Succinimidylation and nitration of aromatic compounds by photolysis with *N*-nitrosuccinimide

Jane Calvert,[b] **Lennart Eberson,***[a] **Michael P. Hartshorn***[b] **and Jan O. Svensson**[a]
[a] *Chemical Center, Lund University, PO Box 124, S-221 00 Lund, Sweden*
[b] *Department of Chemistry, University of Canterbury, Christchurch, New Zealand*

N-Nitrosuccinimide (S-NO_2) engages in weak charge transfer complexes with aromatic compounds (ArH). Upon photolysis with light of $\lambda > 345$ nm in dichloromethane, electron transfer within the charge transfer complex leads to the triad [$\mathrm{ArH^{\bullet+}\,S^-\,NO_2}$] from which products of eventual succinimidylation and/or nitration develop by initial attack of succinimide anion upon the radical cation. Photolysis in the presence of trifluoroacetic acid (0.4 mol dm^{-3}) causes inactivation of S^- by protonation, making EPR detection of $\mathrm{ArH^{\bullet+}}$ or radical cations formed by its further transformations possible. In acetonitrile, trifluoroacetic acid is too weak effectively to protonate S^-, whereas addition of stronger acids again leads to the development of EPR spectra of $\mathrm{ArH^{\bullet+}}$ in the case of 9,10-dimethylanthracene, the intensity increasing with decreasing p*K* of the acid.

An X-ray crystal structure is reported for *N*-nitrosuccinimide.

Tetranitromethane forms charge-transfer complexes with aromatic substrates (ArH), photolysis of which induces 1,2- and/or 1,4-addition of tetranitromethane across the aromatic nucleus in the nitro–trinitromethyl and/or nitrito–trinitromethyl fashion.[1] The adducts are thermally and chemically labile but can be isolated and characterized after careful work-up. The mechanism has been shown[2] to involve initially the light-promoted formation of a triad of $\mathrm{ArH^{\bullet+}}$, trinitromethanide ion and NO_2 within 3 ps [eqn. (1)]. Out of the possible combinations

$$\mathrm{ArH}\cdots\mathrm{C(NO_2)_4} \xrightarrow[<3\,\mathrm{ps}]{h\nu_{\mathrm{CT}}} \mathrm{ArH^{\bullet+}(NO_2)_3C^-NO_2} \qquad (1)$$

of pairwise reactions within the triad, the $\mathrm{ArH^{\bullet+}}$–trinitromethanide reaction has been shown to be the favoured one[3] [eqn. (2)]. Thus the initial selectivity of the reaction is

$$\mathrm{ArH^{\bullet+}(NO_2)_3C^-NO_2} \longrightarrow \mathrm{Ar(H)C(NO_2)_3^{\bullet}} \qquad (2)$$

determined by the nucleophilic reactivity of trinitromethanide ion [$n(\mathrm{CH_3I}) = 2.9$], slightly higher than that of fluoride ion (2.7) but lower than that of acetate ion (4.3), toward $\mathrm{ArH^{\bullet+}}$. In the third step [eqn. (3)], the neutral trinitromethyl-

$$\mathrm{Ar(H)C(NO_2)_3^{\bullet}} + \mathrm{NO_2} \longrightarrow$$
$$\mathrm{Ar(H)C(NO_2)(NO_2)} + \mathrm{Ar(H)C(NO_2)_3(ONO)} \qquad (3)$$

cyclohexadienyl radical is attacked by NO_2, the radical coupling nature of this process ensuring a fairly low regioselectivity.

There is evidence that other species formally carrying nitronium ion react in a similar way upon photolysis with ArH, for example nitropyridinium ion, $\mathrm{NO_2Py^+}$, or its substituted derivatives. Here adducts have been characterized, and assumed to be formed by a reaction analogous to eqn. (2) with pyridine replacing trinitromethanide ion.[4] Pyridine is a stronger nucleophile than trinitromethanide ion, on the $n(\mathrm{CH_3I})$ scale by 2.3 units, and known to react very fast with radical cations.[5]

A similar situation, avoiding the polarity of nitropyridinium ions and the complication that they might participate in an ionization equilibrium generating nitronium ion, can be created by using *N*-nitrosuccinimide (to be denoted S-NO_2) as the acceptor molecule in the CT complex. Photolysis of such a complex [eqn. (4)] would create a triad of $\mathrm{ArH^{\bullet+}}$, succinimide

$$\mathrm{ArH}\cdots\mathrm{S\text{-}NO_2} \xrightarrow{h\nu_{\mathrm{CT}}} \mathrm{ArH^{\bullet+}S^-NO_2} \qquad (4)$$

anion (S^-) NO_2, where S^- is a base/nucleophile of higher strength than pyridine (p*K* of SH 9.5, $\mathrm{PyH^+}$ 5.2). Since little is known about the reactivity of S^- toward radical cations, it is not obvious what kind of reactivity would determine the fate of such a triad, but in view of its higher basicity–nucleophilicity one might anticipate that the $\mathrm{ArH^{\bullet+}}$–S^- interaction would be predominant, leading to bond formation and/or proton abstraction depending on the structure of $\mathrm{ArH^{\bullet+}}$. The succinimide anion is difficult to oxidize [$E^\circ(\mathrm{S^\bullet/S^-}) = 2.2$ V][6] and it is therefore unlikely that electron transfer between $\mathrm{ArH^{\bullet+}}$ and S^- would take place. We now describe the results of an exploratory study of the photolysis of a few S-NO_2–ArH pairs. The main conclusion is that S-NO_2 engages in rather weak CT complexes with ArH which limits the productive photochemistry to ArH with $E^\circ(\mathrm{ArH^{\bullet+}/ArH}) < 1.5$ V (*vs.* Ag/AgCl).

Results

N-Nitrosuccinimide is a surprisingly little studied compound.[7] It is reported to be 'only barely explosive' upon strong heating, and to be ineffective as a nitrating agent under thermal conditions. S-NO_2 is best prepared by treatment of succinimide by ammonium nitrate and trifluoroacetic anhydride,[7d] which in our hands gave a 10% yield of purified material. The crude compound contained succinimide, most of which could be removed by recrystallization from ethanol. The experiments described here were made with samples containing *ca.* 5% of succinimide, unless otherwise stated.

