Reaction of Nitrile Oxides with *N*-Aryl-*S*,*S*-dimethylsulfimides

Shinsaku Shiraishi, Tadashi Shigemoto, and Shojiro Ogawa
Institute of Industrial Science, The University of Tokyo, Roppongi Minato-ku, Tokyo 106

(Received July 21, 1977)

Both benzimidazole 3-oxides and 1,2,4-benzoxadiazines were formed in reactions of sterically-stabilized benzonitrile oxides with *N*-aryl-*S*,*S*-dimethylsulfimides, whereas only 1,2,4-benzoxadiazines were produced in reactions of 2,6-unsubstituted benzonitrile oxides. The reactions are thought to proceed *via* the intermediacy of a nitroso compound formed by the nucleophilic attack of sulfimide on the carbon atom of the nitrile oxide and the subsequent release of dimethyl sulfide. The nitrogen or the oxygen atom of the nitroso group of this intermediate can attack the ortho position of the benzene ring originating from sulfimide to form benzimidazole 3-oxide or 1,2,4-benzoxadiazine, respectively, Conjugation of the nitroso group with the *C*-aryl group can be attained in *s-cis* form for the intermediate derived from 2,6-unsubstituted benzonitrile oxide, and thus, exclusive O-attack takes place to afford 1,2,4-benzoxadiazines. On the other hand, conjugation of the nitroso group with the *C*-aryl group cannot be considered for the intermediate derived from 2,6-disubstituted benzonitrile oxide because of the steric hindrance of the substituents. In this case, the intermediate nitroso compound is either in *s-cis* or in *s-trans* form. This causes the formation of both benzimidazole 3-oxide and 1,2,4-benzoxadiazine. Characterization data of benzimidazole 3-oxides are also described.

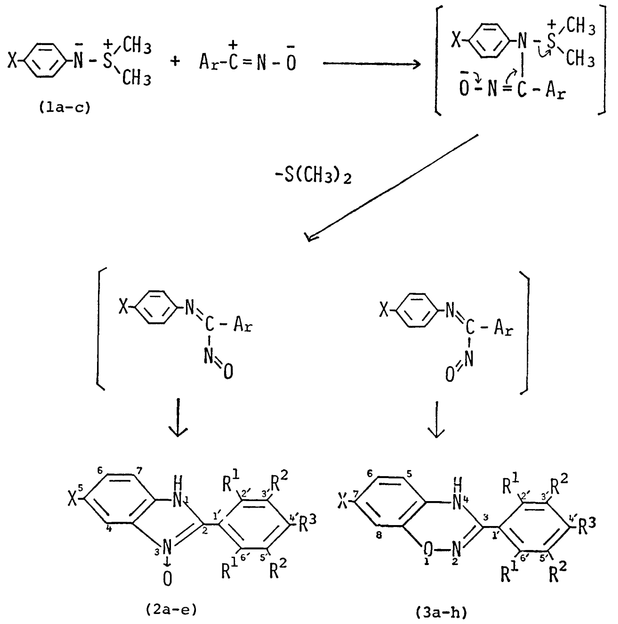
In the field of heterocyclic chemistry, the 1,3-dipolar cycloaddition reaction represents a very useful synthetic method. Nitrile oxides, which are typical 1,3-dipoles, are known to react with various unsaturated bonds to form heterocycles. Furthermore, many studies have been reported on the reactions of nitrile oxides with ylide compounds.[1] However, very few examples of reactions with N–S unsaturated bonds have been reported.[2–4] This is due to the difficulty of synthesizing compounds having such functional groups, except for *N*-(*p*-tosyl)-sulfimides.[5] *N*-(*p*-Tosyl)sulfimides are very stable and easily synthesized, but do not react with nitrile oxides and nitrones.

