where k_+ was relatively secure, an iterative procedure was used. First K was estimated from the measured absorbances. Then k_- was calculated from eq 1. A new value of K was given by k_+/k_-. This process was repeated until input and output K values differed by less than 1%. Usually no more than three calculations of k_- was required to meet this criterion. Table III shows the course of a typical iteration. For reactions involving **5**, where the k_+ values were less secure, the iterative procedure was not used in order to avoid compounding the error in k_+. Fortunately, these reactions were faster than others, and satisfactory approximations of K could be obtained from the absorbances at 10 or more half-lives. Nevertheless, values of K given by k_+/k_- were judged to be more reliable than those obtained from final absorbances and are the values reported in Table I. In no case did the two values of K differ by more than 50%, and typical discrepancies were around 25%. On replication, values of K and k_- determined by eq 11 typically showed an average deviation from the mean of ~10% and a probable error ~4%. The largest probable error in these constants was 6%. When possible systematic errors are also considered (errors in k_+ and K_R), it seems reasonable to assign an uncertainty of ±10% to the K values. For reaction of **5** with **3Hd** and the reverse it was possible to measure k_1 both in pseudo-first-order (eq 8) and in second-order (eq 11) conditions, by suitably adjusting the concentration of **3Hd** or **3d**. The values of k_+ were 3.18 and 3.66×10^{-2} M^{-1} s^{-1}, from the pseudo-first-order and the second-order experiments, respectively, and for k_-, 3.48 and 3.66×10^{-2} M^{-1} s^{-1}. The discrepancies between these values are entirely consistent with the uncertainties estimated above.

All values of k_1 were fitted to the data using a linear least-squares program in a programmable calculator. The correlation coefficients were all above 0.99. The absence of curvature was verified graphically. In a few cases the average discrepancy between measured absorbances and those calculated from eq 8 or 11 was calculated, by using the determined values of the constants. This was less than 0.001 in each case. Thus the scatter in the constants originates in such factors as temperature control or pH measurement, rather than inaccuracies in absorbances or the bias of the linear least-squares evaluation of k_1.

Values of pH were determined using a Radiometer pH meter with a glass pH electrode and a calomel reference electrode. The glass electrode was calibrated by using dilute perchloric acid solutions in the 2-isopropanol–water mixed solvent.

Absorbance was measured at a fixed wavelength using a hybrid spectrophotometer: the monochromator of a Beckman DU spectrophotometer with Gilson source, detector, and digital readout.

Nitration of Bis(amido)naphthalenes[1]

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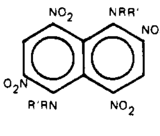
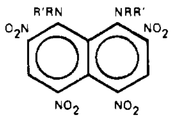
Nitration studies have been conducted on the bis(acetamido), bis(p-toluenesulfonamido), and bis(trifluoroacetamido) derivatives of 2,6-diamino-4,8-dinitro- and 1,5-diaminonaphthalene. The bis(trifluoroacetamides) were nitrated readily to produce tetranitro derivatives, whereas the p-toluenesulfonamides and acetamides gave predominantely dinitro products. The tetrakis(trifluoroacetyl) and tetraacetyl derivatives of 1,3,5,7-tetraaminonaphthalene were nitrated to yield di- and mononitro products, respectively. Solvolysis of some of the amides was successful (most facile with trifluoroacetamido), leading to the first preparations of 2,6-diamino-1,4,5,8-tetranitro-, 1,5-diamino-4,8-dinitro-, and 1,5-dinitro-2,4,6,8-tetraaminonaphthalenes. Peracid oxidation of the new diamines or amides failed to yield polynitronaphthalenes. The effect of structure on the course of nitration, solvolysis, and oxidation of the new nitrated naphthalene derivatives is discussed.

Introduction

As part of our investigation of synthetic routes leading to new polynitronaphthalenes, we have studied the nitration of selected bis(acetamido)-, bis(p-toluenesulfonyl)-, and bis(trifluoroacetamido)naphthalenes. These studies have led to the synthesis of some new polynitronaphthalenediamines. Synthetic methods leading to these materials are discussed as well as results of some unsuccessful attempts to convert them into hexa- and octanitronaphthalene. Of the 75 possible nitronaphthalenes, none are known which contain more than four nitro groups, nor are any such derivatives known, with the exception of 3,4,5,6,8-pentanitroacenaphthene.[3] The extensive studies by Hodgson[4] and Ward[5] and co-workers describe syntheses and structure assignments of many polynitronaphthalenes and their amino derivatives.

Nitrations of bis(amido)naphthalenes have been described by others. Two tetranitronaphthalenediamines and their derivatives have been reported[4a,6]—1,5-diamino-2,4,6,8-tetranitronaphthalene (**1a**) and 1,8-diamino-2,4,5,7-tetranitronaphthalene (**2a**). These compounds





1a; R = R' = H
1b; R = H, R' = 4-$CH_3C_6H_4SO_2$
1c; R = H, R' = 3-$NO_2C_6H_4SO_2$

2a; R = R' = H
2b; R = H, R' = 4-$CH_3C_6H_4SO_2$
2c; R = R' = CH_3

were obtained by nitration of the N,N'-bis(p-toluene-

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[1] Presented, in part, at the Pacific Conference on Chemistry and Spectroscopy, San Francisco, CA, Oct. 10, 1985.

[2] National Research Council/Naval Weapons Center Postdoctoral Research Associate, 1981–1982.

[3] Webb, B. C.; Wells, C. H. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 166.

[4] (a) Hodgson, H. H.; Whitehurst, J. S. *J. Chem. Soc.* **1947**, 80. (b) Hodgson, H. H.; Dean, R. E. *Ibid.* **1950**, 822. (c) Hodgson, H. H.; Ward, E. R. *Ibid.* **1949**, 1187 and other papers by H. H. Hodgson and coworkers.

[5] (a) Ward, E. R.; Johnson, C. D. *J. Chem. Soc.* **1961**, 4314. (b) Ward, E. R.; Wells, P. R. *Ibid.* **1961**, 4866 and other papers by E. R. Ward and coworkers.

[6] (a) Buckley, E.; Everard, J. E.; Wells, C. H. *J. Chem. Ind. (London)* **1978**, 124. (b) Buckley, E.; Houiellebecq, T. F.; Wells, C. H. J. *Ibid.* **1981**, 774.

sulfonamides) of 1,5- and 1,8-naphthalenediamines (**1b**, **2b**), followed by solvolysis with sulfuric acid; similarly **1a** was also prepared from the *N*,*N'*-bis(3-nitrobenzenesulfonamide), **1c**. An *N*,*N*,*N'*,*N'*-tetramethyl derivative of **2a** (**2c**) has recently been reported to form quantitatively by nitration of 1,8-bis(dimethylamino)naphthalene.[7] [Our efforts to repeat the preparation of **1a** from **1b** by the procedure described (and other procedures) were unsuccessful; instead we isolated a 4,8-dinitro derivative.]

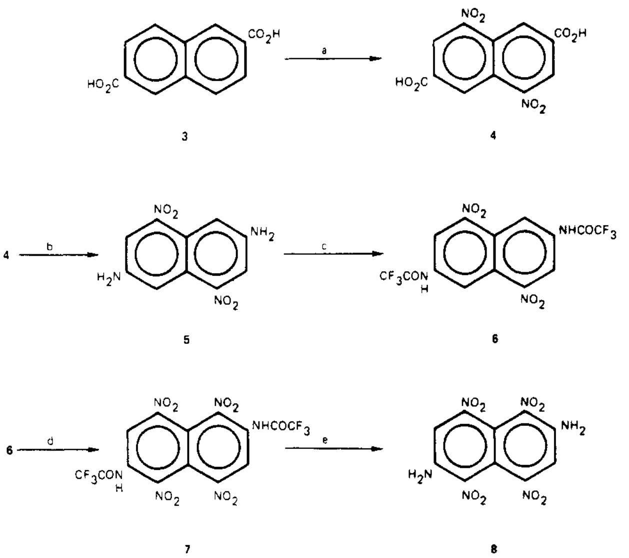
Other nitrations of bis(amido)naphthalenes (the 1,2-, 1,4-, and 2,7-isomers) have produced mono-, di-, and trinitro derivatives. 2,7-Bis(amido)naphthalenes (acetamido, benzamido, and *p*-toluenesulfonamido) have been nitrated to yield 1,8-dinitro derivatives; the *p*-toluenesulfonyl derivative also gave a 1,5,8-trinitro bisamide, and the acetyl compound gave a mononitro product.[8] The corresponding amines were prepared from the *p*-toluenesulfonyl derivative.[8] Nitration of 1,4-bis(acetamido)naphthalene gave either the 2-nitro or 2,3-dinitro derivative, but the corresponding diamines were not prepared.[9-11] Nitration of 1,2-bis(acetamido)-4-nitronaphthalene gave the 3,4-dinitro derivative which was not converted into the diamine.[12] These reported results reveal that the sulfonamides more readily produce nitrated naphthalene products than do the carboxamides and that the resulting polynitronaphthalenesulfonamide derivatives are much more easily hydrolyzed to the free diamines. The polynitrobis(acetamido)naphthalenes are hydrolyzed to diamines with great difficulty and often yield phenols wherein the amido group is replaced by hydroxyl.[10] Our present results agree with these observations.

