# Synthesis of Isotopic Forms of Dilithiomethane [$(CH_2{}^6Li_2)_n$ and $(CD_2Li_2)_n$] and Preliminary Structural Information Obtained by X-ray Powder and Solid-Phase $^{13}C$ NMR Techniques

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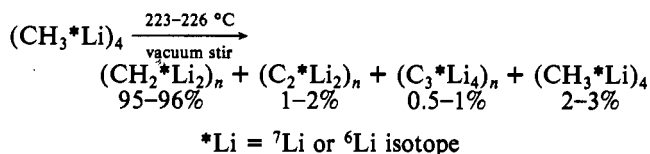
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New synthetic methods have been developed to alter the Ziegler procedure[1] for synthesis of dilithiomethane of various isotopic compositions. $[CH_2(^6Li_2)]_n$ has been prepared to facilitate solid $^{13}C$ NMR spectra. $(CD_2Li_2)_n$ has been prepared, and preliminary X-ray powder pattern data are reported. The first solid-state $^{13}C$ NMR spectrum on any organolithium compound has been obtained. The $^{13}C$ NMR spectra of solid samples of $[CH_3(^6Li)]_4$ and $[CH_2(^6Li_2)]_n$ are discussed.
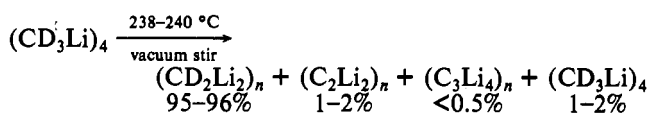
## Introduction

There is unusual interest in the structures of polylithium compounds such as dilithiomethane.[2-5] Although it may soon be possible to grow crystals of dilithiomethane, its limited solubility has made this initially very difficult. Also, it is possible to observe $^7Li$ resonance in certain solvents for dilithiomethane. At the present time no satisfactory solvents have been found such that natural-abundance $^{13}C$ spectra are possible for unsubstituted polylithium compounds.

Quite interestingly the experimental conditions for the synthesis of isotopically substituted dilithiomethane differ substantially in reaction conditions from those that we have reported for substituted-hydrogen and substituted-lithium-7 dilithiomethane:[3]

dilithiomethane

$$(CH_3{}^*Li)_4 \xrightarrow[\text{vacuum stir}]{223-226\ ^\circ C}$$
$$\begin{array}{cccc} (CH_2{}^*Li_2)_n & + (C_2{}^*Li_2)_n & + (C_3{}^*Li_4)_n & + (CH_3{}^*Li)_4 \\ 95-96\% & 1-2\% & 0.5-1\% & 2-3\% \end{array}$$

$$^*Li = {}^7Li\ \text{or}\ {}^6Li\ \text{isotope}$$

dilithiomethane-$d_2$

$$(CD_3Li)_4 \xrightarrow[\text{vacuum stir}]{238-240\ ^\circ C}$$
$$\begin{array}{cccc} (CD_2Li_2)_n & + (C_2Li_2)_n & + (C_3Li_4)_n & + (CD_3Li)_4 \\ 95-96\% & 1-2\% & <0.5\% & 1-2\% \end{array}$$

The cross-polarization magic-angle-spinning (CPMAS) NMR technique[6] combines pulsed NMR with high-speed sample rotation and can produce high-resolution NMR spectra of a solid material approaching the quality of those obtained in liquids. The narrow line widths combined with the high resolution of individual carbon chemical shifts obtained from the CPMAS experiment provide a method for obtaining new information about solid-state structure and dynamics on the atomic level. Thus application of the CPMAS NMR technique to dilithiomethane seemed especially attractive.

