On the Reaction between Anthracene and the Nitrosonium Ion. A Simple Method for the Preparation of 9,10-Anthraquinone and Some Comments on its Formation in Aromatic Nitration*
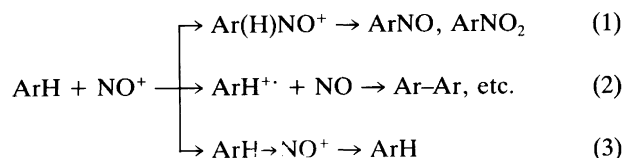
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A summary of the possible electron-transfer reactions between anthracene and the nitrosonium ion, and a convenient and simple method for the synthesis of 9,10-anthraquinone from anthracene, $NaNO_2$ and CH_3OH in CH_2Cl_2/CF_3COOH are presented.
The suggestion that the formation of 9,10-anthraquinone in the N_2O_4 nitration of anthracene originates from trapping of the anthracene radical cation by water is demonstrated to be invalid, e.g., by experiments involving $H_2^{18}O$. Instead, 9,10-anthraquinone is suggested to be formed in the N_2O_4-based and in other related systems via follow-up reactions to an initial 1,4-addition across the 9,10 positions of anthracene.

The nitrosonium ion, NO^+, generally interacts with aromatic compounds either to yield products of initial nitrosation[1,2] [eqn. (1)], i.e. via electrophilic aromatic substitution, or to yield NO and products resulting from the aromatic radical cation[3-6] [eqn. (2)], i.e. via an outer-sphere electron transfer (ET) reaction.[†] A third, very common, possibility is the formation of a charge-transfer complex which after work-up reverts into the aromatic compound and hydrolysis products of NO^+ [eqn. (3)].[6] At present our

$$\text{ArH} + \text{NO}^+ \longrightarrow \begin{cases} \rightarrow \text{Ar(H)NO}^+ \rightarrow \text{ArNO, ArNO}_2 & (1) \\ \rightarrow \text{ArH}^{+\cdot} + \text{NO} \rightarrow \text{Ar–Ar, etc.} & (2) \\ \rightarrow \text{ArH} \rightarrow \text{NO}^+ \rightarrow \text{ArH} & (3) \end{cases}$$

knowledge of the detailed relationship between eqns. (1)–(3) is limited, but it has been suggested that (a) the first step of eqn. (2) is an initial step of eqn. (1), i.e. that the formation of the Wheland intermediate occurs by radical coupling[1,2] [eqn. (4)] as has been extensively discussed in

$$\text{ArH}^{+\cdot} + \text{NO} \rightarrow \text{Ar(H)NO}^+ \qquad (4)$$
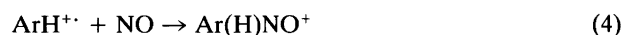
the case of aromatic nitration,[7] and that (b) the first step of eqn. (1) is an initial step of eqn. (2), i.e. that the formation of the radical pair occurs by dissociation of the Wheland

$$\text{Ar(H)NO}^+ \rightarrow \text{ArH}^{+\cdot} + \text{NO} \qquad (5)$$

intermediate [eqn. (5)] via an overall inner-sphere ET step.[2,7] Eqn. (3) probably precedes both pathways, and upon irradiation of the CT absorption band in the presence of O_2 formation of nitrated products results.[6]

We have earlier examined the behaviour of a series of naphthalenes and anisoles towards NO^+, and observed that while 1-methoxynaphthalene was converted into the corresponding biaryl (Ar–Ar, [eqn. (2)]) with O_2 and catalytic amounts of NO^+,[5] anisole resisted such treatment but underwent nitrosation and nitrous acid catalyzed (NAC) nitration with excess NO^+ (i.e. $NaNO_2$ in CF_3COOH).[2] Since the formation of 9,10-anthraquinone (**1**) in the nitration of anthracene by N_2O_4[8] (a reaction closely related to NAC nitration) has been cited in favor of an ET mechanism for N_2O_4-mediated nitration[9] [i.e. via eqn. (6)] we decided to examine the reactions of anthracene with NO^+ under different conditions.


$$\qquad (6)$$
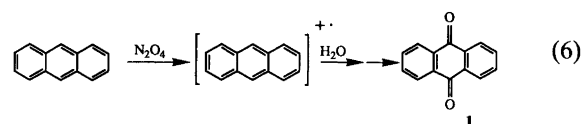
One set of experiments was performed with O_2 and catalytic amounts of NO^+ in order to check for biaryl and quinone formation, and to find out whether the formation of **1** would increase on addition of H_2O or alcohols. A second set of experiments was performed with stoichiometric quantities of NO^+ ($NaNO_2$ in CF_3COOH) in the presence or absence of water or alcohols, and finally the

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* Aromatic Nitration via Electron Transfer. IX. For Part VIII, see Ref. 2.

