The Unusual Behaviour of Nitro-substituted Radical σ-Complexes. The Reactions of Alkyl Radicals with 9-Nitroanthracene

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Alkyl radicals react with 9-nitroanthracene to give the nitro-substituted σ-complex intermediate (III) derived from addition at the 10-position. This radical does not rearomatize, but gives rise to rearrangement of the nitro-group which eventually leads to the formation of alkylanthrones. However, in the presence of stabilized radicals, intermediate (III) is trapped to give products of addition at the 9- and 10-positions. In some cases these latter products can suffer hydrogen abstraction, followed by elimination of the NO_2· radical, to afford 9,10-dialkylanthracenes.

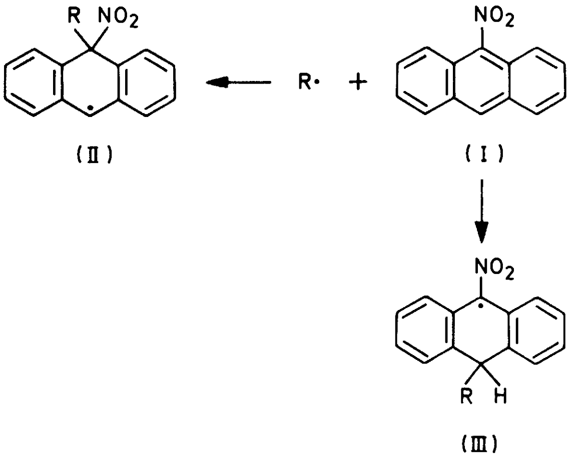
A substantial contribution to the knowledge of the mechanism of homolytic aromatic alkylation has been made by Beckwith and Waters in their investigation of the radical benzylation of anthracene.[1] The results of this study exemplified several possible ways through which a radical σ-complex intermediate can decay. We have recently studied homolytic aromatic *ipso*-substitutions;[2] the reactions of alkyl radicals with aromatic nitro-derivatives give important information about the factors which control the positional selectivity of radical addition. Thus, depending on the polar character of the attacking radical and on the structure of the aromatic nitro-derivative, one can observe addition at unsubstituted ring positions or at the *ipso*-position of the nitro-group to afford products of alkyldenitration. However, radical *ipso* σ-complexes do not always evolve towards the *ipso*-substitution products, but can also give rise to other processes;[2] the results of the homolytic alkylation of polynitrobenzenes,[3] thiophencarbaldehydes,[4] nitrothiophens,[5] and nitrofurans[6] substantially contributed to clarify the factors which control the fate of radical *ipso*-intermediates.

The results obtained by Beckwith and Waters indicated that radical addition to anthracene occurs exclusively at the 9-position. Thus, the use of 9-nitroanthracene as substrate can give interesting information about the selectivity of the addition of alkyl radicals and about the possible behaviour of the σ-complex intermediates. Both these aspects will be influenced by the properties of the radicals employed and we have therefore used alkyl radicals with different polar character and different stabilization energy. It can be expected that alkyl radicals will add to 9-nitroanthracene (I) either at the 9-position to give the *ipso* σ-complex (II) or to the 10-position to give the nitro-substituted σ-complex (III). Radical (II) is expected to give the alkyldenitration product by eliminating the stable $\dot{N}O_2$ radical;[2] radical (III), instead, can rearomatize or, because of the low energy gain in rearomatization, give rise to other processes.

The results demonstrate that radical addition is highly selective but that the course of the reaction is strongly influenced by the requirements of the alkyl radical employed.

Results and Discussion

The alkyl radicals investigated were 1-adamantyl (Ad·) (IV), 1-cyano-1-methylethyl (V), dioxanyl (VI), and benzyl (VII). Whereas radicals (IV),[7] (VI),[8] and (VII)[9] have nucleophilic character, radical (V) is expected to be slightly electrophilic.[10] These radicals were produced according to reactions (1)—(4), respectively.



