Photochemical Nitration by Tetranitromethane. Part VII.[1] Mode of Formation of the Nitro Substitution Products from 1,4-Dimethylnaphthalene in Dichloromethane and Acetonitrile

Lennart Eberson,* Michael P. Hartshorn† and Finn Radner
MAX Chemistry, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

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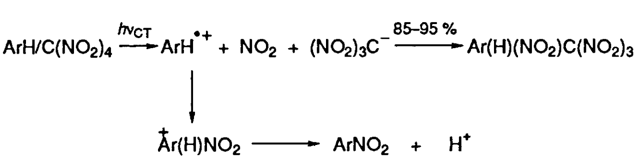
Photolysis of tetranitromethane and 1,4-dimethylnaphthalene at low temperature in dichloromethane gives predominantly addition products, *trans*- and *cis*-1,4-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (**1** and **2**, together 90%), in addition to the side-chain nitration product (**3**, 7%). At higher temperature, **3** becomes the major product [ratio (**1** + **2**):**3** 30:65]. With external acid present during the run, partial formation of the 2-nitro substitution product (**4**) was an additional feature.

In acetonitrile, the phenomenology is similar, except that the corresponding nitrito adducts were also present at the beginning of the reaction (maximally 20%) and disappeared toward the end; the 2-nitro substitution product also appeared toward the end of the run at higher temperature.

It was shown separately that pure **1** rearranges to an equilibrium mixture with **2** in both acetonitrile and dichloromethane (rate constants 0.11 and 8×10^{-4} min^{-1}, respectively). From **2**, the corresponding nitrito adducts are slowly formed in acetonitrile *via* a, presumably, homolytic nitro/nitrito rearrangement. The latter reaction has the 1-trinitromethylnaphthalenyl radical as the intermediate, capable of existing in equilibrium with both trinitromethanide ion/(1,4-dimethylnaphthalene)$^{\bullet+}$ and trinitromethyl radical/1,4-dimethylnaphthalene. Chemical consequences of these equilibria were found in both acid/base promoted reactions and trapping of trinitromethyl radical by the spin trap, α-phenyl-*N*-*tert*-butylnitrone.‡ The 2-nitro substitution product **4**, in all probability, was formed as a consequence of acid-induced reactions of **2**, indicating that in the photochemical experiments **4** is also formed *via* this pathway.

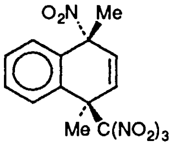
In the preceding paper[1] we showed that the photochemical reaction between naphthalene (NpH) and tetranitromethane takes place predominantly (85–95%) with nitro/trinitromethyl adduct formation. The adducts undergo elimination of nitroform to give nitro-substitution products under forcing conditions such as base catalysis, high temperature (GLC) and long-term storage (50–100 h) in acetonitrile solution. Further, a minor pathway (15–5%) was shown directly to give nitro substitution products with a high α/β ratio, assumed to occur by coupling between photochemically generated $Np^{\bullet+}$ and NO_2 (Scheme 1, ArH = NpH).



Scheme 1

1,4-Dimethylnaphthalene has been shown[2] to react according to a similar pattern, giving a 3:1 mixture of *trans*- and *cis*-1,4-nitro/trinitromethyl adducts (**1** and **2**), the former being isolated and characterized by X-ray crystallography. Adduct **1** underwent slow elimination in acetonitrile at room temperature with exclusive formation of **3**, the side-chain nitration product.[2]

The photochemical reaction in acetonitrile at 25 °C also afforded small amounts (*ca.* 9%) of the nuclear nitration product, **4**, which was assumed to originate from coupling between (1,4-dimethylnaphthalene)$^{\bullet+}$ and NO_2 at the 2-position, as shown in the general case in Scheme 1.[2] Being aware of the complexity of the photochemical system at hand,[1,3] and suspecting the possibility of adduct reactions of as yet unknown character, we have undertaken a more detailed study of the photonitration of 1,4-dimethylnaphthalene by tetranitromethane in dichloromethane or acetonitrile. In what follows we show that complex thermal transformations of the initially formed adducts **1** and **2** give rise to the nitro-substitution products **3** and **4**, *via* a combination of radical and polar steps.



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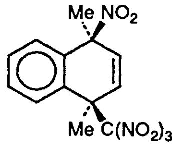

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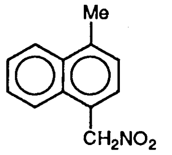

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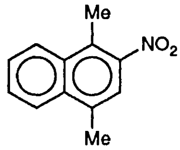

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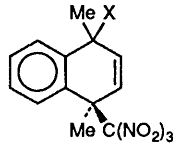

5, **6** epimers X = ONO
5a, **6a** epimers X = OH

Results

Photochemistry in Dichloromethane.—Reactions were performed at −50, −20 and +20 °C and were monitored by ^1H NMR spectral analysis at regular intervals. The results are given in Table 1. At the two lower temperatures adduct **1** was the predominant product, together with its *cis* isomer **2** and the side-chain nitro derivative **3**. At 20 °C, **3** was the major product

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† *Permanent address:* Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

‡ *N*-*tert*-Butylbenzylideneamine *N*-oxide.

already at 21% conversion and its proportion increased during the run at the expense of **1**. An unknown product, labile under the conditions used and with the NMR spectral characteristics of a side-chain derivative, was formed in a maximum proportion of 8% in the beginning of the reaction. Presumably, this product was the nitrito isomer of **3**. Under no conditions was the nuclear nitro product **4** detectable (limit of detection $\leq 0.5\%$).

Since the photolysis mixtures were always acidic toward the end of the reaction, the effect of having acid present during the whole reaction period was studied by conducting a run at 20 °C with dichloromethane, saturated with toluene-*p*-sulfonic acid (≈ 12 mmol dm^{-3}), as the medium. At 100% conversion, the crude product consisted of **1** (8%), **2** ($<1\%$), **3** (79%) and **4** (13%), to be compared with **1** (30%), **2** (4%), **3** (65%) and a trace of **4** at long reaction times from a run with no external acid present (Table 1). The acid thus promoted further reactions of the adducts and induced a new mode of nitration to give the nuclear nitro isomer, **4**.

Photochemistry in Acetonitrile.—Reactions were performed at −20 and +20 °C. The pattern of reactivity was similar to that seen in dichloromethane, except that two new adducts, **5** and **6**, appeared (Table 2) at the beginning of the runs and slowly disappeared during the reaction period. In acetonitrile at +20 °C, **4** was observed (see also ref. 2) in the later part of the run, suggesting that it was formed *via* secondary reactions of the initially formed products.

