, was isolated. Careful repeated fractional recrystallization of the product from hot 2:1 ethanol/benzene solution yielded 5.21 g. of the 2,4-dinitrophenyl sulfide of β -thionaphthol (XIV), a golden yellow solid, m.p. 149–150°, (reported m.p. of 145°^{12b}), 0.33 g. of di- β -naphthyl disulfide, m.p. 141.5–142.5° (which did not depress the m.p. of authentic II, but did depress the m.p. of XIV) and about one gram of a solid of m.p. 103–135°, believed to be a mixture of II and XIV. No trace of the α -2,4-dinitrophenyl sulfide (known to melt at 176°^{12b}) could be found.

1-Naphthyl-methanethiol (VI). This compound was prepared by converting 1-chloromethyl-naphthalene (obtained by chloromethylating naphthalene¹³) to the corresponding thiol by the method of Urquhart *et al.*¹⁴

To 19.4 g. (0.110 mole) of 1-chloromethylnaphthalene, b.p. 122–124°/1.8 mm., was added 8.4 g. (0.11 mole) of thiourea, and 60 ml. of 98% aqueous ethanol. After refluxing the mixture for 7 hr., it was treated with a solution of 6.8 g. of sodium hydroxide, and refluxed for another 2 hr. Most ethanol was removed by distilling *in vacuo*. The residue was acidified with mineral acid, treated with brine solution, and extracted with benzene. The benzene extract was washed, dried, and the benzene removed by distillation *in vacuo*. The residual 17.5 g. of yellow oil (consisting of desired mercaptan of 91.2% purity on basis of an amperometric titra-

(12) a. R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932); b. R. W. Bost, J. O. Turner, and M. W. Conn, *J. Am. Chem. Soc.*, **55**, 4956 (1933).

(13) A. Cambron, *Can. J. Research*, **17B**, 10 (1939); *cf. Org. Reactions*, **I**, 70 (1942).

(14) G. G. Urquhart, J. W. Gates, Jr., and R. Connor, *Org. Syntheses*, **21**, 36 (1941).

TABLE I
PREPARATION OF MIXED NAPHTHALENE-CONTAINING SULFIDES

Sulfide	Formula	M.P. ^a , °C.	Recryst. Solvent	Crude Yield, ^b %	Reactants		Carbon, %		Hydrogen, %		Sulfur, %	
					Thiol	Halide	Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Naphthyl benzyl (III)	C ₁₆ H ₁₄ S	89.8-90.5 ^c	Abs. EtOH	49	2-Naphthalene	Benzyl chloride	81.58	81.25	5.64	5.78	12.81	12.67
1-Naphthyl phenyl (IV) ^d	C ₁₆ H ₁₂ S	39.0-40.5	95% EtOH	12	2-Naphthalene	Iodobenzene	81.34	80.88	5.12	5.08	13.56	13.98
2-Naphthyl phenyl (V) ^d	C ₁₆ H ₁₂ S	50.7-51.7	Abs. EtOH	18	2-Naphthalene	Iodobenzene	81.34	81.35	5.12	5.07	13.56	13.85
1-Naphthylmethyl benzyl (VIII)	C ₁₈ H ₁₆ S	57.0-57.3	95% EtOH	85	1-Naphthyl- methane	Benzyl chloride	81.77	81.55	6.10	5.73	12.12	12.08
2-Naphthylmethyl β-hydroxyethyl (IX)	C ₁₈ H ₁₄ OS	52.0-53.5 ^e	65% EtOH	100	2-Naphthyl- methane	Ethylene chloro- hydrin	72.76	71.65	6.18	6.38	14.04	14.45
Bis(β-naphthylmethyl) pentamethylene (X)	C ₂₇ H ₂₀ S ₂	97.6-98.6	CHCl ₃ / <i>n</i> - C ₆ H ₁₄	34	Pentamethyl- ene di- ^g	2-Bromomethyl- naphthalene	77.84	77.50	6.77	6.87	15.39	15.13
1-Naphthyl allyl (XIII)	C ₁₃ H ₁₂ S	.	—	78	1-Naphthalene	Allyl bromide	77.93	78.08	6.04	5.79	16.01	15.60

