

Figure 1. ORTEP drawings for 3b and 5b.5

In spite of the above structural reassignment, the results do not deny assumption of formation of the thiaziridineimine intermediate 12 from oxaziridine 1 and isothio-

$$1 + 2 \xrightarrow{-PnCHO} \left[ PhN \xrightarrow{S} N \xrightarrow{R} \right] \xrightarrow{2} 3-5$$

cyanate 2 with loss of benzaldehyde.<sup>1</sup> The intermediate also well explains formation of carbodiimide 6 in one case analogously to formation of isothiocyanates from 1 and carbon disulfide.<sup>1</sup> The product distribution summarized in Table I seems to be delicately affected by rearrangement among the isomers 3-5, which would be dependent on the substituents, and by reaction conditions.

## **Experimental Section**

Melting points (uncorrected), IR, and mass spectra (70 eV) were obtained as reported earlier.<sup>7</sup> NMR spectra were taken on JEOL JNM PMX-60 and FX-90Q spectrometers in  $CDCl_3$  solutions using tetramethylsilane as internal standard. Reactions were carried out under nitrogen.

**Materials.** Phenyl isothiocyanate was obtained commercially. Preparation and determination of purity of the oxaziridine 1b were done by described procedures.<sup>7</sup>

**Reaction of Oxaziridine 1b with Isothiocyanate (2).** To a solution of 2 (10.9 g, 81 mmol) in benzene (10 mL) was added 1b (6.35 g, 40 mmol, active oxygen content 94%) in benzene (10 mL) dropwise with stirring, and the solution was allowed to stand at 80 °C for 5 h. Distillation of the reaction mixture gave 4.1 g (97%) of benzaldehyde and addition of a mixture of ether-hexane to the residue afforded crystalline sulfur (140 mg) and a large 409

nylimino)-1,2,4-dithiazolidine (**3b**), 218 mg (2%) of 3-(ethylimino)-4-phenyl-5-(phenylimino)-1,2,4-dithiazolidine (**4b**), 436 mg (4%) of 2-ethyl-4-phenyl-5-(phenylimino)-1,2,4-thiadiazolidine-3-thione (**5b**), and 357 mg of sulfur (total yield 39%) after repeated crystallization of the eluted fractions.

Dithiazolidine **3b** was recrystallized from EtOH-benzene as colorless needles: mp 156.5-157.5 °C; IR (Nujol) 1580 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.43 (t, 3 H, J = 7.0 Hz, Me), 4.31 (q, 2 H, J = 7.0 Hz, CH<sub>2</sub>), 6.8-7.6 (m, 10 H, 2 Ph); <sup>13</sup>C NMR (see, Table II); MS, m/e 313 (M<sup>+</sup>).

Anal. Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>S<sub>2</sub>: C, 61.31; H, 4.82; N, 13.41. Found: C, 61.35; H, 4.74; N, 13.23.

Dithiazolidine 4b was obtained as pale yellow needles from EtOH-benzene: mp 169-170 °C; IR (Nujol) 1615 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.16 (t, 3 H, J = 7.3 Hz, Me), 3.33 (q, 2 H, J = 7.3 Hz, CH<sub>2</sub>), 6.7-7.6 (m, 10 H, 2 Ph); <sup>13</sup>C NMR (see, Table II); MS, m/e 313 (M<sup>+</sup>).

Anal. Calcd for  $C_{16}H_{15}N_3S_2$ : C, 61.31; H, 4.82; N, 13.41. Found: C, 61.31; H, 4.98; N, 13.08.

Thiadiazolidinethione **5b** was obtained as colorless needles from CH<sub>2</sub>Cl<sub>2</sub>-hexane: mp 153-154 °C; IR (Nujol) 1625 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.29 (t, 3 H, J = 6.8 Hz, Me), 4.07 (q, 2 H, J = 6.8 Hz, CH<sub>2</sub>), 6.7-7.5 (m, 10 H, 2 Ph); <sup>13</sup>C NMR (see, Table II); MS, m/e 313 (M<sup>+</sup>).

Anal. Calcd for  $C_{16}H_{15}N_3S_2$ : C, 61.31; H, 4.82; N, 13.41. Found: C, 61.29; H, 4.83; N, 13.41.

