

Photochemical Nitration by Tetranitromethane. XV.* Formation of Adducts and their Secondary Products in the Photochemical Reaction between Benzene and Tetranitromethane

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Ebersson, L., Calvert, J. L., Hartshorn, M. P. and Robinson, W. T., 1994. Photochemical Nitration by Tetranitromethane. XV. Formation of Adducts and their Secondary Products in the Photochemical Reaction between Benzene and Tetranitromethane. – Acta Chem. Scand. 48: 347–355 © Acta Chemica Scandinavica 1994.

Photolysis of benzene/tetranitromethane in dichloromethane or acetonitrile with light of $\lambda > 435$ nm gives four main product categories, namely, in dichloromethane at +20°C (relative yield, products): adducts **1** of hydroxy/trinitromethyl type (total 54%, see below), nitro substitution products (total 8%, nitrobenzene, 1,3-dinitrobenzene and 1,3,5-trinitrobenzene), trinitromethyl substitution products (26%, trinitromethylbenzene, 1-nitro-4-trinitromethylbenzene, 1,3-dinitro-5-trinitromethylbenzene) and phenols (total 12%, 2,4- and 2,6-dinitrophenol, 2,4,6-trinitrophenol). In acetonitrile at +20°C the same product groups comprised 15, 24, 39 and 18%, respectively, and, in addition, a low yield (1.7%) of what is formally a cycloaddition product between 4-nitrobenzonitrile *N*-oxide and acetonitrile, 5-methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole **2**. The structure of **2** was determined by single crystal X-ray analysis.

The main adducts were assigned the structures of a *cis/trans* pair of 1-hydroxy-4-trinitromethylcyclohexa-2,5-diene (NMR). Their formation in both dichloromethane and acetonitrile shows that adduct formation from photolysis of tetranitromethane/aromatics is not only confined to polycyclic aromatics but can occur with a maximally resonance-stabilized system, like benzene itself. The high complexity of the product mixture can be explained partly by elimination reactions of adducts, combined with further thermal and photochemical transformations.

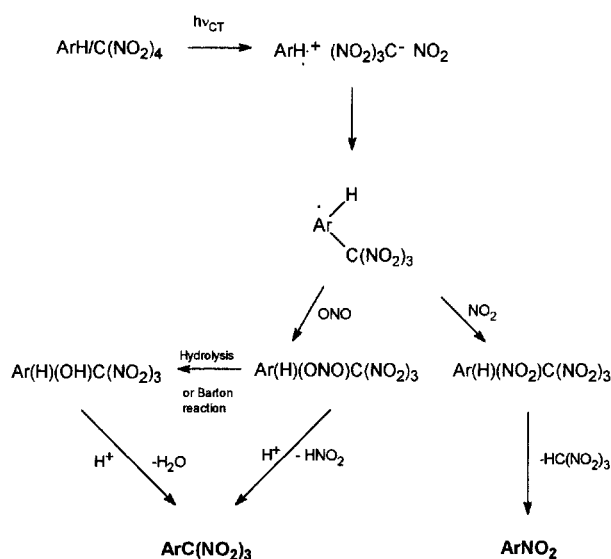
The photochemical reaction between aromatics (ArH) and tetranitromethane leads predominantly or partially to the formation of nitro/trinitromethyl adducts of the aromatic system (naphthalene,^{2,3} 1,4-dimethylnaphthalene,^{4,5} 1,2-dimethylnaphthalene,^{6,7} 1,4,5,8-tetramethylnaphthalene,⁸ anthracene and its derivatives,⁹ dibenzofuran,¹⁰ fluoranthene,¹¹ 4-chloroanisole¹²). In some cases, nitro/trinitromethyl adducts are also formed and detected after work-up as the corresponding hydroxy/trinitromethyl adducts.^{2,4,7,9,12} A novel recent finding was the X-ray crystallographic characterization of products of *intramolecular* 1,3-dipolar cycloaddition in primarily formed *vicinal* nitro/trinitromethyl or hydroxy/trinitromethyl adducts.^{6,7} This definitively demonstrated the presence of hydroxy/trinitromethyl adducts, so far only characterized by their NMR spectral properties. It was conclusively

shown^{2,10,11} that nitro/trinitromethyl adducts undergo elimination of nitroform under mild thermal conditions and thus are at least partially the origin of nitro *substitution* products, whereas it has been inferred¹² that nitro/trinitromethyl and/or hydroxy/trinitromethyl adducts might give rise to trinitromethyl *substitution* products by elimination of nitrous acid and/or water under thermal, acid-catalyzed conditions. The whole spectrum of reactions is summarized in Scheme 1.

One can criticize the list of substrates above on the grounds that they are mostly polycyclic ArH, which are more prone to give addition products than their monocyclic counterparts. We therefore chose to study the photolysis of benzene/tetranitromethane in order to check the possibility of adduct formation under what we deem to be *structurally* unfavorable conditions. As reported in a short communication,¹³ hydroxy/trinitromethyl adducts **1** were indeed obtained from this reaction in both dichloromethane and acetonitrile. We now report the results of

* Parts XIII and XIV, see Refs. 1 and 7, respectively.

