A New Cycloaddition Process Involving Nitro Group Participation in Polynitroaromatic Chemistry

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The reaction of ethyl vinyl ether (2 equiv) with 4,6-dinitrobenzofuroxan (DNBF, 1 equiv) in dichloromethane affords a mixture of two diastereomeric dihydrooxazine *N*-oxide adducts, **5a** and **5b**, in a 4:1 ratio. Further addition of the enol reagent to this mixture results in a second cycloaddition process with formation of a bis(dihydrooxazine *N*-oxide) product **6**, which can also be obtained directly upon treatment of DNBF with excess ethyl vinyl ether. The observed condensations are accounted for in terms of inverse electron demand Diels−Alder cycloaddition processes between the enol ether dienophile and the heterodienyl moieties of DNBF, constituted first, by the 6-NO$_2$ group conjugated to the 6,7-double bond and then by the 4-NO$_2$ group and the 4,5-double bond of the carbocyclic ring. The configurations of the cycloadducts **5a** and **5b** have been determined on the basis of collected ¹H NMR parameters, as well as NOE experiments. It thus appears that the configuration of the major diastereomer corresponds to the endo product while that of the minor one corresponds to the exo product of the first cycloaddition process. The results obtained emphasize a low aromatic character for the DNBF molecule.

4,6-Dinitro-2,1,3-benzoxadiazole 1-oxide, commonly known as 4,6-dinitrobenzofuroxan (DNBF), is a neutral 10π-electron heteroaromatic substrate which exhibits an extremely high electrophilic character in many instances.[1−6] In particular, DNBF is capable of reacting quantitatively with a number of weakly nucleophilic carbon centers which are inert to coupling with the common reference aromatic electrophile 1,3,5-trinitrobenzene (TNB) under similar experimental conditions. A prototype example is shown in eq 1 which refer to the σ-complexation of DNBF by indoles.[5c,e,f] In fact, many π-excessive aromatics and heteroaromatics react with DNBF in a similar manner to indoles, affording very stable anionic C-bonded σ-adducts which are formally the products of S$_E$Ar substitution of the aromatic or heteroaromatic ring.[1−5,7]

(1)
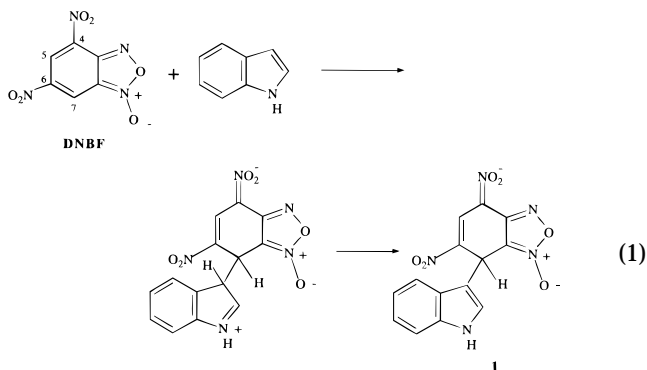
In all of the above processes, covalent addition of the carbon nucleophile takes place at C-7 of the carbocyclic ring of DNBF to give a stable anionic σ-complex (**1** in our example). The same principle applies in all reported interactions of DNBF with oxygen, nitrogen, or sulfur nucleophiles.[1−3] Accordingly our discovery in 1988 that the interaction of DNBF with indene affords the neutral dihydrooxazine *N*-oxide **2**, and not the related σ-zwitterionic adduct **3**, as a stable product (eq 2) was a rather surprising result in view of the classical chemical reactivity of this extremely electron-deficient heteroaromatic.[8]

(2)
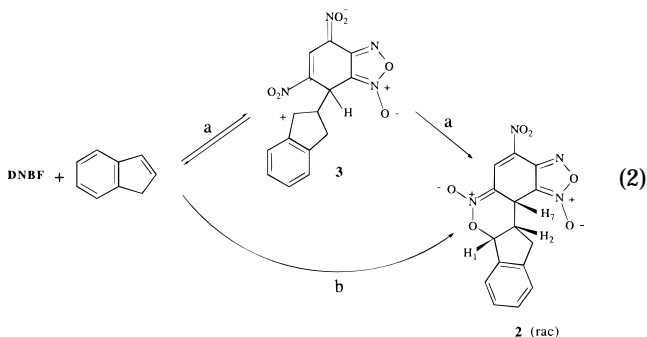
So far, the obtention of the cycloadduct **2** remained the unique example of neighboring nitro group participation

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(2) (a) Terrier, F.; Millot, F.; Norris, W. P. *J. Am. Chem. Soc.* **1976,** *98,* 5883. (b) Terrier, F.; Chatrousse, A. P.; Soudais, Y.; Hlaibi, M. *J. Org. Chem.* **1984,** *49,* 4176.

