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Photochemical Nitration by Tetranitromethane. VIII.† Isolation, X-Ray Structural Analysis and Chemical Properties of a *Vicinal* Nitro/trinitromethyl Adduct from Fluoranthene

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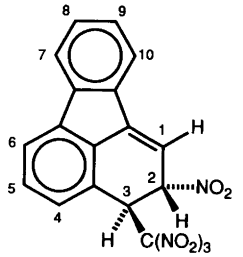
The photolysis of a dichloromethane solution of fluoranthene and tetranitromethane by light with cut-off at $\lambda < 435$ nm gave a mixture of nitro/trinitromethyl adducts (≈10%) and nitrofluoranthenes (≈60%). One of the adducts could be isolated and proved to be a *vicinal* one, *trans*-2-nitro-3-trinitromethyl-2,3-dihydrofluoranthene (**1**), as demonstrated by an X-ray crystallographic analysis. Adducts were formed in acetonitrile too, but the adduct yield was smaller. Adduct **1** was stable for many days in dichloromethane but slowly ($\tau_{1/2}$ about 19 h) eliminated nitroform to give 2-nitrofluoranthene in acetonitrile, whereas added hindered or unhindered bases strongly accelerated the reaction in both dichloromethane and acetonitrile. Under GLC conditions **1** analyzed as 2-nitrofluoranthene. The spin adduct of trinitromethyl radical and α-phenyl-*N*-*tert*-butylnitrone (PBN) was formed and detected by EPR spectroscopy in low concentration and persisted for a long time when **1** and PBN were kept in dichloromethane solution.

The photolysis of aromatic compounds in the presence of tetranitromethane leads to the partial, sometimes predominant, formation of two types of adduct, *viz.* nitro/trinitromethyl and hydroxy/trinitromethyl adducts, the latter type presumably being formed via nitrito/trinitromethyl adducts which decompose photochemically and/or by hydrolysis during work-up. The adducts then decompose either spontaneously (for example in acetonitrile) or thermally (for example during GLC) to give nitro and/or trinitromethyl substitution products.[1–4]

Naphthalene gave mainly a mixture of *cis*- and *trans*-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (total ≈44% yield in dichloromethane or acetonitrile at −20°C), from which the *cis* isomer was isolated in pure form and identified by an X-ray structural study.[1,2] NMR spectral analysis also showed the presence of a small amount (16%) of an isomer of 1-nitro-2-trinitromethyl-1,2-dihydronaphthalene which could, however, not be obtained in pure form. Other naphthalene derivatives were then explored in order to find additional examples of isolable adducts, so that the novel chemistry of these compounds—a key to the understanding of aromatics/tetranitromethane photochemistry—could be further studied. Fluoranthene (numbering, see formula of adduct **1** below) turned out to provide one missing class of adduct, namely a *vicinal* nitro/trinitromethyl adduct. This paper describes the isolation of *trans*-2-nitro-3-trinitromethyl-2,3-dihydrofluoranthene (**1**), its characterization by X-ray crystallography and a study of its chemical properties insofar as they are related to the elimination of nitroform with formation of nitro-substitution products.



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Results

Formation and isolation of adduct **1**. The photolysis of the orange–red charge-transfer (CT) complex of fluoranthene/tetranitromethane in dichloromethane at 20°C for 21.5 h gave a product mixture, containing about 25% of **1**, other adducts (17%) and nitrofluoranthenes (58%). From this mixture **1** was isolated in pure form by crystallization from dichloromethane and dichloromethane/pentane at −5°C.

† Part VII, see Ref. 3.
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Table 1. Overview of yields of products from the photolysis of fluoranthene (0.31 mol dm^{-3}) and tetranitromethane (0.62 mol dm^{-3}) in dichloromethane at −20°C.

t/h	Conversion(%)	Adduct 1(%)	Other adducts(%)	Total $ArNO_2$(%)
2	23	33.0[a]	—	67.0[a]
3	33	19.5	8.1	72.4
4	43	23.5	7.9	68.6
5.5	59	14.9	5.7	78.7
8.5	75	10.7	7.0	82.3
23.7	~100[b]	11.5[b]	9.3[b]	79.1[b]

[a] These values are uncertain owing to problems with the integral of the ^1H NMR spectrum at low conversion. [b] These values are uncertain because they are based on a rather complex NMR spectrum which reveals probable products of further reaction of initially formed materials.

