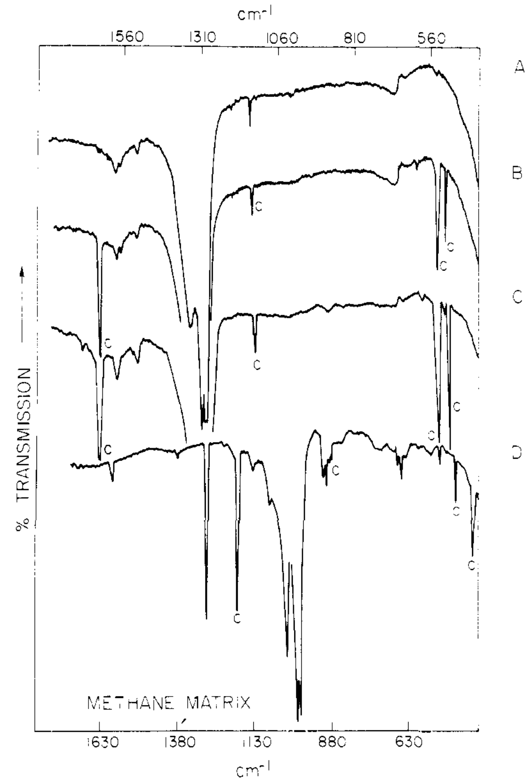

**Figure 1.** Infrared spectra of the reaction products of iron atoms with methane. Spectrum A was recorded after trapping iron atoms vaporized at 1450 °C into a methane matrix. Spectrum B was recorded after photolysis with λ > 330 nm. Spectrum C was recorded after trapping iron atoms vaporized at 1410 °C into a 95% [$^{13}$C]methane matrix with irradiation during trapping. Spectrum D was recorded after trapping iron atoms vaporized at 1410 °C into a 95% deuteriomethane matrix with irradiation during trapping. Absorptions labeled C are product bands.

**Table I.** Product Band Positions (cm$^{-1}$) in Photoexcited Metal Atom/Methane Reactions

| metal atom | band positions, cm$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | $\nu_{C-H}$ | $\nu_{M-H}$ | $\nu_{CH_3}$ | | $\nu_{M-C}$ |
| manganese | 2932.9 | 1582.6 | 1142.3 | 550.3<br>546.2 | 500.7 |
| iron | 2933.5<br>2908.6 | 1653.1 | 1153.4 | 548.8<br>545.9 | 521.1 |
| cobalt | | 1699.5 | | 585.4<br>576.7 | 527.5 |
| copper | | 1855.7 | 1200.1 | 613.8 | 433.9<br>417.4 |
| zinc | | 1845.8 | 1069.5 | 689.1 | 447.1 |
| silver | 2907.6<br>2900.1 | 1725.8 | 1232.4 | 614.7 | |
| gold | | 2195.8 | 1202.8 | 610.9 | |

It is interesting that the first half of the first-row transition-metal series is unreactive with respect to photoinsertion while the second half, with the exception of nickel, is reactive.[8] Similar behavior was observed during recent studies[9] of metal atom reactions with water where all of the second half of the first-row transition-metal series (except nickel) formed a metal atom-water adduct which yielded the insertion product HOMH after photolysis. We suspect that ground-state adducts also exhibit a dominant role in the reactions under investigation here, suggesting that the nickel atom-methane adduct fails to form and that photoexcitation of the metal is then unproductive.

Prolonged irradiation at wavelengths between 200 and 300 nm causes a reduction of the peaks assigned to the $CH_3MH$ species for Fe, Co, and Cu and leads to a new set of peaks. The loss of the metal-hydride stretch and the similarity of the low-frequency peaks suggest these metals undergo further insertion to form the $(CH_3)_2M$ species.

The synthesis of **1** and related compounds on a macroscale level will be reported later.

**Acknowledgment.** We gratefully acknowledge the Robert A. Welch Foundation (Grants C-490 and C-109) and the National Science Foundation for support of this work.

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*Received June 30, 1980*

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(8) The failure of nickel atoms to react is surprising in view of the results of Davis and Klabunde[3] who have shown that clusters of nickel atoms cleave carbon-carbon bonds.

(9) Unpublished observation of R. H. Hauge, A. Kauffman, and J. L. Margrave.

