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THE REACTION OF 2,4,5-TRINITROTOLUENE WITH HYDROXYLAMINE

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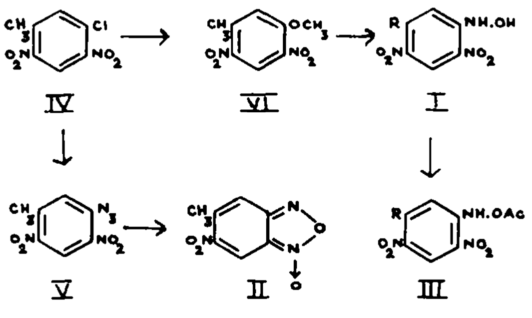
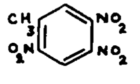
Abstract—Treatment of 2,4,5-trinitrotoluene with hydroxylamine affords O,N-di(5-methyl-2,4-dinitrophenyl)hydroxylamine and not N-(5-methyl-2,4,-dinitrophenyl)hydroxylamine.

The two methods most frequently used for the preparation of benzofuroxans are either heating *o*-nitroaryl azides or oxidizing *o*-nitroarylamines with alkaline hypochlorite.[1]

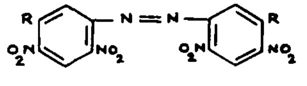
It was reported[2] in 1923 that warming N-(5-methyl-2,4-dinitrophenyl)hydroxylamine (I, R = CH_3) with acetic anhydride afforded 5-methyl-6-nitrobenzofuroxan (II). This did not agree with the observations of Borsche[3] that N-(2,4-dinitrophenyl)-hydroxylamine (I, R = H) formed O-acetyl (III, R = H) and O,N-diacetyl derivatives. The m.p. quoted[2] (209–210°) for II was higher than one would expect for a compound of this structure.[4]

A specimen of II was, therefore, prepared from 5-chloro-2,4-dinitrotoluene (IV) *via* the azide (V). The compound so obtained was low-melting (m.p. 67°), and different from the compound obtained by Giua.[2] We suspected that the product obtained by Giua was the azo compound VII (R = CH_3). A sample of 5,5′-dimethyl-2,2′,4,4′-tetranitroazobenzene (VII, R = CH_3) was prepared by the oxidation[5] of





VIII



VII

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[1] R. C. Elderfield, *Heterocyclic Compounds* Vol. 7; p. 479. J. Wiley (1961).
[2] M. Giua, *Gazzetta*, **53**, 657 (1923).
[3] W. Borsche, *Ber. Dtsch. Chem. Ges.* **56**, 1494 (1923).
[4] A. J. Boulton and A. R. Katritzky, *Revue de Chimie* **7**, 691 (1962).
[5] A. G. Green and F. M. Rowe, *J. Chem. Soc.* 2443 (1912).

5-methyl-2,4-dinitroaniline.[6] The m.p. of VII ($R = CH_3$), 215–216° was close to that reported by Giua.[2] An authentic specimen of N-(5-methyl-2,4-dinitrophenyl)-hydroxylamine (I, $R = CH_3$) was then prepared from 5-methyl-2,4-dinitroanisole (VI). The properties of the compound so obtained were different from those reported by Giua[2] and treatment of I ($R = CH_3$) with cold acetic anhydride yielded an acetyl derivative (III, $R = CH_3$) whose IR spectrum ($CHCl_3$) contained a band at 1780 cm^{-1}, showing it to be an O-acetyl derivative.[7] Giua[2] prepared his so-called N-(5-methyl-2,4-dinitrophenyl)hydroxylamine from 2,4,5-trinitrotoluene (VIII) by reaction with hydroxylamine. This work has been repeated and a solid (designated *Y*) obtained which is different from I, ($R = CH_3$). Compound *Y* is unstable in most hot solvents but may be crystallized from chloroform–petroleum ether, forming pale yellow prisms (m.p. 121°). The mol. wt. (361) of *Y* indicated that the compound contained 2 benzene nuclei; and boiling *Y* in either ethyl acetate or acetic anhydride gave the azo compound VII ($R = CH_3$); which was obtained on shaking a solution of *Y* in chloroform with nickel peroxide.[8]

