

monitored by measurement of the UV absorption at 399 nm. The technique was essentially that reported earlier,²³ except that each rate was the result of only a single trial.

Adducts (17 and 18) of Acridizinium Tetrafluoroborate with 2-Stilbazole. The standard procedure was followed except that only a 3:1 ratio of stilbazole to acridizinium salt was used (46-h reflux) and most of the adduct crystallized from the reaction mixture (overall yield 96%). The ¹H NMR spectrum of the crude product showed that the major regioisomer (17; ~66%) had the phenyl group at position 12 and indicated that the minor isomer (18) consisted of almost equal parts of the two possible geometrical isomers.

Recrystallization from acetonitrile afforded a colorless powder which was analyzed as an isomeric mixture: mp 247–255 °C; ¹H NMR ((CD₃)₂SO) δ 3.89–4.72 (m, 2, C-12, C-13), 5.43 (m, 0.6, C-11 of 17), 5.55 (d, 0.2, *J* = 2 Hz, C-11 of 18), 5.79 (d, 0.2, *J* = 2 Hz, C-11 of 18), 6.70–9.27 (m, 17), and 9.53 (m, 1, C-4); ¹H NMR (CF₃CO₂H) δ 3.91–4.93 (m, 2, C-12, C-13), 5.36 (m, 0.7, C-11 of 17), 5.70 (m, 0.3, C-11 of 18), 6.52 (m, 0.3, C-6 of 18), 6.56–9.01 (m, 17), and 9.30 (m, 1, C-4).

Anal. Calcd for C₂₆H₂₁BF₄N₂: C, 69.66; H, 4.72; N, 6.25. Found: C, 69.70; H, 4.95; N, 6.07.

Registry No.—1 BF₄, 32865-43-3; 1 picrate, 66357-78-6; 1 Br, 7547-88-8; 3 (isomer 1), 66357-80-0; 3 (isomer 2), 66511-02-2; 4, 66357-82-2; 5, 66357-84-4; 6 Br (isomer 1), 66357-85-5; 6 Br (isomer 2), 66511-03-3; 6 ClO₄ (isomer 1), 66511-05-5; 6 ClO₄ (isomer 2), 66537-15-3; 9, 80-62-6; 12 (isomer 1), 66357-87-7; 12 (isomer 2), 66511-07-7; 13 (isomer 1), 66357-89-9; 13 (isomer 2), 66511-09-9; 14 (isomer 1), 66357-91-3; 14 (isomer 2), 66511-11-3; 15, 66357-93-5; 16, 66357-95-7; 17, 66357-97-9; 18, 66357-99-1; indene, 95-13-6; anethole, 104-46-1; *cis*-β-methoxystyrene, 14371-19-8; 1-methoxy-1,3-butadiene, 3036-66-6; ethyl acrylate, 140-88-5; *cis*-crotononitrile, 1190-76-7; 2-stilbazole, 714-08-9.

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Selectivity in Cycloadditions. 6. Cycloadditions of Nitrile Oxides to Benzofuran. Regiochemistry¹

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Received January 6, 1978

Cycloaddition of benzonitrile oxide and mesitonitrile oxide to benzofuran yields the two regioisomeric cycloadducts 1 and 2 in a 70:30 and 26:74 ratio, respectively. Frontier orbital considerations, using ab initio STO-3G calculations, and a comparison with the regioselectivities observed with indene and styrene allow elucidation of the inversion of regiochemistry of the cycloadditions of the two nitrile oxides to benzofuran.

Although much is known about the physical properties of heteroaromatic compounds and the reactivities of these molecules in electrophilic substitution reactions,³ the study of the dipolarophilic reactivities of these molecules toward 1,3 dipoles is by far less developed. The reluctance of heteroaromatics to undergo addition reactions is well known and usually rationalized in terms of loss of aromaticity in the addition step.

The study of cycloaddition reactions of heteroaromatics is

of interest for mechanistic reasons, since the concerted cycloaddition is expected to be slowed down, so that diradical and zwitterionic pathways, which are normally of no importance in 1,3-dipolar cycloadditions,⁴ may become competitive.

The previous paper of this series dealt with the cycloadditions of nitrile oxides to cyclopentadiene,⁵ indene,⁵ and furan.^{1b} In the case of furan a competition between the concerted pathway and a minor two-step pathway was described.