A similar reaction, run at −20°C, was monitored by ^1H NMR spectral analysis (Table 1). The maximum absolute yield of **1** was ≈10% during the run, whereas the yield of 'other adducts' increased from 3 to 9%. The major part of the product consisted of nitrofluoranthenes, increasing in absolute yield from 15 to 62% during the period up to 8.5 h; the yield at full conversion is somewhat uncertain owing to the probably formation of secondary products from initially formed materials. GLC examination of the crude product mixture gave an apparent composition of nitrofluoranthenes of 1-/2-/3-/7-/8-isomers of 6 : 42 : 31 : 6 : 15. Owing to the complexity of the original mixture it was not possible experimentally to establish the origin of these isomers; undoubtedly several nitrofluoranthenes must be formed directly, either by nitration via photochemically generated NO_2 or by coupling between $(fluoranthene)^{\bullet+}$ and NO_2, whereas others wholly or partially stem from elimination of nitroform from the adduct during GLC.

A similar photolysis experiment in acetonitrile at −20°C gave a low final yield, ≈6%, of adduct **1**, practically no other adducts and about 70% of nitrofluoranthenes (Table 2).

X-Ray structure of **1**. The structure of adduct **1** was determined by single-crystal X-ray analysis. A perspective drawing of *trans*-2-nitro-3-trinitromethyl-2,3-dihydrofluoranthene **1**, $C_{17}H_{10}N_4O_8$, m.p. 123.5–124°C (decomp.), is presented in Fig. 1 with corresponding atomic coordinates in Table 3. In the solid state the ring to which addition has occurred is somewhat buckled [torsion angles: C(1)–C(2)–C(16)–C(15) −16(1)°; C(13)–C(14)–C(15)–C(16) −18(2)°; C(2)–C(1)–C(13)–C(14) −9(2)°] and the torsion angle between the substituents at C(15) and C(16) is somewhat enlarged [N(1)–C(15)–C(16)–C(17) −133.4(8)°]. The plane of the NO_2 group at C(15) is close to perpendicular to the C(15)–C(14) bond. The orientation of the trinitromethyl group about the C(16)–C(17) axis is defined by the near perpendicular orientation of the N(4)–C(17) bond relative to the C(2)–C(16) bond [torsion angle: C(2)–C(16)–C(17)–N(4) −82(1)°]. Within the trinitromethyl group the relative orientations of the constituent nitro groups are such that the plane of the $N(3)O_2$ group is close to eclipsed with the C(17)–N(4) bond [torsion angle: O(31)–N(3)–C(17)–N(4) −8(1)°], the plane of the $N(4)O_2$ group is close to eclipsed with the C(17)–N(2) bond [torsion angle: O(41)–N(4)–C(17)–N(2) −7(1)°] and the $N(2)O_2$ group is orientated such that the magnitude of the torsion angles between its plane and the C(17)–N(3) and C(17)–C(16) bonds are similar [torsion-angles: O(22)–N(2)–N(17)–N(3) −32(1)°; O(21)–N(2)–C(17)–C(16) −28(1)°]. The spectroscopic data for adduct **1** were in accord with the established structure.

EPR spectral studies. We have earlier shown that the isolable adducts from naphthalene and 1,4-dimethylnaphthalene, *cis*-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene and *trans*-1-nitro-4-trinitromethyl-1,4-dihydro-1,4-dimethylnaphthalene, upon dissolution in dichloromethane or acetonitrile together with the spin trapping agent, α-phenyl-*N*-*tert*-butylnitrone (PBN) give EPR signals from the trinitromethyl spin adduct.[2,3] In the latter case, the signal was fairly strong and clearly

Table 2. Overview of yields of products from the photolysis of fluoranthene (0.21 mol dm^{-3}) and tetranitromethane (0.42 mol dm^{-3}) in acetonitrile at −20°C.

t/h	Conversion(%)[a]	Adduct 1(%)	Other adducts(%)	Total $ArNO_2$(%)
2	Very low[a]	Trace	—	Trace
4	Low[a]	30.4	—	79.6
8	44.9	18.4	Trace	81.6
24	78.4	7.0	1	92.0

[a] Fluoranthene has limited solubility in acetonitrile at −20°C and early 'conversion' values are meaningless while crystalline fluoranthene was present. This effect also accounts for the lower extent of conversion at 8 and 24 h.