Results and Discussion

In the present work we have studied the nitration of the 1,5- and 2,6-bis(acetamido)-, bis(*p*-toluenesulfonamido)- and bis(trifluoroacetamido)naphthalenes and certain nitro derivatives. To our knowledge trifluoroacetamido derivatives of naphthalenes have not previously been employed in nitration studies. The utility of the trifluoroacetamido group has been demonstrated in at least one related example, the preparation of mono- and dinitrofluorenamines.[13] We find that the bis(trifluoroacetamides) are more readily nitrated to tetranitronaphthalene derivatives than are the corresponding acetamides or *p*-toluenesulfonamides. Also, the nitrated trifluoroacetamides are usually more readily hydrolyzed to the parent polynitrodiamines than are the other bisamides.

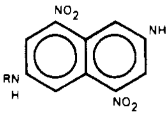
2,6(3,7)-Diaminopolynitronaphthalenes. No nitro derivatives of 2,6-diaminonaphthalene are known, although the diamine itself has been prepared.[14,15] Because we were interested in obtaining a meta-substituted dinitro derivative of 2,6-diaminonaphthalene, we prepared 3,7-diamino-1,5-dinitronaphthalene (**5**) (Scheme I). Nitration of naphthalene-2,6-dicarboxylic acid (**3**) with 90% HNO_3 at 60 °C led to 1,5-dinitronaphthalene-3,7-dicarboxylic acid **4** in 60–66% yield. The Schmidt conversion of **4** to 3,7-diamino-1,5-dinitronaphthalene (**5**) is very efficient (98% yield).

Scheme I[a]

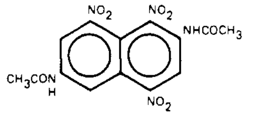


[a] (a) 90% HNO_3, 60 °C; (b) 20% Oleum, NaN_3, 50 °C; (c) $(CF_3CO)_2O$, reflux; (d) 90% HNO_3, concentrated H_2SO_4, 25–55 °C; (e) HCl, CH_3OH, 25–50 °C.

Nitrations of three bis(amides) of 3,7-diamino-1,5-dinitronaphthalene (**5**) were investigated—the bis(trifluoroacetyl), bis(acetyl), and bis(*p*-toluenesulfonyl) derivatives (**6**, **9a**, and **9b**, respectively). These were readily prepared in nearly quantitative yield from the parent diamine and the appropriate acid anhydride or acid chloride. The bis(trifluoroacetamide) **6** was readily nitrated in 90% HNO_3/concentrated H_2SO_4 at 25–55 °C to form 2,6-bis(trifluoroacetamido)-1,4,5,8-tetranitronaphthalene (**7**) in 90% yield (Scheme I). On the other hand, nitration of 3,7-bis(acetamido)-1,5-dinitronaphthalene (**9a**) with the same nitrating mixture at 3–5 °C led to the 1,4,5-trinitro derivative (**10**, 75% yield); use of more vigorous reaction conditions gave a complex mixture of unidentified products. 3,7-Bis-(*p*-toluenesulfonamido)-1,5-dinitronaphthalene (**9b**) was not nitrated with 70% HNO_3 in acetic acid solvent at 25 °C (86% recovery of reactant); the reaction conditions were those employed by Hodgson and Whitehurst[4a] for the synthesis of **1b** and **2b**. More vigorous reaction conditions led to unidentified products. Direct nitration of the diamine **5** (90% HNO_3/H_2SO_4, 40–60 °C) gave only water-soluble products; at 0–20 °C the same nitrating mixture gave traces of a product mixture containing a diazo oxide (2130 cm^{-1}), possibly **13** (vide infra).



9a; R = CH_3CO
9b; R = $4\text{-}CH_3C_6H_4SO_2$



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2,6-Diamino-1,4,5,8-tetranitronaphthalene (**8**) was obtained quantitatively from the corresponding bis(trifluoroacetamide) (**7**) by treatment with methanolic HCl at 25–50 °C (Scheme I); methanolic potassium carbonate or H_2SO_4 (25 °C) was less suitable for this cleavage.

Nitration of the tetranitrodiamine **8** with HNO_3 in 80% H_2SO_4 at 3 °C led to isolation of dinitramine **11**, unstable at ambient temperature. At 25 °C the material spontaneously undergoes decomposition even in the solid state to form a bisdiazo oxide, tentatively assigned structure **13** (ν 2130 cm^{-1}).

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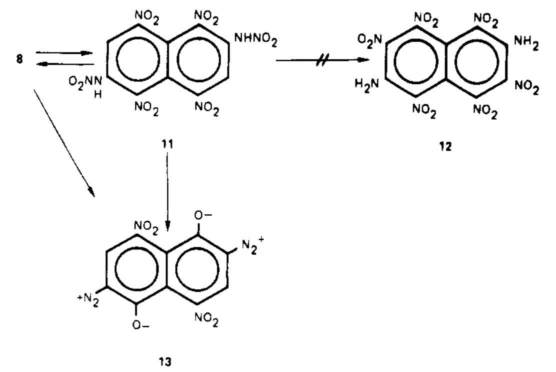
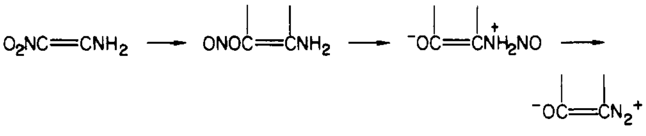
[7] Kurasov, L. A.; Pozharskii, A. F.; Kuz'menko, V. V.; Klyuev, N. A.; Chernyshev, A. I.; Goryaev, S. S.; Chikina, N. L. *Zh. Org. Khim.* **1983**, 590.
[8] Bell, F. *J. Chem. Soc.* **1962**, 4254.
[9] Panizzon-Favre, G. *Gazz. Chim. Ital.* **1924**, *54*, 826.
[10] Hodgson, H. H.; Elliott, R. L. *J. Chem. Soc.* **1936**, 1151.
[11] Hodgson, H. H.; Turner, H. S. *J. Chem. Soc.* **1943**, 635.
[12] Hodgson, H. H.; Elliott, R. L. *J. Chem. Soc.* **1936**, 1762.
[13] Namkung, M. J.; Fletcher, T. L. *J. Org. Chem.* **1960**, *25*, 740.
[14] Leonard, N. J.; Hyson, A. M. *J. Am. Chem. Soc.* **1949**, *71*, 1961.
[15] Chatt, J.; Wynne, W. P. *J. Chem. Soc.* **1943**, 33.

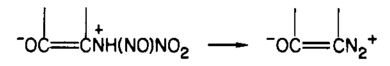


The conversion 11 → 13 also occurs in D_2SO_4 and is complete within 20 h at 25 °C. Rearrangements of polynitroarylnitramines to diazo oxides occur readily and have been encountered frequently in our studies of these compounds.[16,17] Formation of diazo oxide 13 from 11 is much more rapid than rearrangement to 2,6-diamino-1,3,4,5,7,8-hexanitronaphthalene (12), which could not be detected in the reaction products. Nitramine rearrangements of electronegatively substituted arylnitramines to *o*-nitroarylamines are known to be strongly inhibited by the presence of electronegative ring substituents, particularly nitro.[18] The conversion 11 → 13 in D_2SO_4 leads to the appearance of the strong singlet of an intermediate at δ 7.86, much farther upfield than the singlet observed for 11 in acetone-d_6 (δ 9.36); during reaction the δ 7.86 signal becomes completely replaced by that of 13 at δ 8.35 (δ 8.36 in acetone-d_6). The intermediate is possibly 2,6-bis(nitramino)-1,5-dihydroxy-4,8-dinitronaphthalene (formed by solvolysis or nitro → nitrite rearrangement of 11)[19] which is slowly converted to 13. Nitration of 8 with HNO_3 in acetic acid or 65% H_2SO_4 at 25 °C gave 13 directly. Diazo oxide 13 was also formed rapidly upon dissolving 8 in D_2SO_4 at 25 °C. Solvolysis or nitro → nitrite rearrangement of the 1,5-dinitro groups in 8 (or its salt) would be expected to precede formation of 13. However, 8 is stable in concentrated H_2SO_4 for up to 5 h at 25 °C and may be recovered; after 18 h, diazo oxide is produced. Heating 8 alone at 60 °C produced slow conversion to 13 suggesting an intermediate thermal nitro → nitrite rearrangement process leading to a protonated nitrosamine, followed by dehydration to diazo oxide



