# Nitration of Reactive Aromatics *via* Electron Transfer. V.* On the Reaction between Nitrogen Dioxide and the Radical Cation Hexafluorophosphates of Some Methyl-substituted Naphthalenes**

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The coupling reactions of a series of methylnaphthalene radical cation hexafluorophosphates with nitrogen dioxide were studied in dichloromethane at low temperatures. Yields of nitro derivatives were generally higher with the β-methyl- than with the α-methyl-substituted naphthalenes and the isomer distributions were different from those obtained in electrophilic aromatic nitration and nitrous acid catalyzed nitration. This confirms an earlier suggestion that the coupling reaction is not an elementary step of either nitration process. The high regioselectivity of the coupling reaction can only partly be correlated with UHF spin densities.

Pyrene$^{+\cdot}$ hexafluorophosphate does not yield nitropyrenes upon treatment with nitrogen dioxide. This confirms earlier suggestions that only radical cations of aromatics with $E°$ values $\geq 1.7$ V will take part in a successful (exergonic) coupling reaction with nitrogen dioxide.

The proposal that electrophilic aromatic nitration (EAN)[1] might occur *via* an initial electron transfer (ET) step [eqn. (1)] with formation of a radical cation and nitrogen dioxide, has recently been scrutinized by us and others.[2-10] While it is well established that radical cations can be detected in

$$ArH + NO_2^+ \rightleftharpoons \overline{ArH^{+\cdot}NO_2} \rightleftharpoons \overset{\cdot}{Ar}(H)NO_2$$
$$\rightarrow ArNO_2 + H^+ \qquad (1)$$
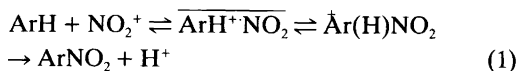
certain cases of EAN, it is not likely that this is a consequence of direct, non-bonded ET between ArH and NO$_2^+$. Nitronium ion is a poor reagent for non-bonded ET due to the very large reorganization energy of the NO$_2^+$/NO$_2$ couple,[3] and we have therefore suggested that radical ca-

tion formation should occur *via* an association-dissociation mechanism [eqn. (2)]. Here radical cation formation is dependent on a favourable

$$ArH + NO_2^+ \underset{}{\overset{a}{\rightleftharpoons}} \overset{+}{Ar}(H)NO_2 \overset{b}{\rightleftharpoons} ArH^{+\cdot} + NO_2 \quad (2)$$

equilibrium constant of the dissociation step (2b).[3,4]

We have earlier suggested on the basis of experimental findings that the coupling betwen ArH$^{+\cdot}$ and NO$_2$ [eqn. (3)] is dependent upon

$$ArH^{+\cdot} + NO_2 \rightleftharpoons \overset{+}{Ar}(H)NO_2 \qquad (3)$$

$E°(ArH^{+\cdot}/ArH)$. For easily oxidizable ArH (*e.g.*, perylene with $E° = 1.30$ V*) the coupling reaction is estimated to be endergonic, and this is manifested in a low or very low yield of ArNO$_2$.[4]

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*Vs.* NHE; all potentials given in this paper are referred to this electrode.

On the other hand, for a difficultly oxidizable ArH (*e.g.*, naphthalene with $E° = 2.08$ V) eqn. (3) is exergonic, thus explaining the obtention of a 100 % yield of the ultimate product after coupling, ArNO$_2$. In this case, it was also noted that the selectivity of this reaction type was high, $\alpha/\beta$ being *ca.* 60 (*cf.* $\alpha/\beta = 10$ for NaphH/NO$_2$$^+$ and 25 for NaphH/NO$_2$).[2]

Since our knowledge of the coupling reaction (3) is confined to the limiting cases mentioned above, we undertook this study to obtain more information on the behaviour of substrates in the critical region of $1.6 \leq E° \leq 2.0$ V. For this purpose, radical cation salts of pyrene ($E° = 1.60$ V) and a series of mono- and dimethylnaphthalenes** ($E° = 1.8$–2.0 V) were prepared by electrocrystallization and subsequently treated with NO$_2$, and the results compared with those obtained from nitration by nitric acid/acetic anhydride and dinitrogen tetroxide/dichloromethane, respectively.

