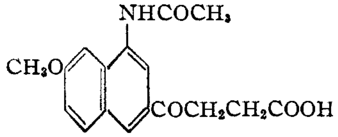
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Succinoylation of 1-Acetylamino-7-methoxynaphthalene

BY LEONARD E. MILLER AND EDWIN F. MORELLO[1]

The reaction of 1-acetylamino-7-methoxynaphthalene with succinic anhydride in nitrobenzene in the presence of aluminum chloride has been found to give β-(1-acetylamino-7-methoxy-3-naphthoyl)-propionic acid (I).



I

The structure of (I) was established by hydrochloric acid hydrolysis, diazotization and deamination using hypophosphorous acid to give the known β-(2-methoxy-6-naphthoyl)-propionic acid (II).[2] The melting points of this acid and its methyl ester were in agreement with those reported. In addition, an alkaline hypochlorite oxidation of (II) produced the known 2-methoxy-6-naphthoic acid (III). Demethylation of (III) with hydrobromic acid in acetic acid gave the known 2-hydroxy-6-naphthoic acid.

Since under similar conditions of reaction the 6-position of 2-methoxynaphthalene is the most reactive one,[2] it may be concluded that the directive influence of the methoxyl group plays the predominant role in the succinoylation of 1-acetylamino-7-methoxynaphthalene in nitrobenzene.

Experimental[3]

1-Acetylamino-7-methoxynaphthalene.—Using Cleve's acid-1,7, this material was prepared by the method of Bachmann and Horton.[4] The procedure used was similar to that given in detail by Wilds and Close[5] for the 1,6-isomer. After distillation at 147° (0.05 mm.), the material crystallized from methanol (Norite) as fine colorless needles, m. p. 160–161°.[4]

β-(1-Acetylamino-7-methoxy-3-naphthoyl)-propionic Acid.—A mixture of 37.6 g. (0.175 mole) of 1-acetylamino-7-methoxynaphthalene and 17.0 g. (0.170 mole) of succinic anhydride was added in small portions to a mechanically stirred, ice-cold solution of 80 g. (0.595 mole) of powdered, anhydrous aluminum chloride in 200 ml. of nitrobenzene. This addition required approximately one hour. After stirring for seventeen hours at 0°, the mixture was poured on 200 g. of ice containing 3 ml. of concentrated hydrochloric acid. The nitrobenzene was distilled off with water vapor at 37° (22 mm.). The solid residue was separated on a filter. The filtrate was heated under reduced pressure once more to remove the residual nitrobenzene. The combined solid residues were treated then with aqueous sodium carbonate. The insoluble material, consisting of starting material and aluminum hydroxide, was removed on a filter. It was treated further with a mixture of ether and aqueous sodium carbonate and was separated on a filter. The combined alkaline filtrates were washed with ether. On acidification with dilute hydrochloric acid, the solid which separated was collected on a filter and permitted to dry in air. It was crystallized from 40% acetic acid to give small colorless needles, m. p. 202–203°; the yield was 45.1 g. (84%). From the ether extracts 1.8 g. of pure starting material was isolated. The yield calculated on the basis of 1-acetylamino-7-methoxynaphthalene consumed was 86%.

Anal. Calcd. for $C_{17}H_{17}O_5N$: C, 64.8; H, 5.4; N, 4.4. Found: C, 64.7; H, 5.7; N, 4.6.

β-(2-Methoxy-6-naphthoyl)-propionic Acid.—A mixture of 43.5 g. of β-(1-acetylamino-7-methoxy-3-naphthoyl)-propionic acid, 150 ml. of water and 300 ml. of concentrated hydrochloric acid was heated under reflux for one hour. On cooling in an ice-bath, the hydrochloride crystallized and was collected on a filter. After one recrystallization from dilute hydrochloric acid, it was used without further purification in the following reaction. The yield was 40.4 g. (94.5%).

Anal. Calcd. for $C_{15}H_{16}O_4NCl$: N, 4.5. Found: N, 4.6.

