

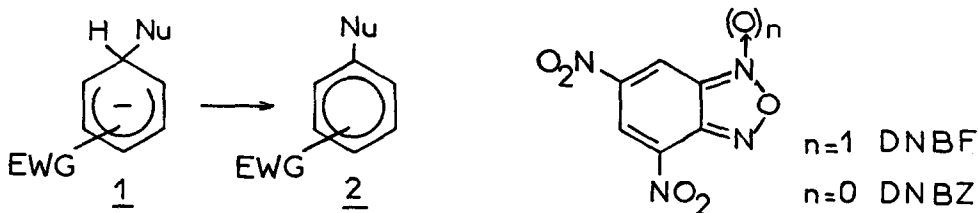
NUCLEOPHILIC DISPLACEMENT OF HYDROGEN IN 4,6-
DINITRO-BENZOFUROXAN AND -BENZOFURAZAN.
SYNTHESIS OF SOME NOVEL 7-SUBSTITUTED 4,6-
DINITRO-BENZOFUROXANS AND -BENZOFURAZANS.

J. C. HALLE*, M. J. POUET, M. P. SIMONNIN and F. TERRIER*

U.A. CNRS 403, E.N.S.C.P. 11 Rue Pierre et Marie Curie, 75231 PARIS Cedex 05, France

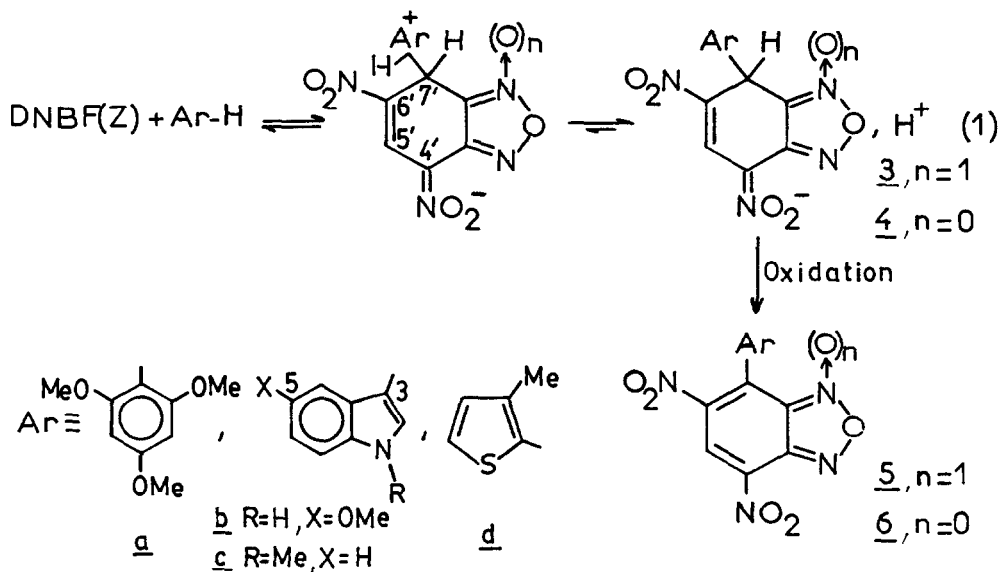
Summary. Formal hydride ion displacement readily occurs in 4,6-dinitro-benzofuroxan and -benzofurazan. This process provides a simple two-step synthesis of some new 7-substituted-4,6-dinitro derivatives.

It is well known that a number of electron-deficient aromatic and heteroaromatic substrates can undergo nucleophilic addition to an unsubstituted ring carbon with formation of σ -adducts like 1.^{1,2} Subsequent conversion of these adducts into the substituted products 2 is not however a common process since it requires the elimination of hydride anion - a very bad leaving group.¹⁻⁵ Only in a few cases has chemical or electrochemical oxidation allowed this process to occur.^{1,6-9} We report here our observation that some carbon-bonded adducts of 4,6-dinitro benzofuroxan (DNBF) and -benzofurazan (DNBZ) oxidize very easily to yield the 7-substituted-4,6-dinitro derivatives 5 or 6.



The high electrophilic character of DNBF and DNBZ has been recently emphasized by its ability to react with a number of very weak carbon nucleophiles. Thus, enols, anilines and π -excessive heterocycles like pyrroles, thiophenes and furans or indoles readily add to DNBF to form C-bonded σ -adducts according to eq. (1).^{1,2,10,11} Further remarkable evidence that DNBF behaves as a superelectrophile is provided by our observation that it also reacts with the weakly basic 1,3,5-trimethoxybenzene (TMB, $pK_a = -5.7$)¹² in Me₂SO at room temperature, yielding quantitatively the C-adduct 3a in its acidic form. Exchanging the H⁺ counterion for a M⁺ (K⁺, Na⁺, Ag⁺) cation allows 3a to be isolated as a very stable crystalline salt 3a, M⁺, which has been structurally characterized by standard methods and ¹H NMR spectroscopy (Table).

The most typical feature of the TMB-DNBF system, however, is that the acidic form of 3a undergoes a "spontaneous" oxidation in Me₂SO solution, yielding the rearomatized product 5a in good yield ($\sim 50\%$). This is evidenced by the evolution of the NMR spectra with time which show a progressive disappearance of the five signals belonging to 3a and the concomitant



appearance of a new set of four signals at lower field, consistent with the presence of only one unsubstituted carbon in the DNBF moiety of 5a (see table). The structure of 5a was also unambiguously established on the basis of elemental analysis¹³ and mass spectroscopy ($m/e=392$). Interestingly, the oxidation reaction also proceeds very smoothly in methanol but, in agreement with previous observations,^{11d,14} formation of 3a,H⁺ in this solvent is preceded by that of a Π -complex.

