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Thermal and Photochemical Decomposition Pathways of Trinitromethylarenes. Part II.† The Effects of Ethanol on the Photolysis Reactions of Some Alkoxy- and Dialkoxyarenes in the Presence of Tetranitromethane. Enhancement of Adduct and Trinitromethyl Substitution Product Formation

Craig P. Butts,[a] Lennart Eberson,[b,*] Michael P. Hartshorn[a,*] and Ola Persson[b]

[a]Department of Chemistry, University of Canterbury, Christchurch, New Zealand and [b]Chemical Center, Lund University, PO Box 124, S-221 00 Lund, Sweden

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The photolysis of the charge transfer (CT) complex of tetranitromethane with 1-methoxynaphthalene, 1,4-dimethoxybenzene, 1,2-dimethoxybenzene, 1,2-methylenedioxybenzene or 2-methylanisole is reported for dichloromethane, acetonitrile, dichloromethane–ethanol and acetonitrile–ethanol solvent systems. The effects of adding ethanol (8% v/v $\sim$1.4 mol dm^{-3}) to dichloromethane or acetonitrile as reaction solvents include: (i) the stabilization of alkoxytrinitromethylarenes, thus reducing their normal tendency for decomposition according to $ArC(NO_2)_3 \rightarrow ArCOOH \rightarrow ArNO_2$, (ii) a reduction in the nucleophilicity of trinitromethanide ion, and (iii) changes in the regioselectivity of trinitromethanide ion attack on the radical cations of alkoxyaromatic compounds away from attack *ipso* to the alkoxy substituent.

Adducts are also stabilized, as shown by the photolysis of the CT complex of 1,4-dimethoxybenzene–tetranitromethane in dichloromethane–ethanol (8% v/v) which gives the epimeric 1,4-dimethoxy-3-nitro-6-trinitromethylcyclohexa-1,4-dienes and 1,4-dimethoxy-2-trinitromethylbenzene, in addition to 1,4-dimethoxy-2-nitrobenzene. The adducts are detected also among the products of photolysis reactions in neat dichloromethane or acetonitrile.

The photochemical addition of tetranitromethane to aromatic compounds ArH has been shown to occur predominantly by *addition* of the elements of tetranitromethane, $-NO_2$ or $-ONO$ (most often ending up as $-OH$ under the conditions employed) and $-C(NO_2)_3$, across the aromatic ring.[2,3] The nitro- and/or nitrito-trinitromethyl adducts are either stable enough to permit isolation or undergo more or less facile elimination of nitroform and/or nitrous acid to give *substitution* products $ArNO_2$ and/or $ArC(NO_2)_3$ [eqn. (1)].

$$ArH + C(NO_2)_4 \xrightarrow{h\nu} ArH^{\cdot+}NO_2(NO_2)_3C^- \rightarrow Ar(H)(NO_2)C(NO_2)_3 + Ar(H)(ONO)C(NO_2)_3 \xrightarrow[\text{or } -HNO_2]{-HC(NO_2)_3} ArNO_2 + ArC(NO_2)_3 \quad (1)$$

For methylated naphthalenes, the regiochemistry of the coupling of the radical cation $ArH^{\cdot+}$ with trinitromethanide ion[4] appears to be determined by the relative stabilities of the various resultant delocalized carbon radicals;[5] subsequent radical coupling of the favoured carbon radicals with nitrogen dioxide yields the predominant, stable nitro–trinitromethyl adducts.

From the reactions of methylated benzenes are obtained a spectrum of nitro–trinitromethyl or hydroxy–trinitromethyl adducts and products of further addition or elimination reactions or rearrangements to give both nuclear and side-chain substituted trinitromethyl derivatives. The ring-substituted trinitromethylarenes, which are relatively stable in this series, are believed to arise during

† Part I, see Ref. 1.
* To whom correspondence should be addressed.

Table 1. Yields of products from the photolysis of 1-methoxynaphthalene (**1**) (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane (DCM) or acetonitrile (AN) at 20 °C (Ref. 7).

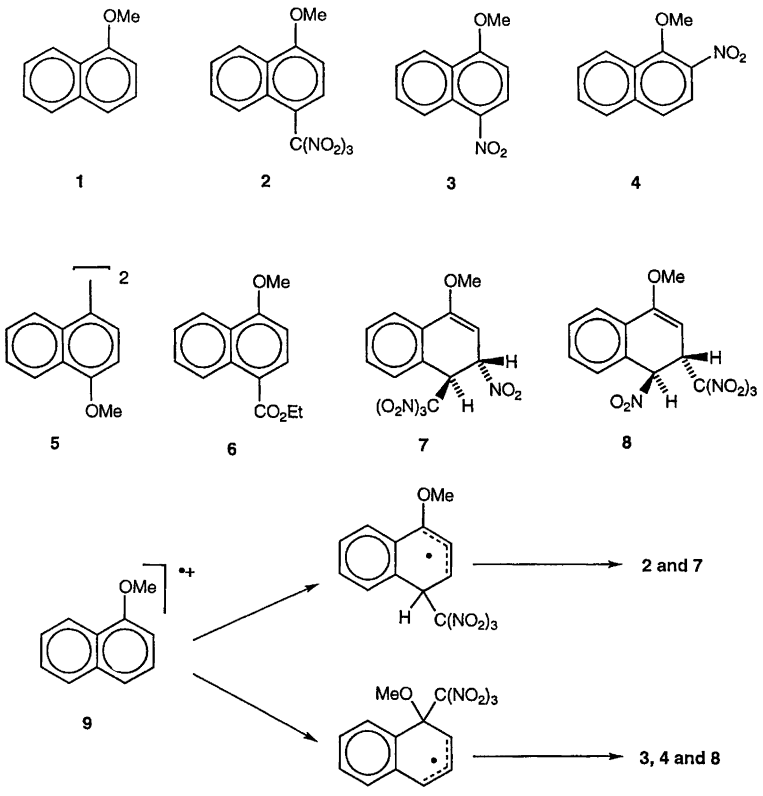
	Yield (%)						
t/h	**2**	**3**	**4**	**5**	**6**	**7**	**8**
In DCM							
0.25	41.3	38.2	2.0	—	—	11.0	7.4
0.5	41.7	41.7	3.0	—	—	7.7	6.2
1	34.6	50.4	5.2	—	—	3.3	6.3
2[a]	24.1	57.4	7.3	—	—	—	6.5
In AN							
0.25	49.5	42.0	3.2	—	—	2.0	2.7
0.5	38.8	50.5	4.1	—	—	3.3	3.3
1	38.0	54.1	4.3	—	—	1.4	2.2
2	17.5	75.5	5.0	—	—	0.7	1.3

[a] 4-Methoxy-1-naphthoic acid (5%) was also formed.

the photolysis reaction by photochemically induced loss of nitrous acid from nitro–trinitromethyl adducts.[6]

The photolysis of the CT complex of 1-methoxynaphthalene (**1**)–tetranitromethane in dichloromethane at 20 °C gives only minor amounts of nitro–trinitromethyl adducts **7** and **8**, the major products being 1-methoxy-4-trinitromethylnaphthalene (**2**) and 1-methoxy-4-nitronaphthalene (**3**) (Table 1).[7] These products arise by decomposition/rearrangement of nitro (or nitrito)–trinitromethyl adducts[7] by attack of trinitromethanide ion either at C4 or C1 of **9** according to Scheme 1. At longer photolysis periods at 20 °C in dichloromethane, and more rapidly in acetonitrile, there is a clear indication of the decomposition of the 3-nitro-4-trinitromethyl adduct **7** to give the 4-trinitromethylarene **2**, which is simultaneously decomposes to give predominantly the 4-nitroarene **3** and minor amounts of the 2-nitroarene **4** (Table 1).

This mode of decomposition has been studied in more detail recently.[1] Using **2** as a model compound for less



Scheme 1.

stable trinitromethylarenes, it was established that **2** undergoes slow thermal decomposition in dichloromethane or acetonitrile to give 4-methoxynaphthoic acid and **3**, the reaction in acetonitrile being the faster one. The reaction was speeded up by added HNO_2 or **1**; under the photolytic conditions used for $ArH–C(NO_2)_4$ reactions, the decomposition was even more strongly accelerated and attained half-lives in a range comparable to the photolysis periods used. It was also shown that 4-methoxynaphthoic acid underwent facile nitrodecarboxylation in the presence of NO_2. It was concluded that this decomposition reaction at least partly accounts for the deceptively simple substitution patterns earlier found for anisoles[8] and dialkoxybenzenes.[9]

Originally,[10] the photolysis of the CT complex of 1-methoxynaphthalene and tetranitromethane was shown to yield some 4-methoxy-1-naphthoic acid at long reaction times (8–16 h). Under similar conditions of long reaction times, but in the presence of added alcohols, alkyl 4-methoxy-1-naphthoates were formed in yields of 30–50%. It was also shown that irradiation for a short period (4 h), followed by dark storage of the reaction mixture for an extended period, increased the yield of the ester strongly, in the case of methanol from 6 to 27% in 16 h. At the time, this effect remained unexplained.

