Photochemical Nitration by Tetranitromethane. Part VI.[1] Predominant Nitro/trinitromethyl Addition to Naphthalene in Dichloromethane and Acetonitrile†

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The photochemical reaction between naphthalene and tetranitromethane in dichloromethane or acetonitrile gave predominantly (85–95%) products of nitro/trinitromethyl addition to the aromatic system, namely *cis*- and *trans*-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene and *trans*-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene. A small amount of *trans*-2-hydroxy-1-trinitromethyl adduct was also formed, presumably originating from an initial nitrito/trinitromethyl adduct.

The minor reaction pathway directly gave product(s) of nitro substitution, the ratio of 1- to 2-nitronaphthalene being high ($\geqslant 25$) in dichloromethane and in the beginning of the acetonitrile runs (up to ≈40% conversion). The temperature dependence of this process suggests that coupling between (naphthalene)$^{+\bullet}$ and nitrogen dioxide is the major pathway leading directly to nitro products. 2-Nitronaphthalene, formed after long reaction periods in acetonitrile runs, was presumably formed *via* elimination of nitroform from the 1,2-adduct.

cis-1-Nitro-4-trinitromethyl-1,4-dihydronaphthalene was isolated in pure form and shown to undergo facile base-catalysed elimination of nitroform in dichloromethane and acetonitrile to give 1-nitronaphthalene. It also underwent a slow spontaneous elimination in acetonitrile. It was stable under acidic conditions. GLC of the pure adduct gave exclusively 1-nitronaphthalene at a low injector-port temperature, whereas at higher temperatures a mixture of products was formed (naphthalene, 1- and 2-nitronaphthalene and 1-naphthonitrile).

The photochemical excitation of charge-transfer complexes between aromatic compounds (ArH) and tetranitromethane (TNM) in dichloromethane or acetonitrile is reported to yield directly nitro- and trinitromethyl-substitution products [ArH and $ArC(NO_2)_3$] for most ArH,[2,3] but nitro/trinitromethyl adducts were found in some cases, such as anthracene derivatives[2b,g] and 1,4-dimethylnaphthalene.[2a] Nitro substitution was apparently favoured in acetonitrile, and trinitromethyl substitution in dichloromethane. The mechanism was assumed to involve reactions mostly within the triad formed upon photoexcitation of the CT complex, the one-electron oxidation of the intermediate trinitromethylcyclohexadienyl radical occurring *via* NO_2 and/or TNM [eqns. (1)–(3)].

We have undertaken an extensive product study of the photonitration of naphthalene by TNM in dichloromethane[4] and concluded that the predominant pathway to nitronaphthalenes was nitro/trinitromethyl addition, followed by elimination of nitroform. This explained the low 1:2 ratio of nitro products, also noticed in a recent study,[2a] since the selectivity of the coupling step between eqn. (2) and (3) would be expected to be low. Such a low ratio (in the range 1.5–10, with most values between 4 and 7, depending upon the reaction conditions chosen) was incompatible with the value independently measured for presynthesized radical cation salt and NO_2, 1:2 ratio ≈ 50.[5–7]

It was noted also that NO_2 leaked from the triad and was present in significant concentrations during the reaction period.[4] The minor nitration pathway, characterized by a 1:2 nitro product ratio of ≈20, was accordingly ascribed to nitration by NO_2.

We showed recently that one of the addition products from the photolysis of naphthalene–TNM in dichloromethane or acetonitrile could be isolated and characterized as *cis*-1,4-dihydro-1-nitro-4-trinitromethylnaphthalene by X-ray crystallography.[8] This adduct was stable for long periods in dichloromethane but underwent slow elimination with half-lives of the order of days in acetonitrile at 20 °C to give exclusively 1-nitronaphthalene. Addition of the hindered base, 2,6-di-*tert*-butylpyridine (DTBPy), to a dichloromethane solution of the adduct promoted rapid elimination of nitroform, again giving 1-nitronaphthalene exclusively. GLC analysis of the adduct gave only 1-nitronaphthalene at low injection-port temperature (< 200 °C), but at higher temperature naphthalene was also formed by elimination of tetranitromethane, 1-cyanonaphthalene by initial elimination of nitrous acid and formal loss of N_2O_6 from 1-trinitromethylnaphthalene, and some 2-nitronaphthalene by rearrangement at the adduct stage.

