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REACTION OF 3,4-DISUBSTITUTED 1,2,5-OXADIAZOLE 2-OXIDES WITH DIPOLAROPHILES

SUBSTITUENT AND SOLVENT EFFECT ON THE REACTION COURSES

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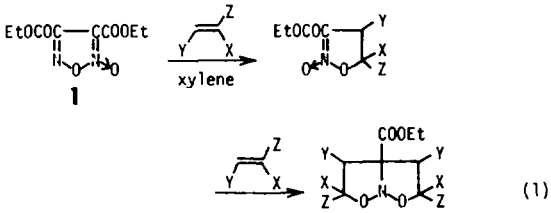
Abstract—A variety of symmetrically or unsymmetrically 3,4-disubstituted furoxans such as dicyano, dialkyl, diacyl, bis(phenylsulfonyl), N,N'-dialkyldicarbamoyl, 3(or 4)-methyl-4(or -3)-phenyl(or nitro, ethoxy, phenoxy, phenylthio, pyrrolidinyl, phenylsulfonyl), 3(or 4)-ethyl-4(or -3)phenyl, and 3(or 4)-ethoxy-4(or -3)-phenylsulfonylfuroxan reacted with dipolarophiles in toluene or xylene at the refluxing temperature to give nitrone-type 1,3-dipolar cycloadducts, 5-substituted 1-aza-2,8-dioxabicyclo-[3.3.0]octanes and/or 3-substituted 2-isoxazoline 2-oxides. On the other hand, some of the furoxans gave 2-isoxazolines via nitrile oxide 1,3-dipolar cycloaddition in a toluene (or xylene)–DMF solvent at the refluxing temperature.

Extensive studies have been carried out on the syntheses and the reaction of 1,2,5-oxadiazole 2-oxides (furoxans). We have recently reported a new type of reaction of 3,4-bis(ethoxycarbonyl)-1,2,5-oxadiazole 2-oxide (**1**) with olefins, where the furoxan behaves as a nitrone as shown in eqn (1).[1]



(1)

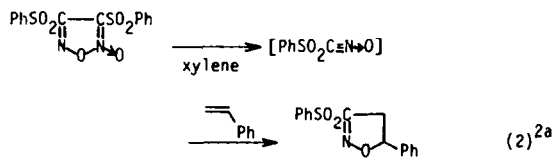
We now report in detail the reactivity of furoxans bearing other various substituents (cyano, carbamoyl, phenylsulfonyl, alkoxy, nitro, pyrrolidinyl, phenylthio, phenyl, and alkyl group) towards dipolarophiles and solvent effect on the reaction.

RESULTS AND DISCUSSION

Furoxans undergo thermal isomerizations or ring-cleavage reactions. Four types of reactions (a)–(d) have been reported when furoxans are thermally treated in the presence of olefins as a trapping agent of the intermediates.

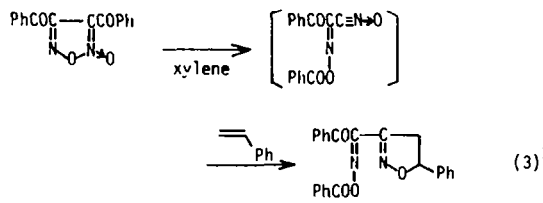
(a) The furoxan (**1**) behaves as a nitrone.[1] (ex. eqn 1).

(b) Thermal reversion into two moles of nitrile oxide.[2]



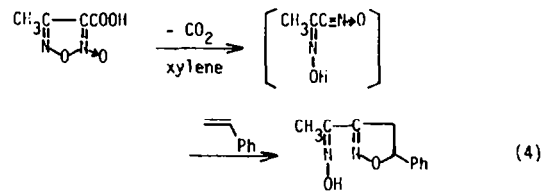
(2)[2a]

(c) Ring interconversion into rearranged nitrile oxide.[3]



(3)[3]

(d) Ring-cleavage reaction with concomitant fragmentation, giving nitrile oxide.[4]



(4)[4]

We reinvestigated the cycloaddition reactions of furoxans (**4**–**9**) (Tables 1 and 2), expecting the possibility of nitrone-type cycloadditions along with the nitrile oxides cycloadditions (eqns 2–4). We found that the furoxans underwent the nitrone-type cycloaddition when the reaction conditions are suitable. It is known that the asymmetrically substituted furoxans (**9**) easily attain an equilibrium with their isomers under our reaction conditions[5] and, therefore, the formation of four nitrone-type cycloadducts may be expected from the reaction of **9** with dipolarophiles (eqn 5). The results are shown in Tables 1 and 2.

Table 1. Reaction courses of symmetrically substituted furoxans (4–8)

Furoxan (R)	Olefin*	Reaction Course** a	b	c	d	Solvent***
4 (CN)	A, B, C, D	○				X, T, or T-D
5a ($CONH_2$)	B, C, D				○	X-D
5b ($CONHCH_3$)	C, D	○				X
5c ($CONHC_2H_5$)	C, D	○				X
6a ($COCH_3$)	A	○				X
	B, C, D			○		X
	C, D				○	T-D
6b (COPh)	A			○		X, T, or B
6c ($COC_6H_4OCH_3$)	A			○		X, T, or B
7 (SO_2Ph)	C	○				X
	A, B, D		○			X
8 (CH_3)	A	○				X

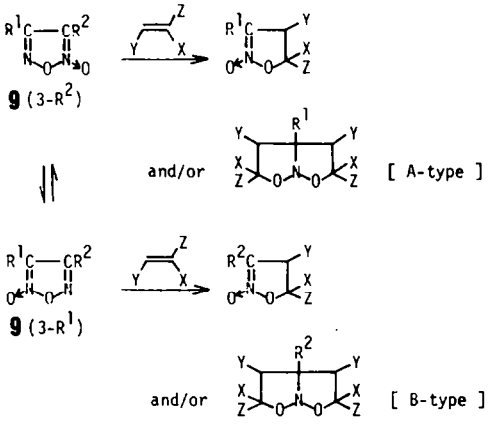
* A; Electron-poor olefins such as maleimides, B; conjugated olefins, C; norbornene or cyclododecene, D; electron-rich olefins except C.

** Circle shows the isolation of the products. *** X; xylene, T; toluene, B; benzene, D; dimethylformamide.

Table 2. Products from the reaction of asymmetrically substituted furoxans (9) with olefins

Furoxan (9)	R^1	R^2	Olefin	Product* A-type	Product* B-type
9a	CH_3	C_2H_5	maleimides	○	
9b	CH_3	$CH(CH_3)_2$	maleimides	○	
9c	CH_3	Ph	maleimides	○	
9d	Et	Ph	maleimides	○	
9e	CH_3	NO_2	maleimides	○	
9e	CH_3	NO_2	electron-rich or conjugated		○
9f	CH_3	SO_2Ph	electron-rich		○
9g	CH_3	OC_2H_5	maleimides	○	
9h	CH_3	OPh	maleimides	○	
9i	CH_3	pyrrolidinyl	maleimides	○	
9j	CH_3	SPh	maleimides	○	
9k	OC_2H_5	SO_2Ph	electron-rich		○

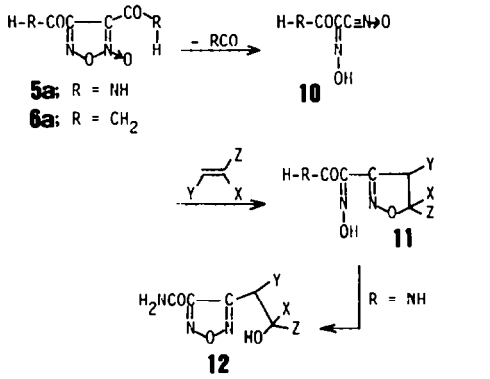
* Circle shows the isolation of the products.



