Photochemical Nitration by Tetranitromethane. X.[†] A Possible Addition/Elimination Pathway to Trinitromethylaromatic Compounds

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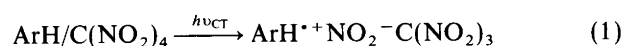[a] Division of MAX Chemistry, Chemical Center, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

Eberson, L., Hartshorn, M. P. and Svensson, O., 1993. Photochemical Nitration by Tetranitromethane. X. A Possible Addition/Elimination Pathway to Trinitro-methylaromatic Compounds. – Acta Chem. Scand. 47: 925–934.

The photolysis of tetranitromethane and 4-chloroanisole in dichloromethane at +20, −20 and −50 °C led to the formation of mainly 4-chloro-2-trinitro-methylanisole (40–50% yield) and a pair of adducts (~30% yield) in which nitrito/trinitromethyl addition had taken place across the 2,5-positions of 4-chloroanisole. Small amounts of a pair of labile adducts (2–3% yield), assigned the structure of the analogous hydroxy/trinitromethyl adducts were formed in the beginning of the runs. In acetonitrile, the major product from the same reaction was 4-chloro-2-nitroanisole at all three temperatures. Only at −50 °C were the nitrito/trinitromethyl adducts detectable in low yield (1–2%).
The pair of nitrito/trinitromethyl adducts spontaneously decomposed in acetonitrile to give 4-chloro-2-trinitromethylanisole with rate constants of $7 \times 10^{-4}\,\mathrm{min}^{-1}$ at 0 °C and $0.020\,\mathrm{min}^{-1}$ at 20 °C, implying that they should be stable in this solvent at −20 and −50 °C, if formed. The adducts also decomposed to 4-chloro-2-trinitromethylanisole under photochemical conditions, accounting for the formation of this compound in low yield also in acetonitrile. The nitration process predominantly observed in acetonitrile presumably occurs via coupling of 4-chloroanisole radical cation and NO_2, both formed in the initial photochemical step.
The nitrito/trinitromethyl adducts were thermally and photochemically stable in dichloromethane under the reaction periods employed for photolysis. The conversion into labile hydroxy/trinitromethyl adducts was assumed to occur via acid-catalysed hydrolysis, eventually leading to 4-chloro-2-trinitromethylanisole via acid-promoted elimination of water from the latter adducts. However, only a minor part of this compound can be accounted for in this way.
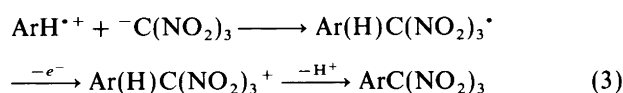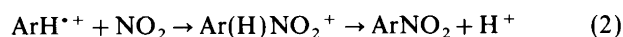
The photochemical excitation of the charge-transfer complex between tetranitromethane and an aromatic compound (ArH) leads to a triad consisting of $ArH^{\cdot +}$, nitrogen dioxide and trinitromethanide ion [eqn. (1)]. It was assumed originally[2] that the products detected, nitro and/or trinitromethyl *substitution* products, were formed in straightforward follow-up reactions from the three components of eqn. (1), *viz.* coupling between $ArH^{\cdot +}$ and NO_2, followed by proton loss and/or nucleophilic attachment of trinitromethanide ion to $ArH^{\cdot +}$, followed by one-electron oxidation and proton loss [eqns. (2) and (3)]. For short, we denote this mechanism as the

$$ArH/C(NO_2)_4 \xrightarrow{h\upsilon_{CT}} ArH^{\cdot +}NO_2{}^-C(NO_2)_3 \qquad (1)$$

$$ArH^{\cdot +} + NO_2 \rightarrow Ar(H)NO_2{}^+ \rightarrow ArNO_2 + H^+ \qquad (2)$$

$$ArH^{\cdot +} + {}^-C(NO_2)_3 \longrightarrow Ar(H)C(NO_2)_3{}^{\cdot}$$

$$\xrightarrow{-e^-} Ar(H)C(NO_2)_3{}^+ \xrightarrow{-H^+} ArC(NO_2)_3 \qquad (3)$$

'triad hypothesis'. However, recent work has shown[2g, 3-7] that nitro substitution was predominantly the result of photochemical nitro/trinitromethyl *addition* to the aromatic ring, followed by thermal elimination of nitroform [eqn. (4)]. Coupling according to eqn. (2)

$$ArH/C(NO_2)_4 \xrightarrow{h\upsilon_{CT}} NO_2Ar(H)C(NO_2)_3$$

$$\xrightarrow{\Delta} ArNO_2 + HC(NO_2)_3 \qquad (4)$$

could not be excluded completely, but in the best studied case, naphthalene, it amounted to only 5–15% of the total reaction[3a] in dichloromethane or acetonitrile. In that case
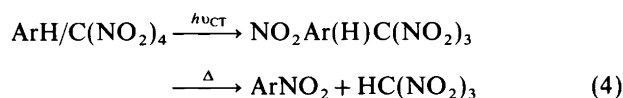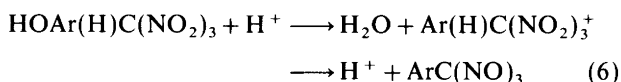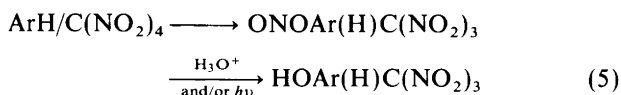

[†] Part IX, see Ref. 1.
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it also was ascertained that the α/β nitro isomer ratio approached that found when presynthesized radical cation salt was allowed to react with NO_2,[8] α/β > 30 vs. ~ 50, respectively. Essentially the same results were later obtained by Kochi et al.[2g]

Another difficulty with the triad hypothesis was encountered when stable radical cations of the triarylaminium type $(Ar_3N^{\cdot +}$, Ar = 4-bromo- or 4-chloro-phenyl) were allowed to react with a trinitromethanide salt, i.e., when the reaction of eqn. (3) was run separately.[9] Unexpectedly, no trinitromethylation product was obtained showing that even with a rather strong oxidant present (the triarylaminium ions have $E°$ around 1.3 V vs. NHE), further oxidation of the trinitromethylcyclohexadienyl radical formed in eqn. (3) did not take place. Instead, the latter radical decomposed in an intramolecular electron-transfer process to give trinitromethyl radical (unstable, decomposing to NO_2 and other low-molecular-weight products) and Ar_3N. The neutral amine then underwent nitration by NO_2, yielding solely nitro substitution products.