## Results

*Nitration of the methylnaphthalenes.* Treatment of the methylnaphthalenes with nitric acid in acetic anhydride at 0 °C yielded mononitromethylnaphthalenes as summarized in Table 1. The isomer distributions were determined by GLC using fused-silica capillary columns and are in reasonable agreement with earlier reports,[11,12] except for 1,4-DMNaphH which was reported[12] to yield the 5-NO$_2$ isomer only. In our hands both the 2- and 5-NO$_2$ isomers, together with the side-chain nitration product, were detected. However, upon treatment with nitric acid and sulfuric acid in acetic acid in the presence of sodium azide, *i.e.* under conditions minimizing[7] the extent of nitrous acid catalyzed (NAC) nitration,[13–15] formation of the 5-NO$_2$ isomer was almost exclusive.

The results from the reactions of the methylnaphthalenes with dinitrogen tetroxide in dichloromethane are summarized in Table 1. There are no earlier reports on this reaction; however, the results parallel those earlier reported for naphthalene in that the preference for $\alpha$-substitution is more pronounced under NAC nitration than under EAN conditions.[2,14] The tendency of 1,4-DMNaphH to undergo side-chain nitration

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**Abbreviations: Methylnaphthalenes MMNaphH, Dimethylnaphthalenes DMNAphH.

has been well documented,[12,16] and for a substrate with no free $\alpha$-position available, 1,4,5,8-tetramethylnaphthalene, the reaction with dinitrogen tetroxide leads solely to 1-nitromethyl-4,5,8-trimethylnaphthalene.

The relative reactivities of the methylnaphthalenes (together with acenaphthene) toward dinitrogen tetroxide were established in a series of competition experiments using 2,3-DMNaphH as the reference compound (Table 1). Naphthalene was also slowly nitrated and 1,4,5,8-tetramethylnaphthalene reacted too rapidly for a comparison of product ratios to be reliable in these cases.

*Synthesis and reactions of (methylnaphthalene)$_2$PF$_6$.* The anodic oxidation of the methylnaphthalenes to yield the dimer monopositive radical ion hexafluorophosphates [(MNaphH)$_2$ PF$_6$] was performed by a modification of the electrocrystallization technique reported by Fritz *et al.*[19] for (NaphH)$_2$PF$_6$. The caramel-like crystal aggregates thus obtained could be kept for at least 2 h at temperatures around −70 °C under argon. UV and ESR spectra were recorded from suspensions of the solids in dichloromethane (Table 2). As earlier reported[19] for (NaphH)$_2$PF$_6$ the ESR spectra of the solids showed no hyperfine structure. When treated with dinitrogen tetroxide in dichloromethane at −70 °C the crystals appeared unaffected but upon warming to *ca.* −20 °C the deep violet suspensions disintegrated, turning to homogeneous yellow or orange solutions. However, the yields reported in Table 2 and isomer distributions given in Table 1 were obtained using excess (MNaphH)$_2$PF$_6$. In these experiments the violet colour therefore persisted on warming and the resulting reaction mixtures were brown-black containing varying amounts of nitro derivatives, dimerized methylnaphthalenes and their nitration products plus unidentified solid material. Regardless of this precaution the isomer distributions reported can, especially for the $\alpha$-substituted dimethylnaphthalenes, be suspected of containing small contributions from those of dinitrogen tetroxide nitration of the neutral methylnaphthalene.

When treated with a small excess of tetrabutylammonium nitrite (TBANO$_2$) at −70 °C a "caramel" of [2-MMNaphH]$_2$PF$_6$ disintegrated within a few s to yield a slightly yellow solution containing 2-MMNaphH and some (1–3 %) monochlorobut no (<0.1 %) mononitro-2-MMNaphH.