Table 3. Fractional coordinates for atoms in *trans*-2-nitro-3-trinitromethyl-2,3-dihydrofluoranthene (**1**). The equivalent isotropic temperature factor is defined as one-third of the orthogonalized *U* tensor.

Atom	$10^4\,x/a$	$10^4\,y/b$	$10^4\,z/c$	$10^3\,U$
C(1)	3863(8)	4522(17)	17542(8)	24(3)
C(2)	3152(9)	5974(18)	17919(8)	26(3)
C(3)	3757(9)	7585(19)	18678(8)	33(6)
C(4)	5042(8)	7588(19)	19076(8)	27(6)
C(5)	5751(9)	6060(18)	18687(8)	30(6)
C(6)	5182(9)	4479(19)	17920(9)	34(3)
C(7)	5605(8)	2663(19)	17355(8)	26(3)
C(8)	6786(10)	1959(20)	17436(10)	40(7)
C(9)	6935(10)	52(23)	16841(9)	44(6)
C(10)	5917(11)	−940(20)	16165(9)	40(8)
C(11)	4726(10)	−216(19)	16058(9)	36(8)
C(12)	4560(8)	1632(18)	16645(8)	25(3)
C(13)	3451(8)	2867(19)	16699(8)	28(3)
C(14)	2279(8)	2798(21)	16078(9)	34(6)
C(15)	1404(9)	4511(19)	16274(8)	31(3)
C(16)	1756(8)	5864(19)	17393(8)	26(2)
C(17)	985(10)	5030(18)	18238(9)	29(3)
O(11)	1730(7)	7659(17)	15286(7)	50(5)
O(12)	444(7)	5332(15)	14337(6)	50(5)
O(21)	−804(6)	6144(14)	16877(7)	48(5)
O(22)	−902(7)	5860(16)	18688(7)	59(5)
O(31)	1853(7)	4559(16)	20242(7)	60(6)
O(32)	1415(7)	7738(18)	19563(7)	53(5)
O(41)	−50(7)	1773(14)	18233(7)	50(5)
O(42)	1940(8)	1806(14)	18465(8)	70(6)
N(1)	1173(8)	5995(21)	15230(8)	39(6)
N(2)	−363(7)	5778(16)	17901(9)	38(5)
N(3)	1469(8)	5796(24)	19478(9)	43(6)
N(4)	957(10)	2656(19)	18324(8)	49(6)

connected with the complex chemistry that this adduct undergoes spontaneously in solution. The signal from the naphthalene adduct was, on the other hand, weak and judged not to be of significance for the elimination chemistry of the adduct.

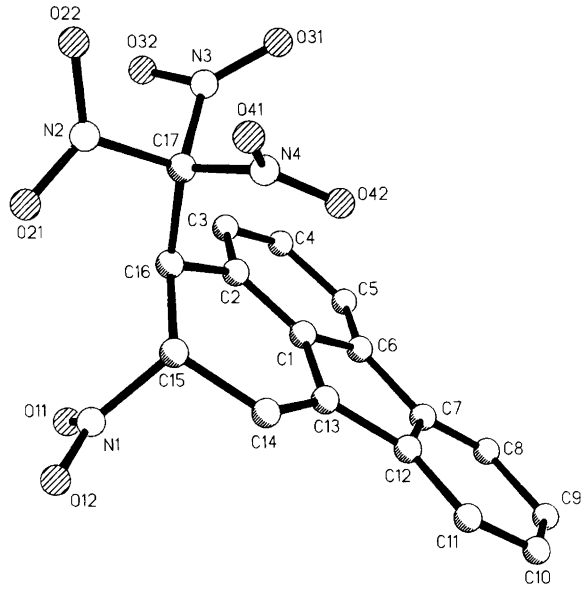

Fig. 1. Perspective view of the structure of **1**.

