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REACTIONS OF SULFONYL SUBSTITUTED FUROXANS WITH OLEFINS

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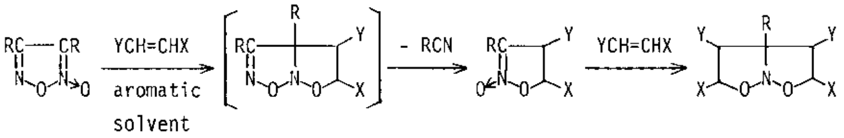
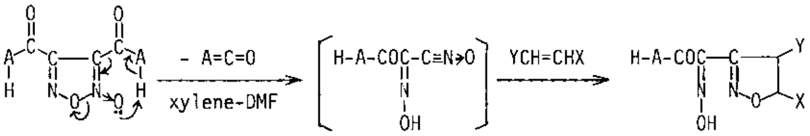
Abstract —— 3,3'-Bi-2-isoxazolines were obtained from the reaction of bis(butylsulfonyl)furoxan with olefins in xylene-DMF (1 : 1) at the refluxing temperature. On the other hand, 3-(1-hydroxyimino)ethyl-2-isoxazolines were obtained from the reactions of 3-methyl-4-methylsulfonylfuroxan with olefins under similar conditions.

Several types of reactions have been known with respect to the reaction of 1,2,5-oxadiazole 2-oxides (furoxans) with olefins.[1-5] Recently, the novel types of the nitrone cycloadditions (eq. 1)[1] and the nitrile oxide cycloadditions (eq. 2)[1b] were reported. We report here some reactions similar to eq. 2 using some sulfonyl substituted furoxans.



(1)



A = NH or CH$_2$

(2)

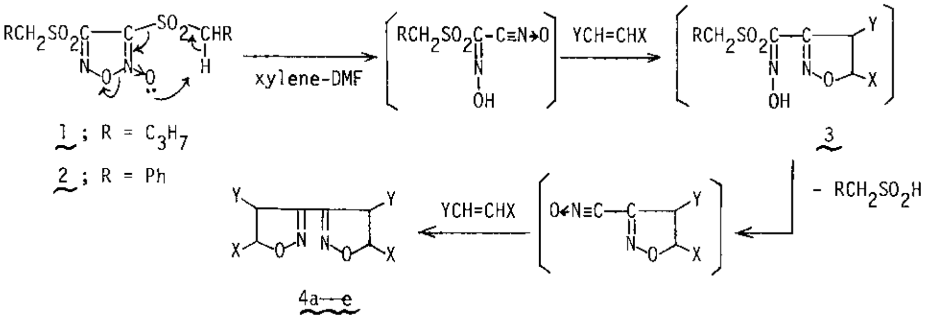
Reactions of bis-butyl (or bis-benzyl)sulfonylfuroxan (1 or 2) with several dipolarophiles were carried out in xylene-DMF (1 : 1) at the refluxing temperature for 10 h. 3,3'-Bi-2-isoxazolines (4a—e) were isolated from the reaction mixture. The results are shown in Table 1. The reaction probably involves concerted elimination of a sulfene and ring opening giving nitrile oxide, followed by cycloaddition with dipolarophiles as shown at first row in Scheme 1. The product (3), similar one to that shown in eq. 2, could not be isolable but undergo further elimination of a sulfinic acid to form another nitrile oxide.

Reactions of 3-methyl-4-methylsulfonyl (or -4-benzylsulfonyl)furoxan (5 or 6) with tetradecene or allylbenzene under the similar conditions began in the same way as with 1, but 3-(1-hydroxyimino)ethyl-2-isoxazolines (7) were isolated because of a poor ability of alkyl group for the