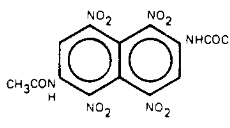
$$O_2NC{=}CNH_2 \longrightarrow ONOC{=}CNH_2 \longrightarrow {}^-OC{=}\overset{+}{C}NH_2NO \longrightarrow {}^-OC{=}CN_2^+$$

The more facile thermal conversion 11 → 13 may be a similar process with loss of nitric acid in the final step



$${}^-OC{=}\overset{+}{C}NH(NO)NO_2 \longrightarrow {}^-OC{=}CN_2^+$$

Nitrations of the *N,N'*-bis(trifluoroacetyl)- and *N,N'*-diacetyl derivatives of diamine 8 (7 and 14, respectively) were also investigated. The bis(acetamide) was readily prepared by reaction of 8 with acetic anhydride (H_2SO_4 catalyst). Attempted further nitration of the bis(trifluoroacetamido) derivative 7 under more vigorous conditions (100% HNO_3, 20% oleum, 55 °C, 6 h) led only to some recovered reactant in addition to water-soluble, nonextractable products. The bis(acetamide) 14, on the other hand, reacting with nitric acid in concentrated H_2SO_4 at 25 °C, although yielding no bis(acetamido) derivative of 12, nor a diazo oxide, produced an unidentified crystalline compound, $C_{10}H_3N_5O_7$; spectral data suggest a quinone structure in one ring with amino and dinitro groups remaining in another. This substance was also obtained by treatment of the parent diamine 8 with peroxydisulfuric acid in H_2SO_4. Several conversions of 1,5- and 1,8-dinitro and 1,4,5,8-tetranitronaphthalenes into 1,4-naphthoquinones have been reported (sulfur/H_2SO_4 or other reducing agents in acidic medium).[20]



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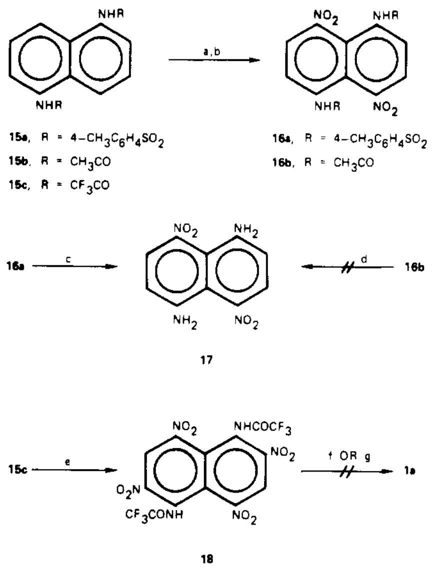
Scheme II[a]



[a] (a) 70% HNO_3, HOAc, 25 °C for formation of 16a; (b) 90% HNO_3, concentrated H_2SO_4, 5–15 °C, for formation of 16b; (c) concentrated H_2SO_4, 43 °C; (d) concentrated H_2SO_4, 65–70 °C; (e) 90% HNO_3, concentrated H_2SO_4, 25 °C; (f) HCl, CH_3OH, 25–50 °C; (g) KOH, CH_3OH, reflux.

1,5-Diaminopolynitronaphthalenes. Hodgson and Whitehurst studied the nitration of 1,5-bis(*p*-toluenesulfonamido)naphthalene (15a) (Scheme II) and reported the formation of the 2,4,6,8-tetranitro derivative **1b** as well as the parent 1,5-diamino-2,4,6,8-tetranitronaphthalene (**1a**) by its hydrolysis.[4a] Apparently, no other nitro derivatives of 1,5-diaminonaphthalene have previously been described in the literature. We have repeated the nitration of **15a** under the conditions described by Hodgson and Whitehurst and obtained only the 4,8-dinitro derivative **16a**, rather than **1b** (Scheme II). The properties of **16a** were found to be virtually identical with those reported by Hodgson and Whitehurst for **1b** (see Experimental Section). Hydrolysis of **16a** led quantitatively to 1,5-diamino-4,8-dinitronaphthalene (**17**) under conditions

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(16) Atkins, R. L.; Nielsen, A. T.; Willer, R. L.; Hollins, R. A. *Nav. Res. Rev.* **1983**, *35*, 25.

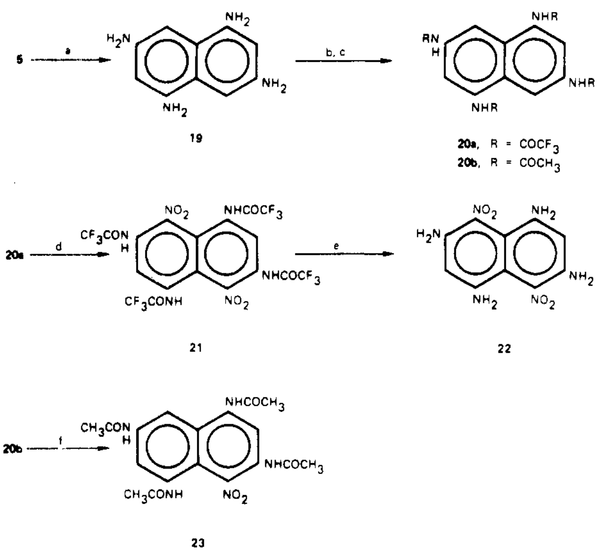
(17) Nielsen, A. T.; Henry, R. A.; Norris, W. P.; Atkins, R. L.; Moore, D. W.; Lepie, A. H.; Coon, C. L.; Spanggord, R. J.; Son, D. V. H. *J. Org. Chem.* **1979**, *44*, 2499.

(18) White, W. N. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 3, p 109–143.

(19) (a) Hartshorn, M. P.; Ing, H. T.; Richards, K. E.; Sutton, K. H.; Vaughan, J. *Aust. J. Chem.* **1982**, *35*, 1635. (b) Mudge, P. R.; Salter, D. A.; Scilly, N. F. *J. Chem. Soc., Chem. Commun.* **1975**, 569.

(20) (a) Bruce, D. B.; Thomson, R. H. *J. Chem. Soc.* **1955**, 1089. (b) Dimroth, O.; Ruck, F. *Justus Liebigs Ann. Chem.* **1925**, *446*, 123. (c) Will, W. *Ber. Dtsch. Chem. Ges.* **1895**, *28*, 2234.

Scheme III[a]



[a] (a) $SnCl_2$, concentrated HCl, 55 °C; (b) $(CF_3CO)_2O$, reflux yields 20a; (c) $(CH_3CO)_2O$, 25 °C yields 20b; (d) 90% HNO_3, concentrated H_2SO_4, 3–5 °C; (e) $(C_2H_5)_3N$, CH_3OH, 25 °C; (f) 90% HNO_3, 25 °C.

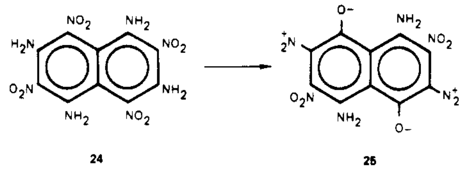
whereby the reported tetranitro bis(amide) **1b** was said to form **1a**; the melting point which we have observed for **17** (300 °C) was close to that reported for **1a** (295 °C).[4a] When we attempted further nitration of **16a** in HNO_3/acetic acid, we obtained only recovered reactant (86%). We have concluded that the products described by Hodgson and Whitehurst as tetranitronaphthalenes **1a,b** are actually dinitro compounds.

We have also prepared 1,5-bis(acetamido)-4,8-dinitronaphthalene (**16b**) by nitration of 1,5-bis(acetamido)naphthalene (**15b**) (Scheme II). However, in this case hydrolysis of the amide to the dinitro diamine **17**, under conditions whereby the bis(*p*-toluenesulfonamide) **16a** was readily hydrolyzed, could not be achieved.

1,5-Bis(trifluoroacetamido)-2,4,5,8-tetranitronaphthalene (**18**) was prepared by nitration of 1,5-bis(trifluoroacetamido)naphthalene (**15c**) (Scheme II). Numerous attempts to hydrolyze **18** to 1,5-diamino-2,4,5,8-tetranitronaphthalene **1a** led to recovered reactant or, under focusing conditions, to unidentified amorphous products. Hydrolysis reaction conditions included those which readily produced 2,6-diamino-1,4,5,8-tetranitronaphthalene (**8**) from the corresponding bis(trifluoroacetamide) **7** (Scheme I). This striking difference in behavior between the two tetranitro bis(trifluoroacetamides) (**7** and **18**) may be associated, in part, with the greater steric hindrance to solvolysis of an amido group (in **18**) which is flanked by ortho- and peri-substituted nitro groups; also, the nitro group substitution pattern differences in the two compounds could produce different solvolysis rates.[21]

1,3,5,7-Tetraaminopolynitronaphthalenes. We have also studied the nitration of 1,3,5,7-tetrakis(trifluoroacetamido)naphthalene (**20a**, Scheme III). 1,3,5,7-Tetraaminonaphthalene (**19**) was prepared by stannous chloride reduction of 3,7-diamino-1,5-dinitronaphthalene (**5**); it had also been prepared previously by stannous chloride reduction of 1,3,5,7-tetranitronaphthalene.[15] Refluxing trifluoroacetic anhydride readily converts **19** into the tetraamide **20a**. Nitration of **20a** gave the 4,8-dinitro derivative **21** in 86% yield (Scheme III). Solvolysis of **21** occurred quantitatively in methanolic triethylamine to yield 1,5-dinitro-2,4,6,8-tetraaminonaphthalene (**22**) (structure supported by ^1H NMR).

