

Table II. Physical Properties of Compounds 5 and 6^a

mp, °C	NMR (CDCl ₃), δ	IR, cm ⁻¹	MS
5b 89.5-90.5	7.5-6.9 (m, 5 H), 4.06 (s, 3 H), 3.98 (s, 3 H), -0.08 (s, 9 H)	2950 (m), 1655 (s), 1645 (s), 1630 (s), 1570 (m), 1450 (m), 1265 (s), 1245 (m), 1100 (s), 840 (s)	316 (43%, EI), 317 (60%, CI)
5c oil	4.00 (s, 3 H), 3.95 (s, 3 H), 2.54 (br t, 2H, J = 7 Hz), 1.5-1.2 (m, 4 H), 0.92 (brt, 3 H, J = 7 Hz), 0.30 (s, 9 H)	2940 (s), 1635 (s), 1575 (m), 1450 (m), 1240 (s), 1190 (m), 1110 (s), 1060 (s), 840 (s)	296 (68%, EI), 297 (91%, CI)
5d 59.5-60	7.5-6.9 (m, 5 H), 3.95 (s, 3 H), 3.90 (s, 2 H), 3.82 (s, 3 H), 0.32 (s, 9 H)	2920 (m), 1630 (s), 1525 (m), 1445 (m), 1245 (s), 1185 (m), 1115 (s), 1080 (m), 840 (s)	330 (7%, EI), 331 (100%, CI)
5e oil	4.47 (s, 2 H), 3.98 (s, 3 H), 3.97 (s, 3 H), 0.32 (s, 9 H), 0.14 (s, 9 H)	2940 (s), 1630 (s), 1580 (m), 1450 (m), 1310 (m), 1250 (s), 1190 (m), 1120 (s), 1080 (s), 840 (s)	342 (14%, EI), 343 (54%, CI)
5f oil	4.52 (brd, 2 H, J = 7 Hz), 4.02 (s, 3 H), 3.97 (s, 3 H), 2.49 (brt, 1 H, J = 7 Hz), 0.33 (s, 9 H)	3600-3100 (s), 2940 (s), 1660-1620 (s), 1580 (s), 1445 (s), 1250 (s), 1190 (s), 1120 (s), 1080 (s), 845 (s)	270 (10%, EI), 271 (15%, CI)
6a 68.5-69.5	¹ H (CDCl ₃) 4.36 (q, 2 H, J = 7 Hz), 4.27 (s, 6 H), 1.35 (t, 3 H, J = 7 Hz), 0.28 (s, 9 H); ¹ H (C ₆ D ₆) 4.32 (q, 2 H, J = 7 Hz), 3.62 (s, 3 H), 3.59 (s, 3 H), 1.18 (t, 3 H, J = 7 Hz), 0.44 (s, 9 H); ¹³ C (CDCl ₃) 184.9, 182.8, 170.6, 153.2, 151.8, 135.4, 61.1, 60.1, 60.0, 14.2, -1.3	2940 (m), 1720-1675 (s), 1630-1590 (s), 1430 (m), 1325 (s), 1215 (s), 1150 (s), 1090 (s), 1020 (m), 840 (s)	312 (7%, EI), 313 (16%, CI)
6b 95-95.5	¹ H (CDCl ₃) 7.4-7.2 (m, 3 H), 6.9-6.7 (m, 2 H), 4.25 (s, 3 H), 4.14 (s, 3 H), 0.11 (s, 9 H); ¹³ C (CDCl ₃) 186.3, 184.2, 163.5, 151.7, 151.6, 142.1, 134.2, 127.7, 126.2, 124.6, 59.9, 59.8, -0.4	2940 (w), 1675 (s), 1620 (s), 1460 (m), 1330 (s), 1070 (s), 835 (s)	316 (11%, EI), 317 (100%, CI)

^a Analytical data are all in agreement with the presented structures.