† The $E°$ values of some of the compounds discussed are anthracene 1.61 V, 1-methoxynaphthalene ca. 1.8 V, and NO^+ 1.51 V.

influence of H_2O and $H_2^{18}O$ on the N_2O_4 nitration of anthracene was examined.

Results

Using an experimental set-up identical with that described earlier for a series of naphthalenes,[5] the reaction of anthracene with stoichiometric and catalytic amounts of NO^+ in CH_2Cl_2 containing 0–40 % CF_3COOH was examined. In pure CH_2Cl_2 the reaction between equimolar amounts of anthracene and $NO^+BF_4^-$ gave results of low reproducibility, due at least partly to the very low solubility of $NO^+BF_4^-$.

$$\text{(7)}$$

2 R = NO₂
3a R = OCOCF₃
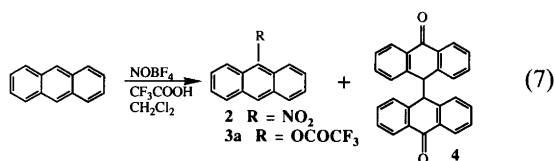
Generally, mixtures of anthracene, 9-nitroanthracene ($ArNO_2$, 2) and bianthrone (4) resulted [eqn. (7)], while the yields of 1 as well as of 9,9'-bianthryl (5) were negligible. In the presence of 20 % CF_3COOH a much cleaner reaction was observed. Equimolar amounts of anthracene

3a,7a Z = COCF₃
3b,7b Z = COCH₃
3c,6a Z = CH₃
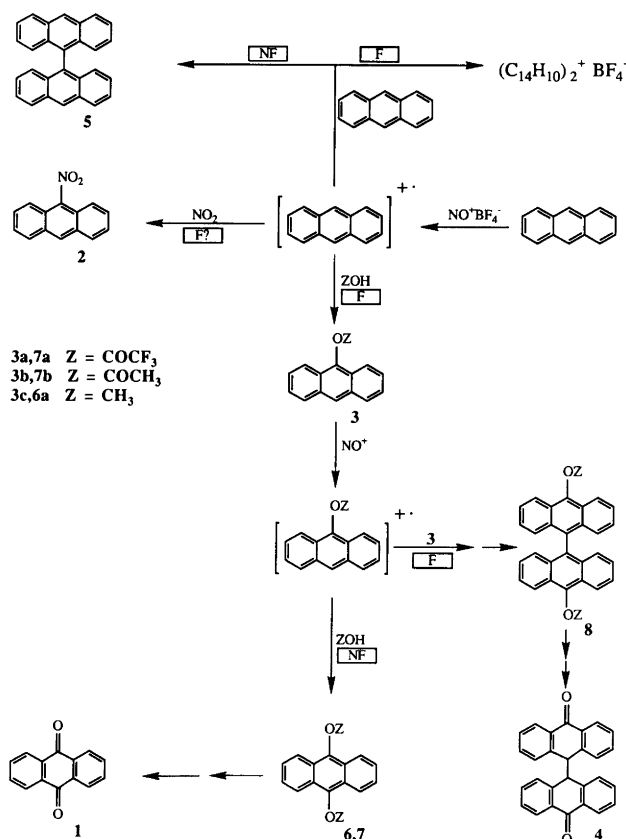
Scheme 1. Possible outer-sphere ET reaction of anthracene and NO^+. F = feasible, and NF = non-feasible follow-up reaction.

Table 1. Reaction of anthracene and O_2 with $NO^+BF_4^-$ in CH_2Cl_2 containing 0–40 vol % of CF_3COOH.[a]

Vol % of CF₃COOH	Yield (%)[b]				
	ArH	ArOCOCF₃	ArNO₂	1	4
0	80	0	4	1	2
10	72	12	4	1	8
20	56	26	3	0	8
30	42	22	4	0	14
40	40	24	4	1	18

[a]Reaction period = 20 h at 25 °C. [ArH] = 0.10 M. $[NO^+BF_4^-]$ = 0.004 M. [b]Determined by GLC.

and $NO^+BF_4^-$ gave, in a typical experiment, after work-up, 19 % anthracene, 10 % 9-trifluoroacetoxyanthracene ($ArOCOCF_3$, 3a) and 44 % 4, i.e. the material balance was above 70 %. Once again, no (< 0.1 %) biaryl or 1 was formed (Scheme 1).

