formation of 6-tosyl-triacetyl-α-methyl-*d*-glucoside in 36% yield and 6-tosyl-triacetyl-β-methyl-*d*-glucoside in 41% yield, respectively. Employing the acylation conditions specified, the differences in spatial arrangement of these isomeric compounds nas little or no effect on the order of reactivity of the various hydroxyl groups.

2. The structure of 6-tosyl-triacetyl-β-methyl-*d*-glucoside, obtained by the unimolar tosylation of β-methyl-*d*-glucoside followed by acetylation, is proven by its identity with 6-tosyl-triacetyl-β-methyl-*d*-glucoside derived from 6-tosyl-monoacetone-*d*-glucose.

3. The structure of 6-tosyl-triacetyl-α-methyl-*d*-glucoside obtained by the unimolar tosylation–acetylation of α-methyl-*d*-glucoside in pyridine solution is proven by the following reactions: 6-tosyl-triacetyl-α-methyl-*d*-glucoside ⟶ 6-iodo-triacetyl-α-methyl-*d*-glucoside ⟶ triacetyl-α-methyl-*d*-glucomethyloside ⟶ acetobromo-*d*-glucomethylose ⟶ triacetyl-β-methyl-*d*-glucomethyloside. The triacetyl-β-methyl-*d*-glucomethyloside obtained in this manner was found to be identical with the reduction product of 6-iodo-triacetyl-β-methyl-*d*-glucoside obtained from 6-tosyl-triacetyl-β-methyl-*d*-glucoside, thus correlating the derivatives of the alpha and beta series.

4. In view of the results of Lieser and Schweizer on the partial benzoylation of α- and β-methyl-*d*-glucosides, the suggestion is made that the order of the reactivity of the hydroxyl groups in these compounds may be influenced by the nature of the acylating reagent.

YONKERS, NEW YORK RECEIVED OCTOBER 28, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

Sulfonic Acid Esters of the Phenylphenols

BY STEWART E. HAZLET

Recently some sulfonic acid esters of the phenylphenols were reported[1] and their characteristics listed. Some of these were rather low melting compounds and not particularly suitable as derivatives for the identification of the phenols. The *p*-bromo- and the *o*-, *m*- and *p*-nitrobenzenesulfonates of the three isomeric phenylphenols have now been characterized and the results are summarized in Tables I, II, III and IV.

TABLE I

ESTERS OF *p*-BROMOBENZENESULFONIC ACID

Starting material	Solvent	Yield, %	M. p., °C.	Formula	Sulfur analyses, % Calcd.	Found
o-Phenylphenol	Methanol	69	69–70	$C_{18}H_{13}O_3BrS$	8.24	8.36
m-Phenylphenol	Dil. alcohol	28	102.5–103.5	$C_{18}H_{13}O_3BrS$	8.24	8.46
p-Phenylphenol	Alcohol	90	185–186	$C_{18}H_{13}O_3BrS$	8.24	8.34

TABLE II

ESTERS OF *o*-NITROBENZENESULFONIC ACID

Starting material	Solvent	Yield, %	M. p., °C.	Formula	Sulfur analyses, % Calcd.	Found
o-Phenylphenol	Dil. alcohol	89	72–73	$C_{18}H_{13}O_5NS$	9.03	9.05
m-Phenylphenol	Methanol	60	69–70	$C_{18}H_{13}O_5NS$	9.03	9.01
p-Phenylphenol	Alcohol	Quant.	138–139	$C_{18}H_{13}O_5NS$	9.03	9.1

TABLE III

ESTERS OF *m*-NITROBENZENESULFONIC ACID

Starting material	Solvent	Yield, %	M. p., °C.	Formula	Sulfur aualyses, % Calcd.	Found
o-Phenylphenol	Alcohol	77	130–131	$C_{18}H_{13}O_5NS$	9.03	9.17
m-Phenylphenol	Alcohol	38	111–112	$C_{18}H_{13}O_5NS$	9.03	9.34
p-Phenylphenol	Alcohol	85	143–144	$C_{18}H_{13}O_5NS$	9.03	9.17

The method of preparation in each instance was the same as that previously used.[1] The phenol was dissolved in pyridine and treated with 1.1 mols of the necessary acid chloride. Yields re-

(1) Hazlet, THIS JOURNAL, 59, 287 (1937).