Reaction of the tetraamide **20a** with nitrating agents under various, more vigorous conditions (e.g., HNO_3, oleum, 25–40 °C, 3 days) led to amorphous degradation products and/or recovered reactant. Nitration of dinitrotetraaminonaphthalene **22** in acetic acid gave a product which revealed a strong diazo oxide signal in its infrared spectrum (2130 cm^{-1}) and no aryl hydrogens in the ^1H NMR spectrum, suggesting the possible formation of **25**. This result would presuppose ring nitration of **22** to occur, leading to the intermediate tetranitrotetraamine **24** (not isolated), precursor of **25**. Mechanisms like those discussed for the **8** → **13** conversion may apply here.



1,3,5,7-Tetraacetamidonaphthalene (**20b**) was prepared in quantitative yield by simply stirring the tetramine **19** with acetic anhydride. Nitration of **20b** proceeded with greater difficulty than with the corresponding trifluoroacetyl compound **20a**, and only a mononitro derivative (**23**) could be prepared (Scheme III). More vigorous reaction conditions (90% HNO_3, concentrated H_2SO_4, 25 °C, 19 h) led to water-soluble, nonextractable products. Hydrolysis of **23** to the corresponding tetraaminonitronaphthalene was not investigated.

Polynitronaphthalenes. One of the objectives of the present research effort is to prepare polynitronaphthalenes, including hexa- and octanitronaphthalene. We have attempted unsuccessfully to oxidize some of the polynitro diamines and diamides described in this study to polynitronaphthalenes. Oxidation of 2,6-diamino-1,4,5,8-tetranitronaphthalene (**8**) with 98% H_2O_2 in trifluoroacetic acid gave a product having a strong diazo oxide band (ν 2130 cm^{-1}), possibly **13**, not further characterized. With peroxydisulfuric acid (H_2O_2 in 100% H_2SO_4, 25 °C, 96 h) **8** gave an unidentified product, $C_{10}H_3N_5O_7$, identical with that observed to form from the nitration of the bis(acetamide) **14**; the corresponding bis(trifluoroacetamide) **7** was recovered when subjected to similar reaction conditions. Attempts were also made to oxidize 3,7-diamino-1,5-dinitronaphthalene (**5**) to known 1,3,5,8-tetranitronaphthalene;[15] the reagents examined, which included peroxydisulfuric acid in H_2SO_4, peracetic acid in acetic acid, and peroxytrifluoroacetic acid in trifluoroacetic acid (25–80 °C), gave unidentified amorphous products but no tetranitronaphthalene. Attempted oxidation of 3,7-bis(acetamido)-1,5-dinitronaphthalene (**9a**) with peroxydisulfuric acid in H_2SO_4 (25 °C) gave unchanged reactant.

Related benzene compounds exhibit behavior contrasting to that of naphthalenes; some phenylenediamines and diamides have successfully been oxidized to the corresponding dinitrobenzene products. For example, 1,3- and 1,4-phenylenediamines gave 1,3- and 1,4-dinitrobenzenes (76% and 86% yields, respectively) with peroxyacetic acid.[22] 1,3-Bis(acetamido)-2,4,6-trinitrofluorobenzene has been oxidized to pentanitrofluorobenzene with peroxydisulfuric acid (23% yield).[23] However, certain other di-

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(21) Krol et al. [Krol, L. H.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 545] discuss the effect of structure on the deacylation of several nitro-substituted 1- and 2-acetamidonaphthalenes. Some rather large effects are noted. For example, 1-acetamido-2-nitronaphthalene is deacylated at a rate 200 times slower than that of 2-acetamido-1-nitronaphthalene.

(22) Emmons, W. D. *J. Am. Chem. Soc.* **1954**, *76*, 3470.

amines could not be oxidized under comparable conditions (1,3-diamino-2,4,6-trinitrobenzene, for example, failed to yield pentanitrobenzene, although tetranitroaniline was readily oxidized to that product).[23] Two examples of oxidation of a naphthylamine to a nitronaphthalene have been reported. 2-Aminonaphthalene gave 2-nitronaphthalene in 40% yield with permaleic acid;[24] however, the yield is 0% with peroxydisulfuric acid[23] or peroxytrifluoroacetic acid.[22] 2-Amino-1-nitronaphthalene gave 1,2-dinitronaphthalene in 25% yield with peroxyacetic acid, but the isomeric 1-amino-4-nitronaphthalene failed to yield 1,4-dinitronaphthalene under conditions whereby 4-nitroaniline gave 1,4-dinitrobenzene in 59% yield.[25] All of these observations are in agreement with our previous conclusion that the oxidizing power of the peracid and the acid strength of the solvent acid must be closely correlated with the basicity of the amine, since the oxidant attack occurs on the free amine.[23] On the other hand, more electronegatively substituted anilines require more powerful oxidants, such as peroxydisulfuric acid.[23] One of the reasons for failure of the $NH_2 \rightarrow NO_2$ oxidation in polynitronaphthalenediamines is believed to be the greater vulnerability of the naphthalene ring itself (relative to benzene) to oxidation, a process more rapid than oxidation of amino to nitro.

Our study of the nitrations of naphthalene bisamides has shown that the trifluoroacetamides are superior to the acetamides and *p*-toluenesulfonamides for polynitration (up to four nitro groups). The acetamides are least readily nitrated. Solvolysis of the trifluoroacetamides is more facile than that of the acetamides. The polynitronaphthalenediamines and diamides are not suitable precursors for oxidation to polynitronaphthalenes containing two additional nitro groups, owing primarily to the great facility of oxidation of the naphthalene rings in these substances.

Experimental Section

Melting points were determined on a Kofler hot stage. NMR spectra were recorded on a Nicolet WB200, Varian XL-100, or Varian EM360 spectrometer (tetramethylsilane internal standard in organic solvents, 3-(trimethylsilyl)propanesulfonic acid in D_2SO_4), mass spectra on a Hewlett-Packard 5985 GC/MS system (70 eV), and infrared spectra on a Perkin-Elmer 137 or Nicolet 7199 FT instrument.

Warning! *All polynitro compounds described are explosives and should be handled with great care.*

Naphthalene-2,6-dicarboxylic acid (3) was most conveniently prepared by aqueous sodium dichromate oxidation of 2,6-dimethylnaphthalene (50-g batches, 90–95% yield).[26] It was also prepared by hydrolysis of 2,6-dicyanonaphthalene with refluxing aqueous sulfuric/acetic acids (92–98% yield).[27] Samples prepared by both methods were obtained as small prisms, mp 366–368 °C.

1,5-Dinitronaphthalene-3,7-dicarboxylic Acid (4). Naphthalene-2,6-dicarboxylic acid (3, 60.0 g, 0.278 mol) was added during 1 h, with stirring, to 700 mL of 90% nitric acid, keeping the temperature below 35 °C. The mixture was heated to 60 °C with continued stirring during 1 h, after which time the reactant had dissolved with evolution of red fumes; stirring was continued at 60 °C for one additional hour. After being allowed to cool to 25 °C, the mixture was poured over 1800 g of ice and the precipitate removed by filtration and washed with water (4 × 200 mL) to yield 51.6 g (61%) of high-purity 4, mp 357 °C; parallel runs gave 60–66% yields; recrystallization from boiling acetic acid (1 g/35 mL) gave pale yellow prisms, mp 370–373 °C (62% recovery); ^1H NMR (Me_2SO-d_6) δ 9.22 (d, J = 1 Hz, 2 H at C-2, C-6), 8.87 (d, J = 1 Hz, 2 H at C-4, C-8). Anal. Calcd for $C_{12}H_6N_2O_8$: C, 47.07; H, 1.98; N, 9.15. Found: C, 47.16; H, 1.87; N, 9.01.

