Studies on Nitroaromatic Compounds. Part III.[1] The Synthesis of Some New Polynitroacenaphthenes

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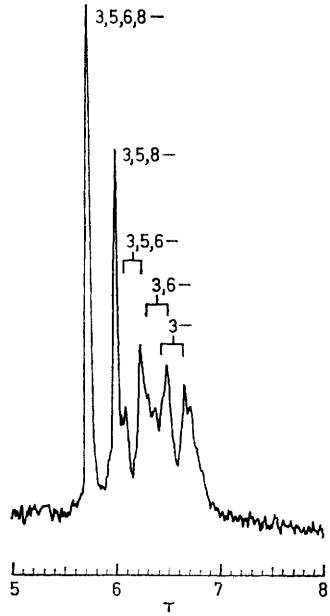
The nitration of mono- and di-nitroacenaphthenes in various media has been investigated, and it has been found that nitration occurs preferentially at the positions *para* to the aliphatic bridge. Methods have been devised for the preparation of 3,7-dinitroacenaphthene, 3,8-dinitroacenaphthene, 4,6-dinitroacenaphthene, 3,5,6-trinitroacenaphthene, 3,5,7-trinitroacenaphthene, 3,5,8-trinitroacenaphthene, 3,6,7-trinitroacenaphthene, 4,5,6-trinitroacenaphthene, 3,5,6,7-tetranitroacenaphthene, and 3,4,5,6,8-pentanitroacenaphthene.

ACENAPHTHENE can be readily nitrated, and a number of mono-, di-, and tetra-nitro-derivatives have been reported.[2-4] Mononitration yields either 5-nitroacenaphthene (VII)[5,6] or a mixture of 3-nitroacenaphthene (I) and 5-nitroacenaphthene,[7,8] depending on the reagent and reaction conditions employed. The third mononitro-isomer, 4-nitroacenaphthene (IX), is not formed to any significant extent in the nitration of acenaphthene, but it may be synthesised *via* the 5-nitro-derivative.[9,10]

Dinitration of acenaphthene and the further nitration of 3- and 5-nitroacenaphthene to dinitro-derivatives have received a good deal of attention;[2,7,11-14] much confusion existed in the literature on the structure of the dinitroacenaphthenes so prepared until the paper of Dashevskii and Malevannaya[15] was published. These workers showed that the dinitration of acenaphthene and the further nitration of 3- and 5-nitroacenaphthene by the methods reported gave only 3,6-dinitroacenaphthene (II) and 5,6-dinitroacenaphthene (VIII). They were unable to obtain 3,8-dinitroacenaphthene (III) by the earlier reported procedure of Morgan and Harrison.[2] Apart from the synthesis of 3,5,6,8-tetranitroacenaphthene (VI)[4] there are no reports on nitroacenaphthenes containing more than two nitro-groups.

One of the important factors controlling the extent of nitration in aromatic systems is the type of nitrating medium used. We have found that it is possible by using nitric acid in various solvents to take the nitration of mono- and di-nitroacenaphthenes to the di-, tri-, tetra-, or penta-nitro stages, and in this way to prepare a number of new polynitroacenaphthenes.

3-Nitroacenaphthene was converted into dinitroacenaphthenes by a mixture of nitric acid and 1,2-dichloroethane. Column chromatography of the product mixture yielded 3,6-dinitroacenaphthene and 3,8-dinitroacenaphthene. The ratio of the two isomers in the product mixture, as determined by n.m.r. spectroscopy, was *ca.* 9 : 1, respectively. Thus the insertion of a second nitro-group occurs preferentially at the position *para* to the aliphatic bridge in the ring remote from the nitro-group. Preferential substitution at the *para*-position also occurs in the nitration of acenaphthene.[16] This most probably arises because the aliphatic bridge distorts the naphthalenic ring system so as to increase the C(5)–C–C(6) bond angle[17] and to expose C-6 to electrophilic attack.