5 and 6. Such migration of a silyl moiety from oxygen to carbon is rare.⁴ However, here it is viewed as being a favorable transformation since such would result in the conversion of zwitterionic intermediates to neutral products. Finally it is noted that the suggested intermediates 3 and 4 are unique. Zwitterion 3 is of particular note since it can be considered as the polar form of a strained cyclic allene.⁵

The cyclobutenones 1a-e were readily prepared from dimethyl squarate.⁶ Thus, treatment of this ester with the pertinent lithium acetylde (-78 °C, THF) followed by quenching with trimethylsilyl chloride resulted in the formation of the cyclobutenones. The crude products were vacuum filtered through Florisil using hexanes-ethyl acetate mixtures to give the purified products in yields ranging from 72% to 88%. The hydrolytic lability of these products precluded their further purification. However, their spectral properties are in agreement with the assigned structures.⁷

The following experimental procedure for the conversion of 1c to 5c is typical. A 20-mL solution of 0.50 g of 1c in *p*-xylene was refluxed under argon for 2 h. During this time the initially colorless solution became dark orange. Analysis of the reaction mixture by TLC showed the presence of one major yellow product which gave an immediate blue spot (positive quinone test) upon treatment with leucomethylene blue solution. Removal of the solvent left a reddish oil. The product was purified by flash chromatography (silica gel, hexanes-ethyl acetate 9:1) to give 5c as a dark orange oil in 75% yield.

In conclusion, we wish to note the significant points of this study: (1) A general synthetic route to (2-alkynylethenyl)ketenes of structural type 2 from dimethyl squarate is now available. (2) Such ketenes readily undergo ring closure and this can be controlled to provide a unique and useful synthesis of trimethyl-

silyl-substituted quinones, a rare class of compounds.⁸ (3) The zwitterionic intermediates 3 and 4 are unique. (4) Finally it is noted that the formation of 5e is of particular interest since it suggests that propargyl alcohols can be utilized in a simple and potentially general route to quinones having those structural features deemed necessary for bioreductive alkylating agents.⁹

Acknowledgment. We thank the National Institutes of Health (CA-11890, AI-15651) and the National Science Foundation (CHE 80-25567) for financial support of this work.

(8) Hashimoto, T. *Yakugaku Zasshi* 1967, 87, 535. Bock, H.; Alt, H. *Angew. Chem., Int. Ed. Engl.* 1967, 6, 941. Razuvaev, G. A.; Vasileiskaya, N. S.; Gorbunova, L. V.; Chevnikova, G. V.; Bortnikov, G. N. *Izv. Akad. Nauk. SSSR Ser. Khim.* 1971, 20, 2392. Vasileiskaya, N. S.; Gorbunova, L. V.; Mamysheva, O. N.; Bortnikov, G. N. *Ibid.* 1972, 21, 2755. Vasileiskaya, N. S.; Gorbunova, L. V.; Mamysheva, O. N.; Makarenko, N. P.; Bortnikov, G. N. *Ibid.* 1975, 24, 2770.

(9) Moore, H. W.; Czerniak, R. *Med. Chem. Rev.* 1981, 1, 249.

Hydrolysis of Mustard Derivatives. Failure of the Raber-Harris Probe in Predicting Nucleophilic Assistance

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Received January 15, 1985

Several years ago Raber, Harris (RH), and co-workers¹ presented convincing evidence that nucleophilic solvent assistance could be detected by analysis of plots of solvolytic rates ($\log k$) of a substrate against those of 1-adamantyl bromide in aqueous ethanols and trifluoroethanols. A single correlation line was shown to be characteristic of substrates reacting by k_c and k_d mechanisms while separate aqueous ethanol and aqueous trifluoroethanol correlation lines were observed for k_s substrates. The method gave excellent predictions for several well-understood reactions, and upon application to controversial substrates,² predictions were made which agreed with a large body of data. Since then the RH

(1) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. M. *J. Am. Chem. Soc.* 1978, 100, 8137.

(2) Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *J. Am. Chem. Soc.* 1978, 100, 8147.

(4) Mora, J.; Costa, A. *Tetrahedron Lett.* 1984, 3493. Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *Organometallics* 1984, 3, 1583. Anderson, G.; Cameron, D. W.; Feutrill, G. I.; Read, R. W. *Tetrahedron Lett.* 1981, 4347.

