

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF QUEEN'S UNIVERSITY]

THE PREPARATION OF 1-NAPHTHOIC NITRILE FROM
1-NAPHTHYLAMINE

BY JOHN A. McRAE

RECEIVED AUGUST 22, 1930

PUBLISHED NOVEMBER 5, 1930

In summing up their results on the preparation of 1-naphthoic nitrile by various methods, Whitmore and Fox¹ stated recently that "treatment of 1-naphthylamine by the Sandmeyer reaction gave none of the nitrile." This statement is surprising in itself and is contrary to previous authors to whose work Whitmore and Fox make no reference. Thus, Bamberger and Philp² reported that the Sandmeyer reaction is a good method for the preparation of 1-naphthoic nitrile and Richter³ commented favorably on the same method. Clarke and Read,⁴ using their modification of the usual Sandmeyer process, obtained a yield of 55% of 1-naphthoic nitrile. It was thought of interest to test the validity of Whitmore and Fox's results and accordingly a study of the preparation of 1-naphthoic nitrile has been carried out, principally as a student's exercise, in the course of which various methods used in well-known laboratory textbooks (Gattermann, Cohen, Henle, Fisher) for preparing *p*-toluic nitrile from *p*-toluidine have been employed as a basis, as well as the important improvements described by Clarke and Read and the interesting process of Korczynski⁵ in which potassium nickel cyanide is substituted for potassium cuprocyanide but which had not been applied hitherto to diazotized 1-naphthylamine.

In agreement with earlier work no difficulty has been encountered in obtaining 1-naphthoic nitrile from 1-naphthylamine by the Sandmeyer reaction, the yields varying from 25 to 35%. We were unable to increase the yield beyond 35% but on the other hand we did not discover conditions under which no naphthoic nitrile was produced. The Korczynski method did not give sensibly greater yields than the ordinary Sandmeyer process but by adding the acid diazo solution to potassium nickel cyanide containing sufficient alkali to neutralize the free acid of the diazo solution, the nitrile has been produced repeatedly in yields of 58 to 65%.

My thanks are due to Messrs. F. S. Wilder and J. W. McCutcheon for their assistance in carrying out most of the experimental work.

Experimental

Preparation of 1-Naphthoic Nitrile from 1-Naphthylamine

(a) Using Potassium Nickel Cyanide.—1-Naphthylamine was diazotized by dis-

¹ Whitmore and Fox, *THIS JOURNAL*, **51**, 3363 (1929).

² Bamberger and Philp, *Ber.*, **20**, 241 (1887).

³ Richter, *ibid.*, **22**, 2449 (1889).

⁴ Clarke and Read, *THIS JOURNAL*, **46**, 1001 (1924).

⁵ Korczynski, Mrozinski and Vielau, *Compt. rend.*, **171**, 182 (1920); Korczynski and Fandrich, *ibid.*, **183**, 421 (1926).

solving the amine (28.6 g. = $1/5$ mole) in 600 cc. of hot water and 20 cc. of concentrated hydrochloric acid. With vigorous mechanical stirring the solution was cooled to 0° and maintained at that temperature during the addition first of 50 cc. of concentrated hydrochloric acid and then of a solution of 14.4 g. of sodium nitrite in 60 cc. of water. Any slight excess of nitrous acid was destroyed by the addition of urea.

The cyanide solution was made by adding a solution of 72.7 g. of a good grade of nickel nitrate in 100 cc. of water to a solution (250 cc.) containing 81.4 g. of potassium cyanide and 20 g. of sodium hydroxide. The cyanide solution, contained in a 5-liter flask, was mixed with 150 cc. of benzene and some crushed ice and vigorously stirred while the diazo solution was added during the course of one-half hour. The stirring was continued for another half hour while the temperature was maintained throughout at $0-5^{\circ}$ and for a further two hours while the mixture was allowed to come to room temperature. It was then heated to 50° , cooled and the aqueous layer removed. The residual benzene solution was steam distilled until 5 liters was collected. The benzene which came off was used to collect the nitrile from the distillate. The benzene extract was washed with caustic soda, dried and after removal of the benzene the residue was fractionated under reduced pressure. Redistillation of the first fraction obtained boiling at $120-200^{\circ}$ (20 mm.) gave 17.8 g. of 1-naphthoic nitrile, b. p. $165-170^{\circ}$ (20 mm.), which quickly solidified.