$$\begin{tikzcd}
\mathrm{ArH\cdots C(NO_2)_4} \arrow[r, "h\nu_{CT}"] & \mathrm{ArH^{+}\,{}^{\bullet}NO_2(NO_2)_3C^{-}} \arrow[r] \arrow[d] & \mathrm{{}^{+}Ar(H)NO_2} \arrow[r, "-H^{+}"] & \mathrm{ArNO_2} & (1) \\
& \mathrm{\dot{A}r(H)C(NO_2)_3} \arrow[r, "-e"] \arrow[d, "NO_2"] & \mathrm{ArC(NO_2)_3 + H^{+}} & & (2) \\
& \mathrm{Ar(H)(NO_2)C(NO_2)_3} & & & (3)
\end{tikzcd}$$

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† Preliminary communication, Ref. 8.

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Table 1 Overview of yields of products from the photolysis of naphthalene (0.50 mol dm^{-3}) and TNM (2.0 mol dm^{-3}) in dichloromethane

		Yield (%) of						
							Nitronaphthalene	
t/h	Conversion (%)	**1**	**2**	**3**	**4**	Total adducts	1-	2-
At −20 °C								
8.75	53	25.5	19.4	18.8	15.0	87.8	12.2	$\leqslant 0.5^a$
24	≈ 90	26.8	16.8	17.7	12.7	86.5	13.5	$\leqslant 0.5^a$
At +20 °C								
2	46	22.7	19.5	21.2	14.3	93.4	6.3	$\leqslant 0.5^a$
4	85	26.3	22.1	22.9	12.5	94.1	5.9	$\leqslant 0.5^a$
7.25	94	23.5	21.3	19.7	8.4	94.3	5.4	$\leqslant 0.5^a$
24	100	24.0	20.4	17.1	$\leqslant 2^a$	95.6	4.4	$\leqslant 0.5^a$

[a] Limit of detection.

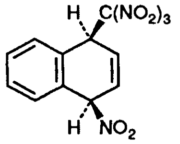
We now present a full account of the photochemical reaction between naphthalene and tetranitromethane in dichloromethane or acetonitrile. It is shown that adduct formation is by far the predominant pathway in both solvents and evidence is given that the minor pathway leading directly to nitro product may actually be the coupling process between naphthalene radical cation and NO_2, the 1:2 nitronaphthalene ratio now approaching agreement with the independently determined ratio.[5–7]

Results

General.—The photochemical experiments were performed with filtered light (cut-off < 435 nm, 5 cm water IR-filter, from a 300 W lamp) as described before,[4] and small samples withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature $\leqslant 0$ °C. The crude product mixtures were stored at −20 °C and were analysed (^{1}H NMR spectroscopy, see the Experimental section) as soon as possible.

All photolysed solutions were slightly acidic immediately after the run, presumably due to the presence of nitroform, a relatively strong acid (pK = 0.2 in water, 7.3 in acetonitrile).[9]

Photochemistry in Dichloromethane.—A solution of naphthalene (1.0 mol dm^{-3}) and TNM (2.0 mol dm^{-3}) in dichloromethane was irradiated at −20 °C. The composition of the reaction mixture was monitored at regular intervals by withdrawing samples for NMR spectral analysis. The final solution (after 24 h, conversion $\approx 90\%$) after work-up contained the *cis*-1,4 adduct (**1**, 25%, isolated and identified by X-ray crystallography), the *trans*-1,4-adduct (**2**, 18%, assigned by its NMR spectral properties), the *trans*-1-trinitromethyl-2-nitro adduct (**3**, 16%, assigned by its NMR spectral properties), the *trans*-1-trinitromethyl-2-hydroxy adduct (**4**, 11%, assigned by its NMR spectral properties), two unidentified adducts (18%; most likely of hydroxy/trinitromethyl adduct type) and 1-nitronaphthalene (13.5%). No 2-nitronaphthalene was detectable at this or earlier stages of the reaction (Table 1), the level of detection being $\geqslant 0.5\%$. Thus the 1:2 ratio was $\geqslant 25$ during the whole run.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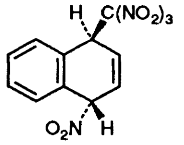
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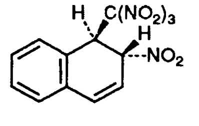
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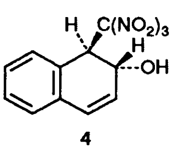
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The predominant existence of adducts in the crude product mixture was completely missed when GLC was employed as the analytical tool. The composition indicated was then naphthalene (20%), 1-nitronaphthalene (56%), 2-nitronaphthalene (11%) and 1-naphthonitrile (13%). GLC checks on all product mixtures containing adducts gave similar results (see below for GLC behaviour of pure **1**).