## A Simple Highly Efficient Asymmetric Synthesis. Preparation and Absolute Configuration of 3(*S*)-(*tert*-Butoxycarbonylamino)-1(*S*)-methyltetrahydrothiophenium Tosylate

*Sir:*

Pyramidal organosulfonium ions occur in living cells.[1] Some methyl derivatives are involved in enzyme-catalyzed methyltransfer reactions.[2] The reaction involving *S*-adenosyl-L-methionine occurs with complete sulfur stereoselectivity.[3] Despite the growing interest in natural, chiral, or prochiral sulfonium compounds, access to optically active alkylsulfonium ions is very limited. So far stereospecific synthesis has been achieved only in one case, where hazardous Cd alkyls or Grignard reagents were employed with optically active sulfoxide.[4] Also, unequivocal information about the absolute configuration of trialkylsulfonium ions is still outstanding.[5] This paper presents an example of a highly stereospecific intramolecular alkylation of a dialkyl sulfide to give an optically active cyclic trialkylsulfonium tosylate whose absolute configuration was confirmed by single-crystal X-ray analysis.

(*S*)-*tert*-Butyl 2-(1-tosyloxy-4-methylthio)butylcarbamate (**1**)[6] was prepared starting from *N*-Boc-(*S*)-methionine ethyl ester.[7]

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(5) Only a few examples are available: (a) Kelstrup, E.; Kjaer, A.; Abrahamsson, S; Dahlen, B. *J. Chem. Soc., Chem. Commun.* **1975**, 629. (b) Cornforth, J. W.; Reichard, S. A.; Talalay, P.; Carrell, H. L.; Glusker, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 7292.

(6) **1**: mp 71-72 °C; $[\alpha]_D^{20}$ -18.8° (*c* 0.76, $CHCl_3$); IR(Nujol) 3352, 1678, 1595, 1508, 1242, 1169, 976, 856, 837, 810 cm$^{-1}$; $^1$H NMR (100 MHz, $CDCl_3$ with $Me_4Si$) δ 1.39 (s, 9 H, *t*-Bu), 1.73 (m, 2 H, $CH_2CH_2CH$), 2.03 (s, 3 H, $SCH_3$), 2.41 (s, 3H, $-C_6H_4CH_3$), ~2.41 (m, 2 H, $CH_2CH_2S$), 3.87 (m, 1 H, $-CH-$), 4.00 (d, *J* = 2.5 Hz, 2 H, $-CH_2O-$), 4.64 (br, 1 H, NH), 7.26 (d, *J* = 12 Hz, 2 H, aromatic), 7.70 (d, *J* = 12 Hz, 2 H, aromatic). Anal. Calcd for $C_{17}H_{27}NS_2O_5$: C, 52.42; H, 6.99; N, 3.60; S, 16.46. Found: C, 52.31; H, 6.96; N, 3.68; S, 16.42.

(7) *N*-Boc-(*S*)-methionine ethyl ester was prepared as a pale yellow oil from (*S*)-methionine ethyl ester *p*-toluenesulfonic acid salt[8] by reaction with *tert*-butyl 4,6-dimethyl-2-pyrimidyl thiocarbonate[9] and converted to the alcohol, (*S*)-*tert*-butyl 2-(1-hydroxy-4-methylthio)butylcarbamate, without purification, by treatment with $LiAlH_4$ in THF at 40 °C (71% yield): mp 44-46 °C; $[\alpha]_D^{20}$ -11.4° (*c* 3.0, $CHCl_3$); IR (Nujol) 3400, 3350, 1680, 1513, 1389, 1375, 1363, 1322, 1300, 1290, 1262, 1240, 1164, 1096, 1072, 1059, 1035, 1015, 1004, 970, 880, 862, 850, 784 cm$^{-1}$; $^1$H NMR (100 MHz, $CDCl_3$ with $Me_4Si$) δ 1.43 (s, 9 H, *t*-Bu), 1.66-2.00 (m, 2 H, $CH_2CH_2CH$), 2.10 (s, 3 H, $SCH_3$), 2.40-2.68 (m, 2 H, $CH_2CH_2S$), 3.11-3.36 (m, 1 H, $-CH-$), 3.42-3.85 (m, 3 H, $-CH_2O-$ + OH), 4.99 (br d, *J* = 8 Hz, 1 H, NH). Anal. Calcd for $C_{10}H_{21}NO_3S$: C, 51.04; H, 8.92; N, 5.95; S, 13.62. Found: C, 50.76; H, 8.92; N, 6.21; S, 13.50.

