The Reactions of Aryldiazomethanes with Sulfur Dioxide in the Presence of Enamines

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The reactions of several arydiazomethanes with sulfur dioxide in the presence of 2-methyl-1-morpholinopropene gave cyclic sulfones, thietane 1,1-dioxides, indicating the existence of sulfene as a reaction intermediate. The stereoselectivity of the sulfene–enamine cycloaddition showed that the less thermodynamically stable *cis* orientation was generally preferred. On the other hand, the reactions in the presence of 1-morpholinocyclohexene, which has a labile proton β to the morpholino moiety, afforded acyclic or cyclic sulfones, depending on the substituents of diazomethanes. The mechanism of these reactions is discussed.

Recently sulfenes, generated by the action of amines on alkanesulfonyl chlorides, have received considerable attention.[1] Though the reactivities of sulfene towards enamines have been extensively investigated, the research on the stereochemistry of the products is meager and the mechanism for sulfene–enamine addition is still not determined.[2] Another useful method for generating sulfene is the reaction of diazoalkanes and sulfur dioxide,[3] but there are only a few publications[4] about this reaction, where episulfones and olefins are formed. In the present paper,[5] we deal with the stereoselecitve formations of thietane 1,1-dioxide in the reactions of aryldiazomethanes with sulfur dioxide in the presence of enamines and with the preference of non-cyclo to cycloaddition.

The mechanism of sulfene–enamine addition has already been discussed in the base-induced β-elimination reaction of alkanesulfonyl chlorides in the presence of enamines.[2] But in this system, the triethylamine used as the elimination reagent is liable to cause a slow post-isomerization[2b] of the cycloadduct, 3-aminothietane 1,1-dioxide. The present system, as compared with the amine–chloride system, could be more favorable for the mechanistic study of sulfene–enamine addition from the stereochemical point of view.

Results and Discussion

Reactions in the Presence of 2-Methyl-1-morpholinopropene (MMP). The reactions of mono- and di-arylsubstituted diazomethanes (**1**) with sulfur dioxide in the presence of MMP, which has no hydrogen atom β to the morpholino moiety, led to the cycloadducts, thietane 1,1-dioxide derivatives (**2**) (Scheme 1).

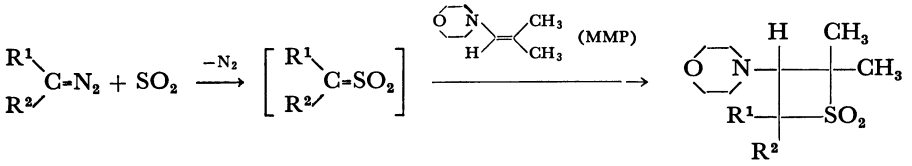
In the reactions of mono-arylsubstituted diazomethanes (**1c**, **1d**, and **1e**) with sulfur dioxide in the presence of MMP, mixtures of *cis* and *trans* isomers were obtained. The less thermodynamically stable *cis* orientation of the morpholino and the aryl groups was preferred in the cycloadducts **2c** and **2d**; on the contrary, the *trans* orientation was preferred in the case of **2e** which has an electron-withdrawing group. The results are summarized in Table 1.

Table 1. The reaction of **1** with SO_2 in the presence of MMP

Diazomethane	R^1	R^2	Solvent	Yield of **2** mol%[a]	*cis* %[b]
1a	fluorenylidene		C_6H_6	99	—
1b	Ph	Ph	C_6H_6	95	—
1c	*p*-Me-Ph	H	C_6H_6	51	73
			THF	57	64
1d	Ph	H	C_6H_6	62	73
1e	*p*-NO_2-Ph	H	C_6H_6	82	29
			THF	82	22

a) Isolated yield calculated on the basis of **1** used.
b) The value shows the ratio of the *cis* isomer in the yield of **2**.