Table I. Chemical Shifts^a and Coupling Constants^b of Cycloadducts^c

Compd	Registry no.	4-H ^d	5-H ^d	J _{4,5}	Other
1a	66303-77-3	6.21 d	6.30 d	8.7	
1b	66357-75-3	6.18 d	6.30 d	8.6	<i>o</i> -Me 2.14 s, <i>p</i> -Me 2.27 s
2a	66303-78-4	5.35 d	7.03 d	7.4	
2b	66303-79-5	5.11 d	6.91 d	7.1	<i>o</i> -Me, <i>p</i> -Me 2.29 s
3a	61495-72-5		8.53 s		OH ^{e,f}
3b	66303-80-8		9.03 s		<i>o</i> -Me 2.02 s, <i>p</i> -Me 2.32 s, OH 6.79 s/

^a Chemical shifts in parts per million (δ) from internal Me₄Si. Multiplicity: s, singlet; d, doublet; m, multiplet. Solvent: CDCl₃. ^b In Hz. ^c Satisfactory combustion analytical data C, H, N ($\pm 0.4\%$) have been obtained for these compounds. ^d Numbering refers to the isoxazoline (isoxazole) ring. ^e Occurs under phenyl multiplet. ^f Exchanges with D₂O.

This paper reports a study of the cycloaddition of benzo- and mesitronitrile oxide to benzofuran. The reactions of benzofuran⁶ in 1,3-dipolar cycloadditions with diphenylnitrilimine⁷ and with 3,5-dichloro-2,4,6-trimethylbenzoxime⁸ have been reported recently.

Results

Benzofuran reacts slowly with benzonitrile oxide (BNO). Generation of BNO in situ in ether in the presence of 10 equiv of benzofuran afforded a 14% yield of cycloadducts **1a** and **2a** (Scheme I) in a ratio of 70:30, along with the dimerization products of BNO. On performing the reaction in benzofuran (100 equiv) as solvent, the dimerization of BNO decreases and the yield of cycloadducts improves to 24%. The reactivity of benzofuran is 180 times less than that of indene, as determined by competition experiments.

No other products could be detected or isolated from the reaction mixtures. The known oximes **4**⁹ and **5**,¹⁰ which are the formal products of 1,3 addition, have been obtained by oximation of the ketones. The oximes are stable under the reaction and separation conditions and could not be detected by TLC or GLC of the reaction mixtures.

The cycloadducts were separated by column chromatography. The structure proofs are based on chemical and NMR evidence (Table I). In adduct **2a** the isoxazoline C-5 proton is deshielded by two adjacent oxygens and occurs as a doublet at low field, δ 7.03, whereas the doublet of the other isoxazoline proton is well separated at δ 5.35, in the usual range reported for isoxazoline C-4 protons.¹¹ In adduct **1a** both the isoxazolinic protons experience the deshielding effect of an oxygen and have similar chemical shifts, appearing as an AB system. The easy acidic hydrolytic cleavage of 5-alkoxyisoxazolines^{12,1a} further supports this structural assignment. Adduct **2a** has

Scheme I

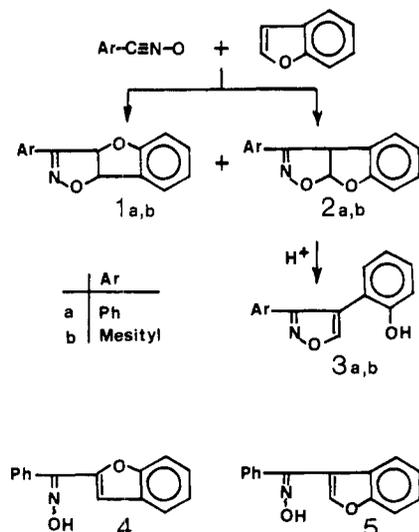


Table II. Regioisomer Distribution in the Cycloaddition of Nitrile Oxides with Styrene, Indene, and Benzofuran

X	I/II		$\frac{\Delta\Delta G^\ddagger_{I/II}}{\text{Ph}}^a$		Change ^{a,b}
	Ph ^c	Mes ^d	Ph	Mes	
H, H	100:0	100:0			
CH ₂	96:4	76:24	1.72	0.68	1.04
O	70:30	26:74	0.46	-0.62	1.08

^a kcal/mol, ± 0.1 kcal/mol. ^b $\Delta\Delta G^\ddagger_{I/II}(\text{Ph}) - \Delta\Delta G^\ddagger_{I/II}(\text{Mes})$. ^c 0 °C, ether, GLC. The regioisomer distribution does not change appreciably for reactions run at 25 °C. ^d 25 °C, benzene, GLC.

