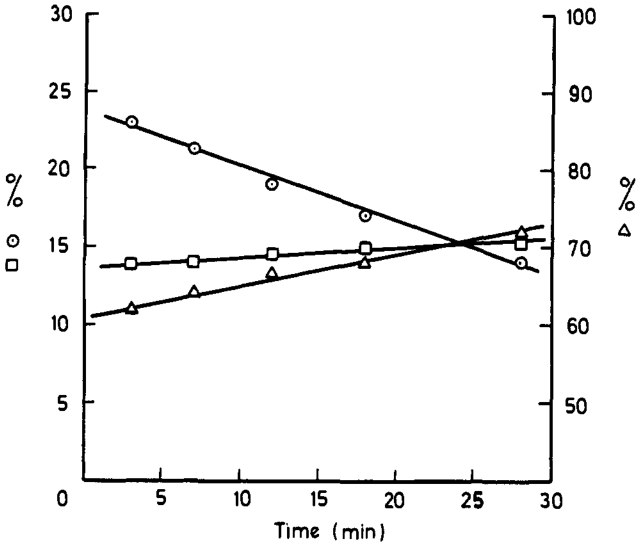
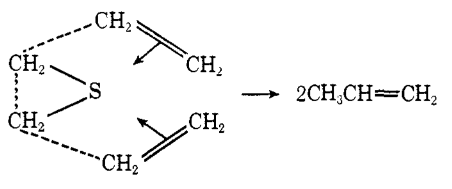


Figure 2. Product distribution on admission of ethylene to a propylene reaction: ⊙, C_2H_4; ◬, C_3H_6; ⊡, C_4H_8.

the sites than higher alkenes. (ii) Reaction 3 is quite rapid when ethylene is added to a system where propylene has already been reacting for some time. (iii) The sites which cause reaction 3 are more labile than those which can only give reactions 1 and 2. (iv) The catalyst is also distinguished from Comox by formation of high yields of pentenes from ethylene at higher temperatures.

The following is an attempt to outline mechanisms involving methylene complexes for reaction 3. The splitting of one ethylene into methylenes, and addition of each of the latter to another ethylene, followed by rearrangement of the resulting trimethylene, seems to be the most straightforward pathway for directly converting ethylene to propylene. However, the possibility that a very different type of mechanism is responsible cannot be discounted. If only two ethylenes are allowed per site then adsorbed methylene is an intermediate. A concerted reaction of three ethylenes per site is also possible. The following diagram attempts to illustrate this without specifying complete details of coordination and bondlng.



The influence of prior addition of propylene is intriguing. Formation of π-allyl complexes is indicated. This would enrich electron density on the metal, thereby enhancing back-donation of charge to π^* orbitals of adsorbed olefin, with consequent easier rupture of ethylene to methylene. In view of the novel arene molybdenum π-allyl derivatives recently described by Green and coworkers,[4] it is possible that allyl and three ethylenes are ligands of one molybdenum which is attached to the support by coordination to one or two oxide or hydroxide ions. π-Allyl could also be the key intermediate in the addition of ethylene to propylene, giving pentenes.

Pettit[5] has argued that the transition state in olefin metathesis is a tetracarbene–metal complex rather than an adsorbed "cyclobutane." Thus, reaction 3 may also have significance in attempting to prove whether carbene complexes can form from olefins on such catalysts, even though the site responsible for different reactions may not be identical.

Acknowledgments. P. P. O'N thanks the Northern Ireland Ministry of Education for a Research Studentship.

---

(4) M. L. H. Green, J. Knight, L. C. Mitchard, G. C. Roberts, and W. E. Silverthorn, *Chem. Commun.*, 1619 (1971).

(5) G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 789 (1971).

P. P. O'Neill, J. J. Rooney*
Department of Chemistry, The Queen's University
Belfast, BT9 5AG, Northern Ireland
Received February 19, 1972

Sodium Magnetic Resonance in Lyotropic Nematic Phases and the Implications for Observation in Living Systems

Sir:

Flautt and Lawson[1] have described the first lyotropic nematic phase which could be used as a solvent for oriented molecule nmr spectra.[2,3] The recommended phase corresponds to the middle soap structures[4,5] in a ternary phase to which sodium sulfate was added for ease of preparation. The ordering of the nematic structure of the phase in a magnetic field has a long relaxation time of several hours and the optic axis is perpendicular to the magnetic field direction.[1] We have investigated the ^{23}Na nmr signals at 8.0 MHz in this phase with and without the addition of sodium sulfate. Typical results are presented in Figure 1. In a ternary phase without addition of sodium sulfate, the signal is a triplet of intensity ratios 3:4:3 arising from an incompletely averaged quadrupole interaction tensor,[6] first order with respect to a nuclear Zeeman splitting. The separation of the outer components of the triplet is given by[6]

$$\Delta\nu = \nu_Q\langle 3\cos^2\theta - 1\rangle = 2\nu_Q S_{zz} \qquad (1)$$

ν_Q is half the quadrupole coupling constant (e^2qQ/h) and θ is the angle between the magnetic field and the principal axis of the electric field gradient (EFG) tensor (axial symmetry). S_{zz} represents the degree of orientation of the EFG axis. The central peak of this triplet is 40% the intensity of the signal from the same concentration sodium ion in water, which has no quadrupole splitting. The intensity of the outer transitions is thus properly accounted for with a ratio 3:4:3. On first observation when inserted into the magnet there is some evidence of the "powder type" spectrum in which the two outer components are broadened and the derivative curve tails toward the central peak. The central peak is always sharp, since it is unaffected by any randomization of the direction of partially averaged

