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High Molecular Weight Fatty Acid Derivatives

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FORMATION OF HETEROCYCLIC COMPOUNDS FROM HALOAMINES

GEORGE H. COLEMAN AND GILBERT E. GOHEEN

N-chloro-N-methyl-n-butylamine has been prepared and found to be a relatively stable substance. Ring closure was effected by heating this compound with concentrated sulfuric acid, N-methylpyrrolidine being formed in 45 per cent yields.

The corresponding bromoamine was prepared by the method of Loffler¹ and ring closure effected by heating with concentrated sulfuric acid. The yield of N-methylpyrrolidine was, however, considerably less than with the chloroamine.

Several reagents other than sulfuric acid were tried in an attempt to bring about the same ring closure. However, positive results were obtained only with 85 per cent phosphoric acid.

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HIGH MOLECULAR WEIGHT FATTY ACID DERIVATIVES

GROVER M. FORD AND HENRY GILMAN

A series of derivatives for identifying lauric, myristic, palmitic, stearic and oleic acids have been prepared.

The ten best series of derivatives may be listed in the following order of decreasing importance: (1) N-acylcarbazole derivatives; (2) N-acyl-*p*-toluenesulfonamides; (3) *p*-phenyl-phenacyl esters; (4) N-acylphenothiazine derivatives; (5) N-acyl-2-nitro-*p*-toluidine derivatives; (6) N-acylsaccharin derivatives; (7) 2, 4-dinitrophenylhydrazides; (8) *p*-nitro-anilides; (9) phenylmercuric salts; (10) *p*-xenylamides.

The N-acylcarbazole derivatives show a difference in melting points of adjacent members of from 3-5°, and a depression of

¹ Loffler, Ber., 42: 3427 (1909).

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*-toluidine derivatives, *p*-toluenesulfonamides, *p*-nitroanilides and *p*-xenylamides were prepared by heating the acid chlorides with carbazole, phenothiazine, 2-nitro-*p*-toluidine, *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.

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MODIFICATION OF THE DIRECTIVE INFLUENCE OF SUBSTITUENTS IN CERTAIN BENZENE DERIVATIVES

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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