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Reactivity of 1-nitronaphthalene and 1,3-dinitronaphthalene with conjugated dienes. An easy access to *N*-naphthylpyrroles

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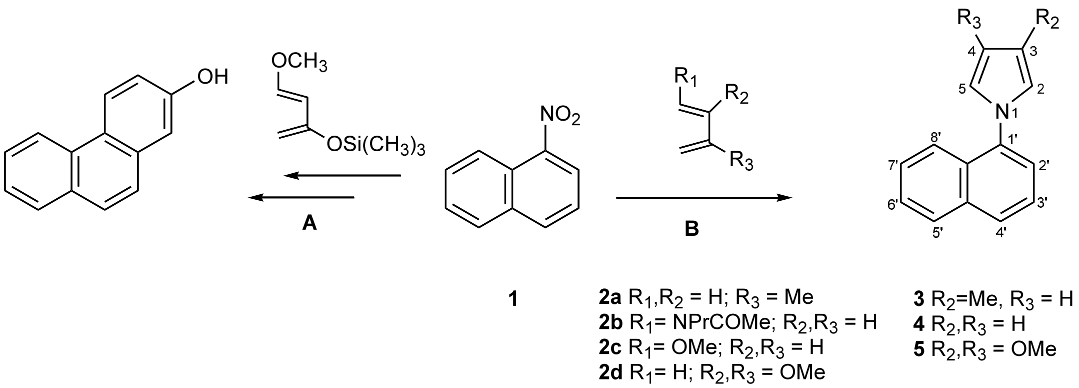
Abstract—1-Nitronaphthalene reacts at high temperature with poor and moderately reactive dienes affording *N*-naphthylpyrroles while, with the same dienes, 1,3-dinitronaphthalene exhibits the dienophilic character of naphthalenic C3–C4 bond producing the corresponding phenanthrenes through a classical Diels–Alder process. © 2003 Elsevier Science Ltd. All rights reserved.

We have recently reported that mono- and dinitronaphthalenes react as dienophiles with a highly activated diene such us *trans*-1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (Danishefsky's diene) by thermal Diels–Alder reactions (with normal electron demand) giving rise to nitro-adducts which suffer aromatization providing the corresponding phenanthrenes (Scheme 1 (A)).[1–3] Interestingly, during the course of extending the above findings to nitronaphthalenes employing less reactive dienes, we found that 1-nitronaphthalene afforded *N*-naphthylpyrroles. The purpose of the present work is to discuss the thermal behavior of nitronaphthalenes with a range of dienes of low to moderately high reactivity. The study was carried out using 1-nitronaphthalene (**1**) and 1,3-dinitronaphthalene (**6**) as substrates. Isoprene (**2a**), 1-(*N*-acetyl-*N*-propylamino)-1,3-butadiene (**2b**), 1-methoxy-1,3-butadiene (**2c**) and 2,3-dimethoxy-1,3-butadiene (**2d**) were chosen as diene components.

The reactions were performed under conditions similar to those reported for nitronaphthalenes with Danishefsky's diene. Thus the substrates were reacted at elevated temperatures with the above cited dienes in ampules using dry benzene as solvent.[4] The results are given in Tables 1 and 2.



Scheme 1. Reactivity of 1-nitronaphthalene with different dienes.

Keywords: 1-nitronaphthalene; *N*-naphthylpyrrole; 1,3-dinitronaphthalene; phenanthrene.

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Table 1. Thermal reactions of 1-nitronaphthalene with dienes of different reactivity

Entry	Diene	Conditions	Product, yield[a] (%)
1	**2a**, 12 equiv.	150°C, 96 h	**3**, 36
2	**2a**, 12 equiv.	180°C, 96 h	**3**, 47[b]
3	**2b**, 3 equiv.	120°C, 72 h	**4**,[1] 43
4	**2c**, 3 equiv.	120°C, 72 h	**4**, 94
5	**2c**, 3 equiv.	150°C, 72 h	**4**, 100
6	**2d**, 2 equiv.	120°C, 72 h	**5**, 15

[a] Based on consumed nitronaphthalene.

[b] 1-Aminonaphthalene in moderate amounts was also detected at this higher temperature.[12]

Table 2. Thermal reactions of 1,3-dinitronaphthalene with dienes **2a**–**d**

Entry	Diene	Conditions	Product, yield[a] (%)	
			Phenanthrene	Pyrrole
1	**2a**, 5 equiv.	120°C, 72 h	**7**, 23.4	Traces
2	**2b**, 3 equiv.	120°C, 72 h	**8**,[14] 26.3	Traces
3	**2c**, 3 equiv.	120°C, 72 h	**8**, 16.5	**10**, 5; **10′**, 1
4	**2d**, 2 equiv.	120°C, 72 h	**9**, 13	Traces

[a] Based on consumed dinitronaphthalene.