In the light of this report, we explored the effect of adding ethanol (8% v/v) to the photolysis reactions under conditions comparable with those in Ref. 7, the most important difference from Ref. 10 being that the reaction was monitored with time during a short reaction period in order to avoid decomposition of **2**. We confirmed that the photolysis of 1-methoxynaphthalene–tetranitromethane over 1 h gave little of the ester, ethyl 4-methoxy-1-naphthoate (**6**). However, more important effects of added ethanol were noticed (Fig. 1). First, the relative yield of 4-trinitromethylarene (**2**) was much higher and remained essentially unchanged with reaction time. The relative yield of adducts (**7**+**8**) was lower than in dichloromethane but stayed almost constant during the run. Second, the yield of the 4-nitroarene **3** was much reduced, and the combined yield of the two nitroarenes **3** and **4** remained essentially unchanged. Finally, the reaction was characterized by the formation of the dehydrodimer **5** in significant yield. A similar pattern of results was found for reactions in acetonitrile–ethanol (8%).

Given the capability of ethanol to promote the formation and stability of the trinitromethylarene **2** in the photoreaction described above, similar reactions were explored for the alkoxybenzenes, 1,4-dimethoxybenzene, 1,2-dimethoxybenzene, 1,2-methylenedioxybenzene, and 2-methylanisole. For these substrates, previous experience[1] suggests that their trinitromethyl derivatives should decompose under photolysis conditions. Clear evidence was obtained that, in the absence of ethanol (8% v/v), nitro–trinitromethyl adducts and trinitromethylarenes were converted into nitroarenes during even short-term

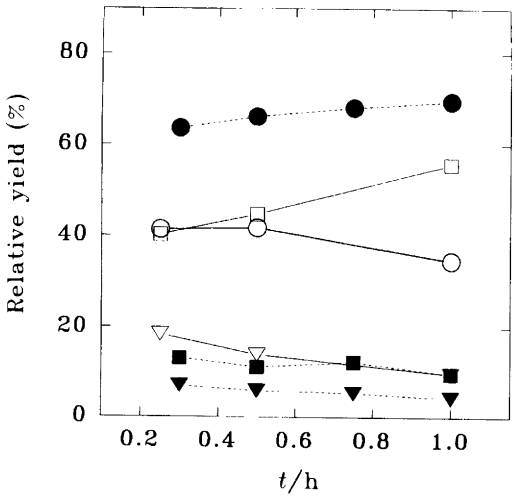


Fig. 1. Time dependence of the yields of trinitromethylarene **2** (circles), nitroarenes (**3** + **4**) (squares) and adducts (**7** + **8**) (triangles) from photolysis reactions of **1** and tetranitromethane in dichloromethane (empty symbols, solid lines) and dichloromethane–ethanol (8% v/v) (filled symbols, dashed lines).

photolysis reactions. We now report the results of these studies.

Results

General. The photochemical experiments were performed with filtered light (cut-off at 435 nm, 5 cm water IR filter, with a 300 W incandescent lamp) as described before,[7] and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature of $\leqslant 0\,^{\circ}C$. The crude product mixtures were stored at $-20\,^{\circ}C$ and were analysed (^1H NMR spectroscopy, see Experimental section; Tables 2–7) as soon as possible.

Photolysis at 20 °C of 1-methoxynaphthalene (**1**) *with tetranitromethane in dichloromethane or acetonitrile containing ethanol (8% v/v).* A solution of **1** and tetranitromethane in dichloromethane containing ethanol (8% v/v) was irradiated at 20 °C, and its composition monitored with time (Table 2). The products were identified by comparison of their ^1H NMR spectra with those for authentic materials.[7] In the presence of ethanol the yields of products **2**–**8** were essentially invariant with reaction time, in contrast to the reaction in dichloromethane where the yields of the 4-trinitromethylarene **2** and the 3-nitro-4-trinitromethyl adduct **7** were always lower and fell markedly with reaction time, with correspondingly increased yields of the nitroarenes **3** and **4** (Table 1 and Fig. 1). Notable also was the formation of significant amounts of the dehydrodimer **5**. The low yield of the ethyl ester **6** confirmed the earlier finding[10] that ester formation is a thermal reaction requiring longer reaction times for substantial yields to build up (see further below).

Table 2. Yields of products from the photolysis of 1-methoxynaphthalene (**1**) (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) at 20 °C in dichloromethane or acetonitrile with ethanol added.

	Yield (%)						
t/h	**2**	**3**	**4**	**5**	**6**	**7**	**8**
In dichloromethane containing ethanol (8% v/v)							
0.3	63.7	10.3	2.8	15.8	0.5	6.0	0.9
0.5	66.2	8.8	2.3	16.0	0.9	4.7	1.1
0.75	68.2	10.7	1.6	13.2	1.0	4.3	1.0
1.0	69.6	7.8	1.8	15.2	1.2	3.4	0.8
In acetonitrile containing ethanol (8% v/v)							
0.3	56.6	31.0	0.9	11.1	0.4	—	—
0.5	52.5	33.7	1.5	11.1	1.1	—	—
0.75	54.5	29.7	1.4	11.7	2.8	—	—
1.0	51.9	29.1	1.6	14.0	3.4	—	—
In ethanol							
0.3	64.7	10.6	2.4	12.9	0.2	8.0	1.2
0.5	66.3	9.4	2.0	13.5	0.8	6.5	1.6
0.75	68.9	7.8	1.3	15.5	1.3	4.3	1.0
1.0	64.5	10.6	2.5	14.7	2.6	4.4	0.7

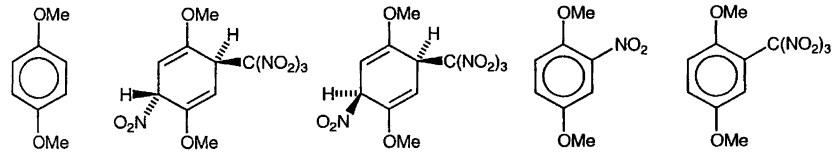
In acetonitrile containing ethanol (8% v/v) only compounds **2**–**6** were detected in the crude product mixtures (Table 2). Nonetheless, the yields of these were also essentially invariant with reaction time, the yield of the 4-trinitromethylarene **2** being somewhat lower than in dichloromethane–ethanol, and that of the 4-nitroarene **3** being somewhat higher. The yields of the dehydrodimer **5** and the ethyl ester **6** were similar to those obtained in the dichloromethane–ethanol reaction above.

Photolysis at 20 °C of 1-methoxynaphthalene (**1**) *with tetranitromethane in dichloromethane containing ethanol (8% v/v), followed by dark storage of reaction mixtures for 1–24 h.* A solution of **1** and tetranitromethane in dichloromethane containing ethanol (8% v/v) was irradiated at 20 °C. Samples of the reaction mixture were withdrawn after 0.5 and 2 h, and stored in the dark. The composition of each reaction mixture was monitored by withdrawing samples for NMR spectral analysis (Table 3). Notably, after storage of either of the reaction mixtures in the dark for 24 h, the yield of **6** increased markedly, reaching 27% in the case of the 0.5 h (light)/24 h (dark) sample. This effect is similar to that observed earlier when adding methanol.[10] The apparent disappearance of the dehydrodimer **5** during the dark reaction periods is worthy of some comment; the ^1H NMR spectra of the 'unknown aromatics' were similar to those of the mixture of nitrated dehydrodimers observed earlier.[7]

Photolysis at 20 °C of 1-methoxynaphthalene (**1**) *with tetranitromethane in ethanol.* A solution of **1** and tetranitromethane in ethanol was irradiated at 20 °C, as above, and gave compounds **2**–**8** in yields presented in Table 2. This pattern of yields is closely similar to that found for the dichloromethane–ethanol reaction, including the relatively low yield of the ethyl ester.

Photolysis at 20 °C of 1,4-dimethoxybenzene (**10**) *with tetranitromethane in dichloromethane containing ethanol (8% v/v).* A solution of **10** and tetranitromethane in dichloromethane containing ethanol (8% v/v) was irradiated at 20 °C and its composition monitored with time as shown in Table 4. After 5 h partial conversion (ca. 84%) had occurred into a mixture of the two nitro–trinitromethyl adducts **11** (6%) and **12** (1.5%), the 2-nitro compound **13** (82%), and the 2-trinitromethylarene **14** (10%). For the structural assignment of **11**, **12** and **14**, see Experimental.

Photolysis at 20 °C of 1,4-dimethoxybenzene (**10**) *with tetranitromethane in dichloromethane, or in dichloromethane containing ethanol (4% v/v).* With the advantage of having established ^1H NMR spectra of the nitro–trinitromethyl adducts **11** and **12**, small amounts of each



10 **11** **12** **13** **14**

Table 3. Yields of products from the photolysis of 1-methoxynaphthalene (**1**) (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) at 20 °C in dichloromethane containing ethanol (8% v/v), followed by dark storage of the reaction mixture for a period of *t* h.