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(5) (a) Simonnin, M. P.; Hallé, J.-C.; Pouet, M.-J.; Terrier, F.; Davoust, D. *Can. J. Chem.* **1987,** *65,* 404. (b) Terrier, F.; Hallé, J.-C.; Pouet, M.-J.; Simonnin, M. P. *J. Org. Chem.* **1986,** *51,* 410. (c) Hallé, J.-C.; Simonnin, M. P.; Pouet, M.-J.; Terrier, F. *Tetrahedron Lett.* **1985,** *26,* 1307. (d) Terrier, F.; Hallé, J.-C.; Simonnin, M. P.; Pouet, M.-J. *J. Org. Chem.* **1984,** *49,* 4363. (e) Terrier, F.; Kizilian, E.; Hallé, J.-C.; Buncel, E. *J. Am. Chem. Soc.* **1992,** *114,* 1740. (f) Terrier, F.; Pouet, M.-J.; Hallé, J.-C.; Hunt, S.; Jones, J. R.; Buncel, E. *J. Chem. Soc., Perkin Trans. 2* **1993,** 1665.

(6) (a) Kind, J.; Niclas, H. J. *Synth. Commun.* **1993,** *23,* 1569. (b) Niclas, H. J.; Göhrmann, B.; Gründemann, E. *Synth. Commun.* **1991,** *333,* 909.

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Table 1. ^{1}H NMR Parameters of DNBF/Ethyl Vinyl Ether Cycloadducts **5a** and **5b**[a,b]

cycloadducts	δ_{H1}	δ_{H2}	$\delta_{H2'}$	δ_{H5}	δ_{H7}	$\delta_{H\alpha}{}^c$	$\delta_{H\alpha'}{}^c$	$\delta_{H\beta}{}^c$
5a (**M**: 79%)	5.72	3.47	1.94	8.31$_6$	4.14	3.73	4.01	1.22
5b (**m**: 21%)	5.69	3.07	2.24	8.30$_6$	4.59	3.81	4.06	1.28

cycloadducts	$^3J_{H1H2}$	$^3J_{H1H2'}$	$^2J_{H2H2'}$	$^3J_{H7H2}$	$^3J_{H7H2'}$	$^2J_{H\alpha H\alpha'}{}^c$	$^3J_{H\alpha H\beta}{}^c$	$^3J_{H\alpha' H\beta}{}^c$	$^3J_{H1^{15}N6}$	$^3J_{H5^{15}N6}$	$^3J_{H7^{15}N6}$
5a (**M**: 79%)	7.4	4.0	13.6	6.5	12.4	9.7	7.1	7.1	6.3	1.9	2.9
5b (**m**: 21%)	2.6	3.4	13.3	5.3	12.2	9.7	7.1	7.1	5.5	1.9	3.1

[a] δ in ppm relative to internal Me$_4$Si. J values in hertz. Solvent, CD$_2$Cl$_2$. [b] See structures **5a** and **5b** in Scheme 1 for numbering of hydrogen. [c] $\delta_{H\alpha}$ and $\delta_{H\alpha'}$ refer to the nonequivalent methylenic protons while $\delta_{H\beta}$ refers to the equivalent methyl protons of the ethoxy group.