(5)

The nitrone-type reaction may be explained on the basis of a considerable lowering of LUMO energy of furoxans (**4**, **5b**, **5c**, **6a**, **7**, **9e**, **9f**, and **9k**) by electron-withdrawing substituents,[6] thus, dipole (LUMO)—dipolarophile (HOMO) interaction is favorable. In other words, a similar reaction observed for furoxans (**8**, **9a–e**, and **9g–j**) bearing electron-donating substituents may be explained by a result of an increase in the HOMO energy of the furoxans,[6] thus, dipole (HOMO)—dipolarophile (LUMO) interaction is favorable. Besides these electronic factors described above, steric factor may play an important role in the nitrone-type cycloaddition of unsymmetrically substituted furoxans.

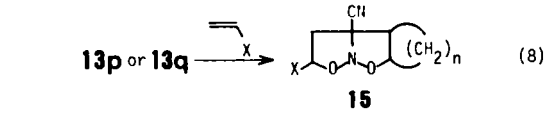
As shown in eqns (4) and (6), some furoxans underwent nitrone O^- assisted elimination followed by rearrangement into nitrile oxide (**10**) (eqn 6).



(6)

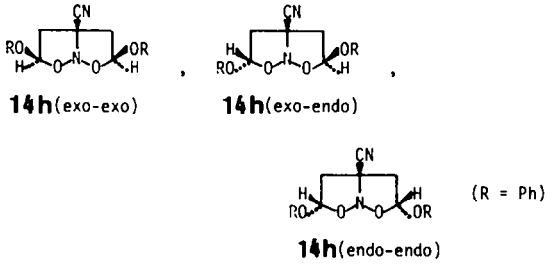
The structure of the products was assigned on the basis of spectral and analytical data. These cycloaddition reactions were rather complex depending on substituents on furoxans and solvent. Therefore, the results are described in detail.

3,4-*Dicyanofuroxan*. The cycloadducts, 5-cyano-1-aza-2,8-dioxabicyclo[3.3.0]octanes (**14**) and/or 3-cyano-2-isoxazoline N-oxides (**13**), could be obtained from the reaction of **4** with several olefins (Table 3). Though the reaction of **1** with olefins proceeds at the temperature of refluxing xylene, the reaction of **4** proceeds with rapid velocity even at the temperature of refluxing toluene. From the reaction with cycloalkenes, 1:1 cycloadducts (**13**) were isolated, which could undergo further cycloaddition (Table 4). From the reaction with phenyl vinyl ether,

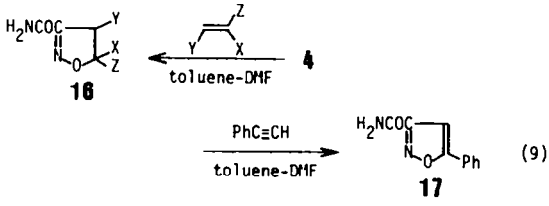


(8)

three stereoisomers (**14h**), i.e. *exo-exo*, *exo-endo*, and *endo-endo* substituted isomers, were isolated in 51, 25, and 3% yields, respectively. A small amount of 3-carbamoyl-5-phenyl-2-isoxazoline (**16g**) was also isolated in addition to **14g** (24%) on the reaction

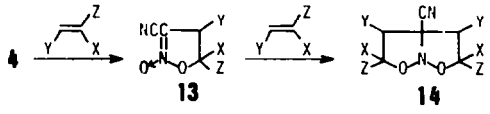


of **4** with styrene in toluene. When the same cycloaddition reactions were carried out in toluene–DMF (1:1), a predominant formation of 3-carbamoyl-2-isoxazolines (**16**) was observed (Table 5)



(9)

and any trace of **13** or **14** could not be detected. Phenylacetylene behaved similarly, giving 3-carbamoyl-5-phenylisoxazole (**17**). Similar results were obtained using dimethylacetamide or dimethylsulfoxide instead of DMF. The compounds **16** are not produced via **13** or **14**, because **13** or **14** was recovered unchanged after the heating in toluene–DMF (1:1). From these results, it can be supposed that dipolar aprotic solvents have some directional effects on the reaction course. One possible mechanism for the formation of **16** consists of the hydration of 3-cyano-2-isoxazolines (**19**) which are produced from the thermal decomposition of **4** to two moles of cyanogen N-oxide (**18**) followed by cycloaddition to dipolarophiles (eqn 10). However, this



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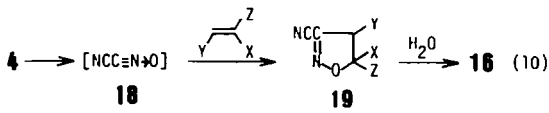
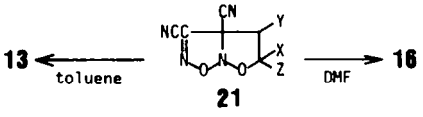


(10)

Table 3. Yields and melting points of the products obtained from the reaction of **4** with dipolarophiles in toluene

Dipolarophile	Product	Yield %	M.p. °C
1-eicosene	14a (X = $C_{18}H_{37}$, Y = Z = H)	61	74- 75
1-octadecene	14b (X = $C_{16}H_{33}$, Y = Z = H)	80	68- 70
1-hexadecene	14c (X = $C_{14}H_{29}$, Y = Z = H)	72	62- 63
1-tetradecene	14d (X = $C_{12}H_{25}$, Y = Z = H)	50	52- 53
allyl *p*-nitrophenyl ether	14e (X = $CH_2OC_6H_4NO_2$, Y = Z = H)	30	174-176
allylbenzene	14f (X = CH_2Ph, Y = Z = H)	35	110-114
styrene	14g (X = Ph, Y = Z = H)	25	139-140
	16g (X = Ph, Y = Z = H)	4	171-172
phenyl vinyl ether	14h(ex-ex) (X = OPh, Y = Z = H)	51	150-153
	14h(ex-en) (X = OPh, Y = Z = H)	25	118-123
	14h(en-en) (X = OPh, Y = Z = H)	3	172-174
2-naphtyl vinyl ether	14i(ex-ex) (X = $OC_{10}H_7$, Y = Z = H)	8	194-196
	14i(ex-en) (X = $OC_{10}H_7$, Y = Z = H)	3	179-180
octadecyl vinyl ether	14j (X = $OC_{18}H_{37}$, Y = Z = H)	14	45- 50
methyl methacrylate	14k(ex-en) (X = CO_2CH_3, Y = H, Z = CH_3)	36	166-167
N-phenylmaleimide	14m(ex-en) [X,Y = -CON(Ph)CO-, Z = H]	46	ca. 300
norbornene	14n(ex-ex) (X,Y = $-C_5H_8-$, Z = H)	85	128-132
cyclododecene	13p (Y,Z = $-C_{10}H_{20}-$, X = H)	61	94- 96
cyclooctene	14q(ex-ex) (X,Y = $-C_6H_{12}-$, Z = H)	3	139-140
	13q (X,Y = $-C_6H_{12}-$, Z = H)	7	oil
cycloheptene	14r (X,Y = $-C_5H_{10}-$, Z = H)	4	162-164

mechanism is ruled out by the results of following experiment; 3-cyano-5-phenyl-2-isoxazoline (**19g**), which was prepared from the reaction of cyanoformhydroximic chloride with styrene[7] was recovered unchanged after treating it in refluxing DMF containing a small amount of water. It is known that aliphatic 1,2-dinitriles are labile to water, giving the ammonium salts of the corresponding acids.[8] Thus, the primary cycloadducts (**21**) would be a precursor of **16**.