Single-crystal X-ray analysis of S-NO_2

The structure of *N*-nitrosuccinimide, $C_4H_4N_2O_4$, mp 86–87 °C, obtained by a further recrystallization of S-NO_2 from dichloromethane–carbon tetrachloride, was determined by single-crystal X-ray analysis. A perspective drawing showing the connectivity is presented in Fig. 1. In this structure the carbon framework is slightly twisted as seen from the torsional

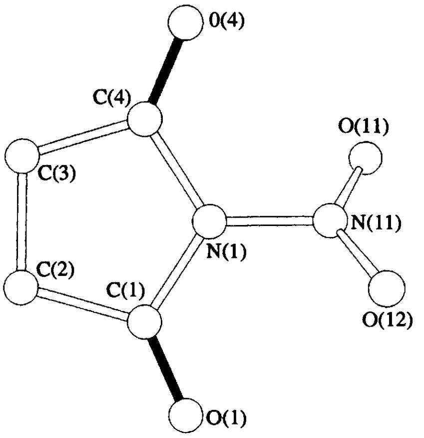


Fig. 1 Perspective drawing of *N*-nitrosuccinimide indicating the connectivity of the structure; double bonds are shown in black

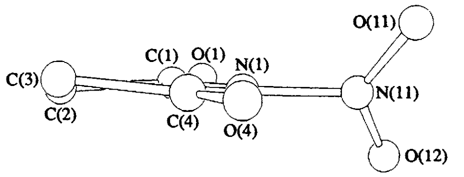


Fig. 2 Perspective drawing of *N*-nitrosuccinimide showing the nature of the buckling of the ring and the orientation of the nitro group.

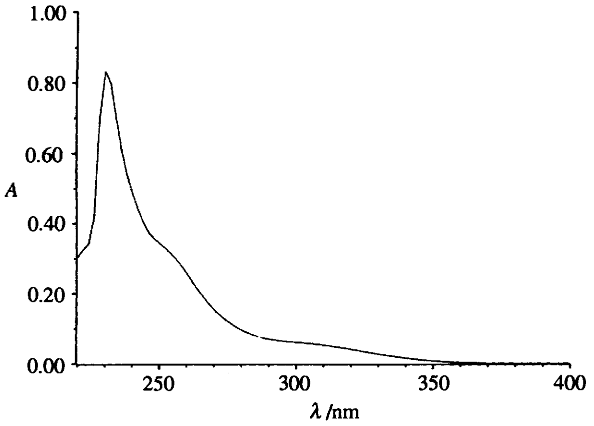


Fig. 3 UV spectrum of *N*-nitrosuccinimide (6.3×10^{-4} mol dm^{-3}) in dichloromethane

angle C(1)–C(2)–C(3)–C(4) −10.5(7)°, and the plane of the nitro group is displaced from coplanarity with the rough plane of the heterocyclic ring [torsional angles: C(4)–N(1)–N(11)–O(11) −49(1)°; C(1)–N(1)–N(11)–O(12) −52(1)° (see Fig. 2)]. The nitrogen atom, N(1), clearly has trigonal coordination (sp^2) as is seen in the closely related structure of *N*-bromosuccinimide,[8] and the N(1)–N(11) bond length is 1.412(6) Å, commensurate with N–NO_2 bond lengths in *N*-nitroamide-type structures,[9] ranging from 1.36 to 1.42 Å.

Cyclic voltammetry

In acetonitrile–tetrabutylammonium hexafluorophosphate S-NO_2 was reduced with E_{pc} at −0.84 V (reference electrode,[10] Ag/AgCl; sweep rate 0.2 V s^{-1}) with no sign of any corresponding reverse current up to a sweep rate of 50 V s^{-1} (technical limit of the instrument). In dichloromethane–tetrabutylammonium hexafluorophosphate E_{pc} was −1.01 V under the same conditions and again irreversibility was observed up to a sweep rate of 50 V s^{-1}.

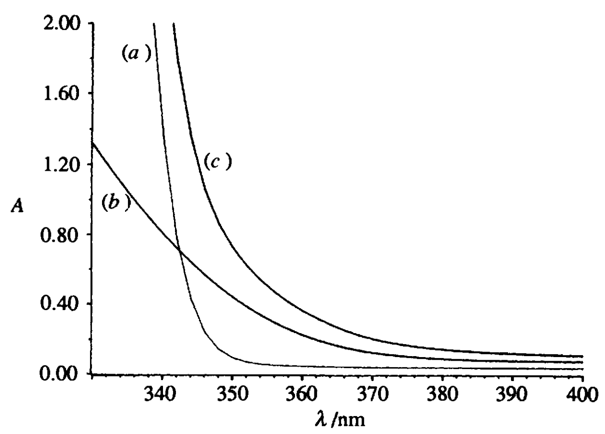


Fig. 4 UV spectra of solutions of (*a*) *N,N*-dimethyl-*p*-toluidine (27 mmol dm^{-3}); (*b*) S-NO_2 (26 mmol dm^{-3}) and (*c*) *N,N*-dimethyl-*p*-toluidine (27 mmol dm^{-3}) and S-NO_2 (26 mmol dm^{-3})

Charge transfer complexes between ArH and S-NO_2

The UV spectrum of a dichloromethane solution of S-NO_2 is shown in Fig. 3. Apart from the apparent maximum at 230 nm (presumably an artefact due to the strong solvent absorption), shoulders at *ca.* 255 ($\log \varepsilon \approx 2.7$) and 310 nm ($\log \varepsilon \approx 1.9$) were the only notable features. The spectrum was unchanged over a period of 2 h after the addition of 0.5 mol dm^{-3} TFA. In acetonitrile, the spectrum was more distinctively defined [λ_{max} 197 nm ($\log \varepsilon$ 3.6), $\lambda_{sh} \approx$ 225 nm ($\log \varepsilon \approx 3.4$), λ_{max} 254 nm ($\log \varepsilon$ 2.7) and λ_{max} 304 nm ($\log \varepsilon$ 2.05)]. Fig. 4 shows that only a weak absorption could be assigned to a CT complex even when a very good donor [4,*N,N*-trimethylaniline, $E°(\mathrm{ArH}^{\bullet+}/\mathrm{ArH})$ = 0.81 V)] was added. Other good donors [tris(4-tolyl)amine, 9,10-dimethylanthracene and dibenzo-1,4-dioxin with $E°(\mathrm{ArH}^{\bullet+}/\mathrm{ArH})$ = 0.80, 1.11 and 1.50 V, respectively] behaved similarly, whereas weaker donors, such as naphthalene and 1,2-dimethylnaphthalene, did not show any sign of charge transfer absorption with S-NO_2. The conclusion from these experiments is that irradiation with light of $\lambda > ca.$ 350 nm should be used for the excitation of any ArH–S-NO_2 charge transfer complex, but that the window for effective photochemistry will be rather narrow. As is the case for tetranitromethane,[11] light of shorter wavelength will also be efficient, but the electron transfer process will then be of different type, excitation of ArH followed by bimolecular electron transfer from ArH* to S-NO_2 [eqn. (5)]. The reverse order of excitation is also a possible sequence.

$$\mathrm{ArH} \xrightarrow{h\nu} \mathrm{ArH}^* \xrightarrow{\text{S-NO}_2} \mathrm{ArH}^{\bullet+}\mathrm{S}^-\mathrm{NO}_2 \qquad (5)$$