^{1}H N.m.r. spectrum of the product mixture from the nitration of 3-nitroacenaphthene in nitric acid–sulphuric acid after 100 min of reaction; solvent nitrobenzene

If the nitration of 3-nitroacenaphthene is carried out in a mixture of nitric acid and sulphuric acid the reaction

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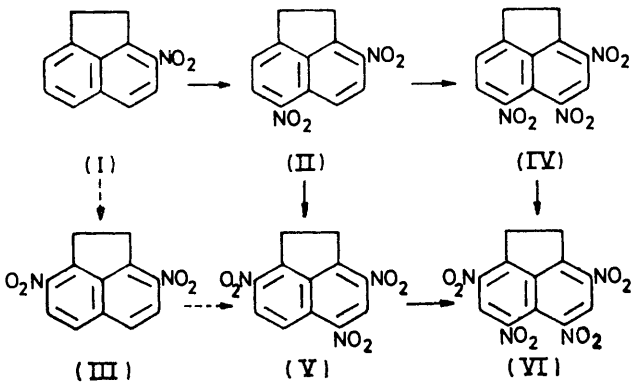
proceeds through to the tetranitro stage to give 3,5,6,8-tetranitroacenaphthene. Quenching the reaction mixture in ice–water at various time intervals after the start of the nitration and comparing the n.m.r. spectrum of the precipitated product (Figure) with the n.m.r. spectra of pure samples of di-, tri-, and tetra-nitroacenaphthenes showed that the 3,5,6,8-tetranitroacenaphthene is formed by a stepwise reaction sequence involving the intermediate formation of 3,6-dinitroacenaphthene, 3,5,6-trinitroacenaphthene (IV), and 3,5,8-trinitroacenaphthene (V). The postulated steps in the nitration of 3-nitroacenaphthene in nitric acid–sulphuric acid are shown in Scheme 1.

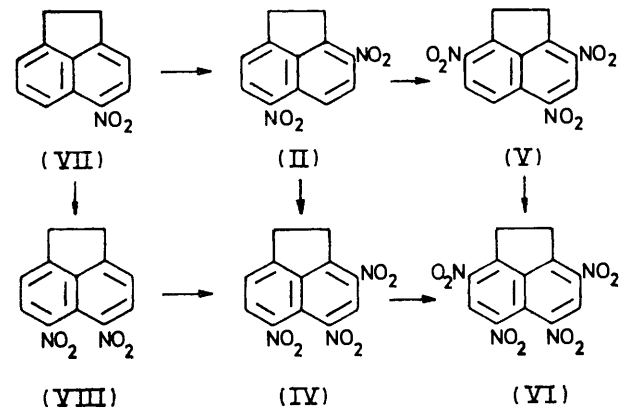


SCHEME 1

Although 3,8-dinitroacenaphthene could not be detected in the product mixture isolated from the reaction of 3-nitroacenaphthene in mixed acid, it is included as a possible reaction intermediate in Scheme 1 on the grounds that it is formed along with 3,6-dinitroacenaphthene when the nitration is carried out in nitric acid–1,2-dichloroethane.

The step in Scheme 1 involving the conversion of 3,6-dinitroacenaphthene into 3,5,6-trinitroacenaphthene and 3,5,8-trinitroacenaphthene was investigated by nitrating the 3,6-derivative in a mixture of fuming nitric acid and nitromethane. Under these conditions nitration of the trinitro-species is sufficiently slow to allow them to be isolated. The 3,5,6- and 3,5,8-trinitroacenaphthenes are formed in the ratio 7 : 3, respectively. Comparison of these figures with those for the conversion of 3-nitroacenaphthene into 3,6-dinitroacenaphthene and 3,8-dinitroacenaphthene (ratio 9 : 1) reveals that the presence of the nitro-group at the 6-position in the 3,6-dinitro-compound reduces the probability of substitution at the position *para* to the bridge relative to that for substitution at the *ortho*-position. This is probably partly owing to the steric effect of the nitro-group in the 6-position.

The course of the nitration of 5-nitroacenaphthene in nitric acid–sulphuric acid was followed, like that of 3-nitroacenaphthene, by using n.m.r. spectroscopy to analyse product mixtures isolated at different times during the reaction. The nitration proceeded *via* 3,6- and 5,6-dinitroacenaphthene and 3,5,6- and 3,5,8-trinitroacenaphthene, and gave 3,5,6,8-tetranitroacenaphthene as the final product. The probable steps in the reaction sequence are given in Scheme 2.