Table 1 Overview of yield of products from the photolysis of 1,4-dimethylnaphthalene (0.50 mol dm^{-3}) and tetranitromethane (2.0 mol dm^{-3}) in dichloromethane

		Yield (%)				
t/h	Conversion (%)	1	2	3	Unknown[a]	Ratio 1:2
At −50 °C						
1	10	70	10	12	8	7
2	26	81	8	7	5	10
4	59	82	9	7	2	9
5.25	74	81	9	7	2	9
At −20 °C						
1	13	68.6	4.6	19.0	7.8	15
2	34	69.9	8.1	15.9	6.1	9
4	61	70.1	10.0	16.9	2.9	7
5.25	81	73.3	7.7	15.4	2.6	8
At +20 °C						
1	21	42.3	4.2	47.1	6.3	10
2	51	44	5.2	48	2.6	8
4	92	33	4.5	60.4	2.2	7
5.25	100	29.5	3.8	64.9	1.8	8

[a] The unknown product has CH_2–X at δ 5.691.

The new adducts **5** and **6** were assigned the structures of the two epimers of 1,4-dimethyl-1-nitrito-4-trinitromethyl-1,4-dihydronaphthalene on the basis of ^1H NMR spectral analysis (see Experimental section). Actually, **5** and **6** were not identified as such but as the corresponding 1-hydroxy-4-trinitromethyl adducts **5a** and **6a** which must have been formed by hydrolysis of the nitrites during photolysis and/or work-up. A similar reaction took place during the photolysis of tetranitromethane/naphthalene.[1] In the following, we report these adducts as **5** and **6**, even if they were analysed as the hydroxy derivatives **5a** and **6a**.

Thermal Rearrangement/Elimination Reactions of **1**.—(*a*) *In acetonitrile*. By analogy with the nitro/trinitromethyl adducts from naphthalene, it would be expected that **1** should undergo elimination reactions,[1] and it has already been shown[2] that it undergoes spontaneously slow elimination of nitroform in acetonitrile to give **3**, the side-chain nitro product. When this reaction was monitored by UV spectroscopy (growth of the 250–350 nm band of **3**), a rate constant of 8.5×10^{-4} min^{-1} ($\tau_{\frac{1}{2}} \approx 14$ h) at 20.0 °C was determined.

Attempts to induce acid-catalysed elimination by adding methanesulfonic acid (5–500 mmol dm^{-3}) to a solution of adduct **1** in acetonitrile indicated initially that the rate of formation of the side-chain nitro product **3** was affected by acid, as monitored by UV spectroscopy in the 250–300 nm region. Pseudo-first-order behaviour was observed, but the rate constants calculated were wildly erratic, showing no relationship whatsoever to the acid concentration. Eventually this behaviour was traced to the practice of using a stock solution for successive runs; even during short storage periods, relatively fast spontaneous reactions in the stock solution evidently interfered with the kinetics of the acid-promoted runs.

Upon closer inspection, the spontaneous elimination of nitroform from **1** showed a more complicated rate pattern. Immediately after dissolution of **1** in acetonitrile, a relatively fast reaction ($k = 0.106$ min^{-1} at 20.0 °C) began with a decrease in absorbance in the 250–300 nm region and was over in *ca*. 40 min [Fig. 1(*a*)]. A slow process then set in, with $k = 6.7 \times 10^{-4}$ min^{-1} at 20.0 °C, building up the absorbance of **3** in the range 250–300 nm [Fig. 1(*b*)].

When this reaction was instead monitored by ^1H NMR spectroscopy, a complex pattern of product evolution was revealed (Table 3; also shown in the plot of Fig. 2). The initial fast process was found to correspond to the rearrangement of the *trans* adduct **1** into its *cis* isomer **2** (**1**:**2** at equilibrium ≈ 2),

Table 2 Overview of yield of products from the photolysis of 1,4-dimethylnaphthalene (0.50 mol dm^{-3}) and tetranitromethane (2.0 mol dm^{-3}) in acetonitrile

		Yield (%)							
t/h	Conversion (%)	1	2	3	4	5	6	Ratio 1:2	5:6
At −20 °C									
1	8.3	61.5	11.6	6.4	—	14.8	5.7	5	2.6
2	24.6	68.7	15.1	6.7	—	6.4	3.2	4.5	2.0
4	45.6	71.6	15.5	7.1	—	3.9	1.8	5	2.2
6.25	60.8	71.5	17.0	6.8	—	3.3	1.4	4	2.4
At +20 °C									
0.5	14.1	41.6	17.4	28.0	—	8.3	4.7	2.4	1.8
1	31.9	40.7	18.5	31.4	—	3.9	1.9	2.2	2.1
2	70.4	33.5	14.6	34.1	15.6	1.1	trace	2.3	—
3.25	97.7	33.7	9.1	43.0	14.1	trace	—	3.7	—

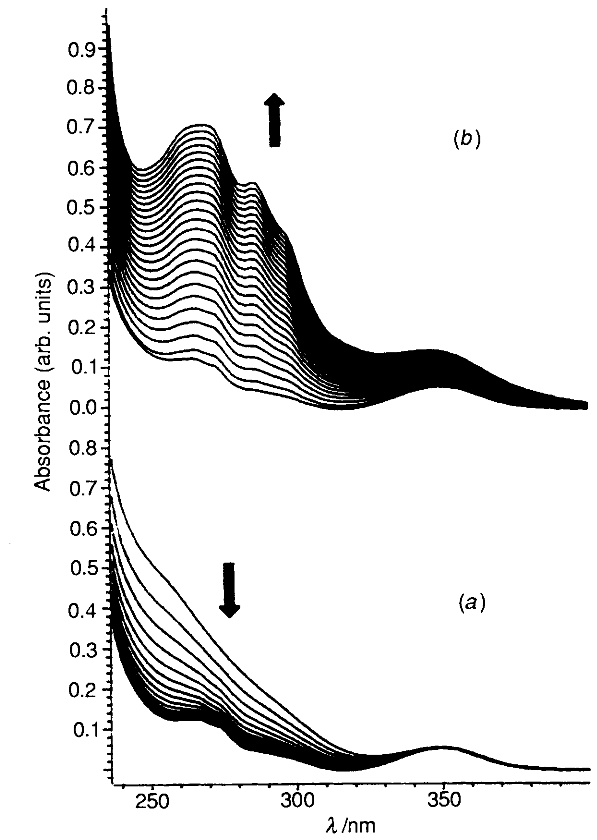


Fig. 1 Repeated UV spectral scans of a solution of adduct **1** in acetonitrile at 20.0 °C: (*a*) 21 × 2 min; (*b*) 21 × 1 h, following (*a*)

