

SYNTHESIS AND THERMAL REARRANGEMENT OF 5-CHLORO-4,6-DINITROBENZOFUROXAN

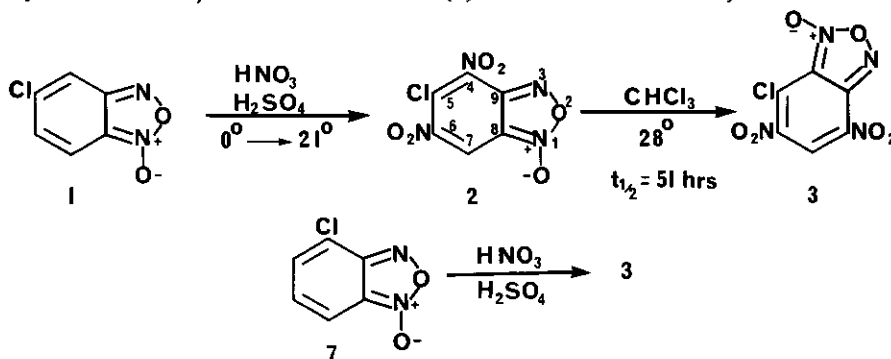
William P. Norris\* and Andrew Chafin  
 Research Department, Naval Weapons Center,  
 China Lake, CA 93555, USA

Robert J. Spear\* and Roger W. Read  
 Materials Research Laboratories, P. O. Box 50,  
 Ascot Vale, Victoria, 3032, Australia

**Abstract** — 5-Chloro-4,6-dinitrobenzofuroxan, prepared by nitration of 5-chloro-benzofuroxan, isomerizes thermally to 7-chloro-4,6-dinitrobenzofuroxan. The latter compound reacts with water, in the presence of potassium bicarbonate, to give the potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan and with methanol, in the presence of potassium bicarbonate, to give potassium 4,7-dihydro-4,6-dinitro-7,7-dimethoxybenzofuroxanide.

4,6-Dinitrobenzofuroxan (DNBF), first prepared by Drost<sup>1</sup> in 1899 and fully characterized in the 1960s,<sup>2</sup> is one of the most electron deficient polynitro aromatics known. It readily forms sigma complexes with nucleophiles such as water,<sup>3</sup> methanol,<sup>4</sup> and amines.<sup>5</sup> We have prepared two reactive derivatives of DNBF, 5- and 7-chloro-4,6-dinitrobenzofuroxan, and have briefly examined their chemistry.

5-Chloro-4,6-dinitrobenzofuroxan (2) was prepared from 5-chlorobenzofuroxan (1)<sup>6</sup> essentially following Drost's<sup>1</sup> procedure for preparation of DNBF, except that the temperature was kept lower. It must be stored below 0° to preserve it for any length of time since (2) rearranges thermally to 7-chloro-4,6-dinitrobenzofuroxan (3). Boulton and Katritzky<sup>7</sup> observed this type



of rearrangement with 5-chloro-4-nitrobenzofuroxan (4) going to 7-chloro-4-nitrobenzofuroxan (5). They suggested that steric inhibition of resonance of the nitro group by chlorine caused (4) to exist at a slightly higher energy level than (5), providing the driving force for the rearrangement. In the case of (2), chlorine causes steric inhibitions of resonance for two nitro groups which by the same reasoning places it at a slightly higher energy level than (3) where steric inhibition affects only one nitro group. The effects of steric interactions are reflected in the NMR spectra for (2) and (3) in Tables I and II.

The structures of (2) and (3) are quite firmly established on several points. The structure of (1), the precursor of (2), was determined by X-ray crystallography.<sup>6</sup> Compound (2) undergoes the Boulton-Katritzky rearrangement<sup>7</sup> to give (3) as expected. Compound (3) reacts with methanol in the presence of potassium bicarbonate to give (6),<sup>8</sup> the molecular structure of which has been determined by X-ray crystallography.<sup>9</sup> Nitration of 4-chlorobenzofuroxan (7)<sup>10</sup> gives only (3). Treatment of (3) with potassium bicarbonate in water gives the potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan (8)<sup>11</sup> which can be converted to 7-hydroxy-4,6-dinitrobenzofuroxan (9).<sup>8,11</sup> The structure of (3) is consistent with the latter three examples.