Reactions of 1-nitronaphthalene proceeded in all the cases to produce the corresponding *N*-naphthylpyrroles **3**–**5**[5] as the only product (Scheme 1 (B)). The yield increases with higher temperatures and more reactive dienes (Table 1).

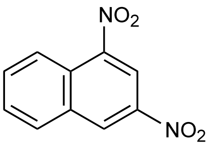
These results evidently involve a condensation between two components with complementary electronic character. On the other hand, it is already known that nitrosobenzene reacts with butadienes afforting the hetero Diels–Alder adduct that becomes *N*-phenylpyrrole by thermal[6,7] and photochemical activation.[8] Therefore, it is reasonable to assume that nitronaphthalenes can react through the heterodienophilic fragment of the nitro group with dienes of low and moderate reactivity producing a heteroadduct which rearranges with high temperature into the observed *N*-naphthylpyrroles.[9] Attempts to isolate intermediate compounds at lower temperatures were unsuccessful.

The low yield obtained with **2d** (Table 1, entry 6) with respect to the increasing yield tendency with the more reactive dienes of the series can be attributed to the difficulty of this diene to reach the *cisoid* conformation required for a [4π+2π] cycloaddition.[10]

When the butadienes **2b** and **2c** which are substituted at position 1 with heteroatoms were used, the loss of the substituent was observed in the resultant pyrroles for both cases which makes this procedure best suited for obtaining naphthylpyrroles substituted at positions 3 and/or 4 of pyrrole.[11]

Other reactions using aromatic hydrocarbons as dienes were also performed; for example 2-hydroxynaphthalenes and 1-vinylnaphthalene were reacted with substrate **1**. However no product was observed in appreciable amounts.

In the case of 1,3-dinitronaphthalene, reaction with dienes **2a**–**d** (Table 2), employing the conditions used with 1-nitronaphthalene, provided phenanthrenes **7**–**9**[5] as the mayor products. The phenanthrenes arise from Diels–Alder cycloaddition at C(3)–C(4) bond of the 1,3-dinitronaphthalene followed by *cis*-extrusion of nitrous acid from the primary nitro-adduct and subsequent aromatization. Traces of the corresponding naphthylpyrroles were also observed.[13] The characterization of a slightly larger quantity of pyrrole **10** obtained with **2c** (Table 2, entry 3) revealed the preferable addition to nitro at position 1 of naphthalene. Small amounts of regioisomer 1-(4′-nitro-naphthalen-2′-yl)-pyrrole (**10′**) (6.44 ppm, t, 2H, $J=2.1$ Hz; 7.22, t, 2H, $J=2.1$ Hz; 8.32 ppm, 1H, d, $J=2.25$ Hz) were also detected together with **10**.



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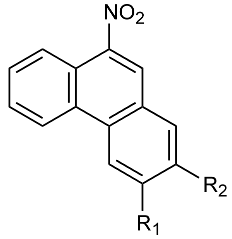
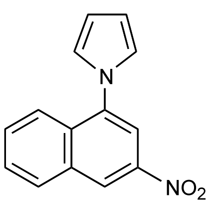


7 R_1= Me; R_2 = H
8 R_1,R_2 = H
9 R_1,R_2 = OMe



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Finally, the results are consistent with the formerly published reaction of 1,3-dinitronaphthalene and Danishefsky's diene that proceeds to yield 3-hydroxy-9-nitrophenanthrene as the principal product at 120°C, 72 h.[1] In the above case, only phenanthrenes and not pyrroles were reported to be obtained. Those previous observations serve to establish that *trans*-1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene due to its strong electron-donor substituents is at the moment the only diene which induces the Diels–Alder cycloaddition selectively to naphthalenic double bonds of both dinitronaphthalenes and mononitronaphthalenes.[1,2]

In conclusion it has been demonstrated that the combination of poor or moderately activated dienes with 1-nitronaphthalene causes the chemospecific obtention of *N*-naphthylpyrroles while a better naphthalenic dienophile such us 1,3-dinitronaphthalene with the same dienes leads mainly to the corresponding phenanthrenes. Thus, the major product of these reactions depends on diene and dienophile type.

These results make a further contribution to nitronaphthalenes reactivity and provide a clean one-pot synthesis of *N*-naphthylpyrroles from ready available 1-nitronaphthalene with several dienes.