Scheme 1
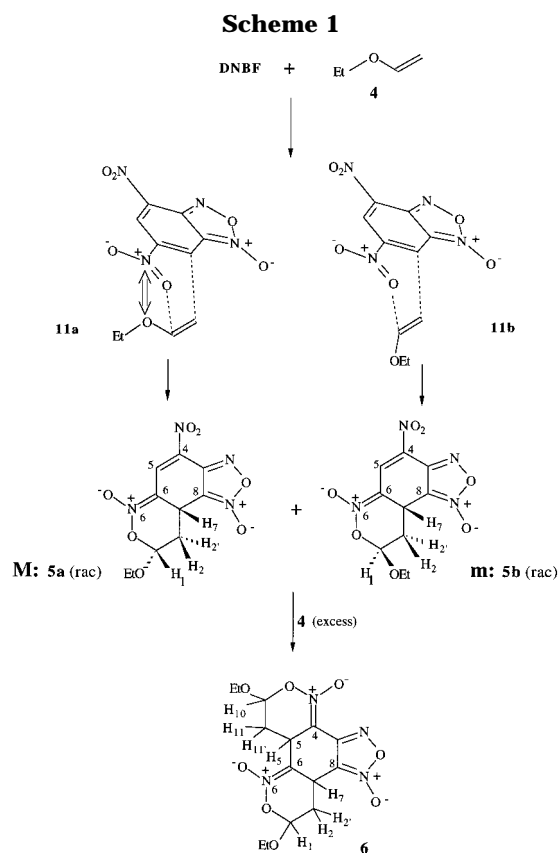
in the chemistry of DNBF. In this paper we report our finding that a similar cycloaddition process occurs upon treatment of DNBF with ethyl vinyl ether (**4**), with formation of the diastereomeric dihydrooxazine *N*-oxide cycloadducts **5a** and **5b** (Scheme 1, only one enantiomer of each is shown). Interestingly, a second cycloaddition takes place upon further addition of the enol reagent to the **5a** and **5b** mixture, leading to the bis(dihydrooxazine *N*-oxide) product **6**. As will be discussed, our results support the view that these cyclizations occur through IEDDA pathways rather than two-step pathways involving zwitterionic σ-complex intermediates.

Results

Addition of 2 equiv of ethyl vinyl ether (**4**) to a solution of DNBF in CD$_2$Cl$_2$ (CD$_3$CN or CDCl$_3$) resulted in the immediate disappearance of the ^{1}H NMR signals due to the two substrates and the concomitant appearance of two sets of signals with intensities in a 4:1 ratio (Table 1). Each of these two sets of signals consisted of a singlet (H5), two doublets of doublets (H7 and H1), and two multiplets (H2, H2′), consistent with the two diastereomeric dihydrooxazine *N*-oxide structures **5a** and **5b**

(Scheme 1).[9] Strong support for the formation of these two neutral cycloadducts was the finding that a ^{15}N labeling of the 6-NO$_2$ group resulted in a large coupling with the H1 proton. Also in accordance with the dihydrooxazine structures **5** was the observation in the ^{1}H NMR spectra of AMXY systems whose AMX parts reflect the coupling of the two nonequivalent methylenic protons H2 and H2′ with the H7 proton of the carbocyclic ring (**M**: δ_{H2} = 3.47, $\delta_{H2'}$ = 1.94 ppm and $^3J_{H7H2}$ = 6.5, $^3J_{H7H2'}$ = 12.4. **m**: δ_{H2} = 3.07, $\delta_{H2'}$ = 2.24 ppm and $^3J_{H7H2}$ = 5.3, $^3J_{H7H2'}$ = 12.2, Table 1). In general, the nonequivalence of the methylenic protons in anionic σ-adducts of type **7** (X = NO$_2$, COCH$_3$, CHO, CH(OH)OEt, CH(OEt)$_2$] is much less pronounced and their coupling with H7 gives rise to ABX rather than AMX systems in the related ^{1}H NMR spectra.[7,10,11] The stereochemical attribution of **5a** and **5b** will be part of the Discussion section.

7a, X = NO$_2$
7b, X = COMe
7c, X = CHO
7d, X = CH(OH)OEt
7e, X = CH(OEt)$_2$

8
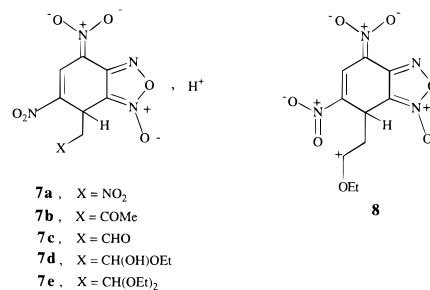
Removing the solvent in the above experiments leads to the isolation of a yellow solid consisting of a mixture of **5a** and **5b**, as evidenced by the NMR spectra recorded after dissolution of this solid in dichloromethane. Attempts to separate these two diastereomers by selective recrystallization have failed, but high-resolution mass spectra have been recorded which are in agreement with the proposed dihydrooxazine *N*-oxide structure **5** (see Experimental Section).