3,7-Diamino-1,5-dinitronaphthalene (5). Sodium azide (13.3 g, 0.204 mol) was added in small portions during 2 h to a stirring suspension of 1,5-dnitronaphthalene-3,7-dicarboxylic acid (4, 25.0 g, 0.0816 mol) in 180 mL of 20% oleum and 75 mL of 1,2-dichloroethane, keeping the temperature below 5 °C. After addition of the sodium azide was complete, stirring was continued for 5 h while the temperature was gradually increased from 5 to 23 °C. The mixture was then heated with stirring for 1 h at 45 °C, then cooled to 10 °C, and poured over 3 kg of ice. The resulting suspension was made strongly basic (pH 12) by addition of 400 mL of 50% NaOH and cooled to 25 °C. The purple solid was removed by filtration, washed with water, and dried under vacuum overnight at 45 °C to yield 20.0 g (98%) of 5, mp 350 °C dec; recrystallization from acetonitrile gave dark prisms with greenish fluorescence, mp 350 °C dec. Failure to make the reaction solution strongly alkaline before filtering off the product results in isolation of a rather insoluble hydrogen sulfate salt of 5; IR of 5 (KBr) 3310, 3400 (NH_2), 1500 (NO_2) cm^{-1} (C=O signals absent); ^1H NMR (Me_2SO-d_6) δ 7.88 (d, J = 2 Hz, 2 H at C-2, C-6), 7.70 (d, J = 2 Hz, 2 H at C-4, C-8). Anal. Calcd for $C_{10}H_8N_4O_4$: C, 48.39; H, 3.25; N, 22.58. Found: C, 48.41; H, 3.38; N, 22.62.

3,7-Bis(trifluoroacetamido)-1,5-dinitronaphthalene (6). 3,7-Diamino-1,5-dinitronaphthalene (5, 8.8 g, 0.0355 mol) was added in small portions to 100 g of chilled (0 °C) trifluoroacetic anhydride. The resulting suspension was heated under reflux for ca. 2 days until all the purple solid reactant had disappeared. After cooling to room temperature, the product was filtered, washed with ether (100 mL), and dried under vacuum over $CaSO_4$ overnight to yield 15.5 g (99%) of 6; recrystallization from acetonitrile gave prisms, mp 350 °C dec; IR (KBr), 3225 (NH), 1730 (C=O), 1515 (NO_2) cm^{-1}: ^1H NMR (Me_2SO-d_6) δ 12.10 (br s, 2 H, NH), 9.30 (d, J = 1.5 Hz, 2 H at C-2, C-6), 9.05 (d, J = 1.5 Hz, 2 H at C-4, C-8). Anal. Calcd for $C_{14}H_6F_6N_4O_6$: C, 38.20; H, 1.37; F, 25.89; N, 12.73. Found: C, 38.33; H, 1.36; F, 25.75; N, 12.79.

2,6-Bis(trifluoroacetamido)-1,4,5,8-tetranitronaphthalene (7). A solution of nitric acid (90%, 6.2 mL) and concentrated sulfuric acid (3.8 mL) was added dropwise during 15 min to a stirring suspension of 3,7-bis(trifluoroacetamido)-1,5-dinitronaphthalene (6, 6.0 g, 0.0136 mol) in concentrated sulfuric acid (50 mL), keeping the temperature at 25–35 °C. After addition was complete, the temperature of the mixture was raised to 55 °C during 2 h. The mixture was cooled to 25 °C and poured over 900 g of ice. The precipitated product was filtered, washed with water until the washings remained clear, and dried under vacuum to yield 6.51 g (90%) of 7 as a yellow microcrystalline solid, mp 290–292 °C dec; recrystallization from ethyl acetate gave pure 7, mp 319 °C dec (67% recovery); IR (KBr), 3300 (NH), 1750 (C=O), 1520 (NO_2) cm^{-1}; ^1H NMR (acetone-d_6) δ 11.33 (br s, 2 H, NH), 9.35 (s, 2 H at C-3, C-7). Anal. Calcd for $C_{14}H_4F_6N_6O_{10}$: C, 31.71; H, 0.76; F, 21.50; N, 15.85. Found: C, 31.90; H, 0.80; F, 21.49; N, 15.64.

3,7-Bis(acetamido)-1,5-dinitronaphthalene (9a). A mixture of 3,7-diamino-1,5-dinitronaphthalene (5, 2.48 g, 0.01 mol), acetic anhydride (20 mL), and concentrated H_2SO_4 (1 drop) was heated under reflux for 4 h. The cooled product mixture was poured into 200 mL of water; the precipitate was filtered and washed with water to yield 3.23 g (98%) of diamide 9a as small prisms, mp 353–355 °C; recrystallization from boiling acetic acid did not change the melting point; ^1H NMR (Me_2SO-d_6) δ 11.0 (br s, 2 H, NH), 9.11 (d, J = 1.5 Hz, 2 H at C-2, C-6), 9.00 (d, J = 1.5 Hz, 2 H at C-4, C-8), 2.18 (s, 6 H, CH_3). Anal. Calcd for $C_{14}H_{12}N_4O_6$: C, 50.60; H, 3.64; N, 16.86. Found: C, 50.43; H, 3.52; N, 16.81.

3,7-Bis(acetamido)-1,4,5-trinitronaphthalene (10). 3,7-Bis(acetamido)-1,5-dinitronaphthalene (9a, 0.25 g, 0.75 mmol) was added during 15 min, with stirring, to a mixture of HNO_3 (90%, 2 mL) and concentrated H_2SO_4 (3 mL), keeping the temperature at 3–5 °C. After addition was complete, the mixture was stirred at 3–4 °C for an additional 15 min, and then poured onto ice and water to yield 0.214 g (75%) of crude 10, mp 215–270 °C dec; recrystallization from acetonitrile gave prisms, 0.05 g, mp 275–278 °C dec; ^1H NMR (Me_2SO-d_6) δ 10.9 (s, 1 H, NH), 10.6

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(s, 1 H, NH), 8.8 (s, 1 H at C-3), 8.7 (d, J = 1.5 Hz, 2 H at C-5, C-7), 1.97 (s, 6 H, CH_3). Anal. Calcd for $C_{14}H_{11}N_5O_8$: C, 44.57; H, 2.94; N, 18.56. Found: C, 44.82; H, 3.00; N, 18.46.

3,7-Bis(*p*-toluenesulfonamido)-1,5-dinitronaphthalene (9b). A solution of 3,7-diamino-1,5-dinitronaphthalene (**5**, 0.248 g, 1.0 mmol) and *p*-toluenesulfonyl chloride (0.418 g, 2.2 mmol) in pyridine (20 mL) was heated under reflux for 1 h. After cooling to 25 °C overnight, the solution was poured into 300 mL of ice water and the solution adjusted to pH 1 by the addition of concentrated hydrochloric acid. The product was removed by filtration and washed with water to yield 0.524 g (94%) of crude **9b**, mp 260–270 °C; recrystallization from aqueous ethanol gave prisms, mp 256–260 °C, with a change to needles, mp 260–275 °C. Anal. Calcd for $C_{24}H_{20}N_4O_8S_2$: C, 51.79; H, 3.62; N, 10.07; S, 11.52. Found: C, 51.65; H, 3.78; N, 10.20; S, 11.48.

2,6-Diamino-1,4,5,8-tetranitronaphthalene (8). Hydrogen chloride was bubbled into a suspension of 2,6-bis(trifluoroacetamido)-1,4,5,8-tetranitronaphthalene (**7**, 5.0 g, 9.4 mmol) in 500 mL of methanol over a 5-h period, during which time the temperature of the reaction mixture was allowed to rise without external cooling to ca. 50 °C. After addition of the HCl was complete the solvent and other volatiles were removed under reduced pressure. Water (300 mL) was added to the remaining solid residue, and the mixture was stirred vigorously until a fine powder had formed. The product was then removed by filtration, washed with water, and dried under vacuum to yield 3.12 g (98%) of **8**, mp 281 °C dec; recrystallization from acetonitrile gave pure **8** as red needles, mp 297 °C dec; IR (KBr) 3300, 3400 (NH_2), 1530 (NO_2) cm^{-1}; ^1H NMR (acetone-d_6) δ 9.23 (s, 2 aryl CH), 8.93 (br s, 4 H, NH_2); MS, *m/e* (relative intensity) M^+ 338 (57), 292 (11), 246 (44), 216 (100). Anal. Calcd for $C_{10}H_6N_6O_8$: C, 35.52; H, 1.79; N, 24.85. Found: C, 35.37; H, 1.75; N, 24.70.

A 100-mg sample of **8** was dissolved by stirring in concentrated H_2SO_4 (5 mL) at 25 °C to obtain a clear orange solution. After standing at 25 °C for 5 h, the solution was poured onto ice to yield a red precipitate having the IR spectrum of unchanged **8**. In a parallel experiment, the H_2SO_4 solution after standing at 25 °C for 18 h gave a product with a strong diazo oxide band at 2130 cm^{-1} (KBr).

A sample of **8** dissolved in D_2SO_4 at 25 °C revealed only a singlet at δ 8.32 (aryl CH of diazo oxide **13**). The solution poured onto ice gave a red precipitate of **13**; ^1H NMR (acetone-d_6) δ 8.36 (s, 2 aryl CH) and no other aryl peaks.

A sample of **8** heated in a vacuum oven at 60 °C over $CaSO_4$ (30 mmHg) for 65 h gave a solid having a strong diazo oxide band at 2130 cm^{-1} as well as NH_2 bands at 3300 and 3400 cm^{-1} (KBr).