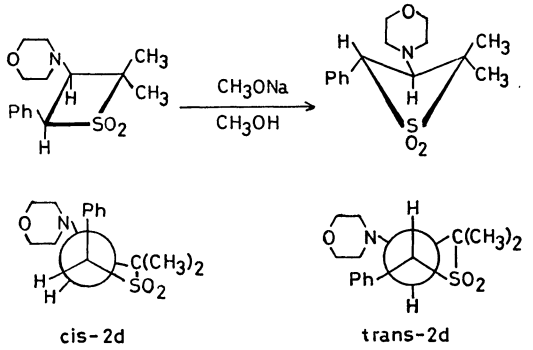
The product, **2d**, obtained from the reaction of **1d** was separated into its *cis* and *trans* isomers (*cis*-**2d** and *trans*-**2d**) by repeated fractional recrystallizations; the isolation of only the *trans* isomer had been made by Truce and Rach.[2b] The isolated isomers were identified on the basis of the NMR spectra. The signals of the phenyl protons appeared as a separate peak in *cis*-**2d** and as a single peak in *trans*-**2d**. The difference between the chemical shifts of the two methyl proton signals was 6 Hz in *cis*-**2d** and 1.8 Hz in *trans*-**2d**, showing an interaction between the phenyl ring and one methyl group in *cis*-**2d**. In the NMR spectra of *cis*-**2d** and *trans*-**2d**, both coupling constants for the two methylidyne protons in the thietane rings were the same and equal to 10 Hz. The large conpling coustant (10 Hz) suggests a dihedral angle between the two protons



1 (**a**) R^1, R^2=fluorenylidene; (**b**) R^1=R^2=phenyl; (**c**) R^1=*p*-tolyl, R^2=H; (**d**) R^1=phenyl, R^2=H; (**e**) R^1=*p*-nitrophenyl, R^2=H. **2a, b, c, d, e**

Scheme 1.

of 0 or 180°.[6] The former angle can be attained only in a planar thietane ring by a *cis* orientation of the morpholino and aryl groups, while the 180° alignment can be achieved only by *trans* substituents in a puckered conformation, as shown in Scheme 2. The assigned stereochemistry was further supported by a study of epimerization: the *cis* isomer or the *cis–trans* mixutre of **2d** was isomerized to the pure *trans* isomer by stirring its methanol solution under the influence of a catalytic amount of sodium methoxide over a period of several days (Scheme 2).



Scheme 2.

The assignment of each of the isomers of **2c** and **2e** was established with their respective NMR spectra, with reference to those of **2d**. And the findings in **2d**, described above, were also applicable to **2c** and **2e**. The *cis* percentages in the yields of **2** were determined by the intensity measurement of the methylidyne proton signals in the NMR spectra of the crude reaction products.

In order to examine the effect of solvent on the stereoselectivity, reactions of **1d** were carried out in various solvents. These results are presented in Table 2. An increasing tendency of the *trans* isomer, though not so drastic, was observed in the polar solvents. Such an effect was also observed in the case of the *para*-substituted phenylsulfene, as seen in Table 1: the reaction of **1c** or **1e** gave the increasing *trans* adduct in THF instead of benzene.

Reactions in the Presence of 1-Morpholinocyclohexene (MCH). A series of reactions of aryldiazomethanes (**1**) and MCH, which has a hydrogen atom β to the morpholino moiety,

TABLE 2. THE REACTION OF PHENYLDIAZOMETHANE (**1d**) WITH SO_2 IN THE PRESENCE OF MMP IN VARIOUS SOLVENTS

Solvent	Yield of **2d** mol%[a]	*cis* %[b]
cyc-C_6H_{12}	80	77
CCl_4	57	77
C_6H_6	62	73
CH_3CN	43	68
THF	50	63
DMF	77	64

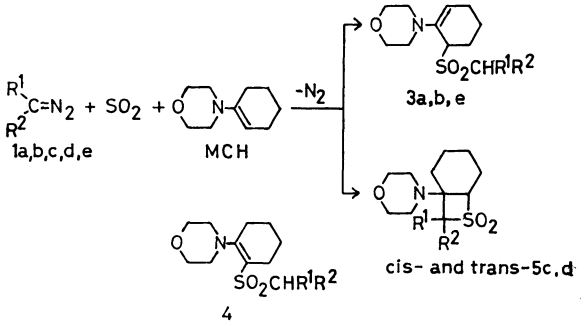
a) Isolated yield calculated on the basis of **1** used.
b) The value shows the ratio of the *cis* isomer in the yield of **2d**.