The reaction of DNBF with **4** was also studied using the enol reagent as solvent. Very rapidly, yellow crystals deposited which were isolated and identified as the bis(dihydrooxazine *N*-oxide) product **6**, on the basis of centesimal analysis and mass spectra experiments (see Experimental Section). Treatment of an isolated mixture of the monoadducts **5a** and **5b** with excess enol ether **4** (8 equiv) similarly afforded the diadduct. Interestingly, recorded ^{1}H NMR spectra revealed that **6** formed as a mixture of several diastereomers, as could be expected from a possible addition of the second enol molecule to

(9) The numbering of the carbon atoms was chosen according to those of the parent molecules. H2 refers to the most deshielded methylenic protons.

(10) Terrier, F.; Goumont, R.; Pouet, M.-J.; Hallé, J.-C. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1629.

(11) Hallé, J.-C.; Vichard, D.; Pouet, M.-J.; Terrier, F. Unpublished results.

Table 2. ^{1}H NMR Parameters of DNBF/Ethyl Vinyl Ether Biscycloadducts 6 (M1, M2)[a,b]

cycloadducts	δ_{H1}	δ_{H2}	$\delta_{H2'}$	δ_{H5}	δ_{H7}	δ_{H10}	δ_{H11}	$\delta_{H11'}$
6 (M1)	5.55	3.16	2.02	4.15	3.91	5.69	3.49	1.74
6 (M2)	5.56	3.34	1.74	4.06	3.90	5.69	3.94	1.64

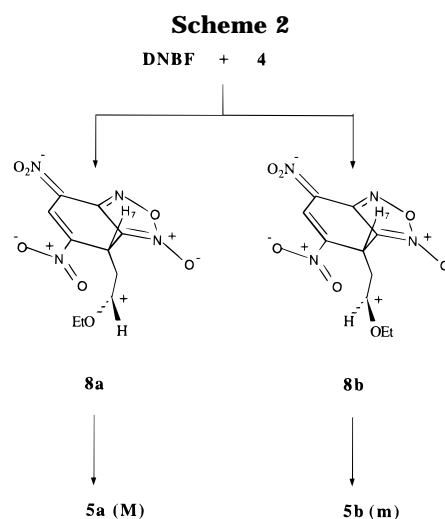| cycloadducts	$^3J_{H1H2}$	$^3J_{H1H2'}$	$^3J_{H10H11}$	$^3J_{H10H11'}$	$^2J_{H2H2'}$	$^2J_{H11H11'}$	$^4J_{H5H7}$	$^3J_{H7H2}$	$^3J_{H7H2'}$	$^3J_{H5H11}$	$^3J_{H5H11'}$	$^3J_{15N6H1}$
6 (M1)	6.8	3.8	7.5	4.2	13.9	13.3	2.4	7.0	10.1	5.8	12.5	5.9
6 (M2)	7.2	3.7	7.5	4.5	13.6	13.3	2.0	6.6	12.2	5.4	12.2	6.1

[a] δ in ppm relative to internal Me$_4$Si. J values in hertz. Solvent, CD$_2$Cl$_2$. [b] See structures **6 M1**, **M2** in Scheme 1 for numbering of hydrogens.

5a and **5b** through both the endo and exo modes. Due to the complexity of the NMR spectra, only resonances pertaining to the two major diastereomers **6**-**M1** and **6**-**M2** resulting from the interaction could be safely assigned using in particular data obtained in COSY and SPID experiments (Table 2). Typical for the formation of each of these two species was the presence in the ^{1}H spectra of two AMXY patterns associated with the H$_1$C$_1$C$_2$H$_2$(H$_2'$)C$_7$H$_7$ and H$_{10}$C$_{10}$C$_{11}$H$_{11}$(H$_{11'}$)C$_5$H$_5$ fragments shown in structure **6**. The unambiguous assignment of these two patterns was made on the basis of experiments carried out with (6-^{15}N)-4,6-DNBF. So far, the configurations of **6**-**M1** and **6**-**M2** have not been determined.

