Competitive and Consecutive Inverse and Normal Electron Demand Cycloadditions in the Reaction of 4,6-Dinitrobenzofuroxan with Cyclopentadiene

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The high susceptibility of nitrobenzofuroxans to undergo covalent nucleophilic addition or substitution processes with very weak nucleophiles has raised considerable interest over the last 2 decades leading to numerous synthetic, biological, and analytical applications.[1-7] In comparison, another field of reactivity of nitrobenzofuroxans, namely the one pertaining to the capability of these compounds to be engaged in Diels–Alder processes, is much less developed. In 1973, Kresze and Bathelt reported that treatment of DNBF (see structure in Scheme 1) with butadiene and 2,3-dimethylbutadiene affords, after several weeks, the diadducts **1a** and **1b** (Chart 1), respectively.[8] Although the formation of these compounds was accounted for in terms of normal electron demand Diels–Alder (NEDDA)-type processes, this promising discovery did not lead to further investigation and neither the stereochemistry nor the mechanistic sequence leading to **1a** and **1b** was elucidated. To
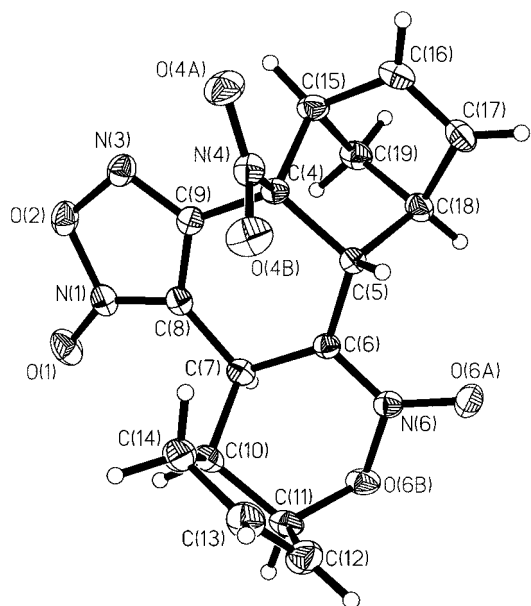
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Figure 1. ORTEP diagram of the diadduct **8**.

Figure 2. ORTEP diagram of the adduct **9**.

explore this potential field of reactivity, our laboratory has recently extended Kresze and Bathelt's work and found in particular that the reaction of DNBF with 1-trimethylsilyloxybuta-1,3-diene proceeds with a high endo stereoselectivity as well as a high regioselectivity, giving rise nearly quantitatively to the monoadduct **2** with no evidence for the formation of a diadduct of type **1**.[9a] At the same time, we found that the reaction of ethyl vinyl ether (2 equiv) with DNBF (1 equiv) in dichloromethane produces a 4:1 mixture of the two diastereomeric dihydrooxazine *N*-oxide adducts **3a** and **3b**.[9b] Use of a large excess of enol reagent afforded the bis-(dihydrooxazine *N*-oxide) product **4**.[9b] In this instance, theoretical calculations have been made which supported the experimental evidence that **3a** and **3b** are the result of inverse electron demand Diels–Alder (IEDDA) condensations and not of two-step addition–cyclization