We then turned to the catalytic system, i.e. the reaction of anthracene with O_2 and small amounts of $NO^+BF_4^-$. From Table 1 it is evident that no conversion of anthracene into 1 (or into 5) occurs under these conditions. The low efficiency of the present system compared with that of 1-methoxynaphthalene[5] is probably due to the more efficient capture of NO_2 (a component of the catalytic system) by anthracene (to yield 2) than by 1-methoxynaphthalene. Apparently, the two major reaction sequences operating are* $ArH \rightarrow ArOCOCF_3 \rightarrow 4$ and $ArH \rightarrow (ArH^+) \rightarrow$ unidentified, probably polymeric products.

The effects of added H_2O and CH_3OH on the reaction are summarized in Table 2. In both cases low material balances were obtained, but with CH_3OH added a 24 % yield of 1 was obtained. In this experiment $(CF_3CO)_2O$ was

Table 2. Reaction of anthracene and O_2 with $NO^+BF_4^-$ in CH_2Cl_2/CF_3COOH containing H_2O or CH_3OH.[a]

Product	Yield (%)[d]	
	H₂O[b]	CH₃OH[c]
ArH	0	16
ArOCOCF₃	38	12
ArNO₂	4	4
1	4	24
4	4	1
Unidentified	50	43

[a]Reaction in 20 vol of CF_3COOH in CH_2Cl_2 for 20 h at 25 °C. [ArH] = 0.10, $[NO^+BF_4^-]$ = 0.004 M. [b]$[H_2O]$ = 0.40 M; no $(CF_3CO)_2O$ was added. [c]$[CH_3OH]$ = 0.40 M; 2 vol % of $(CF_3CO)_2O$ was added. [d]Determined by GLC.

* Control experiments verified that the formation of $ArOCOCF_3$ is due to the action of NO^+; anthracene was quantitatively recovered after treatment with O_2 in CH_2Cl_2 containing 20 % CF_3COOH for 48 h.
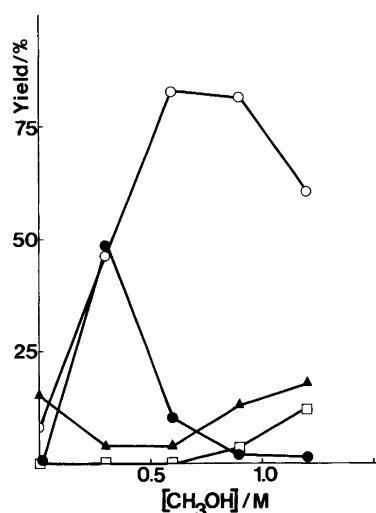
Fig. 1. Plot of formation of 1 (○) and ArNO₂ (▲) vs. [CH₃OH] in the reaction of anthracene (□) with CH₃OH and NaNO₂ in 10 vol % CF₃COOH in CH₂Cl₂ at 25 °C for 20 h. The yield of ArOCOCF₃ was for all [CH₃OH] < 3 %. [ArH] = 0.050 M, [NaNO₂] = 0.24 M.

findings a 'standard' system consisting of anthracene (0.05 M), $NaNO_2$ (0.22 M) and CH_3OH (0.60 M) in CH_2Cl_2 containing 10 % CF_3COOH was considered as optimal, and by this method very pure 1 could be obtained in 80 % isolated yield (see the Experimental). As is evident from Figs. 1–3 the formation of 2 and of 4 can be considerable unless the optimized system is utilized.

The reaction proceeds via the intermediate formation of 9,10-dihydro-9,10-dimethoxyanthracene, 6a, (Scheme 2) which initially created some confusion since 6a was almost quantitatively converted into 10-methoxy-9(10H)-anthracenone (7a) under the GLC conditions employed. This was established by comparison with authentic samples of 7a (and 7d), prepared by literature methods. Moreover, upon all attempted purification procedures including column chromatography, 7a was rapidly and apparently quantitatively transformed into 1, as it was on being heated and treated with base or, albeit more slowly, with acid. Since 1 and 7a exhibit identical retention times in the GLC system employed, the yield attributed to 1 in Figs. 1–3 is actually an approximate value of the sum of the yields of 1 and 6a in the reaction mixture. Since most of the 6a would be converted into 1 upon purification, this approximation was considered acceptable. According to NMR spectroscopy the crude product contains no significant amounts of 7a.