TLC of *Y* showed it to be free of II and *Y* could be chromatographed unchanged on silica. However, chromatography of *Y* on alumina afforded 5-methyl-6-nitrobenzofuroxan (II). The IR spectrum of *Y* (nujol) contained a sharp band at 3300 cm^{-1} (NH) and analytical data was in agreement with structure IX ($R = R' = CH_3$) for *Y*. Reduction of *o*-dinitrobenzene with hydroxylamine gives a mixture of *o*-nitronitrosobenzene and *o*-nitroaniline[9] and IX ($R = R' = CH_3$) could arise by condensation of the nitroso and amino compounds followed by further reduction.[10] This structure would explain the formation of the azo compound VII ($R = CH_3$) but it was difficult to reconcile this structure with the transformation of *Y* into II on chromatography. It was decided to prepare several polynitrohydroazobenzenes in order to examine their behaviour on chromatography and to attempt a synthesis of IX ($R = R' = CH_3$).

Although 2,4-dinitrophenylhydrazine (X, $R = H$; DNP) reacted with picryl chloride to form pentanitrohydrazobenzene, it failed to react with 2,4-dinitrochlorobenzene to form tetranitrohydrazobenzene (IX, $R = R' = H$).[6] However, DNP has been found to react readily with 2,4-dinitrofluorobenzene to form 2,2',4,4'-tetranitrohydrazobenzene (IX, $R = R' = H$) in fair yield. 5-Methyl-2,4-dinitrofluorobenzene (XI) reacted smoothly with DNP forming 5-methyl-2,2',4,4'-tetranitrohydrazobenzene (IX, $R = CH_3$; $R' = H$) and also with 5-methyl-2,4-dinitrophenylhydrazine (X, $R = CH_3$) to form 5,5'-dimethyl-2,2',4,4'-tetranitrohydrazobenzene (IX, $R = R' = CH_3$). This last-named compound has m.p. 244° and is different from *Y*: it gave an intense purple colour (λ_{max} 506 mμ) when dissolved in a solution of potassium hydroxide (1%) in ethanol. A solution of *Y* in this solvent has (λ_{max} 398 mμ). Further, it was observed that tetranitrohydrazobenzenes of type IX were unchanged by chromatography on alumina.

Further analyses of *Y* gave results which were in agreement with a formula

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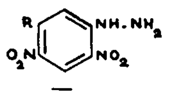
[6] J. W. Cook and O. L. Brady, *J. Chem. Soc.* 750 (1920).

[7] O. Exner and B. Kakáč, Coll. *Czech. Chem. Commun.* **25**, 2530 (1960).

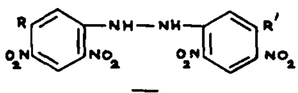
[8] K. Nakagawa and T. Tsuji, *Chem. and Pharm. Bull. Japan* **11**, 296 (1963).

[9] J. Meisenheimer and E. Hesse, *Ber. Dtsch. Chem. Ges.* **52**, 1166 (1919).

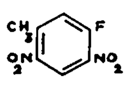
[10] N. V. Sidgwick, *The Organic Chemistry of Nitrogen* p. 252. Oxford University Press (1937).



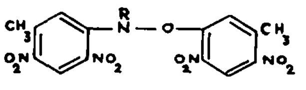
X



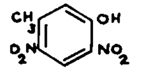
IX



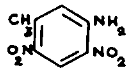
XI



XII



XIII



XIV

$C_{14}H_{11}N_5O_9$ (mol. wt. 393) and not with $C_{14}H_{12}N_6O_8$ (IX, R = R′ = CH_3; mol. wt. 392).