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Scheme 1.

an extended product study. As a novel finding, not directly related to the main theme of this series, we also describe the isolation of a heterocyclic system, 5-methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole **2**, from reactions in acetonitrile.

Results

Photolysis of benzene/tetranitromethane in dichloromethane.

A solution of benzene (0.20 mol dm^{-3}) and tetranitromethane (1.6 mol dm^{-3}) had a very faintly yellow color, common to other ArH/tetranitromethane systems,⁵ assigned to the presence of a weak charge transfer (CT) complex (Fig. 1). From the UV spectrum, it is seen that a narrow part of the CT band is available for irradiation with light which does not at the same time directly excite tetranitromethane. In practice, this means that filtered light with cut-off at $<435 \text{ nm}$ must be used.

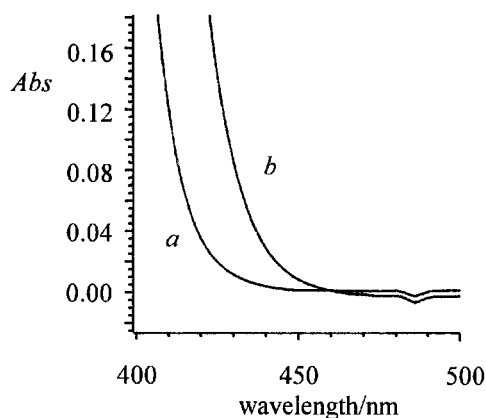
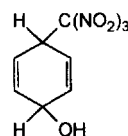
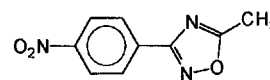


Fig. 1. UV-VIS spectrum of a dichloromethane solution of (a) tetranitromethane (1.6 mol dm^{-3}) and (b) benzene (0.2 mol dm^{-3}) and tetranitromethane (1.6 mol dm^{-3}).

A solution of benzene (0.8 mol dm^{-3}) and tetranitromethane (1.6 mol dm^{-3}) in dichloromethane was irradiated with filtered light ($\lambda > 435 \text{ nm}$) at $+20^\circ\text{C}$. Analyses were performed after 12, 24 and 48 h (Table 1). A large number of products were formed and categorized (see below) as adducts, nitro (substitution) products, trinitromethyl (substitution) products and phenolic products. The time development of these groups of products is shown in Fig. 2 and a summary of the relative percentages of the product groups under different conditions is given in Table 3. After 48 h the total yield of products was 25.8%, adducts **1a** and **1b** comprising 50% of the mixture. 'Other adducts' signifies a set of compounds which have the NMR spectral signature of adducts, but the nature of which are so far unknown. At $+20^\circ\text{C}$, they comprise only 5–10% of the total adduct yield. The structures of the adducts **1** were assigned as the *cis/trans* pair of 1-hydroxy-4-trinitromethylcyclohexa-2,5-diene on the basis of ^1H and ^{13}C NMR spectral data (see the Experimental). The product group next in abundance was trinitromethyl substituted products (26%), followed by phenols (12%) and nitro compounds (8%).

**1****2**

A run at -20°C gave similar results, except that some minor products of further nitro substitution were not detectable. The adduct proportion (53%, Table 3) was the same, but its composition differed owing to the presence of a higher proportion of 'other adducts'. Again, the group of trinitromethyl substituted products was second in abundance (23%), whereas nitrobenzene now came third (19%) and phenols fourth (5%).

Photolysis of benzene/tetranitromethane in acetonitrile.

Photolysis of benzene and tetranitromethane in acetonitrile at $+20^\circ\text{C}$ under the same conditions as above gave a similar set of products (Table 2), developing with time as shown in Fig. 3. The relative yields of the various product groups are given in Table 3. In addition, 5-methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole **2**, formally a 1,3-dipolar addition product of 4-nitrobenzoxazole *N*-oxide and acetonitrile, was formed in 1.7% yield after 48 h. The structure of this compound was determined by single crystal X-ray analysis, as detailed below.

As seen from Table 3, the group of trinitromethyl substituted products was now the dominant one (39%), followed by nitro substitution products (24%), phenols (18%) and adducts (15%). At -20°C , the proportion of adducts approximately doubled, and the proportion of trinitromethyl substituted products increased further (to

Table 1. Overview of product yields from the photolysis of benzene (0.8 mol dm^{-3}) and tetranitromethane (1.6 mol dm^{-3}) in dichloromethane.

Product	Absolute yields (%) after reaction period/h			
	At $+20^\circ\text{C}$		At -20°C	
	12	24	48	56
Adduct 1a	1.2	2.6	6.5	2.6
Adduct 1b	1.2	2.6	6.5	2.6
Other adducts	0.2	0.5	0.9	2.5
Σ Adducts	2.6	5.7	13.9	7.7
Nitrobenzene	0.1	0.3	0.7	2.8
1,3-Dinitrobenzene	0.2	0.4	1.2	—
1,3,5-Trinitrobenzene	—	—	0.1	—
Σ Nitro products	0.3	0.7	2.0	2.8
Trinitromethylbenzene	0.4	1.0	3.3	1.8
1-Nitro-4-trinitro-methylbenzene	0.3	0.9	3.0	1.6
1,3-Dinitro-5-trinitro-methylbenzene	0.1	0.1	0.4	—
Σ Trinitromethyl products	0.8	2.0	6.7	3.4
2,4-Dinitrophenol	0.3	0.6	2.3	0.7
2,6-Dinitrophenol	0.1	0.2	0.6	—
2,4,6-Trinitrophenol	—	—	0.3	—
Σ Phenol products	0.4	0.8	3.2	0.7
Σ All products	4.1	9.2	25.8	14.6

58%) at the expense of nitro substitution products (10%) and phenols (5%).