EPR spectral studies

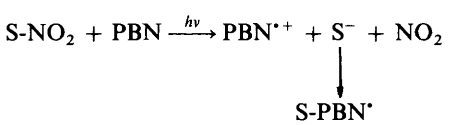
We have shown previously[3] that the reactivity of trinitromethanide ion in eqn. (2) can be suppressed by protonation, simply effected by conducting the photolysis in the presence of trifluoroacetic acid or methanesulfonic acid, the latter acid being used for reactions performed in acetonitrile. This blocks the adduct pathway, initiated by the rapid $\mathrm{ArH}^{\bullet+}$–trinitromethanide interaction, and favours other slower reactions of $\mathrm{ArH}^{\bullet+}$ such as coupling with NO_2 with formation of the Wheland intermediate and eventually nitro-substitution product(s) after proton loss, or self-coupling to give dehydrodimer radical cations ($\mathrm{Ar{-}Ar}^{\bullet+}$).[12,13] The relative slowness of the NO_2 coupling process makes it possible to observe the build-up of a significant radical cation (as monomer, π-dimer or dehydrodimer) concentration by EPR spectroscopy at a suitably low temperature, generally −60 °C. In the absence of TFA but otherwise under identical conditions, the $ArH^{\bullet +}$-trinitromethanide reaction in most cases is too fast for any paramagnetic acitivity to develop. In fact, a more detailed study of one system, 1,2-dimethylnaphthalene, showed that only with [TFA] > *ca.* 0.15 mol dm^{-3} did the radical cation (in this case, that of the dehydrodimer 3,3′,4,4′-tetramethyl-1,1′-binaphthalene[13]) start to develop. This can be traced to the acid–base behaviour of TFA and trinitromethane; TFA is a weaker acid than trinitromethane (apparent $\Delta pK = -0.6$ in dichloromethane) and only at a sufficiently high [TFA] will the trinitromethanide concentration be suppressed to a sufficiently low level to uncouple eqn. (2). Finally, checks on solutions containing ArH and TFA only, run under identical conditions, showed that low concentrations of $ArH^{\bullet +}$ sometimes developed but never to the extent as when tetranitromethane was present. The three sets of conditions will be denoted solution I (ArH–acceptor), solution II (ArH–acceptor–TFA) and solution III (ArH–TFA) conditions in the following.

If S-NO_2 can fulfil the same function as tetranitromethane in photolysis with ArH, one should observe similar phenomena. A first test was carried out with dibenzo-1,4-dioxin which in 40 mmol dm^{-3} concentration upon photolysis with light of $\lambda > 345$ nm with S-NO_2 (100 mmol dm^{-3}, sample with $\leq 1\%$ of SH) in dichloromethane at −60 °C showed no EPR spectral activity (solution I conditions). This shows that both the $ArH^{\bullet +}$-succinimide anion and/or $ArH^{\bullet +}$–NO_2 reactions are fast enough to outrun any accumulation of $ArH^{\bullet +}$. However, in the presence of TFA (0.8 mol dm^{-3}; solution II conditions), the characteristic quintet ($a^H = 0.208$ mT; lit.,[14] 0.210 mT in acetonitrile) of dibenzo-1,4-dioxin$^{\bullet +}$ appeared with high intensity, *ca.* 800 times larger than noise level. Under these conditions, we can be sure that protonation of S^- in eqn. (4) leaves $ArH^{\bullet +}$ and NO_2 behind; since it so happens that the reaction between these reactants is relatively slow, the radical cation can accumulate and be detected. A check with only dibenzo-1,4-dioxin and TFA present showed low EPR spectral activity, *ca.* 20 times larger than noise level.

The second substrate was 9,10-dimethylanthracene, which was EPR silent [Fig. 5(*a*)] upon photolysis with S-NO_2 in dichloromethane (10 and 120 mmol dm^{-3}, respectively; light with $\lambda > 345$ nm, −60 °C). Photolysis in the presence of TFA (0.4 mol dm^{-3}) gave an intense, fully resolved spectrum [Fig. 5(*b*)] of the monomeric radical cation [α^{CH_3} 0.790 (6 H), α^{H1} 0.246 (4 H), α^{H2} 0.123 mT (4 H), the same values as those given in the literature[15]]. Under solution III conditions, the spectrum was very weak (Table 1). 9-Phenylanthracene similarly gave a strong signal (Table 2) which was only moderately well resolved. Other substrates of lower reactivity were tried but in most cases showed solution II activity only slightly larger than that obtained under solution III conditions. However, most spectra were well resolved and permitted the identification of the radical cations. The logarithms of the ratios of the EPR activities of solution II/I and solution III/I conditions are listed in Table 1, together with those obtained earlier[3] using tetranitromethane instead of S-NO_2. The assignments of the radical cation structures are also given in Table 1, since an earlier report[16] had erroneously assigned a number of substituted naphthalene radical cations to the π dimeric type instead of that of the dehydrodimer.[13]

9,10-Dimethylanthracene was studied in acetonitrile as well, using acids of different strength (0.4 mol dm^{-3}) as the protonating agent and at a temperature of −40 °C. A strong to moderately strong signal of the radical cation was obtained under solution II conditions (Table 2 and Fig. 6) for acids with $pK \leq 10$ in acetonitrile. With TFA or trichloroacetic acid as proton donor, no signal appeared.

Another EPR spectrally based method to study the photolysis of S-NO_2 in the presence of an electron acceptor is to use a spin trap in the latter capacity. α-Phenyl-*N*-*tert*-butylnitrone (PBN) is suitable spin trap for this purpose, since its oxidation potential is relatively low, *ca.* 1.55 V.[17] Photoexcitation should bring about the process of eqn. (6) in which


$$S\text{-}NO_2 + PBN \xrightarrow{h\nu} PBN^{\bullet +} + S^- + NO_2 \qquad (6)$$
$$\downarrow$$
$$S\text{-}PBN^{\bullet}$$

$PBN^{\bullet +}$, S^- and NO_2 are formed. Recombination between $PBN^{\bullet +}$ and S^- will lead to S–$PBN^{\bullet}$, the spin adduct which usually is a persistent species. The process of eqn. (6) is a case of *inverse spin trapping*,[18] since the odd electron has been shifted relative to the hypothetical normal spin trapping reaction, PBN + $S^{\bullet}$.

The photolysis of a dichloromethane solution of S-NO_2 (10 mmol dm^{-3}) and PBN (40 mmol dm^{-3}) by UV light at room temperature or −40 °C immediately gave a strong signal of the succinimidyl spin adduct (a^N 1.43, $a^{N'}$ 0.133, a^H 0.54 mT; lit.,[18a] 1.44, 0.135 and 0.54 mT), in accordance with eqn. (6)

5,5-Dimethylpyrroline 1-oxide (DMPO), a spin trap with a somewhat higher redox potential, 1.7 V, when treated similarly gave a strong signal of the succinimidyl spin adduct ($a^N = 1.39$, $a^H = 2.05$, $a^{N'} = 0.22$ mT, $a^{H'}$ not seen; for the corresponding 2,2,3,3-tetramethylsuccinimidyl spin adduct $a^N = 1.38$, $a^H = 2.07$, $a^{N'} = 0.21$, $a^{H'} = 0.015$ mT[18b]).