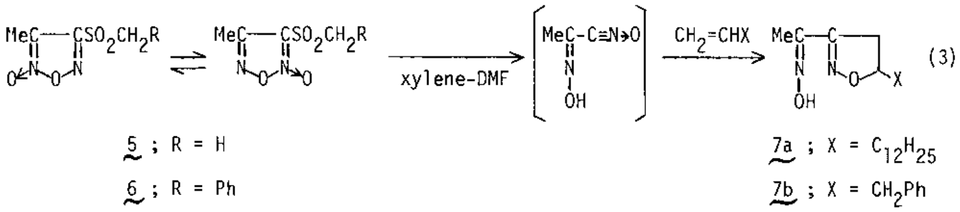
Table 1. Reactions of Sulfonyl Substituted Furoxans with Dipolarophiles

run No	Furoxan	Dipolarophile	Product	Yield[a)] %	Mp (°C)
1	**1**	1-Tetradecene	**4a** ($X = C_{12}H_{25}$, $Y = H$)	17	110—112
2	**1**	1-Nonene	**4b** ($X = C_7H_{15}$, $Y = H$)	12	118—119
3	**1**	Allylbenzene	**4c** ($X = CH_2Ph$, $Y = H$)	8	160—162
4	**1**	Allyl *p*-nitrophenyl ether	**4d** ($X = CH_2OC_6H_4NO_2$, $Y = H$)	12	202—204
5	**1**	Cyclododecene	**4e** ($X, Y = -C_{10}H_{20}-$)	10	216—218
6	**2**	1-Tetradecene	**4a**	8	
7	**5**	1-Tetradecene	**7a** ($X = C_{12}H_{25}$)	14	82—83
8	**5**	Allylbenzene	**7b** ($X = CH_2Ph$)	9	125—127
9	**6**	1-Tetradecene	**7a**	10	
10[b)]	**5**	Norbornene	**12a**	15	101—104
11	**5**	Norbornene	**12a**	20	
12[b)]	**8**	Norbornene	**10a**	41[c)]	120—126
13	**8**	Norbornene	**12a**	18	
14[b)]	**9**	Norbornene	**10a**	25[c)]	
15	**9**	Norbornene	**12a**	14	
16	**9**	1-Eicosene	**13**	11	74—76

a) Isolated yield. b) These runs were underwent in refluxing xylene and the others were in xylene-DMF (1 : 1). c) These data were cited from ref. 1b.

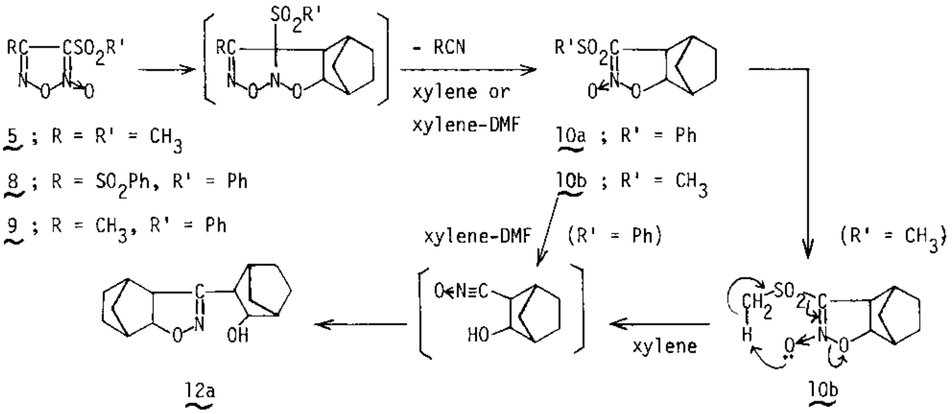


Scheme 1



elimination (eq. 3 and Table 1).

The reactions described above were only feasible when furoxan has sulfonyl (or carbonyl) group with α-hydrogen. On the contrary, when sulfonyl group has no α-hydrogen, nitrone type cycloadduct (10a) was formed from the reaction of bis(phenylsulfonyl)furoxan (8) or 3-methyl-4-phenylsulfonylfuroxan (9) with norbornene in refluxing xylene[1b] (run 12 and 14 in Table 1). However, in xylene-DMF, the reaction of 8 or 9 with norbornene gave an unexpected product, 3-(3-hydroxy-2-norbornyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanobenzoisoxazole (12a) (run 13 and 15). The same compound (12a) was also obtained from the reaction of 5 with norbornene (run 10 and 11). These reaction would proceed by a sequence of reactions shown in Scheme 2 since the reaction of 10a with norbornene in xylene-DMF at the refluxing temperature also gave 12a.