Acknowledgment. We are very grateful to Prof. Gerrit L'abbé and Dr. Suzanne Toppet of University of Louvain, Belgium for helpful discussions and <sup>13</sup>C NMR measurements of some of the products. Thanks are also due to Miss Nobuko Kanehisa who helped us with ORTEP drawings.

**Registry No. 1b**, 7771-15-5; **2**, 103-72-0; **3a**, 61249-39-6; **3b**, 99642-85-0; **3c**, 55210-96-3; **3d**, 55000-06-1; **4b**, 99642-86-1; **4e**, 99642-87-2; **5b**, 99642-88-3; **5c**, 99642-89-4; **5e**, 99642-90-7; **5f**, 99642-91-8; benzaldehyde, 100-52-7; sulfur, 7704-34-9.

### The Proton Sponge as Nucleophile

François Terrier,\* Jean-Claude Halle, Marie-José Pouet, and Marie-Paule Simonnin

Laboratoire de Physicochimie des Solutions, U.A. CNRS 403, Ecole Nationale Supérieure de Chimie de Paris, 11, Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

#### Received July 30, 1985

4,6-Dinitrobenzofuroxan (DNBF) and 4,6-dinitrobenzofurazan (DNBZ) are very strong aromatic electrophiles, which is reflected in their high ability to react with weak bases,<sup>1-3</sup> including very weak carbon bases like enols or II-excessive aromatic or heteroaromatic derivatives.<sup>4,5</sup> In these last cases, the reactions lead to the formation of

<sup>(6)</sup> L'abbé, G.; Timmerman, A.; Martens, C.; Toppet, S. J. Org. Chem. 1978, 43, 4951.

<sup>(7)</sup> Komatsu, M.; Ohshiro, Y.; Hotta, H.; Sato, M.; Agawa, T. J. Org. Chem. 1974, 39, 948.

<sup>(1) (</sup>a) Terrier, F.; Millot, F.; Norris, W. P. J. Am. Chem. Soc. 1976, 98, 5883. (b) Terrier, F. Chem. Rev. 1982, 82, 77. (c) Terrier, F.; Chatrousse, A. P.; Soudais, Y.; Hlaibi, M. J. Org. Chem. 1984, 49, 4176.

<sup>(2)</sup> Strauss, M. J.; Renfrow, R. A.; Buncel, E. J. Am. Chem. Soc. 1983, 105, 2473.

 <sup>(3) (</sup>a) Spear, R. J.; Norris, W. P.; Read, R. W. Tetrahedron Lett. 1983,
 24, 1555. (b) Read, R. W.; Spear, R. J.; Norris, W. P. Aust. J. Chem. 1983,
 36, 1227.

<sup>(4)</sup> Terrier, F.; Simonnin, M. P.; Pouet, M. J.; Strauss, M. J. J. Org. Chem. 1981, 46, 3537.

<sup>(5) (</sup>a) Halle, J. C.; Simonnin, M. P.; Pouet, M. J.; Terrier, F. Tetrahedron Lett. 1983, 24, 2255. (b) Terrier, F.; Halle, J. C.; Simonnin, M. P.; Pouet, M. J. J. Org. Chem. 1984, 49, 4363. (c) Halle, J. C.; Pouet, M. J.; Simonnin, M. P.; Terrier, F. Tetrahedron Lett. 1985, 26, 1307.

carbon-bonded  $\sigma$  adducts in an acidic form, as exemplified in eq 1, which refers to the DNBF (DNBZ)-1,3,5-tri-



methoxybenzene (TMB) systems.<sup>5c</sup> Since these acids have a tendency to undergo a spontaneous oxidation with formation of the corresponding 7-substituted 4,6-dinitrobenzofuroxan or -benzofurazan derivatives, species such as  $1, \mathbf{H}^+$  are not readily isolable. However, exchanging the H<sup>+</sup> counterion for an alkali (Na<sup>+</sup>, K<sup>+</sup>) or silver cation results in the formation of very stable crystalline salts 1,M<sup>+.5c</sup> One drawback of these salts is their poor solubility in most polar solvents, including water.

In order to increase the solubility of the salts  $1, M^+$ , we have been interested in carrying out exchange experiments with amines, especially tertiary amines. When using Proton Sponge, i.e. 1.8-bis(dimethylamino)naphthalene.<sup>6</sup> as the amine we discovered that it acts as a carbon nucleophile, yielding the C-bonded adducts  $2, H^+$  (eq 2). In this report, we characterize this rather unexpected reaction that provides the first evidence that the Proton Sponge (denoted PS in the following) can behave as a nucleophile.