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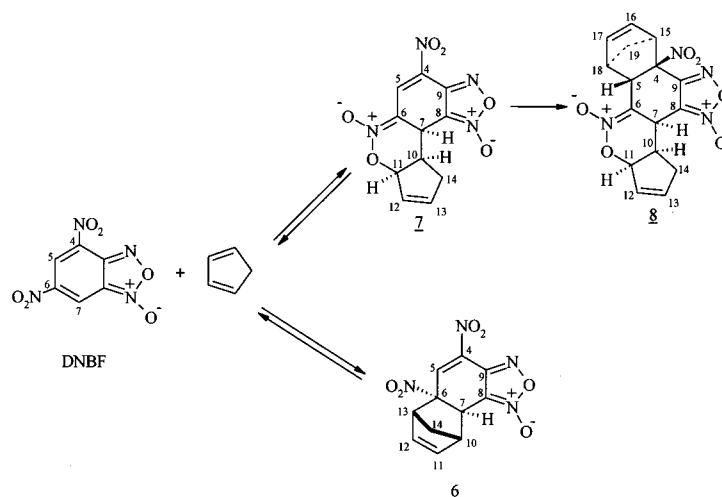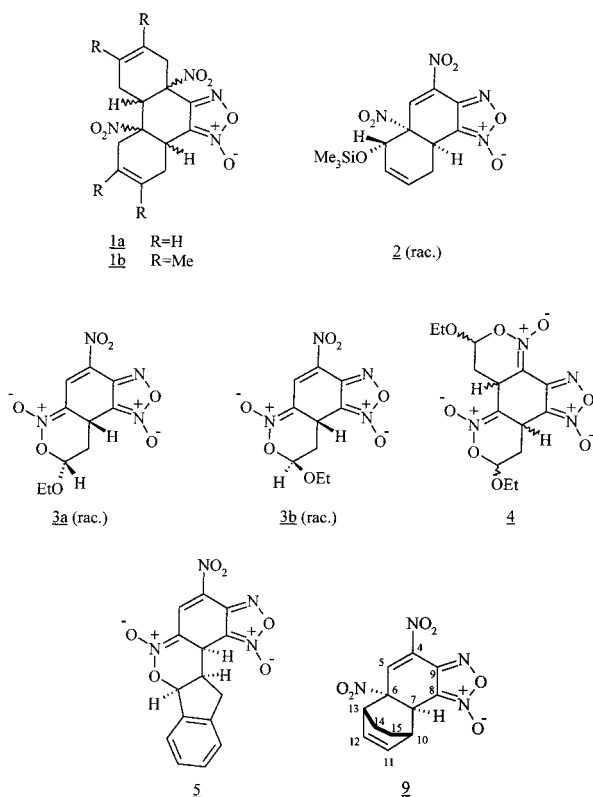
Scheme 1

Chart 1

<u>1a</u>   R=H
<u>1b</u>   R=Me

2 (rac.)

<u>3a</u> (rac.)   <u>3b</u> (rac.)   <u>4</u>

<u>5</u>   <u>9</u>

processes involving the formation of an intermediate zwitterionic σ-adduct.[10] By analogy, it follows that the formation of the indene adduct **5** must preferably be viewed as arising from a concerted cycloaddition reaction rather than an ionic two-step process, as originally suggested.[11]

The importance of the above reactions for synthetic purposes calls for further exploration of these new facets of the reactivity of DNBF. This paper deals with the reaction of DNBF with cyclopentadiene in chloroform or dichloromethane. It leads to the competitive initial

formation of the monoadducts **6** and **7**, which is followed by the stereoselective formation of the highly functionalized diadduct **8**. Inasmuch as the C_6–C_7 double bond is involved in the two initial monocondensation processes, the formation of **6** and **7** constitutes the first clear-cut example of the potentially ambident Diels–Alder reactivity of DNBF. Also reported is the stereoselective and exclusive formation of the DNBF–cyclohexadiene monoadduct **9**.

Addition of excess cyclopentadiene (10 equiv) to a solution of DNBF in $CHCl_3$ or CH_2Cl_2 at 0 °C resulted, after 5 days, in the formation of a product which was readily isolated as white crystals. The ORTEP view in Figure 1 shows that this product is a diadduct which is only obtained as the diastereomer **8** in its racemic form (only one enantiomer is shown in Scheme 1). The ORTEP view of Figure 2 shows the structure of the single product, namely the monoadduct **9**, which is formed in its racemic form under similar experimental conditions in the DNBF–cyclohexadiene system. The stereochemistry of both **8** and **9** in the crystal agrees well with the structural information obtained from a detailed analysis of the ^1H and ^{13}C NMR spectra recorded in Me_2SO-d_6 and/or $CDCl_3$ solution via COSY and HETCOR, as well as NOE[12] and J-modulation experiments (Tables 1 and 2). In particular, 2D-NOE agreed with the space proximity of the H_7, H_{10}, and H_{11} protons in **8**. Among other notable diagnostic features for **8**, we should mention the strong deshielding of the two sp^3 carbons C_4 and C_{11}, which benefit, respectively, from the strong electron-withdrawing inductive effects exerted by a NO_2 group and a O–N^+–O^- fragment of a dihydrooxazine N-oxide ring.[13] A similar situation holds for the sp^3 carbon C_6 of **9**.

Information on the reaction sequence leading to **8** was obtained by carrying out another series of experiments at −30 °C, using lower concentrations of the reagents to overcome solubility problems. In this instance, the spectra recorded immediately after mixing showed the formation of two new products, **X** and **Y**, in a 9:1 ratio. Raising the temperature to −10 °C favors the formation of **Y** at

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(12) In the case of the diadduct **8**, NOE enhancements of about 10% were observed between H_7 and H_{10} as well as between H_{10} and H_{11}. Similarly, irradiation of the H_7 resonance of the monoadduct **7** gave a NOE enhancement of H_{10} (~6%).