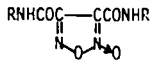


21 (11)

Table 4. Yields and melting points of **15**

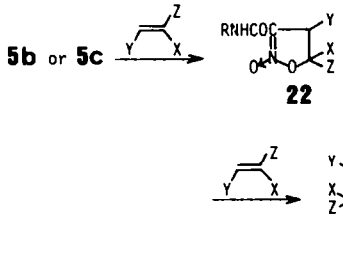
	n	X	Yield %	M.p. °C
15a	10	$CH_2OC_6H_4NO_2$-*p*	20	114-116
15b	10	C_6H_5	16	115-117
15c	6	$CH_2OC_6H_4NO_2$-*p*	7	158-160

Furoxandicarboxamide and its alkyl derivatives. It may also be expected that furoxandicarboxamide (**5a**) and its alkyl derivatives (**5b–d**) show a reactivity similar to **1** or **4** in the reaction with dipolarophiles.



5a R = H
5b R = CH_3
5c R = C_2H_5
5d R = $CH_2CH{=}CH_2$

From the reaction of **5b** or **5c** with dipolarophiles in xylene at refluxing temperature, 5-(N-alkyl) carbamoyl-1-aza-2,8-dioxabicyclo[3.3.0]octanes (**23**) and 3-(N-alkyl)carbamoyl-2-isoxazoline N-oxides (**22**) were obtained in yields shown in Table 6. These carbamoylfuroxans (**5b** and **5c**) were recov-

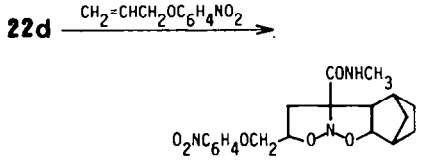


(12)

Table 5. Yields and melting points of the products obtained from the reaction of **4** with dipolarophiles in toluene–DMF

Dipolarophile	Product	Yield %	M.p. °C
1-hexadecene	16c (X = $C_{14}H_{29}$, Y = Z = H)	44	114 - 116
styrene	16g (X = Ph, Y = Z = H)	40	171 - 172
N-phenylmaleimide	16m [X,Y = -CON(Ph)CO-, Z = H]	42	210 - 213
cyclododecene	16p (Y,Z = $-C_{10}H_{20}-$, X = H)	10	127 - 128
phenylacetylene	17	20	206 - 207
N-ethylmaleimide	16s [X,Y = -CON(Et)CO-, Z = H]	48	228 - 229
acenaphthylene	16t (X,Y = $-C_{10}H_6-$, Z = H)	40	250 - 270

ered unchanged in the reaction with other olefins. The 1:1 cycloadduct (**22d**) reacted with allyl *p*-nitrophenyl ether to give a cycloadduct (**24**). While no



(13)

cycloadducts could be obtained from **5a** in xylene probably because of insolubility of **5a** in xylene, 3-carbamoyl-4-(2-hydroxy)ethyl-1,2,5-oxadiazole (**12**) was obtained by heating in xylene–DMF (1:1) (eqn 6). Though it may be possible to assign an alternative structure (**11**) for the products, the validity of the structure **12** was elucidated by the following NMR data; the chemical shift (δ4.5–5.7) of an OH proton observed does not accord with **11** because an acidic oxime proton generally appears at the more down field region of about δ9–12.[9] Furthermore, a characteristic coupling pattern observed in the 2-isoxazoline ring system could not be found. The assignment of the structure was further supported by the isolation of a keto-compound, 3-carbamoyl-4-phenacyl-1,2,5-oxadiazole (**25**), from the reaction of **5a** with phenylacetylene. Isolation of ammonium cyanate and evolution of NH_3 and CO_2 in the reaction also suggest elimination of HNCO from **5a**.

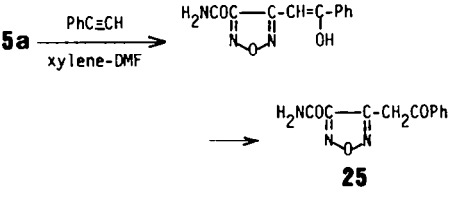


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Table 6. Yields and melting points of the products obtained from the reaction of **5** with dipolarophiles

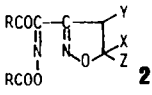
Furoxan	Dipolarophile	Solvent	Product	Yield %	M.p. °C
5b	1-tetradecene	xylene	23a (R = CH_3, X = $C_{12}H_{25}$, Y = Z = H)	7	80- 82
5b	allyl *p*-nitrophenyl ether	xylene	23b (R = CH_3, X = $CH_2OC_6H_4NO_2$, Y = Z = H)	20	163-165
5b	cyclododecene	xylene	22c (R = CH_3, X = H, Y,Z = $-C_{10}H_{20}-$)	4	118-120
5b	norbornene	xylene	22d (R = CH_3, X,Y = $-C_5H_8-$, Z = H)	38	130-131
			23d (R = CH_3, X,Y = $-C_5H_8-$, Z = H)	15	247-249
5c	1-tetradecene	xylene	23e (R = C_2H_5, X = $C_{12}H_{25}$, Y = Z = H)	11	82- 85
5c	1-hexadecene	xylene	23f (R = C_2H_5, X = $C_{14}H_{29}$, Y = Z = H)	11	92- 95
5a	1-tetradecene	xylene-DMF	12a (X = $C_{12}H_{25}$, Y = Z = H)	53	75- 77
5a	allyl *p*-nitrophenyl ether	xylene-DMF	12b (X = $CH_2OC_6H_4NO_2$, Y = Z = H)	43	140-142
5a	cyclododecene	xylene-DMF	12c (X = H, Y,Z = $-C_{10}H_{20}-$)	15	166-168
5a	styrene	xylene-DMF	12g (X = Ph, Y = Z = H)	7	152-154
5a	phenylacetylene	xylene-DMF	25	19	122-125
5a	norbornene	xylene-DMF	22d	5	
			23d	33	

Using **5b** or **5c** instead of **5a** in xylene–DMF, the corresponding N-alkyl derivatives of **12** could not be obtained and starting materials were recovered. Exceptionally, **5b** and norbornene produced the adducts **22d** and **23d** in 5% and 33% yield, respectively. Similarly, N,N,N′,N′-tetramethylfuroxandicarboxamide (**5e**) having no NH proton in carbamoyl groups gave no cycloadducts with various dipolarophiles and **5e** was recovered unchanged quantitatively from the reaction mixture.

3,4-Bis(phenylsulfonyl)furoxan (**7**) *and 3,4-diacylfuroxans* (**6a–c**). Thermal reversion to nitrile oxides is reported on furoxans bearing such elecron-withdrawing groups as phenylsulfonyl[2a] or acyl group.[3] 3,4-Bis(phenylsulfonyl)furoxan (**7**) is decomposed thermally to two moles of phenylsulfonylnitrile oxide at the temperature of refluxing xylene, which undergoes 1,3-dipolar cycloaddition with olefins to give 3-phenylsulfonyl-2-isoxazolines in a good yield (eqn 2).[2a] The reactivity may be interpreted on the basis of the steric hindrance between two phenylsulfony groups of **7**.