Recently, Sharma and his collaborators improved the synthetic method of *N*-arylsulfimides,[6] and Claus *et al.* also synthesized these compounds by a different route.[7] Most are unstable, but *S*,*S*-dimethyl-*N*-(*p*-nitrophenyl)-sulfimide is stable enough to remain unchanged in a refluxing benzene solution for 10 h. The reactions of nitrile oxides with *N*-arylsulfimides are being investigated in this laboratory in order to elucidate the ionic character of 1,3-dipolar cycloaddition reactions. In the course of the investigation, it was found that both benzimidazole 3-oxides and 1,2,4-benzoxadiazines were formed in the reactions of 2,6-disubstituted benzonitrile oxides with *N*-arylsulfimides, though 1,2,4-benzoxadiazines were the sole products in the reactions of 2,6-unsubstituted benzonitrile oxides.

Gilchrist *et al.* have reported on reactions of nitrile oxides with *N*-aryl-*S*,*S*-dimethylsulfimides from the viewpoint of 1,2,4-benzoxadiazine synthesis.[8] They used only 2,6-unsubstituted benzonitrile oxides and other aliphatic nitrile oxides, and therefore, paid no attention to the formation of benzimidazole 3-oxides.

Results and Discussion

Sterically-stabilized 2,3,5,6-tetramethylbenzonitrile oxide (DNO), 2,4,6-trimethylbenzonitrile oxide (MNO), and 2,6-dichlorobenzonitrile oxide (DCNO) were allowed to react with some *N*-aryl-*S*,*S*-dimethylsulfimides (**1**). In almost all cases, two types of products were obtained as main products, benzimidazole 3-oxides (**2**) and 1,2,4-benzoxadiazines (**3**), although the yields were poor. In addition, some minor products formed by the decomposition or isomerization of the starting materials were found. The reaction conditions and yields are shown in Table 1. The reactions of 2,6-unsubstituted benzonitrile oxides with *S*,*S*-dimethyl-*N*-(*p*-nitrophenyl)sulfimide (**1a**) were also carefully studied, but the formation of benzimidazole 3-oxide was not observed. These results are also shown in Table 1.



Scheme 1. Reaction route to the benzimidazole 3-oxide and benzoxadiazine.

The formation of benzimidazole 3-oxides in reactions of benzonitrile oxides with *N*-aryl-*S*,*S*-dimethylsulfimides has not been reported as yet. Characterization data of the benzimidazole 3-oxides are summarized in Table 2. Benzimidazole 3-oxides were formed as fleecy crystals during the reactions. High melting points and poor solubilities in the usual solvents are common to products of this type. Their IR spectra show characteristic broad absorptions in the range from 2100 to 2800 cm^{-1}

TABLE 1. REACTION CONDITIONS AND YIELDS OF REACTIONS OF NITRILE OXIDES WITH *N*-ARYL-*S*,*S*-DIMETHYLSULFIMIDES

Nitrile oxide (Ar)	Sulfimide	Reaction conditions			Yields	
		Solvent	Temp	Time	**2**	**3**
DNO	**1a**	$CHCl_3$	room	190 h	8.3%	14.4%
DNO	**1a**	$CHCl_3$	reflux	10 h	10.7	27.4
DNO	**1a**	PhH	reflux	4 h	11.9	24.7
DNO	**1a**	$PhCH_3$	reflux	2 h	8.5	12.0
DNO	**1a**	Dioxane	reflux	2 h	3.7	trace
DNO	**1a**	THF	reflux	4 h	0.0	6.8
MNO	**1a**	$CHCl_3$	room	18 days	7.6	27.2
MNO	**1a**	PhH	reflux	4 h	7.7	33.8
DCNO	**1a**	$CHCl_3$	room	45 h	14.2	59.5
DCNO	**1a**	$CHCl_3$	reflux	1 h	12.0	65.6
DNO	**1b**	$CHCl_3$	0 °C	a)	16.3	14.3
DNO	**1c**	$CHCl_3$	0 °C	a)	8.1	7.4
Ph-	**1a**	$CHCl_3$	0 °C	a)	0.0	34.6
Ph-	**1a**	THF	0 °C	a)	0.0	61.0
p-ClC_6H_4-	**1a**	$CHCl_3$	0 °C	a)	0.0	37.8
p-ClC_6H_4-	**1a**	THF	0 °C	a)	0.0	68.8
p-$NO_2C_6H_4$-	**1a**	$CHCl_3$	0 °C	a)	0.0	56.3
p-$NO_2C_6H_4$-	**1a**	THF	0 °C	a)	0.0	81.3

a) The reaction mixture was allowed to stand overnight at room temperature.