TABLE 3. THE REACTION OF **1** WITH SO_2 IN THE PRESENCE OF MCH

Diazomethane	R^1	R^2	Solvent	Yield (mol%)[a] cyclic (**5**)	acyclic (**3**)
1a	fluorenylidene		C_6H_6	—	84
1b	Ph	Ph	C_6H_6	—	87
1c	*p*-Me-Ph	H	C_6H_6	49	—
			THF	54	—
1d	Ph	H	C_6H_6	87	—
			THF	87	—
1e	*p*-NO_2-Ph	H	C_6H_6	—	89
			THF	—	93

a) Isolated yield calculated on the basis of **1** used.

was carried out in the same way. The reactions of 9-diazofluorene (**1a**), diphenyldiazomethane (**1b**), and *p*-nitrophenyldiazomethane (**1e**) were carried out and the spectra of IR and NMR for these reaction products could be explained satisfactorily by the structures of the acyclic sulfones (**3**) instead of the other acyclic sulfones (**4**)[7] or the expected cyclic sulfones (**5**). On the contrary, the reactions of *p*-tolyldiazomethane (**1c**) and phenyldiazomethane (**1d**) gave a *cis–trans* mixture of cyclic sulfone (**5**) (Scheme 3). Table 3 shows the results.



Scheme 3.

Three cyclic products (*cis*-**5c**, *cis*-**5d**, and *trans*-**5d**) were isolated respectively by careful recrystallizations from suitable solvents and their configurations were determined by NMR analysis using a shift reagent, Eu(dpm)$_3$.[8] The results of the complexation studies for *cis*-**5d** and *trans*-**5d** are shown in Fig. 1. The primary site of complexation with Eu(dpm)$_3$ is the oxygen of the morpholine ring, since the largest shifts were induced in the protons vicinal to oxygen. In Fig. 1a, the difference in chemical shifts of the two methylidyne protons H_6 and H_8 decreased whereas, in Fig. 1b, the difference remained essentially constant. Thus in *cis*-**5d**, H_8 is deshielded less than H_6, whereas in *trans*-**5d** both protons are deshielded to approximately the same extent. The observed difference in induced shifts must lie in the distance from the chelation site to the protons, establishing the fact that H_6 and H_8 are *trans* to each other in *cis*-**5d** and *cis* to each other in *trans*-**5d**. The induced shift spectra for *cis*-**5c** were similar to those of *cis*-**5d**.

The ratio of the two geometric isomers was deter-

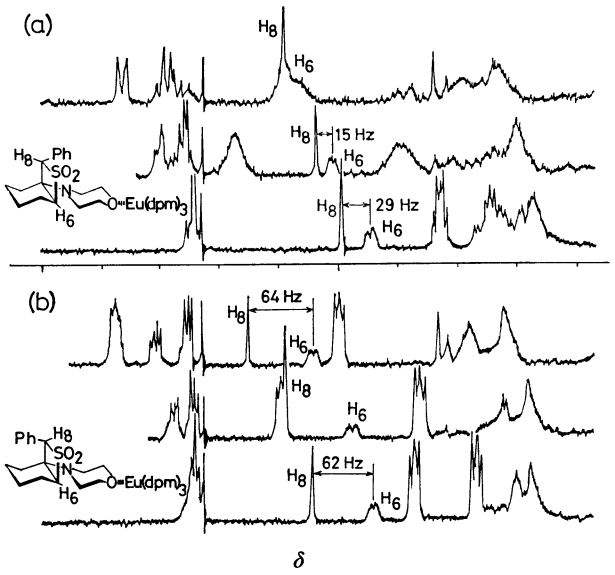


Fig. 1. Succesive scans displaying the effect of the addition of incremental amounts of $Eu(dpm)_3$ on the 60 MHz NMR spectra in $CDCl_3$; (a): for *cis*-**5d**, (b): for *trans*-**5d**.

mined by means of the intensity measurement of the H_8 proton signal in the NMR spectrum of the crude product. In the isomeric mixture of **5d**, the *cis* percentage was as high as 81% in benzene and was lowered to 70% in THF. In the case of **5c**, the predominant yield of the *cis* isomer was evident in the spectrum, though the *cis* percentage could not be determined because the peaks assigned to the *trans* isomer were weak and ambiguous. Interesting to say, the results suggest that the alternative of acyclic (**3**) or cyclic (**5**) is caused by the electronic character of the α-carbon atom in the sulfene.