(5) For example, earlier work has suggested that 1,2-cyclohexadiene may contain a planar zwitterionic structure (Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* 1970, 92, 5469. Bottini, A. T.; Hilton, L. L.; Plott, J. *Tetrahedron* 1975, 31, 1997. Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II *Ibid.* 1972, 28, 4883. Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* 1974, 96, 779). However, more recent investigations have cast doubt on that view and have predicted the diradical to be of lower energy than a zwitterion: Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* 1985, 107, 532. Balci, M.; Jones, W. M. *Ibid.* 1980, 102, 7607. Thus, intermediates 3 and 4 may be diradical rather than dipolar in character.

(6) Cohen, S.; Cohen, S. G. *J. Am. Chem. Soc.* 1966, 88, 1533.

(7) The possibility of 1,4-addition of the lithium reagent leading to 4-alkynyl-3,4-dimethoxy-2-(trimethylsilyloxy)cyclobutenone was ruled out from NMR spectral data. That is, both methoxy signals appear at approximately 4 ppm indicating that they are both situated on a double bond.

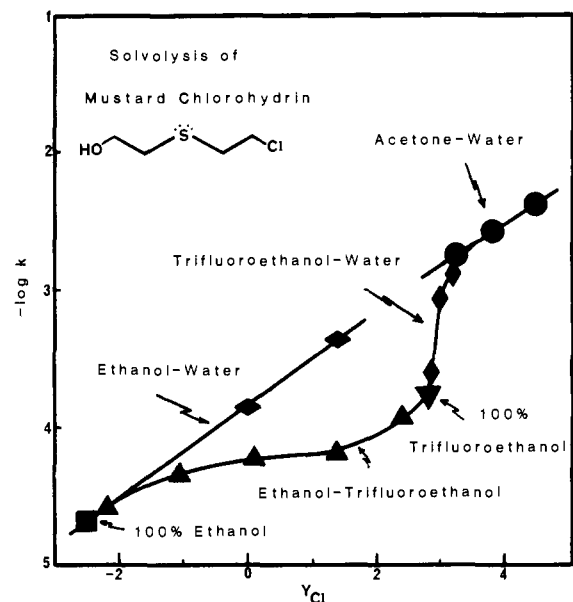
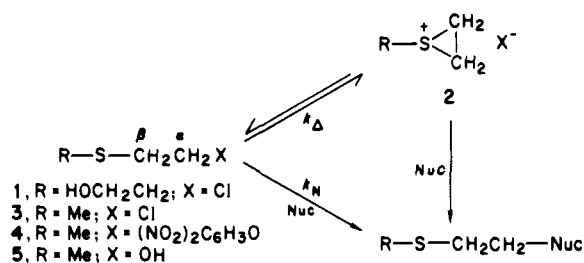


Figure 1. Plot of the logarithms of the rate constants for solvolysis of mustard chlorohydrin (**1**) in various solvents vs. the solvent ionizing power, Y_{Cl} .

Scheme I



method has been applied by several groups³ and is generally recognized as a reliable tool for detecting nucleophilic solvent participation.^{4,5} We wish to report a failure of this method and thus to point out that the method is susceptible to factors previously overlooked.

Mustard chlorohydrin (**1**) has been considered a classical example of a substrate that undergoes hydrolysis with anchimeric assistance by sulfur, a k_A process.⁶ However, when **1** is evaluated utilizing the RH method, nucleophilic solvent participation is strongly indicated by the separate correlations provided by rates of solvolysis of **1** in aqueous ethanols or acetones and aqueous trifluoroethanols⁷ (Figure 1). This finding is surprising in view of the kinetic studies of Bartlett and Swain⁸ which showed that highly nucleophilic anions, such as thiophosphate ion, produce no increase in the rate of chloride ion displacement from **1**. Were Bartlett and Swain wrong in concluding that added nucleophiles do not produce a rate increase with **1** or is the RH method giving a false prediction? To answer these questions we have looked more carefully at solvent effects on the reactivity of **1**, used additional probes for direct nucleophilic assistance (k_N) in the displacement of chloride from **1** (Scheme I), carefully investigated the extent of sulfonium ion **2** involvement using deuterium-labeled mustard analogues, and obtained additional evidence on the reversibility