The t-butoxyl radicals, which effect hydrogen abstraction in reactions (3) and (4), were produced by the thermal decomposition of the t-butyl peroxyoxalate. Reaction conditions are given in the Experimental section.

The reaction of adamantyl radicals with (I) afforded a mixture of two products which were identified as the adamantylanthrone (VIII) and 9,9-dinitro-10-adamantyl-9,10-dihydroanthracene (IX). The yields of these two products were 51 and 22%, respectively; these, however were dependent on the experimental conditions. With prolonged reaction times the amount of compound (IX) decreases and that of compound (VIII) increases. It was proved independently that, under the experimental conditions employed, compound (IX) is transformed into compound (VIII). This behaviour of compound (IX) was also employed to confirm its structure. In fact, when heated above its m.p. (or kept at 100 °C for 8 h in acetonitrile solution), the dinitro-derivative (IX) was quantitatively transformed into the anthrone (VIII) and N_2O_3 was liberated; the effluent gas was collected in an acidic solution of aniline and the formation of the diazonium salt was demonstrated by the characteristic reaction with β-naphthol. This behaviour is similar to that of the related geminal dinitro-derivative 5,5-dinitro-2-adamantyl-2-methoxycarbonyl-2,5-dihydrofuran which was isolated from the reaction of adamantyl radicals with 5-nitro-2-methoxycarbonylfuran.[6] In addition to the anthrone (VIII) and the dinitro-derivative (IX) some anthraquinone was also present in the reaction mixture. It was independently found that, under the experimental conditions employed, 9-nitroanthracene is slowly oxidized to anthraquinone.

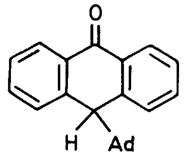
The reaction of (I) with dioxanyl radicals (VI) gave a single product (60% yield), identified as the dioxanylanthrone (X); some anthraquinone was also present.

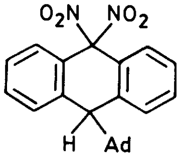
$$\mathrm{AdCOOH} + \mathrm{SO_4^{\cdot-}} \longrightarrow \underset{(\mathrm{IV})}{\mathrm{Ad\cdot}} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{SO_4^{2-}} \qquad (1)$$

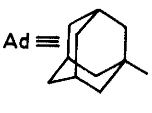
$$\mathrm{Me_2C(CN)N{=}N(CN)CMe_2} \longrightarrow 2\,\underset{(\mathrm{V})}{\mathrm{Me_2\dot{C}(CN)}} + \mathrm{N_2} \qquad (2)$$

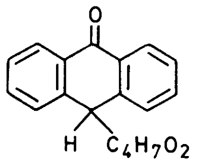
$$\mathrm{Me_3CO\cdot} + \mathrm{C_4H_8O_2} \longrightarrow \mathrm{Me_3COH} + \underset{(\mathrm{VI})}{\mathrm{\dot{C}_4H_7O_2}} \qquad (3)$$

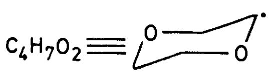
$$\mathrm{Me_3CO\cdot} + \mathrm{C_6H_5CH_3} \longrightarrow \mathrm{Me_3COH} + \underset{(\mathrm{VII})}{\mathrm{C_6H_5\dot{C}H_2}} \qquad (4)$$

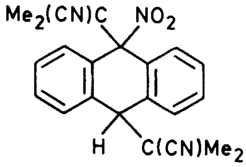

(VIII)

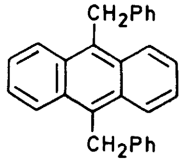

(IX)

