evaporating the mother liquor the yield was increased. It was readily crystallized from acetone or methyl ethyl ketone. It melted at 138–139° (corr.) and the yield was 30 g. or 60%.

Anal. Calcd. for $C_{13}H_9O_3NSI_2$: I, 49.5. Found: I, 49.7, 49.2.

Summary

1. Some new derivatives of diphenyl sulfide and diphenyl ether have been prepared.
2. This work, with the possibility of leading to thyroxine-like compounds, is being continued.

EDMONTON, ALBERTA, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF ALLYL ARYL SULFIDES

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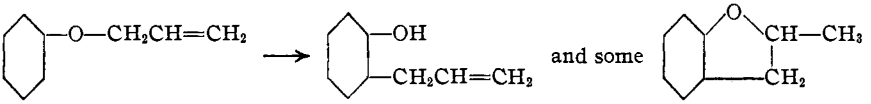
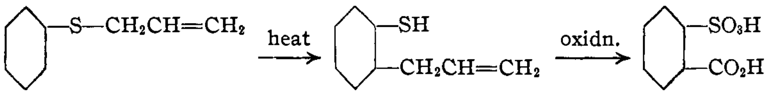
The most striking property of allyl aryl ethers is their rearrangement[1] into *o*-allylphenols when they are heated. In some instances small yields of the isomeric methylcoumaranes have been observed as by-products. Allyl phenyl ether, for example, rearranges into *o*-allylphenol (80% yield) and 2-methylcoumarane (5% yield) by refluxing for six hours.



By analogy, one would infer that allyl aryl thioethers should rearrange similarly, if an ortho position is available, into *o*-allylthiophenols. Small amounts of dihydrothionaphthenes, the sulfur analogs of the coumaranes, might also be anticipated.

This problem has been approached by studying allyl phenyl sulfide and allyl *p*-tolyl sulfide, both of which were prepared in nearly quantitative yields from allyl bromide and the sodium salt of the aryl mercaptan. Allyl phenyl sulfide gradually undergoes rearrangement into *o*-allylthiophenol by refluxing, as witnessed by the increase in the boiling temperature during six hours from 207 to 240°. The *o*-allylthiophenol was identified by analysis of its lead salt, and by oxidation into *o*-sulfobenzoic acid



There is some evidence for the belief that a small amount of the hitherto undescribed 2-methyl-2,3-dihydrothionaphthene, A, was also formed during

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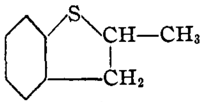
[1] For a survey of this topic, see Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, 1929, pp. 214–228.

the rearrangement. At least, a straw-colored liquid of higher boiling point than the original thioether and of lower boiling point than *o*-allylthiophenol was isolated which failed to form a salt with alcoholic lead acetate solution. The oxygen analog, 2-methylcoumarane, also boils at a higher temperature than phenyl allyl ether and lower than *o*-allylphenol. It is interesting to note that *o*-allylthiophenol is insoluble in alkalies.



A

Allyl *p*-tolyl sulfide yielded 2-allyl-4-methylthiophenol by refluxing for several hours and as before, much of the original thioether was recovered.

Experimental Part

Allyl Phenyl Sulfide.—To an alcoholic solution (30 cc.) of sodium ethoxide (0.1 mole) was added 11 g. (0.1 mole) of thiophenol, followed by 13 g. (0.11 mole) of allyl bromide. There was an appreciable heat of reaction and an immediate precipitation of sodium bromide. The reaction completed itself by standing overnight, at which time it was no longer alkaline toward litmus. The alcohol and the excess of allyl bromide were distilled away on the water-bath, following which water was added to dissolve the sodium bromide. The upper oily layer was separated and the aqueous layer twice extracted with 25-cc. portions of ether. The combined product was dried over anhydrous calcium chloride, the ether removed and the residue vacuum-distilled. The yield was nearly quantitative (15 g.).

Phenyl allyl sulfide was found to have boiling points of 104–106° at 25 mm., and 215–218° at 750 mm. The refractive index, $n_D^{20.5}$, was 1.4772. The thioether was inert toward an alcoholic solution of lead acetate, thus demonstrating the absence of a mercaptan group.

Effect of Prolonged Refluxing.—Twelve grams of phenyl allyl sulfide was refluxed on a fused salt bath in a small flask fitted with an upright air condenser and a thermometer immersed in the liquid. In the course of six hours the temperature rose from 207° to a maximum of 240°. The liquid darkened considerably. Also it acquired a pronounced mercaptan odor which was in decided contrast to the gasoline-like odor of the original thioether. By vacuum distillation, 8 g. of the original allyl phenyl sulfide was recovered and 3 g. of higher-boiling material was obtained. The constants for the latter were: b. p. 183–190° at 17 mm.; n_D^{21} 1.6098. This *o*-allylthiophenol had a decidedly unpleasant odor.