SCHEME 2

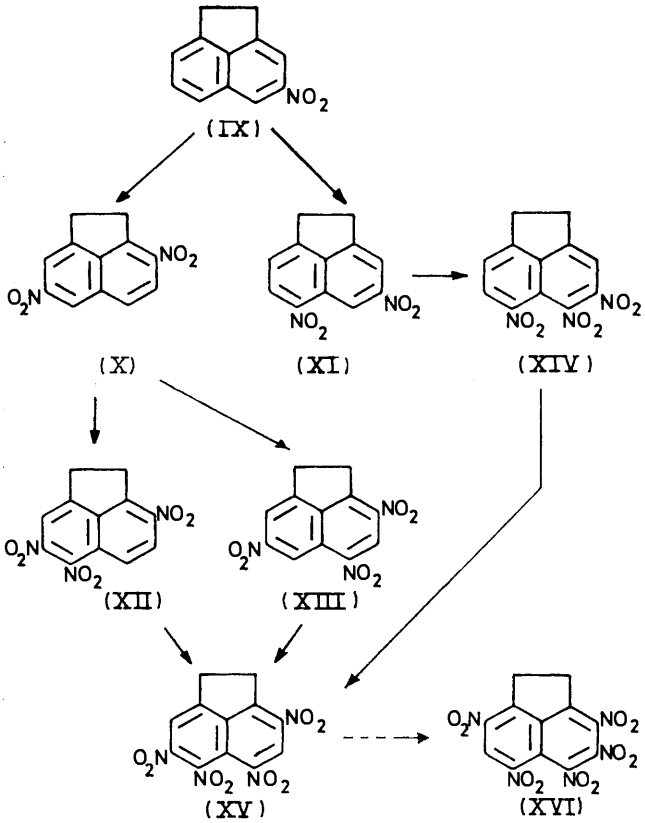
The initial nitration step of Scheme 2 produces the previously characterised 3,6- and 5,6-dinitroacenaphthenes. Further nitration of these dinitroacenaphthenes to the corresponding trinitroacenaphthenes can be studied by use of nitric acid–nitromethane as the nitration medium. Nitration of 3,6-dinitroacenaphthene gave 3,5,6- and 3,5,8-trinitroacenaphthene (see before); nitration of 5,6-dinitroacenaphthene yielded 3,5,6-trinitroacenaphthene.

Polynitroacenaphthenes with a nitro-group *meta* to the aliphatic bridge can be synthesised through the nitration of 4-nitroacenaphthene. The nitration of this compound in nitric acid–acetic anhydride gave a mixture of 3,7-dinitroacenaphthene (X) and 4,6-dinitroacenaphthene (XI) in the ratio 35 : 65, respectively. These figures are similar to those for the formation of 3-nitroacenaphthene and 5-nitroacenaphthene (34 : 66) from the nitration of acenaphthene in nitric acid–acetic anhydride.[16] It thus appears that the presence of a nitro-group *meta* to the aliphatic bridge does not significantly affect the relative reactivities of the *ortho*- and *para*-sites in the unsubstituted ring. However, as would be expected, the presence of a nitro-group at the *meta*-position deactivates the *ortho*- and *para*-positions in the substituted ring towards electrophilic attack, and neither the 3,4- or 4,5-dinitroacenaphthenes could be detected in the nitration of 4-nitroacenaphthene in nitric acid–acetic anhydride.

Carrying out the nitration of 4-nitroacenaphthene in a mixture of nitric acid, sulphuric acid, and nitromethane enables the reaction to be taken through to the trinitro stage. The only product which could be isolated, however, was 4,5,6-trinitroacenaphthene (XIV); either the other possible trinitro-isomers were not formed or else they were present in low concentration in the product mixture. This indicates that the preferred route for the nitration of 4-nitroacenaphthene in nitric acid–sulphuric acid–nitromethane is 4-nitroacenaphthene ⟶ 4,6-dinitroacenaphthene ⟶ 4,5,6-trinitroacenaphthene.

The occurrence of the first step in this sequence is supported by the observation that 4,6-dinitroacenaphthene is the predominant isomer formed during the nitration of 4-nitroacenaphthene in nitric acid–acetic anhydride.