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Table I. Cell Parameters for 1*S*,3*S*-2

| Selected Bond Distances (Å) with Estimated Standard Deviations | | | |
|---|---|---|---|
| S(B)–C(1B) | 1.843 (22) | C(3B)–C(4B) | 1.560 (30) |
| S(B)–C(2B) | 1.841 (22) | C(4B)–C(5B) | 1.502 (33) |
| S(B)–C(5B) | 1.852 (21) | C(3B)–N(B) | 1.441 (28) |
| C(2B)–C(3B) | 1.513 (28) | | |
| **Selected Bond Angles (deg) with Estimated Standard Deviations** | | | |
| C(1B)–S(B)–C(2B) | 102.3 (10) | C(2B)–C(3B)–C(4B) | 105.3 (17) |
| C(1B)–S(B)–C(5B) | 102.0 (10) | C(3B)–C(4B)–C(5B) | 108.6 (18) |
| C(2B)–S(B)–C(5B) | 92.8 (10) | N(B)–C(3B)–C(2B) | 111.8 (17) |
| S(1B)–C(2B)–C(3B) | 105.6 (14) | N(B)–C(3B)–C(4B) | 108.3 (17) |

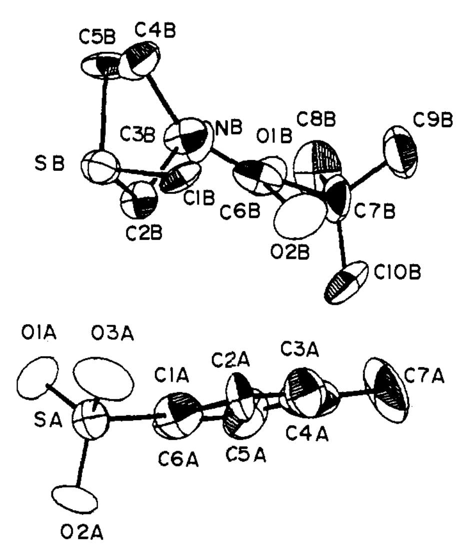
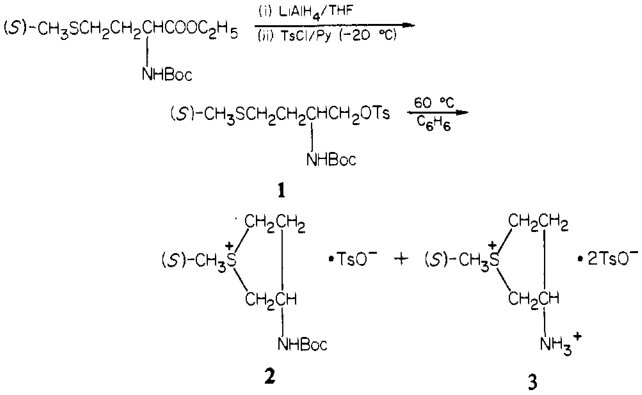


**Figure 1.** ORTEP drawing of (1*S*,3*S*)-**2**. One of the two ion pairs in a unit cell is described. See Table I for all parameters.

When **1** (0.20 g) was heated in benzene (5 mL) at 60 °C for a few hours, the crude tetrahydrothiophenium salt (**2**) precipitated as colorless crystals, mp 145–150 °C (0.11 g), soluble in $CHCl_3$, together with a small amount (0.04 g) of the product **3**,[10] mp 225–227 °C. Since **3** is practically insoluble in $CHCl_3$, it is readily separated from **2**. The $^1H$ and $^{13}C$ NMR spectra indicate that the crude product **2** is a diastereomeric mixture (vide infra). The analytically and optically pure sample of **2**,[11] $[\alpha]_D^{20}$ −14.2° (*c* 2.05, EtOH), can be obtained by recrystallization twice from acetone or chloroform ether.