^a Corrected melting points of analytical samples. ^b Yields are based upon products of less than 4° melting range, or in case of XIII, on oil of 95% purity. ^c Reported melting points for III are 90.7°Sa and 88.5-89.0. ^d Compound was separated from reaction product containing its positional isomer (see experimental section). Reported m.p. of IV is 41.8°, that of V is 51.8°. ^e Compound depressed melting point of pure 2-naphthylmethane thiol (VII) of m.p. 47.2-47.7° to 40-50°. ^f Compound was a yellow, fluorescent oil with garlic like odor, with b.p. 153.3-155.3/4.2 mm., *n*_D²⁰ 1.6162. ^g See reference 17 for source.

tion with silver nitrate solution¹⁵) was distilled. In this way, 15.1 g. of colorless oil, b.p. 142.0–143.0°/0.5.0 mm., n_D^{20} 1.6628 (78.6%) was obtained.⁷

Anal. Calcd. for $C_{11}H_{10}S$: C, 75.79; H, 5.78; S, 18.39. Found: C, 75.25, 75.40; H, 5.78, 5.68; S, 17.75, 18.00.

2-Naphthylmethanethiol (VII). Essentially the same procedure was employed for synthesis of VII as that for synthesis of VI. The 2-bromomethyl-naphthalene used in this preparation was synthesized from 2-methylnaphthalene (Matheson, Coleman & Bell pract. grade) by the procedure of Buu-Hoi.¹⁶ A yield of 26.6 g. of crude mercaptan (VII) (79.9%) was obtained in crops of 18.0 g., m.p. 46–49°, and 8.6 g., m.p. 41–43°, by treating 42.2 g. (0.191 mole) of 2-bromomethyl-naphthalene with thiourea and base in the prescribed manner. By reprecipitating the first crop of mercaptan from aqueous-alcoholic alkaline solution with mineral acid, and recrystallizing the precipitate so obtained from absolute ethanol, 9.5 g. of pure thiol, m.p. 47.2–47.7° was obtained.

Anal. Calcd. for $C_{11}H_{10}S$: C, 75.79; H, 5.78; S, 18.39. Found: C, 75.95, 76.20; H, 6.10, 5.93; S, 18.33, 18.08.

1-(α -Naphthyl)-2-methylpropanethiol-2 (XI). This mercaptan was prepared by hydrosulfurating crude 1-methallylnaphthalene. The hydrocarbon was prepared, essentially, by the method used by Bordwell *et al.*¹⁸ to prepare methallylbenzene.

Crude 1-methallylnaphthalene. A Grignard reagent, obtained by interaction of 104 g. of 1-bromonaphthalene (0.500 mole of Eastman Kodak white label product) with 12.2 g. magnesium turnings (Merck Grignard grade) in 500 ml. abs. ether (predried over sodium) under nitrogen atmosphere, was treated, first, with a solution of 50 ml. anhyd. ether and 200 ml. anhyd. benzene (C.P.), then, with an 0.500 mole quantity of β -methallyl chloride (Matheson, Coleman & Bell pract. grade), added, dropwise, over a 0.5 hr. period to the Grignard system on a warm water bath. The system was refluxed for 2 hr., hydrolyzed with 330 ml. of 10% sulfuric acid, and the layers separated. By removing ether, β -methallyl chloride and benzene from the washed, dried, ether layer, 89.4 g. of amber colored oil was obtained. After removal of a 14 g. forecut of naphthalene and 1-bromonaphthalene between b.p. 78–123°/7.5 mm., a 57.9 g. fraction of crude 1-methallylnaphthalene, b.p. 128–132°/6.9 mm., was obtained (63.6%¹⁹). The product was known to contain some 1-bromonaphthalene (which boils at 122–125°/5 mm.) but was used without further purification.

Hydrosulfuration. The crude 1-methallylnaphthalene was placed in the glass liner for a 1 liter stainless steel autoclave and cooled to -78° . To the hydrocarbon was added 10 ml. of a 48% solution of boron trifluoride in ether and 90 g. of liquid hydrogen sulfide. The glass liner (wiped free of frost)

was inserted into the 1-l. steel autoclave, which had been precooled to -78° , and the autoclave sealed. The autoclave was allowed to warm to room temperature, and to stand at this temperature for 88 hrs. The vessel was opened under a hood, the product poured into water, and extracted with ether. By removing ether from the washed, dried ether extract, 60.5 g. of brown oil was obtained. The product, which contained 83.2% of desired mercaptan (on basis of amperometric titration with silver nitrate¹⁵), could not be purified further by formation of the lead mercaptide (a taffy-like yellow semi-solid) and liberation of the mercaptan with mineral acid. By distilling 27.4 g. of crude mercaptan under nitrogen atmosphere, the following fractions were obtained: 1. 8.6 g. of yellow oil, b.p. 152–155°/5.0 mm. (containing mercaptan of 94.5% purity). 2. 10.2 g. of pale yellow fluorescent oil, b.p. 155.7–160.0°/5.0 mm., n_D^{20} 1.6162 (containing mercaptan of 97.1% purity).