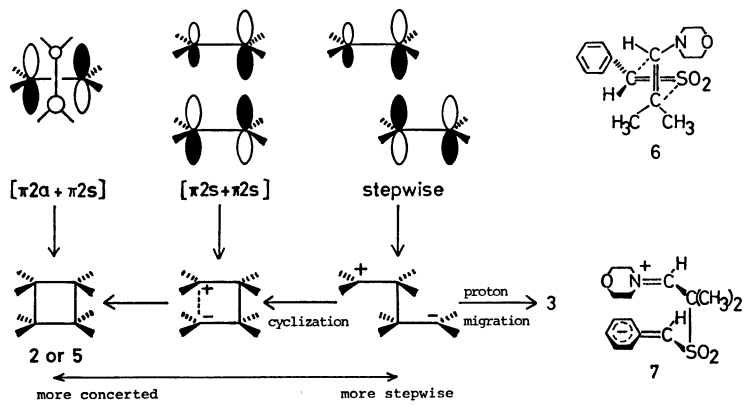
Reaction Mechanism. On the basis of the frontier orbitals' interaction in the [2+2] cycloaddition,[2b,9] different mechanistic processes are possible (Scheme 4). A concerted $[\pi 2_s + \pi 2_s]$ process could conceivably account for the *cis* preference in the cyclic sulfones (**2** and **5**). In this concerted process, one unsaturated system must approach the other with an orthogonal orientation.[12] The most probable transition state is shown for the formation of *cis*-**2**, such as **6**. If the reaction indeed proceeds *via* this concerted process, it should be required that the acyclic sulfones (**3a**, **3b**, and **3e**) were formed through the cyclic sulfones. And so, from the consideration of a steric interaction between the morpholino and the aryl groups, the cyclic isomers of **3a**, **3b**, and **3e** like **5c** and **5d** should also be isolated even in the MCH system, as well as in the MMP system. Actually, however, in the current observation, only acyclic sulfones **3a**, **3b**, and **3e** were afforded without the cyclic isomers in the MCH system. And in the case of the formation of cyclic sulfone, the *cis* preference was lowered when polar solvents were employed.

As an alternative, a concerted $[\pi 2_s + \pi 2_s]$ process can be significantly preferred, as pointed out by Epiotis *et al.*,[13] if one addend is very electron rich and the other is very electron defficient. However, from the evidence of the preference of noncycloaddition when a zwitterionic intermediate (**7**) is stabilized, a stepwise process, which is a third alternative, is rather likely.

The formation of the less stable *cis* isomer of cyclic sulfone (**2** and **5**) can be well explained on the basis of an electrostatic interaction of cisoid 1,4-dipolar intermediate (**7**). In the addition of sulfene to MMP, which has no proton β to the morpholino moiety, the *cis* isomer of **2** was predominantly afforded. If the carbanion is stabilized and given a long lifetime by its substituting group(like *p*-NO_2–Ph) or by a solvation in the polar solvents, the amount of the more thermodynamically stable *trans* isomer of **2** may increase. The addition of sulfene to MCH, which has a labile proton β to the morpholino moiety, resulted in the formation of **5c** and **5d**, where the *cis* isomer was predominant. However, if the carbanion was stabilized or if the negative charge is dispersed and the effective electrostatic attraction is reduced to a great extent by its substituting group, *e. g.* fluorenylidene, diphenyl, or *para*-nitrophenyl group, the proton migration to the carbanion to afford **3** would be more favored than the cyclization of the zwitterion to give **5**.

Experimental

The NMR spectra were recorded on a Varian EM-360 (60 MHz) instrument in $CDCl_3$ with tetramethylsilane as the internal standard. The IR spectra were measured in KBr disks with Hitachi EP-S and 215 spectrophotometers.



Scheme 4. Indicates acceptor(sulfene) LUMO[10]-donor(enamine) HOMO[11] interaction.

Materials. All the diazomethanes were prepared according to the procedures given in the literature: 9-diazofluorene (**1a**),[14] diphenyldiazomethane (**1b**),[15] *p*-tolyldiazomethane (**1c**),[16] phenyldiazomethane (**1d**),[17] and *p*-nitrophenyldiazomethane (**1e**).[18] The enamines were also prepared by the methods in the literature: 2-methyl-1-morpholinopropene(MMP)[19] and 1-morpholinocyclohexene (MCH).[20] Sulfur dioxide, obtained from a commercial source, was dried by passing it through $CaCl_2$ and P_2O_5 tubes. The solvents were purified according to the published directions,[21] stored over sodium wire or calcium hydride, and redistilled just before use.