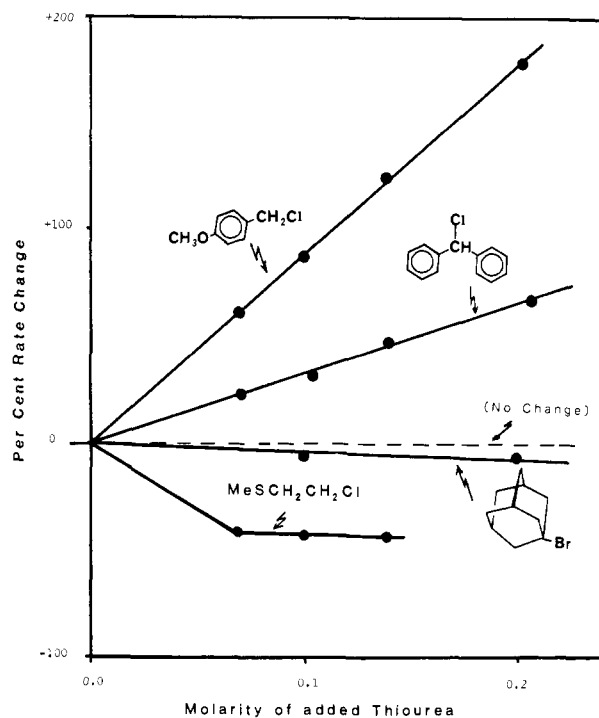


Figure 2. Plot of percent rate change as a function of added thiourea. Benzhydryl and *p*-methoxybenzyl chlorides were run at 19.4 °C in 70% aqueous acetone (v/v);¹² methylthioethyl chloride was reacted at 24.9 °C in 70% aqueous acetone (v/v) and 1-bromoadamantane was reacted at 49.8 °C in 50% aqueous acetone (v/v).

of sulfonium ion formation from **1**.

We have further investigated solvent effects on the rate of hydrolysis of **1** by determining solvolytic rate constants of **1** in mixtures of ethanol and trifluoroethanol. These data are included in Figure 1 and reveal that the aqueous trifluoroethanol data are not in error. Instead, rates in the binary mixtures of trifluoroethanol and ethanol fall on a uniquely shaped curve between the pure solvents.⁹⁻¹¹ In assessing sensitivity to nucleophilicity, we wanted to avoid charged nucleophiles because of possible salt effects on rates and on the stability or reactivity of **2**. Queen¹² and McLennan¹³ have shown that neutral nucleophiles such as thiourea are sensitive probes for direct nucleophilic displacement. In fact we find that a linear relationship exists between the percent rate increase observed for substrates reacting with nucleophilic assistance and thiourea molarity (Figure 2). However, 1-adamantyl bromide, which cannot undergo direct nucleophilic displacement, and the mustard derivative **3** show a depressed solvolytic rate upon addition of thiourea (Figure 2). The retardation presumably results from thiourea reducing the ionizing power of the medium.⁵ The conclusion is obvious: Bartlett and Swain were correct in their assessment of the insensitivity of **1** to added nucleophiles.

When either α,α -*d*₂ or β -*d*₁ (methylthio)ethyl dinitrophenolate (**4**)¹⁴ is subjected to hydrolysis for variable numbers of half-lives in either 50% (v/v) aqueous acetone or 50% (v/v) aqueous ace-

(3) (a) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 1954; (b) Shiner, V. J.; Rutkowske, R. D. *Abstr. Pap.—Am. Chem. Soc.* **187th**, **1984**, ORGN 061; (c) McLennan, D. J.; Martin, P. L. *J. Chem. Soc., Perkin Trans 2* **1982**, 1091.

(4) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89.

(5) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 2.

(6) Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum Press: New York, 1976; Vol. 1.

(7) Harris, J. M.; Paley, M. S.; Hovanes, B. A.; McManus, S. P., unpublished results.

(8) Bartlett, P. D.; Swain, C. G. *J. Am. Chem. Soc.* **1949**, *71*, 1406.