	Yield (%)							
t/h	**2**	**3**	**4**	**5**	**6**	**7**	**8**	Unknown aromatics
Irradiation for 0.5 h, followed by storage in the dark for a period of *t* h								
+0	69.1	17.3	0.2	8.6	0.3	4.2	Trace	—
+1	71.3	10.3	0.2	13.9	2.0	2.0	0.4	—
+2	72.8	8.5	0.2	13.0	3.2	1.1	—	—
+4	68.7	9.2	0.2	12.9	5.8	0.5	—	2.8
+8	62.0	12.4	0.2	8.3	11.4	—	—	5.7
+24	51.6	12.0	0.2	5.0	27.2	—	—	4.0
Irradiation for 2 h, followed by storage in the dark for a period of *t* h								
+0	72.7	14.4	Trace	7.6	2.9	1.4	—	0.7
+1	75.1	14.5	0.2	3.6	3.6	0.5	—	2.4
+2	74.0	16.1	0.1	2.4	4.7	—	—	2.7
+4	72.8	14.1	0.1	2.1	6.6	—	—	4.3
+12	61.5	14.0	0.3	2.4	16.8	—	—	5.0
+24	48.3	18.8	0.1	—	19.1	—	—	13.6

Table 4. Overview of yields of products from the photolysis of 1,4-dimethoxybenzene (**10**) (0.45 mol dm^{-3}) and tetranitromethane (0.9 mol dm^{-3}) at 20 °C.

		Yield (%)			
t/h	Conversion (%)	**11**	**12**	**13**	**14**
In dichloromethane					
1	37	3.6	Trace	96.4	—
2	74	3.1	0.4	96.5	—
3	96	2.7	0.5	96.8	—
In acetonitrile					
1	43	Trace	Trace	~100	—
2	72	0.5	Trace	99.5	—
3	91	0.7	Trace	99.3	—
4	~100	0.9	Trace	99.1	—
In dichloromethane containing ethanol (4% v/v)					
1	31	8.7	1.7	73.8	15.7
2	61	6.4	1.1	81.0	11.4
3	88	5.7	1.5	83.1	9.7
In dichloromethane containing ethanol (8% v/v)					
3	56	8.3	1.5	80.5	9.8
5	84	6.3	1.5	82.5	9.7
In acetonitrile containing ethanol (8% v/v)					
1	23	Trace	Trace	~100	—
2	52	Trace	Trace	~100	—
3	72	0.5	Trace	99.5	—
4	86	0.9	Trace	99.1	—

adduct were identified in the crude reaction product from the photolysis of **10** and tetranitromethane in dichloromethane at 20 °C. The major product was the 2-nitroarene **13**, and none of the 2-trinitromethyl compound **14** could be detected.

Addition of ethanol (4% v/v) to the dichloromethane photolysis solution resulted in the formation of **14**, in addition to **11** and **12**, and reduced amounts of the **13** (Table 4). At this ethanol concentration, it is clear that the yield of the **14** diminishes with photolysis reaction time, with a corresponding increase in the yield of **13**, thus confirming the conclusion drawn in a preliminary study that the conversion **14**→**13** occurs during the photolysis of 1,4-dimethoxybenzene–tetranitromethane.[11] The progressive addition of ethanol (4 and 8% v/v) to the dichloromethane solvent results also in a progressive decrease in the rate of conversion of **10** into products (Table 4).

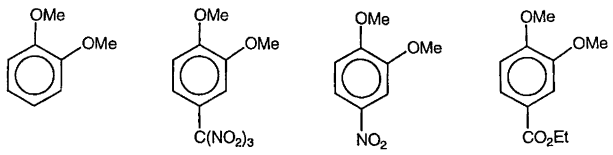
Photolysis at 20 °C of 1,4-dimethoxybenzene (**10**) *with tetranitromethane in acetonitrile or in acetonitrile containing ethanol (8% v/v).* A solution of **10** and tetranitromethane in acetonitrile, or in acetonitrile containing ethanol (8% v/v), was irradiated at 20 °C. The composition of each reaction mixture with time is given in Table 4. The major product of both reactions was the 2-nitroarene **13**, but small amounts of the nitro–trinitromethyl adducts **11** and **12** were also present. The absence of the 2-trinitromethylarene **14** is not surprising in the light of the increased lability of trinitromethylarenes in acetonitrile solution.[1]

Photolysis at −20 °C of 1,2-dimethoxybenzene (**15**) *with tetranitromethane in dichloromethane.* A solution of **15** and tetranitromethane in dichloromethane was irradiated at −20 °C and its composition monitored with time as shown in Table 5. After 3 h partial conversion (ca. 67%) had occurred into a mixture of the 4-trinitromethylarene **16** (5%) and the 4-nitro compound **17**. For the identifica-

Table 5. Overview of yields of products from the photolysis of 1,2-dimethoxybenzene (**15**) (0.45 mol dm^{-3}) and tetranitromethane (0.9 mol dm^{-3}).

		Yield (%)		
t/h	Conversion (%)	**16**	**17**	**18**
In dichloromethane at 20 °C				
1	21	11.4	88.6	—
2	47	11.8	88.2	—
3	64	9.6	90.4	—
In dichloromethane at −20 °C				
1	23	10.8	89.2	—
2	47	6.9	93.1	—
3	67	4.8	95.2	—
In dichloromethane containing ethanol (4% v/v) at 20 °C				
1	43	71.1	28.4	0.5
2	65	50.6	48.9	0.6
3	85	42.9	55.8	1.3
In dichloromethane containing ethanol (8% v/v) at 20 °C				
1	35	82.0	17.0	1.0
2	55	71.0	27.0	1.0
3	72	62.0	36.0	2.0
In acetonitrile at 20 °C				
1	23	3.8	96.2	—
2	41	3.4	96.6	—
3	59	3.4	96.6	—
In acetonitrile at −20 °C				
1	17	4.5	95.5	—
2	35	3.0	97.0	—
3	50	2.9	97.1	—
In acetonitrile containing ethanol (8% v/v) at 20 °C				
1	28	30.9	67.6	1.5
2	49	30.6	66.9	2.5
3	64	26.4	70.8	2.8

tion of **16**, see Experimental. Even in dichloromethane at −20 °C, it is clear that the conversion **16**→**17** occurs during the photolysis reaction.



15 **16** **17** **18**

Photolysis at 20 °C of 1,2-dimethoxybenzene (**15**) *with tetranitromethane in dichloromethane or in dichloromethane containing ethanol (4 or 8% v/v).* A solution of **15** and tetranitromethane in dichloromethane, or dichloromethane containing ethanol (4 or 8% v/v), was irradiated at 20 °C, and its composition monitored with time as shown in Table 5. In the reactions where ethanol had been added to the photolysis solvent medium small amounts of ethyl 3,4-dimethoxybenzoate (**18**) were formed (identification, see Experimental).

The notable outcome of increasing the ethanol content of the reaction medium from neat dichloromethane to dichloromethane–ethanol (8% v/v) is again the marked increase in the yield of the 4-trinitromethyl compound **16** at the expense of the 4-nitro compound **17**. At the most extreme the yield of **16** is 82% after 1 h in dichloromethane–ethanol (8%), but dropping to 62% after 3 h, with a corresponding increase of **17**; the conversion **16**→**17** is apparently associated with some leakage to the formation of ethyl 3,4-dimethoxybenzoate **18**. At the lower ethanol concentration (4% v/v) the yield of the **16** after 1 h is somewhat lower than in dichloromethane–ethanol (8% v/v) and the rate of the conversion into the 4-nitroarene **17** is higher (Table 5).

Photolysis of 1,2-dimethoxybenzene (**15**) *with tetranitromethane in acetonitrile at 20 or −20 °C or in acetonitrile containing ethanol (8% v/v) at 20 °C.* A solution of **15** and tetranitromethane in acetonitrile at 20 or −20 °C, or acetonitrile containing ethanol (8% v/v) at 20 °C was irradiated and its composition monitored with time as shown in Table 5.

In acetonitrile at either 20 or −20 °C the 4-nitroarene **17** was the major product with only small amounts of 4-trinitromethyl compound **16** being detected. In the presence of added ethanol (8% v/v) the yield of **16** was 31% after 1 h (ca. 28% conversion), while **17** remained the major product accompanied by small amounts of **18** (Table 5).

Photolysis at 20 °C of 1,2-methylenedioxybenzene (**19**) *with tetranitromethane in dichloromethane.* A solution of **19** and tetranitromethane in dichloromethane was irradiated at 20 °C and its composition monitored with time as shown in Table 6. After 2 h partial conversion (ca. 66%) had given a mixture of the 4-trinitromethylarene **20** (19%), the 4-nitroarene **21** (75%) and some unidentified aromatic products. For the identification of **20** and **21**, see Experimental. During the the photolysis it was clear that **20** was slowly converted into **21**.

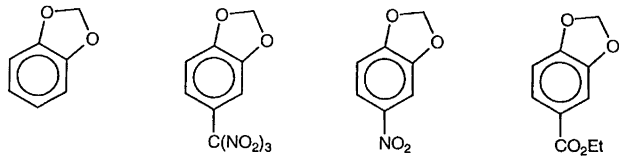
Photolysis of 1,2-methylenedioxybenzene (**19**) *with tetranitromethane in dichloromethane at −20 and −40 °C.* At these lower reaction temperatures the product analysis was rendered unreliable after the 1 h sample because of the crystallization of **21** from the reaction mixture (Table 6).