Discussion

Stereochemical Attribution of 5a and 5b. According to the common reactivity pattern of DNBF, treatment of this compound with ethyl vinyl ether (**4**) might be expected to afford the zwitterionic σ-adduct **8** whose negatively and positively charged moieties could be appropriately located for direct stabilizing interaction. Evidence for such stabilization in zwitterionic σ-adducts has been previously obtained for amidine adducts of 1,3,5-trinitrobenzene and 1,3-dinitronaphthalene.[12] However, there is no doubt that the whole NMR data favor the formation of the cycloadducts **5a** and **5b** rather than the zwitterionic σ-adduct **8**. A major argument supporting the oxazine *N*-oxide structures **5** and **6** is the observation by ^{1}H NMR spectroscopy of a large coupling between H1 and the labeled nitrogen atom of the 6-NO$_2$ group: $^3J_{15N6H1} = 6.3$ Hz (**M**) and 5.5 Hz (**m**). A similar situation holds in the diadducts **6 M1** and **6 M2**: $^3J_{15N6H1} = 5.9$ Hz (**M1**) and 6.1 Hz (**M2**). Interestingly these above coupling constants compare well with that observed for the indene cycloadduct **2**: $^3J_{15N6H1} = 7.1$ Hz.[8] Coupling between the ^{15}N-labeled 6-NO$_2$ group and the H7 and H5 protons of the carbocyclic ring of DNBF are also similar in structures **5** (Table 1) and **2**.[8] An additional but noteworthy feature further supporting the formation of the cycloadducts **5** is the fact that the H5 resonance of these species does not lie in the narrow range of 8.5−8.7 ppm which is known to be typical of the formation of DNBF anionic C-bonded σ-adducts.[1−5,7]

It is noteworthy that notable changes in the intensity of both the H1 and H7 resonances are observed upon irradiation of the most deshielded H2 proton in **M**, indicating that these three protons are located on the same side of the dihydrooxazine *N*-oxide ring, as shown in Scheme 1. In contrast, in the case of the minor isomer **m**, the intensity of the H7 signal is markedly affected

(12) (a) Bard, R. R.; Strauss, M. J. *J. Am. Chem. Soc.* **1975**, *97*, 3789. (b) Bard, R. R.; Strauss, M. J. *J. Org. Chem.* **1976**, *41*, 2421. (c) Reference 1b, p 38.

Scheme 2

DNBF + 4

8a   **8b**

5a (M)   **5b (m)**

upon irradiation of H2 but not that of H1. This fits well the arrangement of the H1, H2, and H7 protons shown in **5b**.

Analysis of the NMR parameters in Table 1 together with the results of NOE experiments thus allow one to attribute the configuration **5a** with H7 and the ethoxy group in a trans orientation to the major diastereomer **M** and the configuration **5b** with H7 and EtO in a cis orientation to the minor one **m**. Owing to chirality of the tetrahedral ring carbon C1, the methylenic protons of the ethoxy group of **5a** and **5b** (Hα,Hα′ in Table 1) are nonequivalent and appear as a pair of double quartets, i.e. the AB part of an ABX3 system. This pattern was also observed in the ethoxy group of the dihydropyrane derivatives **9**, which formed from inverse electron demand Diels−Alder (IEDDA) cycloadditions of ethyl vinyl ether (**4**) with 2-methylene-1,3-dicarbonyl compounds **10**.[13]

9   **10**
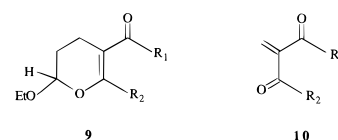
Mechanisms for Formation of 5a and 5b. It is now well-documented that the negative charge on arenide or heteroarenide σ−adducts is largely delocalized onto the NO$_2$ groups in highly activated systems, and hence the formation of the dihydrooxazine *N*-oxides **5** (Scheme 2) may at first be simply viewed as occurring according to a two-step mechanism in which the initially formed zwitterionic adduct **8** undergoes cyclization to **5**, through intramolecular nucleophilic attack of an oxygen atom of the ortho-like 6-NO$_2$ group of the DNBF moiety at the