## Reagents

The $^7Li$ and $^6Li$ metals were obtained from Alfa and Oak Ridge National Laboratory, respectively. Purification of the lithium metal from adherent corrosion products was accomplished by stirring the molten metal in paraffin oil (bp 200–230 °C) under an argon atmosphere. $CD_3I$ (99.5%) was obtained from KOR Laboratories. Diethyl ether was dried by refluxing over sodium ketyl and was freshly distilled and degassed before use. $Hg(CH_3)_2$ was obtained from Alfa. $Hg(CD_3)_2$ was synthesized by the method of Gilman and Brown.[7] $CH_3Li$ and $CD_3Li$ were synthesized by reaction of $^6Li$ or $^7Li$ with

**Table I.** Composition of Hydrolysis Product (%) of $CH_2(^7Li)_2$

| $CH_2D_2$ | 95.1 | $C_2D_2$ | 1.3 |
|---|---|---|---|
| $CH_3D$ | 3.0 | $C_3D_4$ | 0.6 |

**Table II.** Composition of Hydrolysis Product (%) of $CH_2(^6Li)_2$

| $CH_2D_2$ | 94.1 | $C_2D_2$ | 1.5 |
|---|---|---|---|
| $CH_3D$ | 3.9 | $C_3D_4$ | 0.5 |

**Table III.** Composition of Hydrolysis Product (%) of $CD_2(^7Li)_2$

| $CH_2D_2$ | 95.7 | $C_2H_2$ | 2.0 |
|---|---|---|---|
| $CD_3H$ | 2.0 | $C_3H_4$ | <0.3 |

$Hg(CH_3)_2$ or $Hg(CD_3)_2$ in ether. The ether solutions of methyllithium were filtered, and the ether was removed under vacuum. Drying at 120 °C under vacuum resulted in a pyrophoric white powder.

## Synthesis of $CH_2(^7Li)_2$, $CH_2(^6Li)_2$, and $CD_2(^7Li)_2$

$CH_3{}^7Li$, $CH_3{}^6Li$, or $CD_3{}^7Li$ ($\sim$50 mmol) was transferred under argon into the glass system[8] shown in Figure 1. The apparatus was attached to a vacuum line manifold and evacuated. A high-temperature silicone oil bath equipped with a magnetic stirring bar was positioned around the pyrolysis apparatus and elevated so that the inner glass-encapsulated stirring bar (teflon coat removed) was slowly spinning.[9] The oil bath was slowly heated until a temperature between 223 and 226 °C was achieved, and it was maintained at this temperature during the course of the reaction. When $CD_3Li$ was the starting precursor, a temperature range of 238–240 °C was necessary for obtaining high yields of dilithiomethane-$d_2$. It is important that the apparatus be continuously pumped to remove methane gas generated during the pyrolysis. The pyrolysis was complete when the line pressure dropped to $\sim$1 $\mu$m (usually 8–12 h). The golden-brown powder was transferred and stored under an argon atmosphere.

The reactive solid ($\sim$4 mmol) was slowly hydrolyzed with $D_2O$ vapor over a 2-day period on a vacuum line. $H_2O$ was utilized for the hydrolysis of $CD_2Li_2$. The hydrolysis gases were separated on a phenyl isocyanate/Porasil C column

(1) Ziegler, K.; Nagel, K.; Patheiger, M. *Z. Anorg. Allg. Chem.* **1955**, *282*, 345.
(2) Shimp, L. A.; Morrison, J. A.; Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 5951.
(3) Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 2637.
(4) Chinn, J. W., Jr.; Landro, F. J.; Schleyer, P. v. R.; Pople, J. A.; Lagow, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 4275.
(5) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Sieger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419.
(6) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201.
(7) Gilman, H.; Brown, R. E. *J. Am. Chem. Soc.* **1930**, *52*, 3314.
(8) A change in frit porosity from fine to medium has a dramatic effect upon the yield of $CH_2Li_2$. Yields can vary from 15% to 85% with between 5% and 15% $C_2Li_2$.
(9) Alternatively, the oil bath can be lowered every 2 h and the material stirred while cooling. Both procedures yield identical results.