Table 3 Rearrangement of adduct **1** and further reactions in acetonitrile at 20 °C, as monitored by ^{1}H NMR spectral analysis of the δ 5.80–6.75 region

	Percentage of							
t/min	**1**	**2**	**3**	**5**	**6**	1,4-DMN[a]	**1**:**2**	**5**:**6**
0	100	0	0	0	0	0		
2	87.4	6.4	2.6	—	—	3.6[b]	9.3	—
5	81.9	10.4	3.9	trace	—	3.7[c]	7.9	—
10	71.7	16.0	5.4	3.3	—	3.7[c]	4.5	—
20	60.8	22.7	7.1	4.0	2.1	3.3[c]	2.7	1.9
40	51.9	26.2	8.8	6.1	3.7	3.3	2.0	1.6
120	42.1	21.5	17.9	9.5	5.2	4.0	2.0	1.8
220	34.9	18.6	25.3	10.7	6.3	4.1	1.9	1.7
480	24.4	12.7	39.6	11.4	6.3	5.6	1.9	1.8
1440	7.7	4.2	75.7	1.3	trace	10.1	1.8	—
2880	—	—	88	—	—	11	—	—

[a] 1,4-DMN = 1,4-dimethylnaphthalene. [b] Broad signal. [c] Relatively broad signal.

Table 4 Rate constants for the acid-catalysed reaction of adduct **1** at 20 °C in acetonitrile

[CH_3SO_3H]/mmol dm^{-3}	*k*/min^{-1}
5.1	0.039
12.9	0.085
20.6	0.094
30.9	0.107
51.2	0.110
127	0.125
253	0.114
497	0.108

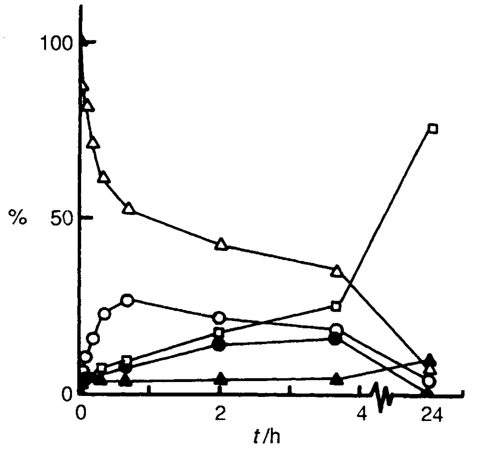


Fig. 2 Plots of the time development of **1** and products from the spontaneous reaction of **1** in acetonitrile at 20 °C. **1**, △; **2**, ○; **3**, □; (**5** + **6**), ●; 1,4-dimethylnaphthalene, ▲. The points for each species are joined by straight lines in order to improve readability. Data at 48 h were omitted for the same reason.

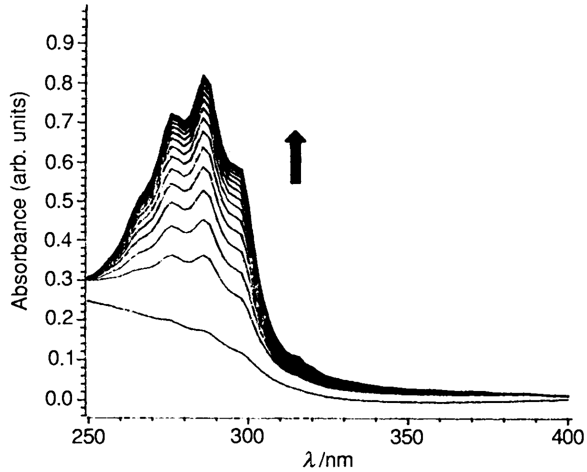


Fig. 3 Repeated UV spectral scans (15 × 2 min) of a freshly prepared solution of **1** in acetonitrile at 20.0 °C with methanesulfonic acid (497 mmol dm^{-3}) added

as shown by the approximate rate constants calculated from the NMR spectral experiment for the disappearance of **1** and appearance of **2**, 0.10 ± 0.4 and 0.10 ± 0.03 min^{-1} (calculated from the first five points), respectively, to be compared with the UV spectrally based value of 0.106 min^{-1}. Once the concentration of **2** has built up (10% within 10 min, maximally 27% after 40 min), the adducts **5** and **6** start to appear and build up to their maximum concentration after 8–10 h. During the whole period, [**3**] increased slowly [rate constant $(1.2 \pm 0.1) \times 10^{-3}$ min^{-1}; *cf.* the UV spectrally obtained value of 8.5×10^{-4} min^{-1} for growth of absorbance due to unconjugated naphthalenes], **3** becoming the only product after a sufficiently long reaction time (Fig. 2). A further feature of the spontaneous reaction was the formal elimination of tetranitromethane with formation of 1,4-dimethylnaphthalene in a final proportion of *ca.* 10%. In the initial part of the run (<40 min) the methyl signal from 1,4-dimethylnaphthalene was significantly broadened.

Against this background, a series of reactions were run with methanesulfonic acid added to freshly prepared solutions of **1** in acetonitrile, the reaction being started ⩽2 min after dissolution of **1** (Fig. 3). At low concentrations of acid, the absorbance/time curve was sigmoidal because of the competition between the decrease in absorbance due to the *trans–cis* rearrangement and the acid-catalysed formation of **3**, leading to an increase in absorbance. Hence rate constants were evaluated from the last

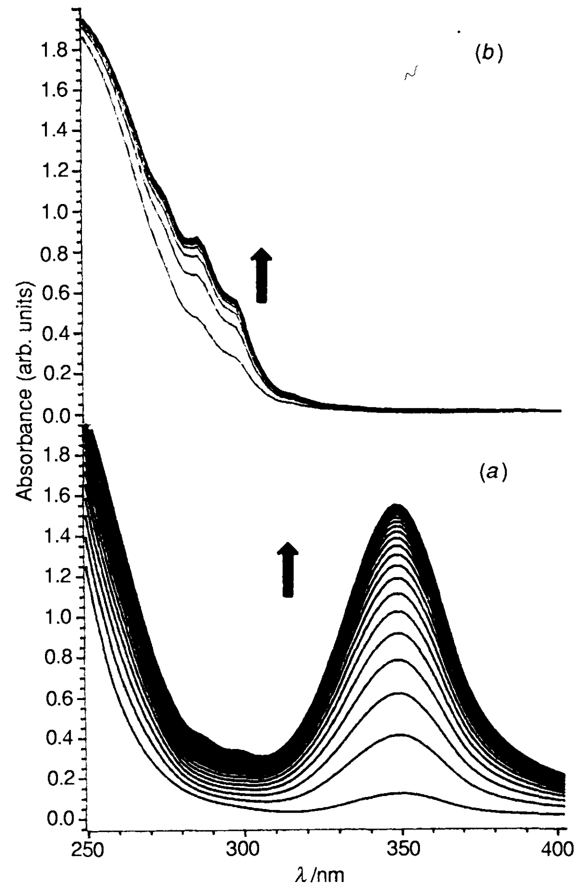


Fig. 4 (*a*) Repeated UV spectral scans (21 × 2 min) of a freshly prepared solution of **1** in acetonitrile at 20.0 °C with pentaisopropylguanidine (21 mmol dm^{-3}) added; (*b*) repeated scans (10 × 20 s) on the final solution from (*a*) after addition of methanesulfonic acid to a final concentration of 200 mmol dm^{-3}