From a comparison of the mass spectra it could be established that after 5 min the ratio of 6a (or rather 7a) to 1 was > 1 while after 20 h this ratio was < 0.01.

The same reaction pattern was observed for all n-alkanols in the series $C_2H_5OH - n\text{-}C_6H_{13}OH$. In every case the mass spectrum and gas chromatogram was in accordance with the formation of 7b–7f, in these cases appearing as separate peaks, but from the NMR spectra of the crude

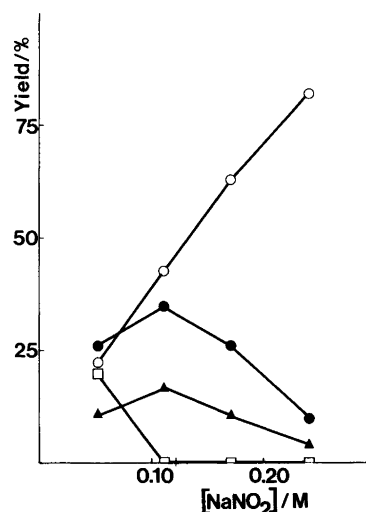present, but in the corresponding experiment with H_2O as the additive [performed in the absence of $(CF_3CO)_2O$] the yield of 1 was 4 %, indicating that H_2O is not an efficient source of oxygen necessary for the formation of 1 in these and related systems.

We then examined the effects of stoichiometric amounts of NO^+, added as $NaNO_2$ as described earlier for the anisole derivatives.[2] Reaction of an excess of $NaNO_2$ with anthracene in CH_2Cl_2/CF_3COOH gave mainly 9-nitroanthracene, together with minor amounts of 1 and 4, and low material balances (Fig. 1). The effects of added H_2O and alcohols on this reaction are summarized in Table 3, and from these results it was evident that CH_3OH was the additive that had the most beneficial effect on the formation of 1. Since this reaction was of considerable interest on its own right, a set of experiments was conducted whereby the concentrations of CH_3OH (Fig. 1), $NaNO_2$ (Fig. 2) and CF_3COOH (Fig. 3) were altered in turn. Based on these-

Table 3. Reaction of anthracene with NaNO₂ in CH₂Cl₂/CF₃COOH in the presence of various additives.[a]

Product	Yield (%)[b]		
	H₂O	CH₃OH	n-C₄H₉OH
ArH	0	0	0
ArOCOCF₃	2	0	1
ArNO₂	23	4	10
1	40	82	53
4	0	10	21

[a]Reaction in 10 vol % of CF₃COOH in CH₂Cl₂ for 20 h at 25 °C. [ArH] = 0.050 M, [NaNO₂] = 0.24 M, [ROH] = 0.60 M. [b]Determined by GLC.

Fig. 2. Plot of formation of 1 (○), 4 (●) and ArNO₂ (▲) vs. [NO₂⁻] in the reaction of anthracene (□) with CH₃OH and NaNO₂ in 10 vol % of CF₃COOH in CH₂Cl₂ at 25 °C for 20 h. The yield of ArOCOCF₃ was 9 % at [NO₂⁻] = 0.005 M and otherwise < 3 %. [ArH] = 0.050 M, [CH₃OH] = 0.60 M.
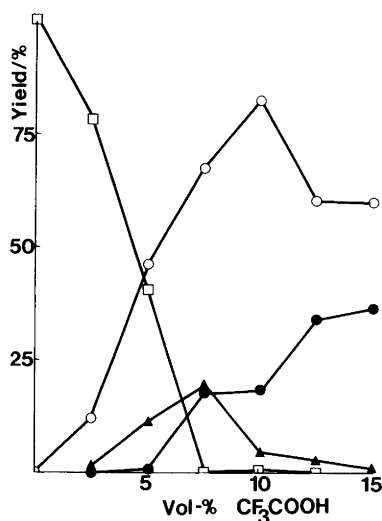
Fig. 3. Plot of formation of **1** (○), **4** (●) and ArNO₂ (▲) vs. [CF₃COOH] in CH₂Cl₂ in the reaction of anthracene (□) with CH₃OH and NaNO₂ at 25 °C for 20 h. The yield of ArOCOCF₃ was for all [CF₃COOH] < 3 %. [ArH] = 0.050 M, [CH₃OH] = 0.60 M, [NaNO₂] = 0.24 M.

products the *absence* of **7b–7f** and the *presence* of the corresponding dialkoxydihydroanthracene (**6**) could be verified.