Addition of PS to freshly prepared solutions of the adducts  $1, H^+$  in methanol or Me<sub>2</sub>SO results in the formation of the expected bis(dimethylamino)naphthalenium salts **1,PSH<sup>+</sup>**, which can be readily isolated as stable orange crystalline solids. In contrast, mixing initially DNBF (or DNBZ), TMB, and PS in equimolecular amounts does not result in the exclusive formation of the salt 1,**PSH**<sup>+</sup>. Instead, a mixture of this salt and another species is obtained. On the basis of the NMR spectra, we could identify the second species as being the zwitterionic C adduct 2a,H<sup>+</sup> or  $2b, H^+$ . As a matter of fact,  $2a, H^+$  or  $2b, H^+$  are the only species formed when equimolar amounts of DNBF or DNBZ and PS are allowed to react in acetonitrile. THF. or Me<sub>2</sub>SO solution. The NMR parameters summarized in Table I are consistent only with DNBF or DNBZ addition taking place at the 4-position of the naphthalene ring. The various chemical shifts of the naphthalene protons were assigned by comparison with those for PS and  $PS, H^+$  in the same solvents. To be noted is that the H-5 and the H-3 resonances are broad when recording the spectra at the probe temperature (32 °C) but become sharper and sharper with increasing temperature. This observation suggests restricted rotation around the  $C_4$ - $C_{7'}$ 

Table I. <sup>1</sup>H NMR Data for the Adducts 2a,H<sup>+</sup> and 2b,H<sup>+ a,b</sup>

	2a,H <sup>+</sup>		2b,H+	
	δ	J	δ	J
H+	18.73		18.75	
$NMe_2$	3.17 (d)	${}^{3}J_{\rm H^{+}NMe_{2}}$ 2.3	3.18	$^{3}J_{\mathrm{H^{+}NMe^{2}}}\mathrm{nr}^{c}$
	3.09 <sub>5</sub> (d)	2.1	3.11	nr <sup>c</sup>
$H_{5'}$	8.83 (s)		9.04 (s)	
$\mathbf{H}_{7'}$	6.43 (s)		6.81 (s)	
$H_2$	7.98 (d)		7.97 (d)	
$H_3$	7.56 (d)	${}^{3}J_{23} = 8.1$	7.50 (d)	${}^{3}J_{23} = 7.8$
$H_5$	8.63 (d)		8.77 (d)	
$H_6$	7.83 (t)	${}^{3}J_{56} = 8.7$	7.90 (t)	${}^{3}J_{56} = 8.3$
$H_7$	8.14 (d)	${}^{3}J_{67} = 7.5$	8.19 (d)	${}^{3}J_{67} = 7.5$

<sup>a</sup> Chemical shifts (ppm) relative to Me<sub>4</sub>Si as internal standard; J in Hertz; solvent Me<sub>2</sub>SO- $d_6$ . <sup>b</sup>See structure 2,H<sup>+</sup> for numbering of the napthalene and DNBF or DNBZ moieties. 'Not resolved.

bond of  $2a, H^+$  and  $2b, H^+$  due to steric hindrance. On the other hand, both the H-5' and H-7' chemical shifts of the DNBF and DNBZ anionic moieties of 2a,H<sup>+</sup> and 2b,H<sup>+</sup> are typical for C-bonded adduct formation in these heterocyclic series.<sup>2-5</sup> Isolation of the zwitterions  $2a, H^+$  and  $2b, H^+$  as orange crystalline solids was readily achieved from acetonitrile or THF solutions.

In contrast with common aromatic amines. PS has an exceptionally high basicity, but the steric hindrance due to the vicinity of the two bulky dimethylamino groups makes it a very poor nitrogen nucleophile.<sup>6</sup> On the other hand, there is normally a strong resonance interaction between an amino group, especially a dimethylamino group, and an aromatic ring. Accordingly, aromatic amines have also some tendency to behave as weak carbon bases under some experimental conditions, and indeed, they do toward DNBF and DNBZ.<sup>2,3</sup> In the case of PS, however, there is no reasonable possibility of bringing even one of the dimethylamino groups into the plane of the ring, resulting in a very low resonance interaction between the nitrogen lone pairs and the aromatic system.<sup>7</sup> Hence, the possibility for PS to act as a carbon nucleophile must be very low, and, in fact, this mode of reaction has never been reported so far. The formation of the C adducts  $2a, H^+$ and  $2b, H^+$  is therefore a noteworthy result.<sup>8</sup> It indicates that, even though weak, the nucleophilic character of Proton Sponge is not completely suppressed. Our results also emphasize the exceptional electrophilic reactivity of DNBF and DNBZ and further confirm that these derivatives constitute very useful probes to assess the reactivity of very weak carbon bases.<sup>10</sup>

