589. *The Preparation of Some Trinitrophenylpyrazoles.*

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1-Phenylpyrazole and nitrophenylpyrazoles have been converted into trinitro-compounds by mixed acids at 100°, and the products orientated by synthesis. Some di- and the tri-nitrophenylpyrazoles give colours in the Janovsky reaction.[1, 2]

Nitration of 1-phenylpyrazole with mixed acids at 100° gives 1-(2 : 4-dinitrophenyl)-4-nitropyrazole; the course of the reaction is indicated by nitration of 1-phenylpyrazole at 12° and 22° which gives the intermediates 1-*p*-nitrophenyl- and 4-nitro-1-*p*-nitrophenylpyrazole, respectively. Nitration of both these compounds at 100° gives the trinitro-compound, which is also obtained by other nitrations (see Table).

1-(2 : 4-Dinitrophenyl)-4-nitropyrazole was characterised by its reaction with boiling methanolic sodium methoxide[3] to give 4-nitropyrazole and 2 : 4-dinitroanisole. It was synthesised by condensation between 4-nitropyrazole [from pyrazole,[4] by nitration with mixed acids at 100° (cf. Buchner and Frisch,[5] and Huttel *et al.*[6])] and 1-chloro-2 : 4-dinitrobenzene in ethanolic potassium hydroxide. Nitration of 1-*m*-nitrophenyl- and 4-nitro-1-*m*-nitrophenyl-pyrazole with mixed acids at 100° gives 1-(3 : 4-dinitrophenyl)-4-nitropyrazole, the orientation of which was established as follows. One nitro-group underwent nucleophilic replacement in ethanolic ammonia at 100°, to give an amine which, on deamination, gave 4-nitro-1-*p*-nitrophenylpyrazole, the presence of a *p*-nitro-group in the trinitro-compound being thus established. This trinitro-compound was synthesised as follows: Partial reduction of 4-nitro-1-*p*-nitrophenylpyrazole with ammonium hydrogen sulphide gave 1-*p*-aminophenyl-4-nitropyrazole (the structure being shown by deamination

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[1] Janovsky, *Ber.*, 1891, **24**, 971.
[2] Bost and Nicholson, *Ind. Eng. Chem. Analyt.*, 1935, **7**, 190.
[3] Crocker and Hall, *J.*, 1955, 4489.
[4] Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 3997.
[5] Buchner and Frisch, *Annalen*, 1893, **273**, 265.
[6] Hüttel, Büchel, and Jochum, *Chem. Ber.*, 1955, **88**, 1582.

to 4-nitro-1-phenylpyrazole), which was acetylated and nitrated with nitric acid in nitromethane, and finally hydrolysed to give 1-(4-amino-3-nitrophenyl)-4-nitropyrazole. The last was characterised by deamination to 4-nitro-1-*m*-nitrophenylpyrazole, and was oxidised with trifluoroperoxyacetic acid [7] to 1-(3 : 4-dinitrophenyl)-4-nitropyrazole, identical with the nitration product.

The series of 4-nitro-1-nitrophenylpyrazoles was obtained by reaction between sodium nitromalonaldehyde monohydrate [8] and the appropriate nitrophenylhydrazine hydrochloride.[9]

1-Phenylpyrazole was obtained in excellent yield by condensation between 1 : 1 : 3 : 3-tetraethoxypropane and phenylhydrazine hydrochloride, using a modification of Jones's method for pyrazole.[4] Ring closure with nitrophenylhydrazines gave the corresponding nitrophenylpyrazoles. This is a particularly simple method for the preparation of 1-*o*-nitrophenylpyrazole (cf. Dal Monte *et al.*[9]).

All the dinitropyrazoles and both trinitropyrazoles gave colour reactions when their acetone solutions were treated with 5% aqueous sodium hydroxide.

EXPERIMENTAL

Nitration of 1-*Phenylpyrazole.*—A mixture of sulphuric acid (30 c.c.; *d* 1·84) and nitric acid (30 c.c.; *d* 1·42) was slowly added to a solution of 1-phenylpyrazole (5 g.) in sulphuric acid (50 c.c.; *d* 1·84). The mixture was heated at 100° for 30 min., then poured on crushed ice. The yellow solid was collected and washed. Recrystallisation from ethanol gave pale yellow needles (8·01 g., 82·7%), m. p. 159—161·5° undepressed on admixture with 1-(2 : 4-*dinitrophenyl*)-4-*nitropyrazole* prepared as below.

