On adding sodium sulfate to the ternary phase the central component of the triplet grows in intensity with respect to the outer transitions, as indicated in the Figure 1 legend. The central component still remains 40% of the intensity of an equivalent aqueous solution of sodium ion, and this indicates the formation of a two-phase system with both phases containing partially ordered sodium ions. The two phases are not immediately apparent, but on standing for 1 week the two layers of approximately equal proportion do appear quite separate. ^{23}Na magnetic resonance signals were investigated in both layers. As expected one layer gave (see Figure 1B) the sharp triplet observed for the pure ternary phase but with a reduced separation between the components. We interpret this result in terms of some excess sodium sulfate being soluble in the ternary phase. The reduced ordering of the sodium ions arises from participation of more ions in the chemical exchange process involving ordered sites. The top layer (see Figure 1A) in the two-phase system has one observable sharp component whose position superimposes with the corresponding central component signal of the other layer. The outer transitions were not observed even though field scans ± 50 kHz each side of this peak were made. This observation is similar to the "hidden sodium" results in actual biological systems where relaxation time studies indicate the presence of normally unobservable resonances.[11-13] We conclude that either the outer transitions are close to those expected from sodium observed in ionic solids and hence derive from a highly ordered environment and/or that the resonances are very broad because of a powder pattern spectrum. The present lyotropic system which separates into two phases does reproduce many of the expected features of a biological system and leads us to anticipate successful experiments in these systems, which will have important bearing on the role and environment of sodium in both the ordered parts (membranes) and isotropic parts of living systems.

Previous studies of the quadrupolar splitting in liquid crystals have appeared in print during this study;[14-17] of especial note is a paper by Schporer and Civan[16] who though failing to find a system with "hidden sodium" correctly demonstrate that such anomalous sodium must be associated with the missing outer transitions.

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[11] F. W. Cope, *Proc. Nat. Acad. Sci. U. S.*, **54**, 225 (1965); J. L. Cziesler, O. G. Fritz, and T. J. Swift, *Biophys. J.*, **10**, 260 (1970).

[12] C. A. Rotunno, V. Kowalewski, and M. Cereijido, *Biochim. Biophys. Acta*, **135**, 170 (1970).

[13] F. W. Cope, *J. Gen. Physiol.*, **50**, 1353 (1967); *Biophys. J.*, **10**, 843 (1970).

[14] B. M. Fung, M. J. Gerace, and L. S. Gerace, *J. Phys. Chem.*, **74**, 83 (1970).

[15] G. Lindblom, H. Wennerström, and B. Lindman, *Chem. Phys. Lett.*, **8**, 489 (1971).

[16] M. Schporer and M. M. Civan, *Biophys. J.*, **12**, 114 (1972).

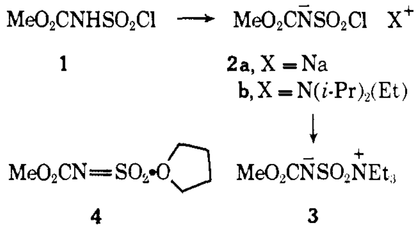
[17] D. Gill, M. P. Klein, and G. Kotowycz, *J. Amer. Chem. Soc.*, **90**, 6870 (1968).

Cycloaddition Reactions of *N*-Sulfonylamines

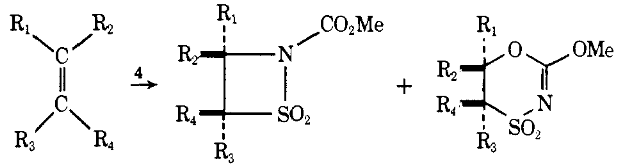
Sir:

The synthetic value of *N*-sulfonylamines[1] ($RN{=}SO_2$) in the form of inner salts with tertiary amines ($RNSO_2^-$-NR_3^+) as reaction partners with alkenes to give cyclic sulfonamides has previously been reported.[2] Such reactions have been limited to strained or nucleophilic olefins with sufficient reactivity to intercept the less electrophilic amine complexed heterocumulene which results from the presence of the base required for the dehydrohalogenation of the precursor N-substituted sulfamoyl chloride ($RNHSO_2Cl$). We now wish to report on an alternative method for the requisite dehydrohalogenation which allows synthesis of *N*-sulfonylamines complexed only by weakly nucleophilic solvents and our observations on the cycloaddition reactions of this species which extend its synthetic utility.