If this behaviour is typical for all kinds of $ArH^{\cdot +}$, how are trinitromethyl substitution products formed? Indisputably, these compounds have been isolated and characterized.[2d] Again an addition/elimination mechanism might be responsible, but now with hydroxy/trinitromethyl adducts as intermediates. Such an adduct (1) was isolated in 20% yield from the

HO Ph

H C(NO₂)₃

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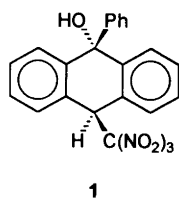
photolysis of tetranitromethane and 9-phenylanthracene and characterized by X-ray crystallography.[2a] It was assumed to be formed by nitrito/trinitromethyl addition followed by hydrolysis during work-up and/or photolytic conversion of –ONO to –OH in an intermolecular version of the Barton reaction [eqn. (5)]. We have detected

$$ArH/C(NO_2)_4 \longrightarrow ONOAr(H)C(NO_2)_3$$

$$\xrightarrow[\text{and/or } h\upsilon]{H_3O^+} HOAr(H)C(NO_2)_3 \qquad (5)$$

$$HOAr(H)C(NO_2)_3 + H^+ \longrightarrow H_2O + Ar(H)C(NO_2)_3^+$$

$$\longrightarrow H^+ + ArC(NO)_3 \qquad (6)$$

hydroxy(nitrito)/trinitromethyl adducts in a number of systems (benzene,[1] naphthalene,[3a, b] 1,4-dimethylnaphthalene[4]) and realized that acid-catalysed solvolysis of such intermediates might provide a pathway to trinitromethyl substitution products [eqn. (6)]. It is also possible that direct acid-promoted solvolysis of the adduct might lead to the trinitromethyl product(s). As pointed out

before,[4, 7] the photolysis solutions gradually become acidic during the run owing to the formation of nitroform, so that significant acid concentrations are always present in the later stages of the reaction. Since substituted anisoles exhibited a clear-cut substitution pattern (nitro substitution in acetonitrile, trinitromethyl substitution in dichloromethane) under conditions of long irradiation times but also gave undefined yields of labile adducts (decomposing to trinitromethyl substitution products upon standing in solution) under conditions of low temperature and short irradiation times,[2d] we chose 4-chloroanisole as a suitable substrate for further study of this problem. In what follows, we show that formation of adducts does take place, but that their chemical/photochemical properties are such that only a small proportion of the nitro or trinitromethyl substitution product can be accounted for by an addition/elimination mechanism.

Results

Photolysis of tetranitromethane/4-chloroanisole in dichloromethane. Table 1 shows the product composition from the photolysis (filtered light, λ > 435 nm) of solutions of tetranitromethane and 4-chloroanisole in dichloromethane at three temperatures, 20, −20, and −50 °C, employing the same mild work-up conditions as before.[3a] Data for analyses at short and long irradiation times are given, whereas the complete product developments with time, normalized with respect to conversion, are shown in Figs. 1–3. The most important feature of these experiments was the parallel growth of the yields of 4-chloro-2-trinitromethylanisole (2, 40–50% yield) and of a pair of relatively stable adducts, most probably cis/trans isomers

Table 1. Products formed from the photolysis of tetranitromethane and 4-chloroanisole in dichloromethane. Absolute yields are given.

Conversion (%)	Un-known 7	4-Cl-2-NO₂-phenol 8	4-Cl-2-NO₂-anisole 6	4-Cl-2-(NO₂)₃C-anisole 2	'Stable' adduct[a] pair 3a,b	Un-stable adduct pair 5a,b
At 20 °C[b]						
15	0.6	—	—	3.6	7.2	3.6
89	1.8	0.9	6.2	48.1	32.3	—
At −20 °C						
78	2.3	0.8	2.3	39.8	32.8	—
16	0.5	0.5	0.5	5.0	6.4	3.2
87	3.5	2.6	6.1	48.7	27.0	—
8	0.6	—	0.3	1.8	3.3	1.9
83	3.3	2.5	5.8	44.8	28.2	—
At −50 °C						
21	0.8	0.8	1.1	8.2	6.3	4.6
65	1.9	1.3	3.9	41	17.0	—

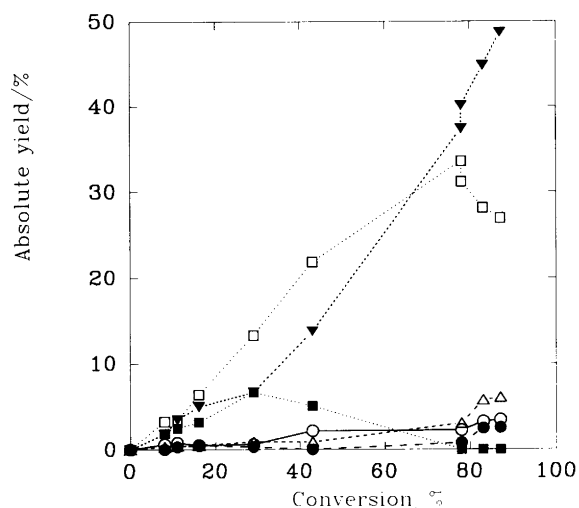[a] A third stable adduct, 4, was formed in ~5% yield.
[b] A previous study [Ref. 2(d)] gave 7% of 6 and 67% of 2.
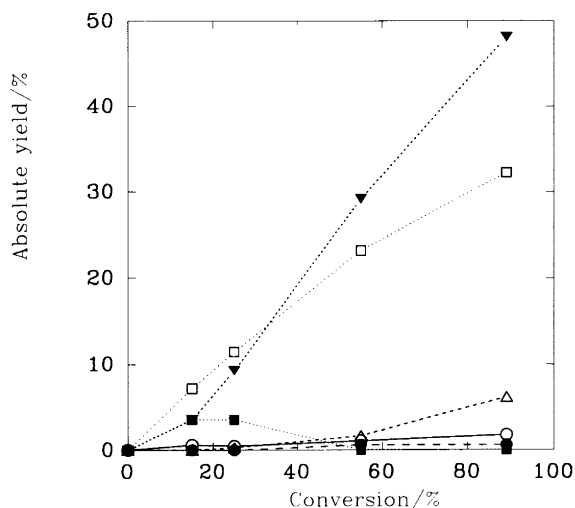
Fig. 1. Development of products as a function of conversion in the photolysis of 4-chloroanisole/TNM in dichloromethane at +20 °C. ○, unknown **7**; ●, **8**; △, **6**; ▲, **2**; □, adduct pair **3a,b**; ■, adduct pair **5a,b**. The points for each species are joined by straight lines in order to improve readability.
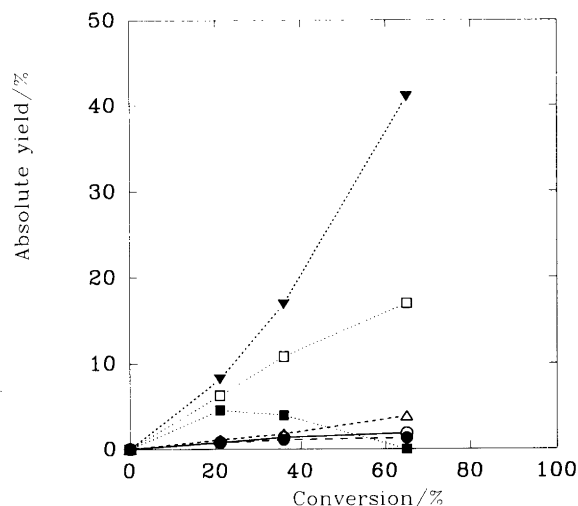

Fig. 3. Development of products as a function of conversion in the photolysis of 4-chloroanisole/TNM in dichloromethane at −50 °C. ○, unknown **7**; ●, **8**; △, **6**; ▲, **2**; □, adduct pair **3a,b**; ■, adduct pair **5a,b**. The points for each species are joined by straight lines in order to improve readability.