Pyrazole nitrated	Product	Yield (%)
Nitrations at 100°, 30 *min.*		
1-*o*-Nitrophenyl-	1-(2 : 4-Dinitrophenyl)-4-nitro-	73
1-*p*-Nitrophenyl-		84
4-Nitro-1-*o*-nitrophenyl-		70·5
4-Nitro-1-*p*-nitrophenyl-		84
4-Nitro-1-phenyl-		85
1-*m*-Nitrophenyl-	1-(3 : 4-Dinitrophenyl)-4-nitro-	57
4-Nitro-*m*-nitrophenyl-		72
Nitrations at 12°, 30 *min.*		
1-Phenyl-	1-*p*-Nitrophenyl	86
4-Nitro-1-phenyl-	4-Nitro-1-*p*-nitrophenyl-	84
Nitrations at 22°, 16 *hrs.*		
1-Phenyl-	4-Nitro-1-*p*-nitrophenyl-	76
1-*p*-Nitrophenyl-	,, ,,	74
1-*o*-Nitrophenyl-	4-Nitro-1-*o*-nitrophenyl-	66
1-*m*-Nitrophenyl-	4-Nitro-1-*m*-nitrophenyl-	73
1-(2 : 4-Dinitrophenyl)-	1-(2 : 4-Dinitrophenyl)-4-nitro-	64

1-(2 : 4-*Dinitrophenyl*)-4-*nitropyrazole.*—(a) *Structure.* The trinitro-compound (5 g.) in methanol (50 c.c.) was refluxed for 5 min. with 0·6N-methanolic sodium methoxide (60 c.c.). Working up was essentially that for fission of 1-(2 : 4-dinitrophenyl)pyrazole (Crocker and Hall [3]), and gave 4-nitropyrazole (1·1 g.), m. p. 161—162° (from benzene), and 2 : 4-dinitroanisole (2·1 g.), m. p. 89—90° (from ethanol).

(b) *Synthesis.* To a refluxing solution of 4-nitropyrazole (1·0 g., 0·009 mole), in ethanol (20 c.c.) containing potassium hydroxide (1 equiv.), was added dropwise a solution of 1-chloro-2 : 4-dinitrobenzene (1·8 g., 0·009 mole) in ethanol (20 c.c.). After 30 min. the solution was filtered from potassium chloride and set aside. The solid obtained was recrystallised from ethanol, giving pale yellow needles of 1-(2 : 4-dinitrophenyl)-4-nitropyrazole (1·1 g., 44·7%),

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[7] Emmons, *J. Amer. Chem. Soc.*, 1954, **76**, 3470.

[8] *Org. Synth.*, 1952, **32**, 95.

[9] Dal Monte, Mangini, and Passerini, *Gazzetta*, 1956, **86**, 797.

m. p. 159—161·5° (Found: C, 39·0; H, 1·9; N, 25·4. $C_9H_5O_6N_5$ requires C, 38·7; H, 1·8; N, 25·1%).

1-(3 : 4-*Dinitrophenyl*)-4-*nitropyrazole*.—(a) *Structure*. The trinitro-compound (2 g.) was heated with 2·4N-ethanolic ammonia (20 c.c.) in a sealed tube for 2 hr. at 100°. The orange solid obtained, coupled, after diazotisation, with alkaline β-naphthol to give a red dye. The crude amine (0·84 g.) was diazotised in sulphuric acid (10 c.c.; *d* 1·84) below 20° with sodium nitrite (0·26 g.), in sulphuric acid (2 c.c.; *d* 1·84). After 1 hr., the solution was diluted with water (12 c.c.) and poured into 31% w/w hypophosphorous acid solution (15 c.c.). Deamination was complete in 2 hr. and the crude product was chromatographed in benzene on alumina. Elution with benzene gave a pale yellow solid, m. p. 136—148°. Two recrystallisations from ethanol gave m. p. 149—150°, undepressed on admixture with 4-nitro-1-*p*-nitrophenylpyrazole.

(b) *Synthesis*. (i) 4-Nitro-1-*p*-nitrophenylpyrazole (5·0 g.) was warmed in ethanol (200 c.c.) containing aqueous ammonia (20 c.c.; *d* 0·880) at 40°. Hydrogen sulphide was passed into the solution for 15 min.; the dinitropyrazole dissolved to give an orange-red solution which was refluxed for 30 min. The hot solution was filtered and the crystals obtained on cooling were collected and extracted with hot 16% hydrochloric acid (250 c.c.). The extract, when made alkaline with ammonia, gave 1-p-*aminophenyl*-4-*nitropyrazole* as an orange solid (needles from ethanol) (3·0 g., 69%), m. p. 190—191° (Found: C, 52·9; H, 4·0; N, 27·3. $C_9H_8O_2N_4$ requires C, 52·9; H, 3·9; N, 27·4%).

