Structure of the Ethanolysis Products from Spruce and Maple Wood

By Leo Brickman, J. J. Pyle, W. L. Hawkins and Harold Hibbert

A re-investigation of the "aldehyde fraction" obtained in the ethanolysis of maple and spruce wood[1] has shown that two of the constituents previously identified (incorrectly) as syringoyl- and vanilloyl-acetaldehydes are, in reality, 1,2-diketones, namely, the benzil derivatives, methyl-4-hydroxy-3,5-dimethoxyphenyl diketone (C_6H_3-$(OH)(OCH_3)_2$-CO-CO-CH_3) (A) and methyl guaiacyl diketone ($C_6H_2(OH)(OCH_3)$-CO-CO-CH_3) (B), respectively. Proof of this has been found in the synthesis of the benzils by oxidation of the corresponding benzoins, namely, α-hydroxypropiovanillone and α-hydroxypropiosyringone, by means of copper sulfate and pyridine. The monosemicarbazone of (A) melts at 213° and its disemicarbazone at 240°, while the mono-2,4-dinitrophenylhydrazone of (B) melts at 226–227° and its monosemicarbazone at 214–215°. No depression in melting point was found on admixture with the corresponding products isolated from the ethanolysis products.

The mistake in identity arose as a result of the aldehyde-like properties possessed by these 1,2-diketones.

A full account of the supporting chemical evidence is to be given in a forthcoming publication.

(1) Pyle, Brickman and Hibbert, This Journal, **61**, 2198 (1939).

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Purification of High Molecular Weight Fatty Esters

By Loran O. Buxton and Roland Kapp

In the course of our research it became necessary to prepare relatively large quantities of substantially acid-free high molecular weight fatty esters. We have found that the following process is more satisfactory for removing substantially all of the unreacted fatty acids than the usual methods.

The procedure most suitable is as follows. The unreacted alcohol is distilled from the esterification mass, and the residual mixture of free fatty acids, crude ester, and catalyst is dissolved in 2 to 5 parts by weight of a solvent such as ethylene dichloride to 1 part of ester. A convenient sample (10 to 20 g.) of the solvent solution of the crude ester is dissolved in an alcohol–ether mixture, and titrated with standard 0.5 N alcoholic potassium hydroxide. On the basis of this titration value an equivalent weight of concentrated aqueous potassium hydroxide, preferably of 38% strength, is added slowly with constant stirring to the solvent solution of the ester mixture. In a relatively short time the potassium soap of the unreacted fatty acids will rise to the surface as a flocculent aggregate, and any mineral acid present as catalyst will also precipitate out as the potassium salt. The solvent solution is filtered without suction, and the soap mass is washed with a small amount of fresh ethylene dichloride to remove traces of neutral ester, and the filtrate distilled. It is not necessary to dry the filtrate.

By this process we have been able to obtain quantitatively the yields of methyl and ethyl esters of lauric, oleic, linoleic, stearic and ricinoleic acids, from the original esterified mass prepared with the respective crude acids. The process also has been applied successfully to the preparation of relatively pure mono- and di-naphthenates of diethylene glycol. The esters obtained in this manner have acid values from 0.5 to 1.0 and can be purified further by vacuum distillation. Relatively large amounts of ester can be purified in this manner without the formation of troublesome emulsions and without the hazards hitherto inherent in the use of ether.

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Lupine Studies. XVI.[1] The Isolation of Nonalupine from *Lupinus andersonii* Wats

By James Fitton Couch

The isolation of nonalupine from *Lupinus sericeus* has been reported recently.[1] In that species this alkaloid is associated with spathulatine first isolated from *L. marianus*.[2] Nonalupine has now been isolated from *L. andersonii*, a perennial, Pacific States lupine, which has not previously been examined chemically. Spathulatine was not found in the last named species.

Experimental

Material.—The plant used in this investigation was collected by the writer on the south road, Crater Lake Mt.,

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(1) Previous paper, No. XV, This Journal, **62**, 554 (1940).

(2) J. F. Couch, *ibid.*, **46**, 2507 (1924).

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.[3]

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 $C_{15}H_{24}ON_2$: 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.

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

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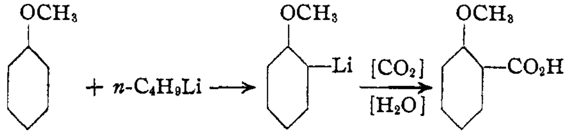
Lateral Metalation of Methyl Phenyl Sulfide

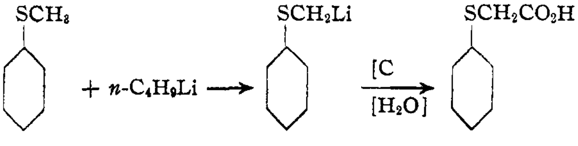
BY HENRY GILMAN AND F. J. WEBB

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-position, metalation by phenylcalcium iodide introduces the metal in the 3-position, or *meta* to the hetero element.[1]

We now find that metalation of methyl phenyl sulfide proceeds quite unlike the related anisole, and instead of giving an *ortho* nuclear metalation product[2] 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 benzylsodium.[3] 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.[4] 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.

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[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**, 673 (1940); Gilman, Pacevitz and Baine, *ibid.*, **62**, May (1940).

[4] Gabriel, *Ber.*, **12**, 1639 (1879).