The apparent absence of both the 3,4,6- and 3,5,7-trinitro-isomers from the product mixture obtained from the nitration of 4,6-dinitroacenaphthene in mixed acid–nitromethane indicates that the position *para* to the aliphatic bridge in this compound is much more susceptible to electrophilic substitution than either of the two *ortho* sites. The predominance of *para*-substitution is also demonstrated in the nitration of 3,7-dinitroacenaphthene. Nitration of this derivative in nitric acid–sulphuric acid gave a 1 : 1 mixture of 3,5,7-trinitroacenaphthene (XIII) and 3,6,7-trinitroacenaphthene (XII). The absence of 3,4,8-trinitroacenaphthene from the product indicates that *ortho*-substitution does not occur to any significant extent. Likewise, *ortho*-substitution does not occur in the nitration of 4,6-dinitroacenaphthene in nitric acid–sulphuric acid, and 4,5,6-trinitroacenaphthene is the only detectable product.



SCHEME 3

Treatment of 4-nitroacenaphthene with excess of nitric acid in sulphuric acid at room temperature affords 3,5,6,7-tetranitroacenaphthene (XV) as the sole product. The fact that the position which is *ortho* to the aliphatic bridge and *ortho* to the *meta*-nitro-group is vacant in this product indicates that compounds (XII), (XIII), and (XIV) are likely trinitro precursors. This, taken in conjunction with the prior observations on the nitrations of the 4-nitroacenaphthene, 3,7-dinitroacenaphthene, and 4,6-dinitroacenaphthene, suggests that the nitration steps leading to the formation of 3,5,6,7-tetranitroacenaphthene are as shown in Scheme 3.

3,4,5,6,8-Pentanitroacenaphthene (XVI) can be synthesised by treating 4-nitroacenaphthene with a mixture of fuming nitric acid and sulphuric acid at 35° for 5 days. Undoubtedly the pentanitro-derivative is formed in a stepwise process involving the intermediate formation of di-, tri-, and tetra-nitro species with the final step presumably being the conversion of 3,5,6,7-tetranitroacenaphthene into 3,4,5,6,8-pentanitroacenaphthene as shown in Scheme 3.

EXPERIMENTAL

Column chromatography was carried out with Merck Kieselgel (0·05—0·2 mm) unless otherwise stated. Mass spectral molecular weights were determined with an A.E.I. MS9 spectrometer. N.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer (tetramethylsilane as internal reference). The structures of the nitration products were assigned from the n.m.r. spectra. In particular, the structures of the isomeric products were assigned by use of the following criteria: (*a*) a single nitro-group *ortho* to the aliphatic bridge resulted in an A_2B_2 pattern for the resonance of the bridge protons, (*b*) nitro-groups in the 4- and 5-positions only affected the resonance position of the bridge protons and not the resonance pattern, and (*c*) the coupling constants for *ortho*-protons in the aromatic system lay in the range 8—10 Hz while those for *meta*-protons lay in the range 0—2 Hz.

Nitration of 3-*Nitroacenaphthene*.—3-Nitroacenaphthene[15] was recrystallised from acetic acid and then washed with water, methanol, and ether, and dried *in vacuo*. The n.m.r. spectrum of the product in nitrobenzene showed it to be free of the 5-isomer.

(a) *In nitric acid*–1,2-*dichloroethane*. Nitric acid (*d* 1·42; 3·5 ml) was added with stirring to a solution of 3-nitroacenaphthene (5 g) in 1,2-dichloroethane (16 ml) so that the temperature did not exceed 40°. After 5 min, more nitric acid (3·5 ml) was added with stirring, again with the temperature kept below 40°. After a further 12 h the resulting precipitate was filtered off, washed with a small quantity of cold 1,2-dichloroethane, then with water, and dried at 70° *in vacuo*. A portion of the mixture was chromatographed on a column (500 × 20 mm) of silica gel. Initially the eluant was 1 : 8 benzene–light petroleum (b.p. 60—80°), but its composition was gradually altered during 10 days to 1 : 4 benzene–light petroleum. Fractions containing each of the three yellow bands were evaporated to dryness. The first two components were identified as 3-nitroacenaphthene and 3,6-dinitroacenaphthene by comparison of their n.m.r. spectra (CD_3NO_2) with those of authentic samples. The third component was 3,8-*dinitroacenaphthene*, m.p. 186° (Found: C, 59·1; H, 3·3; N, 11·4. $C_{12}H_8N_2O_4$ requires C, 59·0; H, 3·3; N, 11·5%); τ (CD_3NO_2) 1·58 and 2·03 (2H, ABq, J_{AB} 10 Hz) and 6·06 (4H, s); *m/e* 244 (M^+).