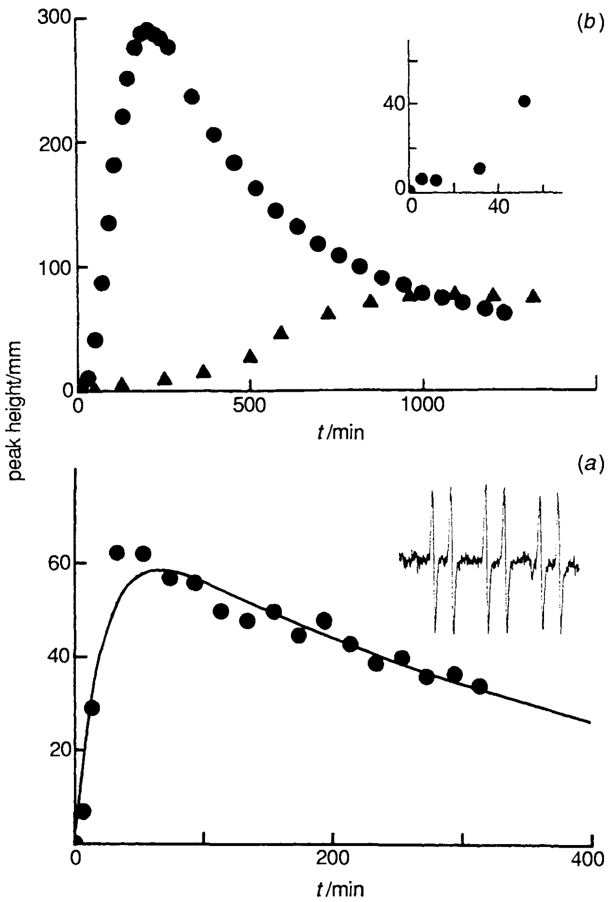


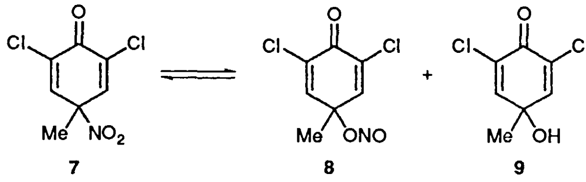
Fig. 5 Time development at ≈24 °C of the EPR spectrum (intensity measured on the outermost low-field signal) of the trinitromethyl spin adduct from: (*a*) a solution of **1** (40 mmol dm^{-3}) and PBN (0.35 mol dm^{-3}) in acetonitrile. The curve represents the best fit to the experimental data, with the rate constants (5 ± 2) × 10^{-2} (up) and (2.5 × 1.0) × 10^{-3} (down) min^{-1}, respectively. The insert shows the EPR spectrum of the PBN trinitromethyl spin adduct in acetonitrile (sweep width 5.0 mT). (*b*) A solution of **1** (47 mmol dm^{-3}) and PBN (0.33 mol dm^{-3}) in dichloromethane (●) and a solution of **1** (42 mmol dm^{-3}), PBN (0.40 mol dm^{-3}) and TFA (0.11 mol dm^{-3}) in dichloromethane (▲). The insert shows the first five points of the first curve on a shorter timescale.

60% of the absorbance/time curve. As shown in Table 4, the rate showed limiting behaviour even at [CH_3SO_3H] ≈ 30 mmol dm^{-3} with k_{lim} = 0.110 min^{-1}. This is, within limits of error, the same value as that of the rate of equilibration between **1** and **2**, indicating that the acid-catalysed step follows the rearrangement, the latter becoming the rate-limiting step at sufficiently high [CH_3SO_3H].

A similar experiment, but with a hindered base (2,6-di-*tert*-butylpyridine or pentaisopropylguanidine) present, led to a build-up of the 350 nm band of trinitromethanide ion with k = 0.114 min^{-1} [Fig. 4(*a*)], independent of the nature or concentration of the base. Again it appears that the rate of rearrangement **1** $\longrightarrow$ **2** is the rate-determining step, followed by a fast reaction which, with base present, ultimately gives trinitromethanide. Acidification of the final solution with methanesulfonic acid after the run immediately bleached the 350 nm band and absorbance originating from an unconjugated naphthalene system then rapidly built up [Fig. 4(*b*)]. The rate of the latter reaction was approximately first order in [CH_3SO_3H], k_2 being *ca.* 0.19 dm^3 mol^{-1} s^{-1}.

An NMR spectrally monitored experiment in which methanesulfonic acid (0.22 mol dm^{-3}) was added to a freshly prepared solution of pure **1** (0.061 mol dm^{-3}) in acetonitrile gave a significantly different result compared with the spontaneous reaction, in that 1,4-dimethylnaphthalene (42%) and the nuclear nitro product **4** (9%) were formed in addition to **3** (49%) in a reaction that was complete within *ca.* 30 min.

At this stage of the investigation, it was apparent that the reaction modes available to adduct **1** and/or **2** might include radical pathways. The nitro–nitrito rearrangement of the *ipso* intermediate **7** in chloroform to give the nitrito isomer **8** and its corresponding hydroxy compound **9** was assumed to be homolytic in nature.[4] The similarity between adducts **1**/**2** and **7** indicated that the formation of **5**/**6** might occur by a homolytic process, and that radical intermediates might play an important role.