Carbomethoxysulfamoyl chloride (**1**) reacts with sodium hydride at −78° in tetrahydrofuran or acetonitrile solution with the evolution of hydrogen to afford salt **2a**.[3] Methyl(carboxsulfamoyl)triethylammonium hydroxide inner salt[2] (**3**), mp 75–76°, is produced when a tetrahydrofuran solution of **2a** is treated with triethylamine at 30°. Structurally analogous salts result from the attempted dehydrohalogenation of **1** with sterically hindered amines, for example, diisopropylethylamine[4] in diethyl ether converts **1** to the unstable salt **2b**.



In tetrahydrofuran solution at 30° **2a** rapidly decomposes to give sodium chloride and the solvent complex of methyl *N*-sulfonylurethan (**4**). This species demonstrates a high degree of electrophilic reactivity in cycloadditions with substituted alkenes to afford the corresponding 2-carbomethoxy-1,2-thiazetidines (**6**),



5 **6** **7**

	R_1	R_2	R_3	R_4
a	Ph	H_x	H_B	H_A
b	*p*-MeOPh	H	H	H
c	Ph	Ph	H	H
d	Me	Me	Me	H
e	H	$-(CH_2)_6-$		H
f	9-carbazolyl	H	H	H
g	1-pyrrolidionyl	H	H	H
h	1-pyrrolidionyl	H	Me	Me
i	1-succinimid ›	H	H	H
j	Ph	H	H	D

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[1] E. M. Burgess and G. M. Atkins, Jr., *J. Amer. Chem. Soc.*, **89**, 2502 (1967).

[2] E. M. Burgess and G. M. Atkins, Jr., *ibid.*, **90**, 4744 (1968).

[3] Attempts to isolate **2a** by removal of the solvent led to the formation of $MeO_2CNSO_2^-N(CO_2Me)SO_2ClNa^+$ and NaCl.

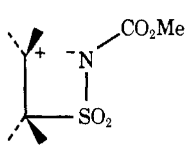
[4] S. Hunig and M. Kiessel, *Chem. Ber.*, **91**, 380 (1958).

Table I. Cycloaddition Product Distribution

Alkene	Temp, °C	Solvent	Mode of addition ratio and melting points (°C) of adducts: **6**	**7**	**8**
5a	4	THF	1 (138–139.5)	4.1 (126–128)	0
	30	THF	1	3.1	0
	4	MeCN	1	1	0
	30	MeCN	1	0.76	0
5b	30	THF	1 (118–119)	1.3 (124–125)	0
5c	30	MeCN	1	0.3	0
	30	THF	1 (175–176)	0	1 (158–159)
5d	30	THF	1 (55–56)	8 (86–87)	0
	30	MeCN	1	1	0
5e	30	THF	0	∞ (143–144)	0
5f	30	THF	0	0	∞ (185–186)
5g	30	THF	0	0	∞ (192–193)
5h	30	THF	∞ (122–123)	0	0
5i	30	THF	0	∞ (157–159)	0

2,3-dihydro-6-methoxy-1,4,5-oxathiazines (**7**), and vinylsulfonamides (**8**).[5] Table I summarizes product distribution and solvent effect for some representative reactions from which a correlation of the (2 + 2) cycloaddition mode with increasing alkene nucleophilicity and solvent dielectric constant is apparent.[6]