of a 2-trinitromethyl-5-nitrito adduct (**3a** and **3b**, 20–30 % yield; structural assignments, see below). A third 'stable' adduct, **4**, of unknown structure was present in ~5 % yield in the −20 °C run (spectral data, see the Experimental). A labile adduct pair, presumably the hydroxy compounds corresponding to **3a** and **3b** (**5a** and **5b**; structural assignments, see below) reached a maximum yield of ~5 % at 20–30 % conversion and disappeared gradually toward the end of the run. Minor aromatic products were 4-chloro-2-nitroanisole (**6**, 4–7 % yield), an unknown compound (**7**, 2–3 % yield, see the Experi-

mental) and 4-chloro-2-nitrophenol (**8**, ~1 % yield). The most remarkable feature of these three experiments is the approximate independence of both the nature and yield of products with temperature.
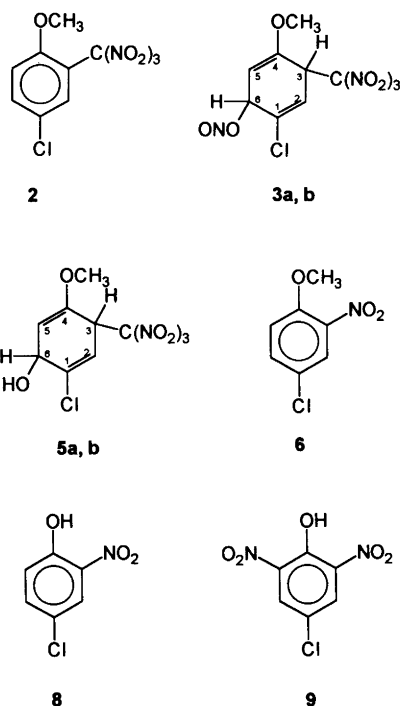

Fig. 2. Development of products as a function of conversion in the photolysis of 4-chloroanisole/TNM in dichloromethane at −20 °C (the results of the two experiments of Table 2 were combined). ○, unknown **7**; ●, **8**; △, **6**; ▲, **2**; □, adduct pair **3a,b**; ■, adduct pair **5a,b**. The points for each species are joined by straight lines in order to improve readability.

In order to check the thermal stability of adducts **3a,b**, an experiment was performed in which half the solution was worked up using the mild procedure (evaporation at 0 °C) and the other half using a more vigorous one (evaporation at 50 °C for 15 min). The latter procedure

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Table 2. Products formed from the photolysis of tetranitro-methane and 4-chloroanisole in acetonitrile. Absolute yields are given.

Conversion (%)	4-Cl-2-NO$_2$-phenol 8	4-Cl-2,6-(NO$_2$)$_2$-phenol 9	4-Cl-2-NO$_2$-anisole 6	4-Cl-2-(NO$_2$)$_3$C-anisole 2	'Stable' adducts 3a,b	Un-known adduct 4
At 20°C [a]						
10			9.1	0.9	—	—
97			95	5	—	—
At −20°C						
14	<1	6.3	4.2	3.1	—	—
71	<1	23.2	37.6	8.5	—	—
10	1	2	5	2	—	—
79	2	35	31	11	—	—
At −50°C						
11	2.8		2.9	2.9	—	2.4
38	11.0		16	8.7	—	2.3
16	5.0	0.3	6.0	5.0	Trace	Trace
41	10.3	1.6	23.0	7.8	1.6	0.6

[a] A previous study [Ref. 2(d)] gave 100% of **6**.

reduced the yield of **3a,b** from 24 to 12%, the ratio of **3a/3b** changing from 1 to 0.5. Since the only other change in product composition was the appearance of small amounts of **9**, it is likely that **3a,b** were thermally decomposed in the 50°C work-up procedure with formation of 4-chloroanisole and/or tetranitromethane/trinitromethyl nitrite, analogously to the behaviour of nitro/trinitro methyl adducts.[3, 4, 6]

Photolysis of tetranitromethane and 4-chloroanisole in acetonitrile. Table 2 shows the product composition from
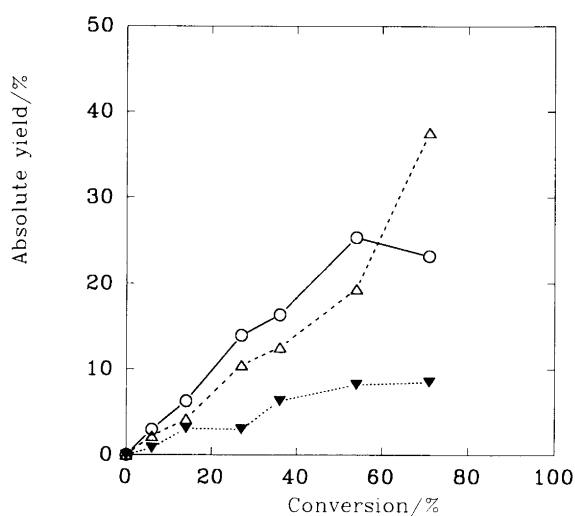
the photolysis of solutions of tetranitromethane and 4-chloroanisole in acetonitrile at three temperatures, +20, −20 and −50°C, employing the same mild work-up conditions as before. Data for analysis at short and long irradiation times are given in Table 2, whereas product development with time, normalized with respect to conversion, is given for the −20 and −50°C experiments in Figs. 4 and 5. We see (Table 2) that the only products detected at +20°C were the substitution products, this time with the nitro compound **6** as the major product (95%) and trinitromethyl compound **2** as the minor one (5%) at both low and high conversion. Only at very low temperature (−50°C) were small amounts of adducts seen (**3a** and **3b**, 1.6% yield, unknown **4**, 0.6% yield). At this temperature, 4-chloro-2-nitrophenol (**8**) was formed in rather high yield (∼10% at 41% conversion), distinctly different from the run at +20°C. A third aromatic product, 4-chloro-2,6-dinitrophenol (**9**) was detected in 1.6% yield.

The −20°C run showed no adducts but gave a fairly high yield of **9** (23%) and some **8**.

Assignments of the structures of adducts 3, 4 and 5. The isolation of even the relatively stable adducts **3a** and **3b** proved not to be possible in the presence of the readily crystallizable and less soluble trinitromethyl compound **2**. Low-temperature recrystallization inevitably provided **2**, and very slow conversion of **3a,b** into **2** seemed to take place during the crystallization procedure. Therefore, the structural assignments had to be based on the NMR spectral characteristics of the adducts, given and discussed below.

As shown in Figs. 1–3, the stable adducts **3a** and **3b**, formed in an approximate ratio of 1:1, reached an appreciable concentration during runs in dichloromethane at any temperature. NMR spectral analysis
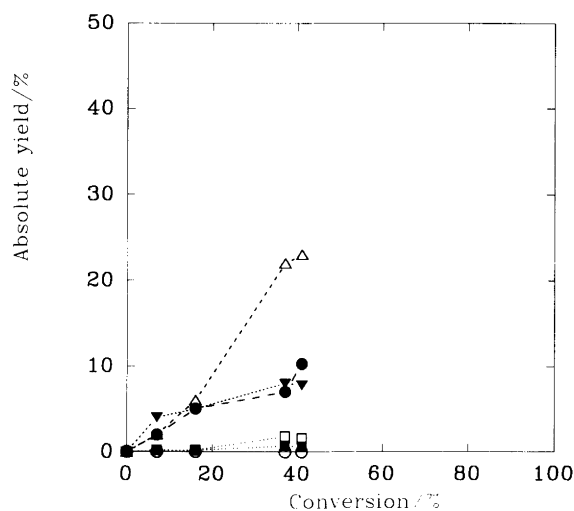

Fig. 4. Development of products as a function of conversion in the photolysis of 4-chloroanisole/TNM in acetonitrile at −20°C. ○, **9**; △, **6**; ▲, **2**. The points for each species are joined by straight lines in order to improve readability.