Nitration of 2,6-Diamino-1,4,5,8-tetranitronaphthalene (8). Procedure A. 2,6-Diamino-1,4,5,8-tetranitronaphthalene (**8**, 100 mg, 0.295 mmol) was added with stirring to a mixture of HNO_3 (100%, 1.87 g, 29.6 mmol) in H_2SO_4 (80%, 10 mL) during 10 min, keeping the temperature at 3 °C by ice-bath cooling. After stirring for 3.5 h at 3 °C, the mixture was filtered and washed sequentially with cold 50% H_2SO_4 (10 mL) and 1 N HCl (10 mL) to yield crude 2,6-diamino-*N*,*N'*,1,4,5,8-hexanitronaphthalene (**11**), yellow powder, 80 mg, 63% after drying at 25 °C, 30 mmHg for 4 h; IR (KBr) 3300 (NH), 1540, 1330 (NO_2) cm^{-1}; diazo oxide and C=O bands absent; ^1H NMR (acetone-d_6) δ 9.36 (s, 2 aryl CH); ^1H NMR (D_2SO_4) δ 7.86 (s, aryl CH); after 20 h at 25 °C the aryl peak at δ 7.86 had disappeared and a strong singlet at δ 8.32 of diazo oxide **13** was formed. Attempts to purify the crude **11** by crystallization from various solvents caused it to decompose rapidly. The substance is unstable in air at ambient temperature and after standing at 25 °C for 24 h revealed a weak diazo oxide band at 2130 cm^{-1} (IR, KBr).

Procedure B. To a suspension of 2,6-diamino-1,4,5,8-tetranitronaphthalene (**8**, 100 mg, 0.295 mmol) in acetic acid (15 mL) HNO_3 (90%, 0.21 g, 2.96 mmoles) was added dropwise with stirring during 5 min, keeping the temperature at 25 °C. Acetic anhydride (2 mL) was added, and stirring of the mixture was continued for 16 h at 25 °C. The mixture was then heated at 55 °C, with stirring for 8 h, cooled to 25 °C, and stirred at 25 °C for 48 h. The reaction mixture, containing a red solid, was poured over 50 g of ice and the crude diazo oxide product **13** filtered on paper and washed with water to yield 53 mg (60%) of **13** as a red powder, explosion point 181 °C; IR (KBr) 3000 (CH), 2130 (diazo oxide), 1525, 1350 (NO_2) cm^{-1}; NH and C=O bands absent; strong bands were seen at 1590, 1220, 1030 and 700 cm^{-1}. ^1H NMR (acetone-d_6) δ 8.36 (s, 2 aryl CH); **Warning!** *Diazo oxide 13 is extremely sensitive to detonation by shock and electrostatic initiation and should not be handled with metal spatulas or contact sintered glass ware.* Elemental analyses were obtained on an unrecrystallized sample. Anal. Calcd for $C_{10}H_2N_6O_6$: C, 39.75; H, 0.67; N, 27.81. Found: C, 39.50; H, 1.18; N, 25.33.

Procedure C. 2,6-Diamino-1,4,5,8-tetranitronaphthalene (**8**, 100 mg, 0.295 mmol) suspended in a solution of HNO_3 (100%, 112 mg, 1.78 mmol) in 65% H_2SO_4 (10 mL) was stirred at 25 °C for 15 h to obtain a clear orange solution. After pouring over 75 g of ice, the product was filtered on paper and washed with cold water to yield 45 mg (45%) of crude diazo oxide **13** having ^1H NMR and IR spectra identical with those obtained for the sample of **13** obtained from procedure B, above.

2,6-Bis(acetamido)-1,4,5,8-tetranitronaphthalene (14). A mixture of 2,6-diamino-1,4,5,8-tetranitronaphthalene (**8**, 0.50 g, 1.48 mmol), acetic anhydride (10 mL), and concentrated H_2SO_4 (3 drops) was stirred at 25 °C for 2 h. The yellow solution was diluted with ether (50 mL), and the precipitated product was filtered, washed with ether, and dried to yield 0.565 g (91%) of crude **14**; recrystallization from acetonitrile gave prisms, mp 294 °C dec; ^1H NMR (Me_2SO-d_6) δ 11.0 (s, 2 H, NH), 9.23 (s, 2 aryl CH), 2.28 (s, 6 H, CH_3). Anal. Calcd for $C_{14}H_{10}N_6O_{10}$: C, 39.82; H, 2.39; N, 19.90. Found, C, 39.76; H, 2.33; N, 19.77.

Nitration of 2,6-Bis(acetamido)-1,4,5,8-tetranitronaphthalene (14). To 2,6-bis(acetamido)-1,4,5,8-tetranitronaphthalene (**14**, 0.50 g, 1.18 mmol) in concentrated H_2SO_4 (25 mL) HNO_3 (100%, 0.24 g, 3.8 mmol) was added, with stirring at 25 °C. After stirring at 25 °C for 6 h, the dark green solution was poured over 250 g of ice. The mixture was extracted with CH_2Cl_2 (6 × 200 mL), and the extracts were dried with $MgSO_4$ and concentrated to yield 0.15 g of crude product; recrystallization from ethylene dichloride gave orange-red prisms, mp 260 °C dec, IR (KBr) 3330, 3220 (NH_2), 1690, 1640 (C=O) cm^{-1}, signals near 2000 cm^{-1} absent; ^1H NMR (acetone-d_6) δ 9.20 (s, CH); MS, *m/e* (relative intensity) 306 (13), 305 (100), 277 (2), 259 (4), 247 (11), 220 (11), 213 (2). Anal. Calcd for $C_{10}H_3N_5O_7$: C, 39.36; H, 0.99; N, 22.94; MW 305.17. Found: C, 39.63; H, 1.36; N, 22.25; MW 311 (osmometry).

The same unknown substance was obtained by oxidation of **8** as follows: To a 100-mg sample of **8** suspended in 100% H_2SO_4 (10 mL) at 0 °C H_2O_2 (98%, 0.5 mL) was added dropwise, with stirring, keeping the temperature below 3 °C. After addition was complete, the mixture was stirred at 25 °C for 96 h and then poured onto ice (75 g). The mixture was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$ and concentrated to yield 30 mg of crude product; recrystallization from $CHCl_3/CH_2Cl_2$ gave prisms, mp 254 °C, having IR and ^1H NMR spectra identical with those of the product obtained by nitration of **14** as described above.

1,5-Bis(*p*-toluenesulfonamido)-4,8-dinitronaphthalene (16a). To a stirred suspension of 1,5-bis(*p*-toluenesulfonamido)naphthalene[4a] (**15a**, 2.0 g, 4.33 mmol) and sodium nitrite (0.02 g) in acetic acid (20 mL) a solution of 70% HNO_3 (3 mL) in acetic acid (2 mL) was added dropwise, causing a temperature increase from 18 to 25 °C. The mixture was stirred at 25 °C for 1.75 h and the tan product removed by filtration, washed with cold acetic acid, and dried under vacuum at 25 °C to yield 1.74 g (73%) of crude **16a**, mp 252–255 °C dec, with previous darkening at 220 °C; recrystallization by dissolving in hot pyridine, followed by dilution with hot water, gave yellow prisms, mp 262–263 °C dec with previous darkening (30% recovery); a sample recrystallized from acetic acid had mp 245 °C dec (46% recovery); ^1H NMR (Me_2SO-d_6) δ 7.90 (collapsed ABq appearing as a singlet, 4 H, naphthalene ring CH), 7.42, 7.28 (AB q, J = 9 Hz, 8 H, tosyl ring CH), 2.37 (s, 6 H, CH_3). Hodgson and Whitehurst[4a] report that their nitration of **15a** by the above procedure gave 1,5-bis(*p*-toluenesulfonamido)-2,4,6,8-tetranitronaphthalene (**1b**); however, the melting behavior of the product which they describe is very similar to our observed value for **16a** (they report mp 257 °C dec with previous darkening at 224 °C for **1b**). Anal. Calcd for $C_{24}H_{20}N_4O_8S_2$: C, 51.79; H, 3.62; N, 10.07; S, 11.52. Found: C, 51.89; H, 3.72; N, 10.04; S, 11.84.

Nitration of **16a** was attempted. To 0.10 g (0.18 mmol) of **16a** suspended in acetic acid (5 mL) HNO_3 (70%, 0.08 g, 1.26 mmol) was added and the mixture stirred at 25 °C for 28 h. Filtration gave 0.033 g (33%) of recovered **16a**, mp 257–273 °C dec; concentration of the filtrate to ca. 2 mL, followed by dilution with water, gave an additional 53 mg of **16a**, mp 240–270 °C dec (needles form near 265 °C; total recovery of **16a**, 86%).

