for the oxidation of toluenes.[2] In the oxidation of naphthalene and 1-nitronaphthalene no carbon dioxide was detected by testing with a solution of barium hydroxide. The determination of the amount of carbon dioxide, evolved during the oxidation of fluorenes, was carried out as follows. The carbon dioxide was swept out by passing dry oxygen-free nitrogen gas. After having been freed of acetic acid with o-chloroaniline and of water with calcium chloride, the carbon dioxide was absorbed by two potash bulbs containing 40% aqueous potassium hydroxide. The increase in weight of the potash bulbs corresponds to that of the carbon dioxide liberated.

DEPARTMENT OF INDUSTRIAL CHEMISTRY
FACULTY OF ENGINEERING
KYOTO UNIVERSITY
KYOTO, JAPAN

A Novel Alkaline Rearrangement in the Naphthalene Series

D. C. MORRISON

Received July 25, 1961

During work in this laboratory on β-substituted naphthalenes, it was decided to attempt to carry out nucleophilic displacement reactions on 2,3-dinitronaphthalene with alkoxides. It was observed that an excess of sodium methoxide in methanol gave, as main product, a compound different from 3-nitro-2-methoxynaphthalene. Further study showed that a nitromethoxynaphthalene had been formed, and it was finally proved by direct comparison to have been 3-nitro-1-methoxynaphthalene. Thus, a rearrangement as well as a displacement had occurred, though the mechanism of this change has not, at present, been demonstrated. It is evidently an addition to the group of cine-substitutions.[1]

Employment of dilute methoxide solution, in a slow reaction, gave some of the 3-nitro-2-methoxynaphthalene, presumably by direct displacement. This isomer can be made the main product, but it is always accompanied by some of the 3-nitro-1-methoxynaphthalene. As the purified 3-nitro-2-methoxynaphthalene did not undergo rearrangement when heated with sodium methoxide solution, simple displacement did not precede rearrangement.

Sodium or potassium hydroxides in methanol also caused the rearranged 3-nitro-1-methoxy compound to form, and the presence of water in the solvent did not prevent the reaction. Higher primary alcohols with potassium hydroxide also reacted with 2-3-dinitronaphthalene to form 3-nitro-1-alkoxynaphthalenes, but at a slower rate than with methanol. Stirring of 2,3-dinitronaphthalene with aqueous potassium hydroxide in the absence of alcohols for twenty-four hours did not give a nitronaphthol but a little unidentified, acidic and perhaps polymeric product.

Authentic 3-nitro-1-naphthol and its methyl ether were prepared from 1-3-dinitronaphthalene by methods described in the literature[2,3] The mixed melting point and infrared spectra of the samples of nitro ether from the two sources were the same.

The 3-nitro-2-methoxynaphthalene was separated from its isomer by crystallization from hexane and from aqueous acetone, and eventually had the same melting point as that given by Woodcock and Clifford.[4] It was hydrolyzed and reduced to 3-amino-2-naphthol, which was also obtained from commercial 2,3-dihydroxynaphthalene by partial amination by Friedlander's method.[5] The infrared spectra of the two preparations were identical.

The fact that 3-nitro-2-methoxynaphthalene can be formed in the reaction would seem to indicate that, in spite of the lower 2,3 bond-order in naphthalene, sufficient activation of one nitro group by the other occurs so that ordinary nucleophilic displacement takes place. Previous efforts in this direction with 3-nitro-2-bromonaphthalene have not succeeded.[6]

Further work on nucleophilic displacements of 2,-3-dinitronaphthalene is being done.

EXPERIMENTAL

Melting points are uncorrected and were taken on a Fisher-Johns block.