Fig. 5. Development of products as a function of conversion in the photolysis of 4-chloroanisole/TNM in acetonitrile at −50°C. ○, **9**; ●, **8**; △, **6**; ▲, **2**; □, adduct pair **3a,b**; ■, unknown adduct **4**. The points for each species are joined by straight lines in order to improve readability.
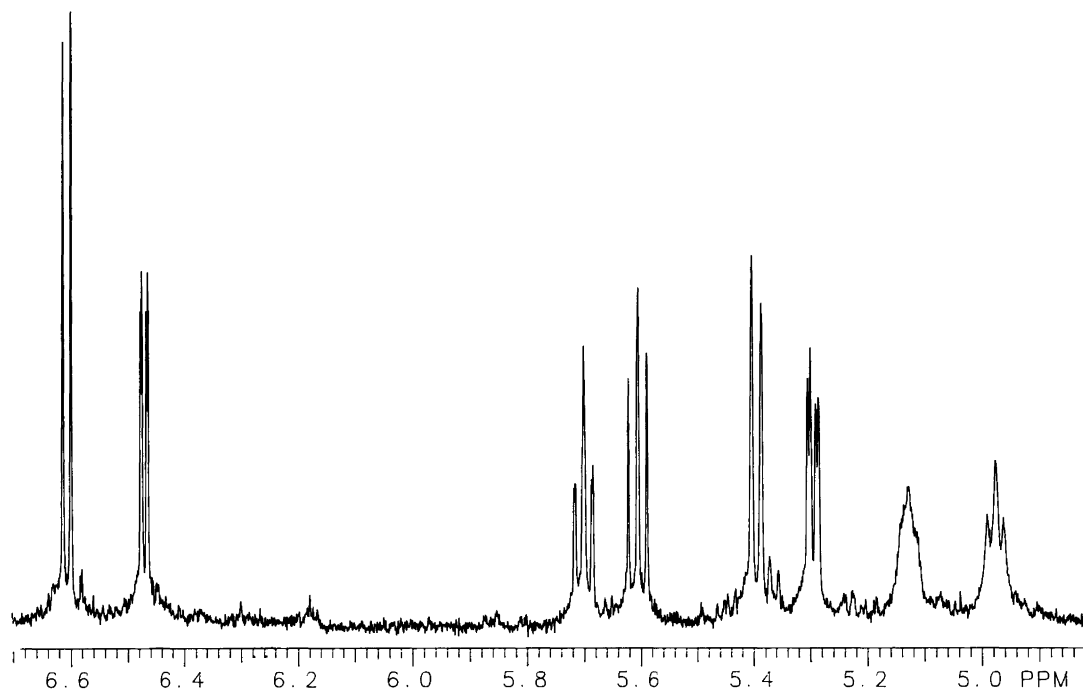
Fig. 6. ^{1}H NMR spectrum of the adduct region from a product mixture obtained by photolysis in dichloromethane at $-20\,°\text{C}$ for 24 h (78% conversion).

could be performed on the crude product mixtures in $CDCl_3$ without problems due to interference from other signals and/or decomposition. The adduct region from a run in dichloromethane at $-20\,°\text{C}$ is shown in Fig. 6; only small amounts of a third adduct (with the same NMR spectral characteristics as an adduct detected in acetonitrile runs at $-50\,°\text{C}$) were detected besides **3a** and **3b**. The signals of **3a** were assigned in the following way. The ^{13}C NMR spectrum had a high-field signal at 45.7 ppm which was assigned to C3, the carbon carrying the trinitromethyl group. The effect of a nitro group at a β carbon is relatively weak,[10] so that the alternative with the 45.7 ppm carbon being C6 (carrying the ONO group) is not tenable. The 121.7 and 85.2 ppm signals were assigned to C2 and C5, respectively, these values being typical of sp^2 carbons β to chlorine and methoxy groups,[11] respectively. The signal at 95.4 ppm thus was left for C6. A HETCOR experiment then connected the four ^{13}C shifts in the order given above to the ^{1}H signals at 4.97, 6.60, 5.6 and 5.4 ppm, with $J_{2,3} = 4.3$, $J_{3,5} = 4.5$ and $J_{5,6} = 5.1$ Hz, as shown by decoupling experiments. The second isomer **3b** in the same way was defined by the following NMR spectral assignments (^{13}C shifts within parentheses): H3 5.12 (45.3), H2 6.45 (122.0), H6 5.30 (94.8) and H5 5.7 (86.2), with $J_{2,3} = 3–4$, $J_{3,5} = 4.0$, $J_{3,6} = 1.4$, $J_{2,5} = 0.7$ and $J_{5,6} = 4.2$ Hz.

Adducts **5a** and **5b** combined instability with low concentration and could thus only be tentatively identified. Their ^{1}H NMR spectral data featured a shift pattern which was similar to those of **3a** and **3b** but displaced 0.4–0.6 ppm toward higher field, in line with the large

upfield shift change of the α hydrogens on going from $-CH_2-O-NO$ to $-CH_2OH$, ~ 1.2 ppm.[11] Again a *cis/trans* relationship was indicated, with a ratio between the isomers of ~ 1.3. The ^{1}H shifts of **5a** (**5b** within parentheses) were thus assigned as follows: H3 4.78 (4.88), H2 6.18 (6.18), H6 4.64 (4.73) and H5 5.29 (5.25) ppm, with $J_{2,3} = 5$ (?), $J_{3,6} = 3–4$ (3–4), $J_{5,6} = 3–4.6$ (3.4), $J_{2,6} = -(1.2)$ and $J_{3,5} = -(0.7)$ Hz.

Control experiments. Various control experiments were performed to track the origin of the aromatic by-products **7–9**. Thus photolysis of 4-chloro-2-nitroanisole (**6**)/TNM in acetonitrile at $-20\,°\text{C}$ led to a slow build-up of **9** to concentrations comparable to those obtained from 4-chloroanisole/TNM runs. It therefore is reasonable to assume that this is the major pathway to **9** in the photochemical experiments. At very long irradiation times (longer than the ones used in the photolysis experiments), the corresponding anisole (4-chloro-2,6-dinitroanisole) was also formed in small amounts. The latter compound was also detected in the thermal nitration of **6** by NO_2 after equally long reaction periods under similar conditions.

Compound **2** also underwent very slow reaction upon photolysis with TNM in dichloromethane at $-20\,°\text{C}$, forming **9** in ~ 2% yield after an irradiation time in excess of that normally used. No thermal reaction between **2** and NO_2 in dichloromethane was apparent, even at ambient temperature.

More importantly, it was established that adducts **3a,b** were *not* influenced by photolysis in dichloromethane

at $-20\,°C$ using reaction periods compatible with the TNM experiments (up to 40 h; some decomposition was observed after 100 h). On the other hand, the same experiment in acetonitrile reduced the proportion of **3a,b** in 24 h from 46 to 27% (**3a** from 27 to 24% and **3b** from 19 to 3.3%); after 76 h, **3a** was left to an extent of 3% whereas **3b** had disappeared completely. Compounds formed were **2** $(18 \rightarrow 33\%)$, **6** $(22 \rightarrow 24\%)$ and **9** $(0.9 \rightarrow 2.4\%)$, approximately corresponding to the **3a,b** consumed.

Since NO_2 has been shown to build up during photolysis in other systems,[3c] the dark reaction between NO_2 and 4-chloroanisole in dichloromethane was monitored at $-20\,°C$, showing that **6** was formed in about 6% yield over 24 h.

Finally, since nitroanisoles are known to undergo photosubstitution of the methoxy group by nucleophiles, e.g., cyanide ion,[12] it was also necessary to check the behaviour of **6** in this aspect. However, the photolysis of **6** in the presence of tetrabutylammonium trinitromethanide in acetonitrile or dichloromethane did not reveal any reactivity of this kind.