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Table 1. ¹H NMR Data for the Monoadducts 6, 7, 9 and the Diadduct 8[a]

adduct	solvent	H_5	H_7	H_{10}	H_{11}	H_{12}	H_{13}	H_{14}	H_{15}	H_{16}	H_{17}	H_{18}	H_{19}	coupling constants (Hz)
6	$CDCl_3$	7.91	3.94	3.81	6.18	6.68	3.63	1.81 1.39	-	-	-	-	-	$^2J_{14a/14b} = 10.5$; $^3J_{12/11} = 5.5$; $^3J_{15N4/H5} = 3.3$
7	$CDCl_3$	8.33	4.32	4.13	5.89	5.92	6.24	2.59 1.96	-	-	-	-	-	$^2J_{14a/14b} = 18.2$; $^3J_{7/10} = 5.9$; $^3J_{12/11} = 2.2$; $^3J_{12/13} = 5.3$; $^3J_{15N4/H5} = 2.6$
8	$CDCl_3$	3.49	4.06	3.98	5.77	5.95	6.21	2.41 2.16	4.06	6.38	6.69	3.49	1.80 1.18	$^2J_{14a/14b} = 18.0$; $^2J_{19a/19b} = 10.2$; $^3J_{11/10} = 8.9$; $^3J_{12/13} = 5.8$. $^3J_{14a/10} = 8.8$; $^3J_{14b/10} = $ $^3J_{16/15} = 2.8$; $^3J_{17/16} = 5.7$
	Me_2SO-d_6	3.30	4.35	3.85	5.86	5.95	6.18	2.35 1.92	3.98	6.34	6.74	3.30	1.61	$^2J_{14a/14b} = 18.6$; $^3J_{7/10} = 5.4$; $^3J_{12/13} = 4.9$; $^3J_{14a/10} = 9.4$; $^3J_{14b/10} = 2.6$; $^3J_{16/15} = 2.9$; $^3J_{17/16} = 5.6$; $^3J_{17/18} = 3.3$; $^4J_{7/5} = 2.8$
9	Me_2CO-d_6	8.02	4.11	3.46	6.67	6.37	3.78	1.83 1.39	1.39 1.18	-	-	-	-	$^3J_{13/14b} = {}^3J_{13/14a} = 3.0$; $^3J_{7/10} = 2.9$; $^3J_{10/11} = 7.5$; $^3J_{12/13} = 7.2$; $^3J_{12/11} = 7.5$

[a] δ in ppm relative to Me_4Si; J in Hertz.

the expense of **X**, both species being present in similar quantities after 30 min at this temperature, when the formation of **8** at the expense of **X** and **Y** begins to be detectable. Warming of the solution to 0 °C accelerated the appearance of **8**, which was the only product eventually present at completion of the reaction process (Scheme 1).

On the basis of the collected ¹H NMR information, there is little doubt that **X** and **Y** are the monoadducts **6** and **7**, respectively, in their racemic forms. This implies that we are dealing with two highly regioselective and diastereoselective normal and inverse electron demand Diels—Alder condensations. The regioselectivity at the C_6–C_7 double bond was readily demonstrated through ¹⁵N-labeling of the 4-NO_2 group of DNBF.[14] In this instance, the only low-field proton observed in the ¹H NMR spectra of **6** and **7** is coupled with the ¹⁵N atom, indicating that this proton is H_5. In addition, the observed $^3J_{N4H5}$ coupling constants of 3.3 and 2.6 Hz, respectively, for **6** and **7** compare well with those previously reported for the parent DNBF molecule ($^3J_{N4H5} = 2.9$ Hz) as well as the monoadduct **2** ($^3J_{N4H5} = 3.1$ Hz).[9a,14]

Regarding the adduct **7**, the first strong, though indirect, evidence for the proposed stereochemistry is that this structure is the only one which can be viewed as a precursor of the diadduct **8**. Indeed, NOE experiments have been carried out which have confirmed experimentally that the H_7 and H_{10} protons of **7** are in a cis arrangement, as found in **8**.[12] In addition, it is worth noting that the H_{10} resonance of **7** appears as a multiplet which is very similar in shape and position to the one observed in the ¹H spectrum of the diadduct **8**, with, in particular, a similar value of the J_{H7H10} coupling constant (Table 1). Regarding the endo configuration assumed for **6**, with the 6-NO_2 group and H_7 being in a trans arrangement to the $C_{13}C_{14}C_{10}$ bridge, it compares well with the situation observed in Figure 2 for the DNBF—cyclohexadiene adduct **9**.[15] Structure **6** is also related to that of the endo adduct **2**, which was previously characterized in the reaction of DNBF with 1-trimethylsilyloxy-buta-1,3-diene.[9a]