TABLE 2. CHARACTERIZATION DATA OF BENZIMIDAZOLE 3-OXIDES (**2**)

Compd No.	X	R^1	R^2	R^3	Mp (dec) °C (recryst. solvent)		Found	Calcd	NMR, δ (in CF_3 COOH)
2a	NO_2	Me	Me	H	334 (DMF)	C: H: N:	65.65 5.45 13.60	65.58 5.50 13.50	2.12 (s, 6H, Me-2′, 6′), 2.37 (s, 6H, Me-3′, 5′) 7.47 (s, 1H, H-4′), 8.17 (d, 1H, H-7), 8.67 (dd, 1H, H-6), 9.02 (d, 1H, H-4) $J_{4,6}$=2.5 Hz, $J_{6,7}$=10 Hz
2b	NO_2	Me	H	Me	306 (DMF)	C: H· N:	64.71 5.35 14.22	64.64 5.09 14.13	2.24 (s, 6H, Me-2′, 6′), 2.44 (s, 3H, Me-4′), 7.20 (s, 2H, H-3′, 5′), 8.11 (d, 1H, H-7), 8.65 (dd, 1H, H-6), 8.93 (d, 1H, H-4) $J_{4,6}$=1.2 Hz,$J_{6,7}$=8.4 Hz
2c	NO_2	Cl	H	H	318 (DMF+H_2O)	C: H: N:	47.34 2.34 12.48	48.17 2.18 12.96	7.69 (s, 3H, H-3′, 4′, 5′), 8.17 (d, 1H, H-7), 8.71 (dd, 1H, H-6), 8.99 (d, 1H, H-4) $J_{4,6}$=1.2 Hz, $J_{6,7}$=9 Hz
2d	Cl	Me	Me	H	319 (DMF)	C: H: N:	67.44 5.62 9.64	67.88 5.70 9.31	2.08 (s, 6H, Me-2′, 6′), 2.36 (s, 6H, Me-3′, 5′) 7.40 (s, 1H, H-4′), 7.76–7.98 (m, 3H, H-4, 6, 7)
2e	Br	Me	Me	H	328 (DMF)	C: H: N:	59.37 5.13 8.20	59.14 4.96 8.11	2.08 (s, 6H, Me-2′, 6′), 2.40 (s, 6H, Me-3′, 5′) 7.39 (s, 1H, H-4′), 7.82–8.13 (m, 3H, H-4, 6, 7)

(Fig. 1). Chua *et al.* have attributed the broad absorption in this range to intermolecular hydrogen bonding.[9] Mass spectra also support the structure. All products of this type show similar fragmentation patterns. It should be emphasized that the (M^+-16) fragment ion peak is very characteristic, because the oxygen atom of usual *N*-oxide compounds is thought to be easily stripped off during the ionization process.[10] And the intensity of the (M^++1) ion peak is much stronger than the value calculated from the natural isotope abundance, because of intermolecular hydrogen bonding. The NMR spectra are understandable on the basis of this structure. The signal due to the proton at the 6-position appears in doublet-doublet form, because of interactions with the protons at the 4- and 7-positions. The coupling constant between the protons at 4- and 6-positions is consistent with those of the protons at the meta-positions. The signal due to the proton at the 4-position appears at a field lower than that of the corresponding signal for the 1,2,4-benzoxadiazines. This suggests that the proton is in the neighborhood of and affected by the magnetic anisotropy of the *N*-oxide moiety.