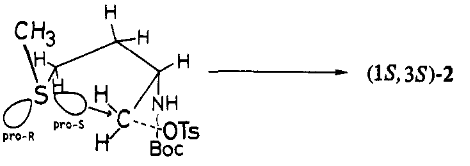


Conversion from **1** to **2** was also carried out in $CDCl_3$ and shown to be complete in 20 h at 30 °C as monitored by $^1H$ NMR. The optical yield of **2** was examined by $^1H$ NMR on the homogeneous reaction (30 °C) carried out in $CDCl_3$. Although the spectrum is complex due to contamination by the byproducts,[12] we could assess the ratio of the two diastereomers in the reaction solution on the basis of the intensity ratio (11:2) of the two $CH_3S^+$ signals at δ 2.97 and 3.18. Therefore, the diastereomeric excess is approximately 85%.[13]

The optical purity of the crude **2** which precipitated during the reaction in $C_6H_6$ was found to be not less than 85% from $^1H$ NMR. $^{13}C$ NMR indicates peaks due to the other diastereomer ((1*S*,3*R*)-**2** at δ 26.92 ($CH_3S^+$), 31.72 (CH*C*$H_2CH_2$), 41.98 ($CH_2$*C*$H_2S^+$), 46.14 (CH*C*$H_2S^+$), 54.84 (–CH–)) besides signals of a pure sample of (1*S*,3*S*)-**2**. The ratio of the two corresponding peaks is also about 11:2 for each pair.

A crystal of **2**, mp 151–153 °C, grown from acetone was used to obtain X-ray data, which were recorded on a Syntex R-3 four-circle diffractometer using graphite monochromated Mo K radiation. Crystal data: triclinic; space group *P*1, $a = 6.319$ (9), $b = 10.144$ (12), $c = 17.218$ (28) Å; $\alpha = 104.3$ (1)°, $\beta = 89.9$ (1)°, $\gamma = 107.8$ (1)°; $U = 1015$ Å$^3$. For the structure determination 1671 reflections were used with $4° \leq 2\theta \leq 40°$ (>1.96 σ(I) background). The structure was solved by using sulfur as the heavy atom; *R* = 7.7%. Each unit cell contains two ion pairs in very similar conformations. Figure 1 shows the ORTEP drawing of one of the two ion pairs, with cell parameters given in Table I. Note the trans disposition of the two substituents in the cyclothiapentane ring. The *S* configuration at the sulfur atom of the predominant diastereomer of **2** is thus established. The thiapentane ring assumes a half-chair conformation where four atoms (S(B), C(2B), C(4B), and C(5B)) are almost coplanar, the C(3B) carbon being displaced 0.65 Å from the plane.

The observed high diastereomeric specificity is in contrast with the complete absence of specificity in alkylations of (*S*)-methionine with alkyl halides[5b] or in S-ethylation of (*S*)-β-thia-δ-caprolactone.[5a] The formation of a cyclic transition state in which the steric requirements of the *S*-methyl and BocNH favor nucleophilic displacement by the pro-*S* lone pair may form the basis of the high stereoselectivity observed.



**Supplementary Material Available:** Two ORTEP drawings of (1*S*,3*S*)-**2** and tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (6 pages). Ordering information

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(10) Compound **3** may be produced from **2** by the reaction with TsOH in the presence of a small amount of water. TsOH could be formed in a side reaction, e.g., via minor E2[12] competing with the intramolecular $S_N2$. **3**: $[\alpha]_D^{20}$ −4.8° (*c* 0.44, $H_2O$); IR (CsI tablet) 3200–2500 (br), 1600, 1540, 1455, 1380, 1373, 1364, 1240–1145, 1115, 1030, 1008, 812, 680, 568 cm$^{-1}$; $^1H$ NMR (60 MHz, $D_2O$ with $H_2O$) δ −2.29 (s, 6 H, $-C_6H_4CH_3$), −1.97 (m, 2 H, $CH_2CH$), −1.77 and −1.70 (2 s in ~6:1 intensity ratio, 3 H, $S^+CH_3$), −1.77 ~ −0.80 (m, 4 H, $CH_2S^+CH_2$), −0.20 (m, 1 H, –CH–), 2.62 (d, *J* = 8 Hz, 4 H, aromatic), 2.97 (d, *J* = 8 Hz, 4 H, aromatic). Anal. Calcd for $C_{19}H_{27}NS_3O_6$: C, 49.44; H, 5.90; N, 3.03; S, 20.83. Found: C, 49.34; H, 5.82; N, 3.03; S, 21.12.