*Synthesis and reactions of (pyrene)$_2$PF$_6$.*

Table 1. Nitration of methylnaphthalenes under different conditions.

| Substrate | Conditions for nitration[a] | $k_{rel}$[b] | Isomer distribution/% | | | | | Other (Yield/%) |
|---|---|---|---|---|---|---|---|---|
| | | | 1– | 2– | 4– | 5– | 8– | |
| 1-Methylnaphthalene | A (ArH$^+$/NO$_2$) | | | 8 | 88 | 1 | 3 | |
| | B (N$_2$O$_4$) | 0.04 | | 18 | 66 | 10 | 6 | |
| | C (AcONO$_2$) | | | 31 | 56 | 8 | 5 | |
| | D (AcONO$_2$) | | | 23 | 43 | 10 | 18 | 3–(6) |
| 2-Methylnaphthalene | A | | 84 | | 10 | 3 | 3 | 6–(0.1) |
| | B | 0.02 | 65 | | 17 | 7 | 9 | (2) |
| | C | | 56 | | 16 | 11 | 12 | (8) |
| | D | | 53 | | 17 | 9 | 14 | (7) |
| 1,4-Dimethylnaphthalene | A | | | 95 | | 5 | | 4-CH$_2$NO$_2$ (<0.1) |
| | B | 9 | | 3 | | 5 | | (92) |
| | C | | | 6 | | 18 | | (76) |
| | E (AcONO$_2$) | | | | | 100[c] | | (trace)[d] |
| | G (NO$_2^+$, N$_3^-$) | | | 14 | | 82 | | (4) |
| 1,8-Dimethylnaphthalene | A | | | <8 | >92 | | | |
| | B | 19 | | 12 | 88 | | | |
| | C | | | 70 | 30 | | | |
| | E | | | 93 | 7 | | | |
| | F (HNO$_3$/AcOH) | | | 21 | 79 | | | |
| | G | | | 14 | 86 | | | |
| 2,3-Dimethylnaphthalene | A | | 90 | | | 10 | | 6–(<0.1) |
| | B | 1 | 77 | | | 21 | | (2) |
| | C | | 77 | | | 18 | | (5) |
| | E | | 73 | | | 21 | | (6) |
| 2,6-Dimethylnaphthalene | A | | 90 | | 10 | | | 3–(<0.1) |
| | B | 2 | 78 | | 22 | | | (<0.1) |
| | C | | 84 | | 15 | | | (1) |
| | E | | 82 | | 16 | | | (2) |

[a]A: Excess radical cation salt/NO$_2$ in CH$_2$Cl$_2$ at −70 to −20 °C. B: MnaphH/N$_2$O$_4$ in CH$_2$Cl$_2$ at 20 °C. C: MNaphH/HNO$_3$ in Ac$_2$O at −10 °C. D: MNaphH/HNO$_3$ in Ac$_2$O at 25 °C; Ref. 11. E: MNaphH/HNO$_3$ in Ac$_2$O at 0 °C; Ref. 12. F: MNaphH/HNO$_3$ in AcOH at 25 °C; Ref. 12. G: MNaphH/HNO$_3$/H$_2$SO$_4$/NaN$_3$ in AcOH at 20 °C. [b]One mmol of MNaphH, 1.0 mmol of 2,3-DMNaphH, 0.15 mmol of N$_2$O$_4$ in CH$_2$Cl$_2$ at 20 °C overnight. Acenaphthene and 1,4,5,8-tetramethylnaphthalene (side-chain nitration only) had $k_{rel}$ > 10$^2$ and > 10$^3$, respectively. [c]After 24 h at −10 °C. [d]After 90 h at −10 °C.

(PyH)$_2$PF$_6$ was prepared by exactly the same technique as earlier reported for (perylene)$_2$PF$_6$.[4] When the resulting black crystals were treated with an equimolar amount of nitrogen dioxide in dichloromethane at 20 °C and stirred for 2 h less than 1 % of 1-nitropyrene was formed, the major reaction product being tarry materials. Treatment with excess TBANO$_2$ resulted in a very rapid 100 % electron transfer reaction yielding pyrene and NO$_2$, which nitrates pyrene only very slowly in the presence of nitrite ion.[20]

## Discussion

Table 3 lists the ratios of the most abundant α-isomer to all other isomers formed (side-chain ni-

*Table 2.* Synthesis, physical data and reactions of (methylnaphthalene)$_2$ hexafluorophosphates.

