

Oregon, on August 24, 1930. At that time the plant was just beginning to bloom. The plants were dried and shipped to Washington, D. C. The whole plant with the exception of the roots was used.

**Isolation of the Alkaloid.**—The finely ground plant (7.415 kg.) was moistened with alcohol containing 75 g. of acetic acid and then extracted with alcohol. The alkaloid was recovered by the process previously described.<sup>3</sup>

The crude alkaloid weighed 130.4 g. or 1.76% of the plant material. It was negative to the modified Grant test for sparteine, practically insoluble in petroleum ether, slightly soluble in ethyl ether, and completely soluble in cold acetone. On standing the sirupy alkaloid solidified to a mass of crystals embedded in a thick sirup.

The mass was washed with cold ethyl acetate, which removed most of the sirup. The crystals were then recrystallized several times from hot ethyl acetate with the addition of a little norit and finally from methyl isobutyl ketone. The melting point was constant at 91–92° (cor.). Mixed with nonalupine from *L. sericeus* there was no alteration in the melting point. The substance was dried to constant weight for analysis.

*Anal.* Calcd. for  $C_{15}H_{21}ON_2$ : C, 72.50; H, 9.74; N, 11.28. Found: C, 72.37, 72.39; H, 9.55, 9.57; N, 11.28, 11.20.

The alkaloid was similar in all chemical and physical respects with nonalupine.

(3) J. F. Couch, *THIS JOURNAL*, **56**, 2434 (1934).

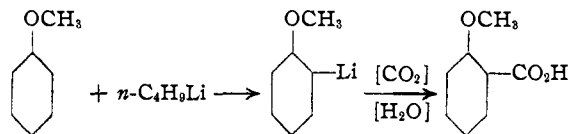
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## Lateral Metalation of Methyl Phenyl Sulfide

BY HENRY GILMAN AND F. J. WEBB

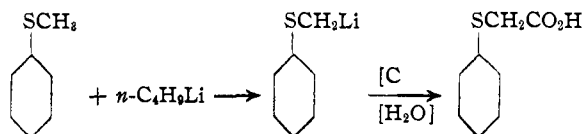
Metalation by organometallic compounds of a great variety of ethers invariably involves hydrogen situated *ortho* to the hetero element. Some of the types examined are: aryl alkyl ethers, diaryl ethers, and cyclic ethers like furan, benzofuran and dibenzofuran. The following reaction with anisole is typical.



The same general reaction takes place with the sulfur analogs of the diaryl ethers and the cyclic ethers mentioned, with but one exception. Metalation of dibenzofuran by a variety of organometallic compounds involves the 4-position (*ortho* to the hetero element); however, the exceptional case has been noted with the related heterocycle, dibenzothiophene. Although metalation of dibenzothiophene by organolithium and organopotassium compounds also involves the 4-posi-

tion, metalation by phenylcalcium iodide introduces the metal in the 3-position, or *meta* to the hetero element.<sup>1</sup>

We now find that metalation of methyl phenyl sulfide proceeds quite unlike the related anisole, and instead of giving an *ortho* nuclear metalation product<sup>2</sup> yields exclusively a lateral metalation product.



There is a possibility that nuclear metalation may have occurred initially, and that the lithium then migrated to the methyl group. This remains to be established. In this connection, it is interesting to note that *o*-, *m*- and *p*-tolylsodiums rearrange laterally to benzylium.<sup>3</sup> The metalation of other sulfur and related types is being examined, together with some syntheses of these new reactive compounds such as the bridging of the 1- and 9-positions in dibenzofuran types by hetero elements and groups.

## Experimental

A solution containing approximately 0.2 mole of *n*-butyllithium was divided into two equal parts. To one portion was added 12.4 g. (0.1 mole) of methyl phenyl sulfide in 30 cc. of ether; and to the other portion was added 10.8 g. (0.1 mole) of anisole in 30 cc. of ether. Each of the mixtures was stirred and refluxed for fifteen hours, and then carbonated by solid carbon dioxide. By means of the usual procedures, there was isolated from the reaction with methyl phenyl sulfide, 7.32 g. (43.5%) of phenylmercaptoacetic acid (m. p., 61–63°). This compound was identified by comparison with an authentic specimen prepared from thiophenol and chloroacetic acid in accordance with the directions of Gabriel.<sup>4</sup> In addition, there was recovered 3.7 g. or 29.8% of methyl phenyl sulfide, which raises the yield of phenylmercaptoacetic acid to 62% on the basis of methyl phenyl sulfide not recovered.

The reaction with anisole gave 4.92 g. or 32.4% of *o*-methoxybenzoic acid; 0.65 g. or 5.37% of 2,2'-dimethoxybenzophenone; and 1.9 g. or 17.6% of recovered anisole. All solids were identified by the method of mixed melting points.

From a check experiment with methyl phenyl sulfide there was obtained 5.9 g. or 35.2% of phenylmercaptoacetic acid (m. p. 61–63°) and 4.5 g. or 36.3% of recovered methyl phenyl sulfide.