Characterization data of the benzoxadiazines are listed in Table 3. In the mass spectra of the oxadiazines obtained here, the (M^+-15) fragment is very characteristic and this is attributed to NH splitting. This agrees well with the results reported by Gilchrist *et al.*[8] A methanolic solution of 7-nitro-1,2,4-benzoxadiazines produced a color change from yellow to violet, upon addition to an alkaline solution. This color change was

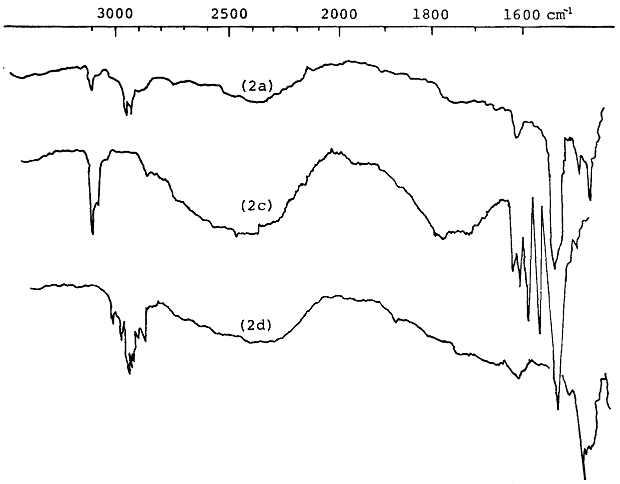


Fig. 1. IR spectra of benzimidazole 3-oxides.

reversible and the violet color returned to its original color upon neutralization.

As seen in Table 1, the reactions of 2,6-disubstituted benzonitrile oxides with *N*-aryl-*S*,*S*-dimethylsulfimides gave both benzimidazole 3-oxides and 1,2,4-benzoxadiazines, whereas 2,6-unsubstituted benzonitrile oxides gave no benzimidazole 3-oxides. The reaction leading to the formation of a benzimidazole 3-oxide or a 1,2,4-benzoxadiazine is considered to proceed by the nucleophilic attack of the nitrogen atom of the sulfimide on the carbon atom of the nitrile oxide followed by the liberation of dimethyl sulfide to form an intermediate nitroso compound. When the nitrogen atom of the nitroso group attacks the ortho-position of the benzene ring, benzimidazole 3-oxide is produced. On the contrary, when the oxygen atom of the nitroso group attacks, 1,2,4-benzoxadiazine is formed (Scheme 1). For the intermediate nitroso compounds, there are two conformational structures, which are *s-cis* and *s-trans* with respect to the –N=C–N=O structure, as shown in Scheme 1. In the *s-trans* form, the lone pair of nitrogen atom faces the *N*-phenyl substituent and, from this structure benzimidazole 3-oxide is produced. In the *s-cis* form, the lone pair faces the opposite side, and nitrogen attack on the *N*-phenyl substituent is inconceivable. Regarding the nitroso intermediate, it is considered to be somewhat more stable when the –N=C–N=O group is in the plane of the aryl group attached to the carbon atom, than when this is not the case. In the case of the reaction of a 2,6-unsubstituted benzonitrile oxide with a sulfimide, the nitroso intermediate can take the more stable *s-cis* form and, therefore, gave only a 1,2,4-benzoxadiazine. However, in the case of the reaction of a 2,6-substituted benzonitrile oxide, coplanarity between the –N=C–N=O and the aryl group attached to the carbon atom is not attained at all due to steric hindrance and thus the intermediate can take either the *s-cis* or the *s-trans* form leading to both 1,2,4-benzoxadiazine and benzimidazole 3-oxide.

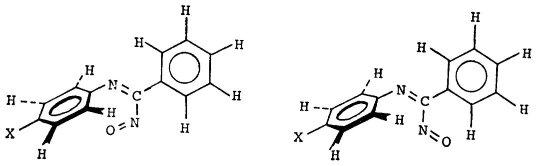
When THF was used as the reaction solvent, no benzimidazole 3-oxide formation was observed and the decomposition of the sulfimide to the corresponding

Table 3. Characterization data of 1, 2, 4-benzoxadiazines (**3**)