(b) *In nitric acid–sulphuric acid* (*preparative run*). 3-Nitroacenaphthene (2·0 g) was added in portions to a mixture of nitric acid (*d* 1·42; 5·0 ml), sulphuric acid

(*d* 1·84; 15 ml). After 2 h the mixture was poured on crushed ice (50 g) and stirred for 15 min. The precipitated solid was filtered off, washed with water, until the filtrate was neutral, dried *in vacuo*, and recrystallised from nitromethane to give 3,5,6,8-*tetranitroacenaphthene* (2·8 g, 85%), m.p. 213° (lit.,[4] 212°), τ (CD_3NO_2) τ 0·75(s) and 5·77(s); *m/e* 334 (M^+).

(c) *In nitric acid–sulphuric acid* (*identification run*). 3-Nitroacenaphthene (0·5 g) was added in portions to a mixture of nitric acid (*d* 1·42; 1·75 ml), sulphuric acid (*d* 1·84; 7·5 ml), and water (0·75 ml). When addition was complete one third of the total volume was withdrawn, poured on crushed ice and stirred; the resulting precipitate was filtered off, washed, and dried. Half of the remaining volume was removed after 30 min and treated likewise, and the remaining mixture was treated similarly after 100 min. The n.m.r. spectra of the solid products in nitrobenzene were recorded over the range τ 5—10 (see Figure).

Nitration of 3,6-*Dinitroacenaphthene*.[15]—(a) *In nitric acid–nitromethane*. 3,6-Dinitroacenaphthene (1·2 g) was added to a stirred mixture of nitric acid (*d* 1·5; 6 ml) and nitromethane (10 ml). After 3 days the mixture was poured on crushed ice (50 g) and stirred vigorously for 2 h. The precipitate was filtered off, washed with water, and dried *in vacuo* at 90° to give a buff-coloured solid (1·32 g). The product (0·4 g) was chromatographed on a column of silica gel (20 × 400 mm; Hopkin and Williams silica gel M.F.C.). Decomposition occurred on the column but elution with benzene at *ca.* 3 ml min^{-1} separated two yellow bands. Evaporation of the first fraction to small volume and addition of excess of light petroleum (b.p. 40—60°) gave 3,5,8-*trinitroacenaphthene* (0·06 g, 17%), m.p. 152—155° (Found: C, 50·4; H, 2·8; N, 14·4. $C_{12}H_7N_3O_6$ requires C, 49·9; H, 2·5; N, 14·5%); τ (CD_3NO_2) 0·60 (1H, s), 1·20 (2H, s, splits into an AB system on addition of benzene), and 5·86 (4H, s); *m/e* 289 (M^+).

Evaporation of the second fraction to small volume and addition of excess of light petroleum (b.p. 40—60°) gave 3,5,6-*trinitroacenaphthene* (0·05 g, 14%), m.p. 202° (Found: C, 50·0; H, 2·9; N, 14·5. $C_{12}H_7N_3O_6$ requires C, 49·9; H, 2·5; N, 14·5%); τ (CD_3NO_2) 0·92 (1H, s), 1·39 and 2·07 (2H, ABq, J_{AB} 8 Hz), and 5·88 and 6·25 (4H, A_2B_2m); *m/e* 289 (M^+).

The n.m.r. spectrum of a sample of the product mixture in nitrobenzene showed that 3,5,6-trinitroacenaphthene and 3,5,8-trinitroacenaphthene were present in the ratio 7 : 3.

Nitration of 5-*Nitroacenaphthene*.[10]—Nitration of 5-nitroacenaphthene by the method of Vernon and Wilson [4] gave 3,5,6,8-tetranitroacenaphthene.

(a) *In nitric acid–sulphuric acid* (*identification run*). 5-Nitroacenaphthene (0·5 g) was added to a mixture of nitric acid (*d* 1·42; 1·75 ml), sulphuric acid (*d* 1·84; 7·5 ml), and water (0·75 ml). When addition was complete one third of the total volume was withdrawn, poured on crushed ice, and stirred; the resulting precipitate was filtered off, washed, and dried. Half of the remaining volume of the reaction mixture was removed after 30 min and treated likewise; the remaining mixture was treated similarly after 100 min. The n.m.r. spectra of the product mixtures in nitrobenzene showed the presence of di-, tri-, and tetranitroacenaphthenes (*cf.* Figure).

