Benzyl ethers are particularly easily oxidized, the peroxides being partly hydrolyzed into hydrogen peroxide, benzaldehyde and alcohols.

Detroit, Michigan

[Contribution from the Laboratory of Organic Chemistry of the State University of Iowa]

THE ROLE OF WEIGHT OF ACYL IN THE MIGRATION FROM NITROGEN TO OXYGEN. I

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It has been shown[1] that when 2-acetylaminophenol is benzoylated by the Schotten-Baumann reaction, the benzoyl radical is attached to nitrogen while acetyl migrates to oxygen. In reporting these results attention was drawn to the fact that of the two acyl radicals thus far studied the heavier one was always found attached to nitrogen, regardless of the order in which they were introduced. It was suspected at the time, however, that factors other than the relative weights of the acyl radicals might be involved in the behavior observed, and it was explicitly stated that in the work already in progress an attempt would be made to determine whether the migration is dependent on the weights of the groups, their chemical characteristics,[2] or some consideration not yet noted. In the present work, however, it was desired to study the question of weight of acyl particularly, because the results thus far reported from this Laboratory do not agree with those obtained by Ransom[3] and extended by Ransom and Nelson,[4] in which it was found that the lighter of the two acyl radicals was always found on nitrogen.

In the work now reported the three aminophenols on which the first observations were made have been employed, and from them mixed diacyl derivatives were prepared by the use of the acetyl, benzoyl and α-naphthoyl radicals. The α-naphthoyl radical was selected because, in the first place, it is sufficiently heavier than benzoyl, so that it might be used not only to cause the migration of acetyl, but if weight alone were the

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[1] Raiford, This Journal, **41**, 2068 (1919).

[2] Beside the difference in weight between acetyl and benzoyl, the only radicals reported on in the preliminary paper, it was recognized that the difference in structure and acidity of these radicals might have a bearing on their behavior. In a report soon to be published, of which the experimental part has been completed, it will be shown that in the study of the mixed diacyl derivatives obtained by the successive introduction, in both possible orders, of thirteen pairs of radicals into a single *o*-aminophenol, 2-amino-4-methyl-6-chlorophenol, the chemical characteristic of the radical (dependent on composition and structure) may exert a very considerable and, in some instances, apparently decisive influence on the migration.

[3] Ransom, *Ber.*, **31**, 1060 (1898); **33**, 199 (1900); *Am. Chem. J.*, **23**, 1 (1900).

[4] Ransom and Nelson, This Journal, **36**, 390 (1914).

deciding factor it might be expected to displace benzoyl as well. Secondly, it is well known[5] that many naphthalene derivatives show a behavior similar to that of an aliphatic rather than that of a true benzene compound. It was hoped, therefore, that the use of the naphthoyl radical might indicate in some degree whether the deciding factor in the migration is weight or those properties that distinguish a compound as "fatty" or "aromatic."

In deciding between the α- and β-naphthoyl radicals our choice was influenced somewhat by the circumstance that the materials from which α-naphthoyl chloride could be prepared were more readily available than the corresponding isomers. It was recognized at the time, however, that some difficulty might be encountered in the preparation and hydrolysis of alpha derivatives as compared with the isomeric beta compounds. As a matter of experiment, Pinner and Klein[6] found that β-naphthonitrile and ethyl alcohol could readily be converted into the imido-ether by treatment with hydrogen chloride in the usual way, while Pinner[7] was unable to obtain the ether from α-naphthonitrile.

That steric hindrance may possibly be a factor in the hydrolysis of the type of compound here under consideration (O-acyl-N-acyl derivative) is indicated by the fact that although 2-acetylaminophenyl acetate is promptly hydrolyzed by a cold aqueous solution of sodium hydroxide,[8] 2-benzoylaminophenyl acetate is but slowly hydrolyzed under similar conditions,[1] while 2-benzoylaminophenyl benzoate requires boiling with an excess of barium carbonate and water for 24 hours,[9] or for a shorter period with sodium hydroxide solution according to our experience (see experimental part). And, finally, it was assumed that if, as in previous cases, the heaviest radicals were here always found attached to nitrogen, the evidence would not only support the view that weight of the acyl radical is an important factor in the migration, but it would tend to indicate that the rearrangement is not prevented by the presence of an *ortho* substituent which in many reactions causes notable retardation.[10]

Experimental Part

α-Naphthoic Acid.—To secure starting material for this work an attempt was made to prepare α-naphthoic acid by hydrolysis of the corresponding nitrile as directed by Hofmann.[11] The nitrile was obtained by

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[5] Graebe, *Ber.*, **13**, 1849 (1880). Liebermann and Hagen, *Ber.*, **15**, 1427 (1882).