1,5-Diamino-4,8-dinitronaphthalene (17). 1,5-Bis(*p*-toluenesulfonamido)naphthalene (**16a**, 0.647 g, 1.16 mmol) was stirred with concentrated H_2SO_4 (10 mL) at 42–44 °C for 1 h to yield a clear, dark solution. After the mixture was poured into 100 g of ice water mixture, the dark purple product which precipitated was removed by filtration, washed with water, and dried to yield 0.281 g (97%) of 17, mp 300–310 °C dec; IR (KBr) 3320, 3220 (NH_2) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 8.6 (br s, 4 H, NH); 8.2, 7.77 (ABq, $J = 10$ Hz, 4 H, aryl CH). Anal. Calcd for $C_{10}H_8N_4O_{10}$: C, 48.39; H, 3.25; N, 22.58. Found: C, 47.92; H, 3.23; N, 22.14.

1,5-Bis(acetamido)-4,8-dinitronaphthalene (16b). 1,5-Bis(acetamido)naphthalene[28] (**15b**, 2.42 g, 0.01 mol) was added with stirring to a solution of concentrated H_2SO_4 (32 mL) and HNO_3 (90%, 20 mL) during 10 min, keeping the temperature at 4–6 °C; stirring was continued while the clear red solution was allowed to warm from 5 to 15 °C during 15 min. After pouring into ice water the precipitated product was removed by filtration and washed with water to yield 1.80 g (56%) of crude orange **16b**, mp 340–345 °C dec. It was purified by stirring under reflux with acetone (250 mL) for 1 h, cooling, and filtering and washing the product with acetone (66% recovery), mp 355–365 °C dec; IR (KBr) 3120 (NH), 1660 (C=O) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 10.25 (s, 2 H, NH), 8.48, 7.88 (ABq, $J = 9$ Hz, 4 H, aryl CH), 2.25 (s, 6 H, CH_3; the ^{1}H NMR spectrum of the crude product was virtually identical with that of the purified material. Anal. Calcd for $C_{14}H_{12}N_4O_6$: C, 50.60f H, 3.64; N, 16.86. Found: C, 50.00; H, 50.60; N, 16.71.

Attempts were made to hydrolyze **16b** to 1,5-diamino-4,8-dinitronaphthalene (**17**) under various conditions: (a) 70% H_2SO_4, 50–70 °C, 7 h gave unchanged **16b** (60% recovery); (b) 85% H_3PO_4, 180 °C, 1 h gave amorphous products, unidentified; (c) acetic acid, H_2SO_4, and water (1:1:1 by vol) refluxed 1 h gave amorphous products; (d) concentrated HCl, acetic acid, and water (1:1:1 by vol) under reflux gave recovered **16b**. Various other nitration conditions with **15b** failed to yield pure products.

1,5-Bis(trifluoroacetamido)naphthalene (15c). 1,5-Diaminonaphthalene[29] (3.0 g, 0.019 mol) was added in small portions to trifluoroacetic anhydride (60 mL) while maintaining the temperature below 5 °C during the addition. The mixture was stirred at 5 °C for 1 h and at 25 °C for an additional hour. The product was removed by filtration, washed with ether (200 mL), and recrystallized from ethyl acetate (400 mL) to yield 6.50 g (98%) of pure **15c**, mp 277–282 °C; IR (KBr) 3250 (NH), 1700 (C=O) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 10.75 (br s, 2 H, NH), 7.7–8.5 (m, 6 H, aryl CH). Anal. Calcd for $C_{14}H_8F_6N_2O_2$: C, 48.01; H, 2.30; F, 32.55; N, 8.00. Found: C, 48.15; H, 2.27; F, 32.37; N, 7.96.

1,5-Bis(trifluoroacetamido)-2,4,6,8-tetranitronaphthalene (18). A solution of HNO_3 (90%, 18 mL) and conc H_2SO_4 (18 mL) was added dropwise during 1 h to a stirring suspension of 1,5-bis(trifluoroacetamido)naphthalene (**15c**, 3.0 g, 8.57 mmol) in concentrated H_2SO_4 (30 mL) keeping the reaction temperature below 10 °C. After addition was complete, the reaction mixture was stirred at 25 °C for 3 days. The mixture was poured over ice (200 g) and the product filtered and washed with water and dried in vacuum to yield 3.27 g (72%) of crude **18**; recrystallization from ethylene dichloride/ethanol gave prisms, mp 242–245 °C; IR (KBr) 3200 (NH), 1720 (C=O), 1525, 1340 (NO_2) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 11.00 (br s, 2 H, NH), 9.35 (s, 2 H, aryl CH). Anal. Calcd for $C_{14}H_4F_6N_6O_{10}$: C, 31.71; H, 0.76; F, 21.50; N, 15.85. Found: C, 31.96; H, 0.76; F, 21.76; N, 15.57.

Attempts to hydrolyze 18 to 1,5-diamino-2,4,6,8-tetranitronaphthalene (**1a**) under various conditions led to unreacted **18**. Methods included (a) methanolic HCl, 30–57 °C, (b) 50% H_2SO_4, 40–50 °C, (c) concentrated H_2SO_4, 90 °C, (d) methanolic NaOH, reflux.

1,3,5,7-Tetraaminonaphthalene (19). 3,7-Diamino-1,5-dinitronaphthalene (**5**, 5.5 g, 0.0222 mol) was added to a stirring suspension of stannous chloride (38.3 g) in concentrated HCl (100 mL) keeping the temperature below 40 °C. After addition was complete, the reaction mixture was heated to 55 °C during 45 min and maintained at 55 °C for 4.5 h, then allowed to cool to 25 °C overnight. After cooling to 0 °C, the reaction mixture was neutralized with NaOH (30% solution, 200 mL), diluted with water (50 mL), and filtered and the product washed with water to yield 2.97 g (71%) of crude **19**, mp 263–265 °C; elemental analyses were obtained on this crude sample. Anal. Calcd for $C_{10}H_{12}N_4$: C, 63.81; H, 6.43; N, 29.77. Found: C, 61.82f H, 6.28; N, 29.03.

1,3,5,7-Tetrakis(trifluoroacetamido)naphthalene (20a). Trifluoroacetic anhydride (100 mL) was added slowly, dropwise, to 1,3,5,7-tetraaminonaphthalene (**19**, unrecrystallized, 4.0 g, 0.0212 mol) so as to avoid an excessively exothermic reaction. After addition was complete the mixture was heated under reflux, with stirring, for 1 h. After the mixture was cooled to 25 °C, ether (100 mL) was added and the product removed by filtration, washed with ether, and dried to yield 9.29 g (76%) of **20a**, mp 356–358 °C dec; recrystallization from acetone lowered the melting point to 344–346 °C dec; IR (KBr) 3150 (NH) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 12.10 (br s, 4 H, NH), 8.49 (d, $J = 2$ Hz, 2 aryl CH), 8.27 (d, $J = 2$ Hz, 2 aryl CH). Anal. Calcd for $C_{10}H_8F_{12}N_4O_4$: C, 37.78; H, 1.41; N, 9.79. Found: C, 37.76; H, 1.45; N, 9.66.

4,8-Dinitro-1,3,5,7-tetrakis(trifluoroacetamido)naphthalene (21). A solution of HNO_3 (90%, 7.7 mL) in concentrated H_2SO_4 (30 mL) was added dropwise with stirring during 0.5 h to a suspension of 1,3,5,7-tetrakis(trifluoroacetamido)naphthalene (**20a**, 9.37 g, 0.0164 mole) in concentrated H_2SO_4 (130 mL), keeping the temperature of the reaction mixture below 5 °C. After addition was complete, the mixture was stirred for 1 h at 3–5 °C. The reaction mixture was poured over 1600 g of ice and the product filtered, washed with water (3 × 500 mL) and $CHCl_3$ (1 L) and dried to yield 9.32 g (86%) of crude **21**, mp 306 °C dec; attempts to recrystallize the substance from various solvents led to its decomposition; an analytical sample was obtained by washing the crude product with dichloromethane and drying under vacuum, mp 318 °C (dec), (82% recovery); compound **21** is somewhat unstable on storage at 25 °C with release of trifluoroacetic acid (odor) occurring after several days; IR (KBr) 3180 (NH), 1735, 1700 (C=O), 1515, 1320 (NO_2) cm^{-1}; ^{1}H NMR (acetone-d_6) 10.73 (br s, 2 H, NH), 10.58 (br s, 2 H, NH), 8.37 (s, 2 aryl CH). Anal. Calcd for $C_{18}H_6F_{12}N_6O_8$: C, 30.54; H, 1.08; N, 11.25. Found: C, 30.99; H, 1.24; N, 11.84.