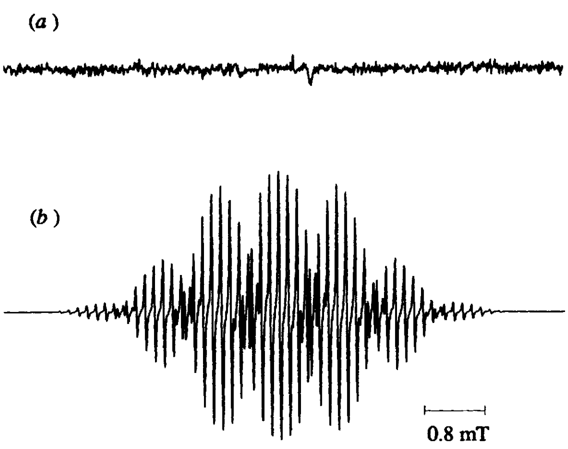


Fig. 5 EPR spectra of photolysed dichloromethane solutions of (*a*) 9,10-dimethylanthracene (10 mmol dm^{-3}) and S-NO_2 (120 mmol dm^{-3}) and (*b*) 9,10-dimethylanthracene (10 mmol dm^{-3}), S-NO_2 (120 mmol dm^{-3}) and TFA (0.4 mol dm^{-3}) at −60 °C

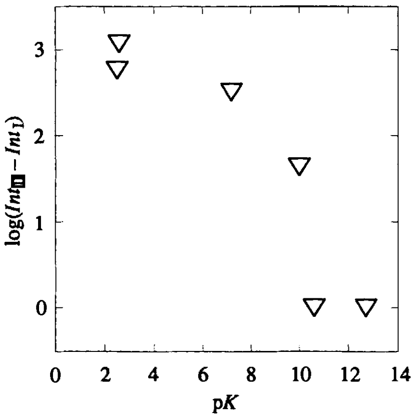


Fig. 6 Plot of log ($I_I - I_{II}$) (see Table 2) *vs.* p*K* of added acid

Table 1 Ratios of EPR spectral intensities (I) from solution II (ArH, acceptor and acid) and solution I (ArH and acceptor) and from solution III (ArH and acid) and I. The acid was TFA (0.4 mol dm^{-3}) and the solvent dichloromethane, unless otherwise specified. Dichloromethane runs were performed at −60 °C, acetonitrile runs at −40 °C

ArH	log (I_{II}/I_I), S-NO_2 as acceptor	log (I_{II}/I_I),[a] $C(NO_2)_4$ as acceptor	log (I_{III}/I_I)[a]	Radical cation type
1,2-Dimethylnaphthalene	1.0	1.3	0.0	$Ar{-}Ar^{\bullet +}$
1,8-Dimethylnaphthalene	1.4	0.9	0.3	$Ar{-}Ar^{\bullet +}$
Acenaphthene	0.9	1.4	0.7	$(ArH)_2^{\bullet +}$
1,4-Dimethylnaphthalene	0.7	0.7	0.0	$(ArH)_2^{\bullet +}$
Dibenzo-1,4-dioxin	2.9	0.4	−1.8	$ArH^{\bullet +}$
in acetonitrile[b]	0.0	0.2	0.0	$ArH^{\bullet +}$
in acetonitrile	0.0	0.0	0.0	—
9-Phenylanthracene	2.0	1.8	0.6	$ArH^{\bullet +}$
9,10-Dimethylanthracene[c]	2.9	2.8	0.7	$ArH^{\bullet +}$

[a] Ref. 3. [b] Acidified with methanesulfonic acid (0.4 mol dm^{-3}). [c] See Table 2 for the effect of variation of the acid component in acetonitrile.

Table 2 EPR spectral intensities (I) of the middle line of the EPR spectrum of 9,10-dimethylanthracene, generated by photolysis (λ > 345 nm) of (I) a solution of *N*-nitrosuccinimide (0.10 mol dm^{-3}), an acid (0.40 mmol dm^{-3}) and 9,10-dimethylanthracene (1.9 mmol dm^{-3}) and (II) a solution of an acid (0.40 mmol dm^{-3}) and 9,10-dimethylanthracene (1.9 mmol dm^{-3}) in acetonitrile at −40 °C

Acid	pK in acetonitrile	I_I	I_{II}	log ($I_I - I_{II}$)
Trifluoroacetic acid	12.7	6[a]	6[a]	0[b]
Trichloroacetic acid	10.6	6[a]	6[a]	0[b]
Methanesulfonic acid	10.0	49	6[a]	1.63
Toluene-*p*-sulfonic acid, H_2O	8.7[c]	—	—	—
Sulfuric acid	7.2	327	11	2.50
Trifluoromethanesulfonic acid	2.6	1239	75	3.07
Perchloric acid, $2H_2O$	2.5[d]	588	8	2.76

[a] Noise level. [b] When ($I_I - I_{II}$) was equal to zero, it was arbitrarily replaced by 1 to provide a meaningful number on the logarithmic scale. [c] The acid crystallized during photolysis. [d] The pK of H_3O^+ was used.

Table 3 Preparative photolyses of solutions of S-NO_2 (0.070 mol dm^{-3}) and ArH (0.14 mol dm^{-3}) in dichloromethane at about 25 °C with light of λ > 345 nm

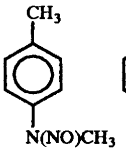
ArH	t/h	Conversion (%)[a]	Product(s)
N,*N*-Dimethyl-*p*-toluidine	2.3	100	*N*-Methyl-*N*-nitroso-*p*-toluidine (**1**), 82% *N*,*N*-Dimethyl-2-nitro-4-toluidine (**2**), 18%
9,10-Dimethylanthracene[b]	3	100	9,10-Dimethyl-9,10-epidioxy-9,10-dihydroanthracene (**3**), 79% 1,2-Bis(10-Methyl-9-anthryl)ethane (**4**), 21%
9,10-Dimethylanthacene[c]	3	100	9-Methyl-9-succinimidyl-10-oxo-9,10-dihydroanthracene (**5**), 60% 1,2-Bis(10-Methyl-9-anthryl)ethane (**4**), 30%
9,10-Dimethylanthracene[d]	6	40	1,2-Bis(10-Methyl-9-anthryl)ethane (**4**), >96%
9-Phenylanthracene	2	100	9-Phenyl-10-succinimidylanthracene (**6**), 65% 9-Phenyl-10-nitroanthracene (**7**), 23%; anthraquinone (**8**), 12%
9-Acetoxyanthracene	1.5	100	9-Acetoxy-10-nitroanthracene (**9**), 38%; anthraquinone (**8**), 62%[e]
1,4-Dimethylnaphthalene	22	40	1-Methyl-4-nitromethylnaphthalene (**10**), 20%
Anisole	22	0	ArH recovered

[a] Based on S-NO_2. [b] Access to air. [c] Ar-protected solution. [d] With 0.4 mol dm^{-3} TFA present. [e] Formed during the work-up procedure.