Photolysis at 20 °C of 1,2-methylenedioxybenzene (**19**) *with tetranitromethane in dichloromethane containing ethanol (8% v/v).* This reaction occurred markedly more slowly than the photolysis reaction in neat dichloromethane, a 10 h reaction time resulting in a conversion of only ca. 50% into products. The 4-trinitromethyl compound **20** was the major product (ca. 60%), with lesser amounts of the 4-nitroarene **21** (ca. 19%), the ethyl

Table 6. Overview of yields of products from the photolysis of 1,2-methylenedioxybenzene (**19**) (0.5 mol dm^{-3}) and tetranitromethane (1.0 mol dm^{-3}).

		Yield (%)			
t/h	Conversion (%)	**20**	**21**	**22**	Unknown aromatics
In dichloromethane at 20 °C					
1	36	31.7	65.3	—	3.0
1.5	59	25.0	70.9	—	4.1
2	66	19.2	75.3	—	5.5
In dichloromethane at −20 °C[a]					
1	30	18.6	76.4	—	5.0
1.5	[a]	12.1	83.5	—	4.4
2	[a]	9.1	89.0	—	1.9
In dichloromethane at −40 °C[a]					
1	32	10.3	86.2	—	3.4
1.5	[a]	7.4	91.6	—	1.0
2	[a]	9.9	87.9	—	2.2
In dichloromethane containing ethanol (8% v/v) at 20 °C					
3	19	61.5	18.5	7.7	12.3
6	29	56.3	19.4	9.7	14.6
10	50	59.9	19.2	9.0	12.0
In acetonitrile at 20 °C					
1	26	—	100	—	—
1.5	43	—	100	—	—
2	62	—	100	—	—
In acetonitrile at −20 °C[a]					
1	29	—	100	—	—
1.5	[a]	—	100	—	—
2	[a]	—	100	—	—
In acetonitrile containing ethanol (8% v/v) at 20 °C					
3	28	10.5	75.6	2.9	11.0
6	35	12.3	72.1	4.9	10.7
10	55	6.3	81.3	8.3	4.2

[a]Some nitro compound (**21**) crystallized from the reaction mixture after 1 h.



19 **20** **21** **22**

ester **22** (ca. 9%) and some unidentified aromatic material (ca. 12%), these proportions remaining essentially constant during the reaction.

Photolysis of 1,2-methylenedioxybenzene (**19**) *with tetranitromethane in acetonitrile or acetonitrile containing ethanol (8% v/v).* In acetonitrile at either 20 or −20 °C the photolysis of **19** and tetranitromethane gave exclusively **21** (Table 6). Addition of ethanol slowed the rate of the photolysis reaction markedly and allowed the detection of **20** and **22** among the products, together with a reduced (but increasing with time) yield of **21**.

Photolysis at 20 °C of 2-methylanisole (**23**) *with tetranitromethane in dichloromethane or acetonitrile, each containing ethanol (8% v/v).* A solution of **23** and tetranitromethane in dichloromethane or acetonitrile, each containing ethanol (8% v/v) was irradiated at 20 °C and its composition monitored with time as shown in Table 7. For comparison, yields for reactions in dichloromethane and acetonitrile[12] are presented also in Table 7.

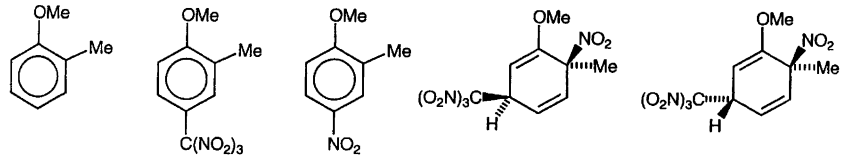
In dichloromethane it is clear that the 4-trinitromethyl compound **24** is converted into the 4-nitroarene **25** during the photolysis reaction.[12] On addition of ethanol (8% v/v) this conversion is apparently suppressed and the yield of **24** remains high (ca. 87%), together with minor amounts of **25** and the epimeric nitro–trinitromethyl adducts **26** and **27**.

The addition of ethanol (8% v/v) to the acetonitrile photolysis reaction medium results in a marked change in product ratio relative to that in pure acetonitrile (Table 7).[12] In this case the higher yield of **24** is accompanied by a marked reduction in the yields of *both* **25** *and* adducts **26** and **27** At longer photolysis times it is clear that some conversion **24**→**25** is occurring.

EPR spectroscopy of some substrate–tetranitromethane combinations. The photolysis of ArH–tetranitromethane solutions in dichloromethane will give EPR spectrally detectable concentrations of $ArH^{\cdot+}$ [cf. eqn. (1)], provided the radical cations are not too reactive.[4] For reactive $ArH^{\cdot+}$, it is necessary to reduce the nucleophilicity of the medium by adding an acid, usually trifluoroacetic acid, in order to protonate trinitromethanide ion. A second possibility to attenuate the nucleophilicity of trinitromethanide ion is to utilize the strong hydrogen-bonding properties of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) for this purpose.[11,13,14] In this solvent, the reactivities of some anionic nucleophiles can be decreased by as much as eight powers of ten in relation to acetonitrile. For trinitromethanide ion, the reactivity decrease was by the more modest factor of 2×10^3.

Some of the substrates used above were photolyzed with tetranitromethane under different conditions, and the radical cations formed were monitored by EPR spectroscopy. The particular aspect studied here was the effect of adding ethanol, and HFP or HFP–EtOH (8% v/v) was used as the solvent in order to make observation feasible. Results in dichloromethane were included for comparison. The results are shown in Table 8.

1-Methoxynaphthalene (**1**) in HFP or HFP–EtOH gave as the only detectable species the radical cation of its dehydrodimer, $\mathbf{5}^{\cdot+}$, as found earlier for reactions in dichloromethane at low temperatures, < -48 °C.[7] The spectral intensity was lower in the presence of ethanol. 1,4-Dimethoxybenzene (**10**) cleanly gave $\mathbf{10}^{\cdot+}$ in both HFP and HFP–EtOH, with a less intense spectrum in



23 24 25 26 27

the latter solvent. No sign of the spectrum of the radical cation of the dehydrodimer (2,2′,5,5′-tetramethoxybiphenyl), was evident. 1,2-Dimethoxybenzene (**15**) behaved in the same way as **10** in both HFP and HFP–EtOH, radical cation **15**$^{\cdot+}$ being the only observable species (spectra of the radical cations of both the dehydrodimer, 3,3′,4,4′-tetramethoxybiphenyl, and the cyclic trimer, 2,3,6,7,10,11-hexamethoxytriphenylene, were recorded under similar conditions and were found to be distinctly different). With ethanol present, the EPR spectral intensity was significantly lower (Fig. 2).

Attempts to study the behaviour of **19** under similar conditions were thwarted by the tendency of **19**$^{\cdot+}$ to dimerize and undergo ring opening;[15] these studies will be reported separately.

In conclusion, the effect of added ethanol in HFP was

Table 7. Overview of yields of products from the photolysis of 2-methylanisole (**23**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}).

	Yield (%)					
t/h	**24**	**25**	Unknown aromatic	**26**	**27**	Unknown adducts
In dichloromethane at 20 °C[12]						
1	75.4	11.7	5.8	2.4	4.7	—
2	70.7	17.4	5.2	2.2	4.5	—
4	65.2	25.0	3.9	1.7	4.1	—
In dichloromethane containing ethanol (8% v/v) at 20 °C						
1	86.9	6.5	—	1.9	4.7	—
2	87.6	7.0	—	1.2	4.1	—
3	87.1	7.5	—	1.2	4.1	—
In acetonitrile at 20 °C[12]						
1	30.7	40.8	4.7	4.2	17.5	2.0
2	26.0	43.3	5.7	4.3	18.3	2.4
4	23.0	44.8	4.5	4.1	19.5	3.2
In acetonitrile containing ethanol (8% v/v) at 20 °C						
1	81.2	12.6	—	1.1	5.0	—
2	80.4	13.3	—	1.5	4.9	—
3	73.7	21.2	—	1.5	3.6	—

Table 8. Detection of radical cations formed in the photolysis of 1-methoxynaphthalene **1**, 1,4-dimethoxybenzene **10** and 1,2-dimethoxybenzene **15** in the presence of tetranitromethane in different solvents.

Substrate	*T*/°C	Solvent[a]	Species detected	Ref.
1	< −48	DCM	**5**$^{\cdot+}$	4, 7
1	22	HFP	**5**$^{\cdot+}$	11, 14
1	22	HFP–EtOH (8% v/v)	**5**$^{\cdot+}$	This work
10	−60	DCM	**10**$^{\cdot+}$ [b]	4
10	22	HFP	**10**$^{\cdot+}$ [b]	11, 14
10	22	HFP–EtOH (8% v/v)	**10**$^{\cdot+}$ [b]	This work
15	−60	DCM	**15**$^{\cdot+}$ [b,c]	This work
15	22	HFP	**15**$^{\cdot+}$ [b,c]	This work
15	22	HFP–EtOH (8% v/v)	**15**$^{\cdot+}$ [b,c]	This work

[a]DCM, dichloromethane; HFP, 1,1,1,3,3,3-hexafluoropropan-2-ol. [b]No dehydrodimer radical cation was detected. [c]The radical cation of 2,3,6,7,10,11-hexamethoxytriphenylene was not detected.

