Preparation of Fluoronitronaphthalenes *via* a Modified Schiemann Reaction

By Earl Brill

1-Fluoro-2-nitro-, and 2-fluoro-1-nitro-naphthalene were prepared in 10—15% yields by the diazotisation of the corresponding nitroamine fluoborate salts in tetrahydrofuran, followed by decomposition of the diazonium fluoborate salts. This is the first reported synthesis of 1-fluoro-2-nitronaphthalene.

DURING our studies on the mechanism of chemical carcinogenesis by the aromatic amines it was necessary to prepare 1-fluoro-2-nitro- and 2-fluoro-1-nitro-naphthalene. [We are investigating the possible use of the fluoro-group as a probe *in vivo* to reveal sites in molecules which participate in the carcinogenic process, as suggested by Dr. J. A. Miller and E. C. Miller.[1]]

2-Fluoro-1-nitronaphthalene was first prepared by Schiemann, Gueffroy, and Winkelmuller[2] by the nitration of 2-fluoronaphthalene. However, the product proved to be a mixture of the desired mononitro-compound and higher nitro-compounds. Steam distillation followed by repeated crystallisation (12) failed to yield the pure 2-fluoro-1-nitronaphthalene. Willstaedt and Scheiber[3] reported the preparation of 2-fluoro-1-nitronaphthalene by the diazotisation of 1-nitro-2-naphthylamine, but Schiemann and Ley[4] demonstrated that the product was 1-chloro-2-fluoronaphthalene.

We have prepared 2-fluoro-1-nitronaphthalene and 1-fluoro-2-nitronaphthalene by a modified Schiemann reaction.[5] Using tetrahydrofuran as solvent, 2-nitro-1-naphthylamine and 1-nitro-2-naphthylamine were converted to their corresponding fluoborate salts upon addition of excess fluoboric acid. Diazotisation to the stable diazonium fluoborate salts in 86—94% yields was accomplished by adding an equivalent of sodium nitrite in a minimum of water.

The diazonium fluoborate salts decomposed with violence, resulting in considerable tar formation and low yield, a result not unexpected for salts containing the nitro-group.[6] The decomposition was best accomplished by the addition of small portions of the carefully-dried salt into a flask held 15—20° below the decomposition temperature. This resulted in 10—15% yields of the desired fluoro-compounds.

4-Fluoro-1-nitronaphthalene, previously prepared by the nitration of 1-fluoronaphthalene,[2] was prepared in 40—50% yields by this method. The decomposition of the diazonium fluoborate salt was quite smooth, and in sharp contrast to the compounds with the nitro-group *ortho* to the diazonium group.

EXPERIMENTAL

Melting points were determined in capillary tubes and were corrected. Infrared spectra were obtained with a Perkin-Elmer model 21 spectrophotometer at concentrations of 25 mg./ml. of chloroform.

2-*Fluoro*-1-*nitronaphthalene*.— 1-Nitro-2-naphthylamine (m. p. 127°; lit.,[7] m. p. 127°) was prepared by the nitration of 2-naphthylamine. To a solution of 1-nitro-2-naphthylamine (9·4 g.) in tetrahydrofuran (100 ml.) was added 48—50% fluoboric acid (100 ml.). A heavy yellow precipitate separated on cooling. To the cooled mixture (0°), a saturated aqueous solution of sodium nitrite (4·15 g.) was added dropwise with stirring. After 1 hr. at 0°, the salt was collected and washed with cold 5% fluoboric acid, methanol, and ether. Vacuum drying over H_2SO_4 afforded the golden-coloured diazonium salt (13·5 g., 94%), decomp. 180—181°. This was decomposed by addition of small portions of the dry salt into a large decomposition flask maintained at 160—165°. Water was added directly into the decomposition flask and the product steam distilled. 2-Fluoro-1-nitronaphthalene (1·4 g., 15% based on fluoborate salt) of m. p. 63—64° was obtained as a pale yellow solid. The material was crystallised twice from 95% ethanol to give 1·1 g. of product, m. p. 64—64·5° (lit.,[3] 59—61°); $\lambda_{\text{max.}}$ 1525, 1351, 1266, 1045, 969, 865 cm.$^{-1}$ (Found: C, 63·0; H, 3·3; N, 7·3; F, 9·9. Calc. for $C_{10}H_6FNO_2$: C, 62·8; H, 3·2; N, 7·3; F, 9·9%).