Lead Salt.—Although it was alkali insoluble, the liquid was considered to be *o*-allylthiophenol. To support this contention, the lead salt was precipitated metathetically by reaction of it with lead acetate, using alcohol as a common solvent. The heavy yellow precipitate which formed was washed with a little alcohol, then with dilute acetic acid, and dried in a desiccator. For analysis it was dissolved in dilute nitric acid and converted into lead sulfate in the usual way with sulfuric acid.

Anal. Subs., 0.2010, 0.2125: $PbSO_4$, 0.1206, 0.1284. Calcd. for $(C_9H_9S)_2Pb$: Pb, 41.0. Found: Pb, 41.0, 41.3.

Oxidation of *o*-Allylthiophenol.—In order to establish the structure of this substance, 1.5 g. of it was converted into *o*-sulfobenzoic acid by oxidation with a solution of 3 g. of potassium permanganate in 75 cc. of water. After two hours of refluxing, the precipitate of manganese dioxide was filtered off, the filtrate was concentrated to 40 cc., cooled and acidified. The white flocculent precipitate which appeared was purified by recrystallization from water; m. p. 66–67°. The pure trihydrate of *o*-sulfobenzoic acid, purified similarly, is known[2] to melt at 69°.

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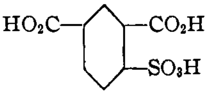
[2] Krannich, *Ber.*, 33, 3485 (1900).

Allyl *p*-Tolyl Sulfide.—This derivative of thiocresol was prepared in 97% yield by a method which was analogous to the one wherein thiophenol was used. Thus, 4.6 g. (0.2 mole) of sodium, 60 cc. of absolute alcohol and 25 g. (0.2 mole) of *p*-thiocresol (m. p. 44°) were admixed and caused to react with 25 g. (0.22 mole) of allyl bromide. The same vigorous reaction was noted but it was necessary to reflux the mixture for a short time to make it neutral to litmus. Upon working up as in the preceding case, there was obtained 32 g. of allyl *p*-tolyl sulfide, boiling at 123–127° and 25 mm.; n_D^{21} 1.5711.

2-Allyl-4-methylthiophenol.—When 11 g. of this thioether was refluxed for four hours, the temperature rose from 228 to 264°. By vacuum distillation, 5 g. of the thioether was recovered and 3 g. of yellow oil was collected at 190–196° and 11 mm.; n_D^{21} 1.6921. This allylthiocresol possessed a pronounced odor. There was a small amount of tarry residue.



B

A portion of the 2-allyl-4-methylthiophenol was oxidized as in the preceding experiment. A white solid subliming at 320° was isolated which is undoubtedly a sulfo-isophthalic acid of the structure shown (B). This compound is not described in the literature.

Lead Salt of 2-Allyl-4-methylthiophenol.—Part of the allylthiocresol was dissolved in alcohol and treated with alcoholic lead acetate solution. Heavy precipitation ensued. The precipitate, when first formed, was orange-colored and amorphous, but on standing for an hour it changed into light yellow needles which melted quite sharply at 330° with decomposition and formation of metallic lead.

Anal. Subs., 0.2100, 0.2236: $PbSO_4$, 0.1190, 0.1286. Calcd. for $(C_{10}H_{11}S)_2Pb$: Pb, 38.9. Found: Pb, 38.7, 38.5.

2-Methyl-2,3-dihydrothionaphthene.—In order to ascertain the presence of a cyclic isomer of *o*-allylthiophenol, 8 g. of the purified rearrangement product, prepared from allyl phenyl sulfide as previously indicated, was treated with alcoholic lead acetate solution until precipitation was complete. The lead salt was filtered off and the alcohol removed from the filtrate by evaporation. The residue was then filtered from the excess of lead acetate and fractionated. In the lower-boiling fraction, about 0.2 g. of a straw-colored liquid was obtained at 103–108° and 8 mm. which yielded no precipitate with lead acetate and which unquestionably was different from *o*-allylthiophenol or the original thioether. Its refractive index was 1.5811, as compared with 1.4772 for the allyl phenyl sulfide and 1.6099 for *o*-allylthiophenol. Work is being continued on this subject.

Summary

A simple method of preparation has been given for allyl phenyl sulfide and for allyl *p*-tolyl sulfide. At the reflux temperature, the former undergoes a partial rearrangement into *o*-allylthiophenol. Small amounts of 2-methyl-2,3-dihydrothionaphthene are also produced. Similarly, allyl *p*-tolyl sulfide was found to pyrolyze into 2-allyl-4-methylthiophenol. The similarity in the pyrolysis of allyl aryl sulfides and of allyl aryl ethers is pointed out.

EVANSTON, ILLINOIS