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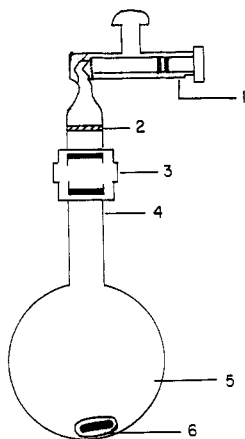
**Figure 1.** The methyllithium pyrolysis unit: (1) valve for evacuation; (2) fine glass frit; (3) $^1/_2$-in. cajon connection; (4) $^1/_2$ in. glass tubing; (5) 50-mL round-bottom flask; (6) glass-encased metal stir bar.

utilizing a temperature-programmed gas chromatographic procedure. The individual compounds were identified and quantified by comparison of their GLC-technique retention times and peak areas with those of known samples. The degree of deuterium substitution, which is indicative of lithium substitution and identity of each species, was determined by high-resolution mass spectrometry. In our 13 years of experience in this field, we have performed many experiments designed to detect spurious hydrolysis results and have come to rely on $D_2O$ hydrolysis. Typical results are listed in Tables I–III.

Optimization of dilithiomethane product yields was achieved by pyrolyzing methyllithium under varying experimental conditions. Methyllithium pyrolyzed under vacuum conditions but not stirred resulted in product yields of $(CH_2Li_2)_n$ (59%), $(CH_3Li)_4$ (40%), $(C_2Li_2)_n$ (1%), and $(C_3Li_4)_n$ (0.5%).

Methyllithium pyrolyzed at 217 °C for 17 h under vacuum conditions and stirred resulted in product yields of $(CH_2Li_2)_n$ (5%), $(CH_3Li)_4$ (95%), and $(C_2Li_2)_n$ (<0.5%) and trace amounts of $(C_3Li_4)_n$.

Methyllithium pyrolyzed under an argon atmosphere and stirred resulted in product yields of $(CH_2Li_2)_n$, $(C_2Li_2)_n$ (9%), and $(C_3Li_4)_n$ (9%). In addition, a significant quantity of hydrogen gas was detected. This indicated formation of substantial quantities of lithium and lithium hydride, and the correct percentages of polylithium compounds are less than indicated. With the exception of $C_3Li_4$, similar results were reported by Ziegler[1] for the pyrolysis of methyllithium between 230 and 240 °C.

Methyllithium-$d_3$ $(CD_3Li)_4$ was pyrolyzed under vacuum, with stirring between 238 and 240 °C. The change in temperature was necessary to overcome kinetic effects associated with the mass change from hydrogen to deuterium. Under normal pyrolysis conditions it was observed after approximately 20 h that the conversion of $CD_3Li$ to $CD_2Li_2$ was only 33% complete, whereas conversion of $CH_3Li$ to $CH_2Li_2$ was 96% complete after 8–12 h.

Dilithiomethane is thermally stable[2] only to 200–225 °C, at which point it begins to disproportionate to species such as $C_2Li_2$ and $C_3Li_4$. Modification of the Ziegler pyrolysis of methyllithium has resulted in the synthesis of high-purity dilithiomethane. The nature of the $(CH_3Li)_4$ precursor, the pyrolysis temperature, and use of a stirring procedure were crucial factors in this modified synthesis. The use of vacuum conditions during the pyrolysis was also necessary for higher yields.[3]

**High-Resolution $^{13}C$ NMR of Solid $CH_2(^7Li)_2$, $CH_2(^6Li)_2$, $CH_3^7Li$, and $CH_3^6Li$**

The low solubility of polylithium organic compounds such
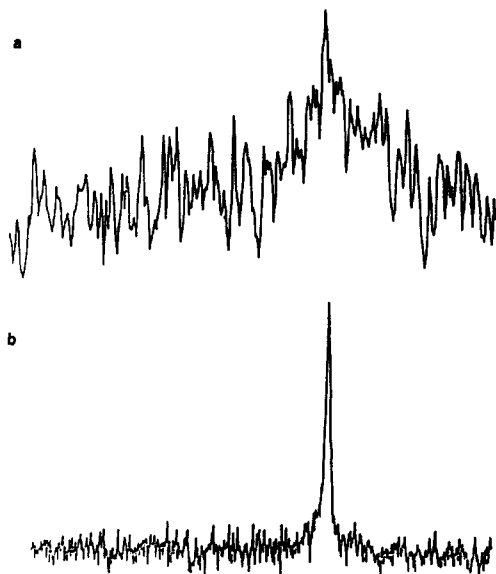