(ii) Nitric acid (20 c.c.; *d* 1·5) in nitromethane (80 c.c.) was slowly added to a stirred suspension of 1-*p*-acetamidophenyl-4-nitropyrazole, m. p. 274—275° (10·0 g.), in nitromethane (160 c.c.) at room temperature, and after 2 hr. the solution was poured into excess of ice-water. The yellow precipitate, on recrystallisation from acetic acid, gave 1-(4-*acetamido*-3-*nitrophenyl*)-4-*nitropyrazole* (10·87 g., 93·5%), m. p. 215—216° (Found: C, 45·6; H, 3·6; N, 23·8. $C_{11}H_9O_5N_5$ requires C, 45·4; H, 3·4; N, 24·1%). This (9·0 g.) was hydrolysed in suspension by boiling hydrochloric acid (*d* 1·18), to 1-(4-*amino*-3-*nitrophenyl*)-4-*nitropyrazole* (7·41 g., 97·3%), m. p. 249—250° (from acetic acid) (Found: C, 43·4; H, 2·9; N, 28·3. $C_9H_7O_4N_5$ requires C, 43·4; H, 2·8; N, 28·1%).

(iii) Hydrogen peroxide (14·1 g.; 30%) was added during 15 min. to a suspension of the dinitroamine (6·2 g.) in refluxing trifluoroacetic acid (25 c.c.). After 1 hr. the solid was recrystallised from acetic acid, and unchanged material obtained (5·0 g.). The mother-liquor was diluted with water, filtered, and kept overnight, to give 0·3 g. of a yellow solid, m. p. 135—138°. Two recrystallisations from ethanol (charcoal) gave 1-(3 : 4-dinitrophenyl)-4-nitropyrazole, m. p. 140—141° (Found: C, 39·0; H, 2·0; N, 24·8. $C_9H_5O_6N_5$ requires C, 38·7; H, 1·8; N, 25·1%).

(iv) The amine (0·5 g.) was diazotised in sulphuric acid (*d* 1·84) with sodium nitrite (0·16 g.) and deaminated, after 1 hr., with 31% hypophosphorous acid. 1-(4-Amino-3-nitrophenyl)-4-nitropyrazole gave pale yellow plates of 4-nitro-1-*m*-nitrophenylpyrazole, m. p. 155—156° (from ethanol; charcoal). 1-*p*-Aminophenyl-4-nitropyrazole gave pale yellow needles of 4-nitro-1-phenylpyrazole, m. p. 129—130° (from ethanol; charcoal). The m. p.s were undepressed when mixed with the relevant authentic specimen.

General Procedure for 4-*Nitro-derivatives*.—Equimol. quantities of sodium nitromalonaldehyde monohydrate and phenylhydrazine hydrochloride, or the relevant nitrophenylhydrazine hydrochloride, were refluxed in 80% ethanol for 30 min. Recrystallisation from ethanol (charcoal) gave 4-nitro-1-phenyl-, m. p. 129—130° (lit.,[9, 10] 126—127°), and 4-nitro-1-*o*-, m. p. 151—152·5° (lit.,[9] 148°), -1-*p*-, m. p. 149—150°, and -1-m-*nitrophenyl-pyrazole*, m. p. 155—156° (Found: C, 46·4; H, 2·5; N, 24·2. $C_9H_6O_2N_4$ requires C, 46·2; H, 2·6; N, 23·9%).

1-*Phenylpyrazole*.—1 : 1 : 3 : 3-Tetraethoxypropane (44 g., 0·2 mole) and phenylhydrazine hydrochloride (28·8 g., 0·2 mole) in 95% ethanol (150 c.c.) were refluxed for 30 min., then worked up as for pyrazole,[4] to give 1-phenylpyrazole (26·1 g., 90·6%), b. p. 74°/0·05 mm.

Nitrophenylpyrazoles.—Equimol. quantities of 1 : 1 : 3 : 3-tetraethoxypropane and the relevant nitrophenylhydrazine hydrochloride were refluxed in 95% ethanol. The nitropyrazole separated out and was recrystallised from ethanol, giving 1-*o*- (83·2%), m. p. 88—89° (lit.,[9] 84—85°), 1-*m*- (88·2%), m. p. 94—95°, and 1-*p*-nitrophenylpyrazole (85·0%), m. p. 169—170°, and 1-(2 : 4-dinitrophenyl)pyrazole (73·4%), m. p. 109—110°.

Janovsky Reaction with the Di- and Tri-nitro-compounds.—Aqueous sodium hydroxide

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[10] Hill and Torrey, *Amer. Chem. J.*, 1899, **22**, 104.

(3 c.c.; 5%) was added to a solution of the nitropyrazole (0·1 g.) in acetone (10 c.c.) with shaking. The following colours were produced: 4-nitro-1-*o*-, reddish-orange; 4-nitro-1-*m*-, wine-red; and -1-*p*-nitrophenyl-, wine-red; 1-(2 : 4-dinitrophenyl)-, bluish-violet; 1-(2 : 4-dinitrophenyl)-4-nitro-, reddish-violet; 1-(3 : 4-dinitrophenyl)-4-nitro-, wine-red. None of the mononitropyrazoles gave a colour.

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