[6] Pinner and Klein, *Ber.*, **11**, 1485 (1878).

[7] Pinner, *Ber.*, **23**, 2917 (1890).

[8] Bamberger, *Ber.*, **36**, 2050 (1903).

[9] Hübner, *Ann.*, **210**, 387 (1881).

[10] Woolfolk (unpublished report), working in this Laboratory, has shown that when the acetyl and benzoyl radicals are used the presence of bromine atoms adjacent to the amino and hydroxyl groups of the base does not prevent the migration.

[11] Hofmann, *Ber.*, **1**, 39 (1868).

dry distillation of a mixture of sodium α-naphthalene-sulfonate and potassium cyanide as directed by Merz and Mühlhäuser[12] in their method for the "preparation of naphthoic acid in quantity." The desired products were obtained in each case, but the yields were so low that other methods were tried. The one finally adopted was a slight modification of that described by Acree[13] which, according to our experience, surpasses any other published method for rapidity, ease of manipulation, high yield and purity of product.

Commercial α-bromonaphthalene was dried for several hours over calcium chloride and distilled. The fraction boiling between 277° and 281° was retained for this work. Fifty g. of this material was dissolved in 250–300 cc. of dry ether, the Grignard reagent prepared in the usual way, and dry carbon dioxide passed in.[14] The reaction mixture was decomposed by 6 N hydrochloric acid instead of sulfuric as used by Acree, and the crude acid isolated in the usual way. Though portions of the product were obtained in a colorless condition by crystallization from 95% alcohol and from glacial acetic acid, the most satisfactory means of purification was that employed by Colver with Noyes[15] for the isomeric beta compound. Treated in this way our product gave, after one crystallization from glacial acetic acid, fine colorless needles that melted at 160°, which is in accord with the literature. Yields varying from 70 to 90% were obtained.

α-Naphthoyl Chloride.—A mixture of equimolecular proportions of the acid and phosphorus pentachloride was heated on a water-bath until the mass was liquid, as directed by Hofmann, after which phosphorus oxychloride was removed, and the acid chloride distilled under reduced pressure. It was obtained as a pale yellow liquid boiling at 187° (23 mm.).[16] Unless protected from the moisture of the air a small portion was hydrolyzed during distillation.

2-Acetylaminophenol.—The first lot of this material we prepared by the method of Tingle and Williams,[17] and obtained a low yield of a highly colored product. A much more satisfactory result was obtained by following the directions of Lumière and Barbier.[18] Forty g. of commercial, highly colored *o*-aminophenol was dissolved in 300 cc. of water containing 1.2 molecular proportions of sodium hydroxide, the mixture filtered, and 1.2 molecular proportions of acetic anhydride added to the filtrate while the mixture was shaken. When the liquid had stood for a few minutes one molecular proportion of hydrochloric acid was added, and the resulting precipitate removed by filtration. Since a considerable amount of the diacylated compound was present in this

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[12] Merz and Mühlhäuser, *Ber.*, **3**, 709 (1870).

[13] Acree, *Ber.*, **37**, 625 (1904).

[14] When too small a volume of ether was used, or the solution was not well stirred during the cooling that immediately preceded the saturation with carbon dioxide, it was found that the reaction product often settled out as a solid mass that did not readily absorb the gas.

[15] Colver with Noyes, THIS JOURNAL, **43**, 902 (1921).

[16] Braun [*Ber.*, **38**, 180 (1905)] recorded 175° (15 mm.), and stated that reduced pressure prevents the formation of a tarry residue, and thus improves the yield. In our work such a residue was observed in each experiment at this point. When distilled at atmospheric pressure the product boiled at 297° as observed by Hofmann, the tarry residue was not appreciably greater than under reduced pressure and the yield was about the same.

[17] Tingle and Williams, *Am. Chem. J.*, **37**, 57 (1907).