Thus, the over-all yield of fairly pure thiol (XI) in two steps from 1-bromonaphthalene is 34.8%.

Fraction 2 was used for determination of ultraviolet absorption spectrum and for element analysis.

Anal. Calcd. for $C_{14}H_{16}S$: C, 77.71; H, 7.45; S, 14.82. Found: C, 77.45, 77.30; H, 7.76, 7.65; S, 14.84, 14.79.

Di-1-naphthyl disulfide (XII). This compound was prepared in two ways. *A. By Leuckart method.* By treating diazotized 1-naphthylamine with potassium ethyl xanthate, and hydrolyzing the resultant xanthate ester with base (following the Tarbell and Fukushima adaptation of the Leuckart method for preparation of *m*-thiocresol²⁰) a 19 g. (48%) quantity of crude brown colored mercaptan oil was obtained. Upon distilling this oil, a total of 5.5 g. of mercaptan, b.p. 131°/4.5 mm., and disulfide, b.p. 165°/3 mm. was obtained. By treating the combined distillate with as much iodine/aqueous potassium dioxide solution as could be decolorized by the oil, extracting the oxidation product with benzene, isolating the product, triturating with hexane, and collecting the crystals, 2.3 g. (5.7%) of yellow-white needles, m.p. 87.1–88.4°, was obtained. By recrystallizing the product from 15 pts. hot *n*-hexane, 1.48 g. of pale yellow needles, m.p. 89.4–89.9°, were obtained. (Compare with needles, m.p. 91°, from pet. ether reported by Leuckart,²¹ and with leaflets, m.p. 85°, from ethanol reported by Schertel²²). This sample was used for ultraviolet absorption spectrum determination.

B. By Grignard method. By converting a 2.00 mole quantity of 1-bromonaphthalene to the Grignard reagent by treatment with a 50% excess of magnesium turnings, in ether solvent, under nitrogen atmosphere, allowing the Grignard to react with two gram atom equivalents of sulfur, hydrolyzing the complex, and isolating the mercaptan in the usual manner,²³ 312 g. of oil, containing a 68:29 ratio of mercaptan to disulfide²⁴ (or a 95.6% yield of naphthylthio units) was obtained. By treating an aliquot portion of the oil mixture with sufficient iodine/potassium iodide solution to oxidize all mercaptan to disulfide, and recrystallizing the

(15) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

(16) Ng. Ph. Buu-Hoi, *Ann.*, **556**, 8 (1944).

(17) This compound was supplied to us by Mr. Max. H. Keck of this laboratory, who prepared it from the dibromide by the thiourea method (see ref. 14) in a manner, similar to that of one of the two methods by which W. P. Hall and E. E. Reid, *J. Am. Chem. Soc.*, **65**, 1466 (1943), prepared this compound. One of the boiling points recorded for this compound by H. and R. is 90.1°/10 mm. These workers also prepared this dithiol by treatment of the dibromide with sodium hydrosulfide.

(18) F. G. Bordwell, C. M. Suter, and A. J. Webber, *J. Am. Chem. Soc.*, **67**, 830 (1945).

(19) H. F. Hipsler and P. H. Wise, *Natl. Advisory Comm. for Aeronaut. Tech. Note No. 2430*, **19** (1951), *cf. Chem. Abstr.*, **46**, 8074 (1952), report preparation of a crude uncharacterized form of this hydrocarbon, in 85% yield, by their own modification of the same general method. They fractionated an undisclosed quantity of crude isomeric 1-(α -naphthyl), 2-methylpropene-1 from this product.

(20) D. S. Tarbell and D. K. Fukushima, *Org. Syntheses, Coll. Vol. III*, 809 (1955).

(21) Leuckart, *J. prakt. Chem.*, [2] **41**, 217 (1890).

(22) A. Schertel, *Ann.*, **132**, 94 (1864).

(23) A method used to prepare a similar mixture by Taboury, *Compt. rend.*, **138**, 982 (1904), who gave no details of the mixture ratio or yield.