| Substrate | $E^\circ/V^a$ | Yield/%$^b$ | Ratio ArNO$_2$:ArAr$^c$ | ESR $g$ value$^d$ | UV $\lambda_{max}$/nm |
|---|---|---|---|---|---|
| 1-Methylnaphthalene | 1.99 | 50 | 1 | – | 560, 480 (sh) |
| 2-Methylnaphthalene | 2.02 | 90 | 7 | 2.00538 | 544, 470 (sh) |
| 1,4-Dimethylnaphthalene | 1.81 | 50 | 1 | 2.00469 | 590 |
| 1,8-Dimethylnaphthalene | – | 5 | 0.1 | 2.00407 | 537, 462, 434 |
| 2,3-Dimethylnaphthalene | 1.90 | 88 | 6 | 2.00577 | 540, 490 (sh) |

$^a$Calculated by methods given in Refs. 17 and 18. $^b$Yield of ArNO$_2$ from ArH$^{+\cdot}$ + NO$_2$ based upon the amount of NO$_2$ added; estimated accuracy ±10 %. $^c$Defined as area-% nitronaphthalenes/area-% dimers + nitrodimers. $^d$Under similar conditions solid (perylene)$_2$PF$_6$ yielded a $g$ value of 2.00472.

tration products omitted) together with our earlier presented results for naphthalene. The preference for α-substitution increases in the order EAN < NAC nitration < ArH$^{+\cdot}$ + NO$_2$ with the exception of 1,4-DMNaphH.
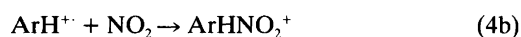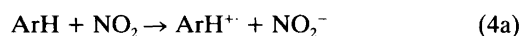
*Table 3.* Ratio of most abundant α-nitro isomer (in EAN) to all other nitro isomers formed in the nitration of naphthalene and some methylnaphthalenes.

| Substrate | NO$_2^+$ | N$_2$O$_4$ | ArH$^{+\cdot}$ + NO$_2$ |
|---|---|---|---|
| Naphthalene[2,14] | 11 | 25 | 40 |
| 1-Methylnaphthalene | 1.3 | 1.9 | 7.3 |
| 2-Methylnaphthalene | 1.3 | 1.9 | 7.0 |
| 1,4-Dimethylnaphthalene | 5.8 | 1.7 | 0.05 |
| 1,8-Dimethylnaphthalene | 2.3 | 7.3 | 12 |
| 2,3-Dimethylnaphthalene | 3.3 | 3.3 | 9 |
| 2,6-Dimethylnaphthalene | 3.5 | 5.3 | 9 |

*Table 4.* Orders of positional reactivities towards NO$_2$ and of UHF spin densities of the naphthalene and some methylnaphthalene radical cations.

| Aromatic | ArH$^{+\cdot}$ + NO$_2$ | UHF spin density |
|---|---|---|
| Naphthalene | 1>2 | 1>2 |
| 1-Methylnaphthalene | 4>2>8>5 | 4>5>8>2 |
| 2-Methylnaphthalene | 1>4>8≈5 | 1>8>4>5 |
| 1,4-Dimethylnaphthalene | 2>5≤6 | 5>2>6 |
| 1,8-Dimethylnaphthalene | 4>2>3 | 4>2>3 |
| 2,3-Dimethylnaphthalene | 1>5>6 | 1>5>6 |
| 2,6-Dimethylnaphthalene | 1>4>3 | 1>4>3 |

For all substrates each of the routes leads to the formation of ArNO$_2$ with different isomer distributions. This confirms our earlier suggestion that the coupling reaction between *free* ArH$^{+\cdot}$ and NO$_2$ is not an elementary step of EAN or NAC nitration. Moreover, since nitrite ion acts as an effective reducing agent towards the radical cations of naphthalene,[2] perylene,[4] 2-methylnaphthalene and pyrene we conclude that the ET step of a recently proposed mechanism[21] for the nitration of polycyclic aromatic hydrocarbons by nitrogen dioxide [eqn. (4)] cannot be feasible for aromatics with $E^\circ$ values higher than *ca.* 1.3 V. A detailed discussion on the nitration

$$ArH + NO_2 \rightarrow ArH^{+\cdot} + NO_2^- \tag{4a}$$
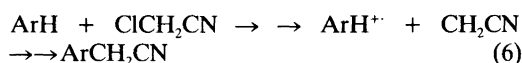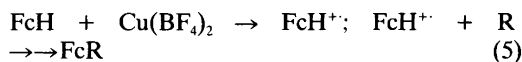
$$ArH^{+\cdot} + NO_2 \rightarrow ArHNO_2^+ \tag{4b}$$

by dinitrogen tetroxide and other cases of NAC nitration and on the properties of nitrogen dioxide as an ET oxidant has recently been presented.[20]

It has been well established that certain compounds, among them anthracene,[20] are very sensitive to and exhibit a special reaction pattern under conditions of NAC nitration. This behaviour is obviously shared by 1,4-DMNaphH and although the products, anthraquinone and 1-nitromethyl-4-methylnaphthalene, cannot be formed *via* the same mechanism, similarities may exist.