Thermal stability of adducts. Low-temperature crystallization of the crude product from photolytic runs in dichloromethane gave mixtures containing, besides **2**, the stable adducts **3a,b** which were used for kinetic studies of adduct stability. Fig. 7 shows the slow decomposition of the adducts **3a,b** in acetonitrile at $0\,°C$ with formation of **2**, as monitored by ^1H NMR spectroscopy. The first-order rate constant for formation of **2** was $7(2) \times 10^{-4}\,min^{-1}$ and the adducts decayed with rate constants $1.3(5) \times 10^{-3}$ and $1.2(8) \times 10^{-4}\,min^{-1}$. Thus knowing the phenomenol-
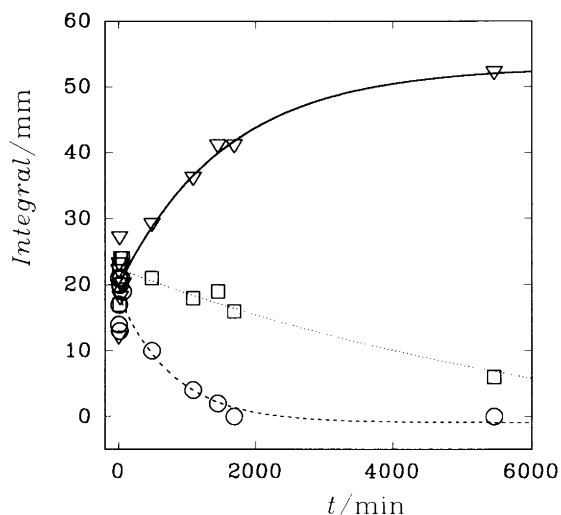
ogy of the reaction, we could use UV spectroscopy to monitor the kinetics in the range 250–360 nm. Compound **2** has a UV spectral maximum at 306 nm and first-order rate constants were determined in an interval around this maximum. At $20\,°C$ in acetonitrile, the average rate constant was $0.020\,min^{-1}$. Addition of methanesulfonic acid approximately doubled the rate constant, regardless of the $[MeSO_3H]$ employed $(0.7–100\,mmol\,dm^{-3})$. Addition of a hindered base, 2,6-di-*tert*-butylpyridine $(0.84\,mmol\,dm^{-3})$ induced a more rapid increase of the absorbance in the region around 306 nm, associated with a rate constant of $2.7(2)\,min^{-1}$.

Spin trapping experiments with the adduct. Pure, recrystallized nitro/trinitromethyl adducts from naphthalene,[3a] fluoranthene[6] and, in particular, 1,4-dimethylnaphthalene[4] have earlier been shown to give the trinitromethyl spin adduct of *N-tert*-butyl-α-phenylnitrone (PBN) upon standing with an excess of PBN in dichloromethane solution. The mixture of products from the dichloromethane runs, freed from tetranitromethane by freeze–drying, upon treatment with PBN (0.15 M) in dichloromethane displayed the same type of homolytic activity. Fig. 8 shows that a strong signal of trinitromethyl-PBN accumulated within 2 h and then slowly decayed over the next few days. If this biphasic process is treated as involving two first-order reactions, the rate constants come out as $k_{up} = 0.033(2)$ and $k_{down} = 0.00160(5)\,min^{-1}$. Under the same conditions, PBN and TNM in a concentration corresponding to the unrealistic assumption that the adduct mixture might contain 10% of remaining TNM after the freeze–drying procedure, initiated as very slow development of the trinitromethyl
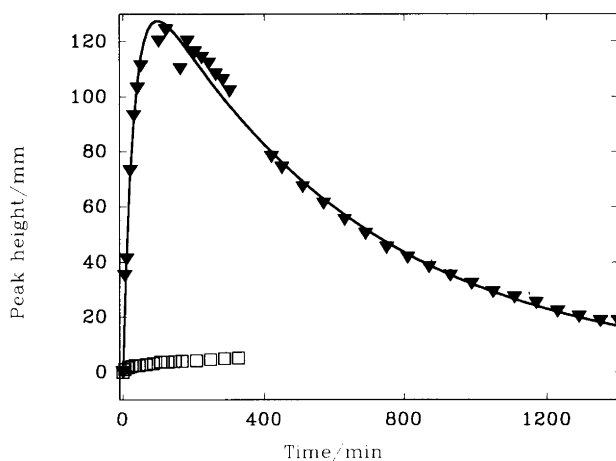

Fig. 7. Plots of the disappearance of adducts **3a** (○) and **3b** (□) and appearance of **2** (△) in acetonitrile at $0\,°C$. The curves represent the best fits to first-order rate equations with $k = 1.3(5) \times 10^{-3}$, $1.2(8) \times 10^{-4}$ and $7(2) \times 10^{-4}\,min^{-1}$, respectively.

Fig. 8. Plot of the intensity of the left-most line of the EPR spectrum of the trinitromethyl spin adduct, appearing in a solution of PBN $(0.17\,mol\,dm^{-3})$ and product mixture (see the text) containing adducts **3a,b** $(\sim 70\,mmol\,dm^{-3})$ (▲), and in a solution of PBN $(0.17\,mol\,dm^{-3})$ and TNM $(7\,mmol\,dm^{-3})$. Both experiments were conducted in dichloromethane. The curve corresponds to two consecutive first-order reactions with $k_{up} = 0.033(2)$ and $k_{down} = 0.00160(5)\,min^{-1}$.

spin adduct concentration (<5 % of that obtained from the adduct mixture during the build-up of the maximum; Fig. 8, □).

Discussion

Structure of adducts **3a,b**. The assignment of the nitrito/ trinitromethyl addition mode for the photochemical formation of **3a,b** from 4-chloroanisole and TNM rests mainly on NMR spectral analysis of the adducts in admixture with other products formed. Theoretically, this is expected from a mechanism in which the initial attack upon the radical cation of 4-chloroanisole[2d] is by trinitromethanide [eqn. (3)], followed by trapping of the intermediate trinitromethylcyclohexadienyl radical by NO_2. It is known[13] that attack via oxygen is favoured in the presence of an electron-withdrawing substituent in the substrate.

Circumstantial evidence rests on their behaviour upon standing in acetonitrile which leads to the slow elimination of *nitrous acid* and formation of **2** only. It is known[3,5] that nitro/trinitromethyl adducts undergo facile elimination of *nitroform* in acetonitrile and thus give nitro substitution products. If **3a,b** had the nitro/trinitromethyl connectivity instead, the anomalous nitro substitution product, 4-chloro-3-nitroanisole would have been formed by elimination of nitroform. We specifically looked for this isomer in the product mixtures but could detect none of it.

In principle, other primary adducts are possible after the initial step. Keeping to the nitrito connectivity, a 1,2 (**10**) and an *ipso* adduct (**11**) are other adducts from the same cyclohexadienyl radical leading to **3a,b**. We cannot exclude that such adducts were formed, either in amounts too small to be detectable or analysable or as transients too unstable to accumulate during the run. The unknown adduct **4** is not a likely candidate for **10** or **11**, since its ¹H NMR spectrum does not show any coupling constant of the size expected for *vicinal* olefinic protons.