Compd No.	X	R^1	R^2	R^3	Mp (dec) °C (recryst. solvent)		Found	Calcd	NMR, δ (in DMSO-d_6)
3a	NO_2	Me	Me	H	214—219 (acetone +H_2O)	C: H: N:	65.44 5.39 13.87	65.58 5.50 13.50	2.21 (s, 12H, Me) 6.75 (d, 1H, H-5) 7.02 (s, 1H, H-4′) 7.46 (d, 1H, H-8) 7.82 (dd, 1H, H-6) $J_{5,6}$= 8.4 Hz, $J_{6,8}$=2.4 Hz
3b	NO_2	Me	H	Me	216—220 (acetone +H_2O)	C: H: N:	65.18 5.34 14.21	64.64 5.09 14.13	2.31 (s, 9H, Me) 6.77 (d, 1H, H-5) 7.02 (s, 2H, H-3′, 5′) 7.46 (d, 1H, H-8) 7.85 (dd, 1H, H-6) $J_{5,6}$=8.4 Hz, $J_{6,8}$=2.4 Hz
3c	NO_2	Cl	H	H	183—186 (acetone +H_2O)	C: H: N:	48.25 2.93 12.68	48.17 2.18 12.96	6.82 (d, 1H, H-5) 7.53 (d, 1H, H-8) 7.69 (s, 3H, H-3′, 4′, 5′) 7.89 (dd, 1H, H-6) $J_{5,6}$=8.4 Hz, $J_{6,8}$=2.4 Hz
3d	Cl	Me	Me	H	176—179 ($CHCl_3$+ hexane)	C: H: N:	67.90 5.85 9.55	67.88 5.70 9.31	2.21 (s, 12H, Me) 6.54—7.07 (m, 4H)
3e	Br	Me	Me	H	182—183 ($CHCl_3$+ hexane)	C: H: N:	59.00 5.25 8.33	59.14 4.96 8.11	2.20 (s, 12H, Me) 6.52 (d, 1H, H-5) 6.83—7.08 (m, 3H) $J_{5,6}$=8.4 Hz
3f	NO_2	H	H	H	179—182[a] ($CHCl_3$)	C: H: N:	61.36 3.58 16.57	61.18 3.55 16.46	6.93 (d, 1H, H-5) 7.40—7.97 (m, 7H) $J_{5,6}$=8.4 Hz
3g[b]	NO_2	H	H	Cl	217—219 ($CHCl_3$)	C: H: N:	54.01 2.94 14.77	53.90 2.78 14.51	5.99 (d, 1H, H-5) 6.65 (d, 1H, H-8) 7.53 (d, 2H, H-3′, 5′) 7.59 (dd, 1H, H-6) 8.01 (d, 2H, H-2′, 6′) $J_{5,6}$=8.4 Hz, $J_{6,8}$=2.4 Hz, $J_{2',6'}$=$J_{3',5'}$=28.8 Hz, $J_{2',3'}$=$J_{5',6'}$=8.4 Hz
3h[b]	NO_2	H	H	NO_2	228—230 (THF)	C: H: N:	51.97 2.82 19.14	52.01 2.69 18.66	6.15 (d, 1H, H-5) 6.59 (d, 1H, H-8) 7.35 (dd, 1H, H-6) 8.10 (d, 2H, H-2′, 6′) 8.15 (d, 2H, H-3′, 5′) $J_{5,6}$=8.4 Hz $J_{6,8}$=2.4 Hz, $J_{2',6'}$=$J_{3',5'}$=1.2 Hz, $J_{2',3'}$=$J_{5'6'}$=3 Hz

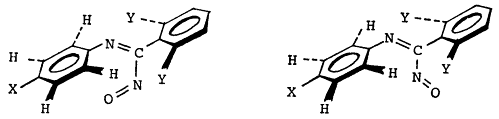
a) Mp lit,[8] 178 °C. b) In measurements of MNR spectra, 1,5-diazabicyclo[5,4,0]undecene-5 (DBU) was added to enhance the solubility of 1,2,4-benzoxadiazine by proton abstraction at the 4-potition due to its strong basicity.

The intermediate nitroso compound derived from 2,6-unsubstituted benzonitrile oxide.



s-cis form *s-trans* form

The intermediate nitroso compound derived from 2,6-substituted benzonitrile oxide.



s-cis form *s-trans* form

Fig. 2. Conformational structures of the intermediate nitroso compounds.

aniline was marked. The reason is not clear, but this may be attributed to the solvation of the zwitterionic intermediate which permits annellation only by the attack of anionic oxygen.