Attempted photoreactions between tetranitromethane and some of the primary products. The large number of apparently secondary products raised problems regarding their origin, and several check experiments were performed to test this aspect. Thus the following compounds were photolyzed with tetranitromethane for 48 h at $+20^\circ\text{C}$ in acetonitrile: nitrobenzene, 2,6-dinitrophenol and a 3:4 mixture of trinitromethylbenzene and 4-trinitromethylnitrobenzene; the nitrobenzene reaction was also attempted in dichloromethane. In all these cases the starting material(s) was recovered in excellent yield and no product was detectable (NMR).

Thermal stability of adducts 1. Unfortunately, it was not possible to isolate either of the adducts **1** in pure state. We were therefore limited to studies of their thermal stability by experimentation with the crude mixture obtained from the dichloromethane photolyses at -20°C , containing about 36% of a 1:1 mixture of **1a** and **1b** plus 17% of 'other adducts'. It should be noted that such studies may be subject to uncontrolled effects due to catalyzing

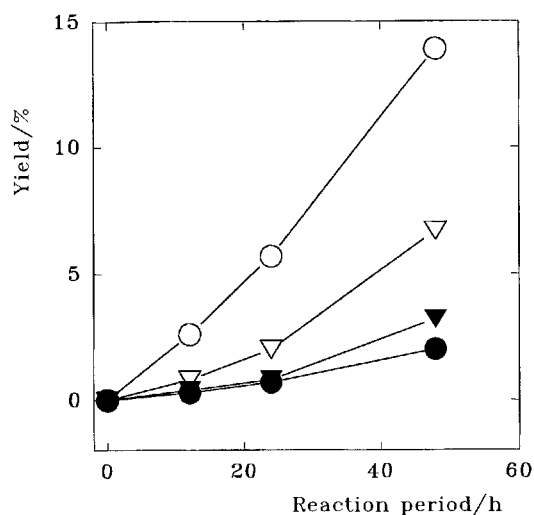


Fig. 2. Growth of product yields with time of a photolyzed solution of benzene (0.8 mol dm^{-3}) and tetranitromethane (1.6 mol dm^{-3}) in dichloromethane at 20°C : \circ , adducts; \bullet , nitro compounds; ∇ , trinitromethyl substitution products; \blacktriangledown , phenols.

acidic components (such as the nitrophenols) in the crude mixture.

The 2,6-di-*tert*-butylpyridine (DtBPy) catalyzed decomposition of **1** in acetonitrile at 20°C caused the relatively fast appearance of the 350 nm UV spectral maximum of trinitromethanide ion in a concentration significantly lower ($\sim 1/3$) than [**1**] at zero time. Runs at several [DtBPy] under pseudo-first-order conditions gave a rate constant of $11(1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In dichloromethane under otherwise identical conditions, the rate constant was $0.8(1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Without base addition, the same batch of crude mixture decomposed much more slowly in acetonitrile under the same conditions as above. The change in the UV spectrum in this case was much less specific, amounting to a relatively small increase in absorbance in the 270–320 nm region, with very little change in the region around 350 nm. First-order rate constants calculated for this change were erratic, varying between 0.003 and 0.006 min^{-1} for the same batch of crude mixture and with intra-batch variability of as much as one power of ten.

Structure determination of the heterocyclic product 2. The structure of this 5-methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole **2**, $\text{C}_9\text{H}_7\text{N}_3\text{O}_3$, m.p. $142\text{--}144^\circ\text{C}$, was determined by single crystal X-ray analysis. A perspective drawing of compound **2** is presented in Fig. 4, and the corresponding atomic coordinates are given in Table 4. In the solid state the heterocyclic ring is essentially planar, and that plane is slightly displaced from coplanarity with the benzene ring [torsional angles: $\text{N}(3)\text{--C}(7)\text{--C}(4)\text{--C}(5)$ $10.6(2)^\circ$, $\text{N}(2)\text{--C}(7)\text{--C}(4)\text{--C}(3)$ $10.0(2)^\circ$], as is the plane of the nitro group [torsional angles: $\text{O}(1)\text{--N}(1)\text{--C}(1)\text{--C}(6)$

Table 2. Overview of product yields from the photolysis of benzene (0.8 mol dm^{-3}) and tetranitromethane (1.6 mol dm^{-3}) in acetonitrile.