10   **11**
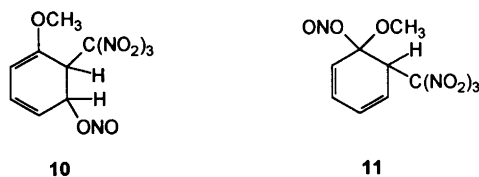
Structures of **5a,b**. The formulation of the two unstable adducts, **5a,b** which were formed in the dichloromethane experiments, as the hydroxy compounds corresponding to **3a,b** is based on the similarity of their NMR spectra, except for a general upfield shift of the ring proton signals, as expected for a replacement of ONO by OH.[11] The chemistry behind the formation of **5a,b** is not yet possible to define with certainty; the reaction cannot be of a photochemical nature since **3a,b** were stable under photolytic conditions in dichloromethane at −20 °C. It remains, then, that **3a,b** may have been hydrolysed by

adventitious water in the beginning of the run, causing **5a,b** to accumulate until the acidity of the medium had increased to the extent that acid-promoted elimination of water from **5a,b** began to predominate.

Photolysis of tetranitromethane/4-chloroanisole in dichloro methane. Besides the major product, **2**, and the aromatic derivatives **7** and **8**, the pair of 'stable' adducts (**3a,b**) was formed to an extent of 20–30 % in the whole temperature interval studied. The adducts were found to be stable under photochemical conditions at −20 °C, showing that **2** cannot be a product originating from **3a,b** at this temperature or the other temperatures employed.

The unstable adduct pair (**5a,b**) was detected in the beginning of the photolytic runs in dichloromethane, independent of the temperature. As suggested before,[2a] hydroxy derivatives can be formed by hydrolysis and/or photolysis of nitrito compounds, so that, in principle, there would seem to be no difficulty in explaining the presence of hydroxy compounds. However, it was shown above that **3a,b** do not undergo the Barton reaction under the conditions employed, and therefore **5a,b** must be formed by hydrolysis of **3a,b**. Their appearance at the beginning of the run and disappearance in the later stages, largely independent of the temperature in the interval +20 to −50 °C might be explained by their high sensitivity to acid-catalysed solvolysis and the limited access to water. As the acid concentration builds up with time, the rate of solvolysis of **5a,b** will increase and eventually these adducts will be destroyed. Results on nitrite hydrolysis[14] show that uncatalysed hydrolysis is very slow, but that the acid-catalysed reaction is reasonably fast. Thus, in principle, it would be possible to explain the formation of hydroxy adducts **5a,b** by acid-catalysed hydrolysis of **3a,b** with adventitious water.

Concluding, it is probable that only a small part of the amount of **2** formed from the photolysis of 4-chloroanisole/TNM in dichloromethane originates from adducts **3a,b** by an elimination mechanism. One cannot exclude the possibility that the remaining part stems from elimination mechanisms operating on **10** and/or **11**, but no positive evidence in this direction was obtained. In particular **11** would be an interesting candidate since its major elimination pathway must be loss of nitrous acid to give **2**. As an *ipso* adduct, **11** would be expected to be less stable than **3a,b** and **10**.

Photolysis of tetranitromethane/4-chloroanisole in acetonitrile. For substituted anisoles, it has been claimed earlier[2d] that a clear-cut distinction could be made between photolyses run in dichloromethane and acetonitrile, trinitromethyl substitution being favoured in a non-polar solvent like dichloromethane and nitro substitution in a polar solvent, e.g., acetonitrile. No such distinction was, however, found for the case of naphthalene.[4]

A comparison between our room-temperature results at high conversion and earlier ones[2d] shows the following

pattern of the most important products from 4-chloro-anisole:

	Dichloromethane		Acetonitrile	
	This paper	Ref. 2(d)	This paper	Ref. 2(d)
Yield of **2** (%)	48	67	5	0
Yield of **6** (%)	6	7	95	100
Yield of **3a,b** (%)	32	—	—	—

The same overall pattern prevails in our study: dichloromethane favours trinitromethyl substitution and acetonitrile nitro substitution, although the difference is not as decisive as in the previous study.[2d] Some trinitromethyl compound is formed in acetonitrile, and its yield increases with lowering of the temperature.
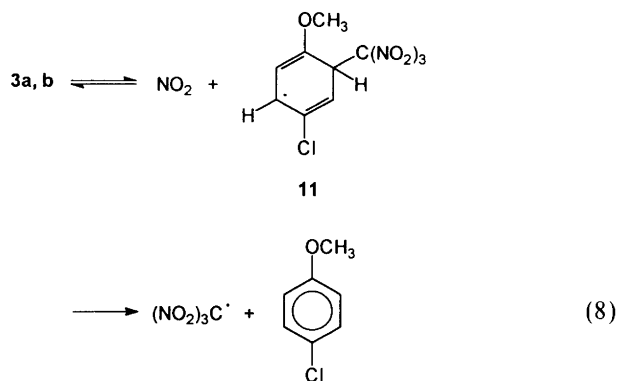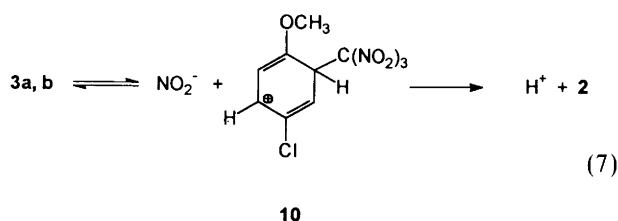
At $-50\,°C$ in acetonitrile, adduct formation was detected. Both **3a,b** and unknown **4** were seen in small amounts at the end of the reactions.

Thermal and photochemical reactions of adducts in acetonitrile. Fig. 7 demonstrates that adducts **3a,b** slowly decompose in acetonitrile with formation of **2**. The rate constant for formation of **2** was $7(2) \times 10^{-4}\,min^{-1}$ at $0\,°C$ and $0.020\,min^{-1}$ at $20\,°C$, corresponding to half-lives of 16 h and 0.6 h, respectively. Thus any adduct **3a,b** formed during the low-temperature runs in acetonitrile should be thermally stable. Only by photochemically induced changes would transformation of **3a,b** into other products, such as **5a,b** and eventually **2**, be possible.

The photochemical control experiment in acetonitrile at $-20\,°C$ indeed showed that this is a feasible process. In a reaction period (24 h) corresponding to those used for substrate/TNM photolyses, **3a,b** are thermally stable but are photolytically converted into **2** to an extent of about 50% (and also give some **6** and **9**). Thus, if **3a,b** are formed in small proportions at all temperatures (note that we have only detected **3a,b** at $-50\,°C$), their likely fate would be to be photochemically transformed into **2**. Since it seems as if the proportion of **3a,b** increases with lowering of the temperature, this process would neatly explain why the yield of **2** increases at lower temperature.

The nature of the reaction $\mathbf{3a,b} \rightarrow \mathbf{2}$ might be of the solvolysis type [eqn. (7)], as proposed earlier for the 1,4-nitro/trinitromethyl adducts of 1,4-dimethylnaphthalene.[4] The stability difference between solutions of **3a,b** in dichloromethane and acetonitrile is then explicable. An alternative would be homolysis of the C–ONO bond according to eqn. (8), followed by one-electron oxidation of radical **13** (by TNM and/or NO_2; see below) to give cation **12**. A second reactivity mode of **13**, proposed earlier in the 1,4-dimethylnaphthalene system,[4] would then be loss of trinitromethyl radical, detected as its spin adduct with PBN (Fig. 8).