Products from photolyses of ArH/S-NO_2 mixtures

Photolyses of ArH/S-NO_2 solutions in dichloromethane were carried out at *ca.* +25 °C with light of λ > 345 nm. Under these conditions, productive photochemistry was restricted to donors of $E°(ArH^{\bullet +}/ArH)$ < *ca.* 1.5 V, as seen from the results listed in Table 3. Thus anisole was recovered unchanged after photolysis with S-NO_2, which is not surprising in view of its relatively high oxidation potential. On the other hand, good donors reacted completely within a photolysis period of 2–3 h, whereas an intermediate case, 1,4-dimethylnaphthalene, reacted partially in 22 h.

N,*N*-Dimethyl-*p*-toluidine, the best donor of the substrates of Table 3, gave mainly the product of *N*-nitrosation–demethylation (**1**) and a small yield of the nuclear nitration product **2**. 9,10-Dimethylanthracene predictably[19] gave predominantly the product of 9,10-addition of dioxygen (**3**) if air was admitted to the reaction vessel during photolysis, whereas runs under dioxygen-free conditions gave the anthrone derivative, 9-



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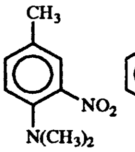

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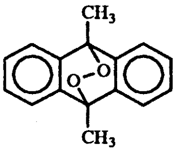

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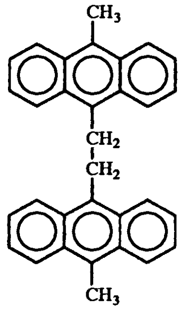

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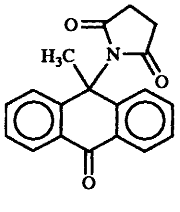

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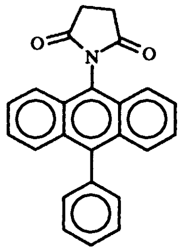

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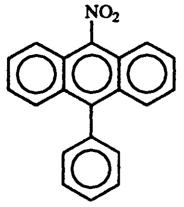

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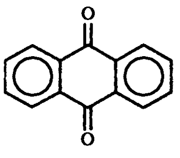

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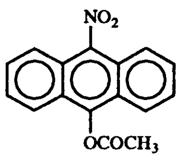

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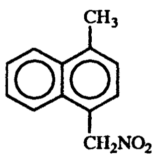

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methyl-9-succinimidyl-10-oxo-9,10-dihydroanthracene (**5**); in both cases the dimeric product, 1,2-bis(10-methyl-9-anthryl)ethane (**4**) was formed as a minor product. When the same reaction was carried out in the presence of 0.4 mol dm^{-3} TFA, only **4** was formed and no sign of the anthrone **5** was detected (detection level ≈ 4%). 9-Phenylanthracene gave mainly the product of 10-succinimidyl substitution (**6**) and some 10-nitro substitution product (**7**) and anthraquinone (**8**). 9-Acetoxyanthracene also gave the corresponding 10-nitro substitution product (**9**), in addition to a sizable yield of anthraquinone **8** which was formed from labile intermediates during the work-up procedure. Finally, the product from 1,4-dimethylnaphthalene was that of side-chain substitution, 1-methyl-4-nitromethylnaphthalene (**10**).

Discussion

Intermediates from the photochemical step and their reactivity

At the outset, we had anticipated that S-NO$_2$ would behave in the photolysis with ArH qualitatively in the same way as other nitro-substituted donors (X-NO$_2$), such as tetranitromethane and nitropyridinium ions. Quantitatively, both the voltammetric and UV spectral results show that S-NO$_2$ is a weaker acceptor than the latter, engaging only in weak CT complexes even with good donors. Therefore, the preparative chemistry available by photoexcitation of mixtures of S-NO$_2$ and donors is limited to good donors, say with $E°(\mathrm{ArH}^{\bullet +}/\mathrm{ArH}) < 1.5$ V. The EPR technique, with its high sensitivity, extends the limit for observation of the consequences of the photoexcitation of ArH–S-NO$_2$ to compounds with $E°(\mathrm{ArH}^{\bullet +}/\mathrm{ArH}) \approx 1.6$ V. Compounds of lower reactivity do give rise to weak spectra under solution II conditions, but considering the fact that weak signals also develop under solution III conditions, these findings cannot be interpreted unambiguously, as could be done in the case of tetranitromethane,[3] a much stronger acceptor capable of sustaining efficient production of the reactive intermediates.

With spin traps PBN or DMPO as the donor, the formation of the succinimidyl spin adduct [as shown for PBN in eqn. (6)] provides strong evidence for the intervention of the [spin trap]$^{\bullet +}$ S$^-$ ion pair.[18] We therefore assume that the primary event is described by eqn. (7); whether the radical anion,

$$\mathrm{ArH}\cdots\mathrm{S\text{-}NO_2} \xrightarrow{h\nu_{\mathrm{CT}}} [\mathrm{ArH}^{\bullet +}\mathrm{S\text{-}NO_2}^{\bullet -}] \longrightarrow \mathrm{ArH}^{\bullet +}\mathrm{S}^{-}\mathrm{NO_2} \quad (7)$$

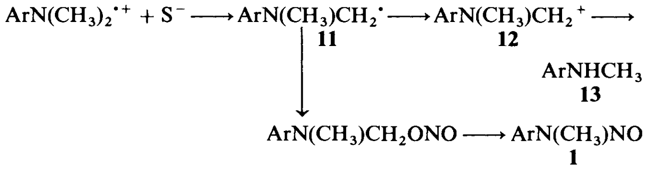
S-NO$_2$$^{\bullet -}$, is a transient intermediate is not yet known. For the moment, this problem is not important since any intermediacy of S-NO$_2$$^{\bullet -}$ would presumably only affect the photochemical yield by introducing a non-productive back electron transfer step.