Product	Absolute yields (%) after reaction period/h			
	At $+20^\circ\text{C}$		At -20°C	
	12	24	48	48
Adduct 1a	0.7	1.2	2.9	1.4
Adduct 1b	0.7	1.2	1.9	0.8
Other adducts	0.5	0.5	0.5	0.6
Σ Adducts	1.9	2.9	5.3	2.8
Nitrobenzene	0.3	0.5	7.0	1.0
1,3-Dinitrobenzene	0.2	0.4	1.2	—
1,3,5-Trinitrobenzene	—	—	0.2	—
Σ Nitro products	0.5	0.9	8.4	1.0
Trinitromethylbenzene	1.7	3.8	10.9	4.9
1-Nitro-4-trinitro-methylbenzene	0.4	0.8	2.4	1.0
1,3-Dinitro-5-trinitro-methylbenzene	0.1	0.1	0.4	—
Σ Trinitromethyl products	2.2	4.7	13.7	5.9
2,4-Dinitrophenol	0.8	1.1	5.3	0.5
2,6-Dinitrophenol	0.3	0.4	—	—
2,4,6-Trinitrophenol	0.2	0.2	1.1	—
Σ Phenol products	1.3	1.7	6.4	0.5
1,3-Dipolar adduct 2	0.4	1.1	1.7	—
Σ All products	6.9	9.3	35.5	10.2

$-10.6(2)^\circ$, $\text{O}(2)-\text{N}(1)-\text{C}(1)-\text{C}(2) -9.9(2)^\circ$]. The bond lengths in the heterocyclic ring are closely similar to those found¹⁴ for the pyridyl derivative **3** (Fig. 5).

Discussion

As before, we assume that the triad of radical cation, trinitromethanide ion and nitrogen dioxide is formed in the photochemical step, followed by the reaction between the radical cation and trinitromethanide ion to give a trinitromethyl substituted cyclohexadienyl radical (Scheme 1). The latter is trapped by nitrogen dioxide, giving a nitro- and/or nitrito-/trinitromethyl adduct, addition taking place 1,2 and/or 1,4 to the aromatic system. The reaction between the radical cation and trinitromethanide ion has recently been shown to be faster than the radical cation/ NO_2 reaction for a number of radical cations in both dichloromethane and acetonitrile,¹ and there is no reason to assume that the reactions of $(\text{benzene})^{\bullet+}$ should deviate from this reactivity order. Thus the reaction between $(\text{benzene})^{\bullet+}$ and NO_2 should

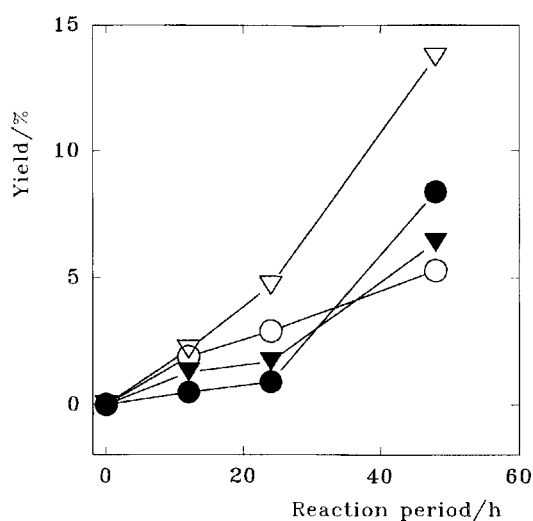


Fig. 3. Growth of product yields with time of a photolyzed solution of benzene (0.8 mol dm^{-3}) and tetranitromethane (1.6 mol dm^{-3}) in acetonitrile at 20°C : ○, adducts; ●, nitro compounds; ▽, trinitromethyl substitution products; ▼, phenols.

Table 3. Overview of product yields of photolyses of benzene/tetranitromethane solutions after ca. 50 h, arranged according to product categories (see Tables 1 and 2).

Solvent ^a ($T/^\circ\text{C}$)	Yield (%) of			
	Adducts	Nitro substitution products	$(\text{NO}_2)_3\text{C}$ substitution products	Phenolic products
DCM ($+20$)	54	8	26	12
DCM (-20)	53	19	23	5
AN ($+20$)	15	24	39	18
AN (-20)	27	10	58	5

be of some, but not dominant importance for the formation of nitrobenzene.

Once adducts have been formed, it is their reactivity toward elimination that decides the product composition. The rules of this type of chemistry have not yet been fully established, but so far we know that nitro/trinitromethyl adducts with the nitro and trinitromethyl groups at secondary carbons are reasonably stable in dichloromethane but slowly undergo spontaneous elimination of nitroform in acetonitrile.^{2,10,11} With the nitro and trinitromethyl

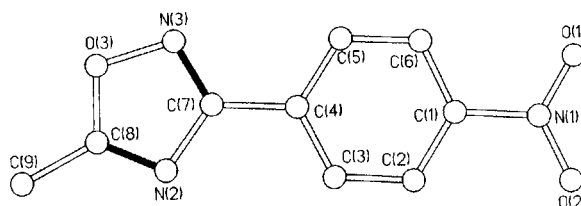


Fig. 4. Perspective drawing of compound **2**. Double bonds are shown in black.

Table 4. Fractional coordinates for atoms in 5-methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole (**2**). The equivalent isotropic temperature factor is defined as one-third of the orthogonalized U tensor (\AA^2).