Gilchrist and co-workers have reported the formation of 1,2,4-triazolo[1,5-*a*]pyridin 3-oxides in the reactions of nitrile oxides with *S*,*S*-dimethyl-*N*-(2-pyridyl)sulfimide.[11] In these reactions, the intermediates are also thought to be nitroso compounds, however, the reaction proceeds by attack of the nitrogen atom of the pyridine ring on the nitroso group. If the lone pair of nitrogen atom of the nitroso group attacks, annellation on the carbon atom at another ortho-position of the pyridine must also occur. However, no such product has been reported.

Furthermore, other two reaction products, isocyanate and 2-amino-5-nitrobenzyl methyl sulfide which are isomerization products of each starting material, were isolated in a reaction of a sterically-stabilized nitrile oxide with *S*,*S*-dimethyl-*N*-(*p*-nitrophenyl)sulfimide. It is well known that sterically-stabilized benzonitrile oxides isomerize to the appropriate isocyanates either thermally or photochemically.[2] However, when the sulfimide alone was subject to the identical and more severe conditions, it remained unchanged. The decomposition of sulfimide to the *p*-nitroaniline is induced also in alcohols. The mechanism is now under investigation.

Experimental

Melting points were measured using a micro-melting-point measuring apparatus (Yazawa Co., Ltd.) and are uncorrected. IR spectra were recorded with a Hitachi infrared spectrometer 215. Mass spectra were recorded with a Hitachi RMU-7M high-resolution mass spectrometer. NMR spectra were recorded with a Hitachi Perkin-Elmer 20R-A high-resolution NMR spectrometer (60 MHz).

Materials. Stable nitrile oxides were synthesized using the method of Grundmann *et al.*[12] 2,6-Unsubstituted benzonitrile oxides were generated *in situ* from the appropriate benzhydroxamoyl chlorides, which were synthesized by the usual methods.[13] *N*-Aryl-*S*,*S*-dimethylsulfimides were synthesized with DMSO, substituted anilines, and sulfur trioxide.[6]

Reaction of 2,3,5,6-Tetramethylbenzonitrile Oxide (DNO) with S,S-*Dimethyl*-N-(p-*nitrophenyl)sulfimide (**1a**).* *a) In Chloroform under Reflux*: A solution of 351 mg (2.00 mmol) of DNO and 377 mg (1.90 mmol) of **1a** in 30 ml of chloroform was heated to reflux with the precipitation of fleecy crystals. After 10 h, the solid product was separated by filtration while the reaction mixture was hot, and was then washed with hot chloroform. The solid product weighed 67 mg (11.3%) and was identified to be 2-duryl-5-nitro-1*H*-benzimidazole 3-oxide (**2a**). The combined filtrate and washing were evaporated giving an oily residue, which was worked up using column chromatography on silica gel (Wacogel C-200) eluted with chloroform. From the elutes, the following were isolated; 199 mg of DNO (56.7% recovery), 19 mg of 2-amino-5-nitrobenzyl methyl sulfide (5.1%), 171 mg of 3-duryl-7-nitro-4*H*-1,2,4-benzoxadiazine (**3a**) (28.9%), and 19 mg of *p*-nitroaniline (7.2%).

b) In Benzene under Reflux: In 50 ml of dry benzene, 877 mg (5.01 mmol) of DNO and 992 mg (5.00 mmol) of **1a** were dissolved and the solution was heated to reflux. Fleecy crystals were deposited during the reaction. After 4 h, the crystals were separated by filtration while hot and washed with hot benzene. They were identified to be **2a**, which weighed 186 mg (11.9%). The combined solution was allowed to stand overnight at room temperature to precipitate the starting ylide, which was removed by filtration (328 mg, 33.1% recovery). The filtrate was evaporated under reduced pressure to give a viscous oil, the trituration of which with a small amount of ether gave a solid. This solid was identified to be **3a** and weighed 286 mg. From the residual ethereal solution, further 48 mg of **3a** was obtained upon trituration with benzene. The residual solution was evaporated and treated on silica-gel column chromatograph with chloroform, and the following substances were isolated: 2,3,5,6-tetramethylphenyl isocyanate (128 mg, 15.7%), DNO (289 mg, 32.9% recovery), 2-amino-5-nitrobenzyl methyl sulfide (109 mg, 11.0%), and **3a** (50 mg). The total amount of **3a** was 384 mg (24.7%).