Given that the triad of eqn. (7) is formed, it is expected that it will exhibit qualitatively the same kind of reactivities as the corresponding one from tetranitromethane–ArH, *i.e.*, very rapid reaction between the radical cation and the nucleophile, and slower reaction between the radical cation and NO$_2$ or any possible self-coupling reactions of the radical cation.[1,3] However, important differences between trinitromethanide ion and S$^-$ reside in their basicity (nearly 10 powers of ten in the p*K*s of the conjugate acids) and nucleophilicity [an estimated[20] difference in $n(\mathrm{CH_3I})$ of *ca.* 3], both factors making S$^-$ a more reactive species. Since the effect on basicity is the larger one, it is expected that reactions related to basicity should be relatively more favoured in the case of S$^-$. Also it should be possible to manipulate the triad reactivity of eqn. (7) by protonation in the same way as can be done for the triad of eqn. (1). The results from application of EPR spectroscopy (Table 1) to neutral and acidified ArH–S-NO$_2$ systems demonstrate convincingly for the more reactive substrates (9,10-dimethylanthracene, 9-phenylanthracene and dibenzo-1,4-dioxin) that the ArH$^{\bullet +}$–S$^-$ reaction must be faster than the ArH$^{\bullet +}$–NO$_2$ process. For the less reactive substrates, the background photolysis reaction of ArH–TFA can sometimes contribute significantly to the overall effect, and thus no firm conclusions can be drawn.

The photolysis of 9,10-dimethylanthracene–S-NO$_2$ in acetonitrile allowed for a comparison between proton donors of different strength. This could not be done with tetranitromethane as acceptor, since TFA is too weak an acid in acetonitrile for complete protonation of trinitromethanide ion to occur at a practically usable [TFA], nor could it be done in dichloromethane for solubility reasons.[3] With SH being a much weaker acid than the acids used here, solution II experiments in acetonitrile could be performed at acid concentrations around 0.4 mol dm^{-3}. Such experiments would be expected to distinguish these acids according to their acidity. This is borne out by the results shown in Table 2 where the stronger acids are much more efficient in promoting the development of the radical cation in the photolysis of 9,10-dimethylanthracene. In fact, TFA has no effect in this respect. Fig. 6 shows the variation of the intensity with p*K*, demonstrating not only the negligible effect of TFA and trichloroacetic acid, but also that the intensity levels off for very strong acids, owing to the levelling effect of acetonitrile (p*K* of protonated acetonitrile *ca.* −11).[21] This finding contradicts the view[22] that TFA has a special cation stabilizing affect; it does stabilize radical cations by preventing loss of ionizable protons and/or protonating any nucleophiles present, like S$^-$ or trinitromethanide ion, but so does any protic acid of comparable acidity. As Fig. 6 shows, the p*K* of the acid is the factor which influences the stabilization of the radical cation.

Photolysis products

The photolysis of S-NO_2 together with *N,N*-dimethyl-*p*-toluidine resulted in mainly *N*-nitrosation–demethylation of the substrate with formation of **1**, which can be understood in terms of Scheme 1. It was shown recently[23] that radical cations of *N,N*-dimethylanilines exhibit C-H acidity of the *N*-methyl groups, making the radical cation of *N,N*-dimethyl-*p*-toluidine an acid with $pK \approx 12$ in acetonitrile. Thus these radical cations underwent facile proton transfer reactions with acetate ion or pyridine, resulting in the removal of one of the *N*-methyl groups. In combination with the high basicity of S^-, it is logical to assume that the first reaction from the triad components is removal of a proton from $ArN(CH_3)_2^{\cdot+}$ with formation of the neutral radical **11**. The latter is an easily oxidizable species and will be rapidly oxidized to the carbocation **12** which eventually results in the demethylated product **13**. Nitrosation of **13** by NO_2 would complete the route to **1**.[24] An alternative pathway from **11** directly to **1** would be *O*-coupling with NO_2 and subsequent expulsion of CH_2O *via* a cyclic transition state.

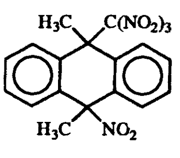


$$\begin{tikzcd} \mathrm{ArN(CH_3)_2^{\cdot+} + S^-} \arrow[r] & \underset{\mathbf{11}}{\mathrm{ArN(CH_3)CH_2^{\cdot}}} \arrow[r] \arrow[d] & \underset{\mathbf{12}}{\mathrm{ArN(CH_3)CH_2^{+}}} \arrow[r] & \underset{\mathbf{13}}{\mathrm{ArNHCH_3}} \\ & \mathrm{ArN(CH_3)CH_2ONO} \arrow[r] & \underset{\mathbf{1}}{\mathrm{ArN(CH_3)NO}} & \end{tikzcd}$$

Scheme 1 Ar = 4-tolyl

The 9,10-dimethylanthracene radical cation also undergoes proton abstraction with formation of a radical **14** which self-couples to give **4**. This reaction type is known from the anodic oxidation of 9,10-dimethylanthracene in the presence of a base, such as pyridine.[25] However, the major reaction involves nucleophilic attack at C9 by S^-, followed by trapping of ONO by the neutral radical **15** to give the nitrito–succinimidyl adduct **16**. This type of addition to a radical cation is well known from the photochemistry of tetranitromethane. Oxidation of the adduct with formal elimination of CH_3NO from the adduct, a reaction with some precedents in 9,10-dialkylanthracene chemistry,[26] gives the anthrone derivative **5** (Scheme 2). In agreement with previous tetranitromethane findings, photolysis in the presence of TFA results in the protonation of S^-, and hence the pathway to **15** will become blocked. The next favoured reaction is proton abstraction, leading to the formation of **4** only.

The photoaddition of tetranitromethane to 9,10-dimethylanthracene has been shown to give a labile adduct, decomposing in the solid state even at −20 °C. It was tentatively assigned the structure of a 9,10-nitro–trinitromethyl adduct **17**, formed *via* initial trinitromethanide attack on the radical cation.[27] Another product was 9-methyl-10-(2,2,2-trinitroethyl)anthracene **18**, presumably formed from **17** by an elimination–rearrangement reaction.[28]



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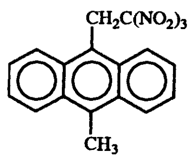

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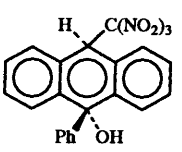

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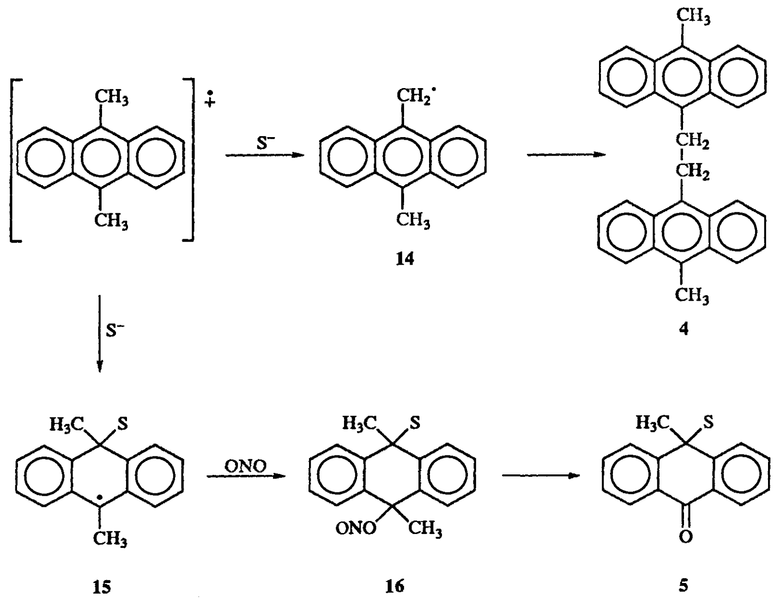
The formation of the 10-succinimidyl substitution product **6** from 9-phenylanthracene can, in principle, occur as a direct oxidative substitution process [eqn. (8)] where the intermediate

$$\mathrm{ArH^{\cdot+} + S^- \longrightarrow Ar(H)S^{\cdot} \longrightarrow Ar(H)S^+ \longrightarrow Ar\text{–}S} \quad (8)$$
$$\mathrm{Ar = 10\text{-}(9\text{-}phenylanthryl)}$$