[18] Lumière and Barbier, *Bull. soc. chim.*, [3] **33**, 784 (1905).

solid (although no reference was made to this by the authors) it was at once dissolved in a solution of caustic alkali, which rapidly hydrolyzed the diacyl derivative at the O connection, the liquid was filtered and the N-acylated compound reprecipitated by the addition of acid. The product was highly colored and melted at 199–200°. After partial decolorization by boiling its solution in 30% acetic acid with bone black, the filtered liquid deposited plates that melted at 201° as observed by Ladenburg.[19]

2-α-Naphthoylaminophenyl Acetate.—An attempt was made to prepare this compound by the Schotten-Baumann method by treatment of 2-acetylaminophenol in a solution of caustic alkali with α-naphthoyl chloride. A brownish liquid separated which after a few hours' standing became a sticky solid. It was removed by filtration and crystallized from dil. alcohol. α-Naphthoic acid was identified, and 2-acetylaminophenol was found in the filtrate. When the whole experiment was repeated with the exception that 2-acetylaminophenol was substituted by phenol, a quantitative yield of α-naphthoic acid was recovered, which indicated that α-naphthoyl chloride does not readily participate in the Schotten-Baumann reaction.[20]

The method finally adopted for the introduction of this acyl radical was that employed (with other acylating agents) by Einhorn and Hollandt,[21] with the modifications mentioned below. Three g. of 2-acetylaminophenol was dissolved in 20 cc. of pyridine, and 4 g. of α-naphthoyl chloride added, which caused the evolution of considerable heat. The mixture was allowed to stand overnight after which it was poured into 200 cc. of dil. sulfuric acid. It was subsequently found that the precipitate which separated at this point could be more easily handled when the pyridine solution was treated with an equal volume of water before being mixed with the acid. The solid obtained in this experiment weighed 6.5 g., which is nearly a quantitative yield. It was washed with ammonium carbonate solution to remove traces of α-naphthoic acid, and then with dil. sulfuric acid and finally with water. When dried on a clay plate, it melted at 120–130°. Repeated crystallization from alcohol gave fine pinkish-colored needles that radiated from common centers, and melted at 133°. The compound is soluble in most organic solvents except ligroin. Caustic alkali solution does not dissolve it at once, which indicates a diacyl derivative. Analyses for nitrogen indicate the presence of both acetyl and naphthoyl radicals.

Analyses. Subs., 0.1160, 0.2950: 4.43 cc., 10.56 cc. of N (corr.). Calc. for $C_{19}H_{15}O_3N$: N, 4.59. Found: 4.77, 4.55.

2-α-Naphthoylaminophenol.—Two g. of the diacyl derivative just described was allowed to stand overnight in contact with 100 cc. of a 1% solution of sodium hydroxide. Only a small portion of solid remained, and this was removed by filtration, after which the filtrate, which was yellow, was acidified with hydrochloric acid. A white flocculent precipitate settled out. When this was collected and dried it weighed 1.7 g., nearly a quantitative yield. The crude material melted at 183–184°; repeated crystallization from alcohol gave colorless masses which to the unaided eye had the appearance of cotton, but under the lens were seen to be very fine needles. They melted at 190°. The compound was soluble in a solution of caustic alkali from which it was precipitated unchanged by acids, indicating its phenolic character. Analysis for nitrogen agreed with the presence of a naphthoyl radical.

Analysis. Subs., 0.1560: 6.37 cc. of N (corr.). Calc. for $C_{17}H_{13}O_2N$: N, 5.32. Found: 5.11.

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[19] Ladenburg, *Ber.*, **9**, 1524 (1876).

[20] Further work by Miss E. A. Mackintosh (unpublished research) in this Laboratory has shown that the reaction does take place with amines, unless they contain highly acidic substituents, but not with phenols so far as tested.

[21] Einhorn and Hollandt, *Ann.*, **301**, 99 (1898).

Proof of the Structure of 2-α-Naphthoylaminophenyl Acetate.—*o*-Aminophenol was purified by crystallization from water, dried and suspended in ether as directed by Ransom for the preparation of N-acyl derivatives. The mixture was shaken while one-half molecular proportion of α-naphthoyl chloride was added to it. The resulting solid was collected on a filter, washed well with water and dried. After two crystallizations from dil. alcohol it melted at 190°, and showed the same solubility relations as the product obtained by hydrolysis of the diacyl derivative described above. A mixture of the two products melted at 190°.

The material here in question was further characterized by converting it into a diacyl compound by heating it with an equal weight of anhydrous sodium acetate and acetic anhydride. After extraction with water to remove sodium salt, the residue was crystallized from alcohol. It melted at 132–133° and did not depress the melting point of the acetyl-naphthoyl derivative described above.