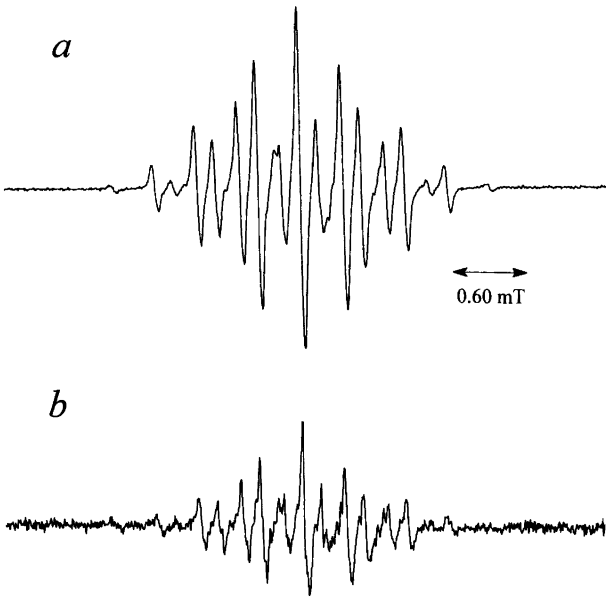


Fig. 2. EPR spectrum of a solution of **15** (0.02 mol dm^{-3}) and tetranitromethane (0.50 mol dm^{-3}) in (*a*) HFP and (*b*) HFP–ethanol (8% v/v). The ratio of the intensities of the spectra in (a) and (b) is ~10.

to decrease the EPR spectral intensity of the primary or secondary radical cations, but no qualitative difference was seen.

Discussion

Overview of the photolysis reactions of substrates 1, 10, 15, 19 and 23 in dichloromethane or acetonitrile containing ethanol (8% v/v) or in ethanol. Table 9 compares data on the final product distributions of the reactions described above, as well as pertinent data from previous work. It is evident that the addition of ethanol (8% v/v ~1.4 mol dm^{-3}) has a beneficial effect on the formation and persistence of trinitromethylarenes under photolytic conditions, the change in the trinitromethyl–arene: nitroarene ratio in going from dichloromethane to dichloromethane–ethanol (8% v/v) amounting to a factor of ca. 19 (**1**), >12 (**10**), 15 (**15**), 13 (**19**) and 4 (**23**). In the change from acetonitrile to acetonitrile–ethanol (8% v/v) the corresponding factors were ca. 4.5 (**1**), not measurable (**10**), 12 (**15**), >7 (**19**) and 7 (**23**).

Also adduct stability was influenced by the addition of ethanol, as shown by the almost time-invariant yields (**1**, **10**, **23**) and the detection of adducts in a critical case like **10**.

The possible factors behind the ethanol effect will be discussed below under the individual compounds.

1-Methoxynaphthalene (**1**). In dichloromethane–ethanol the relative yields of the products **2**–**8** were essentially invariant with reaction time (Table 2). Compared with the reaction in neat dichloromethane (Table 1) the yields were much reduced for the 4-nitroarene **3** and the 4-nitro-3-trinitromethyl adduct **8**, both formed by initial attack of trinitromethanide ion at C1 of the radical cation of 1-methoxynaphthalene.[5,7] Correspondingly the yield of the 4-trinitromethylarene **2** was higher than in dichloromethane. Notable in the dichloromethane–ethanol reaction was the formation of the 4,4′-dehydrodimer **5**, an indication of the reduced nucleophilicity of the trinitromethanide ion in this solvent system. Reaction in neat ethanol gave an essentially identical product yield profile to that found for the dichloromethane–ethanol system.

In acetonitrile–ethanol the reaction products were compounds **2**–**6**, the nitro–trinitromethyl adducts **7** and **8** not being detected among the products (Table 2). Again, the relative yields of products were essentially invariant with time and, compared with the reaction in pure acetonitrile (Table 1), the yield of the 4-trinitromethylarene **2** was higher at the expense of the 4-nitroarene **3**.

Features of the reactions in which ethanol had been added were the marked stability of the **2** under photolytic conditions and the formation of the 4,4′-dehydrodimer **5**. These effects are seen as the consequence of hydrogen bonding by ethanol. Such stabilization of the trinitromethyl group in **2** by hydrogen bonding would be expected to reduce the tendency for the rearrangement/fragmentation of the trinitromethyl group.[1] Further, hydrogen bonding of ethanol to the trinitromethanide ion would be expected to have two effects: first, its nucleophilicity would be reduced, facilitating the reaction pathway for 4,4′-dehydrodimer **5** formation and second, the bulkier solvated trinitromethanide ion might be expected to favour attack at the less-hindered C4-position in $\mathbf{1}^{\cdot+}$ (denoted **9** in Scheme 1).

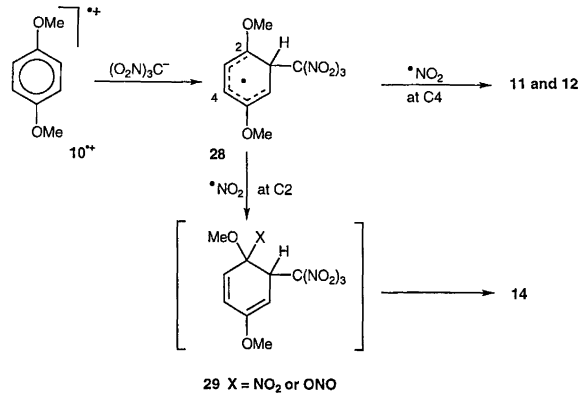
For the reactions with added ethanol the relative stability of the 4-trinitromethylarene **2** and the low yield (<4%) of the ethyl ester **6**, the product of its decomposition in the presence of ethanol, are in agreement with results of an earlier report.[10] As shown in Table 3, short-time irradiation gives a low yield of **6**, and the yield of **6** builds up during the following 'dark' period. The yield was higher if the conversion of **1** into products was incomplete (after 0.5 h conversion ca. 68%); this finding is in accord with the recent report that the decomposition of the 4-trinitromethylarene **2** is promoted by the presence of **1**.[1]

1,4-Dimethoxybenzene (**10**). In dichloromethane containing ethanol (4 or 8%) two nitro–trinitromethyl adducts **11** and **12** were formed in addition to significant amounts of the 2-trinitromethylarene **14** (Table 4). These products are seen as arising from initial attack of trinitromethanide ion at C2 in the radical cation of 1,4-dimethoxybenzene $\mathbf{10}^{\cdot+}$ to give the delocalized carbon radical **28** (Scheme 2). Radical coupling of nitrogen dioxide at C4 in **28** would yield adducts **11** and **12**. An alternative radical coupling of nitrogen dioxide at C2 in carbon radical **28**, which might occur with either C–ONO or C–NO_2 bond formation, would give adduct

Table 9. Overview of the effect of ethanol on the photolyses of **1**, **10**, **15**, **19** and **14** with tetranitromethane.

Compound	Reaction time/h	Solvent[a]	Relative yields		
			$ArC(NO_2)_3$	$ArNO_2$	Adducts
1	2	DCM	24	65	6
	1	DCM–8% EtOH	70	10	4
	2	AN	18	81	2
	1	AN–8% EtOH	52	31	—
	1	EtOH	65	13	5
10	3	DCM	—	97	3
	4[b]	DCM	—	100	—
	3	DCM–8% EtOH	10	83	8
	4	AN	—	99	1
	5.5[b]	AN	—	100	—
	4	AN–8% EtOH	—	99	1
15	3	DCM	10	90	—
	Not given[b]	DCM	—	100	—
	3	DCM–8% EtOH	62	36	—
	3	AN	3	97	—
	Not given[b]	AN	—	100	—
	3	AN	26	71	—
19	2	DCM	19	75	—
	10	DCM–8% EtOH	60	19	—
	2	AN	—	100	—
	10	AN–8% EtOH	6	81	—
23	4	DCM	65	25	6
	3	DCM–8% EtOH	87	8	5
	4	AN	23	45	24
	3	AN–8% EtOH	74	21	5

[a]DCM, dichloromethane; AN, acetonitrile. [b]Ref. 9.



Scheme 2.

29, which is likely to eliminate nitrous acid readily to yield **14**. In photolyses in acetonitrile containing ethanol (8%) **14** was not detected among the products, but small amounts of the adducts **11** and **12** were seen.

For photolyses in both dichloromethane and acetonitrile solution small amounts of the adducts **11** and **12** were detected, with the 2-nitroarene **13** as the major product (Table 4). In the light of an earlier study[11] and the foregoing it seems likely that the 2-trinitromethylarene **14** is formed as a transient intermediate and rapidly decomposes to augment the yield of the 2-nitroarene **13** formed by direct radical coupling of nitrogen dioxide with $\mathbf{11}^{\cdot+}$.