Owing to their instability with respect to transformation into **1**, none of the different dialkoxydihydroanthracenes could be obtained in a pure state. Fortunately, a set of well-resolved NMR spectra could be obtained from a 1:1 mixture of **6d** and **1**. Table 4 demonstrates the outcome of the reaction of anthracene, NaNO₂ and *n*-C₄H₉OH with respect to time, although the yield of **6d** (taken as the GLC

Scheme 2. Possible modes of formation of 9,10-anthraquinone from anthracene, NO⁺ and CH₃OH not involving ET steps.

yield of **7d**) must be considered approximate. The other alkanols all exhibited similar reaction patterns, and out of these the highest yield of **1** (64 %) was obtained when C₂H₅OH was used. Interestingly, the use of H₂O resulted in a lower yield of **1**, higher yield of 9-nitroanthracene and lower material balance than was obtained with any of the *n*-alkanols (cf. Table 3).

Finally, a few experiments concerning the reaction of anthracene with N₂O₄ in CH₂Cl₂ were performed. It has been suggested that the formation of **1** as a by-product in this reaction would be a consequence of the presence of adventitious water.[9] When dry CH₂Cl₂ was saturated with H₂O/H₂¹⁸O (^{16}O:^{18}O = 4:1), redried and used as a solvent for the reaction of N₂O₄ with anthracene no signs of an increase in the amount of (^{16}O^{18}O)-**1** (M = 210) over (^{16}O₂)-**1** (M = 208) was observed in the mass spectrum. Moreover, addition of an equimolar amount (to anthracene) of H₂O or of the labelled mixture did not effect the 9-nitroanthracene:**1** ratio and did not lead to any significant enhancement of the peak at 210 relative to that at 208 in the mass spectrum. Therefore, the formation of **1** in this reaction does not appear to be a consequence of the presence of trace amounts of H₂O. Another clue to the mode of formation of **1** may be found in the reaction of 9-phenylanthracene with N₂O₄ in CH₂Cl₂. According to GLC, in addition to 9-nitro-10-phenylanthracene two other products are formed, with parent peaks in their mass spectra at m/z = 290 and m/z = 286. The latter spectrum is in accordance with structure **9**, which in turn may be formed during the GLC procedure from the corresponding dihydroxy compound **10** (R = H), analogous to the transformation **6a** → **7a**. A more detailed investigation on these findings is in progress, but it appears likely that the formation of **9** via **10** as well as of **1** via **7a**, may be a consequence of 1,4-addition across the 9,10-positions, while the formation of 9-nitroanthracene and 9-phenyl-10-nitroanthracene largely results from direct substitution. When anthracene and N₂O₄ were allowed to react in the presence and absence of CH₃OH in different solvents, the ratios of 9-nitroanthracene to anthraquinone presented in Table 5 were obtained. Note
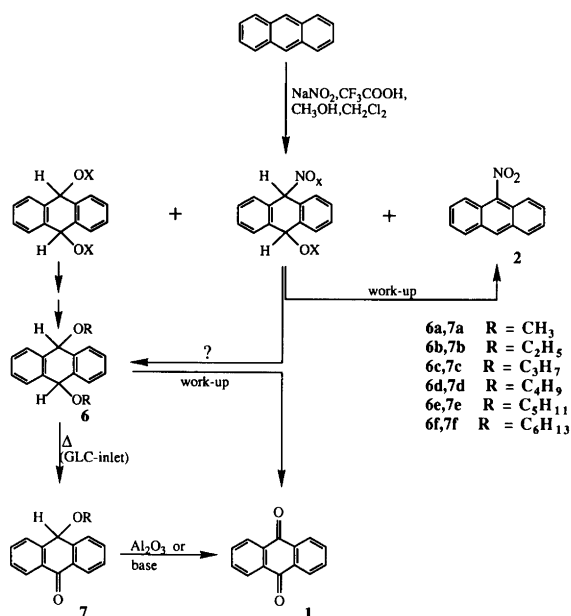
Table 4. Reaction of anthracene and *n*-C₄H₉OH with NaNO₂ in CH₂Cl₂/CF₃COOH.[a]

Product	Yield after t/h			
	0.3	1	3.5	20
ArH	1	0	0	0
ArOCOCF₃	7	3	2	1
ArNO₂	0	5	8	10
1	15	23	33	53
4	15	19	19	21
6a	61	45	32	10

[a]Reaction in 10 vol % of CF₃COOH in CH₂Cl₂ at 25 °C. [ArH] = 0.050 M, [NaNO₂] = 0.24 M, [*n*-C₄H₉OH] = 0.60 M.
[b]Determined by GLC.