7 **8** **9**

The formation of the trinitromethyl radical was shown by a spin trapping experiment where **1** (20 mmol dm^{-3}) was allowed to undergo the spontaneous reaction in acetonitrile at 24–25 °C in the presence of α-phenyl-*N*-*tert*-butylnitrone (PBN, 220 mmol dm^{-3}) in an EPR tube protected from light. The characteristic signal (a^N = 1.47 mT, a^H = 0.51 mT; literature values[5,6] 1.46–1.47 and 0.46–0.50 mT, respectively) of the trinitromethyl spin adduct started to appear immediately [Fig. 5(*a*)] and reached a maximum concentration after *ca.* 100 min. The EPR signal then slowly decayed and was almost gone after

Table 5 Rearrangement of adduct **1** and further reactions in dichloromethane at 20 °C, as monitored by ^1H NMR spectral analysis of the δ 5.80–6.75 region. Experiment 1 was run in CD_2Cl_2, experiment 2 in CH_2Cl_2 (see the Experimental)

t/h (exp. no)	Conversion (%)	Percentage of 1	2	3	Ratio 1:2
0 (1)	0	100	0	0	—
1 (1)	1.7	98.3	1.55	0.18	63
2 (1)	3.2	96.8	2.9	0.3	33
4.17 (1)	5.8	94.2	5.0	0.8	19
7 (1)	9.3	90.7	8.2	1.0	11
18.45 (2)	17.6	82.4	15.8	1.8	5.2
22.18 (1)	21.3	78.7	18.8	2.6	4.2
24.28 (2)	20.5	79.5	18.1	2.4	4.4
42.48 (2)	26.2	73.8	22.0	4.1	3.4
46.08 (1)	28.0	72.0	22.9	5.1	3.1
63.42 (2)	30.1	69.9	23.0	7.1	3.0
87.45 (2)	33.2	66.9	22.4	10.8	3.0

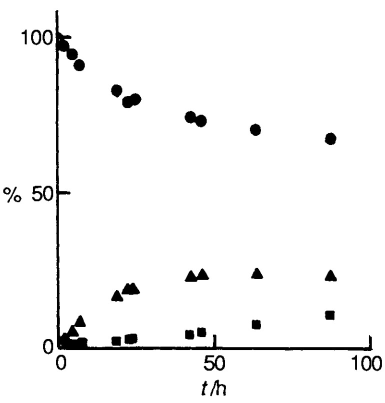


Fig. 6 Plots of the time development of **1** and products from the spontaneous reaction of **1** in dichloromethane at 20 °C: **1**, ●; **2**, ▲; **3**, ■

24 h. The rate constants of the biphasic reaction were evaluated to be (3.5 ± 1.0) × 10^{-2} and (2.5 ± 1.0) × 10^{-3} min^{-1} [average of two runs; one is shown in Fig. 5(*a*)].

(*b*) *In dichloromethane.* With the results from the acetonitrile experiments in mind, it was possible to demonstrate that the same type of chemistry occurs in dichloromethane as well, although the experimental conditions were not as favourable as in the acetonitrile case. Thus the initial **1** $\longrightarrow$ **2** transformation was much slower and difficult to detect and monitor by UV spectroscopy owing to the small accompanying change in absorbance. Moreover, methanesulfonic acid is insufficiently soluble in dichloromethane to be a feasible reagent, so that trifluoroacetic acid, a weaker acid than methanesulfonic acid, had to be used as the acidic component and then at a concentration level that, in fact, might cause a solvent effect.

Thus, the first clues to the spontaneous chemical reactivity of **1** in dichloromethane were obtained by long-term NMR spectral monitoring. The results are shown in Table 5 and Fig. 6. The rate of equilibration between **1** and **2** was slow, the effective rate constant k for approaching equilibrium from **1** at 20 °C being (8.5 ± 1) × 10^{-4} and (11 ± 1) × 10^{-4} min^{-1}, as calculated from the time dependence of [**1**] and [**2**], respectively (using the first four points). This is 100–130 times slower than in acetonitrile. The ratio **1**:**2** at equilibrium was 3 ± 0.3. The only other product seen was **3**, the concentration of which built up very slowly. The nitrito compounds **5** and **6** were not detectable (limit $\leqslant$0.5%).

When monitored by UV spectroscopy, the spontaneous rearrangement of **1** to **2** took place with a decrease in absorbance in the range 240–270 nm and with a rather small but reproducible change (*ca.* 0.04 absorbance units over 20 h at $[\mathbf{1}]_0 \approx 0.5$ mmol dm^{-3}). The rate constant of equilibration came out at (8 ± 1) × 10^{-4} min^{-1} at 20.0 °C, in good agreement with the value obtained by NMR spectral analysis. Addition of trifluoroacetic acid in high concentration (0.43–1.57 mol dm^{-3}) caused the build-up of absorbance in the 250–350 nm region, rate constants ([TFA]/mol dm^{-3}) being 0.034 (0.43), 0.092 (0.84) and 0.26 (1.57) min^{-1}. The order in [TFA] was 1.5. The predominant products formed in this reaction were **3** (23%) and 1,4-dimethylnaphthalene (59%).

Addition of a base (pentaisopropylguanidine) to a solution of adduct **1** in dichloromethane caused a very slow, linear build-up (7.0 × 10^{-4} absorbance units per min at $[\mathbf{1}]_0 \approx 0.2$ mmol dm^{-3}) of absorbance in the 300–400 nm region. Again it seems as if the **1** $\longrightarrow$ **2** equilibration rate is the slow step of the reaction series.

A spin-trapping experiment again gave the signal of the trinitromethyl spin adduct (a^N = 1.47 mT, a^H = 0.44 mT; lit.,[6] 1.46 and 0.44 mT), the maximum concentration of which was *ca.* 5 times larger than at its maximum intensity in the acetonitrile experiment. The maximum concentration was reached after ≈4 h at 24 °C. The initial shape of the spin adduct/time curve was sigmoidal [see the insert of Fig. 5(*b*)]. Leaving out the first three points, the first-order rate constants of the biphasic system were calculated to be (1.3 ± 0.5) × 10^{-2} and (2.0 ± 0.8) × 10^{-3} min^{-1} [Fig. 5(*b*)]. Addition of TFA (0.19 mol dm^{-3}) from the beginning of a second experiment significantly reduced the spin adduct concentration and the rate of its build-up [Fig. 5(*b*)].

Gas-phase Elimination of Tetranitromethane and Nitroform from **1**.—As seen from Table 6, **1** was thermally unstable when exposed to GLC conditions. Both elimination of tetranitromethane (formally) and trinitromethane took place, and both the side-chain nitro product **3** and the 2- and 5-nitro nuclear products were formed.

Discussion

General Remarks on the Nitration of 1,4-*Dimethylnaphthalene*.—The tendency of 1,4-dimethylnaphthalene to undergo nitration in the side-chain is well documented[7] and has been shown to proceed *via* adduct intermediates in some systems.[8] A comparative study[9] showed that two extreme cases, with bearing on the photonitration reaction, could be realized. First, nitration of 1,4-dimethylnaphthalene with nitrogen dioxide in dichloromethane led to almost exclusive side-chain substitution [92%, also 3 and 5% of the 2- (**4**) and 5-nitro isomer, respectively, were formed]. Second, coupling between the radical cation of 1,4-dimethylnaphthalene, presynthesized as the hexafluorophosphate salt, and nitrogen dioxide in dichloromethane gave 95% 2-nitro (**4**) and 5% 5-nitro product. In general, the extent of formation of the 2-nitro isomer **4** by other nitration mechanisms was found to be small, reaching 18% in, for example, the nitration by nitronium ion in the presence of azide to prevent the nitrous acid catalysed reaction. In this case, the 5-nitro isomer was the major product.