TABLE IV

ESTERS OF *p*-NITROBENZENESULFONIC ACID

Starting material	Solvent	Yield, %	M. p., °C.	Formula	Sulfur analyses, % Calcd.	Found
o-Phenylphenol	Alcohol	93	110–111	$C_{18}H_{13}O_5NS$	9.03	9.01
m-Phenylphenol	Methanol	31	97–98	$C_{18}H_{13}O_5NS$	9.03	8.84
p-Phenylphenol	Alcohol	92	148.5–149.5	$C_{18}H_{13}O_5NS$	9.03	9.19

ported are for crude products. Crystallizations from the solvents indicated in the tables yielded small, colorless crystals in each instance.

That these esters may serve as satisfactory derivatives for the phenylphenols is indicated by the following experiment. One gram of *p*-phenylphenol was treated in the usual manner with *o*-nitrobenzenesulfonyl chloride and the corresponding ester was obtained in 96% yield. After two crystallizations from alcohol the derivative melted between 138 and 139°, as had been found for the product prepared on a larger scale and carefully purified.

The *m*-phenylphenol used in this work was supplied by the Dow Chemical Company. This kindness is gratefully acknowledged.

Summary

1. Some new sulfonic acid esters of the phenylphenols have been prepared and their properties reported.

2. Most of the esters will serve as satisfactory derivatives for the identification of these phenols.

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[CONTRIBUTION NO. 41 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Syntheses in the Pyrazine Series. I. The Curtius and Hofmann Degradation of Pyrazine-2,5-dicarboxylic Acid[1]

BY PAUL E. SPOERRI AND A. ERICKSON

The wide use of pyridium as a urinary antiseptic has resulted in the preparation of many related compounds and in an investigation of their bacteriological properties. These compounds usually differ from pyridium by the introduction of functional groups in the pyridine or benzene ring. The present investigation has as its ultimate goal the preparation of a dye of a similar structure in the pyrazine series with the hope that this may have superior bactericidal properties.

As a starting point certain diaminopyrazines such as the 2,5- or the 2,6-diamino compounds which might be coupled with diazonium salt were needed.

The immediate object of this experimental study has therefore been to investigate possible methods of preparing aminopyrazines.

The usual reduction methods of preparing primary amines are evidently not applicable to pyrazine. Attempts to nitrate the pyrazine ring have been unsuccessful apparently due to the stability of the pyrazine nucleus. Further, the pyrazine ring is quite easily reduced which eliminates the possibility of employing methods which involve the reduction of other substituent groups (*e. g.*, NO, NHOH, CN).

The possibility of employing the reaction of ammonia on a halogen substituted pyrazine in the presence of a suitable condensing agent is not very hopeful since the halogen compounds are reported to be extremely unstable, liberating halogen upon mere standing.

The introduction of the amino group directly by the use of sodamide has been suggested. Some work in this direction is reported in the literature. Tschitschibabin and Shukina[2] have investigated the action of sodamide on 2,5-dimethylpyrazine in xylene. They were able to isolate among other products a small quantity of 3-amino-2,5-dimethylpyrazine. The yield, however, is poor and the product not entirely satisfactory for coupling reactions. Bergstrom and Ogg[3] found that potassium amide in liquid ammonia solution attacks pyrazine but were unable to isolate any definite product.

(1) Paper read at the Rochester meeting of the A. C. S., Division of Organic Chemistry, September 9, 1937.

(2) Tschitschibabin and Shukina, *C. A.*, **25**, 2728 (1931); *J. Russ. Phys.-Chem. Soc.*, **62**, 1189–99 (1930).

(3) Bergstrom and Ogg, THIS JOURNAL, **53**, 249–250 (1931).