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Selective Action in the Zincke Nitration

L. Chas. Raiford
State University of Iowa

G. R. Miller
State University of Iowa

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MONOBROMOAMINE WITH ORGANOMAGNESIUM HALIDES

GEORGE H. COLEMAN AND CHARLES B. YAGER

The reaction of monobromoamine with organomagnesium halides has been studied and compared with that of monochloroamine¹ with the same reagents. The yields of primary amines obtained from monobromoamine are considerably smaller than those from monochloroamine. Otherwise the reactions are similar.

On account of the instability of monobromoamine it was necessary to develop special methods of preparing, analyzing and working with solutions of this compound.

STATE UNIVERSITY OF IOWA,
IOWA CITY, IOWA.

SELECTIVE ACTION IN THE ZINCKE NITRATION

L. CHAS. RAIFORD AND G. R. MILLER

Zincke¹ studied the action of nitrous acid on the bromine derivatives of the cresols, and found that in the meta series the halogen atom para to hydroxyl is replaced by the nitro radical, while in the ortho and para series the atom ortho to hydroxyl is replaced. In no case did he report the formation of isomeric compounds as a result of a single nitration.

Raiford and collaborators² have shown that isomeric nitro compounds may be obtained from both ortho- and meta-cresol derivatives, as well as from those of phenol, when the halogen is other than chlorine. Recent work has proved that when the starting material contains both chlorine and bromine, the latter only is replaced by the nitro group. If both ortho and para positions are occupied by bromine or by hydrogen, two different products may be obtained. In nearly every instance where isomers are demanded by theory they have been obtained in this work. The relative positions of the hydroxyl and nitro group was determined by reduction to the corresponding aminophenols, and study of the mixed diacyl derivatives. When the amino and hydroxyl radicals are adjacent (ortho) only one acetyl-benzoyl derivative can be prepared, regardless of the order in which these groups are introduced, and in that one the benzoyl radical is attached to nitrogen.

STATE UNIVERSITY OF IOWA,
IOWA CITY, IOWA.

¹ Coleman & Hauser, *J. Am. Chem. Soc.*, 50, 1193 (1928). Coleman & Yager, *J. Am. Chem. Soc.*, 51, 567 (1929).

² Zincke, *J. prakt. Chem.*, (2) 61, 561 (1900).

³ Raiford, *J. Am. Chem. Soc.*, 46, 2246 (1924).