

Syntheses of *N*-(2,4-Dinitrophenyl)nitroazoles

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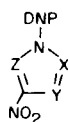
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Several *N*-(2,4-dinitrophenyl)nitroazoles which cannot be obtained by direct nitration of *N*-phenylazoles have been prepared by condensation of 2,4-dinitrofluorobenzene with the appropriate nitroazoles. The structures of the products are assigned on the basis of their proton magnetic resonance spectra; in all the examples studied, condensations occur at positions remote from the nitro group of the nitroazole.

Nucleophilic fission of the 2,4-dinitrophenyl fragments of 1-(2,4-dinitrophenyl)pyrazole and of 2-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole occurs readily (1-4), and this type of reaction allows uninvolved syntheses of 4-nitro-1,2,3-triazole and of 4-methyl-5-nitro-1,2,3-triazole (4); these compounds have not been obtained by direct nitration. The inverse of this fission reaction, in which azoles are condensed with 2,4-dinitrofluorobenzene, has been explored by Jacquier and his co-workers (5-8) and by Wilshire (9), and the dinitrophenylazoles are easily available by such routes.

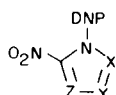
We have found that species which are inaccessible by direct nitration reactions are prepared easily by condensation of the appropriate nitrodiazole or nitrotriazole with 2,4-dinitrofluorobenzene, and this paper is concerned with their syntheses and structural assignment.

Thus, condensation of 2,4-dinitrofluorobenzene in dimethyl sulfoxide with 4-nitro-1,2,3-triazole afforded a mixture of two 2,4-dinitrophenylation products in good yield, readily separable by adsorption chromatography. One of these products is 2-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole, identical with the product obtained by direct trinitration of 2-phenyl-1,2,3-triazole (3), and the other is assigned as the 1-isomer (1a). Similar reaction with 4(5)-nitroimidazole gave a 1-(2,4-dinitrophenyl)nitroimidazole, m.p. 151-153°, as reported previously by Wilshire (9) without assignment of structure: we suggest that the product is 1-(2,4-dinitrophenyl)-4-nitroimidazole (1b).



Type I

- Ia: X = Y = N; Z = CH
 Ib: Y = N; X = Z = CH
 Ic: X = Y = CH; Z = N
 Id: Y = Z = N; X = CH



Type II

- IIa: X = Y = N; Z = CH
 IIb: Y = N; X = Z = CH
 IIc: X = N; Y = Z = CH
 IId: X = Z = N; Y = CH

3(5)-Nitropyrazole and 3-nitro-1,2,4-triazole (which cannot be obtained by conventional nitrations, but are accessible *via* the amines (10,11)) similarly provided condensation products: 3-nitropyrazole gave a single compound assigned as 1-(2,4-dinitrophenyl)-3-nitropyrazole (1c) and 3-nitro-1,2,4-triazole also afforded a single product, assigned as 1-(2,4-dinitrophenyl)-3-nitro-1,2,4-triazole (1d).

As Neuman (12) has shown for 1,2,3-triazole derivatives, this indirect approach to polynitrated phenyl-substituted heterocyclic species may be applied to the synthesis of pieryl derivatives.

Evidence for Structural Assignments.

The structures 1a-1d assigned to the various condensation products are those in which the dinitrophenyl moiety attacks the nitrogen atom(s) remote from the *C*-nitro group of the heterocycle, so that no *ortho-ortho* type nitro-group interactions occur. Exclusion of struc-

TABLE I

N.M.R. Signals of the Dinitrophenyl Protons of DNP-Nitroazoles (a)

Compound	Proton Signals		
	3'	5'	6'
1-DNP-4-nitropyrazole	8.90	8.70	8.22
1-DNP-3-nitropyrazole	8.97	8.77	8.25
1-DNP-4-nitroimidazole	9.00	8.73	8.17
1-DNP-3-nitro-1,2,4-triazole	9.03	8.85	8.17
2-DNP-4-nitro-1,2,3-triazole	9.05	8.80	8.40
1-DNP-4-nitro-1,2,3-triazole	9.07	8.90	8.33

(a) DNP = 2,4-dinitrophenyl; spectra were recorded for solutions in dimethyl sulfoxide-d₆; coupling constants were $J_{5'6'} = 9.0 \pm 0.1$ Hz; $J_{3'5'} = 2.6 \pm 0.1$ Hz. Signals are in p.p.m. from internal TMS.