1,2-Dimethoxybenzene (**15**). In reactions in dichloromethane or acetonitrile at 20 and −20 °C the 4-nitroarene **17** is formed as the major product accompanied by relatively minor amounts of the 4-trinitromethylarene **16** (Table 5). In these reactions there is evidence for the transformation **16**→**17**, even at −20 °C in dichloromethane.

In the reactions in dichloromethane containing ethanol (4 or 8%) a large change in product composition occurs, the 4-trinitromethylarene **16** now being the major product accompanied by the 4-nitroarene **17** and minor amounts of the ethyl ester **18**. Even in dichloromethane–ethanol (8%) it is clear that **16** is converted during the photolysis reaction into **17**, and it seems possible that *all* of **17** is formed via **16** under these reaction conditions. In this connection it is relevant that the ethyl ester **18** is present in significant amounts after 1 h. In acetonitrile solutions the yields of **17** and **18** were characteristically higher than in corresponding dichloromethane solutions; these observations are consistent with the known greater labil-

ity of alkoxytrinitromethylarenes in acetonitrile compared with dichloromethane.[1]

The likely mode of formation of the 4-trinitromethylarene **16** is given in Scheme 3. Trinitromethanide ion attack at C4 in the radical cation of 1,2-dimethoxybenzene (**15**$^{\cdot+}$) would give the delocalized carbon radical **30**, which on radical coupling with nitrogen dioxide at C4 would yield the adduct **31** (X = NO_2 or ONO). This type of adduct has been postulated earlier[7] as the source of 1-methoxy-4-trinitromethylnaphthalene **2**, and an analogous loss of nitrous acid would yield **16**.

1,2-Methylenedioxybenzene (**19**). In dichloromethane solution the 4-trinitromethylarene **20** and the 4-nitroarene **21** were formed, the latter predominating (Table 6). For the reactions at −20 and −40 °C the interpretation of the yield data is made hazardous because of the crystallization of the 4-nitroarene **21** from the reaction medium. However, for the reaction at 20 °C it is clear that **20** is being converted into **21** during the photolysis reaction.

The reaction in dichloromethane–ethanol (8%) occurs markedly more slowly than in neat dichloromethane, the conversion reaching 50% only after 10 h in the former case; this is in keeping with the proposition that ethanol reduces the nucleophilicity of the trinitromethanide ion by hydrogen bonding. The data (Table 6) may be interpreted in terms of initial formation of the 4-trinitromethylarene **20** in a manner analogous to that for 1,2-dimethoxy-4-trinitromethylbenzene (**16**) (Scheme 3), followed by conversion of **20** into **21** with some leakage of material into the formation of the ethyl ester **22**.

In acetonitrile only the 4-nitroarene **21** is detected in the products of the photolysis (Table 6). Addition of ethanol again markedly reduces the rate of the reaction and both the 4-trinitromethylarene **20** and the ethyl ester **22** appear among the products. These data are rationalized as for the dichloromethane reactions, except that the transformation of **20** into the 4-nitroarene **21** would be expected to be facilitated by the acetonitrile-containing solvent system.[1]

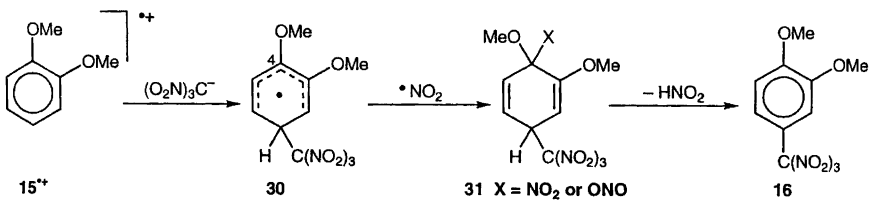
2-Methylanisole (**23**). The formation of the products of photolysis of 2-methylanisole **23** has been rationalized as outlined in Scheme 4.[12] The 4-trinitromethylarene **24** was seen as arising from initial attack of trinitromethanide ion at C4 in the radical cation of 2-methylanisole (**23**$^{\cdot+}$), while the 4-nitroarene **25** and the epimeric adducts **26** and **27** were assumed to arise via attack of trinitromethanide ion *ipso* to the methoxy group in radical cation **23**$^{\cdot+}$. In terms of the data in Table 7 for the dichloromethane and acetonitrile reactions, it is clear that at longer reaction times some **25** arises by transformation of **24**, but the mechanistic conclusions embodied in Scheme 4 remain essentially valid.

In dichloromethane–ethanol (8%) the yields of the 4-trinitromethylarene **24** and the 4-nitroarene **25** are essentially invariant with reaction time, pointing to some stabilization of the trinitromethyl group in **24** by ethanol. The addition of ethanol in acetonitrile results in a marked change in product composition. The 4-trinitromethylarene **24** in acetonitrile–ethanol appears to be somewhat less stable than in dichloromethane–ethanol, but the major effect in acetonitrile–ethanol appears to be a shift in the regiochemistry of attack of trinitromethanide ion on the radical cation of 2-methylanisole **23**$^{\cdot+}$ from *ipso* to the methoxy group towards attack at C4; this leads to an enhanced yield of **24** at the expense of **25** and adducts **26** and **27**. This shift in regioselectivity is presumably a consequence of trinitromethanide ion being solvated in the presence of ethanol.

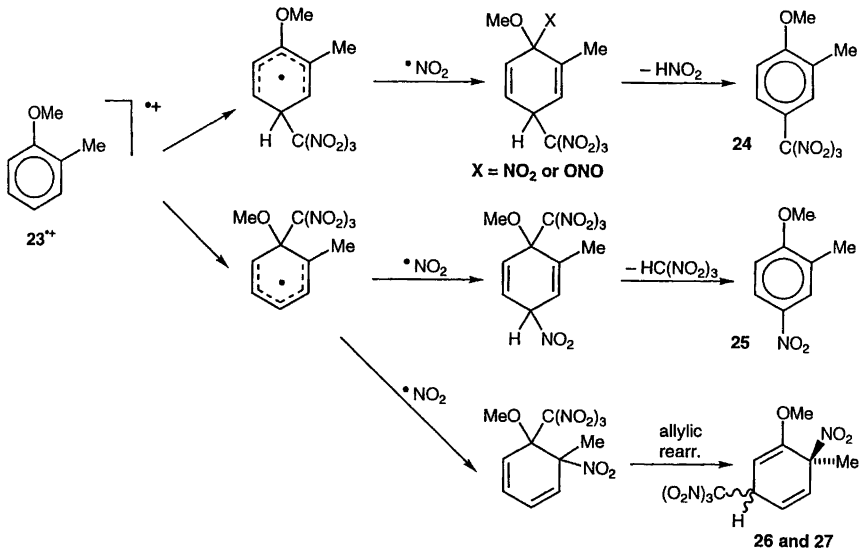
EPR spectral observations. The effect of the addition to ethanol to ArH–tetranitromethane photolyses was briefly studied in HFP for **1**, **10** and **15** by EPR spectral observation of the radical cations formed. The results were as expected: **1** gave the spectrum of its dehydrodimer radical cation **5**$^{\cdot+}$, whereas **10** or **15** cleanly gave their primary radical cations **10**$^{\cdot+}$ or **15**$^{\cdot+}$ (Fig. 2). The addition of ethanol (8% v/v) caused no qualitative changes, but the intensity of the spectra decreased significantly.

Conclusions

From the foregoing it is clear that the tendency for the conversion of alkoxytrinitromethylarenes into alkoxynitroarenes is a general phenomenon; as found also earlier,[1] this process is facilitated by acetonitrile as the solvent and accounts for some of the 'solvent effects' observed in the photolyses of CT complexes of alkoxyarenes and tetranitromethane.[8,9] The addition of ethanol (8% v/v) to either dichloromethane or acetonitrile solvent systems has the effects of: (i) reducing the nucleophilicity of the trinitromethanide ion, (ii) stabilizing alkoxytrinitromethylarenes and (iii) leading to changes in the regioselectivity of attack of trinitromethanide ion on the



Scheme 3.



Scheme 4.

radical cations of alkoxyarenes towards unsubstituted ring positions.

Experimental

Methods and materials. Melting points are uncorrected. IR spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer with $SiMe_4$ as an internal standard. EPR spectra were recorded as published.[4,11,13,14]

Tetranitromethane, 1-methoxynaphthalene, 1,4-dimethoxybenzene, 1,2-dimethoxybenzene, 2,3,6,7,19,11-hexamethoxytriphenylene, 1,2-methylenedioxybenzene, and 2-methylanisole were purchased from Aldrich. 2,2′,5,5′- And 3,3′,4,4′-tetramethoxybiphenyl were prepared according to literature procedures. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH.

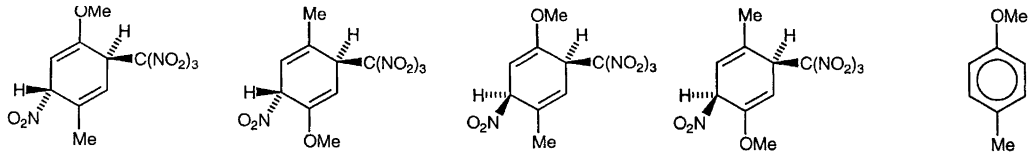
WARNING. While we did not experience any incidents in working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be taken in handling mixtures of tetranitromethane and organic molecules.[16]

General procedure for the photonitration of 1-methoxynaphthalene (**1**) *with tetranitromethane.* A solution of **1** (500 mg, 0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) at 20 °C in either dichloromethane or acetonitrile, each containing ethanol (8% v/v), or in ethanol was irradiated with filtered light (λ_{cutoff} 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition of each sample determined by NMR spectral analysis (Table 2).

