An examination of the dry, solid residues remaining after the reaction of ethyl acetate and ethyl isobutyrate with sodium ethoxide has been made and from the results obtained the conclusion is drawn that the so-called "primary reaction product" postulated by Scheibler as the intermediate in the acetoacetic ester condensation and ketene acetal formation does not exist.

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Notes

Aryl *p*-Bromobenzenesulfonates as Derivatives for the Identification of Phenols

BY VLADIMIR C. SEKERA

In connection with the work on the higher alkyl sulfonates[1] one or two aryl esters were prepared. These beautifully crystalline compounds were so readily prepared and so easily purified that further examples were characterized in order to show their value as derivatives for identification of phenols.

The general method of preparation consisted of mixing equimolecular quantities of the phenol and *p*-bromobenzenesulfonyl chloride with about four equivalents of pyridine and stirring the mixture for about three hours at 15° or lower. With small quantities, less time was needed for the reaction. The reaction mixture was decomposed with ice water containing enough dilute hydrochloric acid to combine with the pyridine. The aryl sulfonate was collected on a Buchner funnel and air dried. One recrystal-

TABLE I

SOME ARYL *p*-BROMOBENZENESULFONATES

Phenol	Yield, %	M. p., °C.	Anal., % Br Calcd.	Anal., % Br Found
Phenol	86	115.5	25.5	25.5
α-Naphthol	81	104	22.0	21.9
β-Naphthol	69	151–152	22.0	22.4
o-Cresol	75	78–79	24.4	24.6
m-Cresol	74	69–70	24.4	24.3
p-Cresol	76	100	24.4	24.5
o-Nitrophenol	70	97–98	22.3	22.6
m-Nitrophenol	70	108–109	22.3	22.4
p-Nitrophenol	69	112	22.3	22.6
o-Bromophenol	57	125	40.8	41.0
Thymol	71	103.5	21.6	21.5
Guaiacol	61	103–104	23.3	23.6
2,4,6-Tribromophenol	85	139–140	58.1	58.4

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[1] Sekera and Marvel, THIS JOURNAL, **55**, 345 (1933).

lization from alcohol using a little decolorizing carbon usually gave a pure product. Table I contains a description of these compounds.

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Note on the Occurrence of Dehydrodeguelin and Dehydrotoxicarol in Some Samples of Derris Root

BY E. P. CLARK AND GEORGE L. KEENAN

On several occasions during the past two years, specimens of derris root were encountered which yielded no rotenone, but gave instead mixtures of yellow crystals whose melting points ranged from 200 to 225°. After purification by recrystallization from various solvents, these materials gave mixtures of dehydrodeguelin and dehydrotoxicarol. The identity of the substances was proved by the optical immersion method. In two instances, dehydrotoxicarol predominated so that it was possible by fractional crystallization to isolate this substance in an analytically pure condition and identify it by comparison with an authentic sample as to melting point, mixed melting point and optical properties. The materials remaining in the mother liquors were recovered and after recrystallization were shown to consist of mixtures which were impossible to resolve but which when examined by the optical method referred to above were conclusively shown to be essentially dehydrodeguelin and dehydrotoxicarol.

Recently there was obtained from a manufacturer of rotenone an interesting sample of yellow crystals derived from derris root which yielded no rotenone. Upon recrystallization this material yielded a beautiful yellow preparation which melted sharply at 217°. Repeated recrystallizations from various solvents failed to alter the melting point, and it was thought that possibly it was a dehydro derivative of an isomer of deguelin or rotenone. Upon subjecting the material to hydrolysis with alcoholic alkali, an acid corresponding to derrisic acid was readily obtained but it melted at 178° (derrisic acid melts at 158° while deguelic acid melts at 186°). The melting point of this acid did not change after several recrystallizations, which was in harmony with the assumption stated above, especially since analysis of the acid showed its molecular formula to be the same as that of derrisic acid. In the meantime, oxidation of the dehydro derivative (m. p. 217°) with permanganate in acetone and in alkaline aqueous solutions, and also with alkaline hydrogen peroxide, yielded 2-hydroxy-4,5-dimethoxybenzoic, nicouic, risic and derric acids.[1] These facts, especially the isolation of nicouic acid in essentially the same yield as is obtained from dehydrodeguelin, proved that at least the greater part of the original

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[1] Clark, THIS JOURNAL, **54**, 3000 (1932).