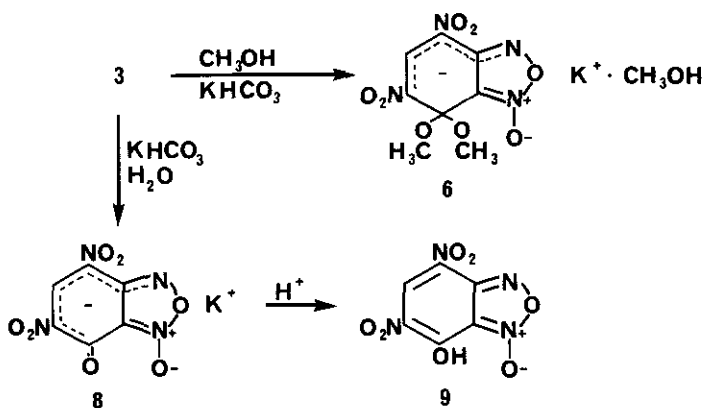


Table 1 gives the  $^1\text{H}$  NMR data for the compounds. It is interesting to note that Brown and Keyes<sup>12</sup> found the  $\text{H}_5$  signal upfield from the  $\text{H}_7$  signal in DNBF in their deuterium labeling experiment while the reverse is true for  $\text{H}_5$  in (3) and  $\text{H}_7$  in (2). The chlorine atom interferes with the resonance of both nitro groups in (2) and the  $\text{H}_7$  signal is moved upfield significantly, with respect to  $\text{H}_7$ -DNBF, while the signal for  $\text{H}_5$  in (3) is little affected, with respect to  $\text{H}_5$ -DNBF, by interaction of chlorine with the one nitro group.

TABLE I.  $^1\text{H}$  NMR Spectra, ppm. TMS Reference.

Compound	H <sub>5</sub>	H <sub>7</sub>	Other
(2) <sup>a</sup>		8.23	
(3) <sup>a</sup>	8.87		
DNBF <sup>b</sup>	8.77	9.04	
(6) <sup>c</sup>	8.79		(CH <sub>3</sub> ) 3.09
(8) <sup>c</sup>	9.05		
(9) <sup>a,c</sup>	9.05		(OH) exchanges with H <sub>2</sub> O

<sup>a</sup> CDCl<sub>3</sub>.    <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub>, see Reference 13.    <sup>c</sup> DMSO-d<sub>6</sub>.

Exactly the same effect is seen in the  $^{13}\text{C}$  NMR spectra for (2) and (3). The observed spectrum of (3) is quite close to its predicted spectrum, taking into account the substituent effect<sup>13</sup> of chlorine on the DNBF spectrum. For (2) the observed spectrum deviates markedly from the predicted spectrum at C<sub>5</sub> and C<sub>7</sub> and in an upfield direction as for H<sub>7</sub>.

 TABLE II.  $^{13}\text{C}$  NMR Spectra, ppm. TMS Reference.<sup>a</sup>

Compound	Position	Observed Spectrum	Predicted Spectrum	Difference
(2)	4	138.6	136.6	-2.0
	5	126.8	131.4	4.6
	6	144.4	145.0	0.6
	7	115.8	122.7	6.9
	8	112.8	115.4	2.6
	9	147.1	146.6	-0.5
(3)	4	136.3	135.3	-1.0
	5	129.2	128.5	-0.7
	6	144.2	145.0	0.8
	7	127.5	125.6	-1.9
	8	115.9	116.7	0.8
	9	145.5	146.6	1.1

<sup>a</sup>CDCl<sub>3</sub> solvent.

The chemistry of (2) and (3) is being explored in more detail.

REFERENCES AND NOTES

1. P. Drost, Justus Liebigs Ann. Chem., **307**, 49 (1899).
2. A. J. Boulton and P. B. Ghosh, 'Benzofuroxans' in 'Advances in Heterocyclic Chemistry' (Eds A. R. Katritzky and A. J. Boulton) Academic Press, New York, 1969, Vol. 10, pp. 1-41 and references cited therein.
3. W. P. Norris and J. Osmundsen, J. Org. Chem., **30**, 2470 (1965); F. Terrier, F. Millot and W. P. Norris, J. Am. Chem. Soc., **98**, 5883 (1976).
4. F. Terrier, Chem. Rev., **82**, 108 (1982).
5. W. P. Norris, R. J. Spear and R. W. Read, Aust. J. Chem., **36**, 297 (1983).
6. D. Britton and W. E. Noland, J. Org. Chem., **27**, 3218 (1962).
7. A. J. Boulton and A. R. Katritzky, Proc. Chem. Soc., **1962**, 257; A. J. Boulton and A. R. Katritzky, Rev. Chim. Acad. Rep. Populaire Roumaine, **7**, 691 (1962).
8. E. Buncel, N. Chuaqui-Offermanns, R. Y. Moir and A. R. Norris, Can. J. Chem., **1979**, 494.
9. The molecular structure of potassium 4,7-dihydro-4,6-dinitro-7,7-dimethoxybenzofuroxanide (6) was determined by C. K. Lowe-Ma, Naval Weapons Center, China Lake, CA, by X-ray crystallography. Full details will be published elsewhere.
10. L. K. Dyal and K. H. Pausacker, Aust. J. Chem., **11**, 491 (1958); L. K. Dyal, Aust. J. Chem., **28**, 2147 (1975).
11. W. Borsche and H. Weber, Justus Liebigs Ann. Chem., **489**, 270 (1931).
12. N. E. Brown and R. T. Keyes, J. Org. Chem., **30**, 2452 (1965).
13. D. F. Ewing, Org. Magn. Reson., **12**, 499 (1979).

Received, 20th October, 1983