(13) Yamauchi, M.; Katayama, S.; Baba, O.; Watanabe, T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3041.
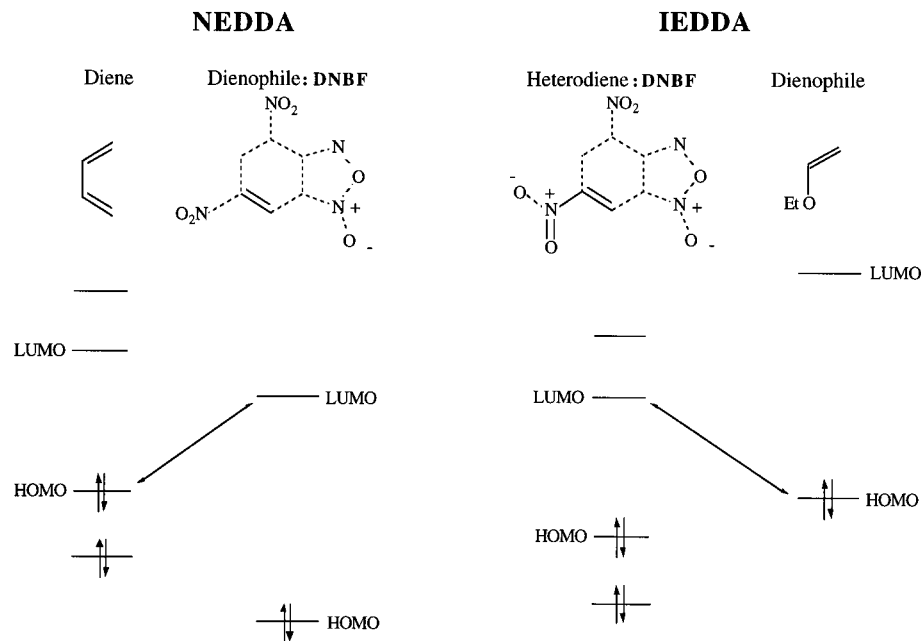
NEDDA   **IEDDA**

Figure 1. Qualitative diagram showing the ambident reactivity of DNBF as dienophile (NEDDA) or heterodiene (IEDDA).

positively charged carbon of the exocyclic vinyl ether structure. In fact, this mechanism is analogous to that previously postulated to account for the formation of **3** in the reaction of DNBF with indene[8] (eq 2). However the formation of **5** may also be envisioned as the result of a one-step [4 + 2] cycloaddition process in which the ethyl vinyl ether acts as a dienophile while the DNBF fragment derived from the 6-nitro group and the 6,7-conjugated double bond acts as an heterodiene moiety. As illustrated in Scheme 1, **5a** and **5b** would then be the products of inverse electron demand Diels−Alder (IEDDA) condensations proceeding through the endo mode and exo mode transition states **11a** and **11b**, respectively.

Considering only the monoaddition process, it would be difficult to definitely choose between the above two mechanisms but the finding that **5a** and **5b** undergo a second cycloaddition to provide **6** strongly suggests that these adducts are actually the result of the Diels−Alder condensations depicted in Scheme 1 rather than of the cyclization of the zwitterionic intermediates such as **8** (Scheme 2). Interestingly, ab initio and semiempirical calculations have been carried out which clearly rule out a contribution of the two-step pathways involving zwitterionic intermediates to the formation of **5a**, **5b**, and **6**.[14] Instead, these calculations favor a pericyclic process and account quite well for the observed enhanced reactivity of the 6-nitro heterodienyl moiety of DNBF relative to that of the 4-nitro analogue.[14]

Assuming that the formation of the cycloadducts proceeds according to the two-step mechanism of Scheme 2, one would also reasonably expect that the major diastereomer will form through cyclization of the less strained and therefore more populated conformation of the zwitterionic intermediate, i.e. **8b**. On this basis **5b** should be favored relative to **5a** in contrast with what we have observed. Considering next the [4 + 2] cycloaddition mechanism, shown in Scheme 1, the endo transition state **11a** is stabilized by a secondary orbital interaction between the oxygen atom of the enol ether

and the nitrogen atom of the 6-NO₂ group.[15] On the basis of this, one would instead expect the formation of the diastereomer **5a** with the trans EtO/H7 stereochemistry to be favored relative to **5b**, as is indeed borne out by experiments. Thus the cycloaddition mechanism is preferred.

Conclusion

It is noteworthy that this study has revealed for the first time the inverse electron demand Diels−Alder reactivity for the DNBF system, and this may be contrasted with the normal electron demand Diels−Alder (NEDDA) behavior previously observed in the reactions of 4-nitrobenzofuroxan (NBF) and 4,6-dinitrobenzofuroxan with butadiene or/and 2,3-dimethylbutadiene which give rise to the 1:1 and 2:1 adducts, **12** and **13**, respectively.[16]

12

13a. R = H
13b. R = Me
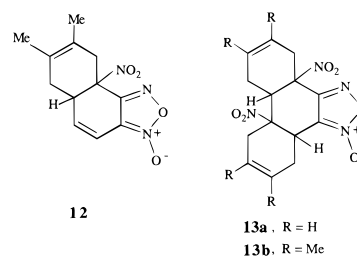
Clearly in the NEDDA addition the strongly electron withdrawing NO₂ group in DNBF or NBF facilitates dienophilic behavior in these molecules toward butadiene for example. However, in the IEDDA behavior of DNBF acting as a heterodiene, there is lowering of energy of the LUMO of this portion, but importantly, the LUMO of the enol ether becomes raised significantly, thereby disfavoring the normal LUMO−HOMO interaction. As a result, the inverse interaction becomes energetically

(14) Pugnaud, S.; Masure, D.; Hallé, J.-C.; Chaquin, P. *J. Org. Chem.* Submitted.