(11) (1*S*,3*S*)-**2**: IR (Nujol) 3220, 1718, 1535, 1364, 1290, 1205, 1190–1175, 1122, 1033, 1010, 813 cm$^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$ with $Me_4Si$) δ 1.38 (s, 9 H, *t*-Bu), 2.34 (s, 3 H, $-C_6H_4-CH_3$), 2.49 (m, 2 H, $CH_2CH_2CH$), 2.97 (s, 3 H, $S^+CH_3$), 3.50 (ddd, *J* = 13.9, 7.8, 5.6 Hz, 1 H, $CH_2CH_2S^+$, H cis to $MeS^+$), 3.59 (dd, *J* = 13.7, 6.8 Hz, 1 H, $CHCH_2S^+$, H cis to $SMe^+$), 3.95 (dd, *J* = 13.7, 4.2 Hz, 1 H, $CHCH_2S^+$, H trans to $SMe^+$), 4.00 (ddd, *J* = 13.9, 7.8, 5.6 Hz, 1 H, $CH_2CH_2S^+$, H trans to $SMe^+$), 4.72 (m, 1 H, –C*H*–), 6.65 (d, *J* = 7.1 Hz, 1 H, N*H*), 7.14 (d, *J* = 8.1 Hz, 2 H, aromatic), 7.72 (d, *J* = 8.1 Hz, 2 H, aromatic); $^{13}C$ NMR ($CDCl_3$ with $Me_4Si$) δ 21.25 ($-C_6H_4CH_3$), 25.71 ($CH_3S^+$), 28.36 ($C(CH_3)_3$), 33.82 ($CHCH_2CH_2$), 42.39 ($CH_2CH_2S^+$), 48.96 ($CHCH_2S^+$), 54.01 (–CH–), 79.61 ($C(CH_3)_3$), 125.70, 128.81, 139.61, 143.19 (aromatic), 155.40 (C=O). Anal. Calcd for $C_{17}H_{27}NS_2O_5$: C, 52.42; H, 6.99; N, 3.60; S, 16.46. Found: C, 51.96; H, 6.88; N, 3.59; S, 16.30.

(12) In addition to the distinct signals of (1*S*,3*S*)-**2** and (1*R*,3*S*)-**2**, the $^1H$ NMR spectra show several small singlets at δ 1.23 (*t*-BuO), 1.33 (*t*-BuO), ~2.0 ($CH_3S$), 4.23, and 4.40 ($CH_2$=C ?) which may be due to the byproducts, $CH_3SCH_2CH_2C(NHBoc)=CH_2$.

(13) These reaction conditions may not be optimal to obtain the maximum optical yield.

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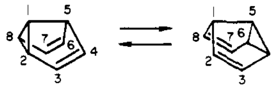
## High-Resoultion NMR Studies of Solid-State Effects on Fluxional Behavior: Semibullvalene

*Sir:*

Over the years, NMR spectroscopy has proved to be an extremely valuable tool for the study of molecular dynamics in solution.[1] For systems undergoing rapid degenerate transformations, it is the only technique available on a routine basis which is capable of providing structural information on the nature of the relevant ground and transition states. Although certain types of molecular motion involving the movement of atoms, or groups of atoms, can be accommodated in solids,[2] the solid state could impose a barrier on a valence isomerization which would compound the usual electronic barrier. The low activation energy for the rearrangement shown coupled with minimal expected geometry change marks I as sensitive material for the study of solid-state effects on processes driven primarily by electronic, as opposed to conformational, dynamics.[3] We report here demonstration of a dramatic solid-state effect on the degenerate Cope rearrangement of semibullvalene (I), a transformation which proceeds with extreme facility in solution ($\Delta G^{\ddagger} = 5.5$ kcal/mol).[4]