A mechanically stirred mixture of 10.9 g. (0.035 mole) of the hydrochloride, 100 ml. of glacial acetic acid and 75 ml. of concentrated hydrochloric acid was cooled in an ice-water-bath to 0°. To this suspension of the hydrochloride, 2.9 g. of sodium nitrite in 14 ml. of water was added dropwise very slowly (two hours). At this time 0.5 g. of urea in 5 ml. of water was added to destroy the excess nitrous acid; the mixture was stirred for an additional hour. To the stirred solution at 0°, 87 ml. of ice-cold 50% hypophosphorous acid was added over a fifteen minute period. After being stirred for an additional two hours, the mixture was placed in a refrigerator for thirty-eight hours. After heating on a steam cone for ten minutes, the liquids were removed at 32° (22 mm.). The solid residue was dissolved in aqueous sodium carbonate, filtered and then acidified with dilute hydrochloric acid. After collection on a filter, it was treated with an ethereal solution of diazomethane for a short time (five minutes). The ether solution was washed with cold 2% sodium hydroxide and was dried over magnesium sulfate. After removal of the ether, the residue was evaporatively distilled at 190–195° (0.02 mm.). It crystallized from methanol in long needles, m. p. 97–97.5°.[2]

A solution of 1.8 g. of the methyl ester of β-(2-methoxy-6-naphthoyl)-propionic acid and 4.0 ml. of 10% sodium hydroxide in 100 ml. of methanol was heated under reflux for two hours. On evaporation of the methanol, the solid residue was dissolved in 100 ml. of water. Upon acidification with dilute hydrochloric acid, the free acid precipitated. It crystallized from methanol in shiny colorless plates, m. p. 149.5–150.5°.[2] The yield was 1.6 g. (17.7% based on amine hydrochloride).

2-Methoxy-6-naphthoic acid was prepared from (II) according to Short, Stromberg and Wiles.[2] After five recrystallizations from ethyl acetate colorless needles were isolated, m. p. 200–202° (reported, 205°).

2-Hydroxy-6-naphthoic acid was prepared by the method of Knowles, Kuck and Elderfield[6] from 110 mg. of the methoxynaphthoic acid after heating under reflux for two and one-half hours with 1 ml. of acetic acid, 1 ml. of 48% hydrobromic acid and 1 ml. of acetic acid saturated with hydrogen bromide. It was recrystallized from water (Norite) three times; m. p. 240–242° (reported, 240–241°,[7] 242–244°,[8] 245–248[7]).

---

[1] Present address: University of Minnesota, Minneapolis, Minn.

[2] Short, Stromberg and Wiles, *J. Chem. Soc.*, 319–322 (1936).

[3] All melting points are uncorrected.

[4] Bachmann and Horton, THIS JOURNAL, **69**, 58 (1947).

[5] Wilds and Close, *ibid.*, **69**, 3080 (1947).

[6] Knowles, Kuck and Elderfield, *J. Org. Chem.*, **7**, 380 (1942).

[7] Butler and Royle, *J. Chem. Soc.*, **123**, 1649 (1923).

[8] Cason, THIS JOURNAL, **63**, 828 (1941).

Summary

The reaction of 1-acetylamino-7-methoxynaphthalene with succinic anhydride in the presence of aluminum chloride using nitrobenzene as a solvent proceeds smoothly to give β-(1-acetylamino-7-methoxy-3-naphthoyl)-propionic acid in 86% yield. The structure of the reaction product has been established.

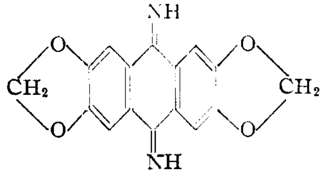
URBANA, ILLINOIS RECEIVED FEBRUARY 4, 1948

[COMMUNICATION NO. 1141 FROM THE KODAK RESEARCH LABORATORIES]

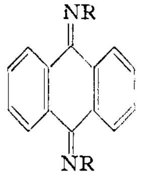
The So-Called "Anthraquinonediimines"; Symmetrical Trisubstituted Triazines