2-Fluoro-1-nitronaphthalene was converted to 2-ethoxy-1-nitronaphthalene (m. p. 102·5—103°; lit.,[2] 103°) by treatment with 2N-ethanolic KOH.

1-*Fluoro*-2-*nitronaphthalene*.— 2-Nitro-1-naphthylamine

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[2] G. Schiemann, W. Gueffroy, and W. Winkelmuller, *Annalen*, 1931, **487**, 270.

[3] H. Willstaedt and G. Scheiber, *Ber*, 1934, **67**, 466.

[4] G. Schiemann and E. Ley, *Ber.*, 1936, **69**, 960.

[5] T. L. Fletcher and M. J. Namkung, *Chem. and Ind.*, 1961, 179.

[6] A. Roe, *Org. Reactions*, 1949, **5**, 210.

[7] C. R. Saunders and C. S. Hamilton, *J. Amer. Chem. Soc.*, 1932, **54**, 636.

(m. p. 142—143°; lit.,[7] m. p. 143°) was prepared by the nitration of 1-naphthylamine. To a solution of 2-nitro-1-naphthylamine (9·4 g.) in tetrahydrofuran (100 ml.) was added 48—50% fluoboric acid (100 ml.). To the cold mixture (0°), an aqueous solution of sodium nitrite (4·2 g.) was added dropwise with stirring. After 1 hr. at 0°, the salt was filtered off and washed with cold 5% fluoboric acid, methanol–ether (1 : 1), and ether. Vacuum drying over H_2SO_4 gave the dark golden-coloured salt (12·3 g., 86%), decomp. 168—169°. The salt (10 g.) was decomposed as described at 140—145° and the product steam distilled. 1-Fluoro-2-nitronaphthalene (0·9 g., 13·53% based on fluoborate salt) of m. p. 96—96·5° was obtained as a bright yellow solid. This was crystallised once from 95% ethanol to yield 0·85 g. of *product*, m. p. 96—96·5°; $\lambda_{\text{max.}}$ 1525, 1350, 1266, 1080, 910, 870 cm.$^{-1}$ (Found: C, 62·7; H, 3·4; N, 7·6; F, 9·8. $C_{10}H_6FNO_2$ requires C, 62·8; H, 3·3; N, 7·3; F, 9·9%).

1-Fluoro-2-nitronaphthalene was converted to 1-methoxy-2-nitronaphthalene (m. p. 80—81°; lit.,[8] 80—81°) by treatment with 2N-methanolic KOH. A mixed m. p. and infrared spectra showed this product to be identical with that produced by the reaction of sodium 2-nitro-1-naphthoxide with methyl sulphate.[8]

1-*Fluoro*-4-*nitronaphthalene*.— 4-Nitro-1-naphthylamine (m. p. 191—192°; lit.,[7] 191°) was prepared by the nitration of 1-naphthylamine. To 4-nitro-1-naphthylamine (9·4 g.) in tetrahydrofuran (100 ml.) was added 48—50% fluoboric acid (100 ml.). Addition of sodium nitrite (4·15 g.) in a minimum of water, as described, yielded a golden-yellow precipitate. The salt was collected by suction filtration, washed with 5% fluoboric acid, methanol, and ether; and vacuum-dried over H_2SO_4; yield 12·0 g., 84%; decomp. 125—126°. The decomposition was carried out by the addition of small portions of the dried salt (10 g.) to a flask at 130°, and the product steam distilled. 1-Fluoro-4-nitronaphthalene (3·4 g., 51% based on fluoborate salt) of m. p. 78—79° was obtained as a bright yellow solid. Crystallisation from 95% ethanol raised the melting point to 80—81° (lit.,[2] 80°). A mixed m. p. and infrared spectra showed this product to be identical with that produced by the nitration of 1-fluoronaphthalene.[2]

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