While the results from EAN and to some extent NAC nitration readily can be compared with earlier reports, the reaction between aromatic radical cations and NO$_2$, although suggested in many reaction schemes of later years,[5–10,14,15,21,22] has only occasionally been the subject of detailed

experimental work. Studies in the gas-phase[9] and on the electrochemical generation of $ArH^{+\cdot}$ in solutions containing nitrogen dioxide[4,8,10] indicate, together with our own results, that the coupling reaction can indeed take place. Since neither the radical cation of perylene nor that of pyrene *but* that of 1,4-dimethoxybenzene[6] ($E° = 1.89$ V), anodically generated in micellar solution, and the various naphthalene radical cations do couple, we conclude that the reaction is feasible only for radical cations of aromatics with $E°$ values $\geq 1.7$ V. The nitro compounds observed[4,10b,10c] from reactions between nitrogen dioxide and radical cation salts of certain heteroaromatics with low $E°$ values are likely to have been formed *via* nitration by dinitrogen tetroxide.

Very little is known about the coupling reaction of aromatic radical cations with radicals. To out knowledge only two examples have been presented besides the work related to nitration, namely oxidative substitution on ferrocene[23] [eqn. (5); R = *e.g.* $(CH_3)_2CCN$, CN, $COCH_3$] and photochemical aromatic cyanomethylation[24] [eqn. (6); ArH = *e.g.* toluene]. The mode of formation of cyanoisopropylferrocene has later been revised.*

$$FcH + Cu(BF_4)_2 \rightarrow FcH^{+\cdot}; \quad FcH^{+\cdot} + R$$
$$\rightarrow \rightarrow FcR \tag{5}$$

$$ArH + ClCH_2CN \rightarrow \rightarrow ArH^{+\cdot} + CH_2CN$$
$$\rightarrow \rightarrow ArCH_2CN \tag{6}$$

In our opinion the isomer distributions presented for the cyanomethylation reaction (*e.g.*, for toluene *o:m:p* = 33:47:20) fall more in line with a process of the type reported by Olah and Overchuck[25] for the high temperature free radical nitration of toluene by nitrogen dioxide (*o:m:p* = 37:38:25) than with the results presented here. Perrin[5] has suggested that radical pair collapse will exhibit selectivity due to the non-uniform spin density of the radical cation and that bond formation is likely to predominate at the positions with (a) the highest spin density and (b) where the most stable σ-complex will be produced. We therefore continue to consider radical cation – radical coupling a reaction of high regioselectivity.

How then do our results correlate with calcu-

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*The following alternative mechanism was proposed:[23b]
$FcH^{+\cdot} + R \rightarrow FcH + R^+ \rightarrow \rightarrow FcR$.

lated spin densities? Presented in Table 4 are the orders of positional reactivities towards nitrogen dioxide and the UHF spin densities[26] of the radical cations. Obviously, the spin density is only one, and perhaps not even the most important, component determining the isomer distribution. More pronounced is the affinity for substitution in the ring bearing the methyl substituent(s), best exemplified by the high preference for 2-substitution in 1,4-DMNaphH$^{+\cdot}$. We have presently no consistent explanation for this behaviour and more experimental and theoretical work will be needed for reliable rationalizations to be possible.

## Experimental

*Materials and methods.* Pyrene, acenaphthene and the methylnaphthalenes (all of >98% purity) were commercial samples and used without further purification. 1,4,5,8-Tetramethylnaphthalene was prepared according to a literature procedure.[27] Dichloromethane (Merck zur Rückstandsanalyse) was dried and stored over 3 Å molecular sieves. Solutions of dinitrogen tetroxide were made up as described previously.[20] All other reagents were commercial samples of highest purity available and used as supplied.