Atom	$10^4 x/a$	$10^4 y/b$	$10^4 z/c$	$10^3 u/\text{\AA}^2$
O(1)	-600(2)	11978(2)	8966(1)	54(1)
O(2)	475(2)	14326(2)	7571(1)	49(1)
O(3)	4751(2)	5570(2)	2235(1)	40(1)
N(1)	312(2)	12658(2)	7825(1)	37(1)
N(2)	4843(2)	8538(2)	2102(1)	37(1)
N(3)	3710(2)	6144(2)	3579(1)	39(1)
C(1)	1235(2)	11417(2)	6694(1)	30(1)
C(2)	1952(2)	12285(2)	5350(2)	31(1)
C(3)	2796(2)	11124(2)	4286(1)	30(1)
C(4)	2921(2)	9132(2)	4577(1)	28(1)
C(5)	2195(2)	8299(2)	5952(2)	32(1)
C(6)	1344(2)	9441(2)	7023(2)	33(1)
C(7)	3824(2)	7925(2)	3426(1)	30(1)
C(8)	5365(2)	7097(2)	1426(2)	38(1)
C(9)	6529(3)	6879(3)	-34(2)	56(1)

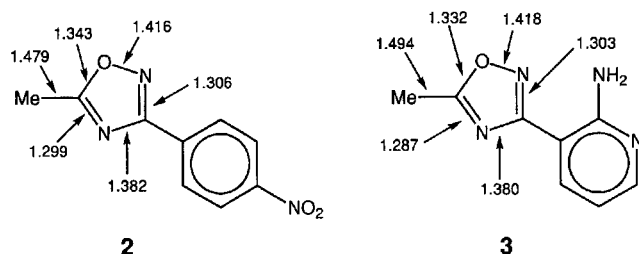


Fig. 5. Selected bond lengths (\AA) for compounds **2** and **3** (Ref. 14).

groups attached to tertiary carbons, an additional, homolytic decomposition pathway becomes available in both dichloromethane and acetonitrile.⁴

Less is known about the stability of nitro/trinitromethyl adducts, mainly because such compounds so far have defied isolation and consequently study in pure form. It was however shown that nitro/trinitromethyl adducts from 4-chloroanisole¹² (in admixture with other products) spontaneously eliminate nitrous acid in acetonitrile to give the trinitromethyl substitution product and that the same reaction also takes place photochemically. Thus we presently have good reasons to assume that trinitromethyl substitution products are also formed via adducts.

In summary, our mechanistic model assumes that adducts are the main primary products, and that secondary products can be formed by elimination reactions of the type discussed above. This model is the basis for the classification of the products into the main groups listed in Tables 1–3, and for the discussion below.

Formation and stability of adducts. In dichloromethane at 20°C, adducts **1** comprise 50% of the product mixture after 24 h reaction time, whereas at -20°C the proportion of adducts is almost identical, albeit with 'other adducts' this time constituting one third of the total yield

of adducts. The structure of 'other adducts' could not be established owing to overlapping NMR spectra. In acetonitrile, the proportion of adducts is low at +20°C and somewhat higher at -20°C, as expected in view of the generally lower thermal stability of adducts in acetonitrile.

The experiments aimed at determining the rate of decomposition of **1** in dichloromethane and acetonitrile were thwarted by the necessity of carrying out the experiments on the crude mixture. Thus one can conclude only that at least one component of the crude mixture is decomposed in a base-induced process with a rate constant of 11(1) $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ in acetonitrile and 0.8(1) $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ in dichloromethane at 20°C. Adducts **1** do spontaneously decompose in acetonitrile at 20°C, but the measured rates are low and erratic. The survival of adducts **1** after photolysis for 48 h in acetonitrile at 20°C indicates that the half-lives of **1** must be put at ≥ 24 h.

Formation of nitro products. Nitrobenzene (from which we assume that 1,3-dinitrobenzene and 1,3,5-trinitrobenzene are derived in secondary/tertiary reactions; see below) can be formed either as a secondary product by the elimination of nitroform from nitro/trinitromethyl adducts, a reaction expected to be rather slow in dichloromethane, or as a primary reaction involving coupling between (benzene) $^{\bullet+}$ and NO_2 . We judge the latter reaction to be of some importance in dichloromethane at -20°C (cf. the naphthalene/TNM reaction,² where the nitro product is more prevalent at lower temperatures). The proportion of nitrobenzene is higher at the lower temperature which is not in accordance with a thermal elimination mechanism.

The formation of 1,3-dinitro- and 1,3,5-trinitrobenzene from nitrobenzene under what appears to be fairly mild conditions is of some interest, since it is not immediately obvious which nitrating reagent accomplishes these reactions. One possibility is that nitrogen dioxide can be oxidized to nitronium ion by (benzene) $^{\bullet+}$, a process which is exergonic by 1–1.5 eV, depending on which value of $E^\circ(\text{NO}_2^+/\text{NO}_2)$ is chosen.¹⁵ This reaction would then compete with the coupling process, both reactions presumably occurring at diffusion-controlled rates. Nitronium ion is known to react^{16a} with nitrobenzene to give 1,3-dinitrobenzene with great ease, but further nitration to 1,3,5-trinitrobenzene requires a high reaction temperature and above all, activation of the nitronium ion by a superacid, fluorosulfuric acid.^{16b,c} In this case, the active reagent was assumed to be protonitronium dication, HNO_2^+ . It is therefore not easy to propose a credible pathway to 1,3,5-trinitrobenzene under photolysis conditions.