General Procedure. In a 100 ml three-necked flask equipped with a magnetic stirrer, a dropping funnel, a thermometer, and a calcium chloride drying tube were placed 70 ml of a dry solvent containing 50 mmol of sulfur dioxide and 10 mmol of an enamine, and the flask was kept at 20 °C. To this solution, 30 ml of dry solvent containing 5 mmol of diazomethane was added dropwise over a period of 15 minutes with stirring. After the addition was complete, the mixed solution was stirred for an additional 45 minutes. Then the solvent and the excess sulfur dioxide were removed as quickly as possible *in vacuo* at room temperature. After an aliquot of the oily residue was dissolved in $CDCl_3$ and analyzed by NMR, the NMR solvent was removed at reduced pressure and the combined residue was crystallized from a suitable solvent. The NMR data for *cis* isomers were obtained from the mixtures except where noted. An analytically pure sample was obtained by recrystallization.

*2-Fluorenylidene-3-morpholino-4,4-dimethylthietane 1,1-Dioxide (**2a**).* The white powder was obtained in 99% yield by adding a small amount of cold petroleum ether to the oily residue. The recrystallization from methanol gave the colorless leaflets, mp 156—157 °C. IR(KBr): 1106 and 1315 cm^{-1} (SO_2). NMR($CDCl_3$): δ 1.55—2.33[4H, broad m, $(CH_2)_2N$], 1.84(3H, s, CH_3), 2.01(3H, s, CH_3), 3.43[5H, m, $(CH_2)_2O$ and methylidyne], and 7.3—8.1(8H, m, aromatic). Found: C, 68.12; H, 6.42; N, 3.89%. Calcd for $C_{21}H_{23}NO_3S$: C, 68.28; 6.28; N, 3.79%.

*2,2-Diphenyl-3-morpholino-4,4-dimethylthietane 1,1-Dioxide (**2b**).* The white powder was obtained in 95% yield in the same manner as described above. The recrystallization from benzene–ethanol(1 : 1) gave the colorless plates, mp 136—137 °C. IR(KBr): 1112 and 1305 cm^{-1} (SO_2). NMR($CDCl_3$): δ 1.64(3H, s, CH_3), 1.70(3H, s, CH_3), 2.37[4H, m, $(CH_2)_2N$], 3.64[4H, m, $(CH_2)_2O$], 3.77(1H, s, methylidyne), 7.15—7.65 (8H, m, C_6H_5 *trans* to morpholine ring and 3H of C_6H_5 *cis* to morpholine ring), and 7.8—8.2(2H, m, 2H of C_6H_5 *cis* to morpholine ring). Found: C, 68.01; H, 6.82; N, 3.85%. Calcd for $C_{21}H_{25}NO_3S$: C, 67.90; H, 6.78, N, 3.77%.

*3-Morpholino-2-*p*-tolyl-4,4-dimethylthietane 1,1-Dioxide (**2c**).* The *cis–trans* mixture was obtained in the yield of 51% in benzene and 57% in THF by adding a small amount of cold methanol to the oily residue. NMR($CDCl_3$) (*cis* isomer): δ 1.62 and 1.73(each 3H, s, *gem*-dimethyl), 2.28[4H, m, $(CH_2)_2N$], 2.32(3H, s, CH_3–Ph), 3.30(1H, d, J=10 Hz, CHN), 3.60[4H, m, $(CH_2)_2O$], 5.27(1H, d, J=10 Hz, $CHSO_2$), and 7.17 and 7.53(each 2H, d, J=7.8 Hz, phenyl). Repeated recrystallization of the crude product from methanol gave analytically pure *trans* isomer, colorless plates, mp 167—168 °C. IR(KBr): 1098, 1118, 1292, and 1304 cm^{-1} (SO_2). NMR ($CDCl_3$): δ 1.63 and 1.67(each 3H, s, *gem*-dimethyl), 2.29 [4H, m, $(CH_2)_2N$], 2.35(3H, s, CH_3–Ph), 3.08(1H, d, J= 10 Hz, CHN), 3.65[4H, m, $(CH_2)_2O$], 5.08(1H, d, J=10 Hz, $CHSO_2$), and 7.25(4H, broad s, phenyl). Found: C, 61.72; H, 7.37; N, 4.52%. Calcd for $C_{16}H_{23}NO_3S$: C, 62.12; H, 7,49; N, 4.53%.