It was impossible to obtain an NMR spectrum of *Y* in chloroform; in dioxan the spectrum contained 5 bands of equal intensity (all singlets); $\tau = -1{\cdot}05$ (NH or OH, exchange with D_2O) and $\tau = 1{\cdot}00, 1{\cdot}18, 2{\cdot}28, 2{\cdot}60$ (aromatic protons). Structure IX (R = CH_3) ought to give only two signals in the aromatic region [one from the H at C_3 (τ approx 1·3) and one for the H at C_6 (τ approx 2·7)) since the two aromatic rings are identical. These results indicated that the molecule was not symmetrical. The mass spectrum of *Y* was determined by Dr. A. E. Williams. Only a small peak at *m/e* 393 was observed, the first prominent ion was detected at *m/e* 198 and an accurate mass determination established the formula as $C_7H_6N_2O_5$ suggesting structure XIII. An ion at *m/e* 197 was found to be a doublet, the low-mass fragment having the formula $C_7H_5N_2O_5$ (1H atom less than XIII) and the high-mass fragment the formula $C_7H_7N_3O_4$, a possible structure being XIV. This pattern of fragmentation can readily be explained if *Y* is O,N-di(5-methyl-2,4-dinitrophenyl)hydroxylamine (XII, R = H). It was found possible to acetylate *Y* in pyridine; the IR spectrum of this acetyl derivative (XII, R = .CO.CH_3) containing a band at 1730 cm^{-1} ($CHCl_3$), indicating that this compound is an N-acetyl derivative; O-acetyl-N-(2,4-dinitrophenyl)hydroxylamine (:CO 1798 cm^{-1}) and N,O-diacetylhydroxylamine (:CO bands at 1794 and 1725 cm^{-1}).[7] The NMR spectrum ($CDCl_3$) of XII (R = CO.CH_3) contained bands at $\tau = 7{\cdot}26$ (2 ar-CH_3 groups), $\tau = 7{\cdot}62$ (:CO.CH_3) and 4 aromatic protons τ; 1·14, 1·30, 1·89 and 2·15.

Finally structure XII (R = H) was confirmed by a synthesis of the compound from I, (R = CH_3) and XI; the product of this reaction being identical (mixed m.p. and IR spectrum) with *Y*.

It is likely that XII (R = H) is formed from VIII by two displacement reactions. It has been shown[11] that the 1 nitro group of 1,2,4-trinitrobenzene is very rapidly displaced by nucleophiles, the compound being more reactive than 2,4-dinitrofluorobenzene. We suggest that VIII is attacked by hydroxylamine forming I (R = CH_3)

[11] R. E. Parker and T. O. Read, *J. Chem. Soc.* 9 (1962).

which is then attacked by a second molecule of VIII yielding XII (R = H). Acylation of N-arylhydroxylamines which contains nitro groups (such as I) occurs on oxygen and not on nitrogen.[7] We hope to report later on the reactions of hydroxylamines of type XII.

EXPERIMENTAL

5-Methyl-6-nitrobenzofuroxan (II). 5-Chloro-2,4-dinitrotoluene (21 g, m.p. 92°)[12] was dissolved in a mixture of acetone (40 ml) and MeOH (40 ml). The solution was stirred and sodium azide (6·5 g) in a mixture of water (50 ml), MeOH (20 ml) and acetone (10 ml) added during 30 min; after stirring for a further 3 hr, the mixture was poured into water and the solid collected. The *azide* (V, 12·5 g) crystallized from MeOH as yellow prisms, m.p. 71° with dec. (Found: C, 38·4; H, 2·4; N, 30·3. $C_7H_5N_5O_4$ requires: C, 37·7; H, 2·3; N, 31·4%.) The azide was decomposed by heating in acetic acid solution until evolution of N_2 ceased.[13] The furoxan (II) formed pale yellow prisms from MeOH, m.p. 67°. (Found: C, 43·3; H, 2·6; N, 21·2. $C_7H_5N_3O_4$ requires: C, 43·1; H, 2·6; N, 21·5%.) The compound is soluble in all the common organic solvents except pet. ether and MeOH.