At 20 °C, the reaction after irradiation for 7 h (conversion 94%) gave **1** (24%), **2** (21%), **3** (20%), **4** (8%), unidentified adducts (13%) and 1-nitronaphthalene (6%), again with no detectable amount of the 2-isomer present (see Table 1). The most noticeable difference from the run at −20 °C is the disappearance of adduct **4** toward the end of the reaction.

Adduct **1** was isolated from a reaction mixture by removal of volatile material at 0 °C under reduced pressure and trituration of the residue with cold dichloromethane. Recrystallization of the solid material from dichloromethane at −20 °C gave pure adduct **1**, the identity of which was determined by X-ray crystallography.[8]

Photochemistry in Acetonitrile.—In this solvent, irradiation for 28 h (82% conversion) at −20 °C gave a product mixture containing **1** (27%), **2** (17%), **3** (17%), **4** (12%), unidentified adducts (17%), 1-nitronaphthalene (10%) and 2-nitronaphthalene (1%). At the early stages of the run (Table 2), the 2-nitro isomer level was very low (level of detection in the actual reaction mixture $\leqslant 0.5\%$), indicating that this compound was formed by elimination of nitroform from **3** (see below), and thus appears only in the later part of the run.

At +20 °C, the same photolysis reaction after 28 h gave **1** (21%), **2** (23%), **3** (20%), unidentified adducts (24%), 1-nitronaphthalene (11%) and 2-nitronaphthalene (2%), again noting (Table 2) that no 2-nitro isomer was detectable during the first 40% of the run. Adduct **4** was present too at this stage but later disappeared.

Elimination of Nitroform from **1**.—Earlier work[4] had shown that the presence of the hindered base, DTBPy, in the concentration range of 0.16 to 0.68 mol dm^{-3} during photolysis led directly to the formation of nitronaphthalenes in a low 1:2 ratio, around 1.5. This was interpreted as being due to base-promoted elimination of nitroform from photochemically produced adducts, essentially as they were formed.

Table 2 Overview of yields of products from the photolysis of naphthalene (1.0 mol dm^{-3}) and TNM (2.0 mol dm^{-3}) in acetonitrile

		Yield (%) of						
							Nitronaphthalene	
t/h	Conversion (%)	**1**	**2**	**3**	**4**	Total adducts	1-	2-
At −20 °C								
6.5	33	22.9	20.2	12.4	12.4	87.0	13.0	$\leqslant 0.5^a$
8.25	37	26.8	17.0	13.6	10.3	84.2	15.8	$\leqslant 0.5^a$
24	79	26.2	19.3	17.1	11.2	91.4	8.0	0.6
28.5	82	27.3	16.7	16.7	11.5	88.8	10.3	0.9
At +20 °C								
4	40	24.1	20.7	21.9	15.0	94.1	5.9	$\leqslant 0.5^a$
25.5	100	26.2	24.1	17.2	$\leqslant 2^a$	87.9	12.1	$\leqslant 0.5^a$
28.2	100	21.1	22.7	19.8	$\leqslant 2^a$	87.4	10.6	2.0

[a] Limit of detection.