c) In THF under Refulx: DNO and **1a** (5.00 mmol each) were dissolved in 50 ml of THF and the solution was heated to reflux for 4 h. No crystal formation was observed even upon prolonged heating. The solution was evaporated under reduced pressure. Trituration of the residual oil with cold chloroform gave 144 mg of the starting ylide (14.6% recovery). The chloroform solution was worked up using column chromatography on silica gel (Wacogel C-200) with chloroform. The following substances were isolated: DNO (729 mg, 93.0% recovery), 2-amino-5-nitrobenzyl methyl sulfide (38 mg, 3.8%), **2a** (106 mg, 6.8%), and *p*-nitroaniline (502 mg, 72.6%).

Reaction of p-*Chlorobenzonitrile Oxide with **1a**.* *In Chloroform*: In a cold solution (below 0 °C) of 496 mg (2.50 mmol) of **1a** in 30 ml of chloroform, 0.40 ml of triethylamine was added with stirring, and then a solution of *p*-chlorobenzhydroxamoyl chloride (475 mg, 2.50 mmol) in 20 ml of chloroform was added dropwise for thirty minutes. After the addition, the cooling bath was removed and the reaction mixture was allowed to stand overnight at ambient temperature. The solvent was removed by evaporation under reduced pressure. The residue was washed with THF to give white crystals of triethylammonium chloride (316 mg, 91.7%). From the THF-soluble part, 274 mg (37.8%) of 3-(*p*-chlorophenyl)-7-nitro-4*H*-1,2,4-benzoxadiazine (**3g**) was obtained upon trituration with chloroform. The residual oil was worked up using column-chromatography on alumina with chloroform to give 260 mg (52.5% recovery) of the starting ylide (**1a**). No 2-(*p*-chlorophenyl)-5-nitrobenzimidazole 3-oxide was obtained.

Reaction of p-*Nitrobenzonitrile Oxide with 1a.* *In Chloroform*: In a cold solution (below 0 °C) of 496 mg (2.50 mmol) of **1a** in 20 ml of chloroform, 0.38 ml of triethylamine was added with stirring, and then a solution of *p*-nitrobenzhydroxamoyl chloride (502 mg, 2.50 mmol) in 30 ml of chloroform was added dropwise for 30 m. During the reaction, a brownish-red precipitate appeared. After the addition, the cooling bath was removed and the reaction mixture was allowed to stand overnight at ambient temperature. The brownish-red precipitate was filtered off and dried, and was identified to be 3-(*p*-nitrophenyl)-7-nitro-4*H*-1,2,4-benzoxadiazine (**3h**). It weighed 396 mg. The filtrate was evaporated under educed pressure to give an oily product. Washing the oily product with THF produced white crystals of triethylammonium chloride (331 mg, 96.2%). The residual THF solution was evaporated and triturated with a small amount of chloroform to give 27 mg of the 3-(*p*-nitrophenyl)-7-nitro-4*H*-1,2,4-benzoxadiazine (**3h**). The total amount of **3h** was 358 mg (56.3%). No 2-(*p*-nitrophenyl)-5-nitrobenzimidazole 3-oxide was found.

Reaction of Benzonitrile Oxide with 1a. *In THF*: In a cold solution (below 0 °C) of 496 mg (2.50 mmol) of **1a** in 30 ml of THF, 0.40 ml of triethylamine was added with stirring, and then a solution of benzhydroxamoyl chloride (391 mg, 2.51 mmol) in 20 ml of THF was added for 30 m. After the addition, the cooling bath was removed and the reaction mixture was allowed to stand over-night at ambient temperature. The first drop of benzhydroxamoyl chloride caused the precipitation of triethylammonium chloride. The precipitate was removed by filtration and washed with THF. The solid was almost pure salt and weighed 296 mg (86.0%). The filtrate was evaporated under reduced pressure giving an oil. Trituration of the oil with a small amount of chloroform gave 250 mg of 3-phenyl-7-nitro-4*H*-1,2,4-benzoxadiazine (**3f**). The residue was worked up employing column chromatography on alumina eluted with chloroform. From the elutes, 139 mg of **3f** and 47 mg of **1a** (5.7% recovery) were isolated. The total amount of **3f** was 389 mg (61.0%).