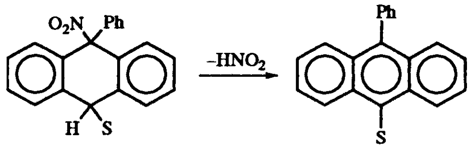
succinimidylcyclohexadienyl radical is oxidized by, for example, a second radical cation molecule to give a Wheland-type intermediate, followed by proton abstraction. Since this reaction does not appear to be the source of trinitromethyl substitution products in the ArH–tetranitromethane photoreaction,[29] by analogy it is deemed less likely to occur in the present case. A more likely possibility is that addition of S-NO_2 takes place, followed by elimination of HNO_2 from the adduct [eqn. (9)]. The formation of the nitro substitution product **7** can be explained similarly [eqn. (10)].

The photoaddition of tetranitromethane to 9-phenylanthracene[27] gave the adduct, 9-nitro-9-phenyl-9-trinitromethyl-9,10-dihydroanthracene (60%), and the corresponding nitrito–trinitromethyl adduct, converted into **19** (22%) during work-up.

The other preparative systems can be understood in similar ways. Clearly, the photolysis of ArH–S-NO_2 systems will not provide such a large and varied range of cases to study as tetranitromethane, which can be induced to add even to benzene.[30] However, the weakness of S-NO_2 as an electron



Scheme 2



(9)

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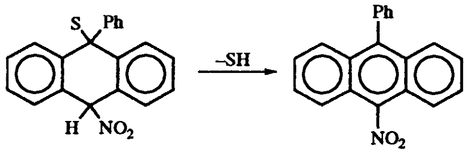

(10)

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acceptor can be a bonus at the other extreme of donor reactivity, where tetranitromethane tends to undergo spontaneous electron transfer.

Experimental

Instruments

NMR spectra were recorded on Varian XL 300 or 200 spectrometers or a Bruker ARX 500 spectrometer. HPLC separations were performed on a Varian 5000 instrument, equipped with a Nucleosil Sil column, and mass spectra were recorded on a JEOL JMS SX-102 instrument. EPR spectra were recorded on the Upgrade Version ESP 3220–200SH of a Bruker ER–200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using the 50 W high-pressure Hg lamp from Bruker (ER 202) and a filter with cut-off at λ < 345 nm from Schott, Germany. Cyclic voltammetry was performed for samples in dichloromethane–Bu_4NPF_6 (0.15 mol dm^{-3}), using the BAS-100 instrument.

Materials

9-Acetoxyanthracene,[31] 1,2-bis(10-methyl-9-anthryl)ethane[32] and dibenzo-1,4-dioxin were available from previous work. 1,2-(Aldrich, 98%) and 1,4-dimethylnaphthalene (Merck, *zur Synthese*, >95%), 9,10-dimethylanthracene (Janssen, 97%), 9-phenylanthracene (EGA-Chemie, 98%), *N*,*N*-dimethyl-*p*-toluidine (Aldrich 99%), anisole (Riedel, 99.5%), PBN (Aldrich), succinimide (Fluka, *purum*), trifluoroacetic anhydride (Riedel, 98%) and ammonium nitrate (M&B, >99%) were used as received. Dichloromethane (Merck, *zur Rückstandsanalyse*) was dried over 4 Å molecular sieves and nitromethane (Merck, *zur Synthese*) was dried over $Mg(SO_4)_2$.

N-Nitrosuccinimide

Trifluoroacetic anhydride (18 ml, 0.13 mol) was added dropwise to a stirred suspension of 5.8 g (0.07 mol) of ammonium nitrate in 20 ml of dry nitromethane at 0 °C.[7d] The mixture was stirred until it became homogeneous and then succinimide (4.95 g, 0.05 mmol), dissolved in 25 ml of dry nitromethane, was added at 0 °C. Stirring was continued for 30 min at room temperature. The solvent was removed under reduced pressure and the residue was treated with CH_2Cl_2–hexane (1:1) to precipitate ammonium trifluoroacetate. The crude product was recrystallised from ethanol, yield 10.5%, mp 86–87 °C, lit.,[7d] 86–87 °C. The *N*-nitrosuccinimide thus obtained was contaminated by 1–6% succinimide.

General procedure for photochemical nitration

The light source was a vertically placed 300 W tungsten lamp (Osram 'Ultravitalux'), above which a combined IR filter and cooling plate (a flat cylindrical glass cell of diameter 15 cm and thickness 5 cm through which a constant flow of tap water was maintained) was located. On top of the glass plate the cut-off filter (cut-off < 345 nm) was placed using black masking tape to prevent unfiltered light from passing through. The samples to be irradiated, kept in small, closed glass vials, were placed on the filter and irradiated for the appropriate reaction period. This arrangement maintained the temperature of the photolysed solution at 25 ± 1 °C.

Photochemical reactions with *N*-nitrosuccinimide: general procedure

A solution of the substrate (0.14 mol dm^{-3}) and *N*-nitrosuccinimide (0.07 mol dm^{-3}) in dichloromethane (4 ml) was irradiated at *ca.* 25 °C, as described above. After the disappearance of *N*-nitrosuccinimide (^1H NMR spectral analysis), the volatile material was removed under reduced pressure at 0 °C. The reaction products were separated by flash chromatography (Silica gel 60H, using pentane–dichloromethane 2:1 and hexane–ethyl acetate 10:1 and 3:2 as the eluent) and in some cases by HPLC (9-phenyl-10-succinimidylanthracene (**6**), 9-methyl-9-succinimidyl-10-oxo-9,10-dihydroanthracene (**5**), *N*-methyl-*N*-nitroso-*p*-toluidine (**1**), with pentane–ethyl acetate 99:1 to 1:2 as the eluent) and characterized by NMR spectroscopy and MS analyses [direct inlet, EI ionisation (70 eV), unless otherwise stated].