Table 3 Base-catalysed elimination of nitroform from *cis*-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (**1**) and crude product mixture at 20.0 °C in dichloromethane (kinetics monitored at 310 nm)

	Pure adduct **1**		Crude product mixture	
[DTBPy]/ mmol dm^{-3}	k/min^{-1}	'k_2'/ dm^3 mol^{-1} s^{-1}	k/min^{-1}	k'/min^{-1}
1.71	0.0094	0.09		
6.5	0.047	0.12		
13.8	0.160	0.19		
34.4	0.41	0.20		
75	0.98	0.22	0.99	0.017
147	2.04	0.23	2.10	0.035

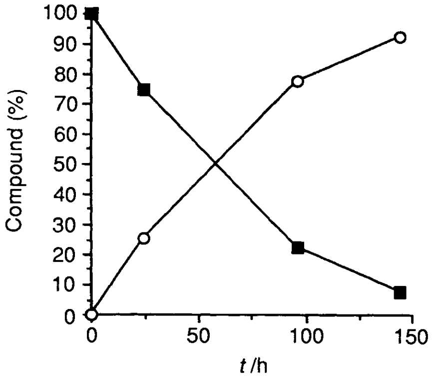

Fig. 1 Spontaneous decomposition of adduct **1** (■) with formation of 1-nitronaphthalene (○) in acetonitrile at 20 °C, as monitored by NMR spectroscopy; $\tau_{\frac{1}{2}}$ in this experiment was *ca.* 43 h

Adduct **1**, available in pure form, was stable for many days in dichloromethane at ambient temperature. Addition of DTBPy caused elimination with formation of nitroform (development of a UV spectral maximum at 352 nm due to partial ionization to trinitromethanide ion with log ε = 4.1) and 1-nitronaphthalene (with development of a maximum at 336 nm, log ε = 3.56). The rate was monitored in the region 290–360 nm and was found to vary by at most 20% over this interval for a given concentration of DTBPy. A flat minimum around 310 nm, exhibited at all [DTBPy] chosen, was deemed best for rate constant calculations. Rate constants in the interval of [DTBPy] = 1.7–150 mmol dm^{-3} are given in Table 3. The order in [DTBPy] was 1.2 ± 0.1. Extrapolated to the range of [DTBPy] used in the preparative experiments, adduct half-lives fall between 20 and 3 s. For the interval of [DTBPy] employed, an average 'second-order' rate constant was calculated to be 0.18 ± 0.5 dm^3 mol^{-1} s^{-1}.

An experiment, in which the composition of a chloroform solution of crude product mixture (from the run in dichloromethane at −20 °C) was monitored by ^{1}H NMR spectroscopy during a base-catalysed run (base = 2,6-di-*tert*-butyl-4-methylpyridine), indicated that adduct **1** disappeared faster than the other adducts. After 30 min the adducts had disappeared and the resulting product mixture was essentially 1- and 2-nitronaphthalene in a ratio of ≈3.7. From the initial composition of the crude product mixture (Table 1), a value of ≈3.2 would be expected.

Monitoring a dichloromethane solution of the same crude product mixture by UV spectroscopy at [DTBPy] = 75 and 150 mmol dm^{-3} showed biphasic behaviour which was analysed in terms of two successive pseudo-first-order reactions with rate constants k and k' ($k > k'$), as shown in Table 3. The first rate constant agreed well with that determined independently for pure **1** under identical conditions. The second rate constant k' was assigned to the elimination of nitroform from **2** and **3**, a composite process which is *ca.* 60 times slower than elimination from **1**.

In acetonitrile, the base-promoted elimination reaction (run at [DTBPy] = 13.8 mmol dm^{-3}) of adduct **1** proceeded with a second-order rate constant of 0.16 ± 0.01 dm^3 mol^{-1} s^{-1} at 20 °C, approximately the same as in dichloromethane. Without any added base, a slow spontaneous elimination process took place with rate constants in the interval of (3–9) × 10^{-4} min^{-1}, corresponding to half-lives between 40 and 13 h. As expected, this rate constant was not very reproducible because of the difficulty in controlling the base concentration in highly purified acetonitrile. A similar experiment, monitored by NMR spectroscopy, showed that only 1-nitronaphthalene was formed by spontaneous elimination from **1** in CD$_3$CN (see Fig. 1).

In view of the behaviour of the corresponding *trans*-1,4-adduct from 1,4-dimethylnaphthalene,[10] a test for the possible intermediacy of trinitromethyl radical during the spontaneous elimination of nitroform was performed by the spin trapping technique. Solutions of adduct **1** (20 mmol dm^{-3}) and 1-phenyl-*N*-*tert*-butylnitrone* (PBN; 200 mmol dm^{-3}) in acetonitrile or dichloromethane were monitored by EPR spectroscopy for a period of 48 h. Only 5 min after mixing a very weak signal of the trinitromethyl spin adduct[11] was detectable in both solvents; however, no further development of the signal took place during 48 h and we therefore do not consider this phenomenon significant for the spontaneous decomposition of **1**.