The purity of the nitrile was confirmed by hydrolysis to 1-naphthoic acid, the yield being almost quantitative. No difficulty was experienced in obtaining pure 1-naphthoic acid of m. p. 161° by distillation of the crude acid under reduced pressure, b. p. $229-231^{\circ}$ (50 mm.), and recrystallization of the distilled acid from toluene. This obviated the more lengthy purification of the acid by conversion into the ethyl ester followed by purification and hydrolysis of the ester which Whitmore and Fox found necessary.

(b) **Using Potassium Cuprocyanide.**—1-Naphthylamine was diazotized as described above in preference to diazotization in more concentrated solution corresponding with the laboratory directions given for *p*-toluidine by Fisher⁶ and with that and the further exception that after steam distillation the nitrile was isolated as described above, the diazotized amine was converted into the nitrile according to Fisher's directions for *p*-toluic nitrile. Eight experiments using each time 28.6 g. of amine gave an average yield of 27%. Steam distillation under reduced pressure of the crude product recommended by Clarke and Read⁴ did not increase the yield appreciably. The addition of sodium carbonate to the diazotized naphthylamine seemed to result always in considerable decomposition and to avoid this the acidic diazo solution in several experiments was poured into potassium cuprocyanide solution containing alkali sufficient to neutralize the free acid of the diazo solution as used above with potassium nickel cyanide and as described by Henle⁷ for *p*-toluic nitrile but without more favorable results. Increasing the ratio of potassium cyanide to correspond with $K_3Cu(CN)_4$ gave no better results. To avoid the lengthy steam distillation, extraction of the reaction mixture with ether-benzene was tried but the separation of the extracting liquid is poor and tedious. However, a yield of 26% of the nitrile was obtained from the extract. Addition of the acidic diazo solution to cuprocyanide solution made from potassium cyanide and copper sulfate as described in many laboratory manuals gave similar results.

1-Naphthoic acid may be obtained directly from the crude reaction mixture. The tar which separates in the absence of benzene or after the benzene is removed hardens on cooling and may be collected easily. The tarry residue from treatment of 28.6 g. of 1-naphthylamine was heated for seven hours under a reflux with 100 cc. each of sulfuric

⁶ Fisher, "Laboratory Manual of Organic Chemistry," 2d ed., p. 187.

⁷ Henle, "Anleitung für das organisch-chemische Praktikum," Zweite Auflage, p. 120.

acid, acetic acid and water—the hydrolyzing mixture used by Whitmore and Fox. The mixture was poured into water and from the solid which separated the 1-naphthoic acid was extracted with dilute ammonia. After precipitation from its ammoniacal solution, the crude naphthoic acid was purified as described above. The yields obtained were from 20–25% of the calculated.

Summary

1. Contrary to a recent statement, 1-naphthoic nitrile is produced readily from 1-naphthylamine by the Sandmeyer reaction.
2. Very good yields of this nitrile can be obtained by a slight modification of the Korczynski method.

KINGSTON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE CHEMICAL BEHAVIOR OF SOME BENZENOID HYDROCARBONS IN THE TESLA DISCHARGE

BY JAMES BLISS AUSTIN¹ AND IAN ARMSTRONG BLACK²

RECEIVED AUGUST 22, 1930

PUBLISHED NOVEMBER 5, 1930

Several years ago, during the course of a study of the Tesla luminescence spectra of benzene and some of its simple derivatives, some very interesting facts came to light in connection with the decomposition and behavior of these substances under the action of the Tesla discharge. Aside from the recent note of Harkins³ and Gans on the decomposition of benzene, there appears to be no reliable literature on the subject of the chemical behavior of organic vapors in the electrical discharge; hence it has been thought worth while to record our experiences. It should perhaps be mentioned here that in our preliminary work several methods of excitation were tried. The results with the electrodeless discharge, later discarded because it failed to produce the desired spectra, have already been published⁴ and are in agreement with the findings of Harkins and Gans.

The method finally selected was the Tesla discharge and is described in our previous paper.⁵ However, it soon became evident that even with this discharge chemical changes were occurring in the vapors. This was indicated primarily by the formation on the discharge tube of shellac-like coatings similar to those formed in the electrodeless discharge, although no trace of the hydrogen lines, Swan bands, or ionized carbon lines appeared in the spectra obtained by this method. Moreover, further investigation

¹ From a dissertation presented by J. B. Austin to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

² Commonwealth Fellow 1926–1928.

³ Harkins and Gans, *THIS JOURNAL*, **52**, 2578 (1930).

⁴ Austin, *ibid.*, **52**, 3026 (1930).

⁵ Austin and Black, *Phys. Rev.*, **35**, 452 (1930).