9   10

that in the presence of CH_3OH the amount of **1** presented actually represents the sum of the amounts of **1** and **6a**. The reactions in CCl_4 were considerably slower than those in the other solvents. This suggests the possibility of a different, probably free-radical mechanism, in media of such low polarity, similar to findings earlier reported for perylene[10] and fluoranthene.[11]

Discussion

The reaction between anthracene and $NO^+PF_6^-$ in CH_2Cl_2 in the absence of air has been demonstrated to yield the radical cation salt $(ArH)_2^{+\cdot}PF_6^-$ and $NO\cdot$.[6] In the presence of O_2 the same reaction gives good yields of 9-nitroanthracene. Owing to the low solubility of $NO^+BF_4^-$, resulting in reactions at the crystal surfaces, the results from the preparative experiments described here can only be used in a qualitative manner. It can be stated, that anthracene is indeed oxidized but that the resulting $ArH^{+\cdot}$ has no reaction paths available since coupling to yield **5** apparently does not occur. The formation of 9-nitroanthracene and **4** (no **1** was formed) are probably due to reactions during work-up, e.g. of NO with O_2 to yield NO_2 and subsequent nitration. The reluctance of $ArH^{+\cdot}$ to yield **3** is similar to the behavior of the naphthalene radical cation.[5,12]

Turning to the systems containing CF_3COOH, a more readily analyzable reaction pattern emerges, partly due to the increased solubility of NO^+ and partly to the possibility

$$ArH \xrightarrow{-e^-} ArH^{+\cdot} \xrightarrow[-H^+]{CF_3COO^-} \xrightarrow{-e^-} ArOCOCF_3 \quad (8)$$

$$ArOCOCF_3 \xrightarrow[-2H^+]{-2e^-} 7a \rightarrow \rightarrow 4 \quad (9)$$
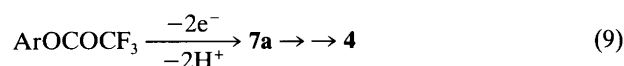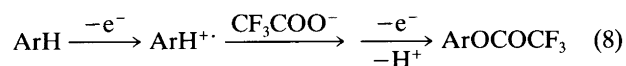
Table 5. Ratio of formation of 9-nitroanthracene to 9,10-anthraquinone in the reaction of anthracene and N_2O_4 in different solvents in the presence and absence of CH_3OH. [ArH] = 0.020 M, $[N_2O_4]$ = 0.010 M.[a]

Solvent	Ratio $ArNO_2$:1^b	
	Without CH_3OH	With CH_3OH^c
CCl_4	> 100	No reaction
CH_2Cl_2	8.1	0.09
CH_3CN	3.1	0.06
CH_2Cl_2:CF_3COOH (9:1)	> 100	> 100

[a]Reaction in 50 ml of solvent for 20 h at 25 °C. [b]Determined by GLC. [c]$[CH_3OH]$ = 0.20 M.

of follow-up reactions of $ArH^{+\cdot}$, i.e. the formation of **3a** [eqn. (8)] and subsequent reactions [eqn. (9)]. The oxidative formation of **4** (but not **1**) from 9-alkoxy- and 9-acyloxy-anthracenes is a well established process.[13,*] Since the formation of **1** in these experiments was negligible, it appears that **4**, rather than **1**, is the product most readily formed following initial ET.

When the catalytic system (NO^+/O_2), which was very efficient for the production of 4,4'-dimethoxy-1,1'-binaphthyl from 1-methoxynaphthalene, was used with anthracene as the substrate, conversion into **3a** and **4** once again dominated the outcome of the reaction. The lower efficiency of the present system relative to that of 1-methoxynaphthalene was, as stated above, caused by the reaction of ArH (or $ArH^{+\cdot}$) with NO_2 to yield 9-nitroanthracene. In the absence of CF_3COOH, obviously, no **3a** (and only a tiny amount of **4**) was formed, emphasizing the importance of eqns. (8) and (9).