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* IUPAC-recommended name: *N*-*tert*-butylbenzylideneamine *N*-oxide.

Table 4 Product composition in the GLC analysis of a solution of adduct **1** in dichloromethane as a function of injection-port temperature

	Products (%)			
Injection port temperature/°C	Naphthalene	1-NO_2-naphthalene	2-NO_2-naphthalene	1-Naphthonitrile
100		100		
150		100		
200	<0.2	100		
250	3	96		1
300	13	80	<0.2	3
350	32	61	<0.5	4
400	56	38	0.5	2

Since the solutions obtained after photolysis were invariably slightly acidic, adduct **1** (88 mmol dm^{-3}) was treated with (220 mmol dm^{-3}) methanesulfonic acid in [$^2H_3$]acetonitrile in order to simulate this condition. No change (^1H NMR) took place over a period of 24 h, showing that **1** is stable against acid under any conditions that might reasonably be expected to prevail during photolysis. This is contrary to the behaviour of nitro/trinitromethyl adducts of 1,4-dimethylnaphthalene (see ref. 10).

It was found earlier[4] that the addition of methanol to the photolysis solution resulted in the formation of methoxycarbonyl substitution products, for example methyl naphthoate (1% yield) from naphthalene or methyl 4-methoxy-1-naphthoate (up to 50% yield) from 1-methoxynaphthalene. In order to shed some light on this pathway, adduct **1** was treated with 0.17 mol dm^{-3} methanol in dichloromethane. The ensuing reaction was monitored in the range 250–280 nm by UV spectroscopy; good first-order behaviour was observed with a rate constant of 0.11 min^{-1} at 20 °C. From a preparative experiment in neat [$^2H_4$]methanol, ^1H NMR spectroscopy showed that adduct **1** was converted into 1-nitronaphthalene to an extent of $\geqslant 90\%$, no other product being detectable. It appears then that the function of methanol toward **1** is only that of a weak base, promoting elimination of nitroform.

GLC analysis has sometimes been used for analyses of products from the photolysis of ArH–tetranitromethane mixtures.[2a,c,f] However, if adducts are significant components of the initial reaction mixture, it is necessary to establish their fate under GLC conditions. We assumed earlier[4] that elimination of nitroform with formation of nitronaphthalenes must take place predominantly and that elimination of nitrous acid with formation of trinitromethylnaphthalenes might take place to some extent—mainly to explain why ArCN were detected in small amounts during GLC. In addition, we inferred that elimination of trinitromethyl nitrite might be possible, with apparent recovery of starting material as a result.

With access to pure **1**, these features could be more conclusively established. Table 4 shows the variation of product composition from the GLC analysis of **1** as a function of injection-port temperature. At low temperatures (<200 °C) only 1-nitronaphthalene was formed (elimination of nitroform), whereas elimination of nitrous acid and trinitromethyl nitrite was clearly evident above 250 °C. Some migration of the nitro group also took place at high temperature. The GLC analysis of the crude product mixture from the -20 °C run in dichloromethane showed similar features, except that now more 2-nitronaphthalene was formed, presumably most of it by elimination from **3** (see above).

Discussion

Photochemistry in Dichloromethane.—We have previously favoured the hypothesis that the photonitration of naphthalene takes place *via* predominant nitro/trinitromethyl addition, accompanied by slow elimination of nitroform from the adduct(s).[4] In parallel, direct nitration of naphthalene takes place, ascribed to nitration by nitrogen dioxide that had escaped from the products of the initial photochemical process. Known rate data about the latter process[12] made it a logical candidate for a nitration reaction with a high 1:2 nitro isomer ratio.

We can now assess the situation starting from a much better set of data, chosen to illuminate the competition between addition and direct nitration processes, by summarizing the runs in dichloromethane at long reaction times (24 h).

