probably chiefly gorlic acid. Assuming this to be the case, the calculated result would be +54.32°, which is still in very close agreement with the actual value.

Summary

The qualitative and quantitative analysis of the fatty acids of *Oncoba echinata* (gorli) oil has been made by the methods given in the first article of this series. The percentage composition of the fatty acid is as follows: palmitic acid, 7.8%, oleic acid, 2.2%, gorlic acid, 14.7% and chaulmoogric acid, 74.9% (loss, 0.4%).

RIO DE JANEIRO, BRAZIL RECEIVED JANUARY 8, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Reactions between Mercury Diaryls and Selenium Tetrabromide

BY HENRY M. LEICESTER

Since mercury diaryls have been shown to react readily with diaryl selenium dihalides[1] it seemed desirable to test the action of the mercury compounds on simpler selenium derivatives such as selenium tetrabromide. In the course of this work, a new method for the synthesis of aromatic selenides was developed.

When mercury diaryls were added to a solution of selenium tetrabromide in carbon bisulfide, it was found that three molar equivalents of the mercury compound were required to discharge the red color from one molar equivalent of the tetrabromide. The reaction was rapid and a heavy precipitate of aryl mercuric bromide settled out almost quantitatively. From the solution were isolated aryl bromides and diaryl selenides. Thus, the reaction was entirely analogous to that found with diaryl selenium dibromides, and was represented by the equation

$$SeBr_4 + 3R_2Hg = R_2Se + RBr + 3RHgBr \quad (1)$$

It is clear that this reaction gives a very rapid and easy method for synthesizing diaryl selenides. Such a synthesis is especially important in the case of compounds containing heavy organic radicals, such as naphthyl or biphenyl. When attempts were made to synthesize these selenides by the diazo reaction[2] the chief products were tars from which the selenides could not be isolated in a pure condition. In this new reaction, they were readily obtained pure.

It was found that when an excess of selenium tetrabromide was present in reaction (1), mercuric bromide was also formed. Aryl mercuric bromides reacted with selenium tetrabromide to give the same salt. The other products formed were again aryl bromides and diaryl selenides. Thus, the second reaction was

$$SeBr_4 + 3RHgBr = R_2Se + RBr + 3HgBr_2 \quad (2)$$

Therefore, the total reaction which can be obtained with an excess of the tetrabromide is

$$2SeBr_4 + 3R_2Hg = 3HgBr_2 + 2R_2Se + 2RBr$$

Experimental

Selenium tetrabromide was prepared by adding excess bromine to gray, powdered selenium and driving off the unreacted bromine by gentle warming.

When dry mercury diphenyl and selenium tetrabromide were mixed, a reaction of almost explosive violence occurred. Therefore, the reaction always was carried out in carbon bisulfide, in which all the reagents were at least partly soluble. When three moles of mercury diphenyl was added with shaking to one mole of selenium tetrabromide in carbon bisulfide, heat was evolved and the red color faded rapidly as a heavy white precipitate came down. Mercury di-*p*-tolyl reacted in a similar way. When mercury di-β-naphthyl and mercury dibiphenyl were used, the reaction was much more sluggish, and the mixtures were warmed gently on the water-bath and stirred during the addition of the mercury compound. The precipitate was filtered off, and in all cases was identified as the aryl mercuric bromide by m. p. and mixed m. p. with authentic specimens. The yields were as follows: phenylmercuric bromide 95%, *p*-tolylmercuric bromide 82%, β-naphthylmercuric bromide 87% and biphenylmercuric bromide 100%. In one case, one mole of selenium tetrabromide was treated with four of mercury diphenyl, but the yield of phenylmercuric bromide was not increased. It thus appears that the reaction is practically quantitative in the sense of equation (1) above, and the failure to obtain 100% yields in all cases was probably due to the difficulty in handling the small amounts of material used.

After separation of the aryl mercuric bromides, the carbon bisulfide solutions were evaporated to dryness. Phenyl and *p*-tolyl selenides and bromides were separated by fractionation. In the case of the naphthyl and biphenyl compounds, the residue was taken up in alcohol, and the selenide was crystallized from this solvent. Careful addition of water to the mother liquors from the crystallizations at first precipitated a small amount of selenide and then, suddenly, the bromide. In view of the difficulty of quantitative isolation of these compounds,

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[1] Leicester, THIS JOURNAL, **57**, 1901 (1935).