**Figure 2.** proton-decoupled solid-phase $^{13}C$ NMR spectra of dilithiomethane: (a) $CH_2(^7Li)_2$, spectrum obtained at –150 °C; (b) $CH_2(^6Li)_2$, $^6Li$-decoupled spectrum obtained at 25 °C. Peak is 10.5 ppm downfield from $Me_4Si$.
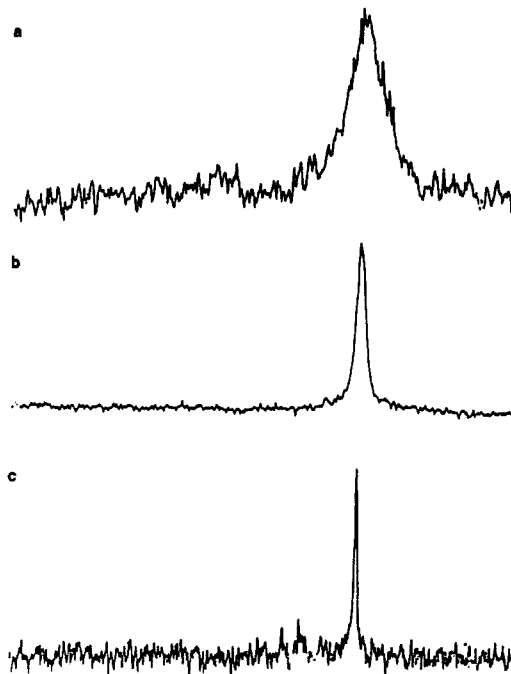


**Figure 3.** Proton-decoupled solid-phase $^{13}C$ NMR spectra of methyllithium obtained at –150 °C: (a) $CH_3^7Li$; (b) $CH_3^6Li$, no $^6Li$ decoupling; (c) $CH_3^6Li$, $^6Li$ decoupled. Peak is 16 ppm upfield from $Me_4Si$.

that $^7Li$ spectra but not $^{13}C$ spectra are possible makes application of the CPMAS NMR technique to dilithiomethane especially attractive. A detailed account of the CPMAS NMR technique and its chemical application in solids has recently appeared.[6]

$^{13}C$ spectra of solid $CH_2(^7Li)_2$, $CH_2(^6Li)_2$, $CH_3^7Li$, and $CH_3^6Li$ were obtained by using $^1H$–$^{13}C$ cross-polarization magic-angle-spinning techniques.[6] Rotors filled with the material were loaded (within seconds) into the spinning apparatus under a strong flow of nitrogen gas after removal from ampules in which they had been sealed under an atmosphere of argon. After being loaded in the spinner, the samples were continuously bathed in an atmosphere of the helium gas used for spinning and, if necessary, cooling.[10]

The proton-decoupled $^{13}C$ spectra (15 MHz) of $CH_2(^7Li)_2$ and $CH_3{}^7Li$ are shown in Figures 2a and 3a, respectively. These spectra were obtained at $-150$ °C, since sensitivity was found to be higher at lower temperatures. Nonetheless, the signal is weak, due to broadening from dipolar coupling with the $^7Li$ nucleus. The $^7Li$ nucleus has a spin quantum number of $^3/_2$ and possesses a sizable electric quadrupole moment. In general, $^{13}C$ spectral broadening due to dipolar coupling to a quadrupolar nucleus cannot be removed either by conventional decoupling techniques or by magic-angle spinning.[11] However, the possibility for removal of this kind of broadening by decoupling or spinning increases as the electric quadrupole moment of the nucleus decreases. Since $^6Li$ has a quadrupole moment that is only $\sim 0.5\%$ of that of $^7Li$, it was felt that it might be possible to achieve higher resolution in the $^{13}C$ spectrum of $CH_2(^6Li)_2$ and $CH_3{}^6Li$ using $^6Li$ decoupling in addition to $^1H$ decoupling.