Constant currents were provided by a Radiak or an Amel 552 power supply. GLC analyses were performed on capillary columns (12.5 m × 0.2 mm SE-30 or 25 m × 0.2 mm OV 1701) on a Varian 3400 gas chromatograph equipped with a Varian 4270 integrator. Column chromatography was performed on 20×700 mm columns on silica gel 60 (Merck, 230–400 mesh) using hexane with 0–50% chloroform as eluent.

^{1}H NMR spectra were recorded at a Nicolet Model 360 WB or a Varian XL 300 spectrometer. UV/VIS spectra were recorded on a Cary 219 spectrophotometer. Mass spectra were recorded on a Finnegan 4021 instrument at 70 eV. ESR spectra were recorded on a Bruker ER 200D SRC spectrometer.

*Nitration of methylnaphthalenes with nitric acid in acetic anhydride.* One mmol of MNaphH in 10 ml of acetic anhydride was treated with 1.1 mmol of $HNO_3$ in 2 ml of acetic anhydride at $-10°C$. After hydrolysis, neutralization, extraction, addition of internal standards, washing and drying the resulting mixtures of isomers were analyzed for yields and isomer distributions by GLC. The sep-

*Table 5.* Mass spectrometric fragmentation of methylnitronaphthalenes.[a]

| Compound | M | M-17[b] | M-30[c] | M-45[d] | M-46[e] | M-47[f] | M-58[g] |
|---|---|---|---|---|---|---|---|
| 2-Nitro-1-methylnaphthalene[i] | 49 | 66 | 1 | 48 | 30 | 19 | 7 |
| 4-Nitro-1-methylnaphthalene[i] | 71 | 2 | 9 | 17 | 29 | 15 | 32 |
| 5-Nitro-1-methylnaphthalene[i] | 95 | 2 | 10 | 12 | 31 | 12 | 55 |
| 8-Nitro-1-methylnaphthalene[i] | 30 | 70 | 1 | 5 | 20 | 25 | 5 |
| 1-Nitro-1-methylnaphthalene[i] | 78 | 13 | 17 | 35 | 35 | 19 | 49 |
| 4-Nitro-1-methylnaphthalene[i] | 72 | 2 | 4 | 15 | 35 | 20 | 52 |
| 6-Nitro-1-methylnaphthalene | 100 | 0 | 5 | 5 | 43 | 5 | 18 |
| 8-Nitro-1-methylnaphthalene[h] | 100 | 0 | 19 | 17 | 40 | 14 | 56 |
| 2-Nitro-1,4-dimethylnaphthalene[j] | 60 | 65 | 5 | 78 | 28 | 55 | 3 |
| 5-Nitro-1,4-dimethylnaphthalene[k] | 30 | 95 | 8 | 8 | 6 | 15 | 1 |
| 1-Nitromethyl-4-methylnaphthalene | 5 | 7 | 11 | 15 | 85 | 35 | 15 |
| 2-Nitro-1,8-dimethylnaphthalene | 92 | 100 | 2 | 73 | 32 | 70 | 3 |
| 4-Nitro-1,8-dimethylnaphthalene[l] | 85 | 1 | 8 | 13 | 11 | 22 | 18 |
| 1-Nitro-2,3-dimethylnaphthalene[l] | 93 | 22 | 15 | 51 | 28 | 28 | 20 |
| 5-Nitro-2,3-dimethylnaphthalene[l] | 98 | 1 | 10 | 27 | 39 | 32 | 20 |
| 6-Nitro-2,3-dimethylnaphthalene[l] | 100 | 2 | 9 | 12 | 68 | 15 | 35 |
| 1-Nitro-2,6-dimethylnaphthalene[l] | 88 | 22 | 18 | 55 | 29 | 27 | 20 |
| 3-Nitro-2,6-dimethylnaphthalene[m] | 83 | 69 | 13 | 22 | 34 | 45 | 10 |
| 4-Nitro-2,6-dimethylnaphthalene[l] | 81 | 0 | 12 | 28 | 31 | 30 | 31 |

[a]In % of the base peak, not adjusted for the $^{13}C$ isotope contribution. [b]M-OH. [c]M-NO. [d]M-NO$_2$+1. [e]M-NO$_2$. [f]M-HNO$_2$. [g]M-NOCO. [h]In mixture with the 5-NO$_2$ isomer. [i]Base $m/z$ at 115. [j]Base $m/z$ at 129. [k]Base $m/z$ at 43. [l]Base $m/z$ at 128. [m]Base $m/z$ at 152.