### **Experimental Section**

Materials. 4,6-Dinitrobenzofuroxan and 4,6-dinitrobenzofurazan were prepared according to previously described methods:<sup>11,1c</sup> DNBF, mp 173 °C (lit.<sup>11,12</sup> mp 172-174.5 °C); DNBZ, mp 133 °C (lit.<sup>1c,3b</sup> mp 129-132 °C). 1,8-Bis(dimethylamino)naphthalene (PS)<sup>6</sup> was reagent grade obtained from Aldrich and was used without further purification.

The zwitterionic adducts  $2a, H^+$  and  $2b, H^+$  were prepared by the addition of an equimolar amount of PS to an acetonitrile or

<sup>(6) (</sup>a) Alder, R. W.; Bowman, P.; Steel, W. R. S.; Winterman, D. R. Chem. Commun. 1968, 723. (b) Awwal, A.; Hibbert, F. J. Chem. Soc. Perkin Trans. 2 1977, 1589. Proton Sponge (PS) is a trademark of Aldrich Chemical Co.

<sup>(7)</sup> Einspahr, H.; Robert, J. B.; Marsh, R. E.; Roberts, J. D. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1973, B29, 1611.

<sup>(8)</sup> A kinetic study of the TMB-DNBF system in water-Me<sub>2</sub>SO and methanol-Me<sub>2</sub>SO mixtures has fully confirmed the mechanism proposed in eq 1.9 On grounds of analogy, there is little doubt that the formation of the PS adducts 2a,H<sup>+</sup> and 2b,H<sup>+</sup> proceeds in a similar way, as shown in eq 2

<sup>(9)</sup> Kizilian, E.; Halle, J. C.; Terrier, F., unpublished results.

<sup>(10)</sup> Buncel, E.; Crampton, M. R.; Strauss, M. J.; Terrier, F. In "Electron-Deficient Aromatic and Hteroaromatic-Base Interactions"; Elsevier: Amsterdam, Holland, 1984; p 166. (11) Drost, P. Liebigs Ann. Chem. 1899, 307, 49.

<sup>(12)</sup> Norris, W. P.; Spear, R. J.; Read, R. W. Aust. J. Chem. 1983, 36, 297.

THF solution of DNBF or DNBZ (110 mg in 2 mL). The reaction mixtures turned immediately dark orange and were allowed to stand at room temperature for about 1 h. The orange crystals that formed were filtered, ground to a fine powder, washed with copious amounts of ether, and dried in vacuo to eliminate any associated solvent. The two solid adducts darkened at ca. 200-230 °C but failed to melt below 300 °C.

Anal. Calcd for  $2a, H^+$  ( $C_{20}H_{20}N_6O_6$ ): C, 54.54; H, 4.58; N, 19.08. Found: C, 54.20; H, 4.46; N, 18.89. Calcd for  $2b, H^+$  ( $C_{20}H_{20}N_6O_5$ ): C, 56.60; H, 4.75; N, 19.80. Found: C, 56.22; H, 4.67; N, 19.27. The <sup>1</sup>H NMR spectra were recorded at 100 MHz (Varian XL

100) in the CW mode, using Me<sub>4</sub>Si as an internal standard.

Registry No. 1a,H<sup>+</sup>, 97670-24-1; 1b,H<sup>+</sup>, 99808-95-4; 2a,H<sup>+</sup>, 99808-93-2; 2b,H+, 99808-94-3; PS, 20734-58-1; DNBF, 5128-28-9; DNBZ, 70264-71-0; TMB, 621-23-8.