$CH_3Li$ and $CH_2Li_2$ were synthesized with an enrichment of 100% in the $^6Li$ isotope (as previously described), and a CPMAS probe was built with the capability of strong irradiation at the $^6Li$ (8.83 MHz), $^1H$ (60 MHz), and $^{13}C$ (15 MHz) Larmor frequencies. The result of a $^{13}C$ CPMAS experiment at ambient temperatures on $CH_2(^6Li)_2$ with $^1H$ *and* $^6Li$ decoupling is shown in Figure 2b. The spectrum consists of a single line, 80-Hz full width at half-maximum. The chemical shift is 10.5 ppm downfield from $Me_4Si$.

The $^1H$- and $^6Li$-decoupled $^{13}C$ spectrum for $CH_3{}^6Li$ is shown in Figure 3c. The spectrum consists of a single line with a chemical shift of 16 ppm upfield from $Me_4Si$. This value is in good agreement with those obtained in solution. The $^{13}C$ chemical shifts for $CH_3{}^7Li$ range from 15 (THF) to 11 ppm ($Et_3N$) upfield from $Me_4Si$. The small upfield displacement of the $^{13}C$ chemical shift of methyllithium (relative to methane) was interpreted as evidence for predominant $sp^3$ hybridization of carbon in this species.[12] Furthermore, excess charge density on the carbon was indicated to be small. The downfield $^{13}C$ chemical shift is indicative of diminishing charge density on the carbon-bearing lithium upon complexation.[12]

The downfield $^{13}C$ shift in $CH_2Li_2$ relative to that of methyllithium may be attributed to an increase in charge density at the methylene carbon with increasing lithium substitution. Electropositive substituents are known to function as effective $\sigma$ donors.[1]

The very small line widths for $CH_2(^6Li)_2$ and $CH_3{}^6Li$ compared with those observed for $CH_2(^7Li)_2$ and $CH_3{}^7Li$ show that the strategies of using $CH_2(^6Li)_2$ and $CH_3{}^6Li$ and decoupling $^6Li$ work and should prove useful for $^{13}C$ studies of other organolithium materials. Such studies are currently under way.[13]

The fact that a sharp singlet is observed in the $^{13}C$ NMR spectrum of dilithiomethane is highly encouraging. This implies that solid aggregate $(CH_2Li_2)_n$ may contain only one carbon environment and that the symmetry is very high. This forecasts very favorable conditions for solution of this important and novel structure.

## Powder X-ray Diffraction

Samples of dilithiomethane were sealed under an argon atmosphere in quartz capillaries (0.3–0.5 mm) and mounted into a Debye–Scherrer powder camera of 114-mm diameter. X-ray analyses were carried out by employing Ni-filtered Cu Kα radiation ($\lambda = 1.540\,51$ Å). Typical exposure times were 8 h.

(10) Fyfe, C. A.; Mossbrugger, H.; Yannoni, C. S. *J. Magn. Reson.* **1979**, *36*, 61.
(11) Menger, E. M.; Veeman, W. S. *J. Magn. Reson.* **1982**, *46*, 257.
(12) McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1969**, *91*, 1057.
(13) Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J.; Yannoni, C. S., to be submitted for publication.
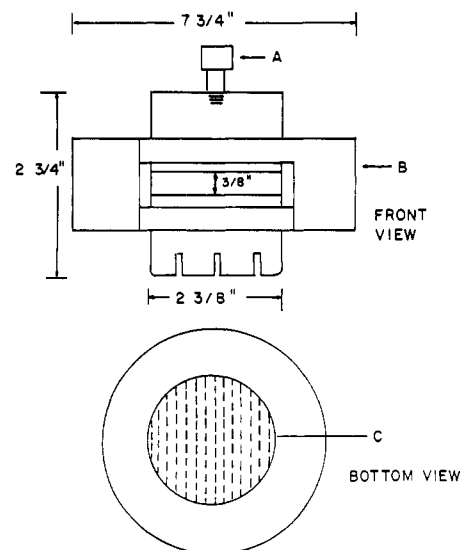
**Figure 4.** Sample holder for air-sensitive powders: (A) $^3/_8$-in. cajon; (B) radiation scattering shield; (C) copper foil (holes drilled $^3/_8$ in. apart).