The chemistry described above indicates that the initial photochemical process, formation of the set of intermediates shown in Scheme 1, gives, in principle, at least one trivial pathway leading to **3**, the side-chain nitration product. We have earlier[3] shown for two substrates that the nitrogen dioxide concentration builds up during photolysis, and thus homogeneous nitration of 1,4-dimethylnaphthalene by nitrogen dioxide to give **3** must also occur to some extent.

Photochemistry in Dichloromethane.—We will start from the assumption that adducts **1** and **2** are the primary products from the initial photochemical reaction and that nitro substitution products are formed in secondary reactions from the adducts. This hypothesis is in best agreement with our findings.

Table 6 Product composition in the GLC analysis of a solution of adduct **1** in dichloromethane as a function of injection port temperature

Injection port temperature/°C	Product (%) 1,4-DMH	3	4	5-NO_2	Unidentified
100	27	25	13	10	23
200	36	21	11	11	20
300	47	18	9	7	14

The experiment in dichloromethane at −50 °C was run in order to minimize the occurrence of secondary reactions. Accordingly (Table 1), the combined yield of the primary products, adducts **1** and **2**, was very high, 90%, and the yield of the secondary product, **3**, only 7%. In this case, **3** is presumably formed by thermal nitration of 1,4-dimethylnaphthalene by photochemically generated nitrogen dioxide.[3] At −20 °C the amount of **3** had increased to 15% at the expense of **1** and **2** (82%), and at +20 °C **3** predominated (65%) over adducts (34%). Under the latter conditions, externally added acid further promoted the conversion of the adducts into nitro products, **3** and the nuclear substitution product **4**. It is thus established that **4** originates from an acid-promoted follow-up reaction of **1** and/or **2**.

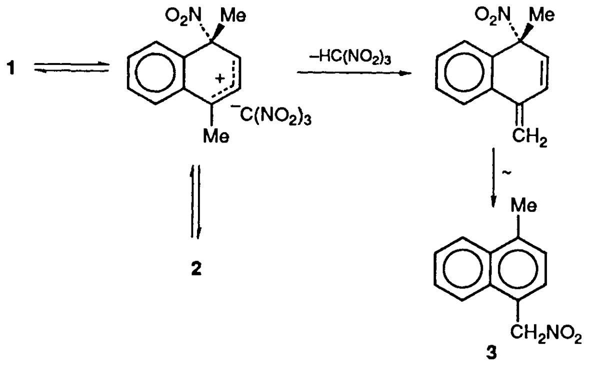
Photochemistry in Acetonitrile.—At −20 °C, the run in acetonitrile after 1 h gave adducts **1** and **2** (62 and 12%, respectively), **3** (6%) and two new adducts, **5** and **6**, assigned the structure of the epimers of 1,4-dimethyl-1-nitrito-4-trinitromethyl-1,4-dihydronaphthalene on the basis of ^1H NMR spectroscopy. As shown in Fig. 2, **5** and **6** originated from the thermal rearrangement of **2**; on the timescale of the photochemical experiment and with the analytical limitations imposed by the NMR spectral technique, it was not possible to establish whether **5** and **6** might be primary products as well.

At +20 °C, the pattern of products showed similar features, except that the proportion of **3** was larger and grew with time owing to the slow overall elimination of nitroform from **1**, which occurred spontaneously at this temperature with $\tau_{\frac{1}{2}} \approx 14$ h. A new feature was the formation of the 2-nitro isomer **4** toward the end of the photolysis period in a proportion of *ca.* 15%. Thus **4** again turns out to be a secondary product, formed in a thermal process from the adducts. The formation of **4** in acetonitrile is most likely induced by acid (nitroform), formed during photolysis and with maximum concentration toward the end of the run.

Thermal Rearrangement of **1** *to* **2**.—The key processes for a full understanding of the photochemical experiments are the further thermal reactions of the initially formed adducts, **1** and **2**. Pure **1** rearranged in acetonitrile (Fig. 2, Table 3) to give **2** which then underwent further rearrangement to **5** and **6** (see below). The reaction **1** ⟶ **2** was fast in acetonitrile, the first-order rate constant for reaching equilibrium being 0.11 min^{-1} at 20 °C, but *ca.* 1.4×10^2 times slower in dichloromethane ($k \approx 8 \times 10^{-4}$ min^{-1}). In the latter solvent, the degree of conversion of **1** into **2** at equilibrium was about 30%; this change was reflected in minor UV spectral changes only, making kinetic experiments dependent on NMR spectroscopy for their correct interpretation.

Once **2** was present in solution, it underwent further reactions, spontaneously as well as in the presence of additives. In acetonitrile addition of methanesulfonic acid led to a build-up of absorbance in the 250–300 nm region (Fig. 3), characteristic of naphthalenes with non-conjugated substituents. The products from the acid-promoted reaction were predominantly 1,4-dimethylnaphthalene (42%) and **3** (49%) which, for all practical purposes at hand, have indistinguishable UV spectra, and some **4** (9%), too small an amount to be reliably detectable by its UV spectral characteristics. An important aspect of the acid-promoted reaction was its rate behaviour (Table 4), showing limiting behaviour with $k_{\lim} \approx 0.11$ min^{-1} even at low [acid]. This is the same rate constant as that of the rearrangement of **1** to **2**. The same rate constant also was determined [Fig. 4(*a*)] when base was added to **1** in acetonitrile, again demonstrating the key nature of the rearrangement step for further thermal reactions in the system. We did not pursue studies of the base-promoted reaction with respect to products, since such conditions are not relevant to the problem at hand, except for noting that extensive changes did take place (^1H NMR spectroscopy).