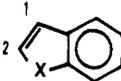
an acetal moiety at the C-5 isoxazolinic carbon and is cleaved by heating with methanol and HCl, affording isoxazole **3a**. This latter compound shows in the NMR spectrum, besides the phenyl protons and the OH signal, a singlet at δ 8.53, in the range reported for isoxazole C-5 protons.¹³ Under similar conditions **1a** was recovered unchanged.

Mesitronitrile oxide, a stable nitrile oxide which does not dimerize at room temperature, reacted with excess benzofuran very slowly. After 4 months cycloadducts **1b** and **2b** were obtained in a 26:74 ratio (89% yield). Structures rely upon the close resemblance of the NMR spectra to those of the corresponding BNO adducts and on the easy hydrolytic cleavage of adduct **2b**.

Discussion

The main products of the reactions are the pairs of regioisomeric cycloadducts, BNO yielding mainly cycloadduct I and mesitronitrile oxide cycloadduct II (Table II). The change of $\Delta\Delta G^\ddagger$ for formation of the two adducts on going from BNO to mesitronitrile oxide amounts to 1.08 kcal/mol. With the carbocyclic indene, the cycloadditions are more regioselective in the direction of I,¹⁴ but the change of $\Delta\Delta G^\ddagger$ on going from BNO to mesitronitrile oxide is a similar value, 1.04 kcal/mol, and the adduct of the type I is still favored slightly. With the parent styrene, only adducts of type I could be isolated.¹⁵

The observed regioselectivities are satisfactorily accounted for by a frontier molecular orbital (FMO) treatment.¹⁶ The shapes of the FMO's of the two dipolarophiles and those of styrene are shown in Figure 1. The ab initio STO-3G eigenvectors and eigenvalues of the FMO's are given in Table III along with the ionization potentials (IP's) and electron affinities (EA's) for the molecules. We have also carried out EHT and CNDO/2 calculations on all these systems, with results similar to those given for STO-3G calculations. Also

Table III. STO-3G Eigenvectors and Eigenvalues of the Frontier Orbitals^{a,d}


Registry no.	HOMO						LUMO						
	C ₁	C ₂	X	ε, eV	IP, eV ^a	P ^b	C ₁	C ₂	X	ε, eV	EA, eV ^c	P ^b	
Styrene	100-42-5	0.31	0.45		-6.61	8.55	0.11	0.36	-0.53		6.17	-0.25	0.15
Indene	95-13-6	0.30	0.45	-0.006	-6.33	8.20	0.11	0.35	-0.54	0.025	6.32	-0.49	0.17
Benzofuran	271-89-6	0.37	0.47	-0.17	-6.54	8.66	0.08	0.31	-0.54	0.26	6.31	-0.11	0.20

^a Geometries and IP's have been taken from M. H. Palmer and S. M. F. Kennedy, *J. Chem. Soc., Perkin Trans. 2*, 1893 (1974).

^b Polarization defined as $C_2^2 - C_1^2$. ^c Styrene: P. D. Burrow, J. A. Michejda, and K. D. Jordan, *J. Am. Chem. Soc.*, **98**, 6392 (1976); for indene and benzofuran, electron affinities were estimated from IP's and $\pi\pi^*$ transition energies²³ from the empirical relationship, $\Delta E(\pi\pi^*) = IP - EA - 3.67$ eV, where the value of $J_{ij} - 2K_{ij}$ is derived for styrene.²⁴ ^d W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1973).