I

We have used high-resolution solid-state $^{13}$C NMR methods to obtain these results. The technique combines cross-polarization and high-power decoupling with "magic angle" spinning.[5] For the studies reported here, low temperatures were required, and were achieved by using an apparatus described previously.[6] Samples of I were prepared as described by Paquette and coworkers[7] and purified by gas chromatography. The liquid was loaded into a Kel-F rotor and frozen at 77 K. The cold rotor was then transferred to a precooled probe and spun at 4 kHz. Sample temperatures are quoted from measurements on the exit driving gas (helium).[6] Spectra obtained in this fashion from samples of $\sim$25 mg are shown in Figure 1. At −155 °C, semibullvalene shows five clearly resolved carbon resonances. The chemical shifts and intensities are consistent with a static structure for I and correspond closely to those reported by Anet and co-workers in solution at −160 °C with a $^{13}$C frequency of 63 MHz.[4] For this reason, the original assignments are retained and shown in the figure. Retention of the liquid-state chemical shifts indicates the absence of large solid-state pertubations on the molecular electron distribution. The averaged solution chemical shifts of semibullvalene appear as arrows in Figure 1.[4] No significant change was observed in the spectrum upon raising the sample temperature to −110 °C (Figure 1). In fact, over the entire temperature range (this range was limited by the melting point of the sample at $\sim$−85 °C), no change was observed even in the line widths. Thus, the normally rapid Cope rearrangement which would be expected to average the nonequivalent carbons (2 and 8 with 4 and 6; 1 with 5) is slow in the solid state relative to the rather long time scale dictated by the smallest chemical shifts and spectrometer frequency (15.087 MHz). Using carbons 1 and 5 ($\Delta\delta = 5.1$ ppm) as guides, we conservatively estimated the rate constant at −110 °C at $\leq 400$ s$^{-1}$. The corresponding rate constant for semibullvalene in solution at the same temperature is $2.2 \times 10^{-5}$ s$^{-1}$![4] We have therefore conclusively demonstrated a dramatic solid-state suppression of the rate of a degenerate rearrangement which proceeds with great ease in solution and which presumably also involves little geometric distortion in the transition state.[4]

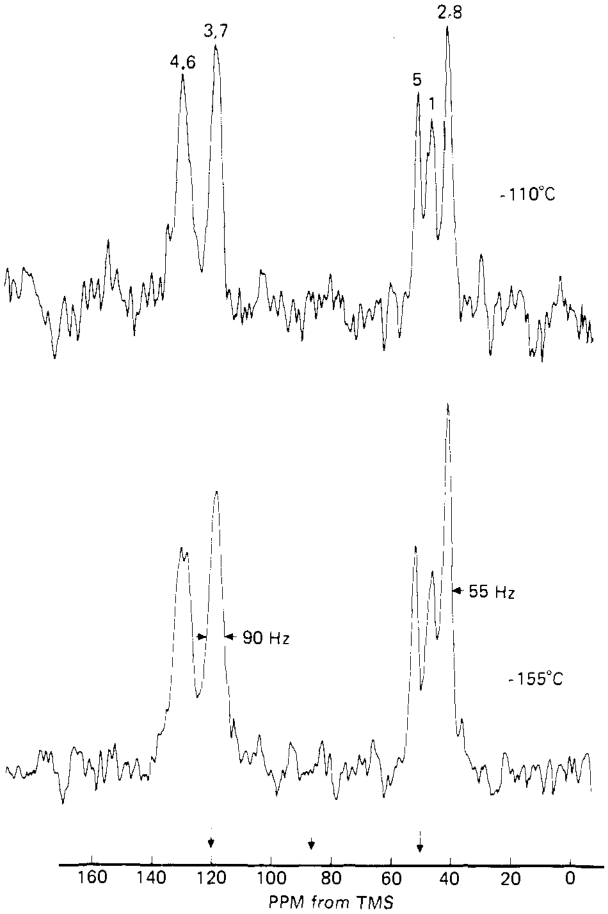


**Figure 1.** $^{13}$C NMR spectra of solid semibullvalene, showing suppression of the degenerate Cope rearrangment. the arrows show the position of the averaged chemical shifts found in solution. Spectral parameters include: $^{13}$C–$^{1}$H cross polarization for 5 ms with 48-kHz Hartmann–Hahn matching.[5] Number of scans (delay between scans) for −155 and −110 °C are 30700 (1 s) and 76242 (2s), respectively.

The spectral line widths are relatively large and deserve special mention. They vary from 55 to 90 Hz, and are probably due mostly to residual chemical shift anisotropy from a misalignment of the magic angle setting. This is likely since (1) olefinic carbons have a much larger anisotropy than aliphatic carbons[8] and (2) residual broadening due to misadjustment of the spinning axis is proportional to the size of the chemical shift anisotropy.[9]

The results presented here clearly bear on the prognosis for using high-resolution NMR in solids for the study of molecular dy-

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