2-α-Naphthoylamino-4-methyl-6-bromophenyl Acetate.—The starting material in this preparation was *p*-cresol which was converted into the 2,6-dibromo derivative (OH = 1) as directed by Zincke and Wiederhold.[22] The product was nitrated by a modification[23] of Zincke's method which replaced one of the bromine atoms by a nitro group. The substance thus obtained melted at 68–69° and showed the other properties recorded by Thiele and Eichwede[24] who prepared it in a different way. Reduction of this material with stannous chloride and hydrochloric acid in the usual manner gave the hydrochloride of the amino cresol which was immediately converted into the N-acetyl derivative by Lumière and Barbier's method which was previously referred to. The resulting compound had the melting point and other properties recorded by Raiford[1] who obtained it by hydrolysis of the diacetylated derivative. Three g. of the 2-acetylamino-4-methyl-6-bromophenol was dissolved in 10 cc. of pyridine, and 2.5 g. of α-naphthoyl chloride added while the solution was shaken. The solid that rapidly formed was allowed to stand overnight, after which it was collected on a filter, washed successively with ammonium carbonate solution and dil. sulfuric acid and water, and dried. The product weighed 3.4 g. and melted at 218°. From the filtrate 0.5 g. of additional material melting at the same temperature was recovered, which made a total yield of 78%. The ammonium carbonate washings gave 0.3 g. of α-naphthoic acid. The diacyl derivative was repeatedly crystallized from alcohol from which it separated as colorless fern-like growths of needles that melted at 218°. Analysis for bromine agreed with the presence of both an acetyl and a naphthoyl radical.

Analysis. Subs., 0.1497: AgBr, 0.0703. Calc. for $C_{20}H_{16}O_3NBr$: Br, 20.10. Found: 19.98.

2-α-Naphthoylamino-4-methyl-6-bromophenol.—Two g. of the diacyl derivative described above was mixed with a solution of sodium hydroxide containing 1.5 g. of alkali in 80 cc. of water, and the mixture allowed to stand for 24 hours. The portion of solid that had not been hydrolyzed was removed by filtration, the clear filtrate acidified, and the precipitated mono-acyl compound removed, washed and dried. In this condition it melted at 149–150°, while crystallization from alcohol gave colorless needles melting at 151°. Further treatment of the non-hydrolyzed residue for 24 hours with a 10% solution of alkali gave 0.7 g. of the product melting at 151°, and left 0.7 g. of material that was identified by mixed melting point determination as unchanged diacyl derivative. Thus, from 1.3 g. which was hydrolyzed 1.2 g. of product was secured, which is nearly a quantitative yield. The compound was soluble in solutions of caustic alkali

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[22] Zincke and Wiederhold, *Ann.*, **320**, 202 (1902).

[23] Raiford, *Am. Chem. J.*, **46**, 426 (1911).

[24] Thiele and Eichwede, *Ann.*, **311**, 375 (1900).

from which acid precipitated it unchanged, indicating its phenolic character. Analysis for bromine agreed with a formula requiring one naphthoyl radical.

Analysis. Subs., 0.1933: AgBr, 0.1012. Calc. for $C_{18}H_{14}O_2NBr$: Br, 22.44. Found: 22.28.

Proof of the Structure of 2-α-Naphthoylamino-4-methyl-6-bromophenyl Acetate.—2-Amino-4-methyl-6-bromophenol was dissolved in ether and converted into the N-α-naphthoyl derivative by Ransom's method. This was crystallized from alcohol, and was found to melt at 151° and to show also the other properties of the product obtained by hydrolysis of the diacyl derivative described above. A mixture of the two melted at 151°. The identity of the product in question was further established by treatment of its pyridine solution with acetyl chloride as previously described. The resulting compound had all the properties observed for that one obtained by treatment of 2-acetylamino-4-methyl-6-bromophenol with α-naphthoyl chloride, and a mixture of the two products melted without depression of the melting point.

