oxide and the esters over alumina, then the conclusion as to relative tendency for ring formation would be false; for, if the ease of dehydration of *iso*propanol as compared with ethanol had been measured over a certain zinc oxide, the conclusion then would have been that ethanol is more readily dehydrated than *iso*propanol, which we know to be untrue. It is not safe, therefore, to determine susceptibility for a given reaction under conditions such that the product or reaction we are interested in is only one of two or more simultaneous reactions.

Summary[5]

The outline and results of the experimental work have been so concisely stated in the second and in the numbered paragraphs of the paper that they need not be repeated here.

It has been further demonstrated that there are two distinct and almost unrelated sets of factors having to do with the catalytic reactions of the type here considered. One phase of the problem has to do with the amount of material entering into reaction, and the other with the proportions of the competing reactions.

The hypothesis as to the importance of the spacial configuration of the catalyst surface in determining the proportion of reaction products has been concisely restated. The validity of this and other hypotheses has been considered in the light of recent experimental work.

The relative reactivity, even of the members of an homologous series, may not be determined by noting the amount of a given end-product when that product represents only one of two or more simultaneous reactions, for the proportions of this product may be more a function of the particular conditions of the reactions than it is of the compounds under comparison.

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ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. I

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When certain di-acyl derivatives of *o*-aminophenol are prepared in which one acyl group is attached to the oxygen and a different acyl group is attached to the nitrogen, several products are possible, depending on the acyl groups used and the order in which they are introduced into the *o*-aminophenol molecule.

Introduction of two different acyl groups in reverse order does not usually result in an isomeric di-acyl derivative, but either may result in the derivative obtained when the first order of introduction was used, or the

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[5] The formation of carbon dioxide and of resins from alcohols over zinc oxides is discussed by the same authors in the June number of the *Journal of Physical Chemistry*.

product may be an equilibrium mixture of the two isomeric di-acyl derivatives.

A review of the literature on this subject may be had by referring to the work of Ransom,[1] Ransom and Nelson,[2] and Raiford with co-workers.[3]

Nelson and Davis[4] have shown that when closely related alkyl groups such as the methyl or ethyl groups, attached to carbonyl groups, are used in the acylation of *o*-aminophenol, together with the carbethoxy group, the carbethoxy group is attached to the nitrogen regardless of the order in which the groups are introduced. A molecular rearrangement occurs, when necessary, to effect this.

The following experiments were carried out to determine whether closely related alkyl groups, both attached to carbonyl groups, would have any effect on the rearrangement. The following pair of acyl radicals was used: $COCH_3$ and COC_2H_5. *o*-Aceto-aminophenol was acylated with propionic anhydride. The resulting product melted between 57° and 75°, and a constant melting point could not be obtained by repeated recrystallization. The product apparently was an equilibrium mixture of the two di-acyls, *o*-aceto-aminophenyl propionate and *o*-propionylaminophenyl acetate, with the former di-acyl present in the greater amount. Saponification yielded only *o*-aceto-aminophenol. If the acetyl group rearranged from nitrogen to oxygen to some extent in the preparation, the reverse change occurred during saponification.

When *o*-propionylaminophenol was acylated with acetic anhydride, a product identical in appearance with that mentioned above was obtained but it was less soluble in ligroin and melted between 85° and 103°. It could not be recrystallized to a constant melting point.

The product is probably an equilibrium mixture of *o*-propionylaminophenyl acetate, in the greater amount, with *o*-aceto-aminophenyl propionate. Saponification yielded as the sole product *o*-aceto-aminophenol. The propionyl group migrated completely to the oxygen from the nitrogen during saponification.

Experimental Part

***o*-Aceto-aminophenyl Propionate,** ($C_2H_5CO.OC_6H_4NHCOCH_3$).—To a solution of 5.15 g. of *o*-aceto-aminophenol in 20 cc. of 10% potassium hydroxide solution (slightly more than one equivalent) was added 5 cc. (a slight excess over one equivalent) of propionic anhydride. The solution was shaken for some time and allowed to stand for 24 hours. It was then extracted several times with ether. The ether left a light brown solid which was moderately soluble in ligroin, b. p. 60–70°, from which it crys-

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[1] Ransom, *Am. Chem. J.*, **23,** 1 (1900).

[2] Ransom and Nelson, THIS JOURNAL, **36,** 390 (1914).

[3] Raiford and others, *ibid.*, (a) **41,** 2068 (1919); (b) **44,** 1792 (1922); (c) **46,** 430, (d) 2246, (e) 2305 (1924); (f) **47,** 1111 (1925).

[4] Nelson and Davis, *Indiana Acad. Sci.*, **1921,** 201–202.

tallized in clusters of white needles, radiating from a common point. The yield was nearly that calculated. The product was soluble in the ordinary organic solvents.

No definite melting point on this material could be obtained. Different series of crystallizations using products from different preparations gave fluctuating melting points ranging from 57° to 75°.

It is suggested that this product is mostly *o*-aceto-aminophenyl propionate in equilibrium with a small amount of *o*-propionylaminophenyl acetate.

Microscopic examination of the crystals showed only one type of crystals.

The analysis is that required by the presence of an acetyl and a propionyl radical.

Anal. Calcd. for $C_{11}H_{13}NO_3$: N, 6.76. Found: 6.81.

On saponification with 10% alkali and acidulation, a white solid precipitated which after recrystallization melted at 200–201°. A mixed melting point with *o*-aceto-aminophenol showed it to be identical with the latter.

If the two acyl groups had exchanged positions to any extent in the di-acyl compound, the reverse change occurred during saponification. No trace of any other saponification product was found.

***o*-Propionylaminophenyl Acetate,** ($CH_3CO.OC_6H_4NHCOC_2H_5$).—Following a similar procedure of treating *o*-propionylaminophenol with acetic anhydride a product was obtained which was very similar to the product formed when the acyl groups were introduced in the reverse order. However, it was less soluble in ligroin and the melting points were higher, ranging from 85° to 103°.

Microscopic examination of the crystals showed no different forms.

It is suggested that this product is mostly *o*-propionylaminophenyl acetate in equilibrium with a small amount of *o*-aceto-aminophenyl propionate.

The analysis corresponds to that of a di-acyl containing propionyl and acetyl groups.

Anal. Calcd. for $C_{11}H_{13}NO_3$: N, 6.76. Found: 6.69.

On saponification with 10% alkali and acidulation a white solid precipitated which after recrystallization melted at 200–201°. A mixed melting point with *o*-aceto-aminophenol showed it to be identical with the latter.

The saponification shows that the acetyl group occupied the position formerly held by the propionyl group. If the propionyl group had only partly rearranged, the rearrangement was completed during saponification of the di-acyl.

Summary

When the methyl and ethyl groups, both attached to carbonyl groups, are used in the acylation of *o*-aminophenol, a partial rearrangement occurs in the di-acyl, regardless of the order in which the groups are introduced. When the acetyl group is first put on oxygen, although a partial rearrangement may have occurred in the di-acyl, saponification causes a complete rearrangement so that the acetyl group is finally found attached to the nitrogen.

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