methylbromo-ethylene was found to be useless as an intermediate in allene syntheses.

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ACETYLBENZOYL DERIVATIVES OF 2-AMINO-7-HYDROXYNAPHTHALENE

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In studies designed to test the configuration of naphthalene and diphenyl, Kaufler[1] and collaborators found that the behavior of certain naphthalene derivatives indicates that Positions 2,6 and 2,7 are more closely related than the plane-surface formula suggests. Thus, the conversion of 2,7-naphthalene-disulfonic acid completely into the 2,6 acid by long heating was interpreted to mean that these substituents render each other labile and that the effect indicates that radicals in Position 2,7 are more closely related than in the 2,6 isomer. Kaufler and Karrer[2] found that when 2,7-diaminonaphthalene reacts with chlorodinitro- and chlorotrinitrobenzene, respectively, but one amino radical is involved. They were able to diazotize only one amino radical,[3] and argued that these results, taken in connection with the formation of a monophthalylnaphthalenediamine could best be explained by a formula which requires the two rings of naphthalene to lie in different planes. Although the rate of hydrolysis of 2-carboxy-7-cyanonaphthalene[4] indicated that these positions are comparable with the *meta* relationship in a benzene derivative, which might suggest in advance that the migration of acyl between nitrogen and oxygen, which is characteristic of acetylbenzoyl derivatives of *o*-aminophenols, would not occur here, it was a matter of interest to us to examine the behavior of such a compound obtained from 2,7-aminonaphthol, because of the rearrangement observed by Raiford and Clark[5] when 8-acetylamino-1-naphthol was benzoylated. The argument of Huggins[6] to the effect that acenaphthene and naphthalic

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[1] Kaufler, *Ber.*, **40**, 3250 (1907); *Ann.*, **351**, 151 (1907).

[2] Kaufler and Karrer, *Ber.*, **40**, 3262 (1907).

[3] This failure to diazotize the second group was probably due to experimental conditions rather than to steric hindrance, in that the reaction may occur in two stages, producing an intermediate aminodiazonium salt that is insoluble in the medium used. Morgan and Micklethwait [*J. Chem. Soc.*, **97**, 2558 (1910)] carried out the experiment in a medium different from that used by Kaufler and Karrer and succeeded in obtaining a bisdiazonium salt.

[4] Kaufler and Thien, *Ber.*, **40**, 3257 (1907).

[5] Raiford and Clark, THIS JOURNAL, **48**, 483 (1926).

[6] Huggins, *ibid.*, **44**, 1615 (1922).

anhydride should be regarded as 1,5 instead of 1,8 derivatives may be neglected in designating the structure of these products, for Fuson[7] has brought experimental proof for at least one well characterized compound involving these positions. He prepared the so-called 1,5-hydroxynaphthoic acid from *o*-bromophenyl-paraconic acid by the Erdmann and Kirchhoff[8] method of ring closure which, apparently, can be interpreted in but one way.

Experimental Part

2-Acetylamino-7-acetoxynaphthalene.—The starting material used in preparing this compound was the sodium salt of 2,7-naphtholsulfonic acid, known commercially as "F acid." It was kindly supplied us by the Cincinnati Chemical Works, Norwood, Ohio, to whom we here express our thanks.

Three hundred g. of sodium hydroxide in small pieces, mixed with 10 cc. of water, was melted in a large copper crucible as directed by Fischer,[9] modified to the extent of providing an asbestos apron securely fastened around the top of the crucible, and extending downward in such a way as to protect the flame from drafts, and keep the walls of the crucible hot. To the fused mass, at about 290°, 30 g. of the sulfonate was added in 10 g. portions with stirring, and the temperature quickly raised to 310°. The mass stiffened very soon, and was at once poured into a warm evaporating dish and stirred to prevent caking. When cool, the melt was dissolved in water and the solution acidified with hydrochloric acid. The precipitated 2,7-dihydroxynaphthalene, purified by repeated crystallization from water, gave colorless needles; m. p., 185°. Ebert and Merz[10] found 186° while Clausius[11] reported 190°. This product was converted into the mono-amino compound as directed by Franzen and Deibel.[12] This required refluxing the dihydroxyl compound with dilute ammonium hydroxide and ammonium sulfite, the latter obtained by passing ammonia and sulfur dioxide into cold 85% alcohol, rather than into the anhydrous liquid as directed by Muspratt.[13] Treatment of the reaction mixture with acid precipitated some unchanged dihydroxynaphthalene, which was filtered off. Addition of alkali to the filtrate precipitated any diamino compound present. From the second filtrate the aminonaphthol was precipitated by carbon dioxide; yield, 15 to 40% in several experiments.