TABLE II
Heterocyclic Proton Signals in DNP-Azoles and -Nitroazoles

Compound	Proton Signals (differences (p.p.m.) between corresponding signals in azoles and nitroazoles are given in parentheses)			Ref.
1-DNP-pyrazole	3-, 7.88	4-, 6.70	5-, 8.54	(6)
1-DNP-4-nitropyrazole	3-, 8.60 (0.72)		5-, 9.67 (1.13)	
1-DNP-3-nitropyrazole		4-, 7.42 (0.72)	5-, 8.70 (0.16)	
1-DNP-imidazole	2-, 8.07	4-, 7.20	5-, 7.55	(5)
1-DNP-4-nitroimidazole	2-, 8.23 (0.16)		5-, 8.83 (1.28)	
1-DNP-1,2,3-triazole		4-, 8.10	5-, 8.88	(8)
1-DNP-4-nitro-1,2,3-triazole			5-, 10.10 (1.22)	
1-DNP-1,2,4-triazole	3-, 8.36		5-, 9.34	(7)
1-DNP-3-nitro-1,2,4-triazole			5-, 9.55 (0.21)	

TABLE III
N-2,4-Dinitrophenylnitroazoles

Reactant Nitroazole	Product(s)	M.p.	Yield (%)	Analyses, %	
				Calcd. for:	Found
4-Nitro- 1,2,3-triazole	(a) 2-DNP (a) 4-nitro- 1,2,3-triazole	104° (lit. 104)	27	—	—
	(b) 1-DNP-4-nitro- 1,2,3-triazole	158°	27	C ₈ H ₄ N ₆ O ₆ : C, 34.29 H, 1.42	C, 34.10 H, 1.59
(these products were eluted in the order of listing)					
3-Nitropyrazole	1-DNP-3-nitro- pyrazole	100°	75	C ₉ H ₅ N ₅ O ₆ : C, 38.72 H, 1.81 N, 25.09	C, 38.60 H, 2.09 N, 25.10
3-Nitro-1,2,4- triazole	1-DNP-3-nitro- 1,2,4-triazole	98-100°	38	C ₈ H ₄ N ₆ O ₆ : C, 34.29 H, 1.42 N, 30.00	C, 34.70 H, 1.32 N, 29.80

(a) DNP = 2,4-dinitrophenyl.

tures of type II is based upon comparisons of the chemical-shift patterns in various *N*-(2,4-dinitrophenyl)nitroazoles. In compounds of type II the interactions of the *C*-nitro group in the heterocyclic ring and of the 2-nitro group in the dinitrophenyl moiety would be expected to result in mutual loss of planarity with the attached aromatic rings, and consequent decreases in the normal deshielding effects of nitro groups (*ca.* 1 p.p.m. (13)). However, the ABX patterns characteristic of the 2,4-dinitrophenyl groups in the compounds obtained by condensation reactions are closely similar to those observed for com-

pounds known from alternative syntheses to have structure of type I (see Table I, and Wilshire (9)), indicating very strongly that the 2,4-dinitrophenyl groups are conformationally similar in all members of the series listed in Table I.

Further support is afforded by comparison of the heterocyclic ring proton shifts in the 2,4-dinitrophenylnitroazoles and in the corresponding dinitrophenylazoles lacking heterocyclic nitro groups (see Table II). Marked deshielding effects are observed for protons adjacent to the nitro groups, and again the effects are closely similar to those

observed in species known to have structures of type I rather than II.

EXPERIMENTAL

General.

N.m.r. measurements were made using a Varian A-60D spectrometer. Combustion analyses were carried out by Mrs. M. Petranovic of this laboratory using a Hewlett-Packard Model 185 CHN Analyzer.

Sources of Materials.

4-Nitro-1,2,3-triazole, m.p. 160-161°, was prepared by nucleophilic fission of 2-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (4). 3(5)-Nitropyrazole, m.p. 175°, was prepared by the method of Bagal and co-workers (10). 3-Nitro-1,2,4-triazole, m.p. 215-216°, was prepared by Browne's method (11). 1-(2,4-Dinitrophenyl)-4-nitropyrazole, m.p. 160° was prepared by trinitration of 1-phenylpyrazole (2). 4(5)-Nitroimidazole, m.p. 312°, was prepared by nitration of imidazole.

General Condensation Procedure

2,4-Dinitrofluorobenzene (Aldrich Chemical Co.) (4.65 g., 0.025 mole), triethylamine (5.0 g., 0.05 mole), and the nitroazole (0.025 mole) were added successively to dimethyl sulfoxide (50 ml.). The solutions were stirred at 20° for 1 hour and poured onto ice-water (500 g.). The crude solids were collected, dried, and chromatographed on silica gel or on alumina using benzene as solvent and eluent. The eluates were evaporated and solid fractions were screened for uniformity using n.m.r. spectroscopy. The appropriate fractions were combined and crystallized from ethanol. Table III lists yields, melting points and analyses.

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