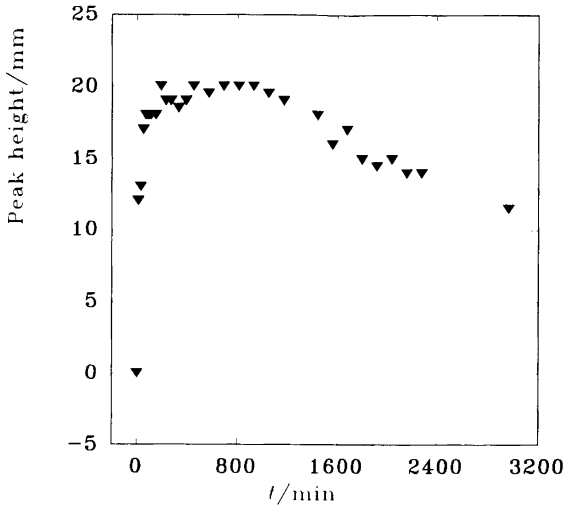

Fig. 2. EPR signal (peak height/mm) from the trinitromethyl-PBN spin adduct as a function of time in a dichloromethane solution of adduct **1** (27 mmol dm^{-3}) and PBN (0.22 mol dm^{-3}).

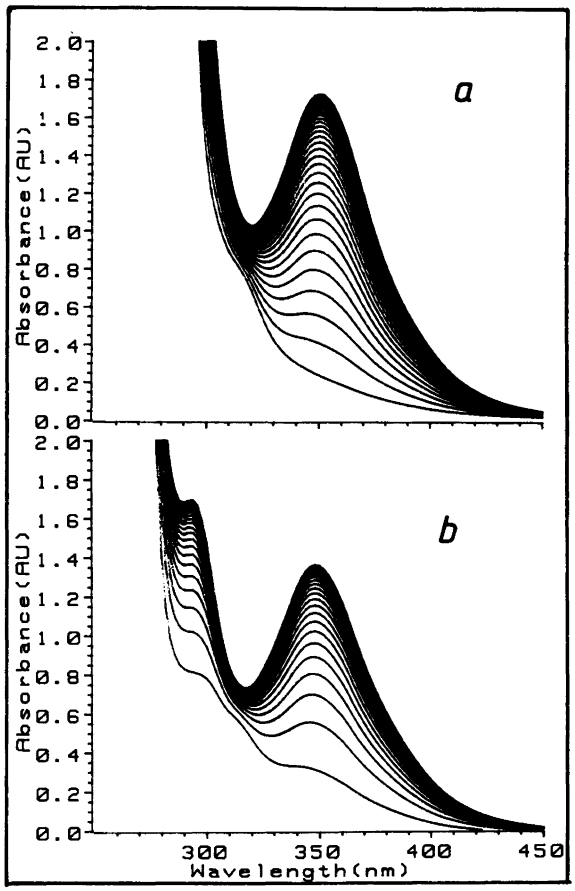

Fig. 3. Repeated UV spectral scans at 20.0°C from solutions of (a) **1** (0.097 mmol dm^{-3}) and 2,6-di-*tert*-butylpyridine (75 mmol dm^{-3}) in dichloromethane (30 s between spectra) and (b) **1** (0.087 mmol dm^{-3}) and 3,5-dimethylpyridine (1.38 mmol dm^{-3}) in acetonitrile (40 s between spectra).

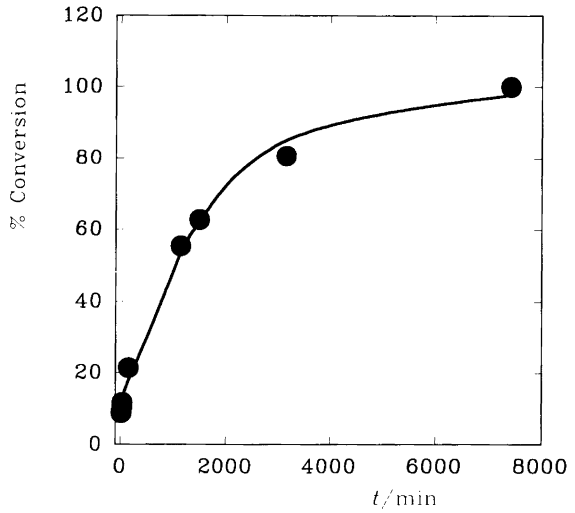

Fig. 4. Formation of 2-nitrofluoranthene from **1** in acetonitrile at 20°C. The first-order rate constant was 5.9×10^{-4} min^{-1} (curve).