---

(1) K. D. Lawson and T. J. Flautt, *J. Amer. Chem. Soc.*, **89**, 5489 (1967).

(2) K. D. Lawson, P. J. Black, and T. J. Flautt, *Mol. Cryst. Liquid Cryst.*, 7, 201 (1969).

(3) K. D. Lawson and T. J. Flautt, *J. Phys. Chem.*, **72**, 2066 (1968).

(4) V. Luzzati, H. Mustacchi, and A. Skoulis, *Discuss. Faraday Soc.*, **25**, 43 (1958).

(5) L. Mandell, Krister Fontell, and P. Ekwall, *Advan. Chem. Ser.*, No. **63**, 89 (1967).

(6) M. H. Cohen and F. Reif, *Solid State Phys.*, *Suppl.*, **5**, 321 (1962).

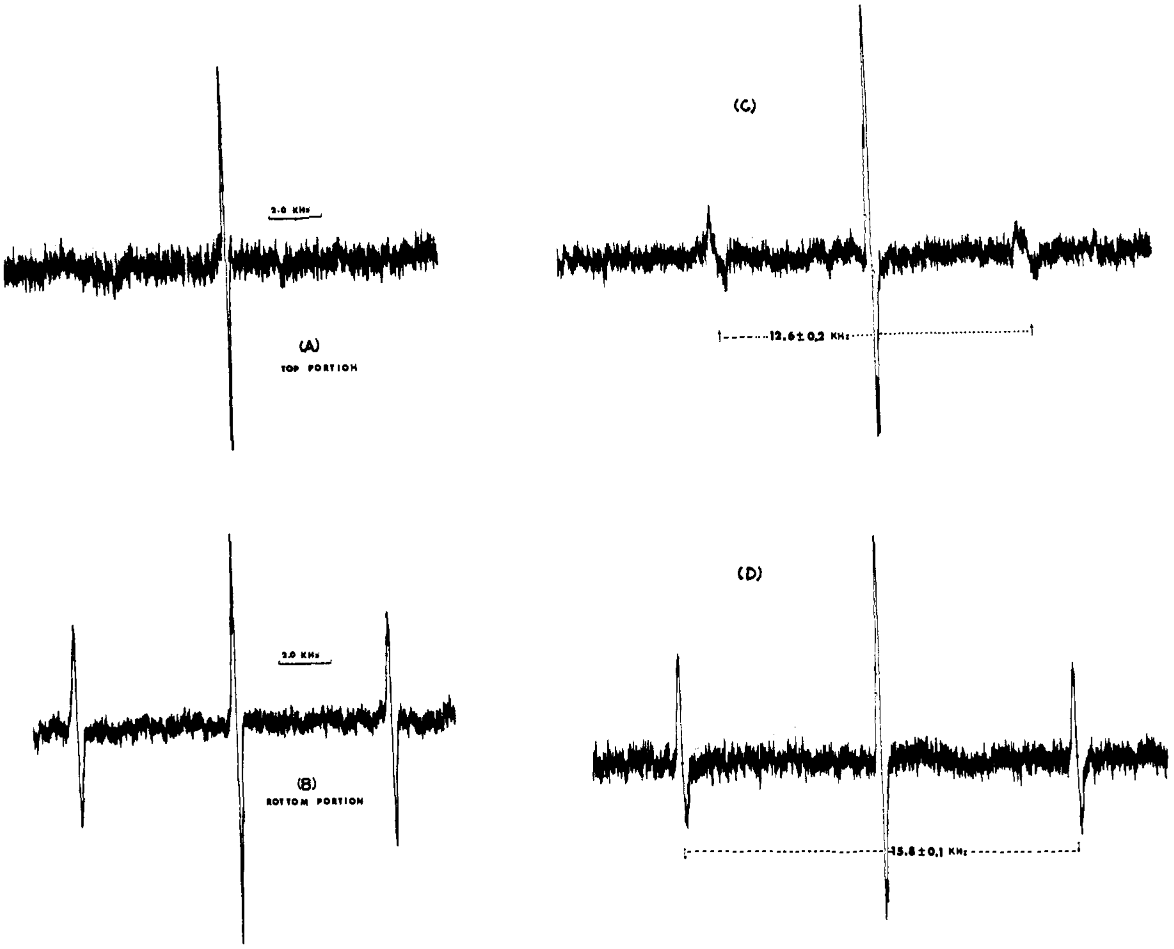


Figure 1. Sodium-23 nuclear magnetic resonance signals in lyotropic nematic phases; frequency 8.0 MHz. The temperature of the probe was 26.4 ± 0.1°. All spectra were recorded with the same gain and modulation settings. (A) Signal from upper layer of the two-phase system whose overall composition was (wt %): 35.0% sodium decyl sulfate (SDS), 7.0% decyl alcohol (DA), 51.0% water (as H_2O), 7% Na_2SO_4 (anhydrous). The only observable resonance has the same half-width within experimental error as the central components in (B), (C), and (D); all are slightly modulation broadened. The existence of other transitions is inferred from intensity comparisons, *cf.* (C), and hence this signal arises from sodium ion in an ordered environment. (B) Signals from the lower layer of the two-phase system described in (A). The separation of the outer observable transitions is 12.6 ± 0.2 kHz as in (C). This phase is composed of a solution of sodium sulfate in the pure ternary phase (D). Intensity ratios are 3:4:3 in agreement with a first-order quadrupolar splitting and the almost uniform line widths of the outer and central peaks indicate uniform ordering throughout the sample. (C) The ^{23}Na signal in the composite two-phase system represented by (A) and (B) before separation into two layers. Inhomogeneity of ordering is reflected in the width of the outer transitions. As in (B) the separation of peaks is 12.6 ± 0.2 kHz. The intensity of the central peak is 40% that of an equimolar aqueous sodium ion solution. The intensity ratios of the three observable peaks are not 3:4:3. The outer components are much less intense than this ratio indicates. The "hidden sodium" is associated with the top layer on phase separation, see (A). (D) Spectrum of the ^{23}Na resonance in the pure ternary phase with no added sodium sulfate: 38.1% SDS, 7.6% DA, 54.3% H_2O. The outer components are sharp, indicating homogeneity of ordering throughout the sample. Intensity ratios are 3:4:3 and the central peak is 40% as intense as an equimolar aqueous Na^+ solution.