3,4-Diacylfuroxans (**6**) undergo N–O bond fission of the oxadiazole ring with a concomitant migration of an acyl group to give a nitrile oxide at relatively low temperature (80–120°), which undergoes 1,3-dipolar cycloaddition with olefins to give cycloadducts (eqn 3).[3] Such reactivity of diacylfuroxans has been explained in terms of the high migratory aptitude of the acyl groups.[3]

Compound **26** was the only isolable cycloadduct from the reaction of 3,4-diaroylfuroxans (**6b** and **6c**) with N-phenylmaleimide in aromatic solvents under various thermal conditions (80–150°). On the other



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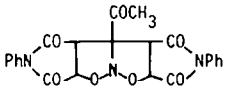

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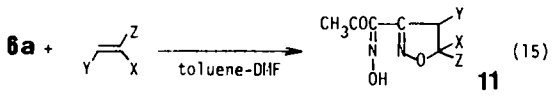
hand, **27** was obtained as a major product from the reaction of 3,4-diacetylfuroxan (**6a**) with N-phenylmaleimide in refluxing xylene. However, none of analogous cycloadducts could be obtained from the reaction of **6a** with other olefins listed in Table 7, and the only isolable adducts were **26**. On the other hand, 3-[1-(hydroxyimino)-2-oxo]propyl-2-isoxazolines (**11a** and **11b**) were obtained in high yields from the reaction of **6a** with olefins in toluene–



(15)

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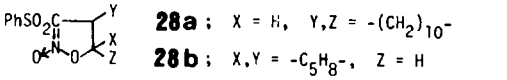
DMF (1:1). The structure of **11a** and **11b** was established from the characteristic coupling pattern for the isoxazoline ring protons and the acidic OH proton for oximes at δ 12–13.

The nitrone-type cycloadducts, 3-phenylsulfonyl-2-isoxazoline N-oxides (**28a** and **28b**), could be obtained from the reaction of **7** with electron-rich dipolarophiles such as cyclododecene and norbornene (Table 8). With other dipolarophiles, **7** gave

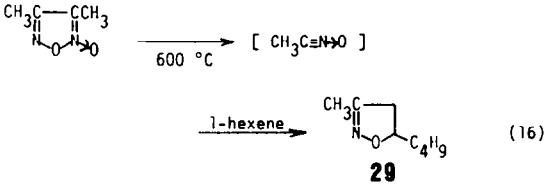


28a; X = H, Y,Z = $-(CH_2)_{10}-$

28b; X,Y = $-C_5H_8-$, Z = H

the same type of adducts as reported in the literature.[2a]

3,4-Dialkylfuroxans. 3,4-Dialkylfuroxans are known to react with electron-rich alkenes at elevated temperature (200°) to give 3-alkyl-2-isoxazolines (**29**) via a nitrile oxide intermediate.[2b] We reinvestigated the



(16)

29

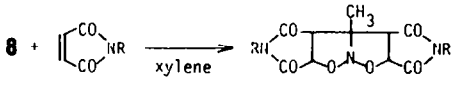
reaction of 3,4-dimethylfuroxan (**8**) with various olefins at the temperature of refluxing xylene and observed the formation of nitrone-type cycloadducts, 5-methyl-1-aza-2,8-dioxabicyclo[3.3.0]octanes (**30a–c**), in the case of the reaction with maleimides (Table 8).

Table 7. Yields and melting points of the products obtained from the reaction of **6** with dipolarophiles

Furoxan	Dipolarophile	Solvent	Product	Yield %	M.p. °C
6a	1-tetradecene	xylene	26a (R = CH_3, X = $C_{12}H_{25}$, Y = Z = H)	70	45- 50
6a	cyclododecene	xylene	26b (R = CH_3, X = H, Y,Z = $-C_{10}H_{20}-$)	40	124-125
6a	styrene	xylene	26c (R = CH_3, X = Ph, Y = Z = H)	22	128-129
6a	*N*-phenylmaleimide	xylene	27	35	257-260
6b	*N*-phenylmaleimide	benzene	26d [R = Ph, X,Y = -CON(Ph)CO-, Z = H]	32	191-194
6c	*N*-phenylmaleimide	toluene	26e [R = $C_6H_4OCH_3$, X,Y = -CON(Ph)CO-, Z = H]	42	
6a	1-tetradecene	toluene-DMF	11a (R = CH_2, X = $C_{12}H_{25}$, Y = Z = H)	46	61- 63
6a	cyclododecene	toluene-DMF	11b (R = CH_2, X = H, Y,Z = $-C_{10}H_{20}-$)	70	130-132

Table 8. Yields and melting points of the products obtained from the reaction of 7–9 with dipolarophiles

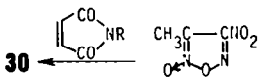
Furoxan	Dipolarophile	Product	Yield %	M.p. °C
7	cyclododecene	28a	35	90 - 91
7	norbornene	28b	41	120 - 126
8	*N*-phenylmaleimide	30a	15	ca. 350
8	*N*-ethylmaleimide	30b	20	264 - 266
8	*N*-propylmaleimide	30c	18	252 - 253
9a	*N*-phenylmaleimide	30a	75	
9b	*N*-phenylmaleimide	30a	10	
9c	*N*-phenylmaleimide	30a	29	
9d	*N*-phenylmaleimide	31a	6	257 - 267
9e	*N*-phenylmaleimide	30a	7	
9e	*N*-propylmaleimide	30c	12	
9e	norbornene	32a	10	159 - 161
9e	styrene	32b(ex-ex)	10	177 - 180
		32b(ex-en)	10	158 - 160
9e	2-naphthyl vinyl ether	32c	7	206 - 207
9f	norbornene	28b	25	
9g	*N*-phenylmaleimide	30a	70	
9g	*N*-propylmaleimide	30c	65	
9h	*N*-phenylmaleimide	30a	63	
9h	*N*-ethylmaleimide	30b	22	
9h	*N*-propylmaleimide	30c	55	
9i	*N*-phenylmaleimide	30a	26	
9i	*N*-propylmaleimide	30c	15	
9j	*N*-phenylmaleimide	30a	8	
9j	*N*-propylmaleimide	30c	5	
9k	norbornene	33	36	183 - 184



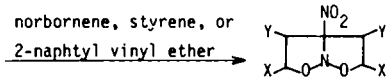
30a; R = Ph
30b; R = C_2H_5 (17)
30c; R = C_3H_7

3,4-*Di-unsymmetrically substituted furoxans*. As mentioned previously, cycloadducts bearing a Me group at the 5-position of bicyclo[3.3.0]octane were the only isolable compounds from the reaction mixture of **9a–c** and maleimides (Table 8). Using other dipolarophiles, the starting materials were recovered quantitatively. Similarly, the corresponding 5-ethyl derivative (**31a**) was obtained from the reaction of **9d** with N-phenylmaleimide. Though the exclusive formation of one of nitrone-type cycloadducts in the reaction of **9a** or **9b** with maleimides can be explained on the basis of the thermodynamic stability of 3-methylfuroxan isomers (eqn 5) [the isomer ratio of **9a**(3-CH_3)/**9a**(4-CH_3) is *ca* 2.0 by the NMR spectra at room temperature], the exclusive formation of the nitrone-type cycloadduct (A-type) is supposed to be the steric effect in the transition state of the cycloaddition. The exclusive formation of one of nitrone-type cycloadducts in the reaction of **9c** or **9d** with maleimides can be explained on the basis of a similar steric effect.

An interesting result was observed in the reaction of **9e** with olefins; **9e** reacts with electron-rich or conjugated olefins such as norbornene, 2-naphthyl vinyl ether, or styrene to give 5-nitro-1-aza-2,8-dioxabicyclo[3.3.0]octanes (**32**), while **30** was obtained from the reaction of **9e** with maleimides.