Acknowledgements

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4. General procedure: The temperature, the length of reaction and the diene/dienophile ratio are given in Tables 1 and 2 for **1** and **6**, respectively. An ampule containing 1.0 mmol of the dienophile and the required amount of diene in 0.5 ml of dry benzene was cooled in liquid nitrogen, sealed and then heated in an oil bath. After the reaction time was completed, it was cooled once more in liquid nitrogen and opened. The solution was evaporated and the residue purified by column chromatography in silica gel using hexane/ethyl acetate mixtures as eluent.
5. Spectral data. ^{1}H and ^{13}C NMR, 200 and 50 MHz, respectively, δ (ppm), J (Hz). **3**: ^{1}H NMR δ (Cl_3CD) 2.20 (s, 3H, Me), 6.20 (dd, 1H, $J=2.1$, $J=1.9$), 6.70 (dd, 1H, $J=1.9$, $J=1.6$), 6.80 (dd, 1H, $J=2.1$, $J=1.6$), 7.38–7.52 (m, 4H), 7.82 (d, 2H, $J=8.2$), 7.9 (d, 1H, $J=8.3$); ^{13}C NMR δ (Cl_3CD) 12.00, 110.60, 119.71, 121.18, 123.02, 123.45 (2 C), 125.31, 126.45, 126.77, 127.49, 128.07, 129.83, 134.33, 138.44; MS (EI) *m*/*z* M+ 207. **5**: ^{1}H NMR δ (Cl_3CD) 3.82 (s, 6H, 2 OMe), 6.48 (s, 2H), 7.36–7.56 (m, 4H), 7.80 (dd, 1H, $J=8.1$), 7.88–7.97 (m, 2H); MS (EI) *m*/*z* M+ 253; IR 1020.76, 1201.80 cm^{-1}. **7**: ^{1}H NMR δ (Cl_3CD) 2.65 (s, 3H, Me), 7.52 (dd, 1H, $J=8.2$, $J=1.5$), 7.71–7.76 (m, 2H), 7.90 (d, 1H, $J=8.2$), 8.46 (s, 1H), 8.47–8.56 (m, 2H), 8.74 (m, 1H); MS (EI) *m*/*z* M+ 237; IR 1513.23, 1336.50 cm^{-1}. **9**: ^{1}H NMR δ (Cl_3CD) 4.02 (s, 3H, OMe), 4.12 (s, 3H, OMe), 7.24 (s, 1H), 7.64–7.72 (m, 2H), 7.90 (s, 1H), 8.40 (s, 1H), 8.50–8.60 (m, 2H); ^{13}C NMR δ (Cl_3CD) 56.05, 56.09, 103.20, 109.42, 122.49, 122.68, 123.90, 124.06, 125.10, 127.43, 127.46, 127.78, 130.30, 144.06, 152.27, 152.29; MS (EI) *m*/*z* M+ 283; IR 1526.53, 1315.50, 1262.43, 1025.48 cm^{-1}. **10**: ^{1}H NMR δ (Cl_3CD) 6.45 (t, 2H, $J=2.1$), 7.02 (t, 2H, $J=2.1$), 7.65–7.96 (m, 3H), 8.12 (dd, 1H, $J=7.0$, $J=2.9$), 8.21 (d, 1H, $J=2.3$), 8.76 (d, 1H, $J=2.3$); ^{13}C NMR δ (Cl_3CD) 110.20 (2 C), 116.60, 121.00 (2 C), 121.40, 126.40, 128.6, 130.20, 130.50, 132.20, 132.80, 139.50, 145.90; MS (EI) *m*/*z* M+ 238; IR 1532.30, 1355.25 cm^{-1}.
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9. As a separate experiment, nitrobenzene was also tested with diene **2b**. The expected phenylpyrrole was isolated and tested by mass analysis.
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11. The experience of others[8] indicates that when 2,4-hexadiene reacts with nitrosobenzene, the resultant pyrrole retains the methyl groups at its 2 and 5 positions. According to this, in the case of nitronaphthalene reactions, alkylic chains (but not heterosubstituents) present in positions 1 or 4 of diene would remain in *N*-naphthylpyrroles.
12. The appearance of 1-aminonaphthalene as a by-product in reactions of nitrosoarenes with different dienes was already reported. See Refs. 6, 7, and 8.
13. Traces of naphthylpyrroles were detected by TLC. A solution of *p*-methoxybenzaldehyde, acetic acid, ethanol and sulfuric acid (3:1:1:4) develop arylpyrroles as a red pot by heating.
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