Photochemistry of **1** *at 20 °C in dichloromethane containing ethanol (8% v/v) and the identification of products* (**2**–**8**). Reaction of **1**–tetranitromethane at 20 °C in dichloromethane containing ethanol (8%, v/v), as above, for 1 h resulted in partial conversion (ca. 75%) into a product which was shown by ^1H NMR spectra to be a mixture of 1-methoxy-4-trinitromethylnaphthalene (**2**) (70%),[7] 4-nitro- and 2-nitro- compounds (**3**) (8%)[7] and (**4**) (2%),[7] respectively, the 4,4′-dehydrodimer (**5**) (15%),[7] the ethyl ester (**6**) (1%), and the nitro–trinitromethyl adducts (**7**) (3%) and (**8**) (1%).[7]

Photochemistry of **1** *at 20 °C in dichloromethane containing ethanol (8% v/v) for 0.5 h and 2 h, followed by storage in the dark for up to 24 h.* Reaction of **1**–tetranitromethane at 20 °C in dichloromethane containing ethanol (8%, v/v), as above, gave reaction mixtures after 30 min and 2 h which were then stored in the dark for up to 24 h. Aliquots were removed from each mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition of each sample determined by NMR spectral analysis (Table 3).

General procedure for the photonitration of 1,4-dimethoxybenzene (**10**) *with tetranitromethane.* A solution of **10** (500 mg, 0.45 mol dm^{-3}) and tetranitromethane (0.9 mol dm^{-3}) at 20 °C in dichloromethane or acetonitrile, in dichloromethane containing ethanol (4 or 8% v/v), or in acetonitrile containing ethanol (8%) was irradiated with filtered light (λ_{cutoff} 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition of each sample determined by NMR spectral analysis (Table 4).



32 33 34 35 36

Photochemistry of 1,4-dimethoxybenzene (**10**) *at 20 °C in dichloromethane containing ethanol (8% v/v) and the identification of nitro–trinitromethyl adducts* (**11** *and* **12**), *1,4-dimethoxy-2-nitrobenzene* (**13**) *and 1,4-dimethoxy-2-trinitromethylbenzene* (**14**). Reaction of **10**–tetranitromethane at 20 °C in dichloromethane containing ethanol (8%, v/v), as above, for 5 h resulted in partial conversion (ca. 84%) into a product which was shown by ^{1}H NMR spectra to be a mixture of the nitro–trinitromethyl adducts (**11**) (6%) and (**12**) (1.5%), the 2-nitro compound (**13**) (82%) and the 2-trinitromethyl compound (**14**) (10%).

The two nitro–trinitromethyl adducts **11** and **12** were insufficiently stable for their isolation by HPLC at −20 °C, but were identified by comparison of their NMR spectra with those of the four nitro–trinitromethyl adducts **32–35** formed from photolysis of 4-methylanisole **36** and tetranitromethane.[17] For the major adduct **11** the connectivity was established from a consideration of the results of decoupling and NOE ^{1}H NMR experiments together with reverse detected heteronuclear correlation spectra (HMQC) which allowed the assignment of the ^{13}C NMR resonances to the crucial carbon atoms, C2, C3, C5 and C6. For the minor adduct **12** only a partial ^{1}H NMR could be discerned but the chemical shifts of H2, H3, H5 and H6, together with the various H–H coupling constants could be determined. The stereochemistry of adducts **11** and **12** were determined by a comparison of their ^{1}H NMR data with those for the epimeric and regioisomeric adducts **32–35** derived from 4-methylanisole (**36**) (Fig. 3). The chemical shift differences for H2 and H6 in the two nitro–trinitromethyl adducts **11** and **12** were comparable with those for the epimeric 3-nitro-6-trinitromethyl adducts **32** and **34**, and the chemical shift differences for H3 and H5 in **11** and **12** exhibited the same trends as for the 6-nitro-3-trinitromethyl adducts **22** and **35**. For each of the above ^{1}H NMR chemical shift comparisons the proton resonances being considered are for resonances of protons flanking the methoxy group in the relevant nitro–trinitromethyl adducts **32–35**. [15]

The 2-nitroarene **13** was identified by comparison with authentic material. The 2-trinitromethyl compound **14** could be isolated, but only in low yield, by chromatography of the crude reaction product on a silica gel Chromatotron plate; the mass spectrum and ^{1}H NMR spectrum of compound **14** were consistent with the structure assigned.

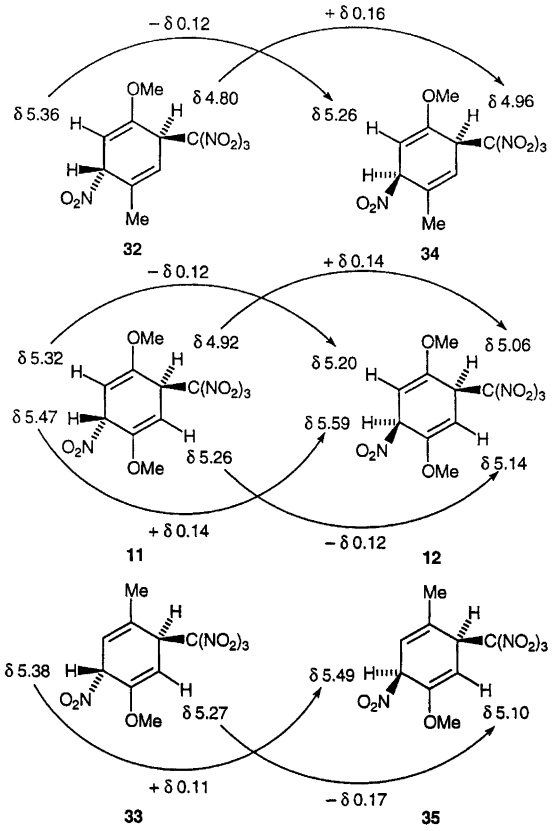


Fig. 3. Comparison of ^{1}H NMR data for the nitro–trinitromethyl adducts **11** and **12** from 1,4-dimethoxybenzene **10** with the nitro–trinitromethyl adducts **32–35** derived from 4-methylanisole **36**.[15]

*1,4-Dimethoxy-*r*-3-nitro-*t*-6-trinitromethylcyclohexa*-1,4-*diene* (**11**). ^{1}H NMR ($CDCl_3$): δ 3.62 (s, 1-OMe), 3.63 (s, 4-OMe), 5.06 (ddd, $J_{H6,H3}$ 4.4 Hz, $J_{H6,H5}$ 3.9 Hz, $J_{H6,H2}$ 1.0 Hz, H6), 5.14 (d, $J_{H5,H6}$ 3.9 Hz, H5), 5.20 (dd, $J_{H2,H3}$ 4.4 Hz, $J_{H2,H6}$ 1.0 Hz, H2), 5.59 (dd, $J_{H3,H2}$ 4.4 Hz, $J_{H3,H6}$ 4.4 Hz, H3). The above assignments were confirmed by double irradiation experiments. Nuclear Overhauser experiments gave the following results: irradiation at δ 5.20 gave an enhancement at δ 5.59 (4.2%); irradiation at δ 5.59 gave an enhancement at δ 5.20 (2.9%). ^{13}C NMR ($CDCl_3$): δ 44.6 (C6), 55.9 (1-, 4-OMe), 83.1 (C3), 90.8 (C5), 94.4 (C2), the remainder of the spectrum was obscured; the above ^{13}C NMR assignments were made from reverse detected heteronuclear correlation spectra (HMQC).

1,4-Dimethoxy-r-3-nitro-c-6-trinitromethylcyclohexa-1,4-diene (**12**). ^{1}H NMR ($CDCl_3$): δ 4.92 (br dd, $J_{H6,H5}$ 4.4 Hz, $J_{H6,H3}$ 3.9 Hz, $J_{H6,H2}$ small, H6), 5.26 (d, $J_{H5,H6}$ 4.4 Hz, H5), 5.32 (br d, $J_{H2,H3}$ 5.3 Hz, $J_{H2,H6}$ small, H2), 5.47 (dd, $J_{H3,H2}$ 5.3 Hz, $J_{H3,H6}$ 3.9 Hz, H3).

The 2-nitro compound **13** was identified by comparison with authentic material. The 2-trinitromethyl compound **14** was isolated in low yield by chromatography of the product mixture on a silica gel Chromatotron plate to give *1,4-dimethoxy-2-trinitromethylbenzene* (**14**), as a yellow oil (insufficient for elemental analysis). Found: M^+ 287.038 86. $C_9H_9N_3O_8$ requires 287.038 96). ^{1}H NMR ($CDCl_3$) δ 3.78, 3.79 (both 3H s, 1-OMe, 4-OMe), 6.82 (d, $J_{H3,H5}$ 2.9 Hz, H3), 7.04 (d, $J_{H6,H5}$ 8.8 Hz, H6), 7.23 (dd, $J_{H5,H6}$ 8.8 Hz, $J_{H5,H3}$ 2.9 Hz, H5).