Addition of a hindered base (2,6-di-*tert*-butylpyridine) to an acetonitrile solution of the mixture of products from a photolytic run in dichloromethane induced a much

$$\mathbf{3a,b} \rightleftharpoons NO_2^- + \mathbf{10} \longrightarrow H^+ + \mathbf{2} \qquad (7)$$

$$\mathbf{3a,b} \rightleftharpoons NO_2 + \mathbf{11}$$

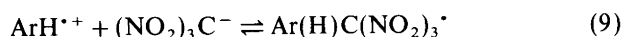$$\longrightarrow (NO_2)_3C^\bullet + \qquad (8)$$

faster process, proceeding with formation of **2** (development of a UV spectral maximum at 306 nm). The rate constant approximately first-order in [base], giving $k_2 = 7(2) \times 10^1\,dm^3\,mol^{-1}\,s^{-1}$. We ascribe this rate process to the elimination of HNO_2 from **3a,b**. Pure nitro analogues of **3a,b** have earlier been shown to undergo a similar elimination of nitroform [1,4-adduct from naphthalene, $k_2 = 0.18(5)\,dm^3\,mol^{-1}\,s^{-1}$ in dichloromethane;[3a] 1,2-adduct from fluoranthene, $k_2 = 0.048\,dm^3\,mol^{-1}\,s^{-1}$ in dichloromethane and $0.112\,dm^3\,mol^{-1}\,s^{-1}$ in acetonitrile;[6] adduct mixture from dibenzofuran, $k_2 \sim 2.5\,dm^3\,mol^{-1}\,s^{-1}$ in dichloromethane,[7] all values being obtained with 2,6-di-*tert*-butylpyridine as the base and at $20\,°C$].

Mechanistic problems. Trinitromethylation. The trinitromethylation reaction observed during the photolysis of tetranitromethane/ArH is favoured in a non-polar solvent, and was seen as proceeding as predominant ion-pair collapse within the triad of eqn. (1), leading to a trinitromethylcyclohexadienyl radical (**13**) via the left-hand reaction of eqn. (3). It must then be assumed that some 1e-oxidant present must be capable of further oxidizing **13** to the corresponding carbocation in order to complete the 2-electron oxidative substitution process. In principle, two species present or formed in the solution might fulfil the role of ET oxidant: tetranitromethane with a tentatively estimated redox potential of $\sim 0.2\,V$ vs. $Ag/AgCl^{3c}$ and NO_2 with a redox potential of $0.7\,V$ vs. $Ag/AgCl$.[15]
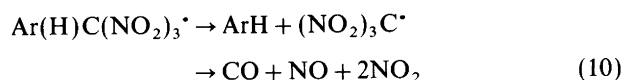
However, we have shown recently[9] that the reaction between representative stable aromatic radical cations with redox potentials around $1.1\,V$ vs. $Ag/AgCl$ and tetrabutylammonium trinitromethanide in dichloromethane or acetonitrile did not give trinitromethylation products, in spite of the presence of an ET oxidant, i.e.,

the radical cation, stronger than both tetranitromethane or NO_2. Instead, nitro-substitution products were formed, most likely by nitration of the parent compound by NO_2 (this reaction was separately shown to be fast under the prevailing conditions). The latter was assumed to originate from the decomposition of the radical intermediate **13** in an intramolecular ET process, as depicted in eqns. (9) and (10). The formulation of reaction (9)

$$ArH^{\cdot +} + (NO_2)_3C^- \rightleftharpoons Ar(H)C(NO_2)_3^{\cdot} \qquad (9)$$

13

$$Ar(H)C(NO_2)_3^{\cdot} \rightarrow ArH + (NO_2)_3C^{\cdot}$$
$$\rightarrow CO + NO + 2NO_2 \qquad (10)$$

(Ar = 4-chloro-2-anisyl) as an equilibrium is necessitated by the saturation-type kinetics observed,[3c] the limiting rate constant being $\sim 13\ min^{-1}$. It is also a commonly found feature in reactions between radical cations and nucleophiles.[16]

If the reaction scheme of eqns. (9) and (10) is generally valid, it follows that trinitromethyl substitution must follow a different mechanism from that defined in eqn. (3), If not, the reasons for the need of different mechanisms for different substrates must be found.

However, the data presented in this paper do not positively support one possible alternative mechanism, involving capture of **13** by NO_2 as a nitrito/trinitromethyl adduct, followed by elimination of HNO_2 from the latter. The various pieces of the mechanism are there, but they do not presently fit together to explain the chemistry observed under all conditions. Of course the very fact that some adducts are detectable suggests that other, less stable ones (such as **11**) might be formed in low concentration and be the [so far] undetected precursors of the trinitromethylation products.

Mechanistic problems. Nitration. This reaction mode has already been shown to occur via at least two pathways in the photolysis of naphthalene/tetranitromethane in dichloromethane or acetonitrile, namely direct coupling [eqn. (2)] to a fairly low extent (5–15%) and nitro/trinitromethyl addition (85–95%), followed by thermal elimination of nitroform. These pathways accordingly give rise to quite different isomer distributions: direct coupling[8] $\alpha/\beta \sim 50$, addition/elimination[2g, 3] $\alpha/\beta \sim 5$. Thus coupling between $ArH^{\cdot +}$ and NO_2 should be feasible in the 4-chloroanisole system too, and it then remains only to explain why nitration is favoured in acetonitrile and trinitromethylation in dichloromethane. We propose that the reactivity of trinitromethanide is generally higher in dichloromethane than in acetonitrile, owing to less pronounced solvation in the former solvent, favouring ion-pair collapse to give **13** in dichloromethane and inducing trapping of the latter by NO_2. As experimental evidence we can point to the reaction between trinitromethanide ion and tris(4-bromophenyl)aminium

ion which is $> 10^3$ times faster in dichloromethane than in acetonitrile,[3c] although it must be noted that this rate ratio is estimated for conditions of low $[(NO_2)_3C^-]$ where saturation kinetics has not been reached in dichloromethane. At higher $[(NO_2)_3C^-]$, the ratio will be lower. Thus the coupling between $ArH^{\cdot +}$ and NO_2 in acetonitrile occurs mainly by default, trinitromethanide reacting much more sluggishly in this medium. It should be noted that the reaction between $(naphthalene)_2^{\cdot +}$ and NO_2 or trinitromethanide ion in acetonitrile[2g] proceeded with rate constants of $8(1) \times 10^5$ and $\sim 6 \times 10^6\ A^{-1}\ s^{-1}$ (A = absorbance units; the disappearance of the radical cation was monitored in both cases), thus indicating higher reactivity of trinitromethanide ion than NO_2 even in acetonitrile.*

Experimental

Materials. 4-Chloroanisole (EGA-Chemie, 99 + %), 4-chloro-2-nitrophenol (**8**, Aldrich, 98%), and tetranitromethane (Aldrich) were used as received. Acetonitrile (Merck, UVASOL) was used as supplied and dichloromethane (Merck, *zur Rückstandsanalyse*) was dried over 4 Å molecular sieves. Solutions of NO_2 in dichloromethane or acetonitrile were made up as previously described.[17] Literature procedures were used for the synthesis of 4-chloro-2-nitroanisole (**6**) and 4-chloro-2,6-dinitrophenol (**9**).[18]

Instrumentation. The GLC instrument[19] was equipped with a fused silica column (25 m, OV-1701). NMR spectra were recorded on a Varian XL 300 spectrometer and UV–VIS-monitored kinetics were recorded on a Hewlett-Packard 8452A diode array spectrophotometer, equipped with a 89500 ChemStation. EPR spectra were recorded on a Bruker ER-200D SRC instrument, spectra collection being performed in the automatic mode.

Methods. The procedure for carrying out photolysis experiments has been described before.[3] The lamps were of Osram 'Ultravitalux' type (300 W). For irradiation at low temperatures a doubly jacketed (vacuum/cooling liquid) vessel was employed, cooling being effected by means of a Colora cooling thermostat ($-20\,^{\circ}C$) or by ethanol–dry ice ($-50\,^{\circ}C$).