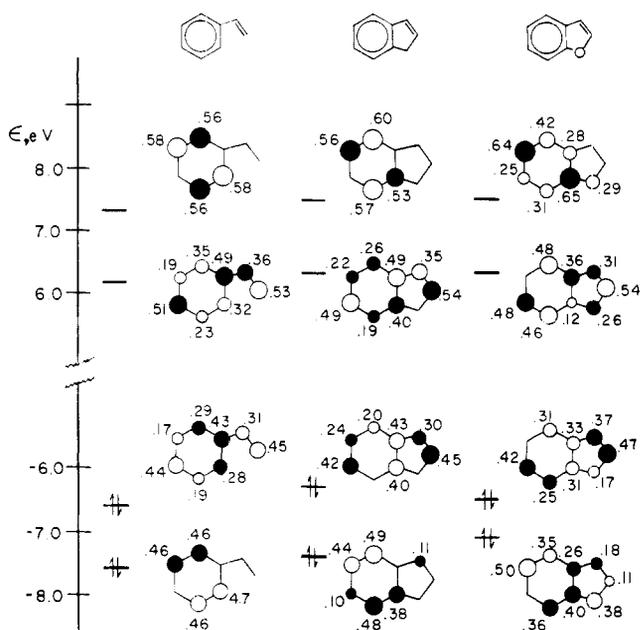


Figure 1. Frontier molecular orbitals of styrene, indene, and benzofuran (STO-3G).

reported in the table is the polarization of the FMO's, defined as the difference between the squares of the coefficients.

The shapes of the FMO's of indene and benzofuran correspond essentially to the familiar FMO's of styrene, whose alkene double bond is polarized toward the terminal carbon as a consequence of phenyl conjugation. All three methods of calculation indicate, however, that the polarization of the HOMO is reduced in benzofuran. On the contrary the polarization of the LUMO increases in indene¹⁷ and to an even larger extent in benzofuran.

The changes in the shapes of FMO's can be qualitatively understood on deriving the MO's of the dipolarophiles from those of styrene and of the ring element X by perturbation theory.¹⁸ The interaction of the styrene orbitals with the oxygen lone pair to form benzofuran and with the π_{CH_2} to form indene is shown in Figure 2. For the sake of simplicity and because the main changes arise from mixing of orbitals of different phases on the double bond of interest, only the FMO's of styrene are displayed in the interaction diagram.

The mixing causes the familiar repulsion of levels as well as a change of the shapes of orbitals. When the X perturber is at lower energy than the orbitals of the other fragment, the X donor causes some of the π^* orbital to be mixed into the π in a negative fashion at the site of substitution, whereas the π mixes into the π^* in a positive fashion.¹⁹ As a result, the

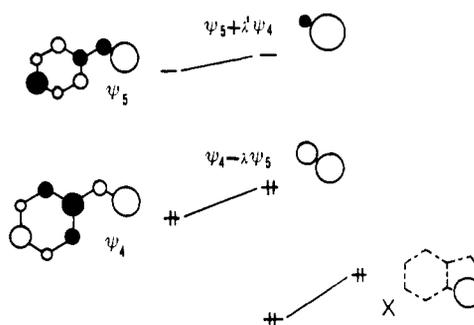


Figure 2. Interactions of the lone pair or π_{CH_2} orbital (shown on the right) with styrene HOMO (ψ_4) and LUMO (ψ_5) (shown on the left) cause polarization of alkene orbitals (shown on the middle).

HOMO polarization decreases and the LUMO polarization increases, as observed in the calculations. The mixing of π with π^* is proportional to the overlaps between X and the styrene orbitals and inversely proportional to both the energy difference between the styrene orbitals and to the energy difference between the orbital of the X fragment and the styrene orbital being polarized. Since the overlaps of the oxygen lone pair and π_{CH_2} with the styrene MO's are similar, the changes of the MO's are greater in benzofuran than in indene because of the higher orbital energy of the oxygen lone pair orbital than the π_{CH_2} orbital.