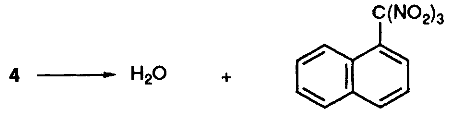
T/°C	Yield of total adducts (%)	Yield of $NpNO_2$ (%)	1:2
-20	87	14	>27
$+20$	96	5	>10

The fact that the yield of nitronaphthalene is nearly three times higher at -20 than at $+20$ °C suggests immediately that nitration of neutral naphthalene by NO_2 cannot be the reaction leading directly to nitro product. This reaction is far too slow to occur to such an extent at -20 °C, and, if responsible for all of the nitro substitution, should yield a lot more at $+20$ °C, contrary to what is observed. Since no elimination of nitroform from the adducts takes place in dichloromethane under neutral or acidic conditions, the nitronaphthalene cannot originate from this pathway either.

Thus we conclude that in dichloromethane at -20 °C we are actually seeing direct coupling between $ArH^{+\bullet}$ and NO_2, either within the triad [eqn. (1)] or in solution (with escaped NO_2). In agreement with earlier data[5] from the direct coupling between presynthesized naphthalene radical cation salt and NO_2, the 1:2 nitro isomer ratio is high for this reaction; we obtain $\geqslant 28$, but this is a lower limit set by experimental restrictions.

However, it should be emphasized that the major products are the adducts **1**–**4**, stable under the reaction conditions used in dichloromethane where conditions range from neutral at the beginning to slightly acidic at the end of the run. Relatively slow base-induced elimination of nitroform takes place in the presence of the hindered pyridine base, DTBPy or 2,6-di-*tert*-butyl-4-methylpyridine, or methanol. With strong bases, elimination is instantaneous.

The assignment of **4** as a 1-trinitromethyl-2-hydroxy adduct deserves some comment. We suggest that this compound is derived by decomposition of an initial 1-trinitromethyl-2-nitrito adduct, formed by attack of NO_2 *trans* to the bulky trinitromethyl group *via* one of its oxygens upon the cyclohexadienyl radical of eqn. (2). Such C–O bond formation occurs in circumstances of steric compression around the reacting centre[13a] and where electron-withdrawing neighbouring groups are present.[13b] The nitrito ⟶ hydroxy transformation might occur during photolysis and/or work-up. Adduct **4** disappeared toward the end of the runs in both dichloromethane and acetonitrile (Table 3), which we ascribe to acid-catalysed solvolysis according to eqn. (4). This would then



(4)

constitute a pathway to 1-trinitromethylnaphthalene, detected as 1-naphthonitrile in the GLC analysis carried out on the crude product mixture.

Photochemistry in Acetonitrile.—The reactions carried out in acetonitrile after *ca.* 30 h can be summarized as follows.

T/°C	Yield of total adducts (%)	Yield of $NpNO_2$ (%)	1:2
−20	89	11	11
+20	87	13	5

In these runs, the 2-nitronaphthalene was detectable only after long reaction times, about 30 h. This time period is comparable to the rate constant of spontaneous elimination of nitroform at least from adduct **1** (Fig. 1) and it is probable that the 2-isomer is formed similarly from **3**. At short reaction times at −20 °C, the direct coupling between $NpH^{+\bullet}$ and NO_2 is probably solely responsible for the formation of nitronaphthalene and accordingly shows high ratios of 1:2 nitro isomers ($\geqslant 32$ after 8.25 h; Table 2); elimination, as well as direct nitration of naphthalene itself by NO_2, would be far too slow to compete.

Conclusions

From the above results, it is clear that adduct formation, possibly followed by elimination, plays the major role in determining the outcome of the photochemical reaction between naphthalene and tetranitromethane in both dichloromethane and acetonitrile. GLC cannot be used for the correct analysis of product mixtures from these reactions because of the facile thermal elimination of nitroform to give nitronaphthalenes and trinitromethyl nitrite to form naphthalene. The resulting product distributions have little or no relevance for the mechanisms leading to the primary photolysis products. By inference, this caveat should be extended to all substrates where significant amounts of adducts can be detected using milder analytical methods, such as NMR spectroscopy. In all cases, adducts being detectable or not, nitro isomer distributions should be treated with proper scepticism, since the formation of transient adducts can never be excluded even in cases where they are not detectable. This makes any nitro isomer distribution from the tetranitromethane-induced photonitration of aromatics of limited use for mechanistic discussions of electrophilic nitration by nitronium ion.[2a,h–j]

Experimental

Materials.—Tetranitromethane was purchased from Aldrich and naphthalene was from BDH. 2,6-Di-*tert*-butyl-4-methylpyridine was from Fluka and 2,6-di-*tert*-butylpyridine from Merck, as were dichloromethane (*zur Rückstandsanalyse*) and acetonitrile (UVASOL). The nitronaphthalenes were available from earlier work.