BY C. V. WILSON

Some years ago Brown and Robinson[1] treated 3,4-methylenedioxybenzonitrile with chlorosulfonic acid in chloroform and obtained a substance that was sparingly soluble in the usual solvents, but dissolved in sulfuric acid to give a deep crimson solution. The color of the solution resembled those which are obtained with methoxyanthraquinones and sulfuric acid. On reduction with hydriodic acid followed by zinc dust distillation and subsequent oxidation a product was obtained which gave a positive color test in the oxanthranol reaction. This was interpreted as indicating the presence of anthracene. From these properties and the analysis of the compound, and despite the recorded fact that the substance was unchanged by boiling hydrochloric acid, Brown and Robinson assigned to it the structure I.



I



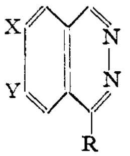
II

Later Keffler[2] attempted a molecular weight determination on the substance but found it so insoluble that he was unable to accomplish his purpose. However, he synthesized two closely related products from veratronitrile and 3-methoxy-4-ethoxybenzonitrile and found them sufficiently soluble in thymol to make possible molecular weight determinations by the cryoscopic method. On the basis of the results he concluded that the products were dimerides of the related nitriles and that the Brown and Robinson formulation was correct.

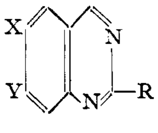
However, the properties recorded for these substances do not resemble those of 9,10-diiminoanthracene (II, R = H). The latter is prepared from the corresponding diamino compound with silver oxide, is soluble in ether, and is easily changed to anthraquinone with aqueous acids.[3] The latter property is also observed for the substituted diiminoanthracenes (II, R = C_6H_5, $CH_3C_6H_4$, etc.).[4] The great stability of the compounds reported by Keffler[2] toward concentrated hydrochloric acid is not compatible with the properties of the simple, unsubstituted 9,10-diiminoanthracene (II, R = H). It is difficult to believe that the substituents would alter this property of the diimine so markedly.

Since substituted anthraquinones that should be obtainable from these diiminoanthracenes were required in connection with another problem in these Laboratories, they were investigated further. A Zerewitinoff determination on the "piperonitrile dimer," prepared as described by Keffler,[2] showed no active hydrogen. This is not in agreement with the proposed structure, which should show two active hydrogens.

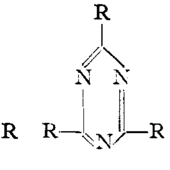
It is possible for the nitriles to polymerize in other ways. Thus they may dimerize by the diene synthesis to give phthalazines (III) or quinazolines (IV), or they may trimerize to triazines of structure V. Unlike the diiminoanthracene structure (I) these compounds would have no active hydrogen.



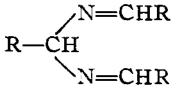
III



IV

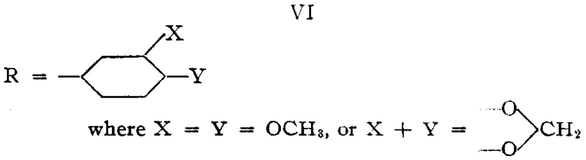


V



$$R-CH\begin{matrix}N=CHR\\N=CHR\end{matrix}$$

VI



where X = Y = OCH_3, or X + Y = $\begin{matrix}-O\\-O\end{matrix}\!\!>CH_2$

A literature survey revealed that the triazine (V, X + Y = $-OCH_2O-$) has been prepared by two different methods, and, surprisingly enough, the melting points recorded were the same as those given by Robinson[1] and Keffler[2] for the so-called dimer. In one of these methods[5] nitro-

---

[1] Brown and Robinson, *J. Chem. Soc.*, **111**, 957 (1917).

[2] Keffler, *J. Chem. Soc.*, **119**, 1476 (1921).

[3] German Patent 590,366 [*Frdl.*, **19**, 1908 (1934)].

[4] German Patent 529,484 [*Frdl.*, **19**, 1907 (1934)].

[5] Davis, *J. Chem. Soc.*, **87**, 1835 (1905).