**Table IV.** Powder X-ray Diffraction Data for Dilithiomethane[a]

| $2\theta$, deg | $d$, Å | $I/I_0$ | $2\theta$, deg | $d$, Å | $I/I_0$ |
|---|---|---|---|---|---|
| 17.62 | 5.039 | 5 | 45.62 | 1.993 | 11 |
| 27.63 | 3.228 | 100 | 46.13 | 1.968 | 16 |
| 31.85 | 2.810 | 5 | 48.70 | 1.870 | 1 |
| 36.65 | 2.452 | 2 | 49.42 | 1.844 | 2 |
| 40.00 | 2.254 | 4 | 54.26 | 1.691 | 7 |
| 43.75 | 2.069 | 4 | 55.48 | 1.656 | 3 |

[a] Si reference standard; corrected values.

**Table V.** Triclinic Unit Cell Parameters for Dilithiomethane

$a = 5.808$ Å $\quad \alpha = 89.65°$ $\quad V = 188.65$ Å$^3$

$b = 6.515$ Å $\quad \beta = 102.55°$ $\quad$ 12/12 lines indexed; FOM = 23.7

$c = 5.158$ Å $\quad \gamma = 97.88°$

Fourteen lines were observed in the diffraction pattern of dilithiomethane. Except for an intense line at $2\theta = 27.63°$, all lines were of weak intensity.

For quantitative intensity measurements a sample of dilithiomethane pressed into pellet form was prepared. The sample was transferred under an argon atmosphere to a Philips diffractometer equipped with a graphite-diffracted-beam monochromator, and Cu Kα radiation was used to obtain a diffraction pattern while the sample was kept under a continuous flow of helium (Figure 4).

The diffraction pattern and relative peak intensities are shown in Table IV. Except for the peak at $2\theta = 27.63°$, all peaks are of low intensity. The high sensitivity necessary to observe the diffraction pattern of $CH_2Li_2$ also enhanced peaks due to impurities (i.e., $C_2Li_2$ and LiH) formed during the pyrolysis. After subtraction of impurity peaks, 12 lines, several of which overlap, were observed in the room-temperature diffraction pattern of dilithiomethane (Table IV).

An attempt to index the lines on the basis of a cubic or a uniaxial crystal system was unsuccessful. A tetragonal cell, $a = 10.070$ Å and $c = 8.424$ Å, indexed 12 of the 12 lines, but the figure of merit (FOM) was only 4.1. A computer program based on one written by Visser[14] was used to analyze the 12-line diffraction pattern. A triclinic unit cell was obtained, and the parameters are shown in Table V. Although

(14) Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89.

the FOM of 23.7 is in an acceptable range, the triclinic cell cannot be considered as definitive. Certainly the low-symmetry crystal system and the limited number of lines have made attempts at solving the crystal structure so difficult that we are now relying on neutron and pulsed-neutron diffraction data for a solution to this problem.[15]

There is a longstanding effort under way, which involves G. D. Stucky, J. Faber, and M. H. Mueller of Argonne National Laboratory, to index and elucidate the structure by neutron diffraction by using Visser programs and other programs of deuterium substitution of dilithiomethane.[15] There is a second project under way at Brookhaven National Lab-

oratory, involving G. D. Stucky, for a pulsed-neutron study of the structure of deuterium-substituted dilithiomethane.[16]

(15) Neutron diffraction data are currently being utilized to derive the crystal structure to dilithiomethane-$d_2$: Stucky, G. D.; Faber, J.; Mueller, M. H.; Knott, H.; Steinfink, H.; Gurak, J. A.; Lagow, R. J., to be submitted for publication.

(16) Stucky, G. D.; Gurak, J. A.; Lagow, R. J., to be submitted for publication.