[2] Leicester and Bergstrom, *ibid.*, **53**, 4428 (1931).

they were identified only qualitatively. The selenides were identified by conversion to their dibromides or dichlorides, the aryl bromides by nitration. In every case, the expected compounds were obtained.

When the mercury diaryls and selenium tetrabromide were allowed to stand together in carbon bisulfide without shaking or stirring, or when an excess of selenium tetrabromide was used, the precipitated aryl mercuric bromide was contaminated with mercuric bromide. The presence of the latter was shown by the formation of yellow mercuric oxide when sodium hydroxide solution was added to the precipitate. When one mole of selenium tetrabromide and three of phenylmercuric bromide were shaken together for six days, pure mercuric bromide was formed and identified by its reaction with mercury diphenyl in acetone solution to form phenylmercuric bromide. The other reaction products were diphenyl selenide and bromobenzene. Even when less than the theoretical amount of phenylmercuric bromide was shaken with selenium tetrabromide, these were the only products, and no trace of diphenyl selenium dibromide was found. Owing to the insolubility of the naphthyl- and biphenylmercuric bromides in carbon bisulfide, it was impossible to carry this reaction to completion with them in a reasonable time.

Summary

Diaryl mercury compounds react with selenium tetrabromide to give almost quantitative yields of aryl mercuric bromides, diaryl selenides and aryl bromides. The aryl mercuric bromides can react with more selenium tetrabromide to give mercuric bromide, diaryl selenides and aryl bromides. These reactions can be used for the synthesis of diaryl selenides, especially those of the type of dinaphthyl or dibiphenyl selenides.

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Arsenicals Containing the Furan Nucleus. III. Some beta-Substituted Furan Arsenicals

BY WILLIAM W. BECK[1] AND CLIFF S. HAMILTON

Furan arsenicals, in which arsenic is linked to the furan nucleus in the alpha position, have been reported in previous communications.[2,3] The availability of certain beta-substituted furan mercurials suggested the possibility of synthesizing and studying furan arsenicals containing arsenic in a beta position.

When three equivalents of 3-chloromercurifuran was treated with one equivalent of arsenic trichloride in benzene solution, there was obtained tri-3-furylarsine. Arsenation proceeded less rapidly than in the case of 2-chloromercurifuran under similar conditions. When the arsine was treated with one equivalent of mercuric chloride in alcoholic solution, the complex addition product, tri-3-furylarsine mercurichloride, was obtained. Under similar conditions, the 2-isomer undergoes cleavage of the carbon–arsenic bond to form 2-chloromercurifuran. Thus, tri-3-furylarsine resembles triphenylarsine, which also forms an addition product with mercuric chloride,[4] more than it does its isomer, tri-2-furylarsine, as regards stability of the carbon–arsenic bond. If cleavage of the carbon–arsenic linkage in aromatic arsenicals by mercuric chloride be considered as one of the criteria of aromaticity, it may be concluded that the beta positions in furan are less aromatic in character than are the alpha positions.[5]

The mercurial was recovered unchanged when methyl 4-chloromercuri-5-bromo-2-furoate was refluxed with arsenic trichloride in xylene solution. When arsenic tribromide was substituted for arsenic trichloride, arsenation proceeded rapidly and completely, and 2-carbomethoxy-5-bromo-4-furyldibromoarsine was obtained. Scission of the carbon–arsenic linkage was not caused by mercuric chloride or iodine. Prolonged boiling with water cleaved the bond, and methyl 5-bromo-2-furoate was obtained.

Mercuration of ethyl 5-bromo-2-furoate gave the ethyl analog of the methyl mercurial, and arsenation of the ethyl mercurial gave a dibromoarsine.

Attempts were made to apply other standard methods of preparing aromatic arsenicals to the furan series. No furan arsenicals were obtained by direct arsonation of furoic esters with arsenic acid nor by the Rosenmund reaction[6] with halogen-substituted furans.

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[1] Parke, Davis and Company Fellow.

[2] Lowe and Hamilton, THIS JOURNAL, **57**, 1081 (1935).

[3] Lowe and Hamilton, *ibid.*, **57**, 2413 (1935).

[4] LaCoste and Michaelis, *Ann.*, **201**, 241 (1880).

[5] Gilman and Towne, *Rec. trav. chim.*, **51**, 1056 (1932).

[6] Rosenmund, *Ber.*, **54**, 438 (1921).