

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.

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

(15) Chemical shifts (ppm) for the methylene protons for **4** in 50% aqueous acetone are δ 2.69 (SCH_2) and 4.60 (CH_2) and those for alcohol **5** are δ 3.00 (SCH_2) and 3.74 (CH_2).

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

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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

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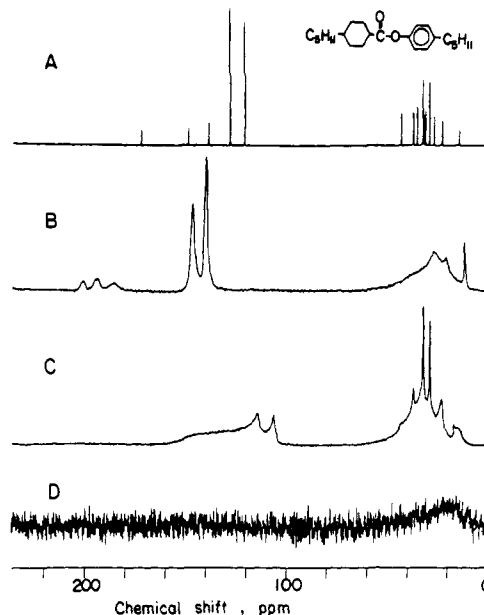


Figure 1. Carbon-13 NMR spectra of **I** at 75.4 MHz: (A) 50 °C, (B) 40 °C, (C) 22 °C with gradual cooling of (B) (1 °C/min) in a water bath, (D) 22 °C with sudden cooling of (B) in an ice bath. The decoupler power was $\gamma B_2/2\pi = 12$ kHz and an ALPHA decoupling sequence¹¹ was used for (B), (C), and (D). The solid spectra (C and D) were taken without spinning.

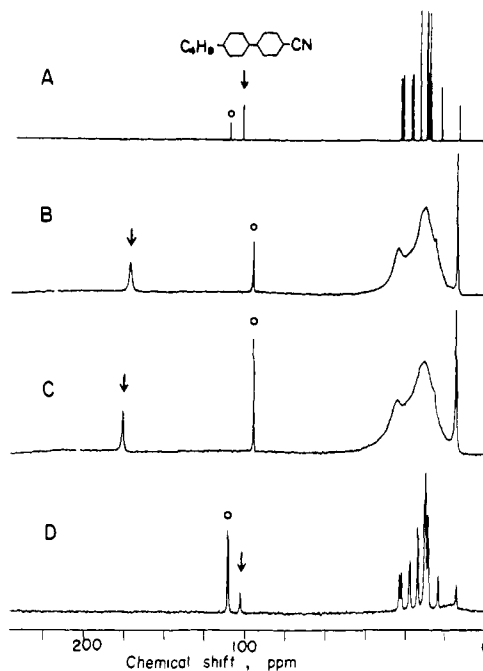


Figure 2. Carbon-13 NMR spectra of **II** with 3.4% benzene at 75.4 MHz: (A) 65 °C, (B) 45 °C, (C) 30 °C, (D) 11 °C with gradual cooling (1 °C/min) from (C). The decoupler power was $\gamma B_2/2\pi = 12$ kHz and an ALPHA decoupling sequence¹¹ was used for (B), (C), and (D). The solid spectrum (D) was 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 (**I**; 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

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spectra of I at 75.4 MHz are shown in Figure 1. When the compound was cooled from the isotropic phase to the nematic phase, large anisotropic shifts were observed (Figure 1B). When the nematic phase of I was gradually cooled (1 °C/min) to the solid phase, the aliphatic peaks moved downfield and the aromatic peaks moved upfield (Figure 1C). In the meantime some of the aliphatic peaks became very sharp. The polycrystalline state of I formed by rapid cooling gave a featureless broad spectrum (Figure 1D) using the same spectrometer setting.

A single crystal can show sharp ¹³C peaks,^{7,8} but this is not likely to be the case for the spectrum in Figure 1C. When the solid was formed by slow cooling in the superconducting magnet, in an electromagnet, or outside a magnet, there were no changes in the chemical shifts of the ¹³C peaks. Since the molecules in the nematic phase of I aligned differently in the three situations, it is highly unlikely that a single crystal with the same orientation was formed under these different conditions.

The major contribution to the aromatic part of the spectrum in Figure 1C may be due to the 2- and 3-carbons in the benzene ring, because the 1- and 4-carbons and the carbonyl carbon are not protonated and have low intensities (Figure 1A,B). The spectral shape appears like the superposition of two powder-pattern signals with axial symmetry. The anisotropy (<5/ ppm) is considerably smaller than that of normal aromatic compounds (>200 ppm).^{8,9} The appearance of the rather narrow "powder-pattern" spectrum is probably due to some kind of motional averaging, possibly a rotation about the para-substituted axis. This feature plus the sharpness of some of the aliphatic peaks led us to believe that the molecules in I undergo rapid but anisotropic rotations after they are gradually solidified from the nematic phase.

A more dramatic case is 1-(*trans*-4-*n*-butylcyclohexyl)-*trans*-4-cyanocyclohexane (II; ZLI 1538 from EM Chemicals). It has a smectic phase from 28 to 54 °C and a nematic phase from 54 to 78 °C. Gradual cooling of II itself from isotropic to nematic to smectic to solid always resulted in a normal polycrystalline solid which gave an extremely broad, featureless ¹³C spectrum without magic angle spinning. However, when a small amount of benzene (≥3%) was dissolved in II, the liquid crystal solution formed a plastic solid upon gradual cooling. The temperatures of phase transitions for a sample with 3.4% benzene were lowered to 28,

39, and 68 °C, respectively, as determined by differential scanning calorimetry (DSC). The carbon-13 spectra of the four phases of this sample are shown in Figure 2. The solid-state spectrum without sample spinning (Figure 2D) is almost identical with that of the isotropic liquid, except with larger line widths (ca. 50 Hz). Again, the spectrum of the solid state did not change with the cooling condition (inside the superconducting magnet, in an electromagnet, or outside a magnet). The proton spectra of this sample in the nematic and smectic phases show the usual splitting pattern of benzene due to partial orientation.¹⁰ The solvent peak has widths of 3000 and 3400 Hz, respectively, which are somewhat less than that of many other liquid crystals. Upon solidification with gradual cooling to 11 °C, the width of the aliphatic protons in II is reduced to 360 Hz and the benzene peaks collapse to one peak with a width of 200 Hz. Thus, the features in the ¹³C and ¹H spectra of II with 3.4% benzene suggest that a plastic solid was formed.

The plastic phase of I and II seems to be a metastable phase, which is not unusual for plastic crystals.¹ When the samples were suddenly cooled from the liquid-crystalline phase or when the plastic solids were further cooled to temperatures 20–30 °C below the freezing points and then warmed up again, "hard" polycrystalline solids were formed as judged from the carbon-13 NMR spectra. We were not able to detect a clear transition between the plastic solid and the ordered solid with DSC.

In view of the molecular structures of I and II, the formation of plastic solids is quite surprising. In the crystal phase, the molecules are elongated and locally aligned. When plastic crystals of I and II are formed, the ¹³C spectra seem to indicate that the molecules do not merely rotate about their long axes. Molecular models show that they can coil up and undergo less restricted rotations. Whether this is true remains to be determined. We are also trying to determine whether the plastic solids of I and II are crystals or glasses.

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