Five g. of 2-amino-7-hydroxynaphthalene, which softened at 197° and melted at 199°,[14] was dissolved in pyridine, treated with a slight excess of acetic anhydride, allowed to stand several hours and poured into water.[15] The precipitate crystallized from dilute alcohol in pale brown needles or leaflets, according to the concentration of the solution; m. p., 156°.

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[7] Fuson, This Journal, **46**, 2779 (1924).

[8] Erdmann and Kirchhoff, *Ann.*, **247**, 372 (1888).

[9] Fischer, "Anleitung zur Darstellung organischer Präparate," Vieweg, Braunschweig, **1922**, p. 63.

[10] Ebert and Merz, *Ber.*, **9**, 610 (1876).

[11] Clausius, *Ber.*, **23**, 520 (1890).

[12] Franzen and Deibel, *J. prakt. Chem.*, [2] **78**, 155 (1908).

[13] Dammer, "Handbuch der anorganischen Chemie," Enke, Stuttgart, **1894**, vol. 2, pt. 2, p. 265.

[14] Franzen and Deibel recorded 201°.

[15] Dimroth, Friedemann and Kämmerer, *Ber.*, **53**, 481 (1920).

Anal. Subs., 0.4862: 19.55 cc. of 0.1 *N* acid. Calcd. for $C_{14}H_{13}O_3N$: N, 5.76. Found: 5.60.

Hydrolysis of the above product with alcoholic sodium hydroxide containing 2.5 molecular proportions of alkali gave the corresponding acetylaminonaphthol, which crystallized from alcohol in plates; m. p., 232°.[16]

2-Acetylamino-7-benzoyloxynaphthalene was prepared from the naphthol described above in 52% yield by the Schotten-Baumann method. Crystallization from absolute alcohol gave colorless needles; m. p., 177°.

Anal. Subs., 0.3236: 10.46 cc. of 0.1 *N* acid. Calcd. for $C_{19}H_{15}O_3N$: N, 4.59. Found: 4.36.

Hydrolysis of this product caused loss of the benzoyl radical and gave the phenolic starting material.

2-Benzoylamino-7-benzoyloxynaphthalene.—This was prepared from the aminonaphthol in nearly quantitative yield by the method indicated above. Crystallization from glacial acetic acid gave colorless needles; m. p., 181°. Sachs[17] found 187.5°. Hydrolysis of this material gave a phenolic compound that was purified by treatment of its sodium salt solution with hydrochloric acid; m. p., 243–246°.[18] Analysis for nitrogen indicated the presence of one benzoyl radical.

Anal. Subs., 0.5066: 19.34 cc. of 0.1 *N* acid. Calcd. for $C_{17}H_{13}O_2N$: N, 5.32. Found: 5.20.

2-Benzoylamino-7-acetyloxynaphthalene was prepared in 96% yield by acetylation of the above-described benzoylaminonaphthol by Dimroth's method. Crystallization from absolute alcohol gave colorless crystals; m. p., 177°. The fact that this melting point is identical with that found for 2-acetylamino-7-benzoyloxynaphthalene, and the further fact that a heavier and more acidic radical in a previous study by Raiford and Couture[19] was found to be replaced by acetyl, suggested the migration of benzoyl from nitrogen to oxygen in this case. A mixture of the N-acetyl-O-benzoyl derivative described above and the product here in question melted at 148°, and hydrolysis of the latter gave the benzoylaminonaphthol from which this diacyl derivative was prepared. Analysis for nitrogen indicated the presence of both acetyl and benzoyl radicals.

Anal. Subs., 0.3980: 12.72 cc. of 0.1 *N* acid. Calcd. for $C_{19}H_{15}O_3N$: N, 4.59. Found: 4.47.

Summary

The acetylbenzoyl derivatives of 2-amino-7-hydroxynaphthalene have been prepared and examined. They were obtained in isomeric forms which did not suffer the rearrangement characteristic of those obtained from *o*-aminophenols.

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[16] Kehrmann and Wolff [*Ber.*, **33**, 1538 (1900)] recorded 220° for this compound. That our product was probably pure is indicated by analysis of the benzoyl derivative given below.

[17] Sachs, *Ber.*, **39**, 3026 (1906).

[18] Repeated attempts to purify this material in other ways failed to change the melting point. The failure to melt sharply was probably due to slight decomposition, which was indicated by change in color during the heating.

[19] Raiford and Couture, THIS JOURNAL, **46**, 2309 (1924).