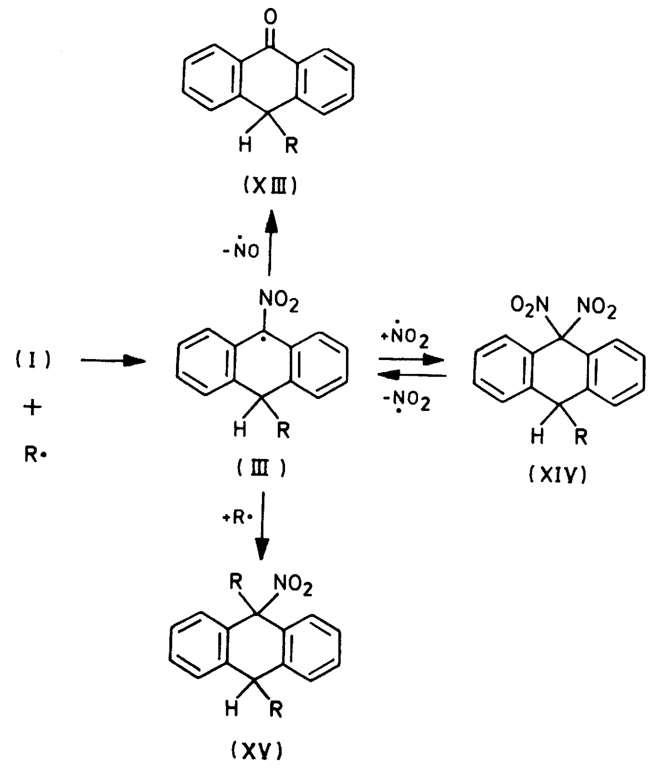



(X)




(XI)


(XII)

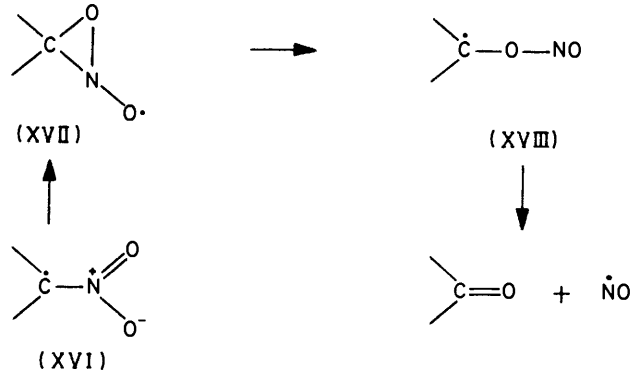


Scheme 1.

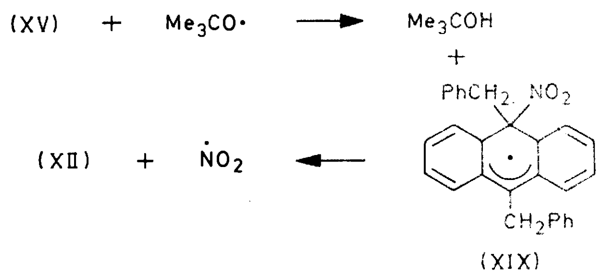
The reaction of 1-cyano-1-methylethyl radicals (V) with 9-nitroanthracene afforded the 9,10-bis-(1-cyano-1-methylethyl)-9-nitro-9,10-dihydroanthracene (XI) in 31% yield; small amounts of other unidentified products were also present. Finally, benzyl radicals gave a 60% yield of the 9,10-dibenzylanthracene (XII).

The first point of interest which emerges from the results concerns the selectivity of the radical addition to 9-nitroanthracene (I). 9-Alkylanthracenes were not obtained and this indicates that the addition at the *ipso* 9-position does not occur effectively with any of the radicals employed. The reaction products obtained clearly indicate that the alkyl radicals selectively attack the 10-position to give the σ-complex intermediate (III). It can therefore be concluded that with 9-nitroanthracene polar effects are not important and that the only factor which controls the positional selectivity of the radical addition is the relative stability of possible σ-complex intermediates. Radical (III) can be considered to be much more stable than (II) because the unpaired electron can be stabilized by the nitro-group and this explains why addition occurs exclusively at the 10-position.