In the presence of H_2O the catalytic system yielded mainly **3a**, while the formation of **1** was anything but impressive, adding additional doubts regarding the efficiency of the reaction between $ArH^{+\cdot}$ and H_2O as a route to **1**. Using CH_3OH as the additive, significant formation of **1** resulted, albeit not at a preparatively useful level. The mechanism of the formation of **1** in this experiment is probably catalytic and reminiscent of that of the reaction between anthracene and $NaNO_2$/CF_3COOH/CH_3OH. Regarding this reaction a few conclusions can be drawn from the data presented above, while the mechanistic considerations necessarily have to be kept at a fairly speculative level.

In the presence of both CF_3COOH and CH_3OH the reaction of anthracene with $NaNO_2$ gave low yields of **3a** whereas no 9-methoxyanthracene (**3c**) (sought by GC and MS) could be detected. Since CH_3OH would be expected to be more efficient for the capture of $ArH^{+\cdot}$ than CF_3COOH, and since any **3c** formed would, in all likelihood, be rapidly converted into **8** (Z = OCH_3) or **4** rather than into 9,10-dimethoxyanthracene (**6a**)[13] (a possible precursor of **1**, see Scheme 2), the outcome of the reaction, i.e. a high preference for the formation of **1** over **4** is not in accordance with the operation of an ET mechanism. Scheme 1 summarizes the possible outer-sphere ET reactions of anthracene and NO^+. (F symbolizes a feasible, NF a non-feasible follow-up reaction to the different ET steps.)

Since outer-sphere ET does not appear to the involved, it seems very likely that the formation of **1** in the 'standard system' *and also in the N_2O_4 nitration* of anthracene is a consequence of a polar 1,4-addition across the 9,10-position. The results presented in Table 5 show that the preference for polar addition during N_2O_4 nitration (i.e. more **1**

* In this paper the yields of **4** listed may include contributions from e.g. **6a** and **7a**, since these compounds cannot be separated properly under the GLC conditions employed. After work-up, the NMR spectrum of the fraction connected to the longest GLC retention times invariably showed the presence of essentially pure **4**. Note that **6a** has been reported as the major product of anodic oxidation of anthracene in the presence of CH_3OH.[13b]

was formed) increased with increasing solvent polarity (i.e. with an enhanced capacity of stabilizing ion pairs such as $NO^+NO_3^-$ or $NO^+OCH_3^-$) in the series CCl_4, CH_2Cl_2, CH_3CN. In the presence of CF_3COOH the direct formation of 9-nitroanthracene is strongly catalyzed,[8] and hence even in the presence of CH_3OH addition cannot compete with substitution. In CCl_4 another reaction path is followed; no formation of NO^+ occurs and formation of 9-nitroanthracene instead is brought about via another route (free radical substitution or addition/elimination). The formation of large amounts of 1 by N_2O_4 in dry CH_3CN, and also of the smaller amounts associated with reaction in CH_2Cl_2, cannot be explained by the presence of adventitious water. Instead, the oxygen atoms incorporated into 1 either must originally have been present in $NO^+NO_3^-$ or another lower nitrogen oxide compound, or originate from the H_2O used during work-up to hydrolyze or substitute an unstable reaction product as has been schematically represented in Scheme 2. The more efficient production of 1 in the presence of CH_3OH in CH_3CN, as well as in CH_2Cl_2, suggests that in these cases one of the oxygen atoms of 1 was originally present in CH_3OH; i.e. via (at least formally) addition of $NO^+OCH_3^-$. We have earlier pointed out that the N_2O_4 nitration of anthracene does not give a quantitative yield of 9-nitroanthracene unless acid is added, whereas that of pyrene does.[8b] In the uncatalyzed reaction, formation of 9-nitroanthracene probably also occurs via a 'normal' substitution, as in the case of pyrene, via an addition/elimination mechanism involving adducts[14] that can yield either 9-nitroanthracene or 1 from further transformations. Lack of data prevents us from further speculations on the nature of such adducts, or on their mode of formation.* The discussion will be continued in a future study, where $CH_3^{18}OH$ and $NaN^{18}O_2$ will be used.