Adduct **1** behaved in the same way as the naphthalene adduct, a weak EPR signal being observed as early as 5–10 min after mixing **1** (27 mmol dm^{-3}) and PBN (0.22 mol dm^{-3}) and persisting for a long period; after ≈50 h about 50% of the maximal concentration was still present (Fig. 2).

Kinetics of base-induced elimination. Adduct **1** was stable for long periods of time in dichloromethane but underwent elimination of nitroform in the presence of bases [for an example, see Fig. 3(a)]. The strongly hindered bases, 2,6-di-*tert*-butylpyridine and 2,6-dimethylpyridine, reacted at 20.0°C with second-order rate constants k_2 of 0.048 and 0.162 dm^3 mol^{-1} s^{-1}, whereas the unhindered 3,5-dimethylpyridine gave $k_2 = 27.7$ dm^3 mol^{-1} s^{-1}. Acetate ion (in the form of tetrabutylammonium hydrogendiacetate) reacted very fast, k_2 being $> 7 \times 10^3$ dm^3 mol^{-1} s^{-1}. In acetonitrile, the rate constants for elimination by 2,6-di-*tert*-butylpyridine and 2,6-dimethylpyridine were somewhat higher than in dichloromethane, 0.112 and 0.85 dm^3 mol^{-1} s^{-1}. For 3,5-dimethylpyridine, the reaction was not first-order in base in the concentration interval studied, k_2 varying between 2.6 and 5.3 dm^3 mol^{-1} s^{-1} between 2.59 and 0.71 mmol dm^3 in [base] [Fig. 3(b)].

The spontaneous elimination of nitroform in acetonitrile occurred with $k = 0.00061$ min^{-1} at 20.0°C, corresponding to $\tau_{1/2} = 19$ h, as measured by UV monitoring of the emerging trinitromethanide absorption band at 350 nm. The same constant was obtained by NMR spectral monitoring of the progress of the reaction (Fig. 4).

Discussion

The existence of adduct **1** was confirmed by an X-ray crystallographic study and thus also *vicinal* nitro/trinitromethyl adducts from aromatics are reasonably stable species in the solid state at ≤20°C, similarly to 1,4-adducts.[2,3] In dichloromethane solution, **1** is stable for long periods, whereas it slowly eliminates nitroform when allowed to stand in acetonitrile with a half-life of ≈20 h, a time period compatible with the irradiation times employed. If acetonitrile acts as the base in this reaction, the second-order rate constant comes out at $\approx 5 \times 10^{-6}$ dm^3 mol^{-1} s^{-1}. However, we suspect that traces of basic impurities in the acetonitrile may also affect the rate of elimination. Added bases, even hindered ones like 2,6-dimethyl- or 2,6-di-*tert*-butyl-pyridine, strongly increase the rate of elimination ($k_2 = 0.162$ and 0.048 dm^3 mol^{-1} s^{-1} in dichloromethane and 0.85 and 0.112 dm^3 mol^{-1} s^{-1} in acetonitrile, respectively). An unhindered pyridine base (3,5-dimethylpyridine) raises k_2 in dichloromethane to 27.7 dm^3 mol^{-1} s^{-1} and hydrogendiacetate ion to >7000 dm^3 mol^{-1} s^{-1}. In acetonitrile, elimination by 3,5-dimethylpyridine did not follow simple first-order kinetics, but the apparent k_2 was about 3 dm^3 mol^{-1} s^{-1} at [base] = 1.4 mM. The elimination of nitroform from a *vicinal* nitro/trinitromethyl compound, 1,1,1,3-tetranitro-2-phenylpropane, has been studied[5] and it was concluded that the mechanism is of the E1cB type, with the formation of the carbanion as the rate-determining step under basic conditions.

