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Studies on 2,4,6-Trinitrophenyl Substituted Naphthalenes. Part 1. Synthesis of Nitro- and Polynitro- 2-(2,4,6-Trinitrophenyl)Naphthalenes

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Abstract: Three nitro-, two dinitro-, and five trinitro- derivatives of 2-(2,4,6-trinitrophenyl)naphthalene have been synthesised using a variety of nitration procedures. Some of these derivatives have also been synthesised from 2-bromonaphthalene via a combination of nitration and Ullmann reactions.

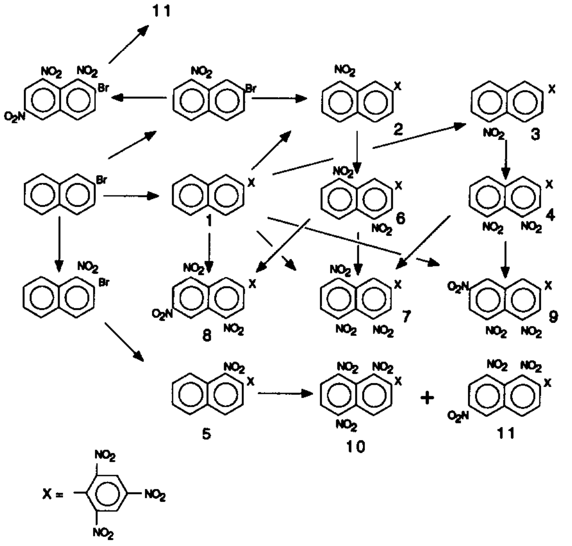
INTRODUCTION

Polynitroaromatic compounds are well known for their explosive properties, with 2,4,6-trinitrotoluene (TNT) being the best known example. Polynitroaromatic compounds which combine explosive properties with thermal stability are of commercial interest because of their potential application in the space industry[1,2]. In general, for a series of related compounds the melting point increases with molecular mass, and hence high molecular mass polynitroaromatic compounds are likely to fulfil the criteria required for thermally stable explosives. In view of this, we have studied the nitration of 2-(2,4,6-trinitrophenyl)naphthalene (**1**), a compound in which the naphthalene ring provides a moiety for futher substitution with energy rich nitro groups, and the substituent provides molecular mass and explosive properties. Previous work on the nitration of naphthalenic compounds has been concerned mainly with the nitration of methyl- and dimethyl- substituted derivatives.[3-8]

RESULTS AND DISCUSSION

Nitration of **1** with nitric acid in glacial acetic acid gave a product mixture from which two mono-nitro derivatives, **2** and **3** (see Scheme), were isolated by fractional crystallisation. The structure of **2** was confirmed by its synthesis via nitration of 2-bromonaphthalene with nitric acid in acetic acid to give 2-bromo-8-nitronaphthalene, followed by reaction of this compound with 1-chloro- 2,4,6-trinitrobenzene to give **2**. Since the 2,4,6-trinitrophenyl substituent in **1** deactivates the substituted ring relative to the unsubstituted ring with regard to nitration, the second product from the nitration of **1** was assigned as 5-nitro-2-(2,4,6-trinitrophenyl)naphthalene (**3**). This assignment was confirmed by further nitration of **3** to yield 4,5-dinitro-2-(2,4,6-trinitrophenyl)naphthalene (**4**). Compound **4** was identified as having nitro groups on adjacent *peri*-positions by the fact that the base peak in its mass spectrum corresponded to loss of NO_2 from the molecular ion through *peri*-nitro group interaction.[9,10] Nitro group substitution into the (2,4,6-trinitrophenyl) substituted ring in 1 was achieved by nitration of 2-bromonaphthalene to give 2-bromo-1-naphthalene followed by reaction of this compound with 1-chloro-2,4,6-trinitrobenzene to give 1-nitro-2-(2,4,6-trinitrophenyl)naphthalene (**5**).