5,5′-Dimethyl-2,2′,4,4′-tetranitroazobenzene (VII, R = CH_3). 5-Methyl-2,4-dinitroaniline (m.p. 193°)[5] was prepared[14] from 5-chloro-2,4-dinitrotoluene. A solution of NaClO (10% active Cl_2, 115 ml) was neutralized with acetic acid (phenolphthalein) and added during 1·5 hr to a stirred solution of 5-methyl-2,4-dinitroaniline (1 g) in *sym*-tetrachloroethane (80 ml) at 70°. After stirring for a further hr the tetrachlorethane was removed by distillation, water being added to the flask to keep the volume of liquid constant. The azo compound, yield 4%, formed orange-red prisms from acetic acid, m.p. 215–216° with dec. (Found: N, 21·2. $C_{14}H_{10}N_6O_8$ requires: N, 21·5%.) The amine was recovered in 60% yield. Oxidation of 2,4-dinitroaniline gave 2,2′,4,4′-tetranitroazobenzene (3·2% yield, m.p. 221°). Green and Rowe[4] report m.p. 220° and do not state a yield.

N-(*5-Methyl-2,4-dinitrophenyl*)*hydroxylamine* (I, R = CH_3). A solution of Na (1 g) in MeOH (25 ml) was added to a stirred suspension of 5-chloro-2,4-dinitrotoluene (10 g) in MeOH (100 ml). After 8 hr the mixture was warmed to 50°, filtered, cooled, the solid (VI) which separated, yield 59%, collected and crystallized from pet. ether–benzene (9:1) as colourless needles, m.p. 101° (reported[15] value 101°). Sodium (0·4 g) was dissolved in EtOH (8 ml) and the solution mixed with hydroxylamine hydrochloride (1·15 g) in hot EtOH (15 ml). The liquid was made neutral (phenolphthalein) by the addition of a small quantity of ethanolic hydroxylamine hydrochloride, filtered from NaCl, and added to a solution of 5-methyl-2,4-dinitroanisole (3·15 g) in EtOH (15 ml). The mixture was boiled for 12 hr and then the solvent evaporated to dryness *in vacuo* at 25°. The product was crystallized from benzene (keeping the solution below 70°). N-(5-methyl-2,4-dinitrophenyl)hydroxylamine formed orange needles, m.p. 88° with dec the yield varying between 27–43%. (Found: C, 39·7; H, 3·2; N, 19·9. $C_7H_7N_3O_5$ requires: C, 39·4; H, 3·3; N, 19·7%.) The IR spectrum (nujol) contained a broad band at 3350 cm^{-1}; in $CHCl_3$ solution bands were observed at 3360 cm^{-1} and 3220 cm^{-1}; λ_{max} 272 (ε 12,400); 338 m (ε 9,400). The hydroxylamine (350 mg) was dissolved in acetic anhydride (0·7 ml) which had previously been warmed to 30°. The solution was immediately placed in an ice bath. After 1 hr the *acetyl* derivative was collected and washed with water. Crystallization from aqueous acetic acid afforded 68% of orange needles, m.p. 115°. (Found: C, 42·3; H, 3·4; N, 17·0 $C_9H_9N_3O_6$ requires: C, 42·4; H, 3·6; N, 16·5%); λ_{max} 216 mμ (ε 11,900); 267 mμ (ε 13,500); 322 mμ (ε 9,300) ($CHCl_3$).

2,2′,4,4′-Tetranitrohydrazobenzene (IX, R = R′ = H). 2,4-Dinitrophenylhydrazine (4 g) was suspended in boiling n-butanol (60 ml) and 2,4-dinitrofluorobenzene (6 g) added, followed by powdered $CaCO_3$ (2 g). The mixture was refluxed and stirred for 4 hr, cooled, the solid collected, washed with dil HClaq, and crystallized from acetone–EtOH. The hydrazo compound (38% yield) formed yellow prisms m.p. 250° (dec) reported[5] m.p. 250°. (Found: C, 39·3; H, 2·2; N, 22·6. Calc. for $C_{12}H_8N_6O_8$: C, 39·6; H, 2·2; N, 23·1%.)

