

It has been shown that reduction of 3,4-dinitro-5-bromocatechol methylene ether may give an aminonitrobromo, a diaminobromo or a diamino compound containing no bromine, depending on conditions of reduction.

Nitration of an acetic anhydride solution of 6-bromopiperonal, as described, replaced the aldehyde radical by the nitro group, split the methylene oxide ring, and gave 3,4-dihydroxy-6-bromonitrobenzene.

Further work is in progress.

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## The Influence of the Migrating Group in the Fries Isomerization

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It has hitherto been supposed that the position taken up by the migrating group in the Fries isomerization was determined chiefly, if not entirely, by the structure of the phenol whose ester was used and by the temperature of the reaction mixture. Differences in the metallic halide used as catalyst, and in the solvent, have been considered to affect the speed and completeness of the reaction, but not its direction. That among the esters of normal, fatty acids the nature of the acyl group might be significant has, in fact, been denied by Rosenmund and Schnurr<sup>1</sup> in their work on the course and mechanism of this reaction. In his criticism of Rosenmund's conclusions, v. Auwers<sup>2</sup> did not attack this point. At the same time, Coulthard, Marshall and Pyman<sup>3</sup> have reported formation of *o*-hydroxy ketones of the *m*-cresol series under those conditions in which Rosenmund and Schnurr predicted and *reported formation* of the *para* compounds.

It was of some importance to us to be sure of the nature of the products, so we have carried out isomerizations in this series both at low temperature in nitrobenzene and at high temperature without solvent, and have found that with the esters of the higher fatty acids the same ketone was obtained under both sets of conditions. The products had the properties of *o*-hydroxy ketones and could be methylated and then oxidized to methoxyterephthalic acid.

The *m*-cresyl esters of the lower acids gave varying amounts of *p*-hydroxy ketone. Only in the case of the acetate could Rosenmund's results

(1) Rosenmund and Schnurr, *Ann.*, **460**, 56 (1926).

(2) v. Auwers and co-workers, *Ber.*, **61**, 416, 1495 (1928); **64**, 2216 (1931); *Ann.*, **460**, 240 (1928); **464**, 293 (1928); **483**, 44 (1930).

(3) Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930). It is to be noted here that these authors employ a system of numbering beginning at the methyl group in the cresol series, whereas we prefer to start with the hydroxyl. Consequently, our 6-butyryl-*m*-cresol is their 4-butyryl compound, and *vice versa*.

be reproduced. The propionate and butyrate gave merely traces when the reaction was run at room temperature, but when the temperature of the reaction mixture was 2°, the butyrate yielded about 3% of the *p*-hydroxy ketone, while the propionate gave 10% (about 14% of the reacting substance). Lower temperatures of reaction might increase the yield of *p*-hydroxy ketone somewhat, but technical difficulties have prevented our examining this possibility. Lederer,<sup>4</sup> in a study of the behavior of  $\alpha$ -naphthyl esters in the Fries isomerization, reports slightly higher yields of *p*-hydroxy ketone with the acetate than with the butyrate, but this may not be significant.

It is probable that the nature of the migrating group exercises a constant effect, larger groups tending to go to the ortho position, but this effect is small compared to that of the structure of the phenol, and the temperature of the reaction. Where these two influences largely counteract each other, the influence of the acyl group may, however, be dominant.

### Experimental Part

**Fries Isomerizations at High Temperature.**—The ester to be isomerized was placed in a flask protected from moisture by a capillary tube, and about 1.1 equivalents of powdered anhydrous aluminum chloride was added as rapidly as the reaction permitted. The flask was placed immediately in an oil-bath and kept at 120–140° until evolution of gas had largely ceased. This usually took 10–20 minutes. The orange-colored mixture was then allowed to cool to around 60° and decomposed with dilute hydrochloric acid. The mixture was extracted with ether, the extract washed with water and dried over calcium chloride. The ether was boiled off and the product fractionated under diminished pressure.

**Isomerizations at Low Temperature.**—The procedure was essentially the same as that worked out by Rosenmund and Schnurr. The aluminum chloride (1.3 equivalents) was dissolved in a quantity of nitrobenzene five times the weight of ester to be used, and cooled in an ice-bath. The ester was added with vigorous stirring, and the reaction mixture permitted to rise to room temperature. These reactions were allowed to run at least twenty-four hours with stirring. As the higher ketones have only a limited solubility in alkali, it was found more convenient to separate the whole product, after decomposition of the reaction mixture and drying of the extracts, by fractional distillation under diminished pressure.