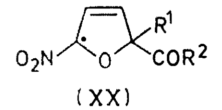
On the other hand, the way in which the intermediate (III) subsequently evolves is strongly dependent on the nature of the alkyl radical employed. The energy gain in rearomatization is very low and hydrogen abstraction from the 10-position does not occur; in no case in fact were 10-alkyl-9-nitroanthracenes obtained. The observed behaviour of (III) is summarized in Scheme 1. If stabilized radicals are not present in solution, radical (III) gives the anthrones (XIII). This behaviour of α-nitroalkyl radicals has already been observed in the cases of nitro-substituted *ipso* σ-complexes derived from furans [6] and thiophens [5] as well as in simple α-nitroalkyl radicals which give rise to ketones.[11] This reaction



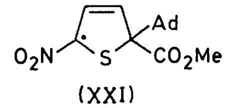
Scheme 2.



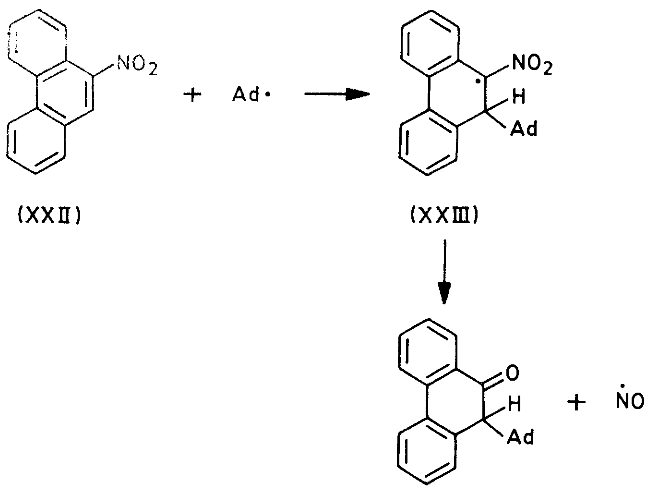
Scheme 3.



(XX)



(XXI)



has been explained[6,11] by assuming that the α-nitroalkyl radical (XVI) rearranges to the α-nitritoalkyl radical (XVIII) *via* intramolecular attack of the carbon-centred radical on the nitro-group to give the oxaziridin-*N*-oxyl (XVII) which fragments at the carbon–nitrogen bond; radical (XVIII) then suffers homolytic β-cleavage to afford the carbonyl group and $\dot{N}O$ (Scheme 2).

The transformation of (IX) into (VIII) can be explained by assuming that the dinitro-derivative (XIV) reverts thermally to radical (III), by losing an $\dot{N}O_2$ radical, and that (III) then rearranges to the anthrone according to Scheme 2.

If however stabilized radicals are present in solution. radical (III) can be trapped to give products of addition at the 9- and 10-positions. This is very likely the way through which the dinitro-derivative (XIV; R = Ad) is formed. Presumably the $\dot{N}O$ produced from the rearrangement of (III) to the anthrone is first oxidized by the persulphate to $\dot{N}O_2$ and this couples with (III) to give (XIV; R = Ad) (Scheme 1). The formation of the dinitro-derivative (XIV; R = $C_4H_7O_2$) was not observed in the reaction of dioxanyl radical with (I); thus, either (XIV; R = $C_4H_7O_2$) is not formed at all, because under the experimental conditions employed $\dot{N}O$ is not oxidized to $\dot{N}O_2$, or if formed it easily decomposes to the anthrone (XIII; R = $C_4H_7O_2$).

The 1-cyano-1-methylethyl and benzyl radicals efficiently trap intermediate (III) to give products with structure (XV). In the first case the reaction stops at this stage because the 1-cyano-1-methylethyl radical is not sufficiently reactive to effect hydrogen abstraction.[12] In the reaction with benzyl radicals, on the other hand, t-butoxyl radicals are present in solution and these can abstract hydrogen from (XV; R = $C_6H_5CH_2$) to give a new σ-complex intermediate (XIX); this is an *ipso* σ-complex in which one of the two *ipso*-substituents is a nitro-group. This kind of intermediate is known[2] to rearomatize rapidly by eliminating the stable $\dot{N}O_2$ radical (Scheme 3). This reaction sequence accounts for the formation of 9,10-dibenzvlanthracene (XII) from the reaction of benzyl radicals with 9-nitroanthracene.