2-α-Naphthoylamino-4,6-dibromophenyl Acetate.—This compound was prepared by dissolving 3.6 g. of 2-acetylamino-4,6-dibromophenol[1] in 20 cc. of pyridine, and adding 2.5 g. of α-naphthoyl chloride. After the mixture had been shaken for a few minutes, a gray precipitate was formed. The mixture was allowed to stand for six hours. The solid was removed by filtration, washed successively with ammonium carbonate solution, dil. sulfuric acid, and water. When dry it weighed 2.5 g. and melted at 226°. When the first filtrate was poured into dil. sulfuric acid 1.0 g. of the diacyl derivative was obtained, which made a total yield of 91%. No α-naphthoic acid was found in the ammonium carbonate washings. The substance was crystallized from glacial acetic acid, and separated in flocculent, pinkish masses that under the lens appeared to be very fine needles. Analysis for bromine showed that an acetyl and a naphthoyl radical were present.

Analysis. Subs., 0.1942: AgBr, 0.1578. Calc. for $C_{19}H_{13}O_3NBr_2$: Br, 34.52. Found: 34.58.

2-α-Naphthoylamino-4,6-dibromophenol.—One g. of the diacylated compound just described was mixed with 100 cc. of a 2% solution of sodium hydroxide, and the mixture allowed to stand for 24 hours. The portion that had not dissolved was removed by filtration, mixed with 200 cc. of 10% solution of alkali and set aside overnight. Beside the colorless non-hydrolyzed portion there was a yellowish solid which was thought to be the sodium salt of the N-acylamino-dibromophenol in question. When the mixture was diluted to 250 cc. the yellow compound dissolved, and the original material that had not been attacked was removed, washed and dried. It weighed 0.2 g. The combined filtrate was acidified with dil. hydrochloric acid, and the precipitate was collected and dried. This weighed 0.7 g., and was found to darken at about 165° and melt at 175°. Crystallization from alcohol gave colorless needles that melted at 175°. To show that the product here in question was not the 2-acetylamino-4,6-dibromophenol (which melts at 174–175° and could have resulted during the hydrolysis if no rearrangement had occurred when the diacylated derivative was prepared) that was used in preparing the diacyl derivative mentioned above, the two were mixed and melted. The mixture began melting at 135° and was entirely liquid at 150°. Its ready solubility in sodium hydroxide solution indicated a free hydroxyl group, and analysis for bromine agreed with the presence of a naphthoyl radical.

Analysis. Subs., 0.1766: AgBr, 0.1588. Calc. for $C_{17}H_{11}O_2NBr_2$: Br, 37.96. Found: 38.20.

Proof of the Structure of 2-α-Naphthoylamino-4,6-dibromophenyl Acetate.—A portion of 2-amino-4,6-dibromophenol was dissolved in ether, and converted into the N-acyl derivative by treatment with α-naphthoyl chloride as directed by Ransom.

When recrystallized the product was found to melt at 175°, and when melted with the compound obtained by hydrolysis of the acetyl-naphthoyl derivative described above no depression of the melting point was observed. The material here under consideration was further characterized by acetylation. It was dissolved in pyridine, and treated with acetyl chloride as explained above, but without satisfactory results. A second portion was mixed with anhydrous sodium acetate and a considerable excess of acetic anhydride, and heated in an oil-bath at 130–140° for about ten minutes. Extraction of the cooled mass with water and crystallization of the residue from glacial acetic acid gave pinkish needles that melted at 225° and showed the properties of the compound obtained by treatment of 2-acetylamino-4,6-dibromophenol with α-naphthoyl chloride. The two products melted together without depression of the melting point.

2-α-Naphthoylaminophenyl Benzoate.—Four g. of *o*-benzoylamino-phenol[9] was dissolved in 30 cc. of pyridine, and 4 g. of α-naphthoyl chloride was added. After 24 hours this liquid was poured into 250 cc. of water while the mixture was stirred, and the precipitate was collected on a filter, washed and dried. The filtrate, which was milky in appearance, was poured into 200 cc. of dil. sulfuric acid, and the precipitate that resulted was shaken with ammonium carbonate solution which dissolved all but a very small quantity. From the clear liquid obtained by filtration hydrochloric acid precipitated 2.7 g. of a solid that was identified as α-naphthoic acid, which corresponds to about three-fourths of the α-naphthoyl chloride used in the experiment.[25]

The original precipitate was washed, in a Hirsch funnel, with a 0.5% sodium hydroxide solution to remove any unchanged benzoylaminophenol, and the washings were acidified. The precipitate thus obtained was extracted with a solution of ammonium carbonate (in which benzoylaminophenol is not appreciably soluble) to remove any benzoic or α-naphthoic acid which would have been present if the sodium hydroxide used in the previous treatment had hydrolyzed either of the possible diacyl derivatives. Neither acid was recovered from the washings. The solid remaining was identified as *o*-benzoylaminophenol, and weighed 2.0 g. That portion of the original precipitate which did not dissolve in caustic alkali solution was washed with water and dried. It weighed 1.5 g. Attempts to render the action more complete by allowing it to proceed for a longer time, and by conducting it at a higher temperature gave about the same relative amounts of products. Portions of the diacyl derivative crystallized from alcohol and from benzene, respectively, separated as very fine, colorless needles that melted at 176°. Analyses for nitrogen, carbon and hydrogen agreed with the formula assigned.