5-Methyl-2,4-dinitrofluorobenzene (XI). *m*-Fluorotoluene (13 g) was added during 1·5 hr to a well-stirred ice-cold mixture of fuming HNO_3 (26 g, *d* 1·5) and conc. H_2SO_4 (40 g). After being stirred at

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[12] F. Reverdin and P. Crépieux, *Ber. Dtsch. Chem. Ges.* **33**, 2506 (1900).

[13] A. S. Bailey and J. R. Case, *Tetrahedron* **3**, 113 (1958).

[14] *Organic Synthesis* Col. Vol. 2; p. 221 J. Wiley (1943).

[15] H. Barbier, *Helv. Chim. Acta* **11**, 158 (1928).

room temp for 16 hr, the mixture was poured onto ice; the solid collected, washed with water, and dried. Crystallization from EtOH gave pale yellow needles (yield 59%) m.p. 78·5–79°. (Found: C, 42·4; H, 2·7; N, 13·5; F, 9·3. Calc. for $C_7H_5FN_2O_4$: C, 42·0; H, 2·5; N, 14·0; F, 9·5%.) Ostaszynski[16] reports m.p. 78–78·5° for a material isolated by an elaborate fractionation from the nitration product of *m*-fluorotoluene. The NMR spectrum of XI ($CDCl_3$) was consistent with this structure; the spectrum contained signals at $\tau = 7{\cdot}22$, (C-methyl group); $\tau = 1{\cdot}15$ (proton at C_3 split by F atom, J = 6 c/s); and $\tau = 2{\cdot}60$ (proton at C_6 split by F atom, J = 10 c/s).[17]

5-*Methyl*-2,2′,4,4′-tetranitrohydrazobenzene (IX, R = H, R′ = CH_3). 5-Methyl-2,4-dinitrophenylhydrazine (4 g)[18] was dissolved in n-butanol (60 ml), 2,4-dinitrofluorobenzene (6 g) added followed by $NaHCO_3$ (2 g). The mixture was boiled for 4 hr, cooled, the dark blue Na-salt collected and digested with acetic acid to liberate the free hydrazo compound. Yellow–brown crystals were obtained from glacial acetic acid, m.p. 241°. (Found: C, 41·8; H, 2·9; N, 22·5. $C_{13}H_{10}N_6O_8$ requires; C, 41·3; H, 2·7; N, 22·2%.)

5,5′-Dimethyl-2,2′,4,4′-tetranitrohydrazobenzene (IX, R = R′ = CH_3) was obtained by heating 5-methyl-2,4-dinitrophenylhydrazine (2 g), 5-methyl-2,4-dinitrofluorobenzene (3 g) and $CaCO_3$ (1·5 g) in n-butanol (30 ml) for 6 hr. The compound formed orange-yellow crystals, m.p. 244° from acetic acid. (Found: C, 42·8; H, 3·4; N, 20·7. $C_{14}H_{12}N_6O_8$ requires: C, 42·7; H, 3·1; N, 21·4%.) Ethyl acetate solutions of the three tetranitrohydrazo compounds described above, of 2,2′,4,4′,6-pentanitrohydrazobenzene and of 2,2′,4,4′,6,6′-hexanitrohydrazobenzene[5] were chromatographed on alumina (Spence, grade H). Elution with MeOH–ethyl acetate yielded dark blue solutions of the Na-salts of the unchanged hydrazo compounds. There was no sign of the formation of nitrobenzofuroxans.