As before, we assume that the excitation of the CT complex directly gives a triad (**2**) of the radical cation, trinitromethanide ion and NO_2, from which product formation is initiated by complex formation (assumed to be of the σ type, **3**) between the radical cation and trinitromethanide ion.[6,7] σ-Complex **3** is unstable with respect to decay into substrate and trinitromethyl radical but can be trapped by NO_2, stemming either from the original triad or the supply of NO_2 which builds up in the solution during the run. This must be the mode of formation of the adducts which in most cases are detected. Another reactivity mode of radical cations is coupling with NO_2, earlier studied by us[8–10] and shown to be more selective than nitration both by NO_2 and NO_2^+.

$$\mathrm{ArH\cdots C(NO_2)_4} \xrightarrow{h\nu_{CT}} \mathrm{ArH^{\bullet+}\,(NO_2)_3C^-NO_2}\ (\mathbf{2}) \rightleftharpoons {}^{+}\mathrm{Ar(H)NO_2}$$

$$\Big\downarrow\Big\uparrow$$

$$\mathrm{{}^{\bullet}Ar(H)C(NO_2)_3}\ (\mathbf{3})$$

$$\Big\downarrow \mathrm{NO_2}$$

$$\mathrm{O_2NAr(H)C(NO_2)_3}$$

Contrary to the behaviour of naphthalene,[2] fluoranthene forms a relatively small proportion of adducts upon photolysis with tetranitromethane in dichloromethane, the major product being a mixture of nitrofluoranthenes. Similarly to naphthalene, the proportion of nitro product is higher at −20 than at +20°C (data for naphthalene within parentheses).

T/°C	Adduct(%)	Nitro products(%)
+20	43 (96)	58 (5)
−20	20 (87)	79 (14)

By the same reasoning applied earlier to the naphthalene case, we interpret the higher proportion of nitro product at the lower temperature as indicating that nitro products are at least partially formed by coupling between the radical cation and NO_2; the other feasible reactions, nitration of fluoranthene by NO_2[11,12] and/or elimination of nitroform from adducts would be expected to be slowed down at $-20°C$. In both cases the proportion of nitro product is expected to be larger in acetonitrile than in dichloromethane because of slow elimination of nitroform from adducts during photolysis; it may also be that the collapse of radical cation/trinitromethanide to form the neutral radical **3** is disfavoured in the polar acetonitrile compared with dichloromethane. We have shown earlier[7] for tris(4-bromophenyl)aminium ion that this type of reaction is much slower in acetonitrile than in dichloromethane, the ratio being $<10^{-3}$. The $ArH^{\cdot+}/NO_2$ reaction is not expected to be influenced that strongly by solvent effects.

We demonstrated earlier that *cis*-1,4-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (**4**) owes its reactivity in acetonitrile or dichloromethane to homolytic dissociation of the 1-nitro group to give the corresponding trinitromethylcyclohexadienyl radical, the presence of which was detected by its propensity to cleave off trinitromethyl radical.[3] This species was trapped by α-phenyl-*N*-*tert*-butylnitrone (PBN), to give a characteristic and fairly stable spin adduct. The facile cleavage of NO_2 from adduct **4** is explicable by the fact that the nitro group is bound to a tertiary carbon. Since the 1,4-nitro/trinitromethyl adduct from naphthalene also gave a weak, persistent signal of the trinitromethyl-PBN adduct,[2] it is obvious that such an adduct, with the 1-nitro group bound to a secondary carbon atom, also has some homolytic reactivity.

The EPR signal from the trinitromethyl spin adduct of PBN that was obtained from a solution of adduct **1** and PBN in dichloromethane (Fig. 2) shows that *vicinal* nitro/trinitromethyl adducts also possess homolytic reactivity. As in the naphthalene adduct case, we judge that this reaction mode has nothing to do with the more rapid solution chemistry taking place during photolysis. We do however wish to put its existence on record, since it represents an interesting type of radical reaction.

Experimental

Materials. Tetranitromethane, fluoranthene and 2,6-lutidine were purchased from Aldrich Co. 2,6-Di-*tert*-butyl-4-methylpyridine and 2,6-di-*tert*-butylpyridine were from Fluka AG, and dichloromethane (*zur Rückstandsanalyse*) and acetonitrile (UVASOL) were from Merck AG.

Methods. Procedures for carrying out photolyses, kinetic experiments and NMR spectral analysis have been described before.[2,3] The photolysis 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.

WARNING! While we did not experience any incidents in working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be exercised in handling mixtures of tetranitromethane and organic compounds.[13] Nitrofluoranthenes are suspected mutagens and carcinogens and should be handled accordingly.

General procedure for the photonitration of fluoranthene with tetranitromethane. A solution of fluoranthene (1 g, 0.31 mol dm^{-3}) and tetranitromethane (0.62 mol dm^{-3}) in dichloromethane or acetonitrile was irradiated at $+20$ or $-20°C$ with filtered light ($\lambda_{cut\text{-}off} < 435$ nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at $\leqslant 0°C$, and the product composition determined by NMR spectral analysis (Tables 1 and 2).