# Thioquinones. Generation of Dithioanthraquinone

M. V. Lakshmikantham,\*1 Matthew Levinson, Mary Menachery, and Michael P. Cava<sup>1</sup>

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, and Department of Chemistry, University of Alabama, University, Alabama 35486

### Received June 5, 1985

In contrast to the extensive literature on quinones, very little is known about the corresponding sulfur analogues. Attempts to prepare thioquinones date back to 1900.<sup>2</sup> Only recently, Bock et al. have succeeded in the pyrolytic generation and spectroscopic characterization of the mono and dithio analogues 1 and 2 of p-benzoquinone, in an argon matrix.<sup>3</sup> It was felt that the annellation of two



benzene rings to the p-dithioquinone system might render the thioquinone system more stable and lead to the synthesis of a stable member of this class. The recent synthesis of monothioanthraquinone 3 by Raasch<sup>4</sup> by the reaction of diazoanthrone and elemental sulfur in refluxing DMF was encouraging, in view of the remarkable stability of the anthraquinone analogue in comparison to the benzoquinone analogue 1.

Although a substance considered to be dithioanthraquinone (4) has been reported once, it was stated that the experiment could not be reproduced.<sup>5</sup> Several pathways to the synthesis of dithioanthraquinone are possible. The simplest of these, in view of the ready availability of substrates, was the direct thionation of anthraquinone. We now report our results on the thionation of anthraquinone.

Anthraquinone underwent ready reaction with the thionating agent. Lawesson's reagent  $(5)^6$  in a variety of solvents like benzene, toluene, etc. However, apart from traces of monothioanthraquinone, and some unreacted anthraquinone, the other products were nondescript powders with variable analyses.<sup>7</sup> However, when boiling solutions of anthraquinone and the thionating reagent were quickly mixed under nitrogen and refluxed, a series of color changes from yellow to green to a red brown was visible, and within an hour a cinnabar-like red microcrystalline material was thrown out of solution. This material after filtration and workup by boiling with ethanol analyzed for an oligomer of the expected dithioanthraquinone containing one half unit of a Lawesson's reagent derived moiety for ten units of the thioquinone.



The intermediacy of the monothioanthraquinone was confirmed by subjecting it to the action of Lawesson's reagent under analogous reaction conditions. Thionation occurred rapidly as expected and the red polymeric material with similar elemental analysis was isolated. These observations clearly indicated that, unlike the monothione 3, the dithioquinone 4 was either unstable or too reactive and polymerized to form a polydisulfide. This conjecture was proved by the sodium borohydride reduction of the red material to a water-soluble dithiolate anion which was readily methylated in 70% yield to give the known 9,10dithiomethylanthracene 6.8 The dithiolate anion could also be readily benzoylated to the dibenzoyl derivative 7. Indeed, this procedure of borohydride reduction of the polymer derived from 4 provides a convenient source of 9,10-dithiosubstituted anthracene derivatives.

An alternate route to dithioanthraquinone was sought. It was shown by Raasch that monothioanthraquinone added readily to 2,3-dimethylbutadiene to give spiroadduct  $8.^4$  It was found that adduct 8 could be readily thionated to a blue crystalline compound 9, which corresponds to the monoadduct derived from dithioanthraquinone and 2.3dimethylbutadiene. After considerable experimentation



it was found that adduct 9 could be subjected to retro-

<sup>(1)</sup> Present address: Department of Chemistry, University of Ala-

<sup>bama, University, Alabama 35486.
(2) Zincke, Th.; Frohneberg, W. Ber. Dtsch. Chem. Ges. 1909, 42, 2727.
(3) Bock, H.; Mohmand, S.; Hirabayashi, T.; Maier, G.; Reiseauer, H.</sup> P. Chem. Ber. 1983, 116, 273

<sup>(4)</sup> Raasch, M. A. J. Org. Chem. 1979, 44, 632.

<sup>(5)</sup> Heilbron, I. M., Heaton, J. S. J. Chem. Soc. 1923, 123, 1735.

<sup>(6)</sup> Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S. O. Bull. Soc. Chim. Belg., 1978, 87, 223

<sup>(7)</sup> After the completion of our work, a report by El-Kateb et al. (El-Kateb, A. A.; Hennawy, I. T.; Shabana, R.; Osman, F. H. Phosphorus Sulfur 1984, 20, 329) described the thionation of anthraquinone with Lawesson's reagent in refluxing toluene. We have been unable to reproduce the results claimed in this publication. We thank a referee for drawing our attention to this work.

<sup>(8)</sup> Zweig, A.; Mauer, A. H.; Roberts, B. G. J. Org. Chem. 1967, 32, 1322