Thus, in conclusion, two paths are open to the intermediate (III), *i.e.* coupling with other radicals or rearrangement and fragmentation of the nitro-group; the coupling reaction seems to be faster than the rearrangement, since no anthrone is formed whenever a stabilized radical, which can trap (III), is present in solution.

The rearrangement and fragmentation of the nitro-group is peculiar to those nitro-substituted σ-complexes which do not rearomatize easily. The same process has been in fact observed in some *ipso* σ-complexes, like (XX)[6] and (XXI),[5] where neither of the two *ipso*-substituents can be easily eliminated. From these arguments one can anticipate that other aromatic nitro-derivatives can react with alkyl radicals to give σ-complex intermediates which will decay as described in Scheme 2. Indeed, the reaction of 9-nitrophenanthrene (XXII) with adamantyl radicals gives a 55% yield of the adamantylphenanthrone (XXIV) which clearly originates from intermediate (XXIII).

Experimental

Product characterization was accomplished by n.m.r. (Varian EM 390 and JEOL C 60 HL instruments; $CDCl_3$ solution), i.r. (Beckman AccuLab 5 instrument; CH_2Cl_2 solution), and mass spectrometry (Varian MAT 311 A instrument at 70 eV using an all glass inlet system). M.p.s are uncorrected.

Reaction of 9-*Nitroanthracene* (I) *with* 1-*Adamantyl Radical*.—To a stirred solution of 9-nitroanthracene (0.67 g, 3 mmol), adamantane-1-carboxylic acid (2.7 g, 15 mmol), and $AgNO_3$ (0.05 g, 0.3 mmol) in 4 : 1 v/v acetonitrile–water (50 ml), a saturated solution of $(NH_4)_2S_2O_8$ (20 mmol) in water was added dropwise, under reflux, over *ca.* 20 min. Stirring and heating were continued for 30 min and the cooled solution was then poured onto ice and NH_3; the mixture was extracted with chloroform and the organic layer was washed with 5% NaOH and with water. The solution was dried and the solvent evaporated. The residue was chromatographed through a silica gel column using light petroleum–diethyl ether (97 : 3) as eluant. The separation of the products was monitored by t.l.c. The first fractions contained 10-*adamantyl*-9,9-*dinitro*-9,10-*dihydroanthracene* (IX) (0.27 g, 22%), m.p. 152—153°, δ 7.6 (8 H, m), 3.85 (1 H, s), 2.0br (3 H, s), 1.6br (6 H, s), and 1.45br (6 H, s), $\nu_{max.}$ 2 900, 2 840, and 1 580 cm^{-1}, *m/e* 374 (0.6%, *M* – NO), 328 (9.7, *M* – N_2O_3), 223 (7, *M* – $C_{10}H_{15}$-NO_2), 193 (12.3, *M* – $C_{10}H_{15}N_2O_3$), 165 (11), and 135 (100, $C_{10}H_{15}$) (Found: C, 71.6; H, 6.05; N, 6.7. $C_{24}H_{24}N_2O_4$ requires C, 71.3; H, 5.9; N, 6.9%). Subsequent fractions contained 10-*adamantyl*-9-*anthrone* (VIII) (0.5 g, 51%), m.p. 214—216°, δ 8.1 (2 H, m), 7,4 (6 H, m), 3.7 (1 H, s), 1.85br (3 H, s), and 1.4br (12 H, s), $\nu_{max.}$ 2 900, 2 850, 1 660, 1 600, 1 300, and 900 cm^{-1}, *m/e* 328 (14%, *M*), 193 (13, *M* – $C_{10}H_{15}$), 165 (12), 135 (100, $C_{10}H_{15}$), 106 (5), and 91 (12) (Found: C, 87.5; H, 7.15. $C_{24}H_{24}O$ requires C, 87.8; H, 7.3%). The last fractions contained traces of anthraquinone identified by mixed m.p. with an authentic sample and by its i.r. spectrum.