Reaction in dichloromethane at $+20°C$ and the identification of the major product. Reaction of fluoranthene/tetranitromethane in dichloromethane at $+20°C$, as above, for 21.5 h gave a mixture in which 57% conversion of fluoranthene into products had occurred. The composition of the mixture was shown (^1H NMR spectroscopy) to be: adduct **1** (26%), other adducts (17%) and aromatic nitro compounds (57%). The major adduct **1** was isolated by crystallization of the mixture from dichloromethane and dichloromethane/pentane at $-5°C$ to give trans-2-*nitro-3-trinitromethyl-2,3-dihydrofluoranthene* (**1**, 316 mg), m.p. 123.5–124°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1610, 1590, 1570, 1545, 1295 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.01 (dd, $J_{2,1}$ 5.9 Hz, $J_{2,3}$ 1.1 Hz, H2), 6.06 (br s, H3), 6.60 (d, $J_{1,2}$ 5.9 Hz, H1), 7.09 (dd, $J_{4,5}$ 7.8 Hz, $J_{4,6}$ 0.6 Hz, H4), 7.34–7.50 (m, 3 H), 7.67–7.76 (m, 3 H). ^{13}C NMR ($CDCl_3$) δ 42.7, 80.2, 109.3, 121.5, 122.2, 123.6, 126.2, 128.4, 131.2, 132.0; the remaining carbon resonances were not detected in the weak spectrum.

*GLC examination of adduct **1** and 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 260°C. While the pure adduct **1** decomposed cleanly to give 2-nitrofluoranthene, the crude product from the nitration in dichloromethane at $+20°C$ gave an apparent nitro compound composition of: 1-nitro, 7-nitro- ($\approx 1:1$, total 12.5%), 2-nitro- (41.8%), 3-nitro (30.5%) and 8-nitro-fluoranthene (14.5%).

*Reaction of adduct **1** with 2,6-lutidine in dichloromethane.* A solution of adduct **1** (98 mg) in dichloromethane (2 ml) and 2,6-lutidine (31 mg) was stored at 20°C for 17.5 h, and the volatile material removed under reduced pressure

to give a residue (53 mg) shown (^{1}H NMR) to be essentially pure 2-nitrofluoranthene. Filtration of a dichloromethane solution of the residue through a short silica gel column, followed by recrystallization from dichloromethane/pentane gave pure 2-nitrofluoranthene, m.p. 160–161°C (lit.[14] m.p. 159.5–160°C). ν_{max} (KBr) 1525, 1342, 890 cm^{-1}. ^{1}H NMR (CD_3CN) δ 8.84 (d, *J* 1.7 Hz, 1 H), 8.67 (d, *J* 1.7 Hz, 1 H), 8.15–7.43 (m, 7 H).

Decomposition of adduct **1** *in* CD_3CN. A solution of **1** (9.5 mg) in CD_3CN (0.7 ml) was stored at 20°C and the NMR spectrum of the solution monitored at appropriate time intervals. The spectra revealed an essentially quantitative conversion of **1** into 2-nitrofluoranthene with a half-life of 19.5 h (Fig. 4).

Crystal data for **1**. $C_{17}H_{10}N_4O_8$, $M = 398.29$, monclinic, space group $P2_1$, $a = 11.124(25)$, $b = 6.286(4)$, $c = 11.856(4)$, $\beta = 103.84(4)°$, $V = 804.9$ Å^3, $Z = 2$, μ(Mo-Kα) 1.34 cm^{-1}, MoKα radiation ($\lambda = 0.71073$ Å). Data were collected at 123 K using a Stoe 4-circle diffractometer for a blade-shaped transparent yellow crystal of dimensions $1.0 \times 0.1 \times 0.02$ mm. The number of independent reflection intensities measured was 1452 for which the value of $wR_2 = 0.178$ (the weighted *R*-factor fased on F^2). The subset for which $I > 2\sigma(I)$ had a conventional agreement factor $R_1 = 0.069$% based on *F*. All refinement and geometry calculations were carried out using SHELXL92. Atomic coordinates, bond lengths and angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre in cif format.

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