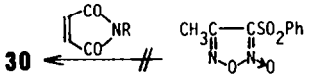


9e

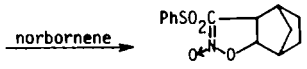


32a; X, Y = $-C_5H_8-$
32b; X = Ph, Y = H
32c; X = $OC_{10}H_7$, Y = H (18)

While an expected cycloadduct (**28b**) was obtained from the reaction of **9f** with norbornene, **30a–c** could not be detected from the reaction of **9f** with maleimides. While furoxans (**9g–j**) bearing efficient



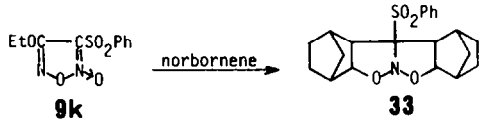
9f



28b (19)

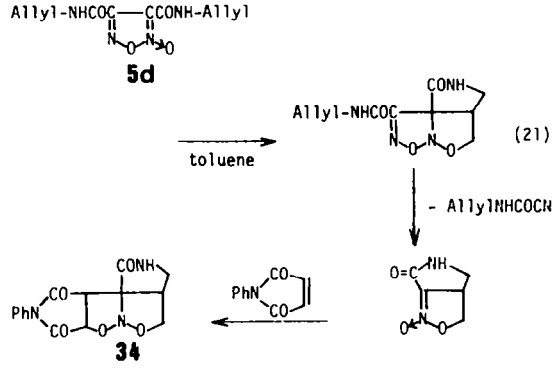
electron-donating substituents were expected to react with electron-poor olefins such as maleimides to give the corresponding 5-ethoxy (or phenoxy, pyrrolidinyl, phenylthio) derivatives of **30**, the actually isolated products were **30a–c**.

It is interesting to research the reactivity of furoxan (**9k**) bearing both a powerful electron-withdrawing substituent and an electron-donating substituent. Though the cycloadduct (**33**) was obtained from the reaction of **9k** with norbornene, none of the cycloadducts could be obtained from the reaction of **9k** with maleimides.



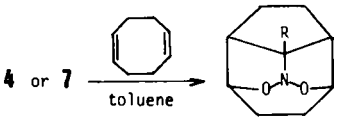
9k **33** (20)

Intramolecular nitrone-type cycloaddition of furoxans. Facile trapping of a nitrone dipole was observed in furoxans bearing appropriately located olefins. The application to intramolecular cycloaddition was attractive for the syntheses of heteropolycyclic compounds. In fact, tetracyclic compound **34** was obtained in a good yield *via* primarily intramolecular cycloaddition from the reaction of **5d** with



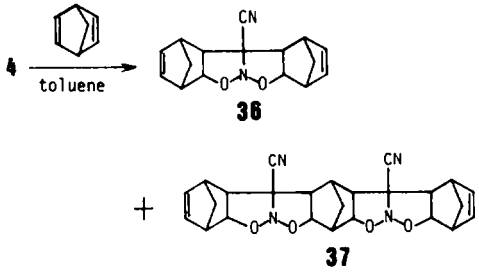
5d **34** (21)

N-phenylmaleimide. Intramolecular cycloadducts could also be obtained from the reaction of furoxan with polyenes in which two double bonds are located in an appropriate position. For example, **4** or **7** reacted with 1,5-cyclooctadiene to give intramolecular cycloadducts (**35a** or **35b**, respectively).



35a; R = CN (22)
35b; R = SO_2Ph

However, **4** reacts with norbornadiene to give only intermolecular cycloadducts (**36** and **37**).



36 **37** (23)

EXPERIMENTAL

Measurements. All m and b pts are uncorrected. IR spectra were determined on a Hitachi 215 IR Spectrophotometer. ^{1}H-NMR spectra were measured on Valian T-60A instrument with Me_4Si as an internal standard. All new products gave correct elemental analyses which are shown in Table 9 along with ^{1}H-NMR data.

Materials. Compounds **4**,[10] **5a**,[11] **5e**,[12] **7**,[13] **6a**,[14] **6b** or **6c**,[11] **8**,[15] **9c**,[15] **9e**,[16] **9f**,[5e] **9g**,[5e] **9h**,[5e] **9i**,[5e] **9j**,[5e] **9k**,[13] and 3-cyano-5-phenyl-2-isoxazoline[7] were prepared according to the method described in the literature. Compounds **9a**, **9b**, and **9d** were prepared according to a method similar to the preparation of **8** or **9c**;[15] **9a**: 55% yield, b.p. 105–108°/20 mmHg; **9b**: 76% yield, b.p. 88–90°/3 mmHg; **9d**: 80% yield, b.p. 135–145°/3 mmHg.

Preparation of N,N'-*dimethyl(or diethyl or diallyl)furoxandicarboxamide* **5b** (*or* **5c** *or* **5d**). To a stirred 15% methylamine (or 25% ethylamine or 20% allylamine) soln (50 ml), was added dropwise 10 g (43 mmol) of 3,4-bis(ethoxycarbonyl)furoxan[11] at 0–5°. After stirring the mixture for several hours at room temp, the ppt was filtered off. **5b**: 52% yield, m.p. 169–170° (from EtOH); **5c**: 21% yield, m.p. 118–119° (from CCl_4); **5d**: 25% yield, m.p. 100–101° (from CCl_4).

Reaction of furoxans with dipolarophiles

General procedure. A mixture of furoxan (10 mmol) and dipolarophile (20 mmol) was refluxed in xylene or toluene (or a mixed-solvent consisting of same volume of one of these aromatic solvents and DMF) (30 ml) for 24 hr. In the case of the reaction with styrene or maleimide, a small amount of hydroquinone was also added. Evaporation of the solvent and other low-boiling products from the mixture in a rotary evaporator gave the crude product. The crystalline crude products were recrystallized from EtOH and the oily crude products were chromatographed (silica gel) with $CHCl_3$ to give the crystalline products, which were recrystallized from EtOH. Yields and m.p. are shown in Table 3 and Tables 5–8. The separation of the three isomers of **14b** was accomplished by combination of the fractional crystallization and the chromatographic technique (silica gel–$CHCl_3$).

Table 9. Analytical and ^{1}H NMR spectral data of the components listed in Tables 3–8