(24) As determined by a method developed by Dr. Glen E. Meyer of this laboratory, as reported by G. E. Meyer, R. J. Coleman, and R. M. Pierson, "Behavior of Some Bis-Type Modifiers in Emulsion Butadiene Polymerization," private communication to Office of Synthetic Rubber, FFC 1954, based upon the fact that di-aryl disulfides are cleaved quantitatively by treatment with sodium sulfite, generally to one mole of sodium mercaptide and one mole of Bunte salt, and in special cases to two moles of sodium mercaptide. The mercaptide content is then determined by potentiometric titration with standardized silver nitrate solution.

crude solid disulfide from a 95% aqueous ethanol/*n*-hexane mixture, disulfide was obtained in two crops of 117 g. of yellow-orange crystals, m.p. 87.3–88.3°, (36.8%) and 17.5 g. of very fine pale yellow crystals, m.p. 81–83° (5.3%). The melting point of the higher melting crop was increased to m.p. 89.7–90.6° by recrystallization from 95% aqueous acetic acid. Titrimetric analysis of this product by the sodium sulfite silver nitrate method,²⁴ indicated a purity of 99% of XII.

1-Naphthyl allyl sulfide (XIII). By treating 60.8 g. of 1-thionaphthol (0.380 mole) with equivalent quantities of alcoholic potassium hydroxide and allyl bromide (Halogen Chem. Co.) in much the same manner as that used to prepare III, the crude mixed sulfide was isolated as a golden oil. By distilling this oil, two fractions of desired sulfide were obtained: 1. 26.8 g., b.p. 153.3–155.3°/4.2 mm., and 2. 22.3 g., b.p. 154.3–157.4°/4.2 mm., both distillates being

fluorescent yellow oils (78%) with distinct garlic-like odors. Fraction 1 was used as a sample for both ultraviolet absorption spectrum determination and element analysis.

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AKRON, OHIO

(CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY AND ENZYMOLOGY, FORDHAM UNIVERSITY)

Studies on the Chemistry of Heterocyclics. XXXII.* Preparation and Absorption Spectra of Triarylmethane Dyes Containing a Thiophene or a Thianaphthene Ring

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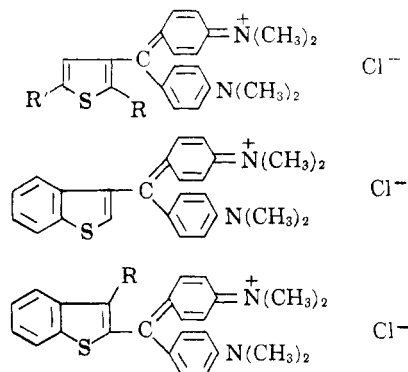
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The preparation of some new thiophene and thianaphthene dyes and their derivatives has been presented and discussed. The absorption spectra of 3-Thianaphthene Malachite Green, 2-Thianaphthene Malachite Green and its derivatives, 3-Thiophene Malachite Green and its derivatives have been determined and compared with the absorption spectra of Malachite Green. An interpretation of the bathochromic effects of the thiophene and thianaphthene rings in triarylmethane dyes has been offered.

It was demonstrated earlier³ that replacement of one of the phenyl rings in Malachite Green by a thiophene ring produces a bathochromic shift of the secondary absorption band. In a continuation of the study of the effect on the absorption spectrum of Malachite Green, of replacing one of the phenyl rings by a heterocyclic ring, a number of dyes containing either a thiophene ring or a thianaphthene ring were prepared and their absorption spectra measured. Furthermore, dyes containing various substituents on the heterocyclic moiety were also prepared to investigate the effects of these substituents.

The dyestuffs studied were those shown in the accompanying formulas.

The general method of preparation consisted of the condensation of the appropriate aldehyde or the substituted aldehyde with two molecules of dimethylaniline using anhydrous zinc chloride as the condensing agent. The oxidation of the leuco compounds so obtained to the dyes was achieved



Where R = H, CH₃, Br or Cl and R' = H, CH₃.

using manganese dioxide and sulfuric acid. The dyes were isolated as their zinc chloride complex salts. The dye bases were prepared by basification of the dye solutions with aqueous sodium hydroxide solution. During the course of purification of the dye bases, a considerable polymerization was encountered. This observation was first made in the case of the dye base of 2-Thiophene Malachite Green.³ It could be avoided to a certain extent by isolating the dye bases immediately upon formation.

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(3) C. D. Mason and F. F. Nord, *J. Org. Chem.*, **16**, 722 (1951).