Nitration of 5,6-*Dinitroacenaphthene*.[15]—(a) *In nitric acid–nitromethane*. 5,6-Dinitroacenaphthene (24 g) was added to a stirred mixture of nitric acid (*d* 1·42; 200 ml) and nitromethane (200 ml). The mixture was stirred at room temperature for 5 days then poured on crushed ice (200 g) and stirred for 2 h. The precipitate was filtered off, washed with water, and dried *in vacuo* at 90°. Recrystallisation from 1 : 1 nitromethane–glacial acetic acid gave 3,5,6-trinitroacenaphthene (20·3 g), m.p. 199° (Found: C, 49·8; H, 2·4; N, 14·3. Calc. for $C_{12}H_7N_3O_6$: C, 49·9; H, 2·5; N, 14·5%), identical (n.m.r. and mass spectra) with the sample produced in nitration of 3,6-dinitroacenaphthene in nitric acid–nitromethane.

Nitration of 4-*Nitroacenaphthene*.[10]—(a) *In nitric acid–acetic anhydride*. 4-Nitroacenaphthene (4 g) was suspended in acetic anhydride (150 ml) by vigorous stirring and cooled to −10° in an ice–salt bath. An ice-cold solution of nitric acid (*d* 1·5; 2·5 ml) in acetic anhydride (40 ml) was added dropwise during 30 min, and the mixture was then maintained at 10—20° for 3 days. It was then poured into distilled water (1 l) and the precipitated product was filtered off, washed with water, and dried *in vacuo* at 90° to give a yellow solid (3·85 g). The product (0·1 g) was chromatographed on a column of silica gel (20 × 400 mm) with 1 : 1 diethyl ether–benzene as eluant and an elution rate of 0·7—0·8 ml min^{-1}. The product separated into two yellow bands. Evaporation of the first fraction to small volume and addition of excess of light petroleum (b.p. 40—60°) gave 3,7-*dinitroacenaphthene*, m.p. 275° (Found: C, 58·5; H, 3·5; N, 11·2. $C_{12}H_8N_2O_4$ requires C, 59·1; H, 3·4; N, 11·5%); τ (CD_3NO_2) 1·28 and 1·78 (2H, ABq, J_{AB} 2 Hz), 1·67 and 1·96 (2H, ABq, J_{AB} 9 Hz), and 6·04 and 6·35 (4H, A_2B_2m); *m/e* 244 (M^+).

Evaporation of the second fraction to small volume and addition of excess of petroleum (b.p. 40—60°) gave 4,6-*dinitroacenaphthene*, m.p. 200—202° (Found: C, 58·7; H, 3·7; N, 11·3. $C_{12}H_8N_2O_4$ requires C, 59·1; H, 3·4; N, 11·5%); τ (CD_3NO_2) 0·61 and 1·80 (2H, ABq, J_{AB} 2 Hz), 1·33 and 2·24 (2H, ABq, J_{AB} 8 Hz), and 6·40 (4H, s); *m/e* 244 (M^+).

The n.m.r. spectrum of a sample of the crude product in nitrobenzene showed that 3,7-dinitroacenaphthene and 4,6-dinitroacenaphthene were present in the ratio 35 : 65.

(b) *In nitric acid–sulphuric acid–nitromethane*. 4-Nitroacenaphthene (1 g) was dissolved in nitromethane (40 ml) and nitric acid (*d* 1·5; 8 ml) was added, followed by sulphuric acid (*d* 1·84; 4 ml). The mixture was stirred for 3 h and then washed with saturated aqueous magnesium nitrate (4 × 50 ml). The nitromethane solution was then dried ($MgSO_4$) for 24 h and filtered. The clear filtrate was then reduced in volume to (*ca.* 10 ml) and stored at −10° for 6 days. The precipitated crystalline solid was filtered off, washed with dichloromethane, and dried *in vacuo*. Recrystallisation from nitromethane gave the pale yellow 4,5,6-*trinitroacenaphthene* (0·3 g, 24%), m.p. 199° (Found: C, 49·4; H, 2·9; N, 14·4. $C_{12}H_7N_3O_6$ requires C, 49·9; H, 2·5; N, 14·5%), τ (CD_3NO_2) 0·90 (1H, s), 1·17 and 2·10 (2H, ABq, J_{AB} 9 Hz), and 6·20br (4H, s); *m/e* 289 (M^+).

