

ACYL DERIVATIVES OF O-AMINOPHENOL.

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When o-aminophenol, ($\text{HOC}_6\text{H}_4\text{NH}_2$), is acylated with two different acyl groups, one group attaches itself to the nitrogen and the other to the oxygen, forming a stable diacyl compound. In attempting to prepare the isomer of the above compound, the isomer rearranges spontaneously forming the same diacyl compound. A molecular rearrangement takes place and the group finally found attached to the nitrogen depends on the two acyl groups used.

Saponification of the diacyl compound removes the acyl group attached to the oxygen first.

If the remaining hydrogen of the acylated amino group be replaced by an alkyl group no rearrangement takes place.

A typical example of this rearrangement is found in Ransom's¹ work. He acylated oxyphenylurethane, ($\text{HOC}_6\text{H}_4\text{NHCO}_2\text{C}_2\text{H}_5$), with benzoyl chloride in alkaline solution. The attempt to prepare the isomer of benzoyloxyphenylurethane, ($\text{C}_6\text{H}_5\text{CO.OC}_6\text{H}_4\text{NHCO}_2\text{C}_2\text{H}_5$), by acylating benzoyl-o-aminophenol, ($\text{HOC}_6\text{H}_4\text{NHCOC}_6\text{H}_5$), with ethyl chloroformate in alkaline solution, resulted in the formation of benzoyloxyphenylurethane, the carbethoxy group,— $\text{CO}_2\text{C}_2\text{H}_5$, occupying the position formerly held by the benzoyl group.

Ransom and Nelson² observed similar rearrangement in attempting to prepare the isomer of carbamyl o-oxyphenylethylurethane, ($\text{C}_7\text{H}_{11}\text{CO}_2\text{OC}_6\text{H}_4\text{NHCO}_2\text{C}_2\text{H}_5$).

If an acyl group is attached to the oxygen of o-nitrophenol and the acylated nitrophenol is reduced the resulting free base rearranges. The acyl group exchanges position with one hydrogen of the amino group.

Stieglitz and Upson³ investigated the time of arrangement of a number of substituted monoacyl derivatives of o-aminophenol, substituting chlorine, bromine and the methyl group about the ring, and concluded that, "the more or less positive character of the amino group, as shown by the affinity constants, does not seem to have any paramount influence in determining the tendency of the base to undergo rearrangement, as measured by the rate of rearrangement", but that, "the velocity constant depends more on changes affecting the neighboring carbalkoxyl groups".

Raiford⁴ did not find the rearrangement of diacyl derivatives affected by the substitution of negative groups about the ring.

From the previous work done it seems that the diacyl derivatives of o-aminophenol tend to undergo rearrangement regardless of the

¹ Amer. Chem. Journ. Vol. 23, No. 1, 1.

² Jour. Amer. Chem. Soc. Vol. 36, N 2, 390.

³ Amer. Chem. Journ. Vol. 31, No. 1, 497.

⁴ Journ. Amer. Chem. Soc. Vol. 41, No. 12, 2068.

weight of the two acyl groups concerned, or whether the latter possess carbonyl or carboxyl groups. Neither does the substitution of negative groups about the benzene nucleus affect the tendency to rearrange.

The purpose of this investigation has been principally (1), to determine whether closely related alkyl radicals in the aliphatic acyl groups affected the rearrangement, and (2) to determine whether the same alkyl radical in the different acyl groups affected the rearrangement.

EXPERIMENTAL PART.

Acetyloxyphenylurethane, ($\text{CH}_3\text{CO}.\text{OC}_6\text{H}_4\text{NHCO}_2\text{C}_2\text{H}_5$), was prepared from oxyphenylurethane and acetic anhydride in alkaline solution. White needle-like crystals melting at 72.9° to 73.4° were obtained from ligroin. On saponification oxyphenylurethane was obtained, showing the carbethoxy group to be attached to the nitrogen in acetyloxyphenylurethane.

Action of Ethylchlorformate on o-Acetylaminophenol.

When *o*-acetylaminophenol, ($\text{HOC}_6\text{H}_4\text{NHCOCH}_3$), is treated with ethylchlorformate in alkaline solution acetyloxyphenylurethane, and not its isomer, is obtained. The product of saponification is oxyphenylurethane, showing the carbethoxy group attached to the nitrogen where the acetyl group had been.

In connection with the behavior of the acetyl group, Raiford's work with unsubstituted *o*-aminophenol was repeated and the exchange of position between the acetyl and benzoyl groups observed.

Propionyloxyphenylurethane, ($\text{C}_2\text{H}_5\text{CO}.\text{OC}_6\text{H}_4\text{NHCO}_2\text{C}_2\text{H}_5$), was prepared from oxyphenylurethane and propionic anhydride in alkaline solution. Crystals of long, white, silken needles melting at 41.7° to 42.4° were obtained from dilute alcohol. Saponification showed the carbethoxy group to be attached to the nitrogen.

Propionyl-o-aminophenol, ($\text{HOC}_6\text{H}_4\text{NHCOC}_2\text{H}_5$), was prepared from *o*-aminophenol and propionyl chloride in ether solution. Small white, cubical crystals melting at 76.2° to 77.2° were obtained from ligroin slightly diluted with ether.

Action of Ethylchlorformate on Propionyl-o-aminophenol.

On treating propionyl-*o*-aminophenol, in alkaline solution, with ethylchlorformate a diacyl compound is formed identical with, and in fact is, propionyloxyphenylurethane. Saponification yields oxyphenylurethane, showing that the carbethoxy and the propionyl groups had exchanged places.

When two closely related alkyl radicals, one being attached to the carbonyl group and the other to a carboxy group, are used in the preparation of a diacyl derivative of *o*-aminophenol, the acyl group containing the carboxy group is always found attached to the nitrogen. When necessary a molecular rearrangement takes place to effect this.

When the same alkyl radical is used, in one case attached to a carbonyl group and in the other to a carboxy group, the acyl group containing the carboxy group, again, is found attached to the nitrogen.