Methods.—Procedures for carrying out photolyses, kinetic experiments and NMR spectral analysis have been described before.[4] The photolysis lamps were of Osram 'Ultravitalux' type (300 W). Seemingly widely differing reaction times given for similar reactions merely reflect the age of the lamp used and are not significant in any other respect (the degree of conversion was monitored by NMR spectral analyses at regular intervals). For irradiation at low temperatures a doubly jacketed (vacuum/cooling liquid) vessel was employed, cooling being effected by a Colora cooling thermostat.

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[14] and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.

General Procedure for the Photonitration of Naphthalene with Tetranitromethane.—A solution of naphthalene (1 g, equal to a 0.5 mol dm^{-3} solution) and tetranitromethane (2 mol dm^{-3}) in dichloromethane or acetonitrile (16 cm^3) was irradiated at −20 or +20 °C with filtered light (cut-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 determined by NMR spectral analysis (Tables 1 and 2).

Reaction in Dichloromethane at −20 °C *and the Identification of Products.*—Reaction of naphthalene–tetranitromethane in dichloromethane at −20 °C, as above, gave, after bleaching of the CT band, a product which was shown by ^1H NMR spectra to be a mixture (Table 1) of adducts (total 86.5%), including adducts **1–4** and 1-nitronaphthalene (13.5%). No 2-nitronaphthalene was seen at the detection level of this particular type of mixture ($\leqslant 0.5\%$). The major adduct **1** was isolated by trituration of the crude product with cold dichloromethane; crystallization of the solid from dichloromethane at −20 °C gave *cis*-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (**1**, 450 mg, 18%), m.p. 152.5–153.5 °C,[8] ν_{max}(KBr)/cm^{-1} 1620sh, 1603, 1598, 1580 and 1551; $\delta_H(CD_2Cl_2)$ 5.44 (dd, $J_{4.3}$ 4.1 Hz, $J_{4.1}$ 2.6 Hz, H-4), 6.02 (dd, $J_{1.2}$ 4.66 Hz, $J_{1.4}$ 2.6 Hz, H-1), 6.77 (dd, $J_{3.2}$ 10.2 Hz, $J_{3.4}$ 4.1 Hz, H-3), 6.81 (dd, $J_{2.3}$ 10.2 Hz, $J_{2.1}$ 4.6 Hz, H-2), 7.28 (dd, $J_{5.6}$ 8.0 Hz, $J_{5.7}$ 1.3 Hz, H-5), 7.54 (ddd, $J_{6.5}$ 8.0 Hz, $J_{6.7}$ 7.7 Hz, $J_{6.8}$ 1.3 Hz, H-6) 7.64 (ddd, $J_{7.8}$ 8.0 Hz, $J_{7.6}$ 7.7 Hz, $J_{7.5}$, H-7) and 7.85 (dd, $J_{8.7}$ 8.0 Hz, $J_{8.6}$ 1.3 Hz, H-8); NOE experiments: irradiation at δ 5.44 gave enhancements at δ 6.77 (7%) and at δ 7.28 (8%); irradiation at δ 6.02 gave enhancements at δ 6.81 (7%) and at δ 7.85 (10%); irradiation at δ 7.28 gave enhancements at δ 5.44 (8%) and at δ 7.54 (8%); irradiation at δ 7.85 gave an enhancement at δ 6.02 (6%). $\delta_C(CD_2Cl_2)$ 41.02 (C-4), 76.60 (C-1), 122.29 (C-3), 124.57 (C-5), 126.01 (C-2), 126.57 (C-7), 127.57 (C-6) and 129.79 (C-8), resonances for the remaining carbons were not detected in the weak spectrum. Assignments were confirmed by HETCOR experiments.