aration and purification of the isomeric nitro-1-methylnaphthalenes and nitrodimethylnaphthalenes (Table 1) were performed by flash chromatography (5 % chloroform in hexane; orders of elution peri-, α-, β-, except for 1,8-DMNaphH for which the 2-isomer eluted first) followed by recrystallization (ethanol). The isomers were identified by their mass spectra (Table 5) and, in most cases, by UV/VIS and NMR spectra.[28] 1-Nitro-2-methylnaphthalene eluted prior to an inseparable, though readily analyzable, mixture of the 4-, 5- and 8-isomer and the assignments made have been based on mass spectra, GLC retention times and NMR studies.

*Nitration of the methylnaphthalenes by dinitrogen tetroxide.* One mmol of the methylnaphthalene, 0.80 mmol of N$_2$O$_4$ and 0.1 mmol of methanesulfonic acid were dissolved in 20 ml of dichloromethane, mixed and left overnight. After work-up and addition of internal standard, yields and isomer distributions were determined by GLC. Using flash chromatography, the side-chain nitration products could be eluted with 50 % chloroform in hexane. In this manner *1-ni-*

*tromethyl-4-methylnaphthalene* could be isolated in 87 % yield as white needles, m.p. 106–107 °C and with satisfactory spectral data.[16d] *1-Nitromethyl-4,5,8-trimethylnaphthalene* was isolated in 94 % yield as white needles, m.p. 101–102 °C, $^1$H NMR (300 MHz, CDCl$_3$) 2.75 (s,3), 2.87 (s,3), 2.91 (s,3), 6.02 (s,2), 7.19 (m,2), 7.29 (m,2). MS $m/z$ (% rel. abd.) 229 (5,M$^+$), 183(100), 181(32), 165(23), 153(21).

*Syntheses and analyses of [MNaphH]$_2$PF$_6$.* The methylnaphthalene (0.05 M) and TBAPF$_6$ (0.02 M) in dichloromethane was electrolyzed (1–2 mA for 2–3 h) at −70 °C in a divided cell designed as follows: The side-necks of a 100 ml three-necked flask were equipped with an inlet for argon and a specially designed anode (Pt-gauze)/gas-outlet, respectively. In the middle neck, held by a screw-cap, a cylindrical ceramic cell divider surrounding the cathode (Pt wire) was immersed. The flask was placed in a dry-ice acetone bath, and when the appropriate amount of current had passed, the cathode compartment was taken out and the anolyte removed by suction while continuously flushing with argon. After careful washing

with pre-cooled dichloromethane the violet crystal aggregates, adhering at the anode, were stored at −70 °C under argon. UV spectra were recorded by placing a small amount of crystals in a cuvette with dichloromethane at low temperature under argon, allowing the temperature to rise to around −20 °C by wiping the windows and rapidly transferring the cuvette into the spectrophotometer. Samples for ESR were obtained by transferring a small amount of the crystals together with some dichloromethane into a capillary at low temperature while flushing with argon.

*Reactions of [MNaphH]₂PF₆. With nitrogen dioxide.* Nitrogen dioxide (50 % of the theoretically formed amount of [MNaphH]₂PF₆) in 20 ml of dichloromethane was pre-cooled to −70 °C and added to the flask while vigorously flushing with argon. Magnetic stirring was started and the cooling bath removed. When the temperature had reached 0 °C the reaction mixture was quenched with dilute aqueous sodium bicarbonate solution. After washing and addition of internal standard the mixtures were analyzed by GLC. The dimers and nitrated dimers formed (Table 2) were identified by GLC/MS; no further attempts were made at the isolation and characterization of these compounds. *With tetrabutylammonium nitrite.* Replacing nitrogen dioxide by a 150 % excess of TBANO₂ the procedure above led to almost instantaneous ⋅ decolorization and disintegration of the solid. In a typical experiment, GLC showed the presence of 95 % of the theoretical amount of 2-MMNaphH and, as identified by MS, *ca.* 2 % of monochlorinated 2-MMNaphH.

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