Nitration of **2** with nitric acid in glacial acetic acid/sulphuric acid yielded a dinitro-product assigned as 4,8-dinitro-2-(2,4,6-trinitrophenyl)naphthalene (**6**). This assignment is made on the basis that the 2,4,6-trinitrophenyl group is less deactivating than a nitro group towards ring nitration, and that if nitration occurs in the 2,4,6-trinitrophenyl substituted ring then the preferred site will be at the *peri*-position which is *meta* to the substituent rather than at the position *ortho* to the substituent which is subject to steric hindrance. Furthermore, the base peak in the mass spectrum is that of the M^+ ion, a feature characteristic of polynitronaphthalenes having only one of adjacent *peri*-positions occupied.[9,10] It is noteworthy that the ^1H nmr spectra of **4** and **6** are closely similar as to be expected for compounds which have the same proton substitution pattern in each ring.



SCHEME

Nitration of either **4** or **6** with nitric acid in sulphuric acid resulted in two trinitro-substituted products in each case, one of which is common to both systems. In view of the assigned structures of **4** and **6**, this common product must be 4,5,8-trinitro-2-(2,4,6-trinitrophenyl)naphthalene (**7**). The ^1H nmr spectrum of the product is in accord with this assignment. Furthermore, the mass spectrum exhibits a large $(M\text{-}NO_2)^+$ ion peak indicative of the presence of adjacent *peri*-nitro groups. The mass spectrum of the second trinitro-substituted product formed in the nitration of **6** in mixed acid indicated that there were no adjacent *peri*-nitro groups in the structure. Furthermore, as the ^1H nmr spectrum of the compound is consistent with the presence of two sets of *meta*-coupled protons, the compounds is assigned as 4,6,8-trinitro-2-(2,4,6-trinitrophenyl)naphthalene

(**8**). The second trinitro-substituted product formed in the nitration of **4** in mixed acid is assigned as 4,5,7-trinitro-2-(2,4,6-trinitrophenyl)naphthalene (**9**) since the mass spectrum shows the presence of adjacent *peri*-nitro groups, and the ^{1}H nmr spectrum shows that two sets of *meta*-coupled protons are present.

Nitration of **1** with nitric acid in sulphuric acid gave a product mixture from which the isomers **7**, **8**, and **9** were separated by column chromatography.

Nitration of **5** with nitric acid in sulphuric acid yielded two trinitro-isomers different from **7**, **8** and **9**. One of these isomers is assigned as 1,5,8-trinitro-2-(2,4,6-trinitrophenyl) naphthalene (**10**) on the basis that the mass spectrum shows a large $(M\text{-}NO_2)^+$ ion peak indicative of the presence of adjacent *peri*-nitro groups, and the ^{1}H nmr spectrum shows protons H_3 and H_4 as an *ortho*-coupled doublet of doublets, and protons H_6 and H_7, which are in nearly identical chemical environments, as a singlet integrating to two protons. The other isomer is assigned as 1,6,8-trinitro-2-(2,4,6-trinitrophenyl)naphthalene (**11**) because its mass spectrum shows the presence of adjacent *peri*-nitro groups, and it has an ^{1}H nmr spectrum exhibiting an *ortho*-coupled doublet of doublets for protons H_3 and H_4, and a *meta*-coupled doublet of doublets for protons H_5 and H_7. The structure of **11** was confirmed by unambiguous synthesis via nitration of 2-bromo-8-nitronaphthalene to give 2-bromo-1,6,8-trinitronaphthalene, followed by an Ullman reaction of this compound with 1-chloro-2,4,6-trinitrobenzene to give **11**.

EXPERIMENTAL

Unless otherwise stated, dry-column column chromatography[11] was carried out using Merck silica gel (70-230 mesh). Mass spectra were recorded on an AEI MS 9 mass spectrometer. NMR spectra were recorded on either a Perkin-Elmer R32 spectrometer or a Jeol PS100 spectrometer, with CD_3COCD_3 as solvent and tetramethylsilane as internal reference.

Preparation of 2-(2,4,6-trinitrophenyl)naphthalene (1) via Ullman reaction.