The most reasonable way to account for the initial observation of a mixture of the two monoadducts **6** and **7** in the reaction of DNBF with cyclopentadiene is in terms of the two competitive [4 + 2] cycloadditions depicted in Scheme 1. While the C_6–C_7 double bond of

DNBF behaves as the dienophile in the condensation leading to **6**, it is part of the O_6–N_6–C_6–C_7 fragment, which acts as a heterodienic moiety in the condensation pathway leading to **7**. The formation of **6** and **7** highlights the ambident Diels—Alder reactivity of DNBF while adding to the evidence that nitrobenzofuroxans are 10π-electron heteroaromatics of low resonance energy.[1a,5d,e] In this regard, the behavior of DNBF may be compared to that of nitroalkenes, which are known to react as dienophiles or heterodienes, depending upon the experimental conditions and the systems at hand.[16–20] In particular, Denmark and co-workers have recently reported the formation of a number of dihydrooxazine *N*-oxide structures from Lewis-acid promoted [4 + 2] cycloadditions of nitroalkenes with various dienophiles, including cyclopentadiene.[16,17]

The results obtained tend to indicate that the two monoadducts **6** and **7** have rather similar thermodynamic stabilities but that the NEDDA condensation is kinetically more favored than the IEDDA process. That the diadduct **8** appears as the only final product of the interaction implies, however, that the NEDDA addition of the second molecule of cyclopentadiene is kinetically more favored at the remaining nitroalkene moiety of **7** than of **6**.[21] In as much as **8** is thermodynamically the most stable product, its formation at the expense of **7** has the effect to drive the complete equilibrium system of Scheme 1 toward completion of the second condensation. This reaction proceeds through the endo mode as evidenced by the results of the X-ray analysis (Figure 1).

That the diadduct **8** is the result of two consecutive inverse and normal electron-demand condensations occurring at the C_6–C_7 and C_4–C_5 double bonds of the DNBF moiety is also a new feature of the chemistry of DNBF. So far, only the contrasting "unsymmetrical" NEDDA—IEDDA sequence and the two "symmetrical" NEDDA—NEDDA and IEDDA—IEDDA sequences (see structures **1** and **4**) have been observed.[8,9] Altogether, the present results demonstrate the considerable scope of

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(15) That the adduct **6** is the result of a NEDDA-type condensation is unambiguously demonstrated by the close similarity of its C_6 and C_7 resonances with those found for **9** (Table 2).

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Table 2. ^{13}C NMR Data for the Monoadducts 6 and 9 and the Diadduct 8[a]

adduct	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	coupling constants (Hz)
6[b]	141.24	136.22	97.09	38.07	110.37	144.17	56.05	133.10	141.05	46.45	46.08	-	-	-	-	-	$^1J_{C5H5}$ = 146.9; $^1J_{C7H7}$ = 142.7;
8[c]	91.27	47.54	121.82	32.17	111.35	152.69	36.61	91.67	127.52	139.36	34.60	54.56	134.27	141.90	46.11	46.24	$^1J_{C10H10}$ = 141.3; $^1J_{C11H11}$ = 162.2; $^1J_{C12H12}$ = 170.7; $^1J_{C13H13}$ = 167.6; $^1J_{C14H14}$ = 129.4; $^1J_{C15H15}$ = 156.8; $^1J_{C16H16}$ = 179.2; $^1J_{C17H17}$ = 175.8; $^1J_{C18H18}$ = 156.0; $^1J_{C19H19}$ = 136.8; $^2J_{C8H7}$ = 9.6
9[d]	141.37	137.81	93.83	37.06	110.79	146.00	30.18	136.36	131.50	40.51	21.23	18.45	-	-	-	-	$^1J_{C5H5}$ = 175.8; $^1J_{C7H7}$ = 141.3; $^1J_{C10H10}$ = 144.7; $^1J_{C11H11}$ = 172.4; $^1J_{C12H12}$ = 172.9; $^1J_{C13H13}$ = 145.8; $^1J_{C14H14}$ = 132.2; $^1J_{C15H15}$ = 133.0; $^2J_{C8H7}$ = 9.0; $^2J_{C9H5}$ = 8.5; $^2J_{C9H7}$ = 2.3; $^2J_{C14H13}$ = 5.4; $^2J_{C7H10}$ = 2.3

[a] δ in ppm relative to Me$_4$Si; J in Hertz. [b] In CDCl$_3$. [c] In Me$_2$SO-d$_6$. [d] In Me$_2$CO-d$_6$.

reactivity of DNBF, further emphazising the versatile character of this compound.