From the ^1H NMR spectrum of the crude product, prior to the isolation of adduct **1**, three further adducts **2–4** were identified.

trans-1-*Nitro*-4-*trinitromethyl*-1,4-*dihydronaphthalene*. δ_H-($CDCl_3$) (ddd, $J_{4.3}$ 4.4 Hz, $J_{4.1}$ 2.1 Hz, $J_{4.2}$ 1.0 Hz, H-4), 6.06 (ddd, $J_{2.3}$ 10.2 Hz, $J_{2.1}$ 1.8 Hz, $J_{2.4}$ 1.0 Hz, H-2), 6.24 (ddd, $J_{1.2}$ 1.8 Hz, $J_{1.3}$ 2.0 Hz, $J_{1.4}$ 2.1 Hz, H-1) and 6.66 (ddd, $J_{3.4}$ 4.4 Hz, $J_{3.2}$ 10.2 Hz, $J_{3.1}$ 2.0 Hz, H-3); confirmed by double irradiation experiments.

trans-2-*Nitro*-1-*trinitromethyl*-1,2-*dihydronaphthalene* **3**.

δ_H($CDCl_3$) 5.69 (dd, $J_{2,3}$ 7.1 Hz, $J_{2,1}$ 0.5 Hz, H-2), 5.82 (d, $J_{1,2}$ 0.5 Hz, H-1), 6.05 (dd, $J_{3,4}$ 9.5 Hz, $J_{3,2}$ 7.1 Hz, H-3) and 6.84 (d, $J_{4,3}$ 9.5 Hz, H-4); confirmed by double irradiation experiments.

trans-2-*Hydroxy*-1-*trinitromethyl*-1,2-*dihydronaphthalene* **4**, δ_H($CDCl_3$) 4.83 (d, $J_{1,2}$ 1.2 Hz, H-1), 4.89 (dd, $J_{2,3}$ 5.8 Hz, $J_{2,1}$ 1.2 Hz, H-2), 5.97 (dd, $J_{3,4}$ 9.6 Hz, $J_{3,2}$ 5.8 Hz, H-3) and 6.56 (d, $J_{4,3}$ 9.6 Hz, H-4); confirmed by double irradiation experiments.

Reaction of the Crude Product from Nitration in Dichloromethane at −20 °C *with* 2,6-*Di*-tert-*butyl*-4-*methylpyridine in* $CDCl_3$.—A solution of the crude product (30 mg) from the dichloromethane nitration at −20 °C and the hindered pyridine (15 mg) in $CDCl_3$ (0.7 cm^3) was kept at the temperature of the NMR probe (23 °C) and the ^1H NMR spectrum of the solution monitored at appropriate time intervals. After 30 min the adducts had reacted and the resulting NMR spectrum was essentially that of a mixture (*ca.* 3.7 : 1) of 1- and 2-nitronaphthalene.

GLC *Examination of the Crude Product from the Nitration in Dichloromethane at* −20 °C.—GLC analysis was carried out using a 25 m OV-1701 capillary column at 160–210 °C, the injector port usually being kept at 250 °C. The apparent composition then was: naphthalene, 20.4%; 1-naphthonitrile, 13.2%; 1-nitronaphthalene, 55.8%; 2-nitronaphthalene, 10.5%.

Decomposition of Adduct **1** *in* CD_3CN.—A solution of adduct **1** (10 mg) in CD_3CN (0.7 cm^3) was stored at 20 °C and the ^1H NMR spectrum of the solution was monitored at appropriate time intervals. These spectra revealed a clean conversion of adduct **1** into 1-nitronaphthalene with a half-life of *ca.* 43 h (Fig. 1).

Decomposition of Adduct **1** *in* CD_3OD.—A solution of **1** (10 mg) in CD_3OD (0.7 cm^3) was stored at 20 °C and the ^1H NMR spectrum of the solution monitored at appropriate time intervals. These spectra revealed a conversion of **1** into 1-nitronaphthalene (*ca.* 90%) with a half-life of *ca.* 50 min.

Acknowledgements

Financial support from the Swedish Natural Science Research Council, the Knut and Alice Wallenberg Foundation and the Crafoord Foundation is gratefully acknowledged.

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Paper 2/02676G
Received 22nd *May* 1992
Accepted 2nd *June* 1992