*3-Morpholino-2-phenyl-4,4-dimethylthietane 1,1-Dioxide (**2d**).* The crude isomeric mixtures of the *cis* and *trans* cycloadducts were obtained in the yields of 43—80% according to the solvent used. The mixture was separated into the *cis* and *trans* isomers by repeated fractional recrystallization from a mixed solvent of petroleum ether and benzene. The *cis* isomer: colorless prisms, mp 128—129 °C. IR(KBr): 1089 and 1301 cm^{-1} (SO_2). NMR($CDCl_3$): δ 1.67 and 1.77(each 3H, s, *gem*-dimethyl), 2.33[4H, m, $(CH_2)_2N$], 3.35 (1H, d, J=10 Hz, CHN), 3.63[4H, m, $(CH_2)_2O$], 5.30(1H, d, J=10 Hz, $CHSO_2$), and 7.2—7.8(5H, m, phenyl). Found: C, 61.10; H, 7.23; N, 4.75%. Calcd for $C_{15}H_{21}NO_3S$: C, 61.00; H, 7.17; N, 4.74%. The *trans* isomer was also obtained by treating the *cis* isomer or the isomeric mixture in methanol containing a 0.02 part of sodium methoxide for about a week. The *trans* isomer: colorless plates, mp 179—180 °C(lit, 181—182 °C).[2b] IR(KBr): 1105 and 1298 cm^{-1} (SO_2). NMR ($CDCl_3$): δ 1.65 and 1.68(each 3H, s, *gem*-dimethyl), 2.26 [4H, m, $(CH_2)_2N$], 3.10(1H, d, J=10 Hz, CHN), 3.64[4H, m, $(CH_2)_2O$], 5.13(1H, d, J=10 Hz, $CHSO_2$), and 7.40(5H, s, phenyl). Found: C, 60.89; H, 7.25; N, 4.75%. Calcd for $C_{15}H_{21}NO_3S$: C, 61.00; H, 7.17; N, 4.74%.

*3-Morpholino-2-*p*-nitrophenyl-4,4-dimethylthietane 1,1-Dioxide (**2e**).* The NMR spectrum of the crude product showed the peaks derived from both *cis* and *trans* isomers. The yield of the product was 82% both in benzene and in THF. The *cis* isomer: NMR($CDCl_3$): δ 1.67 and 1.77(each 3H, s, *gem*-dimethyl), 2.25[4H, m, $(CH_2)_2N$], 3.41(1H, d, J=10 Hz, CHN), 3.63[4H, m, $(CH_2)_2O$], 5.40(1H, d, J=10 Hz, CH-SO_2), and 7.79 and 8.32(each 2H, d, J=9 Hz, phenyl). The pure *trans* isomer was obtained by recrystallization of the crude product from methanol: colorless plates, mp 193—194 °C. IR(KBr): 1115 and 1305 cm^{-1} (SO_2). NMR(CD-Cl_3): δ 1.67 and 1.69(each 3H, s, *gem*-dimethyl), 2.23[4H, m, $(CH_2)_2N$], 3.10(1H, d, J=10 Hz, CHN), 3.61[4H, m, $(CH_2)_2O$], 5.17(1H, d, J=10 Hz, $CHSO_2$), and 7.58 and 8.25(each 2H, d, J=9 Hz, phenyl). Found: C, 52.87; H, 5.97; N, 8.46%. Calcd for $C_{15}H_{20}N_2O_5S$: C, 52.93; H, 5.92; N, 8.46%.

*3-(9-Fluorenylsulfonyl)-2-morpholinocyclohexene (**3a**).* A white powder was afforded in 84% yield by adding a small amount of cold petroleum ether to the oily residue. An analytiacally pure sample was obtained by recrystallization from methanol: colorless plates, mp 142—143 °C. IR(KBr): 1120 and 1315 cm^{-1}(SO_2), 1653 cm^{-1}(C=C). NMR($CDCl_3$): δ 1.25—2.75(6H, broad m, cyclohexane ring), 2.58[4H, m, $(CH_2)_2N$], 3.48[5H, m, $(CH_2)_2O$ and $CHSO_2$], 5.28(1H, t, J=3 Hz, vinyl), 5.58(1H, s, SO_2CH–Ar), and 7.2—8.1(8H, m, aromatic). Found: C, 70.48; H, 6.40; N, 3.31%. Calcd for $C_{23}H_{25}NO_3S$: C, 69.85; H, 6.37; N, 3.54%.