Reaction with rearrangement. A solution of 20 g. of sodium methoxide (0.37 mole) in 250 ml. of methanol was treated with 7.5 g. of 2,3-dinitronaphthalene (0.034 mole) with cooling. The mixture was kept in a bath with internal temperature of 45° with stirring for 11 hr. It was then cooled and treated with 1 l. of ice water and kept overnight. The product was filtered, washed with water, and dried. The yield was 6.6 g. or 94.6%. In another run, with 56 g. of sodium methoxide in 700 ml. of methanol, treated with 14 g. of dinitronaphthalene, the mixture was stirred for 4 hr. at 40–45°. The yield was 12.62 g. or 96.8%.

The reaction in methanol with potassium hydroxide was best carried out below room temperature for 1–2 days and yields were poorer than above. By-products were alkali-soluble and seemed to consist of acidic polymers.

After several recrystallizations from aqueous methanol, the 3-nitro-1-methoxynaphthalene had m.p. 103–104°, which was not depressed when mixed with an authentic sample.[2] The infrared spectra of the two samples were identical.

Cleavage of 3-nitro-1-methoxynaphthalene. A solution of 5 g. of the methyl ether in 35 ml. of acetic acid was mixed with 15 ml. of 48% hydrobromic acid and then refluxed for 27 hr. The solution was cooled and diluted with 0.5 l. of water. After 2 hr., the solid was filtered and washed, and then extracted repeatedly with dilute sodium carbonate solution until the extracts were no longer red. The combined dark red extracts were acidified with hydrochloric acid and the

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(1) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(2) A. Bryson, *J. Am. Chem. Soc.*, **82**, 4862 (1960).

(3) D. H. Rosenblatt, M. M. Nachlas, and A. M. Seligman, *J. Am. Chem. Soc.*, **80**, 2463 (1958).

(4) D. Woodcock and D. R. Clifford, *J. Chem. Soc.*, 4139 (1957).

(5) P. Friedlander, *Ber.*, **27**, 761 (1894).

(6) N. McLeish and N. Campbell, *J. Chem. Soc.*, 1103 (1937).

precipitated 3-nitro-1-naphthol filtered and washed. The dry weight was 4.1 g. or 87.2%. The infrared spectrum of this material was identical to that of authentic 3-nitro-1-naphthol,[2] prepared from 1-3-dinitronaphthalene. The ether cleavage could also be carried out by refluxing with 60% sulfuric acid.

Reaction with minimum of rearrangement. A solution containing 10 g. (0.046 mole) of 2,3-dinitronaphthalene and 4 g. (0.074 mole) of commercial sodium methoxide in 0.5 l. of methanol was refluxed for 75 hr. and then cooled and diluted slowly (to prevent oiling out) with 2.5 l. of water. Next day, the deposit was filtered, washed with water and dried; yield, 8.9 g. of product, which by infrared spectra, was about 70% 2,3 isomer and 30% 1,3. The proportion of 2,3 isomer could not be increased beyond about 75% even by very slow addition of the methoxide solution to the refluxing mixture. The ethers were fractionated from hexane and from aqueous acetone, and pure 3-nitro-2-methoxynaphthalene was obtained, m.p. 81–82°. Woodcock and Clifford[4] give m.p. 81–82°.

Cleavage of 3-nitro-2-methoxynaphthalene. A solution of 0.3 g. of the ether in 35 ml. of 60% sulfuric acid was refluxed for 4.5 hr. and cooled. The insoluble product was filtered and washed and then extracted repeatedly with warm dilute sodium carbonate solution. The combined extracts were filtered and acidified. When filtered, washed, and dried, the 3-nitro-2-naphthol weighed 0.25 g. or 89.6% yield. On heating, this substance sintered at 85–90° and melted 102.5–104°; lit.[4] m.p. 103–104°. Cleavage of this ether with hydrobromic acid results in concurrent halogenation, probably to the 1-bromo derivative. Hydrogenation of this nitronaphthol was done with palladium-black on charcoal in methanol solution. The 3-amino-2-naphthol was purified by by making use of its amphoteric properties. It had an infrared spectrum identical to the product obtained by the method of Friedlander,[5] confirming the 2,3 orientation.