General procedure for the photonitration of 1,2-dimethoxybenzene (**15**) *with tetranitromethane.* A solution of **15** (500 mg, 0.45 mol dm^{-3}) and tetranitromethane (0.9 mol dm^{-3}) at 20 °C in dichloromethane or acetonitrile, in dichloromethane containing ethanol (4 or 8% v/v), or in acetonitrile containing ethanol (8%) was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition of each sample determined by NMR spectral analysis (Table 5).

Chromatography of the crude product on a silica gel Chromatotron plate gave a low recovery of the 4-trinitromethylarene **16** which was identified from its mass spectrum, where the $M^+ - NO_2$ fragment was the first peak which could be measured accurately, and from its ^{1}H NMR spectrum which indicated the presence of a C4-substituent. The major product, 4-nitroarene **17**, isolated as above was identical with authentic material.

1,2-Dimethoxy-4-trinitromethylbenzene (**16**), isolated in low yield from the product of a photolysis reaction in dichloromethane at −20 °C by chromatography on a silica gel Chromatotron plate, was a yellow oil (insufficient for elemental analysis). Found: $M^+ - NO_2$ 241.045 70. $C_9H_9N_2O_6$ requires 241.046 06. ^{1}H NMR ($CDCl_3$): δ 3.90, 3.97 (both 3H s, 1-OMe, 2-OMe), 6.97 (d, $J_{H6,H5}$ 8.8 Hz, H6), 7.04 (d, $J_{H3,H5}$ 2.9 Hz, H3), 7.19 (dd, $J_{H5,H6}$ 8.8 Hz, $J_{H5,H3}$ 2.9 Hz, H5).

1,2-Dimethoxy-4-nitrobenzene (**17**), isolated as for the trinitromethyl compound (**16**) above, was identical with authentic material.

Ethyl 3,4-dimethoxybenzoate (**18**), one of the products of photolyses in the presence of ethanol, was identified by comparison with authentic material prepared by reaction of 3,4-dimethoxybenzoyl chloride with ethanol. ^{1}H NMR ($CDCl_3$): δ 1.37 (t, $OCH_2\mathbf{CH_3}$), 3.92 (s, 6H, 3-OMe, 4-OMe), 4.34 (q, $O\mathbf{CH_2}CH_3$), 6.86 (d, $J_{H5,H6}$ 8.3 Hz, H5), 7.53 (d, $J_{H2,H6}$ 2.0 Hz, H2), 7.67 (dd, $J_{H6,H5}$ 8.3 Hz, $J_{H6,H2}$ 2.0 Hz, H6).

General procedure for the photonitration of 1,2-methylenedioxybenzene (**19**) *with tetranitromethane.* A solution of **19** (500 mg, 0.51 mol dm^{-3}) and tetranitromethane (1.02 mol dm^{-3}) in dichloromethane (at 20, −20, or −40 °C) or acetonitrile (at 20 or −20 °C), in dichloromethane containing ethanol (8% v/v), or in acetonitrile containing ethanol (8% v/v) was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition of each sample determined by NMR spectral analysis (Table 6).

Chromatography of this mixture on a silica gel Chromatotron plate afforded small samples of each of the compounds **20** and **21**. The 4-trinitromethylarene **20** was identified from its mass spectrum, where the $M^+ - NO_2$ fragment was the first peak which could be measured accurately, and from its ^{1}H NMR spectrum which indicated the presence of a C4 substituent. The 4-nitroarene **21** was identified in a similar manner.

1,2-Methylenedioxy-4-trinitromethylbenzene (**20**), isolated in low yield from the product of a photolysis reaction in dichloromethane at 20 °C by chromatography on a silica gel Chromatotron plate, was a yellow oil (insufficient for elemental analysis. Found: $M^+ - NO_2$ 225.014 88. $C_8H_5N_2O_6$ requires 225.014 76). IR: ν_{max} (liquid film) 1614, 1583, 1259, 1121, 1038, 797 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.14 (s, O–$\mathbf{CH_2}$–O), 6.94 (d, $J_{H6,H5}$ 8.8 Hz, H6), 7.05 (d, $J_{H3,H5}$ 2.4 Hz, H3), 7.13 (dd, $J_{H5,H6}$ 8.8 Hz, $J_{H5,H3}$ 2.4 Hz, H5).

1,2-Methylenedioxy-4-nitrobenzene (**21**), isolated as for the trinitromethyl compound (**20**) above, was a yellow oil (Insufficient for elemental analysis. Found: M^+ 167.021 97. $C_7H_5NO_4$ requires 167.021 86). ^{1}H NMR ($CDCl_3$) δ 6.14 (s, O–$\mathbf{CH_2}$–O), 6.86 (d, $J_{H6,H5}$ 8.3 Hz, H6), 7.66 (d, $J_{H3,H5}$ 2.4 Hz, H3), 7.89 (dd, $J_{H5,H6}$ 8.3 Hz, $J_{H5,H3}$ 2.4 Hz, H5).

Ethyl 3,4-methylenedioxybenzoate (**22**), one of the products of photolyses in the presence of ethanol, was identified by comparison with authentic material prepared by reaction of piperonyl chloride with ethanol. ^{1}H NMR ($CDCl_3$) δ 1.37 (t, $OCH_2\mathbf{CH_3}$), 4.34 (q, $O\mathbf{CH_2}CH_3$), 6.03 (s, O–$\mathbf{CH_2}$–O), 6.82 (d, $J_{H5,H6}$ 8.8 Hz, H5), 7.46 (d, $J_{H2,H6}$ 1.9 Hz, H2), 7.65 (dd, $J_{H6,H5}$ 8.3 Hz, $J_{H6,H2}$ 2.0 Hz, H6).

General procedure for the photonitration of 2-methylanisole (**23**) *with tetranitromethane.* A solution of **23** (500 mg, 0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) at 20 °C in dichloromethane or acetonitrile, or at 20 °C in dichloromethane or acetonitrile each containing ethanol (8% v/v) was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition of each sample determined by NMR

spectral analysis (Table 7). Compounds (**24–27**) were identified from their known spectroscopic data.[12]

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References

1. Eberson, L., Hartshorn, M. P., Radner, F. and Svensson, J. O. *Acta Chem. Scand. 50* (1996) 885.
2. Eberson, Hartshorn, M. P. and Radner, F. In Coxon, J. M., Ed., *Advances in Carbocation Chemistry*, Vol. 2, JAI Press, London 1995, p. 207.
3. Eberson, L., Hartshorn, M. P. and Radner, F. *Acta Chem. Scand. 48* (1994) 937.
4. Eberson, L., Hartshorn, M. P., Radner, F. and Svensson, J. O. *J. Chem. Soc., Perkin Trans. 2* (1994) 1719.
5. Butts, C. P., Eberson, L., Hartshorn, M. P. and Robinson, W. T. *Aust. J. Chem. 48* (1995) 2011; and references cited therein.
6. Eberson, L., Hartshorn, M. P. and Timmerman-Vaughan, D. J. *Acta Chem. Scand. 50* (1996) 1121; Butts, C. P., Eberson, L., Fulton, K. L., Hartshorn, M. P., Robinson, W. T. and Timmerman-Vaughan, D. J. *Acta Chem. Scand. 50* (1996) 991; Butts, C. P., Eberson, L., Hartshorn, M. P., Robinson, W. T., Timmerman-Vaughan, D. J. and Young, D. A. W. *Acta Chem. Scand. 50* (1996) 29.
7. Butts, C. P., Eberson, L., Hartshorn, M. P., Persson, O. and Robinson, W. T. *Acta Chem. Scand. 49* (1995) 253.
8. Sankararaman, S., Haney, W. A. and Kochi, J. K. *J. Am. Chem. Soc. 109* (1987) 7824.
9. Sankararaman, S., Haney, W. A. and Kochi, J. K. *J. Am. Chem. Soc. 109* (1987) 5325.
10. Eberson, L. and Radner, F. *J. Am. Chem. Soc. 113* (1991) 5825.
11. Eberson, L., Hartshorn, M. P. and Persson, O. *Angew. Chem., Int. Ed. Engl. 34* (1995) 2268.
12. Butts, C. P., Eberson, L., Hartshorn, M. P., Robinson, W. T. and Timmerman-Vaughan, D. J. *Acta Chem. Scand. 51* (1997) 69.
13. For a review, see: Eberson, L. Hartshorn, M. P., Persson, O. and Radner, F. *J. Chem. Soc., Chem. Commun.* (1996) 2105.
14. Eberson, L., Persson, O., Radner, F. and Hartshorn, M. P. *Res. Chem. Intermediat. 22* (1996) 799.
15. Eberson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Perkin Trans. 2* (1995) 1735.
16. Tschinkel, J. G. *Ind. Eng. Chem. 48* (1956) 732.
17. Butts, C. P., Eberson, L., Hartshorn, M. P. and Robinson, W. T. *Acta Chem. Scand. 50* (1996) 122.

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