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

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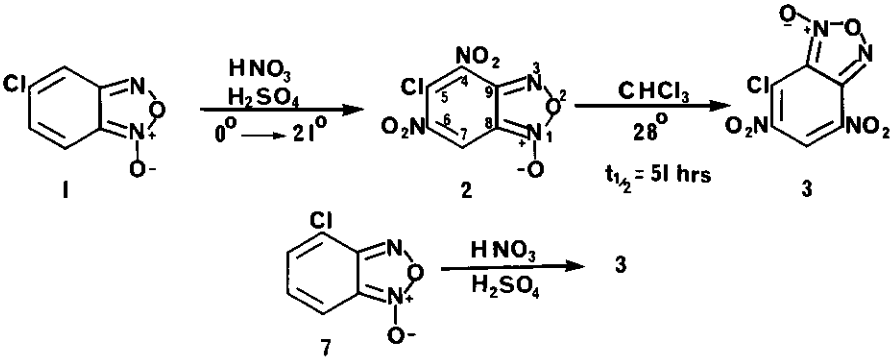
Abstract — 5-Chloro-4,6-dinitrobenzofuroxan, prepared by nitration of 5-chlorobenzofuroxan, isomerizes thermally to 7-chloro-4,6-dinitrobenzofuroxan. The latter compound reacts with water, in the presence of potassium bicarbonate, to give the potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan and with 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[1] in 1899 and fully characterized in the 1960s,[2] is one of the most electron deficient polynitro aromatics known. It readily forms sigma complexes with nucleophiles such as water,[3] methanol,[4] and amines.[5] 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)[6] essentially following Drost's[1] 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[7] 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.[6] Compound (2) undergoes *the Boulton-Katritzky rearrangement*[7] *to give (3) as expected. Compound (3) reacts with* methanol in the presence of potassium bicarbonate to give (6),[8] the molecular structure of which has been determined by X-ray crystallography.[9] Nitration of 4-chlorobenzofuroxan (7)[10] gives only (3). Treatment of (3) with potassium bicarbonate in water gives the potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan (8)[11] which can be converted to 7-hydroxy-4,6-dinitrobenzofuroxan (9).[8,11] The structure of (3) is consistent with the latter three examples.

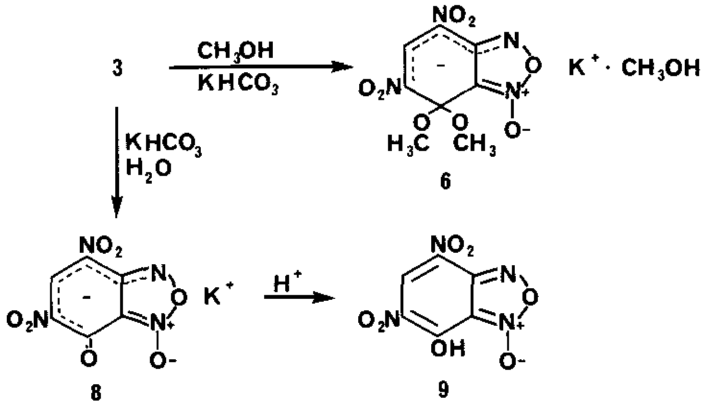


Table 1 gives the ^{1}H NMR data for the compounds. It is interesting to note that Brown and Keyes[12] found the H_5 signal upfield from the H_7 signal in DNBF in their deuterium labeling experiment while the reverse is true for H_5 in (3) and H_7 in (2). The chlorine atom interferes with the resonance of both nitro groups in (2) and the H_7 signal is moved upfield significantly, with respect to H_7-DNBF, while the signal for H_5 in (3) is little affected, with respect to H_5-DNBF, by interaction of chlorine with the one nitro group.

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

Compound	H_5	H_7	Other
(2)[a]		8.23	
(3)[a]	8.87		
DNBF[b]	8.77	9.04	
(6)[c]	8.79		(CH_3) 3.09
(8)[c]	9.05		
(9)[a,c]	9.05		(OH) exchanges with H_2O

[a] $CDCl_3$. [b] CH_2Cl_2, see Reference 13. [c] DMSO-d_6.

Exactly the same effect is seen in the ^{13}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[13] of chlorine on the DNBF spectrum. For (2) the observed spectrum deviates markedly from the predicted spectrum at C_5 and C_7 and in an upfield direction as for H_7.

TABLE II. ^{13}C NMR Spectra, ppm. TMS Reference.[a]

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

[a] $CDCl_3$ solvent.

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

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