O,N-Di(*5-methyl-2,4-dinitrophenyl*)*hydroxylamine* (XII, R = H). 2,4,5-Trinitrotoluene (4·54 g, m.p. 103–104°)[19] was suspended in EtOH (26 ml), the mixture warmed to 50°, stirred and an ethanolic solution of hydroxylamine [from hydroxylamine hydrochloride, (1·47 g) in EtOH, (30 ml) and Na (0·5 g) in EtOH (10 ml)] added during 5 min. The solution became deep red in colour, and solid dissolved and after 5 min bright yellow solid separated. After stirring for a further 10 min the mixture was cooled and the solid (2·2 g) collected, m.p. 115° Giua[8] reports m.p. 97–98° (dec). The compound is very unstable in hot polar solvents but may be crystallized from $CHCl_3$–pet. ether (b.p. 60–80°) as fine ochre needles, m.p. 120–121° with dec. (Found: C, 42·5, 42·6, 42·8; H, 2·9, 3·0, 2·8; N, 18·3, 17·3, 17·6. $C_{14}H_{11}N_5O_9$ requires: C, 42·8; H, 2·8; N, 17·8%.) Compound XII(R = H) was free (TLC) from the azo compound VII(R = CH_3), 5-methyl-2,4-dinitroaniline (I, R = CH_3) and from II. But crystallization of XII(R = H) from ethyl acetate, EtOH or acetic anhydride afforded the azo compound VII(R = CH_3), m.p. and mixed m.p. 215° (IR spectrum). (Found: C, 43·6; H, 2·7; N, 21·4. Cal. for $C_{14}H_{10}N_6O_8$: C, 43·1; H, 2·6; N, 21·5%.) The yields varied from 15–20%, no other crystalline material was obtained. O,N-Di(5-methyl-2,4-dinitrophenyl)hydroxylamine (2 g) in $CHCl_3$ (200 ml was stirred with nickel peroxide (3·7 g) for 3·5 hr, the mixture filtered, the filtrate evaporated to dryness and the residue crystallized from acetic acid. The azo compound VII (R = CH_3; 800 mg, m.p. 220°) was obtained.

A solution of XII(R = H; 500 mg) in ethyl acetate (40 ml) was chromatographed on alumina (Spence, Grade H). Elution with ethyl acetate (600 ml) gave a solid (215 mg) m.p. 65°, unchanged by crystallization from pet. ether, (b.p. 40–60°) and identical with II. When a solution of the hydroxylamine in benzene was chromatographed on silica the azo compound VII(R = CH_3; 6%) was obtained from the early fractions; starting material was then eluted; no trace of II was detected.

N-*Acetyl*-O,N-*di*(*5-methyl-2,4-dinitrophenyl*)*hydroxylamine* (XII, R = CO.CH_3). To an ice-cold solution of XII(R = H; 100 mg) in pyridine (0·2 ml) was added acetic anhydride (0·2 ml). After 24 hr at 0° the solution was poured onto ice and the solid (100 mg, m.p. 120°) collected and washed with water. Crystallization from $CHCl_3$–MeOH gave the acetyl compound, pale yellow needles, m.p. 127–128° with dec. (Found: C, 44·1; H, 3·2; N, 15·9. $C_{16}H_{13}N_5O_{10}$ requires: C, 44·1; H, 3·0; N, 16·1%.) The IR spectrum contained no bands in the region 3000–3500 cm^{-1} (NH or OH).

N-(5-methyl-2,4-dinitrophenyl)hydroxylamine (100 mg) was dissolved in EtOH (2 ml) and the solution added to 5-methyl-2,4-dinitrofluorobenzene (110 mg) in EtOH (3 ml). The mixture was

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[16] A. Ostaszynski, *Bull. Soc. Sci. et des Lettres de Lodz*, Cl. III 3, 15 (1952).

[17] N. S. Bhacca and D. H. Williams, *Applications of* NMR *Spectroscopy in Organic Chemistry* p. 131. Holden-Day (1964).

[19] O. L. Brady and W. H. Gibson, *J. Chem. Soc.* 99 (1921).

warmed to 50°, a solution of KOH (1 %, 1 ml) in EtOH added and the solution refrigerated. After 2 hr the solid (50 mg) was collected, washed with EtOH and dried m.p. 122° (dec); identical (IR spectrum) with a specimen prepared by the action of hydroxylamine on 2,4,5-trinitrotoluene.

TLC were run on unbaked silica plates using chloroform as solvent; results are summarised in Table 1.

TABLE 1

Compound	R_f	Compound	R_f
I(R = CH_3)	0·06	XII(R = H)	0·39
VIII	0·10	IX(R = CH_3)	0·68
X(R = CH_3)	0·21	II	0·69
5-Methyl-2,4-dinitroaniline	0·28	VII(R = CH_3)	0·70

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