In acetonitrile, the proportion of nitrobenzene is higher at +20 than -20°C, presumably because of the faster thermal elimination reaction at the higher temperature.

Formation of trinitromethyl substitution products. Trinitromethylbenzene would be a primary product if the initially

formed trinitromethylcyclohexadienyl radical might somehow be oxidized to the corresponding cation with subsequent loss of a proton from the latter. This mechanism suffers from the uncertainty of assigning a suitable one-electron oxidant to the latter step during photochemical conditions.¹⁷ It has been shown separately that even stable radical cations of the triarylaminium type do not undergo oxidative trinitromethylation but instead exchange an electron with trinitromethanide ion, in spite of the fact that an effective electron transfer oxidant is, in principle, available.¹⁸ We therefore favor the assumption that trinitromethylbenzene is a secondary product, formed by thermal elimination of nitrous acid (water) from nitrito(hydroxy)/trinitromethyl adducts in reactions of E1 mechanistic type [eqns. (1) and (2)]. These reactions are acid-catalyzed¹⁹ and should be accelerated towards the end of the photolysis reaction, when the solution has become markedly acidic.^{2,4}

The now fully established⁷ conversion of a nitrito/trinitromethyl adduct into the hydroxy/trinitromethyl compound is still not clarified beyond earlier assumptions^{9,12} that hydrolysis during work-up and/or an intermolecular version of the Barton reaction might be responsible. Since either derivative can be converted into the trinitromethyl substitution product by an acid-catalyzed process, solution of this problem is not critically important for our reasoning.

Formation of phenolic products. Adducts **1** can, in principle, undergo elimination of nitroform, as shown in eqn. (3), and give phenol which would be rapidly nitrated by, for example, NO₂ to give the products observed. Alternatively, the corresponding nitrites might undergo the same type of reaction [eqn. (4)], thus producing PhONO, which, by analogy with the chemistry of phenyl nitrate,²⁰ might rearrange to 2-nitrosophenol and eventually become oxidized to 2-nitrophenol.

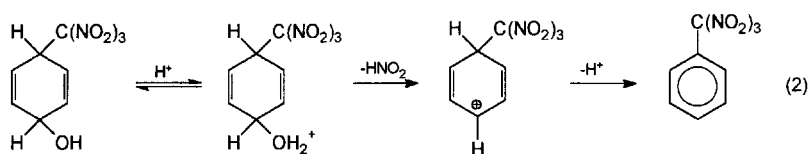
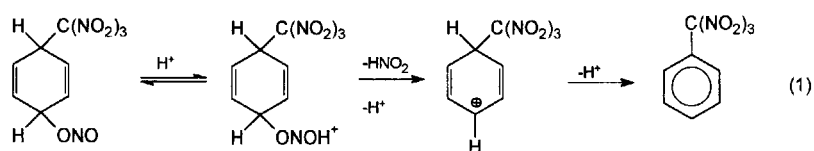
Formation of the 1,3-dipolar addition product 2. The heterocyclic compound **2** is formally the product of 1,3-di-

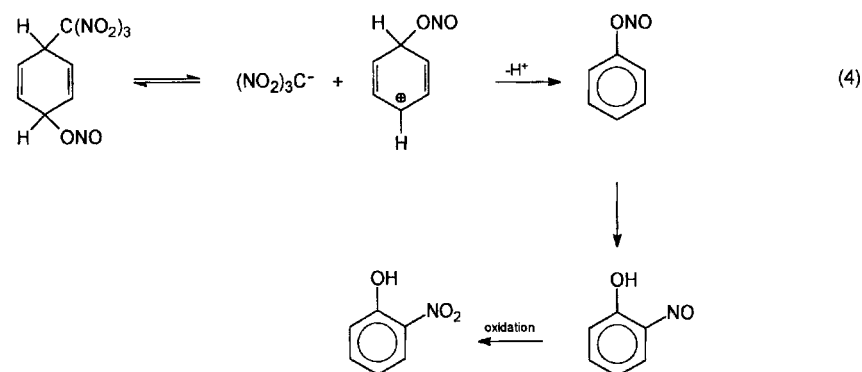
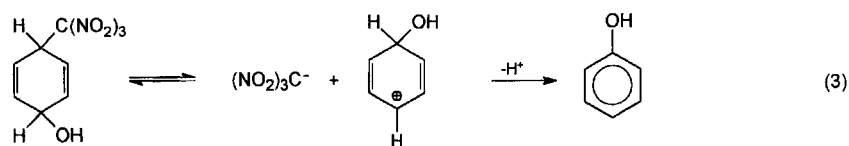
polar addition of 4-nitrobenzocitrile *N*-oxide and acetonitrile (cf. Ref. 21). It seems likely that the nitrile oxide functionality is generated from a trinitromethyl group during the photolysis reaction, the nitrile oxide group then reacting with the solvent, acetonitrile. As one of the products of the photolysis is 4-trinitromethylnitrobenzene, this compound is the probable precursor of the proposed nitrile oxide intermediate. However, as trinitromethylbenzene is also present among the reaction products, one cannot exclude a sequence of steps which includes benzocitrile *N*-oxide formation, cycloaddition with acetonitrile, and nitration at C4 of the phenyl ring of the resulting 1,2,4-oxadiazole. The degradation of a trinitromethyl group to the nitrile function under thermal conditions has been observed upon GLC of product mixtures from photolysis of TNM/naphthalene^{2,17} and TNM/dibenzofuran,¹⁰ so the above reaction has some precedence of similar type.

