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.

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

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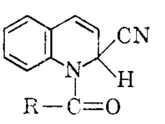
Received July 13, 1961

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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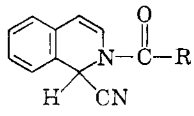
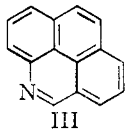


II

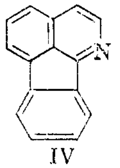
In addition to isoquinoline itself,[6] the formation of Reissert compounds from 6,7-dimethoxyisoquinoline[7,8] and 3-methylisoquinoline[9] has been reported.

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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(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.

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TABLE I

ISOQUINOLINE REISSERT COMPOUNDS

Substituent	M.P.[b]	Yield, % Method A[c]	Yield, % Method B[d]	Calcd., % C	Calcd., % H	Calcd., % N	Found, %[a] C	Found, %[a] H	Found, %[a] N	Yield, % Benzaldehyde[e]
H	125–126[f]	69	72							95
4-Amino-[g]	158[h]	20				11.08			11.12	90
4-Bromo-	173	38	0	60.20	3.27		60.45	3.46		90
5-Hydroxy-[i]	198	68				7.37			7.38	90
5-Nitro-	148	10	0	66.88	3.63	13.77	66.95	3.65	13.82	12
8-Nitro-	181	9		66.88	3.63	13.77	66.77	3.54	13.68	9
3-Methyl-5-cyano-	175[h]	45		76.24	4.38		76.53	4.40		97
3-Methyl-5-nitro-	159[h]	83		67.70	4.10	13.16	67.68	4.23	13.39	63
3-Methyl-8-nitro-	134[j]	28		67.70	4.10	13.16	67.74	4.06	13.29	85
5-Carbomethoxy-	121[h]	29		71.69	4.43		71.81	4.58		98

[a] Analyses by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Drs. Weiler and Strauss, Oxford, England. [b] Melting points are uncorrected. Recrystallized from 95% ethanol unless stated. [c] Methylene chloride–water method, see Experimental. [d] Aqueous method, see Experimental. [e] From acid-catalyzed hydrolysis, isolated as the 2,4-dinitrophenylhydrazone, see ref. 10. [f] Reported m.p. 124–126°, ref. 6. [g] Isolated as the benzoylamino derivative. [h] Recrystallized from 80% ethanol. [i] Isolated as the benzoate derivative. [j] Recrystallized from 75% isopropyl alcohol.

EXPERIMENTAL

Reagents. Reagent grade benzoyl chloride, methylene chloride, and potassium cyanide were used. The isoquinolines were obtained commercially or prepared by standard literature procedures.

Aqueous method of Reissert compound formation. This method was carried out as described in the previous paper of this series. The results are listed in Table I.

Methylene chloride-water method of Reissert compound formation. This method was carried out as described in the two previous papers of this series. The results are listed in Table I.

Reaction of 1-azapyrene. Reaction of 1-azapyrene, benzoyl chloride, and potassium cyanide by the methylene chloride–water method gave a 54% yield of solid, m.p. 212–213° (from 95% ethanol).

Anal. Calcd. for $C_{23}H_{14}N_2O$: C, 82.62; H, 4.22; N, 8.38. Found: C, 82.37; H, 4.23; N, 8.14.

Acid-catalyzed hydrolysis of this compound as described below gave a 95% yield of benzaldehyde-2,4-dinitrophenylhydrazone.

Reaction of 2-azafluoranthene. Reaction of 2-azafluoranthene, benzoyl chloride, and potassium cyanide by the methylene chloride–water method gave a 23% yield of solid, m.p. 158–159° (from 95% ethanol).

Anal. Calcd. for $C_{23}H_{14}N_2O$: C, 82.62; H, 4.22; N, 8.38. Found: C, 82.71; 82.84; H, 4.36, 4.48; N, 8.38, 8.55.

Acid-catalyzed hydrolysis of Reissert compounds. This was carried out with concentrated hydrochloric acid and 2,4-dinitrophenylhydrazine as previously described.[1,10]

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The Formation of the N—N Bond in Pyrazolines

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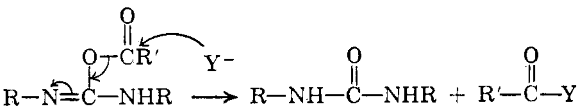
Received July 19, 1961

Syntheses of pyrazolines[1,2] generally require that the N—N bond be formed prior to cyclization. In fact, cyclization reactions of organic compounds involving the formation of an N—N bond are scarcely known. The examples reported[3] for the preparation of triazoles or tetrazoles are usually not applicable to the synthesis of pyrazolines.

While in search for a method of N—N bond closure in the formation of pyrazolines, we felt that a reaction of type (1) might be feasible under special conditions. The case where OX represents a good leaving group, *i.e.*, acylate or tosylate, would appear desirable but the presence of an amino group in oxime I (X = H) precludes the use of acylating agents in the formation of I (OX = acylate).

I II (1)

During the last few years *N,N'*-dicyclohexylcarbodiimide has been used successfully in dehydrative cyclizations of amino acids to lactams[4] and of hydroxy acids to lactones.[5] The mechanism presumably involves[6] the addition of the acid to *N,N'*-dicyclohexylcarbodiimide to give an intermediate *O*-substituted isourea from which urea can be displaced by a nucleophile. We felt that perhaps *N,N'*-



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