Copper powder (4g) was added over 45 min to 2-bromonaphthalene (8g) and 1-chloro-2,4,6-trinitrobenzene (8g) at 150° in an open beaker, and then the mixture maintained at 150° for a further 30 min. After cooling, the reaction mixture was Soxhlet extracted with methylbenzene, the extract evaporated to small volume to which was added an equal volume of hexane. The resulting solution was column chromatographed using methylbenzene:hexane (1:1 v/v) as eluent. After elution of unreacted 2-bromonaphthalene in the first band, the eluent was changed to methylbenzene and the second (yellow) band collected. This solution was evaporated to dryness and fractionally crystallised from propan-2-one:methylated spirits (1:1 v/v) to yield **1** (2.33g, 22%), mp 130-1°. (Found: C, 56.6; H, 2.8; N, 12.5. $C_{16}H_9N_3O_6$ requires C, 56.6; H, 2.7; N, 12.4%).

Nitration of 2-(2,4,6-trinitrophenyl)naphthalene (1).

Nitric acid (*d* 1.42; 10 cm^3) was added dropwise during 10 min to a solution of **1** (1g) in glacial acetic acid (10 cm^3). The reaction mixture was maintained at 100° for 30 min during which time a precipitate appeared. The reaction mixture was poured onto ice, filtered, washed with water, and dried. The product was fractionally crystallised from propan-2-one. The first crystallisation yielded **2** (0.38g, 34%), mp 265-8°. (Found: C, 50.2; H, 2.1; N, 14.4. $C_{16}H_8N_4O_8$ requires C, 50.0; H, 2.1; N, 14.6%. δ, 9.20 (2H,s), 8.25 - 8.56 (4H,m), 7.83 (2H,t). *m/e* 384 (M^+).

The second crystallisation yielded **3** (0.25g, 22%), mp 242-5°. (Found: C, 50.1; H, 2.2; N, 14.4.

$C_{16}H_8N_4O_8$ requires C, 50.0; H, 2.1; N, 14.6%). δ, 9.20 (2H, s), 8.63 (1H, d), 8.31-8.50 (2H, m), 8.22 (1H, s), 7.71 - 7.93 (2H, m). *m/e* 384 (M^+).

Nitration of 5-nitro-2-(2,4,6-trinitrophenyl)naphthalene (3)

Nitric acid (*d* 1.42; 2 cm^3) was added dropwise during 10 min to a solution of **3** (0.12g) in glacial acetic acid (5 cm^3) and sulphuric acid (d 1.84; 2 cm^3). The reaction mixture was heated for 1 hour at 100° and then poured onto crushed ice. The precipitate was filtered off, washed with water, dried, and then recrystallised from propan-2-one:methylated spirits (1:1 v/v) to give **4** (0.11 g, 80%), mp 258-60°. (Found: C, 44.8; H, 1.9; N, 16.3. $C_{16}H_7N_5O_{10}$ requires C, 44.8; H, 1.6; N, 16.3%). δ, 9.33 (2H, s), 8.72 (1H, d), 8.58 - 8.69 (2H, t), 8.53 (1H, d), 8.04 (1H, t). *m/e* 429 (M^+).

Nitration of 2-Bromonaphthalene

Nitric acid (*d* 1.42; 40 cm^3) was added dropwise during 30 min to a solution of 2-bromonaphthalene (10g) in acetic acid (40 cm^3). The reaction mixture was stirred at 60° for 2 hours and then poured onto crushed ice. The precipitate was filtered off, washed with water, and dried. The product was dry column chromatographed, eluting first with hexane, then methylbenzene:hexane (1:1 v/v) and finally methylbenzene. The fractions were monitored by tlc using hexane:methylbenzene (1:1 v/v) as eluent. Similar fractions containing only product(s) were combined, evaporated to dryness, and recrystallised from methylated spirits to yield 2-bromo-1-nitronaphthalene (1.64g; 14%), mp 99-101° (lit[12] mp 100-101°) and 2-bromo-8-nitronaphthalene (3.49g; 29%), mp 110-112° (lit[12] mp 110-111°).