Experimental

Materials and instrumentation. See Refs. 2 and 4. **WARNING.** While we did not experience any incidents whilst working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.²²

General procedure for the photolysis of benzene and tetranitromethane. A solution of benzene (0.8 mol dm⁻³) and tetranitromethane (1.6 mol dm⁻³) in dichloromethane or acetonitrile was irradiated with filtered light (cutoff < 435 nm). Aliquots were withdrawn at appropriate time intervals, the volatile material was removed under reduced pressure at ≤ 0°C and the product composition was determined by NMR spectral analysis (Tables 1 and 2). The runs at -20°C were performed with initial benzene and tetranitromethane concentrations of 0.4 and 0.8 mol dm⁻³, respectively.





Reaction in dichloromethane at +20°C and the identification of products. Reaction of benzene at +20°C, as above, for 48 h gave a product which was shown by NMR spectroscopy to be a mixture of products as summarized in Table 1. The *cis*- and *trans*-1-hydroxy-4-trinitromethylcyclohexa-2,5-dienes **1** could not be isolated but their structures were deduced from the analysis of NMR spectra of the crude mixture in CDCl₃. Isomer **1a**: ¹H NMR: δ 6.59 [ddd, *J*_{3,2} 10.4 Hz, *J*_{3,4} 3.9 Hz, *J*_{3,1} 1.9 Hz, H3 (H5)], 6.22 [ddd, *J*_{2,3} 10.4 Hz, *J*_{2,1} 3.4 Hz, *J*_{2,4} 1.6 Hz, H2 (H6)], ca. 5.48 (m, H4), ca. 4.64 (m, H1). Isomer **1b**: ¹H NMR: δ 6.62 [ddd, *J*_{3,2} 10.4 Hz, *J*_{3,4} 3.1 Hz, *J*_{3,1} 2.1 Hz, H3 (H5)], 6.24 [ddd, *J*_{2,3} 10.4 Hz, *J*_{2,1} 3.5 Hz, *J*_{2,4} 2.2 Hz, H2 (H6)], ca. 5.48 (m, H4), ca. 4.64 (m, H1). By long-range reverse detected ¹H-¹³C heteronuclear correlation spectra (HMBC) the ¹³C NMR spectrum of adducts **1** was partially defined: δ 41.2, C4 (**1a**, **1b**); 77.54, 77.62, C1 (**1a**, **1b**); 123.88, C3, C5 (**1a**, **1b**); 127.65, C2, C6 (**1a**, **1b**).

The following products were isolated from the product mixture by chromatography on a silica gel Chromatotron plate (Harrison & Harrison), using pentane/diethyl ether mixtures as the eluting solvents: (i) nitrobenzene, identical with an authentic sample; (ii) 1,3-dinitrobenzene, identical with an authentic sample; (iii) 1,3-dinitro-5-trinitromethylbenzene, ¹H NMR (CDCl₃): δ 9.42 (dd, *J* = *J*' = 1.9 Hz, H2), 8.91 (d, *J* 1.9 Hz, H4, H6). A sample of 1,3-dinitro-5-trinitromethylbenzene (4.3 mg) was heated under reflux for 16 h with concentrated hydrochloric acid (0.1 cm³). The material (3.9 mg) isolated by diethyl ether extraction was shown (¹H NMR) to be 3,5-dinitrobenzoic acid.

(iv) A mixture of trinitromethylbenzene and 4-trinitromethylnitrobenzene, ¹H NMR (CDCl₃): δ 7.62 (d, *J*

3.4 Hz), 7.63 (s), 7.57–7.66 (m), 7.72–7.79 (m); relative integrals for total regions δ 7.57–7.66: 7.72–7.79, ca. 4:1. A sample (43 mg) of this mixture was heated under reflux for 18 h with concentrated hydrochloric acid (1 ml). The material (38 mg) isolated by diethyl ether extraction was shown (¹H NMR, acetone-*d*₆) to be a mixture (ca. 3:4) of benzoic acid and 4-nitrobenzoic acid.

HPLC separation of the product mixture on a Varian 5000 liquid chromatograph with an Alltech cyanopropyl column and a Varian UV-50 detector, eluting with hexane-dichloromethane mixtures gave: (v) 2,4-dinitrophenol, identical with an authentic sample. The following products were not isolated but were identified by comparison of their ¹H NMR spectra with those of authentic samples: (vi) 2,4,6-trinitrophenol, (vii) 2,6-dinitrophenol and (viii) 1,3,5-trinitrobenzene.