9,10-Dimethylanthracene

Photolysis of 9,10-dimethylanthracene–S-NO_2 under conditions allowing for access of air to the reaction vessel yielded 79% *9,10-dimethyl-9,10-epidioxy-9,10-dihydroanthracene* (**3**), δ(300 MHz; $CDCl_3$) 7.39 (m, 4 H), 7.27 (m, 4 H) and 2.14 (s, 6 H); *m*/*z* (CI NH_3) 239 (100%), 207 (94), 223 (76), EI 206 (100) and 191 (23), and 21% *1,2-bis(10-methyl-9-anthryl)ethane* (**4**), identified by comparison (NMR, MS) with an authentic sample.[32]

Photolysis of 9,10-dimethylanthracene–S-NO_2 under oxygen-free conditions was achieved by bubbling the reaction mixture with argon for 3 min before sealing the vessel with an air-tight cap. The reaction yielded 30% *1,2-bis(10-methyl-9-anthryl)ethane* (**4**, see above) and 60% *9-methyl-9-succinimidyl-10-oxo-9,10-dihydroanthracene* (**5**), δ_H(500 MHz; $CDCl_3$) 2.18 (s, 9-Me), 2.68 (s, 9-succinimidyl), 7.40 (ddd, $J_{1,2}$ = 7.94 Hz, $J_{1,3}$ = 1.15 Hz, $J_{1,4}$ = 0.38 Hz, H1,8), 7.46 (ddd, $J_{3,4}$ = 7.86 Hz, $J_{3,2}$ = 7.29 Hz, $J_{3,1}$ = 1.15 Hz, H3,6), 7.60 (ddd, $J_{2,1}$ = 7.94 Hz, $J_{2,3}$ = 7.29 Hz, $J_{2,4}$ = 1.47 Hz, H2,7) and 8.35 (ddd, $J_{4,3}$ = 7.86 Hz, $J_{4,2}$ = 1.47 Hz, $J_{4,1}$ = 0.38 Hz, H4,5); δ_C($CDCl_3$) 28.55 (9-succinimidyl), 33.73 (9-Me), 61.00 (C9), 124.48 (C1,8), 127.88, 127.92 (C3, 4, 5, 6), 129.916 (C4-C10), 133.92 (C2,7), 146.73 (C1-C9), 177.12 (9-succinimidyl) and 182.64 (C10); *m*/*z* (CI NH_3) 323 (100%), 306 (84), EI: 206 (100) 305 (79), 178 (77) and 290 (31).

9-Phenylanthracene

Photolysis of 9-phenylanthracene–S-NO_2 yielded 65% *9-phenyl-10-succinimidylanthracene* (**6**) δ_H(300 MHz; $CDCl_3$) 7.21–7.80 (m, 13 H) and 3.27 (s, 4 H); δ_C($CDCl_3$) 29.25 (10-succinimidyl), 121.56–131.10 (C–Ar) and 176.84 (10-succinimidyl). The HETCOR technique showed connectivity between ^1H at δ 3.27 and ^{13}C at δ 29.25 and long-range connectivity between ^1H at δ 3.27 and ^{13}C at δ 176.84. *m*/*z* 351 (100%), 352 (22), 268 (18) and 252 (17). There was also isolated a 23% yield of *9-phenyl-10-nitroanthracene* (**7**), δ(300 MHz; $CDCl_3$) 7.96 (d, 2 H), 7.70 (d, 2 H), 7.62 (m, 5 H) and 7.42 (m, 4 H); *m*/*z* 299 (100%), 269 (44), 252 (67) and 250 (34) and 12% *anthraquinone* (**8**) identified by comparison (NMR, MS) with an authentic sample.

9-Acetoxyanthracene

Photolysis of 9-acetoxyanthracene–S-NO_2 yielded 38% 9-

acetoxy-10-nitroanthracene (**9**), δ(300 MHz; $CDCl_3$) 7.99 (m, 4 H), 7.64 (m, 4 H) and 2.68 (s, 3 H); *m/z* 281 (14%), 239 (100), 209 (93) and 163 (58) and 62% *anthraquinone* (**8**) formed during work-up.

N,*N*-Dimethyl-*p*-toluidine

Photolysis of *N*,*N*-dimethyl-*p*-toluidine–S-NO_2 yielded 82% *N-methyl-N-nitroso-4-toluidine* (**1**), δ(200 MHz; $CDCl_3$) 7.42 (m, 2 H), 7.27 (m, 2 H), 3.44 (s, 3 H) and 2.40 (s, 3 H); *m/z* (CI NH_3) 168 (100%), 151 (33) and 121 (24), 18% *N,N-dimethyl-2-nitro-p-toluidine* (**2**), δ(300 MHz; $CDCl_3$) 7.58 (d, $J_{3,5}$ = 2.14 Hz, H3), 7.23 (dd, $J_{5,6}$ = 8.55 Hz, $J_{5,3}$ = 2.14 Hz, H5), 6.93 (d, $J_{6,5}$ = 8.55, H6), 2.83 (s, NMe_2) and 2.31 (s, 4-Me); *m/z* 180 (47%), 163 (54), 120 (100).

Crystallography

Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, λ(Mo-Kα) 0.710 68 Å, from a crystal monochromator] are given below. The space group was determined unambiguously as a result of the structure analysis reported below, but initially indicated by limiting possible reflections. ω-Scans were used to collect reflection intensities out to the maximum Bragg angle θ, given below. The cell parameters were determined by least-squares refinements for which the setting angles of 25 accurately centred high-angle reflections were used.

Crystal data

N-Nitrosuccinimide, $C_4H_4N_2O_4$, *M* 144.1, orthorhombic, space group *Pbca*, $a = 10.463(2)$, $b = 8.210(3)$, $c = 13.523(3)$ Å, $V = 1161.6(5)$ Å^3, $D_c = 1.648$ g cm^{-3}, $Z = 8$, μ(Mo-Kα) = 1.50 cm^{-1}. The crystal was colourless and of approximate dimensions 0.72 × 0.48 × 0.06 mm. Data were collected at 131 K out to a maximum Bragg angle $\theta = 24.96°$. The number of independent reflections measured was 735, 335 with $I > 2\sigma(I)$; absorption corrections, maximum 1.000, minimum 0.786, $g_1 = 0.0291$, $g_2 = 0.0000$; $R_{(obs)} = 0.078$, $wR_{(all\ data)} = 0.132$.

Structure determination

The structure was solved by direct methods and difference-Fourier syntheses. Full-matrix least-squares refinements (SHELXL-93)[33] were employed. This program is based on intensities and uses all data. The observed threshold $I > 2\sigma(I)$ was used only for calculating $R_{(obs)}$, shown here as a comparison for the refinements based on *F*. Reflection weights $1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$, where $P = [F_o + 2F_c^2]/3$, were used.

All non-hydrogen atoms were assigned anisotropic thermal parameters. Final Fourier syntheses showed no abnormal discrepancies between observed and calculated structure factors. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

Acknowledgements

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† For details of the CCDC deposition scheme, see 'Instructions for Authors (1995),' *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

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