(c) *In nitric acid–sulphuric acid*. 4-Nitroacenaphthene (1 g) was added in portions to a stirred mixture of nitric acid (*d* 1·42; 10 ml) and sulphuric acid (*d* 1·84; 10 ml). The solution was stirred for 8 h and then poured on crushed ice (50 g). The precipitate was filtered off, washed with water, and dried *in vacuo* at 90° to give 3,5,6,7-*tetranitroacenaphthene* (1·3 g, 77%), m.p. 157° (Found: C, 43·0; H, 2·1; N, 16·8. $C_{12}H_6N_4O_8$ requires C, 43·1; H, 1·8; N, 16·8%); τ (CD_3NO_2) 0·50 (1H, s), 0·75 (1H, s), and 5·79 and 5·99 (4H, A_2B_2m); *m/e* 334 (M^+).

(d) *In nitric acid–sulphuric acid at elevated temperature*.

4-Nitroacenaphthene (0·5 g) was added in small portions to a stirred mixture of nitric acid (*d* 1·5; 10 ml) and sulphuric acid (*d* 1·84; 10 ml) maintained in an ice-bath so as to keep the temperature below 10°. The mixture was then transferred to a dried flask (50 ml) equipped with a nitrogen inlet and drying tube, and was maintained at 35° under nitrogen for 5 days. (*N.B.* If the solution is left too long, oxidation products also precipitate out.) The crystalline precipitate was filtered off, washed with water, and dried *in vacuo* to give 3,4,5,6,8-*pentanitroacenaphthene* (0·25 g, 26%) (Found: C, 37·8; H, 1·8; N, 18·6. $C_{12}H_5N_5O_{10}$ requires C, 38·0; H, 1·3; N, 18·5%); τ (CD_3NO_2) 0·61 (1H, s) and 5·77 (4H, s); *m/e* 379 (M^+).

Nitration of 3,7-*Dinitroacenaphthene in Nitric Acid–Sulphuric Acid.*—A mixture of nitric acid (*d* 1·5; 0·1 ml) and sulphuric acid (*d* 1·84; 25 ml) was prepared, and a portion (2·5 ml) was added to a solution of 3,7-dinitroacenaphthene (0·06 g) in sulphuric acid (*d* 1·84; 2·5 ml). The mixture was stirred for 20 h and then poured on crushed ice (15 g). The precipitate was filtered off, washed with water, and dried *in vacuo* at 45° to give an ochre-coloured product (0·05 g). All attempts to separate the mixture by column chromatography failed on account of the rapid decomposition of the products on the various stationary phases used. Elemental analysis showed that the product was a mixture of trinitroacenaphthenes (Found: C, 50·4; H, 2·5. Calc. for $C_{12}H_7N_3O_6$: C, 49·9; H, 2·5%).

The n.m.r. spectrum of a sample of the product in [$^2H_3$]-nitromethane showed that it was a 1 : 1 mixture of 3,5,7-trinitroacenaphthene (XIII) and 3,6,7-trinitroacenaphthene (XII): τ (XIII) 0·59 (1H, s), 1·46 (2H, s), and 5·90 and 6·14 (4H, A_2B_2m) (the singlet at τ 1·46 splits into a doublet on addition of C_6D_6); τ (XII) 0·47 (1H, s), 1·33 and 1·74 (2H, ABq), and 5·90 and 6·14 (4H, A_2B_2m).

Nitration of 4,6-*Dinitroacenaphthene in Nitric Acid–Sulphuric Acid.*—A solution of nitric acid (*d* 1·5; 0·1 ml) and sulphuric acid (*d* 1·84; 25 ml) was prepared, and a portion (2·5 ml) was added to a solution of 4,6-dinitroacenaphthene (0·06 g) in sulphuric acid (*d* 1·84; 2·5 ml). The mixture was stirred for 24 h and then poured on crushed ice (20 g). The precipitate was filtered off, washed with water, and dried *in vacuo* at 45° to give 4,5,6-trinitroacenaphthene (0·04 g), identical (n.m.r. and mass spectra) with the sample produced from nitration of 4-nitroacenaphthene in nitric acid–sulphuric acid–nitromethane.

We thank Drs. I. Dunstan and R. J. J. Simkins and Mr. J. A. Bell for discussions, and the Ministry of Defence (Aviation Supply) for financial support.

[1/1571 *Received, August 27th,* 1971]

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