WARNING. While we did not experience any incidents when working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits[20] and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.

* This assessment is made on the basis of rate data given in Tables 4 and 6 of Ref. 2(g). It must however be pointed out that it does not agree with statements appearing in the text which indicate that the trinitromethanide ion data of Table 6 [Ref. 2(g)] should actually be given in $dm^3\,mol^{-1}\,s^{-1}$. Since the nitrogen dioxide second-order rate constant given in Table 5 of Ref. 2(g) appears to be wrong by a factor of 10^3, our assessment may indeed be correct.

General procedure for the photolysis of 4-chloroanisole/ tetranitromethane. A solution of 4-chloroanisole (1.0 g, corresponding to a 0.44 mol dm^{-3} solution) and tetranitromethane (0.88 mol dm^{-3}) in dichloromethane or acetonitrile (16 ml) was irradiated at -20 or $+20\,^{\circ}C$ with filtered light (cut-off <435 nm). For runs at $-50\,^{\circ}C$ half of the above amounts was used. Aliquots were withdrawn at appropriate time intervals, the volatile material removed under reduced pressure at $0\,^{\circ}C$, and the product composition determined by NMR spectral analysis (Tables 1 and 2 and Figs. 1-5).

Reaction in -dichloromethane or acetonitrile and the identification of products. The products detected were the aromatic derivatives 2-nitrochloroanisole (**6**), unknown **7** (characterized by a doublet at 8.5 ppm in the NMR spectrum of the mixture), 4-chloro-2-nitrophenol[2d] (**8**), 2-trinitromethyl-4-chloroanisole[2d] (**2**) and 4-chloro-2,6-dinitrophenol (**9**) and adducts **3a,b**, **5a,b** (NMR spectra and assignments, see the text) and small amounts of unknown **4**. The ^1H NMR (CDCl$_3$) shifts of **4** were 6.59 (H$_a$, dd, $J_{a,b} = 5.8$, $J_{a,d} = 0.7$ Hz), 5.45 (H$_b$, dd, $J_{b,a} = 5.8$, $J_{b,d} = 4$ Hz), 5.35 (H$_c$, d, $J_{c,d} = 4.6$ Hz) and 5.07 (H$_d$, ddd, $J_{d,a} = 0.7$, $J_{d,b} = 4$, $J_{d,c} = 4.6$ Hz). The low concentration precluded the elucidation of its ^{13}C NMR spectral characteristics.

References

1. Eberson, L. and Hartshorn, M. P. *J. Chem. Soc., Chem. Commun.* (1992) 1563.
2. (a) Masnovi, J. M. and Kochi, J. K. *J. Org. Chem. 50* (1985) 5245; (b) Masnovi, J. M., Kochi, J. K., Hilinski, E. F. and Rentzepis, P. M. *J. Am. Chem. Soc. 108* (1986) 1126; (c) Sankararaman, S., Haney, W. A. and Kochi, J. K. *J. Am. Chem. Soc. 109* (1987) 5325; (d) Sankararaman, S., Haney, W. A. and Kochi, J. K. *J. Am. Chem. Soc. 109* (1987) 7824; (e) Masnovi, J. M., Sankararaman, S. and Kochi, J. K. *J. Am. Chem. Soc. 111* (1989) 2263; (f) Sankararaman, S. and Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* (1991) 1; (g) Kim, E. K., Bockman, T. M. and Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* (1992) 1879.
3. (a) Eberson, L., Hartshorn, M. P. and Radner, F. *J. Chem. Soc., Perkin Trans. 2* (1992) 1793; (b) Eberson, L., Hartshorn, M., Radner, F. and Robinson, W. T. *J. Chem. Soc., Chem.*

Commun. (1992) 566; (c) Eberson, L. and Radner, F. *J. Am. Chem. Soc. 113* (1991) 5825.
4. Eberson, L., Hartshorn, M. P. and Radner, F. *J. Chem. Soc., Perkin Trans. 2* (1992) 1799.
5. Eberson, L., Hartshorn, M. P., Radner, F., Merchán, M. and Roos, B. O. *Acta Chem. Scand. 47* (1993) 176.
6. Eberson, L., Hartshorn, M. P., Radner, F. and Robinson, W. T. *Acta Chem. Scand. 47* (1993) 410.
7. Eberson, L., Hartshorn, M. P., Radner, F. and Svensson, J. O. *Extended Abstracts, Sixth International Symposium on Organic Free Radicals*, Noordwijkerhout, The Netherlands, August 23-28, 1992.
8. Eberson, L. and Radner, F. *Acta Chem. Scand., Ser. B 34* (1980) 739; *40* (1986) 71; *Acc. Chem. Res. 20* (1987) 53. The α/β ratio was ~50 in nitromethane: Ross, D. S., Schmitt, R. J. and Malhotra, R. Quoted from *Chem. Abstr. 100* (1984) 155980b.
9. Eberson, L., Radner, F. and Svensson, J. O. *J. Chem. Soc., Chem. Commun.* (1992) 1140.
10. Kalinowski, H.-O., Berge, S. and Braun, S. *Carbon-13 NMR Spectroscopy*, Wiley, Chichester 1988.
11. See, e.g., Piette, L. G., Ray, J. D. and Ogg, R. A., Jr. *J. Chem. Phys. 26* (1957) 1341; Phillips, W. D. and Looney, C. E. *J. Mol. Spectrosc. 1* (1957) 35; Brown, H. W. and Hollis, D. P. *J. Mol. Spectrosc. 13* (1964) 305.
12. For reviews, see Havinga, E. and Cornelisse, J. *Pure Appl. Chem. 47* (1976) 1; Cornelisse, J. and Havinga, E. *Chem. Rev. 75* (1975) 353; Cornelisse, J., de Gunst, G. P. and Havinga, E. *Adv. Phys. Org. Chem. 11* (1975) 225.
13. Amin, M. R., Dekker, L., Hibbert, D. B., Ridd, J. H. and Sandall, J. P. B. *J. Chem. Soc., Chem. Commun.* (1986) 658; Hartshorn, M. P., Martyn, R. J., Robinson, W. T., Sutton, K. H., Vaughan, J. and White, J. M. *Aust. J. Chem. 38* (1985) 1613.
14. See, e.g., Allen, A. D. *J. Chem. Soc.* (1954) 1968; Allen, A. D. and Schonbaum, G. R. *Can. J. Chem. 39* (1964) 940; Oae, S., Asai, N. and Fujimori, K. *J. Chem. Soc., Perkin Trans. 2* (1978) 571; Doyle, M. P., Terpstra, J. W., Pickering, R. A. and LePoire, D. M. *J. Org. Chem. 48* (1983) 3379; Iglesias, E., Garcia-Rio, L., Leis, R., Pena, M. E. and Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* (1992) 1673.
15. Eberson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, Heidelberg, 1978.
16. Hammerich, O. and Parker, V. D. *Adv. Phys. Org. Chem. 20* (1984) 55.
17. Eberson, L. and Radner, F. *Acta Chem. Scand., Ser. B 39* (1985) 343, 357.
18. Bunton, C. A., Hughes, E. D., Ingold, C. K., Jacobs, D. I. H., Jones, M. H., Minkoff, G. J. and Reed, R. I. *J. Chem. Soc.* (1950) 2628.
19. Eberson, L. and Radner, F. *Acta Chem. Scand. 46* (1992) 312.
20. Tschinkel, J. G. *Ind. Eng. Chem. 48* (1965) 732.