order in the sample. The degree of orientation S_{zz} is the ratio of the splitting to the nonaveraged quadrupole coupling constant $2\nu_Q$. Estimating ν_Q as about 0.8 MHz for ^{23}Na[7] from measurements in the solid state gives a degree of orientation of the EFG axis in this nematic phase for the sodium ion of ~0.02. This is typical for a solute molecule in the phase rather than of the phase itself where the degree of orientation associated with the optic axis of the liquid crystal is of the order 0.3–0.5.[8] The sodium ion can be regarded as similar to a solute such as methanol, benzene, or ethylene carbonate[9] with respect to its degree of orientation. There is rapid translational diffusion, but part of the character of the anisotropic tumbling of the molecules of the phase itself is imposed on the sodium ion, possibly in transient ion pair formation with the outer surface of the polar sulfate groups which are arranged cylindrically in a hexagonal packing.[4,5,8] It is expected that the sodium ions will reside in the interstitial water region of the phase, which is itself ordered.[1] The origin of the first-order quadrupolar splitting is a rapidly exchanging mobile sodium ion which for a small fraction of the total time is attached to polar groups which are highly ordered. This fulfills some of the conditions necessary for a biological function of the sodium ion[10] especially in respect of ordering and mobility.

(7) T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, **1**, 1 (1958).

(8) G. H. Brown, J. W. Doane, and V. D. Neff, "A Review of the Structure and Physical Properties of Liquid Crystals," Chemical Rubber Publishing Co., Cleveland, Ohio, 1971.

(9) S. A. Barton, M. A. Raza, and L. W. Reeves, *J. Magn. Resonance*, in press.

(10) R. J. P. Williams, *Quart. Rev., Chem. Soc.*, **24**, 331 (1970).

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.

Acknowledgment. This research was supported by the Defence Research Board and the National Research Council of Canada in grants to L. W. Reeves.

[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).

D. M. Chen, L. W. Reeves*
The Chemistry Department, University of Waterloo
Waterloo, Ontario, Canada

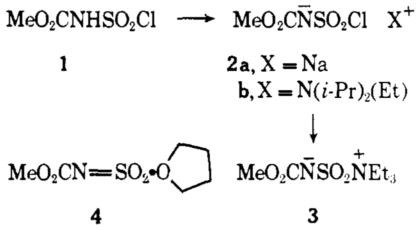
Received Feburary 18, 1972

Cycloaddition Reactions of *N*-Sulfonylamines

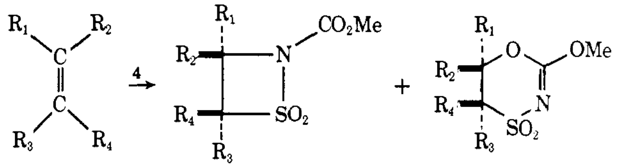
Sir:

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

---

[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).