Attempts to prepare 5a via chemical oxidation of 3a in aqueous acidic solution were also successful, provided that very strong oxidizing agents like potassium permanganate ($\text{MnO}_4^-/\text{Mn}^{2+}$, $E^\circ = 1.51$) be used. Weaker oxidants have no effect on the structure of 3a. For instance, addition of silver nitrate (Ag^+/Ag , $E^\circ = 0.80$) to an aqueous solution of 3a,H⁺ simply results in precipitation of the red colored silver salt 3a,Ag⁺. These observations show that the oxidation potential of 3a is very high, making the "spontaneous" oxidation of this adduct under our experimental conditions in Me_2SO or methanol a rather unexpected result.

Many experiments have been carried out to elucidate the mechanism of this reaction. All of them indicate that the H^+ ions play a primary role in the oxidation process. Thus, trapping the H^+ ions with a tertiary base like 1,8-bis(dimethylamino)naphthalene, i.e. the proton sponge, precludes any conversion of 3a into 5a. Similarly, the silver or alkali salts 3a,M⁺ are stable for several weeks in Me_2SO and /or MeOH solution. Another significant observation is that the presence of an excess of DNBF or of another electron acceptor like unsubstituted benzofuroxan itself strongly accelerates the oxidation of 3a,H⁺. This is consistent with various reports that electron acceptors play an important role in hydride ion transfers in aromatic rings, but we are, as other, presently unable to propose a reasonable mechanism.^{8,9,15}

Our observations with the TMB-DNBF system prompt us to reconsider the behavior of some

Table. ^1H NMR Data of σ -Adducts and Related Oxidation Products ; $t=31^\circ\text{C}$ (i)

COMPOUNDS	δ_{H_5}	δ_{H_7}	δ_{H_2}	δ_{H_4}	δ_{H_5}	δ_{H_6}	δ_{H_7}	δ_{NH}	δ_{NMe}	δ_{Me}	δ_{OMe}
<u>3a</u> , H^+	8.65	5.83	6.19			6.19					(1) 3.74 (3,5) 3.68
<u>5a</u>	8.87		6.38			6.38					(1) 3.90 (3,5) 3.71
<u>3b</u> , H^+	8.75	5.63	7.30	6.80		6.72	7.26	10.87			(5) 3.65
<u>5b</u>	8.94		7.96	6.66		6.87	7.44	12.16			(5) 3.70
<u>4b</u> , H^+	8.83	6.04	7.18	6.90		6.72	7.23	10.78			(5) 3.68
<u>6b</u> (ii)	8.97		8.40	6.50		6.93	7.51	12.60			(5) 3.75
<u>4c</u> , H^+ ($\sim 20^\circ\text{C}$)	8.81	6.03	7.20						3.69		
<u>6c</u> ($\sim 20^\circ\text{C}$)	9.02		8.50						4.00		
<u>4d</u> , H^+	8.73	6.13		6.81	7.19					2.33	
<u>6d</u>	9.15			7.17	7.94					2.12	

(i) δ in ppm relative to internal TMS. Solvent $\text{Me}_2\text{SO}-d_6$. (ii) in the presence of $\text{CF}_3\text{CO}_2\text{H}$.
 $J(\text{Hz})$ 3a, H^+ : $^4J_{5,-7}=0.4$; 3b, H^+ : $^4J_{4-6}=2.4$ $^5J_{4-7}=0.6$ $^3J_{6-7}=8.7$; 5b : $^4J_{4-6}=2.4$ $^5J_{4-7}\sim 0.5$
 $^3J_{6-7}=8.8$ $^3J_{2-\text{NH}}=3.2$; 4b, H^+ : $^4J_{4-6}=2.4$ $^5J_{4-7}=0.5$ $^3J_{6-7}=8.8$ $^3J_{2-\text{NH}}\sim 2.5$; 6b : $^4J_{4-6}=2.4$
 $^5J_{4-7}=\text{n.r.}$ $^3J_{6-7}=8.8$ $^3J_{2-\text{NH}}=3.2$; 4c, H^+ : $^4J_{2-7}=0.5$; 4d, H^+ : $^3J_{4-5}=5.15$ $^4J_{4-\text{Me}}=0.4$
 $^5J_{5-\text{Me}}=0.4$ $^5J_{5-7}=0.5$; 6d : $^3J_{4-5}=5.0$ $^4J_{4-\text{Me}}=0.4$ $^5J_{5-\text{Me}}=0.4$.

previously reported systems which yielded σ -adducts 3 in their acidic form, as depicted in equation (1).^{10b,c} We thus found that not only the DNBF adducts 3 of Π -excessive heterocycles (pyrroles, indoles or thiophenes) but also the desoxygenated 4,6-dinitrobenzofurazan analogs 4 undergo "spontaneous" oxidation in Me_2SO . Again this was evidenced by the NMR spectra which showed a progressive conversion of these adducts into the corresponding C-7 substituted 4,6-dinitrobenzofuroxans 5 or dinitrobenzofurazans 6. The indole derivatives 5b, 6b and 6c, as well as the thiophene analog 6d, have presently been isolated and characterized.¹⁶ The NMR data of these compounds and their parent σ -adducts 3 or 4 are given in the table.

The "facile" oxidation of the afore-mentioned DNBF or DNBZ adducts is of interest in that it provides a route to 7-substituted-4,6-dinitrobenzofuroxans or -benzofurazans which cannot be prepared by usual synthetic methods. It also constituted a novel example of a formal hydride ion displacement from an aromatic ring. Further work in this field is in progress.

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- (16) Mass spectroscopy data and /or elemental analysis are in agreement with the proposed structures.

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