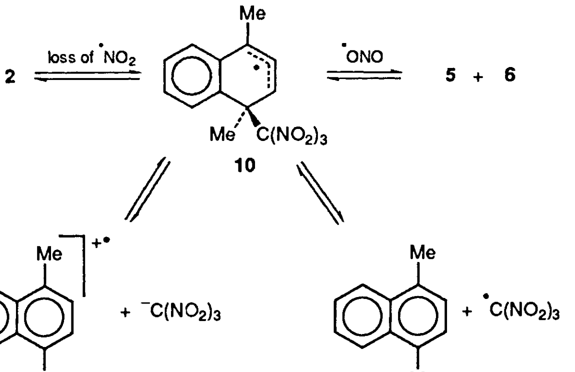
The rearrangement of **1** to **2** is assumed to be polar with trinitromethyl acting as the leaving group, as shown in Scheme 2. The large rate ratio of 1.4×10^2 between acetonitrile and dichloromethane and the fact that nitrito isomers **5** and **6** begin to appear only after a sizeable concentration of **2** has been built up, favour this assumption. The fact that **3** begins to form from the beginning is then explicable by elimination of nitroform from the intermediate nitrocyclohexadienyl cation, analogous chemistry being known from the chemistry of acetoxy–nitro adducts.[8]



Scheme 2

Thermal Rearrangement of **2** *to* **5** *and* **6**.—Once **2** has been formed in acetonitrile solution, a pathway to **5** and **6** opens through a nitro–nitrito rearrangement, the nature of which is usually assumed to be homolytic.[4] This process would proceed *via* a trinitromethylcyclohexadienyl radical (**10**), identical in nature with the cyclohexadienyl intermediate of the oxidative substitution mechanism.[10] As such, it exists in equilibrium with trinitromethanide and the radical cation of 1,4-dimethylnaphthalene, a well-established general mechanism of radical cation chemistry.[10] We propose, on the basis of a recent study of the electron-transfer reaction between trinitromethanide and the radical cation of tris(4-bromophenyl)amine,[11] that **10** is also in equilibrium with 1,4-dimethylnaphthalene and trinitromethyl radical. This is a fundamental assumption for the initial step of homolytic aromatic substitution.[12] The mechanism is shown in Scheme 3.

The intervention of trinitromethyl radical requires further comment. It was recently[11] shown that a stable radical cation, like tris(4-X-phenyl)aminium (**11**; X = Br, Cl), underwent electron transfer from trinitromethanide ion to give trinitromethyl radical, probably *via* the equivalent of **10** in this system. There is reason to generalize this behaviour to the radical cation formed in any known photochemical transformation of an ArH/tetranitromethane (Scheme 1), since in most cases the $ArH^{\bullet +}$/trinitromethanide step is more strongly exergonic than that of the $\mathbf{11}^{\bullet +}$/trinitromethanide case. The reason that products can be formed from the intermediate trinitromethyl-



Scheme 3

cyclohexadienyl radical lies in the fact that it is rapidly trapped by nitrogen dioxide. However, some of this radical will always be present and decompose to give ArH and trinitromethyl radical. The latter is a little known species; it can be trapped with spin traps such as PBN,[5,6] and must therefore possess some stability. Its chemical fate is largely unknown, but a reasonably well founded assumption is that it loses NO_2 to give dinitrocarbene,[11] shown to be a very unstable species which decomposes to NO_2, NO and CO.[13]

The phenomena described above are now readily explained. Formed from **1** in an initially neutral solution in acetonitrile, **2** rearranges to **5** and **6** and an equilibrium is set up between these compounds *via* the common intermediate **10**. In the absence of added acid, the reaction to give the eventual product **3** is slow ($k \approx 6.7 \times 10^{-4}$ min^{-1}) and presumably mostly occurs *via* the polar mechanism of Scheme 2. The trinitromethyl radical can be trapped with PBN and the spin adduct concentration reaches a maximum approximately at the same time as $[\mathbf{2}]_{max}$ has been reached (Figs. 2 and 6). As expected, [spin adduct] is much smaller in the polar solvent, acetonitrile, than that in non-polar dichloromethane.

When acid is added in acetonitrile, the **10**/trinitromethanide + radical cation equilibrium is affected by protonation of trinitromethanide, thus driving the reaction toward formation of (1,4-dimethylnaphthalene)$^{\bullet +}$. One characteristic reaction of this species[9] is its ability to couple with nitrogen dioxide to give predominantly **4**, and we propose that in photolysis **4** will be also formed from the initial adducts by this mechanism. Otherwise, it is not understandable why **4** should not be formed during photolysis in dichloromethane or in the early stages of the acetonitrile runs. Another indication of the intervention of (1,4-dimethylnaphthalene)$^{\bullet +}$ is provided by the broadening of the methyl signal in its NMR spectrum in the early part of the reaction (Table 3), caused by $ArH^{\bullet +}$/ArH electron exchange.[14]

Another, more conventional pathway open to (1,4-dimethylnaphthalene)$^{\bullet +}$ would be deprotonation to give the corresponding benzylic radical, from which **3** might be formed by coupling with nitrogen dioxide and 1,4-dimethylnaphthalene by hydrogen atom abstraction. The experiments with added base are also explained by the base affecting the equilibrium **10**/trinitromethanide + radical cation, now by providing a rapid deprotonation pathway for the radical cation.

In dichloromethane, the reactions of **1** are slower than those in acetonitrile. Owing to experimental problems, it was difficult to obtain full evidence for the same reaction scheme as discussed above for acetonitrile. However, as expected from the non-polar character of dichloromethane, the pathway to 1,4-dimethylnaphthalene + trinitromethyl radical was favoured, as demonstrated by the spin trapping experiment of Fig. 5(*b*). The prediction that added acid would disfavour this pathway was also fulfilled. The fact that acid strongly increased the rate of formation of unconjugated naphthalenes has no counterpart in acetonitrile where the rate-limiting step was the rearrangement of **1** to **2**. A likely explanation of the effect of acid in dichloromethane is assistance to ionization by the strongly hydrogen-bonding trifluoroacetic acid, *i.e.*, a medium effect. This would explain the non-integral order of 1.5 in [TFA].

Conclusions

The primary products formed in the photolysis of 1,4-dimethylnaphthalene are adducts **1** and **2**. Possibly, some side-chain nitro product **3** is formed by nitration of 1,4-dimethylnaphthalene by nitrogen dioxide, formed in the photochemical step. The major part of **3** is formed *via* secondary reactions of the adducts. The nuclear nitration product **4** is also formed from the primary adducts in acid-promoted, non-photochemical processes. The mechanism of the thermal reactions is a complex mixture of polar and radical steps.

Experimental

Materials.—Apart from compounds used in ref. 1, 1,4-dimethylnaphthalene and pentaisopropylguanidine were obtained from Merck, and PBN from Aldrich. The nitro derivatives of 1,4-dimethylnaphthalene were available from earlier work.[9]

Methods.—For photolysis experiments and kinetics methods, see ref. 1. During photolysis, solutions were protected from atmospheric moisture. The EPR spectra were recorded on a Bruker ER-200D SRC instrument at a temperature of 23–24 °C. The measurements were performed in the automation mode, all settings being identical during the whole run and between different experiments. All solutions were prepared under argon.

WARNING. While we did not experience any incidents while working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits[15] and therefore due care should be taken in handling mixtures of tetranitromethane and organic compounds.