# Synthesis, Properties, and Reactions of Bis((trifluoromethyl)sulfonyl) Imide, $(CF_3SO_2)_2NH^1$

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Bis((trifluoromethyl)sulfonyl) imide, $(CF_3SO_2)_2NH$, the parent compound of the bis((perfluoroalkyl)sulfonyl) imides, has been prepared in good yield. The strong electron-withdrawing effect of the $(CF_3SO_2)_2N$ group is borne out by the acidity of the imide and the properties of its derivatives. The synthesis and properties of $(CF_3SO_2)_2NH$ are described, as well as those of the derivatives $(CF_3SO_2)_2NX$, where X = Cs, Cl, NO, $NO_2$, and $Si(CH_3)_3$.

## Introduction

The electronegativity of the $CF_3SO_2$ group and its application in organic chemistry have been well documented.[3-5] As an electron-withdrawing group on nitrogen, for example, it substantially increases the acidity of an amine, imine, or imide. Compounds such as $CF_3SO_2NH_2$ and $CF_3SO_2N(H)C_6H_5$ exhibit $pK_a$ values of weak acids, and in the case of $CF_3SO_2NH_2$, the lone $CF_3SO_2$ group affords the dichloro and disilver derivatives reasonable stability.[6,7]

The presence of two sulfonyl groups on nitrogen drastically increases the acidity of the remaining proton, as shown by $(FSO_2)_2NH$,[8] $(RSO_2)_2NH^5$ (R = aryl), and certain $(R_fSO_2)_2NH^9$ derivatives. However, the simplest member of the $(R_fSO_2)_2NH$ series, $(CF_3SO_2)_2NH$, had not been isolated. Our immediate interest was to compare the properties and reactivity of this imide to those of related $(FSO_2)_2NH$. The

latter has led to a variety of interesting compounds,[10] including one possessing the first example of a xenon–nitrogen bond.[11]

## Experimental Section

The majority of the synthetic work was carried out by using Pyrex and stainless-steel vacuum systems equipped with glass–Teflon and stainless-steel valves. Pressures were measured by using a Wallace and Tiernan differential pressure gauge, Series 1500. Where applicable, amounts of volatile reagents were determined by *PVT* measurements, assuming ideal-gas behavior. All other reagents were measured by direct weighing. Melting points were taken on a standard capillary-tube apparatus or by a modified Stock technique.

$^{19}F$ NMR spectra were normally recorded on a Varian XL-100-15 spectrometer using ~80 mol % $CFCl_3$ as a solvent and internal standard. Chemical shifts are positive when found at a lower field than that of $CFCl_3$. $^1H$ NMR spectra were recorded on a Varian T-60 spectrometer using $(CH_3)_4Si$ as an external standard.

Routine IR spectra were recorded on either a Perkin-Elmer Model 337 or 1330 spectrometer. Spectra for assignment were taken on a Perkin-Elmer Model 180 spectrometer. Gas spectra were taken with use of a 10-cm gas cell fitted with AgCl or KCl windows. Solids were taken as Nujol or Fluorolube mulls on AgCl windows.

Raman spectra were recorded on a Spex Model 14018 double monochromator employing photon-counting detection. Excitation was via the 514.5-nm line of an argon ion laser. Samples were usually run at low temperature in a glass cell similar to that of Brown et al.,[12]

(1) Work carried out in part at Kansas State University.
(2) Present address: Argonne National Laboratory, Argonne, IL 60439.
(3) Senning, A. *Chem. Rev.* **1965**, *65*, 385.
(4) Howells, R. D.; Mc Cown, J. D. *Chem. Rev.* **1977**, *77*, 69.
(5) Hendrickson, J. B.; Sternbach, D. D.; Bair, K. W. *Acc. Chem. Res.* **1977**, *10*, 306.
(6) Nazaretyan, V. P.; Radchenko, O. A.; Yagupolskii, L. M. *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 2476.
(7) Ekkehard, B.; Haas, A. *J. Fluorine Chem.* **1974**, *4*, 99.
(8) Ruff, J. K. *Inorg. Chem.* **1965**, *4*, 1446.
(9) Meussdorffer, J. N.; Niederprum, H. *Chem. Ztg.* **1972**, *96*, 582.

(10) Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 732.
(11) DesMarteau, D. D.; LeBlond, R. D.; Hossain, S. F.; Nothe, D. *J. Am. Chem. Soc.* **1981**, *103*, 7734.