Scheme 2

3-(1-Eicosenyl)-5-octadecyl-2-isoxazoline (13) was obtained from the reaction of 5 with 1-eicosene. The formation of 13 can be explained by a mechanism similar to that of Scheme 2.

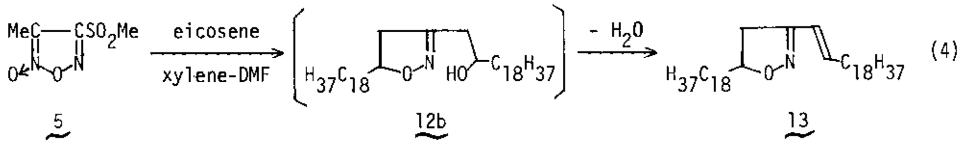
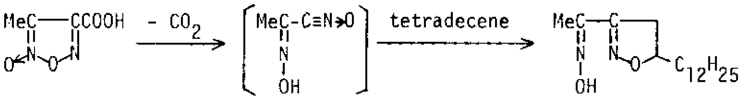


Table 2. Mass and NMR Spectral Data of Cycloadducts

Compd.	Mass ; M/e Found (calcd)	Nmr (δ) [4d was dissolved in DMSO-d_6, the others were in $CDCl_3$]
4a	476.43(476.43)	0.7—1.8(m, 50 H), 2.85(dd, 2 H, J = 8 & 17), 3.33(dd, 2 H, J = 10 & 17), 4.4—5.0(m, 2 H).
4b	336.28(336.28)	0.7—1.8(m, 30 H), 2.83(dd, 2 H, J = 8 & 17), 3.33(dd, 2 H, J = 10 & 17), 4.4—5.0(m, 2 H).
4c	320.15(320.15)	2.7—3.6(m, 8 H), 4.7—5.3(m, 2 H), 7.35(s, 10 H).
4d	442.11(442.11)	3.0—3.7(m, 4 H), 4.3(d, 4 H, J = 4), 4.9 5.5(m, 2 H), 7.15(d, 4 H, J = 9), 8.2(d, 4 H, J = 9).
4e	416.34(416.34)	1.1—2.3(m, 40 H), 3.3—3.7(m, 2 H), 4.5—4.9(m, 2 H).
7a	296.25(296.25)	0.7—1.8(m, 25 H), 2.2(s, 3 H), 2.7(dd, 1 H, J = 9 & 17), 3.2(dd, 1 H, J = 10 & 17), 4.4—5.0(m, 1 H), 8.3(s, 1 H, OH).
7b	218.11(218.11)	2.15(s, 3 H), 2.6—3.5(m, 4 H), 4.7—5.2(m, 1 H), 7.2(s, 5 H), 8.7 (s, 1 H, OH).
12a	247.16(247.16)	0.9—2.0(m, 12 H), 2.0—2.7(m, 5 H), 3.1(d, 1 H, J = 8), 3.4 (br, 1 H, OH), 3.93(d, 1 H, J = 7), 4.35(d, 1 H, J = 8).
13	601.61(601.61)	0.7—1.8(m, 72 H), 2.0—2.6(m, 2 H), 2.7(dd, 1 H, J = 9 & 17), 3.15 (dd, 1 H, J = 10 & 17), 4.4—4.9(m, 1 H), 5.7—6.3(m, 1 H), 6.5(d, 1 H, J = 16).

The structures of the cycloadducts (4a—e, 7a, 7b, 12a, and 13) were assigned on the basis of elemental, mass, nmr, and ir spectral analyses (see Table 2). The assignment of the structure (7a) was further supported by comparison of physical properties of 7a with those of an authentic specimen prepared from the reaction of 3-methylfuroxan-4-carboxylic acid with 1-tetradecene.[4]



(5)

7a

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