(9) Previously unreported Y_{Cl} values were determined by the procedure of Bentley and Carter¹⁰ using their reported rate for solvolysis of 1-adamantyl chloride in 80% aqueous EtOH. The values in 70–100% TFE in binary mixtures of TFE–EtOH were determined by extrapolating rates to 25 °C from rates measured at higher temperatures. The remaining values were extrapolated from the linear relationship ($r = 0.997$) of Y_{Br} at 35 °C¹¹ and Y_{Cl} values for 100% TFE, 90% TFE–EtOH, 70% TFE–EtOH, and 100% EtOH.

(10) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.

(11) Kaspi, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1980**, *102*, 3829.

(12) Queen, A. *Can. J. Chem.* **1979**, *57*, 2646.

(13) McLennan, D. J. *Tetrahedron Lett.* **1975**, 4689.

(14) All new compounds have been fully characterized by elemental analysis, IR, and NMR. The deuterated derivatives **4** were prepared from the respective alcohols without detectable label scrambling. However, conversion of the deuterated alcohol to the respective chloride (using a variety of procedures) gave chloride with the label equally at the α and β positions.

tonitrile, the extent of label scrambling, determined from analysis of the 300-MHz ^1H NMR spectra,¹⁵ can be used to test for formation of the sulfonium ion intermediate and for return to neutral substrate. The average of seven hydrolysis experiments allowed us to determine that complete (100.2 \pm 3.0%) rearrangement has occurred in the product alcohol **5**. These same experiments show that ion pair return is a facile process.

There are two possible reasons for the failure of the RH method. First, return from sulfonium ions to neutral substrate may be more important in trifluoroethanol, a solvent of low nucleophilicity, than in the more nucleophilic water or ethanol. Second, recent evidence^{13,16-21} suggests that electrophilic factors, especially in fluorinated solvents, have been inadequately treated in classical solvolytic theory. Thus, mustard chlorohydrin **1** and 1-adamantyl chloride may respond differently to changes in electrophilicity. In particular, 1-adamantyl chloride may be more susceptible to electrophilic solvation than mustard chlorohydrin **1**, or solvation of the neighboring sulfur group by highly electrophilic solvents like trifluoroethanol may reduce the effectiveness of the sulfur's anchimeric assistance. We are evaluating these factors further and will report our findings in future articles.

Acknowledgment. Support of this research by the U. S. Army Research Office (DAAG29-82-K-018) is gratefully acknowledged. We also thank Dr. Charles Watkins for obtaining the 300-MHz NMR spectra.

Registry No. **1**, 693-30-1.

(15) Chemical shifts (ppm) for the methylene protons for **4** in 50% aqueous acetone are δ 2.69 (SCH₂) and 4.60 (CH₂) and those for alcohol **5** are δ 3.00 (SCH₂) and 3.74 (CH₂).

(16) McManus, S. P.; Zutauf, S. E. *Tetrahedron Lett.* **1984**, 25, 2859; *Isr. J. Chem.*, in press.

(17) Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, 46, 3053.

(18) Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, 105, 502.

(19) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* **1984**, 49, 3639.

(20) Peterson, P. E.; Vidrine, D. W.; Waller, F. J.; Henrichs, P. M.; Magaha, S.; Stevens, B. *J. Am. Chem. Soc.* **1977**, 99, 7968.

(21) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, 23, 4635.

Liquid Crystals and Plastic Solids. A Carbon-13 NMR Study

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Received December 10, 1984

Liquid crystals have local orientational order but positional disorder. Plastic crystals have positional order but orientational disorder. Molecules in plastic crystals undergo rapid rotational motion around one or more axes.¹ Unlike regular polycrystalline solids, plastic crystals without magic angle spinning can show high-resolution ^{13}C or ^{31}P NMR spectra with little or no broadening due to chemical shift anisotropy.²

Some liquid crystals containing one or two cyclohexane rings have interesting properties, such as low-temperature nematic phases³ and negative magnetic anisotropy.⁴⁻⁶ We have found that

(1) Dunning, W. J. In "The Plastically Crystalline State"; Sherwood, J. N., Ed.; Wiley: Chichester, 1979; p 1.