1,5-Dinitro-2,4,6,8-tetraaminonaphthalene (22). Triethylamine (dry, 1.0 mL) was added to a stirring mixture of 4,8-dinitro-1,3,5,7-tetrakis(trifluoroacetamido)naphthalene (**21**, 8.0 g, 0.0121 mol) and methanol (300 mL) at 25 °C. After stirring for 42 h at 25 °C, the mixture was concentrated to dryness. Water (100 mL) was added to the remaining red solid, and the suspension was stirred until a fine powder was produced. The product was removed by filtration, washed with water (4 × 25 mL), and dried in a vacuum at 45 °C to yield 4.2 g (100%) of crude **22**, mp 400 °C after turning black at 200 °C; IR (KBr) 3220 (NH) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 7.54 (br s, 4 H, NH), 6.30 (s, 2 aryl CH), 6.20 (br s, 4 H, NH); an elemental analysis was obtained on the unrecrystallized sample. Anal. Calcd for $C_{10}H_{10}N_6O_4$: C, 43.17; H, 3.62; N, 30.21. Found: C, 42.86; H, 3.70; N, 26.86.

Nitration was conducted by addition of HNO_3 (70%, 0.2 mL) to **22** (100 mg, 0.359 mmol) in acetic acid (1.0 mL), followed by stirring at 25 °C for 3.5 h. After pouring into water (25 mL) the product was removed by filtration (on paper), washed with water, and dried to yield 20.4 mg (17%) of crude diazo oxide, possibly **25**; IR (KBr) 3350 (NH_2), 2130 (diazo oxide), 1530 (NO_2) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) revealed no aryl CH signals. **Warning**! *The diazo oxide should not be handled with a metal spatula or contact sintered glass owing to sensitivity to detonation.*

1,3,5,7-Tetraacetamidonaphthalene (20b). A suspension of 1,3,5,7-tetraaminonaphthalene (**19**, unrecrystallized, 300 mg, 1.59 mmol) in acetic anhydride (5 mL) was stirred at 25 °C for 28 h. Ether (30 mL) was added and the mixture stirred until a fine powder had formed. The product was removed by filtration and dried under vacuum to yield 548 mg (97%) of crude **20b**, mp 380–383 °C (dec); recrystallization from acetic acid gave prisms, mp 405 °C dec; ^{1}H NMR (Me_2SO-d_6) 10.50 (br s, 2 H, NH), 10.25 (br s, 2 H, NH), 8.33 (d, $J = 2$ Hz, 2 aryl CH), 8.02 (d, $J = 2$ Hz, 2 aryl CH), 2.18 (s, 6 H, CH_3), 2.10 (s, 6 H, CH_3). Anal. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.67; H, 5.66; N, 15.72. Found: C, 60.46; H, 5.68; N, 15.57.

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(29) Brown, W. G.; Letang, N. J. *J. Am. Chem. Soc.* **1941**, *63*, 358.

4-Nitro-1,3,5,7-tetraacetamidonaphthalene (23). Nitric acid (90%, 0.2 mL) was added to a stirring suspension of 1,3,5,7-tetraacetamidonaphthalene (**16b**, 300 mg, 0.842 mmol) in acetic acid (13 mL). After the reaction mixture was stirred at 25 °C for 3 days, it was poured into 50 mL of water and the product filtered to yield 273 mg (81%) of crude **23**; recrystallization from acetic acid gave yellow prisms, mp 336–338 °C (dec) (90% recovery); IR (KBr) 3100, 2900 (NH), 1625 (C=O), 1510 (NO_2) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 10.33 (br s, 1 H, NH), 10.15 (br s, 1 H, NH), 9.78 (br s, 1 H, NH), 9.58 (br s, 1 H, NH), 8.25 (d, J = 2 Hz, 1 aryl CH), 7.72 (d, J = 2 Hz, 1 aryl CH), 7.67 (s, 1 aryl CH), 2.17 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3), 1.93 (s, 3 H, CH_3). Anal. Calcd for $C_{18}H_{19}.N_5O_6$: C, 53.86; H, 4.77; N, 17.45. Found: C, 53.69; H, 4.87; N, 17.34.

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Bicyclic Vinyl Sulfides by Ring Expansions of Spirocyclic Dithioketal Systems

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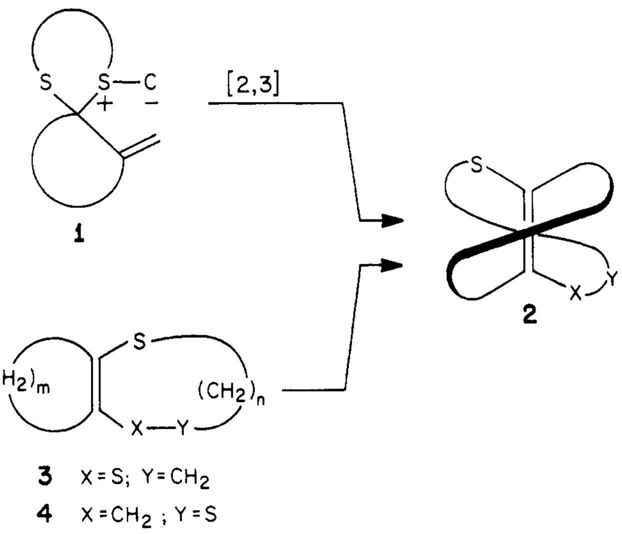
Our objective was to prepare sulfur-containing bicyclo[10.5.0]- and -[10.6.0]alkenes for future photochemical studies. Prototypes having a seven-membered heterocyclic ring with two sulfurs were obtained by one-atom ring expansion of a spirocyclic 1,3-dithiane 1-oxide (**11b**). A similar sequence applied to the homologous 1,3-dithiepine 1-oxide (**17**) enlarged it to its corresponding eight-membered heterocycle (**18**). A two-atom-ring growth of a β-hydroxy-1,3-dithiane promoted by P_2O_5 was developed with a monocyclic model compound (**23a**). The product (**24**) is a 1,5-dithiacyclooctene with one sulfur vinylic and the other allylic. When the scheme was applied to the appropriate spirocyclic 1,3-dithiane system (**29a**), P_2O_5 produced the corresponding 12/8 bicyclic alkene (**31a**) with a tetrasubstituted π bond. With $POCl_3$/Py, the 6 → 8 rearrangement afforded the trisubstituted olefin (**30a**), which separately could be isomerized to alkene **31a**. The action of P_2O_5 on a spirocyclic β-hydroxy-1,3-dithiolane (**29c**) gave the desired 12/7 ring system as a binary mixture of olefins (**30b, 31b**), which converted entirely to the more stable tetrasubstituted isomer when treated with HCl gas. One-atom (6 → 7) ring expansion in α-hydroxy-1,3-dithianes was tested on a monocyclic analogue (**32a**) and its acetate ester (**32b**). Hot $POCl_3$/Py successfully enlarged the alcohol to an alkene having a 1,4-dithiepane skeleton (**36**). Pyrolysis of the acetate (**32b**) effected the same ring expansion.

Recently, we described the first syntheses of doubly transoid, bicyclic olefins (i.e., "betweenanenes") having a heteroatom (sulfur) directly connected to the sheltered double bond (see **2**).[1,2] The approach involved multistep construction of unsaturated spirocyclic sulfur ylides of type **1**, which underwent [2,3]-sigmatropic rearrangement to the desired targets **2** (see Scheme I). Our studies of the chemistry of shielded alkenes make it necessary to develop other (potentially shorter) routes to such structures, and especially to those in which the transoid heterocyclic ring would be highly strained (e.g., eight membered or less).

Photic isomerization of bicyclic cisoid alkenes[3] could provide an entry to strained betweenanenes. One favorable feature of a vinylic sulfur is to shift the UV absorption of the alkene bathochromically to more accessible wavelengths.[4] But it is uncertain whether the heteroatoms would thwart the cis → trans photochemical change because the irradiation behavior of cycloalkenes carrying one or two vinylic sulfurs in unknown. Photochemical approaches to strained heterocyclic betweenanenes require prior syntheses of their appropriate fused bicyclic "cis" counterparts. The present paper describes routes to several "cis" prototypes with a 12-membered carbocyclic ring.

Scheme I



Some of these compounds have two vinylic sulfurs (i.e., type **3** whereas others have one vinylic and one allylic sulfur (i.e., type **4**).

Our first approach to type **3** used a transformation reported by Chen and Donatelli. They found that *p*-toluenesulfonic acid hydrate expands a 1,3-dithiolane 1-oxide (**5a**) to a dihydro-1,4-dithiine (**6a**), presumably via cationic intermediates like those shown in Scheme II.[5] We

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(1) (a) Nickon, A.; Rodriguez, A.; Shirhatti, V.; Ganguly, R. *Tetrahedron Lett.* **1984**, *25*, 3555–3558.

(2) Nickon, A.; Rodriguez, A. D.; Shirhatti, V.; Ganguly, R. *J. Org. Chem.* **1985**, *50*, 2767–2777.

(3) Nakazaki, M.; Yamamoto, K.; Yanagi, J. *J. Chem. Soc., Chem. Commun.* **1977**, 346–347.

(4) Whereas unstrained monoalkenes absorb around 200 nm or less, vinylic sulfurs can shift absorptions as high as 250–285 nm. For example, see Experimental Section for UV of compounds 12, 14, and 31a.

(5) Chen, C. H.; Donatelli, B. A. *J. Org. Chem.* **1976**, *41*, 3053–3054.

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