Compound (IX) (0.1 g) dissolved in acetonitrile (8 ml) and kept at 100 °C for 8 h afforded a quantitative yield of (VIII).

Reaction of 9-*Nitrophenanthrene* (XXII) *with Adamantyl Radical.*—This reaction was carried out under the conditions for compound (I). After column chromatography 10-*adamantyl-9-phenanthrone* (XXIV) (0.54 g, 55%) was obtained, m.p. 126—128°, δ 8.0—7.0 (8 H, m), 3.3 (1 H, s), 1.85br (3 H, s), and 1 .5br (12 H, s), $\nu_{max.}$ 2 900, 2 850, and 1 680 cm^{-1}; *m/e* 328 (7%, *M*), 193 (7, *M* − $C_{10}H_{15}$), 165 (15.5), 135 (100, $C_{10}H_{15}$), 106 (7), and 91 (14) (Found: C, 87.3; H, 7.1. $C_{24}H_{24}O$ requires C, 87.8; H, 7.3%).

Reaction of 9-*Nitroanthracene* (I) *with Dioxanyl Radical.*—A solution of (I) (0.67 g, 3 mmol) and t-butyl peroxyoxalate (1.65 g) in dioxan (20 ml) was kept at 70 °C for 4 h. The solvent was evaporated under vacuum and the residue was chromatographed through a silica gel column using light petroleum–diethyl ether (97 : 3) as eluant. After some fractions containing small amounts of anthraquinone, fractions were collected which contained 10-*dioxanyl-9-anthrone* (X) (0.5 g, 60%), m.p. 95—97°, δ 8.2 (2 H, m), 7.6—7.2 (6 H, m), 4.3 (1 H, d, *J* 4.5 Hz), and 3.9—2.6 (6 H, m), $\nu_{max.}$ 1 635, 1 600, and 1 300 cm^{-1}, *m/e* 193 (100%, *M* − $C_4H_7O_2$), 177 (2.4), 165 (16.1), and 87 (32.3) (Found: C, 77.4; H, 5.7. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.8%).

Reaction of 9-*Nitroanthracene* (I) *with* 1-*Cyano*-1-*methylethyl Radical.*—A solution of (I) (0.67 g, 3 mmol) and azobisisobutyronitrile (1.65 g) in toluene (20 ml) was refluxed for 30 h. The solvent was evaporated under vacuum and the residue was chromatographed through a silica gel column using light petroleum–diethyl ether (95 : 5) as eluant. The first fractions contained traces of the unreacted starting product; subsequent fractions contained 9,10-*bis*-(1-*cyano*-1-*methylethyl*)-9-*nitro*-9,10-*dihydroanthracene* (XI) (0.33 g, 31%), m.p. 194—196°, δ 7.8—7.4 (8 H, m), 4.5 (1 H, s), and 1.0 (12 H, s), $\nu_{max.}$ 2 220 cm^{-1}, *m/e* 292 (20.8%, *M* − 67), 262 (2), 246 (100, *M* − 113), 231 (25), 225 (14.3), 206 (16.2), and 180 (16.2) (Found: C, 73.3; H, 5.8; N, 11.9. $C_{22}H_{21}N_3O_2$ requires C, 73.5; H, 5.8; N, 11.7%). Fractions were then collected which contained minute amounts of other unidentified products.

Reaction of 9-*Nitroanthracene* (I) *with Benzyl Radical.*—A solution of (I) (0.67 g, 3 mmol) and t-butyl peroxyoxalate (1.6 g) in toluene (20 ml) was kept at 70 °C for 4 h. The solvent was evaporated under vacuum and the residue was chromatographed through a silica gel column using light petroleum–diethyl ether (98 : 2) as eluant. The first fractions contained diphenylethane (0.17 g). Subsequent fractions contained 9,10-dibenzylanthracene (XII) (0.64 g, 60%), m.p. 246—248° (lit.,[1] 248°), δ 8.5—8.1 (4 H, m), 7.7—7.1 (14 H, m), and 5.1 (4 H, s).

Acknowledgement

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