*3-Diphenylmethylsufonyl-2-morpholinocyclohexene (**3b**).* A white powder was obtained in 87% yield by adding a small amount of cold petroleum ether to the oily residue and was recrystallized from ethanol, giving the colorless plates, mp 150.5—151.5 °C. IR(KBr): 1112 and 1305 cm^{-1} (SO_2), 1645 cm^{-1} (C=C). NMR($CDCl_3$): δ 1.3—3.2(6H, broad m, cyclohexane ring), 2.76[4H, m, $(CH_2)_2N$], 3.83[5H, m, $(CH_2)_2O$ and $CHSO_2$], 5.43(1H, t, J=4 Hz, vinyl), 6.02(1H, s, SO_2CH–Ar), and 7.3—8.0(10H, m, aromatic). Found: C, 69.41; H, 6.96; N, 3.65%. Calcd for $C_{23}H_{27}NO_3S$: C, 69.50; H, 6.85; N, 3.52%.

*3-*p*-Nitrobenzylsulfonyl-2-morpholinocyclohexene (**3e**).* The NMR spectrum of the residue showed that the reaction products consisted exclusively of acyclic isomer. The crude product was collected as white powder by adding cold methanol to the residue in the yield of 88.5% in benzene and 93% in THF. Recrystallization from methanol afforded analytically

pure **3e**: colorless needles, mp 181—182 °C. IR(KBr): 1128 and 1304 cm^{-1} (SO_2), 1639 cm^{-1} (C=C). NMR($CDCl_3$): δ 1.5—2.7(6H, broad m, cyclohexane ring), 2.48—3.35[4H, broad m, $(CH_2)_2N$], 3.83[4H, m, $(CH_2)_2O$], 3.87 (1H, m, methylidyne), 4.40 and 4.73 (each 1H, ABq, J= 12.5 Hz, SO_2CH_2–Ph), 5.40(1H, t, J=3.5 Hz, vinyl), and 7.53 and 8.22 (each 2H, d, J=8.5 Hz, phenyl). Found: C, 55.55; H, 6.02; N, 7.69%. Calcd for $C_{17}H_{22}N_2O_5S$: C, 55.72; H, 6.05; N, 7.65%.

*1-Morpholino-8-*p*-tolyl-7-thiabicyclo[4.2.0]octane 7,7-Dioxide (**5c**).* The crude product consisted exclusively of cyclic adduct; the peaks in the NMR spectrum which are derived from *trans*-**5c** were weak and ambiguous. After careful recrystallization from cold methanol, analytically pure *cis* isomer was isolated in the yield of 49% in benzene and 54% in THF; its structure was established by means of NMR, using $Eu(dpm)_3$. The *cis* isomer: colorless plates, mp 123—124 °C. IR(KBr): 1120 and 1320 cm^{-1} (SO_2). NMR($CDCl_3$): δ 1.3—2.8(8H, broad m, cyclohexane ring), 2.32(3H, s, CH_3), 2.47[4H, m, $(CH_2)_2N$], 3.30[4H, m, $(CH_2)_2O$], 4.42 (1H, m, H_6), 4.86(1H, s, H_8), and 7.24 and 7.36(each 2H, d, J=8.5 Hz, phenyl). Found: C, 65.06; H, 7.49; N, 4.16 %. Calcd for $C_{18}H_{25}NO_3S$: C, 64.46; H, 7.51; N, 4.18%.