Preparation of 1-nitro-2-(2,4,6-trinitrophenyl)naphthalene (5)

To 2-bromo-1-nitronaphthalene (1.5g) and 1-chloro-2,4,6-trinitrobenzene (2.0g) at 150° was added copper powder (0.75g) over 30 min. The reaction mixture was maintained at 150° for a further 30 mins. After cooling, the reaction mixture was Soxhlet extracted with methylbenzene, the extract evaporated to small volume to which was added an equal volume of hexane. The resulting solution was column chromotographed using methylbenzene:hexane (1:1 v/v). The second band which was eluted was collected and recrystallised from propan-2-one:methylated spirits (1:1 v/v) to give **5** (0.34g, 10%), mp 267-8°. (Found: C, 50.2; H, 2.1; N, 14.4. $C_{16}H_8N_4O_8$ requires C, 50.0; H, 2.1; N, 14.6%). δ, 9.20 (2H, s), 8.40-8.60 (3H, m), 8.10-8.30 (1H, m), 7.70 - 8.02 (2H, m). *m/e* 384 (M^+).

Nitration of 8-nitro-2-(2,4,6-trinitrophenyl)naphthalene (2)

A solution of **2** (0.3g) in glacial acetic acid (10 cm^3), sulphuric acid (*d* 1.84; 5 cm^3), and nitric acid (*d* 1.42; 5 cm^3) was heated at 100° for 4 h, after which time the reaction mixture was poured onto crushed ice. The precipitate was filtered off, washed with water, and dried. The product was dry column chromatographed with methylbenzene as eluent. The fraction containing the single yellow band was collected, evaporated to dryness, and recrystallised from propan-2-one to give **6** (0.13g, 39%), mp 227-230°. (Found: C, 44.8; H, 1.61; N, 16.4. $C_{16}H_7N_5O_{10}$ requires C, 44.8; H, 1.6; N, 16.3%). δ, 9.24 (2H, s), 8.73 - 8.90 (2H, m), 8.68 (1H, d), 8.62 (1H, d), 8.11 (1H, t). *m/e*, 429 (M^+).

Nitration of 4,5-dinitro-2-(2,4,6-trinitrophenyl)naphthalene (4)

A solution of **4** (6.11g) in sulphuric acid (*d* 1.84; 5 cm^3) and nitric acid (*d* 1.41; 2 cm^3) was stirred at

100° for 1 h, after which time the reaction mixture was poured onto crushed ice. The precipitate was filtered off, washed with water, and dried. The product mixture was column chromatographed using methylbenzene as eluent. Fractions were monitored by tlc. The fractions containing the first product eluted were combined, evaporated to dryness, and the residue recrystallised from propan-2-one:methylated spirits (1:1 v/v) to give **9** (0.045g; 37%), mp 243°. (Found: C, 40.6; H, 1.5; N, 18.0. $C_{16}H_6N_6O_{12}$ requires C, 40.5; H, 1.3; N, 17.7%). δ, 9.34 (2H,s), 8.92 (1H,d,J_{AX}2Hz), 8.83(1H,d,J_{AX}2Hz), 8.70(2H,d,J_{AX}2Hz). *m/e*, 474(M^+). The fractions containing the second product eluted were combined, evaporated to dryness, and the residue recrystallised from propan-2-one: methylated spirits (1:1 v/v) to give **7** (0.021g; 17%), mp 271° . Found: C, 40.7; H, 1.3; N 17.9. $C_{16}H_6N_6O_{12}$ requires C, 40.5; H, 1.3; N, 17.7%). δ, 9.51(1H, J_{AX}2Hz), 9.34(2H,s), 9.16(1H, J_{AX}2Hz), 8.95(2H,s). *m/e*, 474(M^+).

Nitration of 4,8-dinitro-2-(2,4,6-trinitrophenyl)naphthalene (6)

A solution of **6** (0.13g) in sulphuric acid (*d* 1.84; 3cm^3) and nitric acid (d 1.42, 1 cm^3) was stirred at 100° for 1 h, after which time the reaction mixture was poured onto crushed ice. The precipitate was filtered off, washed with water, and dried. The product mixture was column chromatographed using methylbenzene as eluent. Fractions were collected and monitored by tlc. The fractions containing the first product eluted were combined, evaporated to dryness, and the residue recrystallised from propan-2-one:methylated spirits (1:1 v/v) to give **8** (0.043g; 33%), mp 224°. (Found: C, 40.3; H,1.6; N, 17.5. $C_{16}H_6N_6O_{12}$ requires C, 40.5; H, 1.3; N, 17.7%). δ, 9.83(1H, d, J_{AX}2Hz), 9.33(2H,s), 9.15(1H,d,J_{AX}2Hz), 8.95(2H,d,J_{AX}2Hz). *m/e*, 474 (M^+). The fractions containing the second product eluted were combined, evaporated to dryness, and the residue recrystallised from propan-2-one: methylated spirits (1:1 v/v) to give **7** (0.056g; 43%).