Compound	Anal., Calcd. (Found) C %	H %	N %	^{1}H—NMR, δ ppm (solvent)
14a	78.20 (78.04)	12.50 (12.60)	4.34 (4.34)	($CDCl_3$) 0.7—2.1 (m, 74 H), 2.1—3.1 (m, 4 H), 3.9—4.9 (m, 2 H)
14b	77.49 (77.49)	12.32 (12.45)	4.76 (4.76)	($CDCl_3$) 0.7—2.1 (m, 66 H), 2.1—3.1 (m, 4 H), 3.8—4.9 (m, 2 H)
14c	76.63 (76.65)	12.11 (12.37)	5.26 (5.29)	($CDCl_3$) 0.7—2.1 (m, 58 H), 2.1—3.1 (m, 4 H), 3.8—4.9 (m, 2 H)
14d	75.57 (75.57)	11.84 (11.96)	5.88 (5.88)	($CDCl_3$) 0.7—2.0 (m, 50 H), 2.1—3.1 (m, 4 H), 3.8—4.9 (m, 2 H)
14e	54.29 (54.52)	4.10 (4.11)	12.66 (12.69)	(DMSO-d_6) 2.65—3.25 (m, 4 H), 4.2—4.4 (m, 4 H), 4.7—5.3 (m, 2 H), 7.1 (d, 4 H, J = 9 Hz), 8.15 (d, 4 H, J = 9 Hz)
14f	74.97 (75.16)	6.29 (6.27)	8.74 (8.80)	($CDCl_3$) 1.75—3.35 (m, 8 H), 4.0—5.0 (m, 2 H), 7.0—7.4 (m, 10 H)
14g	73.95 (74.21)	5.52 (5.49)	9.58 (9.61)	($CDCl_3$) 2.3—3.4 (m, 4 H), 5.0—5.9 (m, 2 H), 7.4 (s, 10 H)
14h(ex-ex)	66.66 (66.97)	4.97 (4.95)	8.64 (8.69)	($CDCl_3$) 3.0 (d, 4 H, J = 4 Hz), 6.05 (dd, 2 H, J = 4 & 5 Hz), 6.8—7.5 (m, 10 H)
14h(ex-en)	66.66 (66.70)	4.97 (4.98)	8.64 (8.61)	($CDCl_3$) 2.9—3.6 (m, 4 H), 5.9—6.2 (m, 2 H), 6.7—7.5 (m, 10 H)
14h(en-en)	66.66 (66.86)	4.97 (4.97)	8.64 (8.64)	($CDCl_3$) 3.0—3.6 (m, 4 H), 6.1 (dd, 2 H, J = 3 & 6 Hz), 6.6—7.4 (m, 10 H)
14i(ex—ex)	73.57 (73.50)	4.75 (4.77)	6.60 (6.58)	(DMSO-d_6) 2.9—3.7 (m, 4 H), 6.58 (dd, 2 H, J = 3 & 6 Hz), 7.1—8.1 (m, 14 H)
14i(ex—en)	73.57 (73.59)	4.75 (4.79)	6.60 (6.56)	(DMSO-d_6) 3.0—3.8 (m, 4 H), 6.4—6.7 (m, 2 H), 7.0—8.0 (m, 14 H)
14j	74.50 (74.78)	11.91 (12.05)	4.14 (4.01)	
14k(ex—en)	50.70 (50.88)	5.67 (5.70)	9.85 (9.75)	($CDCl_3$) 1.45 (s, 3 H), 1.65 (s, 3 H), 2.5 (d, 1 H, J = 13 Hz), 2.53 (d, 1 H, J = 13 Hz), 3.30 (d, 1 H, J = 13 Hz), 3.43 (d, 1 H, J = 13 Hz), 3.73 (s, 3H), 3.77 (s, 3 H)
14m(ex—en)	61.40 (61.35)	3.28 (3.32)	13.02 (12.91)	(DMSO-d_6) 4.8 (d, 1 H, J = 8 Hz), 4.87 (d, 1 H, J = 8 Hz), 5.2 (d, 1 H, J = 8 Hz), 6.07 (d, 1 H, J = 8 Hz), 6.8—7.8 (m, 10 H)
14n(ex—ex)	70.56 (70.55)	7.40 (7.44)	10.29 (10.32)	($CDCl_3$) 0.7—2.1 (m, 12 H), 2.1—2.8 (m, 6 H), 4.5 (d, 2 H, J = 6 Hz)
14q(ex—ex)	71.01 (71.04)	9.27 (9.34)	9.20 (9.20)	($CDCl_3$) 0.9—2.3 (m, 24 H), 2.53 (q, 2 H, J = 7 Hz), 4.53 (q, 2 H, J = 7 Hz)
14r	69.53 (69.40)	8.75 (8.73)	10.14 (10.10)	($CDCl_3$) 1.0—2.3 (m, 20 H), 3.5—3.95 (m, 2 H), 4.9—5.4 (m, 2 H)
13p	67.17 (67.21)	8.86 (8.90)	11.19 (11.29)	($CDCl_3$) 0.8—2.1 (m, 20 H), 3.35 (dt, 1 H, J = 3 & 7 Hz), 4.75(dt, 1 H, J = 3 & 7 Hz)
13q	61.83 (61.80)	7.27 (7.35)	14.42 (14.49)	($CDCl_3$) 1.0—2.1 (m, 12 H), 3.1—3.5 (m, 1 H), 4.5—5.0 (m, 1 H)
15a	64.32 (64.29)	7.28 (7.32)	9.78 (9.79)	($CDCl_3$) 1.2—2.0 (m, 20 H), 2.3—3.2 (m, 3 H), 3.8—4.3 (m, 1 H), 4.28 (d, 2 H, J = 4 Hz), 4.7—5.2 (m, 1 H), 7.0 (d, 2 H, J = 9 Hz), 8.17 (d, 2 H, J = 9 Hz)
15b	74.54 (74.54)	8.53 (8.57)	7.90 (7.93)	($CDCl_3$) 1.2—2.1 (m, 20 H), 2.3—2.8 (m, 1 H), 2.73 (d, 2 H, J = 8 Hz), 3.7—4.1 (m, 1 H), 5.6 (t, 1 H, J = 8 Hz)
15c	61.11 (60.99)	6.21 (6.21)	11.25 (11.15)	($CDCl_3$) 1.0—2.3 (m, 12 H), 2.3—3.3 (m, 3 H), 4.0—4.5 (m, 2 H), 4.5—5.4 (m, 2 H), 6.8—7.3 (m, 2 H), 8.2 (d, 2 H, J = 9 Hz)