(2) Boden, N. In "The Plastically Crystalline State"; Scherwood, J. N., Ed.; Wiley: Chichester, 1979; p 147.

(3) Eidenschink, R. *Mol. Cryst. Liq. Cryst.* **1983**, 94, 119.

(4) Khetrpal, C. L.; Kunwar, A. C. *Mol. Cryst. Liq. Cryst.* **1981**, 72, 13.

(5) Khetrpal, C. L.; Kunwar, A. C. *Chem. Phys. Lett.* **1981**, 81, 170.

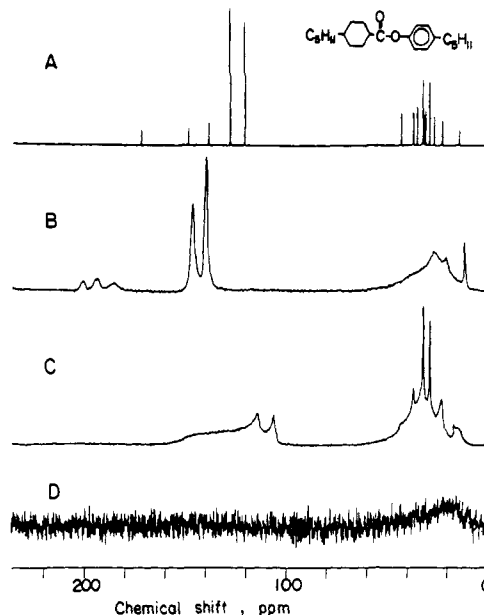


Figure 1. Carbon-13 NMR spectra of **I** at 75.4 MHz: (A) 50 °C, (B) 40 °C, (C) 22 °C with gradual cooling of (B) (1 °C/min) in a water bath, (D) 22 °C with sudden cooling of (B) in an ice bath. The decoupler power was $\gamma\text{B}_2/2\pi = 12$ kHz and an ALPHA decoupling sequence¹¹ was used for (B), (C), and (D). The solid spectra (C and D) were taken without spinning.

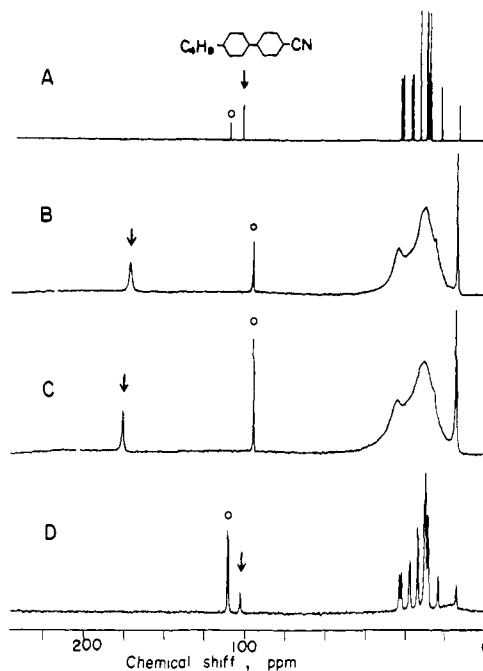


Figure 2. Carbon-13 NMR spectra of **II** with 3.4% benzene at 75.4 MHz: (A) 65 °C, (B) 45 °C, (C) 30 °C, (D) 11 °C with gradual cooling (1 °C/min) from (C). The decoupler power was $\gamma\text{B}_2/2\pi = 12$ kHz and an ALPHA decoupling sequence¹¹ was used for (B), (C), and (D). The solid spectrum (D) was taken without spinning. The arrows indicate the CN peak of the solvent and the circles indicate the benzene peak.

some of these compounds can form plastic solids through the nematic or smectic phase.

A compound that exhibits this behavior is 4-pentylphenyl *trans*-4-pentylcyclohexane/carboxylate (**1**; S1497 from EM Chemicals, Hawthorne, NY). It has a solid-nematic transition at 37 °C and a nematic-liquid transition at 47 °C. The ^{13}C NMR

(6) Khetrpal, C. L.; Yeh, H. J.; Saupe, A. *Mol. Cryst. Liq. Cryst.* **1984**, 92, 243.