Nitration of 2-(2,4,6-trinitrophenyl)naphthalene (1) in mixed acid

A solution of **1** (1.2g) in sulphuric acid (*d* 1.84; 15 cm^3) and nitric acid (*d* 1.42; 15 cm^3) was stirred at 100° for 3 h, after which time the reaction mixture was poured onto crushed ice. The precipitate was filtered off, washed with water, and dried. The product mixture was column chromatographed with methylbenzene as eluent. Three fraction sets were collected, evaporated to dryness, and the residues recrystallised from propan-2-one:methylated spirits (1:1 v/v) to give **7**(0.14g; 8.3%), **8**(0.081g; 4.8%), and **9** (0.053g; 3.2%).

Nitration of 1-nitro-2-(2,4,6-trinitrophenyl)naphthalene (5)

A solution of **5** (0.2 g) in sulphuric acid (*d* 1.84; 3 cm^3) and nitric acid (*d* 1.5; 3 cm^3) was stirred at 55° for 2 h, after which time the reaction mixture was poured onto crushed ice. The precipitate was filtered off, washed with water, and dried. The product mixture was column chromatographed using methylbenzene as eluent. Fractions were monitored by tlc. The fractions containing the first product eluted were combined, evaporated to dryness, and the residue recrystallised from propan-2-one:methylated spirits (1:1 v/v) to give **10** (0.044g; 18%), mp 234-8°. (Found: C, 40.9; H, 1.7; N, 16.4. $C_{16}H_6N_6O_{12}$ requires C, 40.5; H, 1.3; N, 17.7%). δ, 9.33 (2H, s), 8.88(1H,d,J_{AX} 9Hz), 8.73 (2H,s), 8.20(1H,d,J_{AX} 9Hz). *m/e* 474 (M^+). The fractions containing the second product eluted were combined, evaporated to dryness, and the residue recrystallised from propan-2-one:methylated spirits (1:1 v/v) to give **11** (0.037g; 15%), mp 247-51°. (Found: C, 41.0; H, 2.0; N, 16.3. $C_{16}H_6N_6O_{12}$ requires C, 40.5; H, 1.3; N, 17.7%). δ, 9.61(1H,d,J_{AX}2Hz), 9.33(2H,s), 9.16(1H,d,J_{AX}2Hz), 9.03(1H,d,J_{AX}9Hz), 8.19(1H,d,J_{AX}9Hz). *m/e*, 474(M^+).

Preparation of 2-bromo-1,6,8-trinitrobenzene

A solution of 2-bromo-8-nitronaphthalene (3g) in sulphuric acid (*d* 1.84; 10 cm^3) and nitric acid (*d* 1.42; 5 cm^3) was stirred at 100 for 4 h, after which time the reaction mixture was poured onto crushed ice. The precipitate was filtered off, washed with water, dried, and recrystallised from methylated spirits to give 2-bromo-1,6,8-trinitronaphthalene (1.10g; 27.1%), mp 205°(lit[13] mp 205°).

Preparation of 1,6,8-trinitro-2-(2,4,6-trinitrophenyl)naphthalene

A mixture of 2-bromo-1,6,8-trinitronaphthalene (0.75g) and 1-chloro-2,4,6-trinitrobenzene (1.5g) was heated at 150° whilst copper powder (0.75g) was added over 15min. The reaction mixture was maintained at 150° for a further 15 min. After cooling, the reaction mixture was Soxhlet extracted with methylbenzene, the extract evaporated to small volume, and then column chromotagraphed using methylchloride as eluant. The fraction containing the second band eluted was collected, evaporated to dryness, and the residue recrystallised from propan-2-one to give 1,6,8-trinitro-2-(2,4,6-trinitrophenyl)naphthalene (0.14g; 25.3%), mp 247-50°. The nmr parameters and *m/e* were the same as those for **11**.

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