Mass Spectral Data of Benzimidazole 3-Oxides (2). 2-Duryl-5-nitrobenzimidazole 3-oxide (**2a**); $m/e=312$ (M^++1), relative abundance 8; 311.1288 (M^+, calcd for $C_{17}H_{17}N_3O_3=311.1269$), 42; 295 ($M^+-16$), 15; 294 ($M^+-17$), 58; 248, 100: 2-Mesityl-5-nitrobenzimidazole 3-oxide (**2b**); 298 (M^++1), 8; 297.1122 (M^+, calcd for $C_{16}H_{15}N_3O_3=297.1112$), 46; 281 ($M^+-16$), 22; 280 ($M^+-17$), 41; 234, 100: 2-(2′,6′-Dichlorophenyl)-5-nitrobenzimidazole 3-oxide (**2c**); 326 (M^++3), 3; 325 (M^++2), 23; 324 (M^++1), 4; 322.9868 (M^+, calcd for $C_{13}H_7N_3O_3Cl_2=322.9864$), 33; 309 ($M^+-14$), 7; 307 ($M^+-16$), 12; 173, 100; the ($M^+-17$) ion peak was not observed in this case. 2-Duryl-5-chlorobenzimidazole 3-oxide (**2d**); 303 (M^++3), 4; 302 (M^++2), 13; 301 (M^++1), 10; 300.1014 (M^+, calcd for $C_{17}H_{17}N_2OCl=300.1028$), 38; 286 ($M^+-14$), 8; 285 ($M^+-15$), 31; 284 ($M^+-16$), 22; 283 ($M^+-17$), 100: 2-Duryl-5-bromobenzimidazole 3-oxide (**2e**); 347 (M^++3), 7; 346 (M^++2), 50; 345 (M^++1), 8; 344.0530 (M^+, calcd for $C_{17}H_{17}N_2OBr=344.0524$), 52; 330 ($M^+-14$), 22; 329 ($M^+-15$), 100; 328 ($M^+-16$), 24; 327 ($M^+-17$), 100.

References

1) R. Huisgen and J. Wuff, *Chem. Ber.*, **102**, 1833 (1969); *ibid.*, **102**, 1848 (1969).

2) C. Grundmann and P. Grunanger, "The Nitrile Oxides," Springer-Verlag, Berlin (1971), pp. 62, 134.

3) E. S. Levchenko and I. E. Sheinkman, *Zh. Obshch. Kim.*, **36**, 428 and *Chem. Abstr.*, **65**, 643e (1966).

4) P. Rajagopalan and B. G. Advani, *J. Chem. Soc.*, **1965**, 3369.

5) K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Jpn.*, **42**, 2631 (1969).

6) A. K. Sharma, T. Ku, A. D. Dawson, and D. Swern, *J. Org. Chem.*, **39**, 3365 (1974); T. E. Varkey, G. F. Whitfield, and D. Swern, *ibid.*, **40**, 2758 (1975).

7) P. K. Claus, W. Reider, and P. Hofbauer, *Tetrahedron*, **31**, 505 (1975).

8) T. L. Gilchrist, C. J. Harris, F. D. King, M. E. Peek, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 2161 and T. L. Gilchrist, C. J. Harris, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, **1974**, 485.

9) S. O. Chua, M. J. Cook, and A. R. Katritzky, *J. Chem. Soc., B*, **1971**, 2350.

10) K. Volkamer and H. W. Zimmermann, *Chem. Ber.*, **102**, 4177 (1969).

11) T. L. Gilchrist, C. J. Harris, D. G. Hawkins, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 2166.

12) C. Grundmann and R. Richter, *J. Org. Chem.*, **33**, 476 (1968); C. Grundmann and J. M. Dean, *ibid.*, **30**, 2809 (1965).

13) M. H. Benn, *Can. J. Chem.*, **42**, 2393 (1964).