The changes discussed above are however somewhat moderated by minor effects. In benzofuran the oxygen increases the electronegativity of the adjacent carbons, as shown in the ¹³C spectrum.²⁰ This causes the familiar inductive stabilization of the levels as well as an increase of the HOMO polarization and a decrease of the LUMO polarization (static mixing²¹), which oppose the overriding dynamic mixing²¹ of Figure 2. In the case of indene a perturbing $\pi^*_{CH_2}$ orbital is available above the FMO's of styrene. According to the mixing rules,^{19,21} the $\pi^*_{CH_2}$ induces a mixing of the styrene orbitals opposite to that of Figure 2, i.e., π^* mixes into π in a positive fashion. As discussed in the case of propene,¹⁹ the importance of the $\pi^*_{CH_2}$ in the polarization of the HOMO is, however, small with respect to that of the π_{CH_2} , whereas the effect of the $\pi^*_{CH_2}$ on the polarization of the LUMO is noteworthy and partly compensates the opposite overriding influence of π_{CH_2} .

The orbital energies of the dipolarophiles are similar. In the case of indene the FMO's are slightly higher with respect to those of styrene, a result of the mixing discussed above, whereas the MO's of benzofuran are inductively stabilized. The STO-3G calculations reproduce this trend nicely.

BNO should behave mainly as an electrophile in the reaction with these dipolarophiles since the LUMO (dipole)-HOMO (dipolarophile) separation is smaller than the HOMO

(dipole)-LUMO (dipolarophile) separation. That is, the EA of BNO can be estimated as +0.05 eV,^{25,26} whereas the IP is 8.98 eV.²²

The two interactions have opposite regioselectivity consequences, since in nitrile oxides the electrophilic and nucleophilic center are on carbon and on oxygen, respectively, whereas the styrene-like dipolarophiles both have the largest HOMO and LUMO coefficients at the unsubstituted terminal carbon.

The effects of the energies and coefficients on the regioselectivity can be grasped in the framework of the FMO approximation. The stabilization energies ΔE_1 and ΔE_2 for the formation of the two regioisomers 1 and 2 can be calculated from standard perturbation theory.

The difference $\Delta\Delta E$ between the stabilization energies of the regioisomers gives a theoretical measure of the regioselectivity and can be expressed as^{16c}

$$\Delta\Delta E = A \frac{(c^2_{\text{HO,S}} - c^2_{\text{HO,S'}})}{E_{\text{LU,BNO}} - E_{\text{HO,S}} - Q} - B \frac{(c^2_{\text{LU,S}} - c^2_{\text{LU,S'}})}{E_{\text{LU,S}} - E_{\text{HO,BNO}} - Q}$$

where c 's are the coefficients of HOMO and LUMO on the terminal (S) or internal (S') carbon of the styrene-type molecules, E 's are the orbital energies, and Q is a correction factor which takes into account the change of frontier orbital energies during the approach of the molecules to one another. Its value has been estimated at 4–6 eV.^{16c}

The regiochemistry is now expressed as a function of the polarization of the orbitals of dipolarophiles and of the energy separations. The first term of the equation takes into account the regioselectivity effect of the stronger LU(dipole)-HO(dipolarophile) interaction favoring regioisomer I and the second term represents the effect of the weaker interaction favoring regioisomer II. Since the three dipolarophiles have similar orbital energies, the changes in the denominators are small for the three dipolarophiles with respect to the changes in polarizations, even using the maximal values of the Q correction. On going from styrene to indene the leading effects on regioselectivity are the small change of the first term and the increase of the second term of the equation, caused by the increase of polarization of the LUMO. On going from indene to benzofuran, the decrease of the first term and increase of the second term of the equation causes a significant regioselectivity change as a consequence of the strong increase of the LUMO polarization.

With the more nucleophilic mesitronitrile oxide, which has an IP of 10.26 eV²² and an estimated EA of -0.11 eV,²⁵ the HO-(dipole)-LU(dipolarophile) interaction increases at the expense of the LU(dipole)-HO(dipolarophile) interaction. As a consequence, the balance between regioisomers is shifted toward regioisomer II. The effect of regioselectivity is noteworthy, affecting the $\Delta\Delta G^\ddagger$ by about 1 kcal/mol. This causes, in the case of indene, a diminution of regioselectivity and in the case of benzofuran a change in the preferred regioisomer. A similar situation should hold for 2,4,6-trimethyl-3,5-dichlorobenzonitrile oxide,⁸ which gives with benzofuran a ratio of regioisomers I/II of 2:3, close to that observed with mesitronitrile oxide.