Photonitration of 1,4-*Dimethylnaphthalene with Tetranitromethane: General Procedure.*—A solution of 1,4-dimethylnaphthalene (1 g) and tetranitromethane (2 mol dm^{-3}) in dichloromethane (16 cm^3) was irradiated at -50, -20 or $+20$ °C with filtered light (cut-off <435 nm); similar reactions in acetonitrile (16 cm^3) at -20 and $+20$ °C were also studied. Aliquots were withdrawn at appropriate time intervals, the volatile material removed under reduced pressure at $\leqslant 0$ °C, and the product composition determined by ^{1}H NMR spectral analysis (Tables 1 and 2).

Photochemical Reaction in Dichloromethane at -50 °C.—Reaction of 1,4-dimethylnaphthalene (1 g) in dichloromethane at -50 °C, as above, gave a crude product after bleaching of the CT band which was shown by ^{1}H NMR spectroscopy to be a mixture of two adducts, **1** (81%) and **2** (9.3%), the nitromethyl compound **3** (7.4%) and an unidentified compound (2.2%), exhibiting a $-CH_2X$ signal (δ 5.69) in the ^{1}H NMR spectrum (presumably, X is equal to $-ONO$).

The major product was isolated from the crude product by crystallization from dichloromethane at -20 °C to give adduct **1** as plates, m.p. 100–100.5 °C (decomp.), $\delta(CDCl_3)$ 2.11 (s, Me), 2.23 (s, Me), 6.26 (d, *J* 10.5 Hz, H2/H3), 6.68 (d, *J* 10.5 Hz, H3/H2), 7.40–7.51 (m, 3 H) and 7.58–7.61 (m, 1 H) [lit.,[2] δ 2.10 (s, Me), 2.20 (s, Me), 6.24 (d, *J* 10.7 Hz, 1 H), 6.67 (d, *J* 10.7 Hz, 1 H) and 7.75 (m, 4 H)].

The minor adduct **2** was not isolated but was characterized by its ^1H NMR spectrum: δ 2.03 (s, Me), 2.12 (s, Me), 6.49 (d, J 10.5 Hz, H2/H3) and 6.66 (d, J 10.5 Hz, H3/H2) [lit.,[2] δ 1.96 (s, Me), 2.06 (s, Me), 6.41 (d, J 10.7 Hz, H2/H3) and 6.62 (d, J 10.7 Hz, H2/H3)]. The remainder of the spectrum was obscured by signals of other components of the mixture.

The nitromethyl compound **3** was identified by comparison of its ^1H NMR spectrum with that of authentic material: δ ($CDCl_3$) 2.74 (s, Me), 5.89 (s, CH_2NO_2), 7.37 (d, J 7.1 Hz, 1 H), 7.50 (d, J 7.1 Hz, 1 H), 7.62 (m, 2 H) and 8.06 (m, 2 H).

Photolysis of 1,4-*Dimethylnaphthalene in Dichloromethane, Saturated with Toluene*-p-*sulfonic Acid, at* 20 °C.—Photolysis of 1,4-dimethylnaphthalene (1 g) in dichloromethane, saturated with toluene-*p*-sulfonic acid ($\approx$12 mmol dm^{-3}) at 20 °C gave, after bleaching of the CT band, a crude product, shown by ^1H NMR spectroscopy to be a mixture of **1** (8.0%), **2** (<1%), **3** (78.8%) and **4** (13.2%).

Photochemical Reaction in Acetonitrile at −20 °C.—Reaction of 1,4-dimethylnaphthalene (1 g) and tetranitromethane (2 mol dm^{-3}) in acetonitrile at −20 °C as above for 6.25 h gave a crude product (61% conversion into products) which was shown by ^1H NMR spectroscopy to be a mixture of 1,4-dimethylnaphthalene, four adducts **1** (71.5% based on consumed starting material), **2** (17.0%), **5a** (3.3%) and **6a** (1.4%), and the nitromethyl compound **3** (6.8%).

Adduct **5a** was tentatively identified as one epimer of 1-hydroxy-1,4-dimethyl-4-trinitromethyl-1,4-dihydronaphthalene on the basis of its ^1H NMR spectrum: δ($CDCl_3$) 1.65 (s, 1-Me), 2.09 (s, 4-Me), 5.95 (d, J 10.1 Hz, H2/H3) and 6.36 (d, J 10.1 Hz, H3/H2); the remainder of the spectrum was obscured by signals of other components of the mixture.

Adduct **6a** was tentatively identified as the second epimer of 1-hydroxy-1,4-dimethyl-4-trinitromethyl-1,4-dihydronaphthalene: δ($CDCl_3$) 1.57 (s, 1-Me), 1.98 (s, 4-Me), 5.97 (J 10.2 Hz, H2/H3) and 6.29 (d, J 10.2 Hz, H3/H2); the remainder of the spectrum was obscured by signals of other components of the mixture. It is assumed that adducts **5a** and **6a** were formed from the corresponding nitrites **5** and **6** by hydrolysis either during photolysis or subsequently during the work-up procedure.

Rearrangement of trans-1,4-*Dimethyl*-1-*nitro*-4-*trinitromethyl*-1,4-*dihydronaphthalene* (**1**) *in Acetonitrile at* 20 °C.—A solution of adduct **1** (144 mg) in acetonitrile (14 cm^3) was kept at 20 °C. Aliquots were withdrawn at appropriate time intervals, the solvent removed at 0 °C, and the ^1H NMR spectrum in $CDCl_3$ recorded. Although **1** was labile in acetonitrile it underwent no detectable change in $CDCl_3$ for at least 2 h. The composition of each sample is given in Table 3 (see also Fig. 2). Initially, adduct **2** was formed by epimerization of **1**, and the nitromethyl compound **3** by elimination/nitration. Subsequently, the nitrite esters of adducts **5** and **6** increased in concentration and then decreased again, as all adducts were eventually transformed into the nitromethyl compound **3** (final yield >95%).

Rearrangement of trans-1,4-*Dimethyl*-1-*nitro*-4-*trinitromethyl*-1,4-*dihydronaphthalene* (**1**) *in Dichloromethane at* 20 °C.—*Experiment* 1. A solution of **1** (60 mg) in dichloromethane (6 cm^3) was stored at 20 °C and aliquots of 1 cm^3 each removed at appropriate time intervals. The solvent was removed under reduced pressure and the ^1H NMR spectrum recorded in $CDCl_3$.

Experiment 2. A solution of **1** (8 mg) in CD_2Cl_2 (0.7 cm^3) was stored at 20 °C and monitored by ^1H NMR spectroscopy at appropriate time intervals.

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