Acknowledgment. The author is indebted to W. Morgan Padgett II, Dietrich Heinritz, and Mrs. Dobbie Roisen for valuable discussions and spectral work, to H. P. C. Lee for aid in synthetic work, and to Dr. J. Hyman for encouragement and advice during the work.

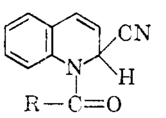
HYMAN LABORATORIES, INC.
BERKELEY, CALIF.

Reissert Compounds Studies. III. Nature of the Isoquinoline[1,2]

FRANK D. POPP AND WILLIAM BLOUNT[3]

Received July 13, 1961

The formation of Reissert compounds[4] (I) from 3-, 4-, 5-, 6-, and 7-substituted quinolines has been shown to be a general reaction[1] when methylene chloride-water is used as the solvent system.[5] In comparison, very little is known about the effect of substituents on the reactivity of the isoquinoline ring in the formation of Reissert compounds (II).



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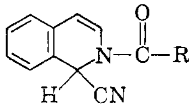
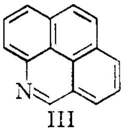


II

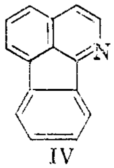
In addition to isoquinoline itself,[6] the formation of Reissert compounds from 6,7-dimethoxyisoquinoline[7,8] and 3-methylisoquinoline[9] has been reported.

The ten isoquinolines shown in Table I and 1-methylisoquinoline have been caused to react with benzoyl chloride and potassium cyanide by the methylene chloride-water method.[5] With the exception of 1-methylisoquinoline each of the isoquinolines gave a Reissert compound. These results indicate that, with the possible exception of 1-substituted isoquinolines, the formation of Reissert compounds from isoquinolines is also a general reaction. In view of the apparent steric effect which prevents Reissert compound formation from 2- and 8-substituted quinolines,[1,4] the failure of 1-methylisoquinoline is not surprising.

Substances giving the correct analysis for Reissert compounds were also obtained from 1-azapyrene (III) and 2-azafluoranthene (IV). Both III and IV can be considered substituted isoquinolines. The formation of a Reissert compound from IV was not expected in view of the failure of 1-methylisoquinoline to react. The nature of this material will be investigated further at a latter date.



III



IV

All the Reissert compounds listed in Table I and the one from III gave benzaldehyde on acid-catalyzed hydrolysis.[10,11] As was the case with the nitroquinolines[1], the Reissert compounds from 5-nitro- and 8-nitroisoquinoline gave only a low yield of benzaldehyde, although a higher yield was obtained from the corresponding nitro-3-methylisoquinolines.

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[1] Part II, F. D. Popp, W. Blount, and P. Melvin, *J. Org. Chem.*, **26**, 4930 (1961).

[2] Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961. This work was supported in part by a grant from the Research Corp.

[3] A portion of this work has been abstracted from the M.S. thesis of W.B.

[4] W. E. McEwen and R. L. Cobb, *Chem. Revs.*, **55**, 511 (1955).

(5) F. D. Popp and W. Blount, *Chem. & Ind.*, 550 (1961).

(6) A. Reissert, *Ber.*, **38**, 3415 (1905).

(7) R. D. Haworth and W. H. Perkin, *J. Chem. Soc.*, **127**, 1434 (1925).

(8) F. D. Popp and W. E. McEwen, *J. Am. Chem. Soc.*, **79**, 3773 (1957).

(9) I. W. Elliott, Jr., *J. Am. Chem. Soc.*, **77**, 4408 (1955).

(10) W. E. McEwen, R. H. Terss, and I. W. Elliott, *J. Am. Chem. Soc.*, **74**, 3605 (1952).

(11) R. L. Cobb and W. E. McEwen, *J. Am. Chem. Soc.*, **77**, 5042 (1955).