With diphenylnitrilimine only a cycloadduct of type I was isolated in a 30% yield.⁷ This is consistent with the known greater LU(dipole) control in the cycloadditions of nitrilimines,²⁷ as a consequence of the easy bending of these dipoles.²⁸

The reactivity of benzofuran decreases by a factor of 180 with respect to indene, but the 1,3-addition reaction to yield oximes is still noncompetitive. The cycloaddition is slowed down because of the loss of aromaticity in the four-center

transition state and in part because of the higher IP of benzofuran. The drop of reactivity corresponds to an increase of the barrier of 2.8 kcal/mol (for furan 4.0 kcal/mol^{1b}). These values are relatively small, when compared to the resonance energies of heteroaromatics, and are compatible with an early transition state for the cycloaddition of nitrile oxides, as suggested by ab initio calculations.²⁹

No oximes could be isolated or detected in significant amounts. 1,3-Additions are known to occur as side reactions in the cycloaddition of BNO to furan^{1b} and phenylacetylene.³⁰ In the case of furan the 1,3 addition is 100 times slower than cycloaddition. The occurrence of the addition was attributed to the reduced 1,3-dipolar reactivity of furan, due to the aromaticity of this molecule and to the stabilizing secondary orbital interactions accompanying the overriding LU-MO(BNO)-HOMO(furan) interaction, which partially compensates for the smaller overlap of the two-center transition state of the 1,3 addition. In the case of benzofuran, the cycloaddition is slowed down less, since, with benzofuran, the loss of aromaticity is smaller than that with furan. Moreover the LUMO(BNO)-HOMO(dipolarophile) interaction, which gives secondary orbital interactions that stabilize the addition pathway,^{1b} becomes less influential with benzofuran, as inferred from the level orderings of Table III and by the easy regioselectivity switch.

Conclusions

Benzofuran is known to react mainly at the α position in electrophilic substitution reactions, a fact which is consistent both with the polarization of the HOMO and with the stability of the Wheland intermediate.³¹ The α position is also the site of attack of nucleophiles.³²

In concerted cycloadditions where the two frontier interactions are similar in magnitude, the regiochemical outcome depends subtly on the 1,3-dipole, i.e., on which interaction is dominant. With the "electrophilic" BNO the major isomer results from attack of the α carbon of benzofuran on the nitrile oxide carbon. With the more nucleophile mesitronitrile oxide the regiochemical control switches to HO(dipole)-LU(dipolarophile) control, and the major isomer arises from the attack of the nitrile oxide oxygen on the α carbon of benzofuran.

Experimental Section

All melting points are uncorrected. NMR spectra: CDCl₃ solution, Me₄Si as internal standard, Perkin-Elmer R12 spectrometer, 60 MHz. Gas-chromatographic analyses were carried out on a glass column, 5% SILAR and 3% OV 17 on Gaschrom P, with a column temperature of 170–200 °C on a "Carlo Erba" Fractovap instrument. Microanalyses were performed by Dr. L. Maggi Dacrema. Satisfactory analytical data ($\pm 0.4\%$ for C, N, H) were obtained for all the compounds listed in Table I. Column chromatography and TLC: silica gel H and GF₂₅₄ (Merck), respectively, eluant cyclohexane-EtOAc = 9:1 to 7:3 unless otherwise specified.

Cycloaddition of BNO to Benzofuran. To a stirred ice-cooled solution of benzhydroxamic acid chloride (1.55 g, 10 mmol) and benzofuran (11.8 g, 100 mmol) in anhydrous ether (50 mL), a stoichiometric amount (10 mmol) of triethylamine was added over a 2-h period. After keeping overnight at 0 °C and 2 days at 25 °C, the triethylamine hydrochloride was filtered off and the filtrate was evaporated under reduced pressure, leaving a residue. Column chromatography gave 3,4-diphenylfuroxan (60%) and 3,5-diphenyl-1,2,4-oxadiazole (13%) along with adduct 1a (7.3%), colorless crystals mp 123–4 °C from EtOH, and adduct 2a (3.2%), colorless crystals mp 168–9 °C from EtOH.

The total yield of adducts 1a + 2a (14% in a 70:30 \pm 2% ratio) was determined by GLC by adding as an internal standard a known amount of the major adduct of BNO to indene.⁵ The area ratio was corrected by using response factors, determined on known mixtures of the adducts and the standard. On performing the reaction in benzofuran (100 equiv) as solvent, the total yield of cycloadducts was found to be 24%.

