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REACTION OF NITRILE OXIDES WITH S,S-DIMETHYL-N-(2,4,6-TRIBROMOPHENYL)SULFIMIDE

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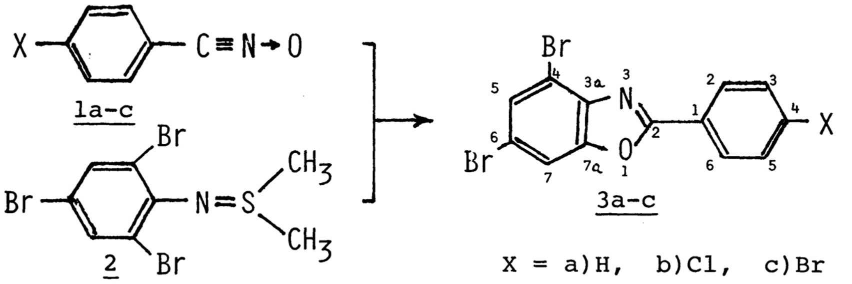
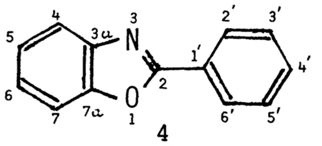
2-Aryl-4,6-dibromobenzoxazoles were isolated in the reaction of benzonitrile oxides with S,S-dimethyl-N-(2,4,6-tribromophenyl)-sulfimide. Structure determination was done by means of spectroscopic and elemental analyses.

In the previous papers,[1,2] we reported the intermediacy of nitroso compounds in the reaction of benzonitrile oxides with N-aryl-S,S-dialkylsulfimides forming benzimidazole 3-oxides and/or benzoxadiazines. During the course of the study, we found a novel reaction forming an unusual product in the reaction of nitrile oxides with S,S-dimethyl-N-(2,4,6-tribromophenyl)sulfimide.

Into a THF solution of benzonitrile oxide (1a), which was prepared from benzohydroximoyl chloride with triethylamine at below -10°C, an equimolar amount of a THF solution of S,S-dimethyl-N-(2,4,6-tribromophenyl)sulfimide 2) was added with cooling to keep the reaction mixture at below -10°C. The mixture was then allowed to stand overnight at ambient temperature. Separation of triethylammonium chloride by filtration, removal of the solvent and subsequent column chromatography of the solid residue on silica gel with chloroform as an eluent gave a crystalline produt, the structure of which was determined to be 2-phenyl-4,6-dibromobenzoxazole (3a). Reactions of p-chloro- (1b) and p-bromobenzonitrile oxide (1c) with 2 in similar manners also gave 2-(p-chlorophenyl)- (3b) and 2-(p-bromophenyl)-4,6-dibromobenzoxazole(3c), respectively.





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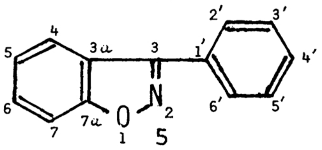

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The results of the reactions and analytical data of the products are shown in Table 1. High resolution mass spectra of the products gave molecular formulae of $C_{13}H_6Br_2NOX$ (X = H, Cl, or Br), which were consistent with the analytical data. Mass fragmentation was very similar to those of benzoxazole and benzisoxazole.[3] UV absorption spectra of 3a-c were very alike to that of 2-phenylbenzoxazole (4)[4] and not to that of 3-phenylbenzisoxazole (5)[5] in shape. PMR spectra measured in $CDCl_3$ and D_2SO_4 were consistent with the structure proposed. ^{13}C-NMR spectral data

Table 1. Yields and analytical data of 2-aryl-4,6-dibromobenzoxazoles (3a-c)

Compd.	Yield (%)	Mp*1) (°C)	Anal.(%) Found(Calcd.)	PMR in $CDCl_3$ (δ)	PMR in D_2SO_4 (*2)	Assignment
3a	37	148-149	C: 44.02(44.23)	7.64(s,2H)	8.59 and 8.50	H-5 and 7
			H: 1.83(2.00)	8.20(m,2H)	8.91	H-2' and 6'
			N: 3.74(3.74)	8.52(m,2H)	8.33	H-3' and 5'
				8.46(m,1H)	8.43	H-4'
3b	50	182-183	C: 40.96(40.30)	7.58(s,2H)	8.56 and 8.50	H-5 and 7
			H: 1.36(1.56)	8.08(d,2H)	8.78	H-2' and 6'
			N: 3.71(3.62)	7.40(d,2H)	8.23	H-3' and 5'
3c	51	181-183	C: 36.08(36.15)	7.61(s,2H)	8.52 and 8.46	H-5 and 7
			H: 1.35(1.40)	8.06(d,2H)	8.67	H-2' and 6'
			N: 3.19(3.24)	7.60(d,2H)	8.36	H-3' and 5'

*1) Recrystallized from methanol. *2) Ppm from external TMS.

Table 2. ^{13}C-NMR spectra of 2-aryl-4,6-dibromobenzoxazoles and related compounds

Compd.	C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	C-1'	C-2',6'	C-3',5'	C-4'
3a	163.8	141.0	113.2	130.5	117.8	113.2	150.8	126.0	127.9	128.8	132.1
3b	163.0	141.1	113.3	130.8	118.2	113.3	-*1)	124.6	129.3	129.3	138.6
3c	162.3	141.5	113.3	130.8	118.2	113.3	150.1	124.5	129.3	129.3	138.6
4 6)	162.1	141.5	119.6	125.1	124.4	110.5	150.1	130.6	127.0	128.8	131.4
5	157.2*2)	120.4	123.8	122.1	130.2	110.1	163.8	134.3	128.0	129.1	129.7

*1) Not observed. *2) C-3.

are listed in Table 2 and they are well consistent with the structure. Especially, the signals due to C-2, 3a, and 7a are in good accordance to those of 2-phenylbenzoxazole (4) reported by Llinares.6) These data shown above cannot definitely rule out the structure of 2-aryl-5,7-dibromobenzoxazoles. But 5,7-dibromo-2-phenylbenzoxazole was reported to melt at 175-176°C by Blatt.7) The melting point is much different from that of 3a. Thus, the structure of the products was determined to be 3.

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