The stereospecificity of the addition was probed using as a model substrate *trans*-styrene-β-d_1[7] in tetrahydrofuran at 30° which afforded **6** and **7** in a ratio of 1:3.1 in 72% overall yield. Nmr analysis ($CDCl_3$, 60 MHz) of both adducts after isolation revealed only a two-doublet AX pattern centered at δ 5.06 and 5.84 for a trans disposition of H_A and H_X with J = 5 and 13 Hz for **6** and **7**, respectively, and we were unable to detect any of the cis adducts in the reaction mixture.[8] Identical results were obtained using acetonitrile as a solvent indicating both the (2 + 2) and (2 + 4) cycloadducts are formed completely stereospecifically in different solvents with a large variance in polarity. In principle, the formation of **6** and **7** may be envisaged to result from a concerted thermal[9] ${}_{\pi}2_s + {}_{\pi}2_a$ and ${}_{\pi}2_s + {}_{\pi}4_s$ cycloaddition, respectively, or either may be nonconcerted. Although the observed stereochemical results seem to demand the former, the adduct distribution with solvent change suggests **6** results from closure of a rotationally rigid[10] dipole **9** formed in a nonconcerted overall process while **7** is derived from the concerted alternative.[11] As expected, addition of **4** to acetylenes proceeds exclusively through the (2 + 4) mode (for example, phenylacetylene gives **10**).



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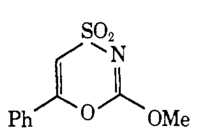

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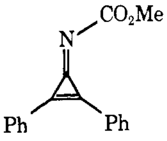
The ability of *N*-carbomethoxysulfonylamine to participate simultaneously and to a comparable extent in both concerted and nonconcerted "polar" stereospecific cycloadditions with certain alkenes is unique among the heterocumulenes examined to date.

Finally, a number of heteroatomic π systems undergo initial (2 + 2) cycloaddition with **4** in tetrahydrofuran at 30° to afford intermediates which spontaneously fragment with the loss of sulfur trioxide in an overall "quasi" Wittig reaction.[12] For example, benzaldehyde gives the corresponding *N*-carbomethoxyimine, diphenylcyclopropenone affords in quantitative yield **11**, mp 193–194° dec, and dimethyl sulfoxide provides the *N*-carbomethoxydimethylsulfimine (**12**), mp 110–111° dec.



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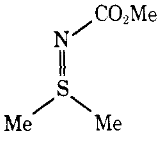

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(5) The stable dioxane complex of sulfur trioxide has been employed in alkene cycloaddition reactions: C. M. Suter, P. B. Evans, and J. M. Kiefer, *J. Amer. Chem. Soc.*, **60**, 538 (1938); F. G. Bordwell and M. L. Peterson, *ibid.*, **76**, 3957 (1954).

(6) The distribution of products was determined by nmr analysis ($CDCl_3$, 60 MHz) of the crude reaction mixture and each component was isolated by fractional crystallization. Consistent nmr and mass spectra as well as correct exact mass and/or elemental analyses were displayed by each product. The appearance of either a 1735 (C=O) or 1605 cm^{-1} (C=N) absorption in the ir spectrum provided an expedient means of differentiating **6** from **7**. The noninterconvertibility of **6** and **7** under the reaction conditions was verified.

(7) T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Amer. Chem. Soc.*, **86**, 4670 (1964).

(8) The nmr spectrum ($CDCl_3$, 60 MHz) of **6** showed an ABX system centered at δ 5.09 (H_X), 4.66 (H_B), and 4.05 (H_A) with J_{AX} = 5, J_{BX} = 8.3, and J_{AB} = 12.5 Hz. Analogously for **7**, signals appeared at δ 5.86 (H_X), 3.72 (H_B), and 3.36 (H_A) with J_{AX} = 11, J_{BX} = 4, and J_{AB} = 14 Hz.

(9) This antarafacial interaction could result from participation of a favorably disposed unoccupied sulfur d orbital with the ethylene components: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Weinheim, West Germany, 1970, pp 163–168.

(10) The conformational integrity is maximized when the 1,4 dipole is internally stabilized by a charge-transfer interaction: R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969).

(11) Where structurally possible the solvent-catalyzed prototropy of **9** gives **8** whose production seems to be proportional to the stability of **9**.

(12) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience, New York, N. Y., 1967, pp 332–337.

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