Analyses. Subs., 0.1718: CO_2, 0.4932; H_2O, 0.0754. Subs., 0.2805: 8.59 cc. of N (corr.). Calc. for $C_{24}H_{17}O_3N$: C, 78.45; H, 4.67; N, 3.81. Found: C, 78.32; H, 4.91; N, 3.83.

Proof of the Structure of 2-α-Naphthoylaminophenyl Benzoate.—One g. of α-naphthoylaminophenol prepared as previously described was dissolved in 100 cc. of water containing 1.2 molecular proportions of sodium hydroxide, 1.2 molecular proportions of benzoyl chloride were added, and the mixture was shaken until the odor of the acid chloride had disappeared. After the resulting solid had been filtered off and dried, it weighed 1.3 g. One-tenth g. of 2-α-naphthoylaminophenol was recovered by treatment of the filtrate with acid. Hydrolysis of the diacyl derivative gave 2-α-naphthoylaminophenol and benzoic acid, both of which were identified by a mixed melting point determination.

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[25] The reason for using this method of freeing the reaction product from α-naphthoic acid instead of pouring the original reaction mixture at once into dilute acid and washing the precipitate thus obtained with ammonium carbonate solution, was that it was feared that if two isomeric diacyl derivatives were present one might be so unstable as to be hydrolyzed by ammonium carbonate.

2-α-Naphthoylamino-4,6-dibromophenyl Benzoate.—To a solution of 1.6 g. of 2-benzoylamino-4,6-dibromophenol in 20 cc. of pyridine was added 1.2 g. of α-naphthoyl chloride. The pink precipitate that formed immediately was allowed to remain overnight, and was then filtered off and washed as previously described. The dry material weighed 1.6 g. and melted at 235°. It was nearly insoluble in alcohol, benzene, ligroin and carbon tetrachloride. It was best crystallized by partial evaporation of its chloroform solution, and gave colorless masses of solid that were crystalline but not well crystallized, and that melted at 235°. When the pyridine filtrate was worked up 0.7 g. additional product was obtained, making the total yield nearly quantitative. Analysis for bromine agreed with the presence of both a benzoyl and a naphthoyl radical.

Analysis. Subs., 0.1029: AgBr, 0.0733. Calc. for $C_{24}H_{15}O_3NBr_2$: Br, 30.44. Found: 30.31.

Proof of the Structure of 2-α-Naphthoylamino-4,6-dibromophenyl Benzoate.—A portion of 2-α-naphthoylamino-4,6-dibromophenol (see above) was benzoylated by the Schotten-Baumann reaction. The crude precipitate obtained melted at 210–215°. After purification as described for the product obtained by treatment of 2-benzoylamino-4,6-dibromophenol with α-naphthoyl chloride, the material here in question melted at 235° also, and a mixture of the two melted at the same temperature. Treatment of the product with a cold 10% solution of sodium hydroxide for three days did not cause appreciable hydrolysis. The mixture was then boiled for an hour, diluted to 400 cc. and filtered. The insoluble residue was identified by its melting point as unchanged material. The filtrate was acidified with hydrochloric acid, and the precipitate collected on a filter and washed with ammonium carbonate solution as indicated above. It melted at 175° and failed to depress the melting point of a known sample of 2-α-naphthoylamino-4,6-dibromophenol when mixed with it.

Summary

1. When the α-naphthoyl radical is introduced into an O-acyl aminophenol in which the acyl is either acetyl or benzoyl, the naphthoyl radical is attached to nitrogen while the lighter radical migrates to oxygen.

2. This work, taken in connection with the fact that benzoyl will cause the migration of acetyl in the same manner, indicates that the relative weight of the acyl radicals is one of the chief factors in the migration.

3. The migration is shown to be more or less independent of the method of acylation, and also of the presence of substituents other than hydrogen in the aminophenol.

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