Experimental Section

General. Melting points were determined on a Kofler-type block and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are reported in ppm (J values in hertz) relative to internal Me$_4$Si. Electronic impact mass spectra (EI, 70 eV) were obtained using a spectrometer equipped with a quadrupole. Elemental analyses were determined by the Microanalytical laboratory of the University Paris VI, Paris, France. X-ray data for adducts **8** and **9** were collected on a three-circle diffractometer equipped with a bidimensional CCD detector. All these data, together with the details of their acquisition, are given as Supporting Information (Tables S$_1$–S$_5$).[22]

Materials. 4,6-Dinitrobenzofuroxan (DNBF) was prepared according to the procedure reported by Drost[23] [mp 173 °C (lit.[4,5a,c,23] 172–174.5 °C)], modified to prepare [4-^{15}N]- 4,6-dinitrobenzofuroxan (mp 173 °C).[11] Cyclopentadiene was obtained from the heating of bicyclopentadiene and was used without further purification. Cyclohexadiene was obtained from ACROS and used as received.

Preparation of 8 and 9. Excess diene (5 mL, >10 equiv) was added to a solution of DNBF (1 g, 4.42 mmol) in CH$_2$Cl$_2$ or CHCl$_3$ (5 mL) at 0 °C. The solution turned rapidly to orange and the reaction mixture was stirred at 0 °C for 5 days. Addition of pentane resulted in the immediate formation of a precipitate which was collected by filtration and dried under vacuum. Cycloadducts **8** and **9** were obtained as pale yellow solids in 60 and 54% yields, respectively. Single crystals of **8** and **9** were obtained by recrystallization in a CHCl$_3$/pentane mixture.

Selected data for 8: mp 184 °C (dec); *m/z* (EI) 359 (M + H)$^{+\bullet}$, 312 (M − NO$_2$)$^{+\bullet}$, 293 (M + H − Cp)$^{+\bullet}$; IR (CHCl$_3$) 2434, 2401, 1636, 1598, 1567, 1485, 1361, 1140, 1097, 1042 cm^{-1}. Found: C, 53.51; H, 3.90; N, 15.70. C$_{16}$H$_{14}$N$_4$O$_6$ requires: C, 53.61; H, 3.94; N, 15.64.

Selected data for 9: mp 180 °C; *m/z* (EI) 307 (M + H)$^{+\bullet}$, 260 (M − NO$_2$)$^{+\bullet}$; IR (CHCl$_3$) 2878, 2436, 2402, 1659, 1566, 1466, 1343, 1139, 1100 cm^{-1}. Found: C, 47.04; H, 3.24; N, 18.13. C$_{12}$H$_{10}$N$_4$O$_6$ requires: C, 47.07; H, 3.29; N, 18.30.

In Situ Preparation of 6 and 7. Cyclopentadiene (2 equiv) was added under stirring to a solution of DNBF (0.025 g, 1.11 mmol) in CDCl$_3$ or in CD$_2$Cl$_2$ (1 mL) at −30 °C, and the resulting mixture poured into a NMR tube. From the analysis of the various NMR spectra recorded at −30 °C and then at −10 °C during the first hour following the mixture of the reagents, ^{1}H NMR data for **6** and **7** and ^{13}C NMR data for **6** could be obtained (see the text).

Supporting Information Available: X-ray data for **8** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) In terms of energy profiles, the finding that the NEDDA addition of the second molecule of cyclopentadiene takes place at the C$_4$−C$_5$ double bond of **7** rather than at the same moiety of **6** indicates that the LUMO of this dienophilic fragment is lower in the IEDDA monoadduct **7** than in its NEDDA counterpart **6**. This situation is consistent with the fact that the C$_4$−C$_5$ double bond of **7** is activated by the strong electron-withdrawing effects of both the 4-NO$_2$ and the 6-*N*-oxide groups while that of **6** is activated only by the effect of the 4-NO$_2$ group. Also to be noted is that the NO$_2$ group at the sp^3-hybridized carbon C$_6$ in **6** must result in some steric hindrance to the endo approach of this adduct by the second cyclopentadiene molecule. Such a steric constraint does not exist in **7**.

(22) All X-ray data pertaining to the adducts **8** and **9** have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 124104 and 124103 for **8** and **9** respectively.

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