It may finally be noted that the method presented above for the synthesis of 1 (i.e. the 'standard conditions') offers a convenient, mild and simple alternative to the established methods for the synthesis of 1 from anthracene. Earlier reports describe the use of HNO_3, $(NH_4)_2Cr_2O_7$, $CuBr_2/O_2$ and many other oxidizing agents,[15,16,17a] and most recently Rodriguez and Tijero described an industrial process in which N_2O_4 in CH_3COOH was used at elevated temperatures.[16b] These oxidations have often been considered to involve $ArH^{+\cdot}$, and the reaction between anthracene and ceric ammonium nitrate was suspected to proceed via reaction of $ArH^{+\cdot}$ and CAN to yield $ArONO_2$.[17a]

Experimental

Materials and methods. Generally the same materials and procedures reported earlier were used.[2,5,8] $H_2^{18}O$ (20 % in $H_2^{16}O$) was obtained from KOR isotopes. GLC analyses

were performed,[8] and NMR and mass spectra recorded[18] as previously described.

Products were identified by comparison of GLC retention times and by their mass and NMR spectra. GLC yields were determined by internal and external standard methods using 1-nitronaphthalene as the reference compound.

Reactions of anthracene with $NO^+BF_4^-$. Reactions were performed exactly as described earlier for the naphthalenes[5] and the amounts employed are summarized in Tables 1 and 2. In the experiments where CH_3OH and H_2O were used as additives, these were added prior to $NO^+BF_4^-$.

Reactions of anthracene with $NaNO_2/CF_3COOH/CH_3OH$. The reactions were performed in Erlenmeyer flasks equipped with an addition funnel, a drying tube and magnetic stirring apparatus. The amounts used are summarized in Figs. 1–3 and Tables 3–4. All reactions were performed analogously to those described below for the 'standard system.'

Synthesis of 9,10-anthraquinone ('standard system'). Anthracene (0.010 mol), $NaNO_2$ (0.044 mol) and CH_3OH (0.120 mol) were mixed in 150 ml of CH_2Cl_2 and a mixture of 20 ml of CF_3COOH and 30 ml of CH_2Cl_2 was added over 5 min.

The reaction mixture turned dark green and nitrogen oxides were evolved. Stirring was continued for 20 h, and the mixture was poured into H_2O, separated, the aqueous layer shaken with CH_2Cl_2, and the combined organic layers were washed with H_2O, aq. $NaHCO_3$, and H_2O and dried. After evaporation and passage through a short column (silica gel 60; pentane/CH_2Cl_2), essentially pure 9,10-anthraquinone (0.080 mol, 80 %) was isolated.

Preparation of 9,10-di-n-butoxy-9,10-dihydroanthracene. Application of the procedure described above (replacing CH_3OH with n-C_4H_9OH), and quenching of the reaction mixture with water after 10 min, resulted in the formation of a slightly yellow solution which, according to GLC, consisted mainly of 1, 4 and 6d (Table 4). The solution was dried and evaporated, and the resulting solid was dissolved in pentane, filtered, evaporated, redissolved in pentane, filtered and evaporated (with benzene added to remove traces of n-C_4H_9OH) to yield an approximately 1:1 mixture of 1 and 6d, which was stable in the dark at 4 °C in C_6D_{12}. The product showed exactly the same GLC retention time and GLC/MS as 7d; prepared by a literature method.[19] ^1H NMR (300 MH$_2$, C_6D_{12}): 0.74 (t, 6), 1.20–1.40 (m, 8), 2.82 (t, 4), 5.65 (s, 2) (Ar$_2CHOR$), 7.29 (m, 4), 7.42 (m, 4). ^{13}C NMR (300 MHz, $CDCl_3$): 13.8, 19.8, 32.1, 63.4, 71.5 (Ar$_2CHOR$), 127.3, 128.5, 135.5. It was not determined whether the reaction yielded the *cis* or *trans* isomer, but from the NMR spectra it was evident that only one of the isomers was formed. The Ar$_2CHOCH_3$ absorptions of *cis* and *trans*-9,10-dimethoxy-9,10-dihydroanthracene appear at 5.25 and 5.38 ppm, respectively, in $CDCl_3$.[17b]

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* Among the possibilities are the initial addition of $NO^+NO_3^-$ or NO^+OZ^- or initial nitrosation followed by capture of $Ar(H)NO^+$ by OZ^-. Note the formation of 1 during anodic oxidation of 9-nitroanthracene in CF_3COOH.[13b]

Reactions of anthracene with N_2O_4. The reactions were performed in stoppered Erlenmeyer flasks as described previously.[8] The additives were weighed in them prior to addition of the N_2O_4 solution.

Note added in proof. Pryor and coworkers have recently [*J. Org. Chem. 55* (1990) 4322] established that the reaction between anthracene and N_2O_4 in CCl_4 initially yields *cis*- and *trans*-9,10-dinitro-9,10-dihydroanthracene.

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