(1) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Gilman, Jacoby and Pacevitz, *ibid.*, **3**, 120 (1938).

(2) Phenoxathiin and *N*-ethylbenzothiazole are known to metalate *ortho* to a hetero element, and with the former compound *ortho* to the oxygen linkage.

(3) Gilman and Pacevitz, *THIS JOURNAL*, **62**, 672 (1940); Gilman, Pacevitz and Baine, *ibid.*, **62**, May (1940).

(4) Gabriel, *Ber.*, **10**, 1629 (1879).

We have just observed that *ethyl* phenyl sulfide with *n*-butyllithium gives *o*-ethylmercaptobenzoic acid.

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### Hydrogenation of Wood

BY H. P. GODARD, JOSEPH L. MCCARTHY AND HAROLD HIBBERT

Studies on hydrogenation of lignin and other plant materials at high pressures have now shown that maple and spruce wood meals readily undergo hydrogenation. The two latter products were first freed from resin, fats, etc., by the customary preliminary extraction treatment with alcohol-benzene, alcohol, and water in the order named, then dried, suspended in anhydrous dioxane, the copper-chromium oxide catalyst added and the mixture then subjected to the action of hydrogen at around 250 to 280° at a pressure of 5000-6000 pounds per square inch (333-400 atm.) for periods of twelve to sixteen hours.

The main products isolated were (a) 4-*n*-propylcyclohexanol-1, b. p. 92-95° (7 mm.), refractive index  $n_D^{25}$  1.4633, and (b) 4-*n*-propylcyclohexanediol-1,2, b. p. 107-110° (1 mm.), refractive index  $n_D^{25}$  1.4808; some higher boiling oils also were obtained. These substances undoubtedly originate from the lignin present in the wood, the combined yields of (a) and (b) in the preliminary work, when calculated on the total (Klason) lignin present originally, amounting to around 60 to 70% in the case of maple and about 35 to 40% in the case of the spruce meal. Similar results were obtained using wood meal previously extracted with cold 5% alkali, although in these cases the yields were somewhat lower.

Presumably other suspending media such as tetralin, decalin, cyclohexane, as well as the above solvents (a) and (b), can be used in place of dioxane, and these are being actively investigated.

It is of considerable interest that the accompanying carbohydrate-polysaccharide components also undergo simultaneous hydrogenation and hydrogenolysis as indicated by the large absorption of hydrogen (about 3.2 moles of hydrogen per 100 g. of wood meal). The nature of these reactions and of the resulting products are also under investigation.

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### The Effect of Chlorine Substitution on the Fungistatic Properties of Acetic and Propionic Acids

BY CHARLES HOFFMAN, T. R. SCHWEITZER AND GASTON DALBY

In a recent paper the fungistatic properties of  $\beta$ -iodopropionic acid were reported in connection with a study of a series of normal, branched-chain, and substituted fatty acids.<sup>1</sup> It was shown that  $\beta$ -iodopropionic acid had remarkable fungistatic properties which apparently depended to some extent on the nature of the iodine atom itself. The effect of substituents is also of interest from the point of view of the relationship of molecular structure to fungistatic power. Monochloroacetic,  $\alpha$ -chloropropionic, and  $\beta$ -chloropropionic acids are readily available and their fungistatic curves illustrate the effect of the introduction of a single chlorine atom in all possible positions.

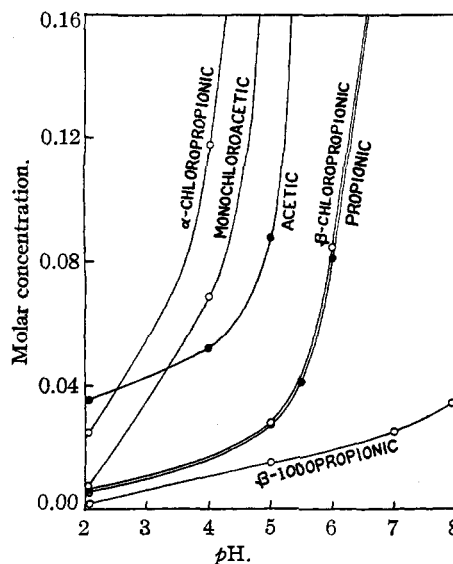


Fig. 1.—Molar concentrations of the indicated acids at various pH values necessary to inhibit mold for forty-eight hours at 37.5°.

The method used was as previously reported.<sup>1</sup>  $\beta$ -Chloropropionic acid has a curve practically identical with that of propionic acid itself and is markedly different from the  $\beta$ -iodopropionic acid curve which is indicated on the graph for comparison. The introduction of chlorine on the alpha carbon of propionic acid sharply decreases its fungistatic properties. Monochloroacetic acid is also much less effective than acetic acid except

(1) Hoffman, Schweitzer and Dalby, *Food Research*, 4, 539 (1939).