Reaction in acetonitrile at +20°C and isolation of 5-methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole **2**. Reaction of benzene at +20°C, as above, for 48 h gave a product which was shown by NMR spectroscopy to be a mixture of products as summarized in Table 2. Chromatography of this mixture on a silica gel Chromatotron plate and elution with pentane gave first a mixture (ca. 5:1) of trinitromethylbenzene and 1-nitro-4-trinitromethylbenzene. The second material eluted was a small amount (yield 1.7%) of a compound the structure of which remains unknown.

Next eluted was 5-methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole **2**, m.p. 142–144°C (X-ray crystal structure determined below), *v*_{max} (KBr): 1612, 1584 (C=N), 1539 cm⁻¹ (NO₂). ¹H NMR (CDCl₃): δ 8.35, 8.27 (AB-system, *J* 9.3 Hz, 4 H, phenyl-H), 2.70 (s, Me). ¹³C NMR (CDCl₃): δ 177.4 (C5), 166.9 (C3), 132.7 (C4'), 129.9 (C1'), 128.3 (C3', C5'), 124.1 (C2, C6'), 12.4 (CH₃).

Further elution with pentane and pentane–diethyl ether gave only mixtures of what appeared to be products of decomposition of materials initially present.

Attempted photolysis of nitrobenzene with tetranitromethane. A solution of nitrobenzene (0.5 mol dm⁻³) and tetranitromethane (1.0 mol dm⁻³) in dichloromethane or acetonitrile at +20°C was irradiated with filtered light (cut-off < 435 nm) for 48 h. The volatile material was removed under reduced pressure at ≤ 0°C and the product composition determined by NMR spectral analysis. In both solvents, only nitrobenzene was recovered in good yield from the attempted reactions.

Attempted photolysis of 2,6-dinitrophenol with tetranitromethane. A solution of 2,6-dinitrophenol (20 mg) and tetranitromethane (43 mg) in acetonitrile (1 cm³) at +20°C was irradiated with filtered light (cut-off < 435 nm) for 48 h. The volatile material was removed under reduced pressure at ≤ 0°C and the product composition determined by NMR spectral analysis. Only 2,6-dinitrophenol was recovered in good yield from the attempted reaction.

Attempted photolysis of a mixture (ca. 3:4) of trinitromethylbenzene and 4-trinitromethylnitrobenzene with tetranitromethane. A solution of a mixture (3:4) (37 mg) of trinitromethylbenzene and 4-trinitromethylnitrobenzene and tetranitromethane (59 mg) in acetonitrile (1 cm³) at +20°C was irradiated with filtered light (cut-off < 435 nm) for 48 h. The volatile material was removed under reduced pressure at ≤ 0°C and the product composition determined by NMR spectral analysis. The product (35 mg) was a similar mixture of trinitromethylbenzene and 4-trinitromethylnitrobenzene to that used for the attempted reaction.

Crystallography

Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, λ (Mo K α) 0.71069 Å, from a crystal monochromator] are given below. The space group was determined unambiguously as a result of the structure reported below, but initially indicated by conditions limiting possible reflections. ω -Scans were used to collect reflection intensities out to a maximum Bragg angle $\theta = 25^\circ$. The cell parameters were determined by least-squares refinements for which the setting angles of 25 accurately centered high-angle reflections were used.

Crystal data. 5-Methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole **2**. C₉H₇N₃O₃, *M* 205.18, triclinic, space group *P*1, *a* = 7.083(3), *b* = 7.336(2), *c* = 10.107(3) Å, α = 76.47(1)°, β = 72.38(3)°, γ = 69.28(2)°, *V* = 463.7(3) Å³, *D*_c = 1.469 g cm⁻³, *Z* = 2, μ (Mo K α) 1.14 cm⁻¹. The

crystal was colorless and of approximate dimensions 0.62 × 0.25 × 0.16 mm. Data were collected at 183 K. The number of independent reflections measured 1615, 1393 with $I > 2\sigma(I)$; absorption corrections were not applied; *g*₁ 0.0522, *g*₂ 0.0948, *R*_(obs) 0.037, *wR*_(all data) 0.098.

Structure determination. The structure was solved by direct methods and difference-Fourier syntheses. Full-matrix least-squares refinements (SHELXL-92)²³ were employed. This program is based on intensities and uses all data. The observed threshold $I > 2\sigma(I)$ was used only for calculating *R*_(obs), shown here as a comparison for the refinement based on *F*. Reflection weights $1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$, where $P = [F_o^2 + 2F_c^2]/3$, were used.

All non-hydrogen atoms were assigned anisotropic thermal parameters. Methyl hydrogen atoms were included as rigid groups pivoting about their carbon atoms. Final Fourier syntheses show no significant residual electron density, and there were no abnormal discrepancies between observed and calculated structure factors. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements. Financial support (to L.E.) from the Swedish Natural Science Research Council and the Knut and Alice Wallenberg Foundation is gratefully acknowledged.

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Received September 24, 1993.