When the reaction temperature was 2°, the reagents were mixed in a flask cooled by a freezing mixture. The stoppers were coated with paraffin to exclude moisture and the reaction was allowed to run ten days in a refrigerating room, with stirring. In the case of *m*-cresol propionate so treated, 4 g. of *m*-cresol was recovered at the end of the reaction, this corresponding to 17% of the ester used.

The quantities used and the yields of the products are summarized in Table I.

Coulthard, Marshall and Pyman have prepared most of these compounds, and their characterizations agree closely with ours. At the same time, the structure of the higher members depended solely on analogy. It was decided to degrade caproyl *m*-cresol by oxidation. When methylated with sodium methylate and dimethyl sulfate, and then oxidized with hot aqueous

(4) Lederer, *J. prakt. Chem.*, [II] **135**, 49 (1932).

TABLE I

Ester of <i>m</i> -cresol used Acyl group	Wt., g.	B. p., °C. (mm.)	Temp. of reaction, °C.	<i>o</i> -Hydroxy ketone		M. p., °C. (mm.)	M. p., phenylhydrazone, °C.	<i>p</i> -Hydroxy ketone		M. p., °C.
				Yield G.	%			Yield G.	%	
Propionyl	30	90-92 (5)	120-140	28	93	M. p. 43-44				
Propionyl	21	90-92 (5)	25	15	67	M. p. 43-44			Trace	
Propionyl	36	90-92 (5)	2	23.5	65	M. p. 43-44			3.5	10 117-118
Butyryl	40	89-93 (4)	120-140	30	75	112-115 (4)	97-98			
Butyryl	43	89-93 (4)	25	28	66	112-115 (4)	97-98		Trace	
Butyryl	33	89-93 (4)	2	24	72	112-115 (4)	97-98	1	3	98-99
Valeryl	30	93-95 (2)	120-140	24	80	121-125 (3)	138-139			
Valeryl	20	93-95 (2)	25	14	67	121-125 (3)	138-139			
Caproyl	68	104-105 (2)	120-140	62	91	134-135 (3)	97-97.5			
Caproyl	26	104-105 (2)	25	16	62	134-135 (3)	97-97.5			
Heptylyl	20	112-115 (2)	120-140	14	67	148 (4)	82-83			
Heptylyl	17	112-115 (2)	25	12.5	73	148 (4)	82-83			
Pelargonyl	91	156-162 (4)	120-140	68	75	175-177 (4)				

permanganate solution, it yielded methoxyterephthalic acid, m. p. 278-280°. Consequently, the caproyl group is para to the methyl. The same acid was obtained by similar treatment of 6-acetyl-*m*-cresol.

### Summary

In the Fries isomerization the tendency of the fatty acid esters of *m*-cresol to change to *o*-hydroxy ketones, rather than to para, is greater than has hitherto been supposed. This tendency becomes more marked with esters of the higher acids.

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## The Anhydrides of N-Arylanthranilic Acids

By M. GOODMAN, N. ARBITER AND GARFIELD POWELL

**Introduction.**—Concerning the formulas for the anhydrides of acyl anthranilic acids, of salicylic acids, and of related compounds, there is still some dispute and obscurity.<sup>1</sup> For example, anhydrides of unknown constitution are reported in attempted preparations of chlorides and esters of anthranilic acid,<sup>2</sup> and the only recognized anhydrides of anthranilic acid itself or N-alkyl or N-aryl anthranilic acids are those reported by Schroeter<sup>1b</sup> of the type 2M-2H<sub>2</sub>O (M is the original acid) which

are formulated as 8-ring compounds . It is the purpose

of this communication to show that the hitherto unrecognized acyl anhydride type must be considered in dealing with dehydration products of N-

(1) (a) G. Heller and H. Lanth, *Ber.*, **52B**, 2295 (1919); (b) G. Schroeter and O. Eisleb, *Ann.*, **367**, 144 (1909); (c) R. Spallino, *Gazz. chim. ital.*, **37**, II, 151 (1907).

(2) H. Meyer, *Ann.*, **351**, 267 (1907).