*1-Morpholino-8-phenyl-7-thiabicyclo[4.2.0]octane 7,7-Dioxide (**5d**).*[22] The mixture of *cis* and *trans* cyclic adducts was obtained when **1d** was used. The NMR spectrum of the residue showed that the reaction product consisted exclusively of cyclic adduct. The yields were 87% both in benzene and THF. The *cis* and *trans* isomers were isolated by careful fractional recrystallization from methanol. The ratios of the *cis* isomer were 81% in benzene and 70% in THF. Each of the structures was confirmed by means of NMR using $Eu(dpm)_3$, as described before. The *cis* isomer: white crystalline, mp 103—104.5 °C. IR(KBr): 1150 and 1314 cm^{-1} (SO_2). NMR($CDCl_3$): δ 1.2—2.8(8H, broad m, cyclohexane ring), 2.50[4H, m, $(CH_2)_2N$], 3.30[4H, m, $(CH_2)_2O$], 4.44(1H, m, H_6), 4.92(1H, s, H_8), 7.37(5H, m, phenyl). Found: C, 64.04; H, 7.09; N, 4.87%. Calcd for $C_{17}H_{23}NO_3S$: C, 63.53; H, 7.21; N, 4.36%. The *trans* isomer; colorless prisms, mp 115—116 °C. IR(KBr):1140 and 1298 cm^{-1} (SO_2). NMR($CDCl_3$): δ 1.2—2.6(8H, broad m, cyclohexane ring), 2.63[4H, m, $(CH_2)_2N$], 3.80[4H, m, $(CH_2)_2O$], 4.37(1H, m, H_6), 5.40(1H, s, H_8), and 7.2—7.7(5H, m, phenyl). Found: C, 63.48; H, 7.22; N, 4.23%. Calcd for $C_{17}H_{23}NO_3S$: C, 63.53; H, 7.21; N, 4.36%.

References

1) For a review, see: a) G. Opitz, *Angew. Chem. Int. Ed. Engl.*, **6**, 107 (1967); b) T. Nagai and N. Tokura, *Int. J. Sulfur Chem.*, **7B**, 207 (1972); c) J. F. King, *Acc. Chem. Res.*, **8**, 10 (1975).

2) a) L. A. Paquette, J. P. Freeman, and S. Maiorana, *Tetrahedron*, **27**, 2599 (1971); b) W. E. Truce and J. F. Rach, *J. Org. Chem.*, **39**, 1109 (1974).

3) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).

4) a) G. Hesse and E. Reichold, *Chem. Ber.*, **90**, 2101 (1957); b) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); c) T. Nagai, H. Namikoshi, and N. Tokura, *Tetrahedron*, **24**, 3267 (1968); d) N. H. Fischer, *Synthesis*, **1970**, 393.

5) Part of this work was reported in a preliminary communication: T. Tanabe, T. Shingaki, and T. Nagai, *Chem. Lett.*, **1975**, 679.

6) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2871 (1963).

7) In discussing the exclusive formation of the acyclic sulfone **3** instead of the isomeric sulfone **4** as shown in Scheme 3, the following consideration may be made: the sulfone **4** is destabilized by steric inhibition of the resonance involving the nitrogen lone pair and the double bond.

8) C. T. Goralski and T. E. Evans, *J. Org. Chem.*, **37**, 2080 (1972).

9) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975).

10) The MO of sulfene was calculated: a) J. P. Snyder, *J. Org. Chem.*, **38**, 3965 (1973); b) K. N. Houk, R. W. Strozier, and J. A. Hall, *Tetrahedron Lett.*, **1974**, 897.

11) In HOMO of enamine, the coefficient magnitude is $c_\beta > c_\alpha$: R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976).

12) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y. (1970), pp. 68—69.

13) N. D. Epiotis, R. L. Yates, D. Carlberg, and F. Bernardi, *J. Am. Chem. Soc.*, **98**, 453 (1976), and references therein.

14) H. Staudinger and O. Kupfer, *Ber.*, **44**, 2207 (1911).

15) L. I. Smith and K. L. Howard, *Org. Synth.*, Coll. Vol. III, 351 (1955).

16) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, **1952**, 4775.

17) C. G. Overberger and J. P. Anselme, *J. Org. Chem.*, **28**, 592 (1963).

18) H. W. Davies and M. Schwarz, *J. Org. Chem.*, **30**, 1242 (1965).

19) E. Benzing, *Angew. Chem.*, **71**, 531 (1959).

20) S. Hünig, E. Lücke, and W. Brenninger, *Org. Synth.*, Coll. Vol. V, 808 (1973).

21) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York (1970).

22) A. M. Hamid and S. Trippett, *J. Chem. Soc., C*, **1968**, 1612, reported the formation of **5d** from the reaction of phenylmethanesulfonyl chloride and MCH in the presence of Et_3N, but the stereochemistry of the reaction was not discussed.