Table 9. *Cont.*

16c	69.63	11.04	9.02	(DMSO-d_6) 0.8—1.9 (m, 29 H), 2.7 (dd, 1 H, J = 8 & 16 Hz),
	(69.77)	(11.12)	(9.00)	3.2 (dd, 1 H, J = 10 & 16 Hz), 4.2—4.8 (m, 1 H), 6.9—7.5 (br, 2 H)
16g	63.15	5.30	14.73	(DMSO-d_6) 3.05 (dd, 1 H, J = 9 & 18 Hz), 3.7 (dd, 1 H, J = 11 & 18 Hz),
	(63.42)	(5.29)	(14.72)	5.73 (dd, 1 H, J = 9 & 11 Hz), 7.37 (s, 5 H), 7.4—8.0 (br, 2 H)
16m	53.52	7.11	15.60	(DMSO-d_6) 5.0 (d, 1 H, J = 10 Hz), 5.73 (d, 1 H, J = 10 Hz),
	(53.49)	(7.10)	(15.58)	7.0—8.2 (m, 7 H)
16p	66.63	9.59	11.10	($CDCl_3$) 1.0—2.2 (m, 20 H), 3.2—3.6 (m, 1 H), 4.5—5.0 (m, 1 H),
	(66.64)	(9.66)	(11.24)	5.8 (br, 1 H), 6.5 (br, 1 H)
16s	45.50	4.30	19.90	(DMSO-d_6) 1.15 (t, 3 H, J = 7 Hz), 3.6 (q, 2 H, J = 7 Hz),
	(45.25)	(4.27)	(19.83)	5.0 (d, 1 H, J = 9 Hz), 5.7 (d, 1 H, J = 9 Hz), 7.5 (br, 2 H)
16t	70.58	4.23	11.76	
	(70.69)	(4.20)	(11.87)	
17	63.82	4.29	14.89	(DMSO-d_6) 7.3 (s, 1 H), 7.3—8.3 (m, 7 H)
	(63.95)	(4.30)	(14.65)	
22c	63.80	9.28	9.92	($CDCl_3$) 0.8—2.1 (m, 20 H), 2.8 (d, 3 H, J = 4 Hz), 3.2—3.6 (m, 1 H),
	(63.76)	(9.25)	(9.92)	4.5—4.9 (m, 1 H), 8.1 (br, 1 H)
22d	57.13	6.71	13.33	($CDCl_3$) 1.0—1.9 (m, 6 H), 2.5—2.9 (m, 2 H), 2.8 (d, 3 H, J = 4 Hz),
	(57.12)	(6.73)	(13.14)	3.53 (d, 1 H, J = 8 Hz), 4.57 (d, 1 H, J = 8 Hz), 8.2 (br, 1 H)
23a	73.17	11.89	5.51	($CDCl_3$) 0.7—3.0 (m, 57 H), 2.8 (d, 3 H, J = 4 Hz), 4.2—4.8 (m, 2 H),
	(73.10)	(12.02)	(5.49)	7.0 (br, 1 H)
23b	53.16	4.67	11.81	($CDCl_3$) 2.6—3.1 (m, 7 H), 4.17 (d, 4 H, J = 4 Hz), 4.6—5.2 (m, 2 H),
	(53.12)	(4.66)	(11.76)	6.7—7.1 (br, 1 H), 6.95 (d, 4 H, J = 9 Hz), 8.15 (d, 1 H, J = 9 Hz)
23d	67.08	7.95	9.20	($CDCl_3$) 0.8—2.0 (m, 12 H), 2.2—2.7 (m, 6 H), 2.85 (d, 3 H, J = 4 Hz),
	(67.12)	(7.95)	(9.23)	4.47 (d, 2 H, J = 6 Hz), 6.8 (br, 1 H)
23e	73.51	11.95	5.36	($CDCl_3$) 0.7—2.0 (m, 57 H), 2.0—3.7 (m, 6 H), 3.8—4.9 (m, 2 H),
	(73.48)	(11.90)	(5.35)	7.0 (br, 1 H)
23f	74.68	12.19	4.84	($CDCl_3$) 0.6—1.9 (m, 61 H), 1.9—3.7 (m, 6 H), 3.8—4.9 (m, 2 H),
	(74.83)	(12.32)	(4.78)	7.0 (br, 1 H)
12a	62.74	9.60	12.91	($CDCl_3$) 0.6—1.8 (m, 25 H), 3.1 (d, 2 H, J = 6 Hz), 3.6—4.6 (m, 2 H),
	(62.95)	(9.67)	(12.91)	7.2—8.1 (m, 2 H)
12b	46.76	3.92	18.18	(DMSO-d_6) 3.2 (d, 2 H, J = 5 Hz), 4.0—4.6 (m, 3 H), 5.4 (d, 1 H, J = 5 Hz),
	(46.75)	(3.86)	(18.03)	7.1 (d, 2 H, J = 9 Hz), 8.18 (d, 1 H, J = 9 Hz), 8.2—8.6 (m, 2 H)
12c	60.99	8.53	14.23	(DMSO-d_6) 0.8—2.1 (m, 20 H), 3.4—4.2 (m, 2 H), 4.57 (d, 1 H, J = 5 Hz),
	(60.89)	(8.58)	(14.22)	7.95 (br, 1 H), 8.3 (br, 1 H)
12g	56.65	4.75	18.02	(DMSO-d_6) 3.3 (d, 2 H, J = 6 Hz), 5.0 (q, 1 H, J = 6 Hz),
	(56.60)	(4.77)	(17.96)	5.55 (d, 1 H, J = 6 Hz), 7.3 (s, 5 H), 8.05 (br, 1 H), 8.4 (br, 1 H)
25	57.14	3.92	18.18	(DMSO-d_6) 4.9 (s, 2 H), 7.3—7.8 (m, 3 H), 7.9—8.2 (m, 2 H),
	(56.65)	(3.86)	(18.17)	8.5 (br, 2 H)
26a	65.54	9.35	7.64	($CDCl_3$) 0.7—1.8 (m, 25 H), 2.17 (s, 3 H), 2.43 (s, 3 H), 2.5—3.5 (m, 2 H),
	(65.49)	(9.31)	(7.66)	3.7—4.2 (m, 1 H)
26b	64.26	8.39	8.33	($CDCl_3$) 1.1—2.0 (m, 20 H), 2.15 (s, 3 H), 2.4 (s, 3 H),
	(64.19)	(8.38)	(8.30)	3.2—3.7 (m, 1 H), 4.5—5.0 (m, 1 H)
26c	61.31	5.15	10.21	($CDCl_3$) 2.17 (s, 3 H), 2.5 (s, 3 H), 3.25 (dd, 1 H, J = 9 & 18 Hz),
	(61.27)	(5.09)	(10.06)	3.73 (dd, 1 H, J = 11 & 18 Hz), 5.8 (dd, 1 H, J = 9 & 11 Hz), 7.35 (s, 5 H)
26d	66.81	3.67	8.99	($CDCl_3$) 5.1 (d, 1 H, J = 10 Hz), 7.0—7.8 (m, 11 H),
	(66.77)	(3.71)	(8.98)	7.9—8.2 (m, 4 H)
26e	63.75	4.01	7.96	(DMSO-d_6) 3.85 (s, 3 H), 3.88 (s, 3 H), 5.42 (d, 1 H, J = 10 Hz),
	(63.69)	(4.01)	(7.98)	5.93 (d, 1 H, J = 10 Hz), 6.9—7.6 (m, 9 H), 7.85—8.3 (m, 4 H)
27	61.74	3.83	9.39	(DMSO-d_6) 2.25 (s, 3 H), 4.37 (d, 1 H, J = 8 Hz), 4.57 (d, 1 H, J = 8 Hz),
	(61.79)	(3.77)	(9.32)	5.03 (d, 1 H, J = 8 Hz), 5.7 (d, 1 H, J = 8 Hz), 7.1—7.8 (m, 10 H)