The relative rate constants for the cycloaddition of BNO to ben-

zofuran and indene were evaluated by the competition method.³⁴ Benzhydroxamic acid chloride (1 mmol), indene (1.8–2.1 mmol), and benzofuran (20–30 mmol) in anhydrous ether (20 mL) were reacted as above. A reactivity ratio of 180 ± 10 was obtained as an average of three different reaction mixtures.

Oximes 4 and 5. The syn and anti oximes **4** have been prepared by oximation of 2-benzoylbenzofuran according to the literature.⁹ Oximes **5**¹⁰ have been obtained with good yield on refluxing 3-benzoylbenzofuran (100 mg) with an excess of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (5 equiv) in ethanol for 24 h. The mixture was concentrated, diluted with water, and extracted with CHCl_3 . The extracts were dried and the solvent was evaporated, yielding a mixture of the two oximes in a ratio ca. 9:1 (TLC). The major oxime crystallized from hexane, colorless crystals mp 152–3 °C in a 60% yield. Anal. Found: C, 75.70; H, 4.83; N, 6.23. $\text{C}_{15}\text{H}_{11}\text{NO}_2$ requires: C, 75.93; H, 4.67; N, 5.90. The minor oxime has a higher R_f value. A sample of this oxime, colorless crystals mp 87–8 °C, from hexane, was obtained by preparative TLC, eluting with benzene. Both the oximes **5** were hydrolyzed to 3-benzoylbenzofuran on boiling with ethanol, water, and concentrated HCl .¹⁰

The oximes are stable under the conditions of the cycloaddition reactions, in ether in the presence of $\text{NEt}_3/\text{NEt}_3\cdot\text{HCl}$. A comparison of the oximes with the cycloaddition mixture by TLC (eluant benzene or ethyl acetate–benzene 1:9) and by GLC allowed the exclusion of the oximes in the cycloaddition mixtures in amounts larger than 1% of the total yield of adducts **1a** + **2a**.

Cycloaddition of Mesitronitrile Oxide to Benzofuran. A solution of 1.61 g (10 mmol) of mesitronitrile oxide and 5 g (42 mmol) of benzofuran in anhydrous benzene (50 mL) was kept at room temperature for 4 months and 1.20 g (43%) of adduct **2b** was crystallized out. Recrystallization from benzene gave an analytical sample of **2b**, mp 173 °C. The mother liquors were evaporated leaving a residue. Column chromatography with CHCl_3 –cyclohexane (6:4) as eluant afforded 0.59 g (21%) of adduct **1b**, colorless crystals from hexane mp 140 °C, and 0.70 g (25%) of adduct **2b**.

The ratio of adducts **1b/2b** was determined by GLC and was found to be 26.74 ± 2 .

Cleavage of Adducts 2a and 2b. A solution of 1 mmol of adduct **2a** in MeOH (10 mL), concentrated H_2SO_4 (1 mL), and water (1 mL) was refluxed for 6 h. After cooling, the mixture was poured in water (20 mL) and extracted with CHCl_3 . The extracts, dried on Na_2SO_4 and evaporated, afforded isoxazole **3a** (60%) as colorless crystals, mp 124–5 °C, from EtOH.

Adduct **2b** was similarly cleaved to the isoxazole **3b** as colorless crystals, mp 160–1 °C from benzene, with a 65% yield.

Under the same conditions cycloadducts **1a** and **1b** were recovered unchanged.

Acknowledgment. We would like to acknowledge a NATO Fellowship (to P.C.) and the financial support of the Italian CNR. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research.

Registry No.—syn-**5**, 66303-81-9; anti-**5**, 66357-76-4; I (X = CH_2 ; Ar = Ph), 27271-35-8; I (X = CH_2 ; Ar = Mes), 61191-73-9; II (X = CH_2 ; Ar = Ph), 42443-92-5; II (X = CH_2 ; Ar = Mes), 61191-74-0; BNO, 873-67-6; benzhydroxamic acid chloride, 698-16-8; mesitronitrile oxide, 2904-57-6.

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