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Modification of the Directive Influence of Substituents in Certain Benzene Derivatives

L. Chas. Raiford
State University of Iowa

M. F. Ravely
State University of Iowa

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mixed melting points of from 4-8°. The N-acyl-*p*-toluenesulfonamides show a depression in mixed melting points of from 8-11°. The *p*-phenylphenacyl esters show a difference in melting points of from 3-6° and a lowering in mixed melting points of from 5-8°.

The carbazole, phenothiazine and 2-nitro-*p*-toludine derivatives, *p*-toluenesulfonamides, *p*-nitroanilides and *p*-xenylamides were prepared by heating the acid chlorides with carbazole, phenothiazine, 2-nitro-*p*-toludine, *p*-toluenesulfonamide, *p*-nitroaniline and *p*-xenylamine, respectively, from 100° to 160° without a solvent. The *p*-phenylphenacyl esters were prepared from *p*-phenylphenacyl bromide and the sodium salt of the acids. The saccharin derivatives were prepared by refluxing the sodium salt of saccharin and the acid chlorides in chloroform. The 2, 4-dinitro-phenylhydrazides were prepared by refluxing the base and the acid chlorides in dry benzene. The phenylmercuric salts were prepared by refluxing diphenylmercury and the acids in xylene.

DEPARTMENT OF CHEMISTRY,
LABORATORY OF ORGANIC CHEMISTRY,
IOWA STATE COLLEGE,
AMES, IOWA.

MODIFICATION OF THE DIRECTIVE INFLUENCE OF SUBSTITUENTS IN CERTAIN BENZENE DERIVATIVES

L. CHAS. RAIFORD AND M. F. RAVELY

Bromination of vanillin, 3-methoxy-4-hydroxybenzaldehyde, gives a yield of 88-90 per cent of the 5-bromo compound which indicates that the chief directive influence is exerted by hydroxyl. If the hydroxyl radical is first acylated and the resulting acetyl or benzoyl vanillin is brominated, an equally high yield of the 6-bromo derivative is obtained, and no other product can be isolated. Vanillic acid and methyl vanillate likewise give good yields of the corresponding 5-bromo compounds, while the acylated derivatives give the 6-bromo substitution products only. These results indicate that acylation of hydroxyl suppresses its orienting effect and the entrance of bromine into position 6 shows that the methoxy radical then exercises the chief directive influence.

When a meta-directing substituent other than the aldehyde radical occupies position one, bromination of the compound having a free hydroxyl group again gives a high yield of the 5-bromo compound. Thus, 3-methoxy-4-hydroxy-benzonitrile and 3-methoxy-4-hydroxynitrobenzene, respectively, give yields of more than 85 per cent of the required 5-bromo compounds. When the corresponding acetyl derivatives are used starting material is recovered. This raises a number of questions which are now being studied.

LABORATORY OF ORGANIC CHEMISTRY,
STATE UNIVERSITY OF IOWA,
IOWA CITY, IOWA.

n-OCTADECYLAMINE AND DI-*n*-OCTADECYLAMINE AND THEIR DERIVATIVES

WILLIAM HARBER AND HENRY GILMAN

n-Octadecylamine and di-*n*-octadecylamine have been prepared by various methods, and particularly by both the wet and the catalytic reduction of stearonitrile. The report includes a study of new derivatives (some useful for purposes of characterization), and rearrangement reactions.

LABORATORY OF ORGANIC CHEMISTRY,
IOWA STATE COLLEGE,
AMES, IOWA.

NITRATION OF THE TRIBROMO SUBSTITUTION PRODUCT OF *SYM*-XYLENOL

L. CHAS. RAIFORD AND DONALD W. KAISER

In previous work Raiford and Miller[1] showed that when a phenol or cresol containing bromine in both ortho and para positions is treated with nitrous acid, a halogen atom may be replaced by the nitro radical and isomeric mononitro compounds may be formed. Chlorine cannot be replaced in this way.

It has now been found that when 2, 4, 6-tribromo-*sym*-xylenol is treated with nitrous acid, in accordance with the Zincke method of nitration, a mixture of the 4-nitro compound and 2, 6-dibromo-

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[1] J. Am. Chem. Soc., 55, 2131 (1933).