(15) Preliminary calculations (ref 14) are in accord with the transition state stabilization depicted in **11a** (cf. Scheme 1).
(16) Kresze, G.; Barthelt, H. *Tetrahedron* **1973**, *29*, 1043.

more favored.[14] These two modes of reaction are illustrated in the qualitative diagram of Figure 1.

In as much as some IEDDA condensations have been observed between enol ethers and α-nitroalkenyl compounds[17] (in order to synthesize, for example, new chiral heterocycles), the fact that DNBF may be able to react as a heterodiene in IEDDA reaction is a result of general significance. Such a behavior will in itself be evidence that this heterocycle has low resonance energy, a feature which is commonly accepted but has never been specifically addressed.[18]

Experimental Section

Materials. 4,6-Dinitrobenzofuroxan (DNBF) was prepared according to the procedure reported by Drost:[19] mp 173 °C (lit.[4b,5,19] mp 172−174.5 °C), modified to prepare [6-^{15}N]-4,6-dinitrobenzofuroxan (mp 173 °C).[8] Ethyl vinyl ether (**4**) (Aldrich) was distilled on sodium.[20]

Preparation of 5. An oven-dried NMR tube was charged with DNBF (0.084 g, 0.37 mmol) and CD_2Cl_2 (1 mL) and capped with a septum. Then **4** (0.090 mL, 0.94 mmol) was added within 15 min and the tube was shaken. A ^{1}H NMR

(17) (a) Denmark, S. E.; Schnute, M. E.; Senanayake, C. B. W. *J. Org. Chem.* **1993**, *58*, 1859. (b) Waldmann, H. *Synthesis* **1994**, 535 and references therein.

(18) Reference 7 and references therein.

(19) Drost, P. *Liebigs Ann. Chem.* **1899**, *307*, 49.

(20) Armarego, W. L. F.; Perrin, D. D. In *Purification of laboratory chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1996.

spectrum was recorded to follow the reaction and to characterize the mixture of **5a**,**5b**. When some higher amounts of the reagents were used, a precipitation finally occurred. Volatiles were removed by oil pump vacuum, and no further purification was required. The reaction was quantitative; mass spectrum (obsd), m/z = 299.0638 (M + 1)$^+$ (reference *m*-nitrobenzyl alcohol); $C_{10}H_{11}N_4O_7$ requires 299.0628. The yellow solid which was obtained is moisture sensitive and turns quickly to a dark brown oil. No melting point could be measured.

Preparation of 6. An oven-dried flask was charged with DNBF (0.120 g, 0.53 mmol) and **4** (2 mL, 0.021 mol). The reaction was exothermic, and an orange precipitate rapidly appeared. The reaction mixture was centrifugated, and the solid was rinsed with pentane, dried under oil pump vacuum, and stored under nitrogen. No further purification was required. The reaction was quantitative: mp 74 °C dec (diastereomeric mixture). Anal. Calcd for $C_{14}H_{18}N_4O_8$: C, 45.40; H, 4.86; N, 15.13. Found: C, 45.62; H, 4.76; N, 14.92. Mass spectrum (obsd): m/z = 371 (M + 1)$^+$, 325 (MH$^+$ − NO$_2$), 299 (MH$^+$ − NO − NO$_2$).

Measurements. ^{1}H NMR spectra were recorded on a Bruker AC300 spectrometer. Chemical shifts are reported in ppm (J values in hertz) with tetramethylsilane (Me$_4$Si) as the internal reference. The high-resolution mass spectra was obtained on a conventional EB-geometry mass spectrometer JEOL-AX-500 and DEC data system (JEOL-Europe-SA, Croissy sur Seine, France). Fast-atom bombardment ionization was performed with xenon atoms at 6 keV formed from a beam of 10 mA flux.