Table 9. *Cont.*

11a	66.63	9.94	8.63	($CDCl_3$) 0.6—2.0 (m, 25 H), 2.45 (s, 3 H), 3.05 (dd, 1 H, J = 9 & 18 Hz),
	(66.64)	(9.89)	(8.64)	3.53 (dd, 1 H, J = 10 & 18 Hz), 4.3—4.9 (m, 1 H), 12.8 (br, 1 H)
11b	65.28	8.90	9.52	($CDCl_3$) 1.0—2.2 (m, 20 H), 2.5 (s, 3 H), 3.7—4.2 (m, 1 H),
	(65.23)	(8.91)	(9.49)	4.5—4.9 (m, 1 H), 12.8 (br, 1 H)
28a	65.31	7.79	4.01	($CDCl_3$) 1.0—2.2 (m, 20 H), 3.3—3.8 (m, 1 H), 4.6—5.0 (m, 1 H),
	(65.48)	(7.86)	(4.10)	7.4—7.9 (m, 3 H), 7.9—8.2 (m, 2 H)
28b	57.33	5.16	4.78	($CDCl_3$) 1.0—1.9 (m, 6 H), 2.5 (br, 1 H), 3.63 (d, 1 H, J = 8 Hz),
	(57.61)	(5.13)	(4.68)	4.6 (d, 1 H, J = 8 Hz), 7.5—7.9 (m, 3 H), 7.9—8.2 (m, 2 H)
30a(ex—en)	63.01	4.08	10.02	(DMSO-d_6) 1.45 (s, 3 H), 3.9 (d, 1 H, J = 8 Hz), 4.4 (d, 1 H, J = 8 Hz),
	(63.32)	(4.08)	(10.01)	4.93 (d, 1 H, J = 8 Hz), 5.75 (d, 1 H, J = 8 Hz), 7.0—7.8 (m, 10 H)
30b(ex—en)	52.01	5.30	13.00	(DMSO-d_6) 1.0 (t, 6 H, J = 7 Hz), 1.3 (s, 3 H), 3.4 (q, 2 H, J = 7 Hz),
	(51.81)	(5.21)	(12.82)	3.6 (d, 1 H, J = 8 Hz), 4.13 (d, 1 H, J = 8 Hz), 4.6 (d, 1 H, J = 8 Hz),
				5.5 (d, 1 H, J = 8 Hz)
30c(ex—en)	54.69	6.02	11.96	(DMSO-d_6) 0.77 (t, 3 H, J = 7 Hz), 0.83 (t, 3 H, J = 7 Hz), 1.1—1.9 (m, 4 H),
	(54.41)	(6.02)	(11.89)	1.27 (s, 3 H), 3.3 (t, 2 H, J = 7 Hz), 3.35 (t, 2 H, J = 7 Hz),
				3.6 (d, 1 H, J = 8 Hz), 4.17 (d, 1 H, J = 8 Hz), 4.6 (d, 1 H, J = 8 Hz),
				5.5 (d, 1 H, J = 8 Hz)
31a(ex—en)	63.73	4.42	9.70	(DMSO-d_6) 1.15 (t, 3 H, J = 7 Hz), 1.5—2.1 (m, 2 H), 3.9 (d, 1 H, J = 8 Hz),
	(63.69)	(4.40)	(9.66)	4.4 (d, 1 H, J = 8 Hz), 4.9 (d, 1 H, J = 8 Hz), 5.7 (d, 1 H, J = 8 Hz),
				7.1—7.8 (m, 14 H)
32a(ex—ex)	61.63	6.90	9.58	($CDCl_3$) 0.8—1.9 (m, 12 H), 2.2—2.6 (m, 4 H), 2.8 (d, 2 H, J = 6 Hz),
	(61.53)	(6.94)	(9.52)	4.6 (d, 2 H, J = 6 Hz)
32b(ex—ex)	65.37	5.16	8.97	($CDCl_3$) 2.9—3.4 (m, 4 H), 5.75 (dd, 2 H, J = 7 & 10 Hz), 7.4 (s, 10 H)
	(65.33)	(5.18)	(8.98)	
32b(ex—en)	65.37	5.16	8.97	($CDCl_3$) 2.3—3.8 (m, 4 H), 5.3 (dd, 1 H, J = 5 & 11 Hz),
	(65.39)	(5.16)	(8.99)	5.9 (dd, 1 H, J = 6 & 11 Hz), 7.4 (s, 10 H)
32c	67.56	4.54	6.30	(DMSO-d_6) 3.4—3.8 (m, 4 H), 6.6 (t, 2 H, J = 4 Hz), 7.0—8.1 (m, 14 H)
	(67.56)	(4.58)	(6.22)	
33	65.09	6.50	3.62	($CDCl_3$) 0.5—2.0 (m, 12 H), 2.0—2.6 (m, 4 H), 3.05 (d, 2 H, J = 6 Hz),
	(65.16)	(6.59)	(3.56)	4.73 (d, 2 H, J = 6 Hz), 7.3—7.8 (m, 3 H), 8.0—8.3 (m, 2 H)

The reaction of 3-*cyano*-4,5-*decamethylene* (or *hexamethylene*)-2-*isoxazoline*-2-*oxide* (**13p** *or* **13q**) *or* 7a,4a-*dihydro*-1,4-*methano*-7-(N-*methyl*)*carbamoyl*-*isoxazolo* [7a,4a-d]*cyclohexene*-6-*oxide* (**22d**) *with dipolarophiles.*

An equimolar mixture of **13p** (or **13q** or **22d**) (2 mmol) and dipolarophile was heated under reflux in xylene (20 ml) for 24 hr. After evaporation of the solvent, the residue was chromatographed (silica gel) with $CHCl_3$ to give cycloadducts (**15** or **24**). Yields and m.p. are shown in Table 4. Those of **24** are as follows; 40% yield, m.p. 220–222°, IR (nujol): 3370(NH) and 1660 cm^{-1} (C = 0), NMR ($CDCl_3$) δ: 0.9–1.8 (m, 6H), 2.2–3.0 (m, 5H), 2.85 (d, 1H, J = 5 Hz), 4.0–5.1 (m, 4H), 6.6–7.1 (br, 1H, NH), 6.9 (d, 2H, J = 10 Hz), and 8.2 (d, 2H, J = 10 Hz). (Found: C, 58.37; H, 5.96, N, 10.93. Calc. for $C_{19}H_{23}N_3O_6$: C, 58.60; H, 5.95; N, 10.79%.)

Reaction of N,N′-*diallylfuroxandicarboxamide* (**5d**) *with* N-*phenylmaleimide*

An equimolar amounts (3 mmol) of **5d** and N-phenylmaleimide were heated under reflux in toluene (20 ml) for 24 hr. After evaporation of the solvent, the residue was recrystallized from EtOH; m.p. 195–197°, yield: 88%, NMR (DMSO-d_6) δ: 2.9–4.6 (m, 5H), 4.1 (d, 1H, J = 8 Hz), 5.43 (d, 1H, J = 8 Hz), 7.1–7.7 (m, 5H), and 8.4 (br, 1H, NH). (Found: C, 57.15; H, 4.15; N, 13.60. Calc. for $C_{15}H_{13}N_3O_5$: C, 57.14; H, 4.16; N, 13.33%.)

Reaction of **4** *or* **7** *with* 1,5-*cyclooctadiene*

Equimolar amounts (10 mmol) of **4** (or **7**) and 1,5-cyclooctadiene was heated under reflux in toluene (30 ml) for 24 hr. After evaporation of the solvent, the residue was chromatographed (silica gel) with $CHCl_3$ to give cycloadducts (**35a** or **35b**); **35a**: 15% yield, m.p. 196–198° (from EtOH); IR (nujol): 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ: 1.9–2.5 (m, 8H), 3.3–3.7 (m, 2H), and 4.5–4.85 (m, 2H); mass spectrum; *m/e* 192 (M^+). (Found: C, 62.33; H, 6.32; N, 14.58. Calc. for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58.)

Compound **35b**: 30% yield, m.p. 199–201° (from EtOH); IR (nujol): 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) δ: 1.7–2.8 (m, 8H), 3.3–3.7 (m, 2H), 4.4–4.8 (m, 2H), 7.3–7.8 (m, 3H), and 7.95–8.25 (m, 2H); mass spectrum; *m/e* 307 (M^+). (Found: C, 58.82; H, 5.63; N, 4.60. Calc. for $C_{15}H_{17}NO_4S$: C, 58.63; H, 5.58; N, 4.56%.)

Reaction of **4** *with norbornadiene*

A mixture of **4** (1.36 g, 10 mmol) and norbornadiene (1.5 g, 16 mmol) was heated under reflux in toluene (30 ml) for 24 hr. After evaporation of the solvent, the residue was

chromatographed (silica gel) with $CHCl_3$ to give the crystalline products. Fractional recrystallization from EtOH gave **36** (30%) and **37** (14%).

Compound **36**: m.p. 158–160°, IR (nujol): 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ: 1.6–2.3 (m, 4H), 2.6–2.8 (m, 2H), 2.9–3.3 (m, 4H), 4.6–4.9 (m, 2H), and 6.0–6.4 (m, 4H). (Found: C, 71.25; H, 5.98; N, 10.51. Calc. for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44%.)

Compound **37**: m.p. 280° (dec.), IR (nujol): 2250 cm^{-1} (CN); NMR ($CDCl_3$: DMSO-d_6 = 1:1) δ: 1.55–2.2 (m, 6H), 2.5–3.5 (m, 10H), 4.05–4.35 (m, 2H), 4.7–5.0 (m, 2H), and 6.1–6.6 (m, 4H). (Found: C, 67.36; H, 5.46; N, 12.49. Calc. for $C_{25}H_{24}N_2O_2$: C, 67.55; H, 5.44; N, 12.61%.)

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