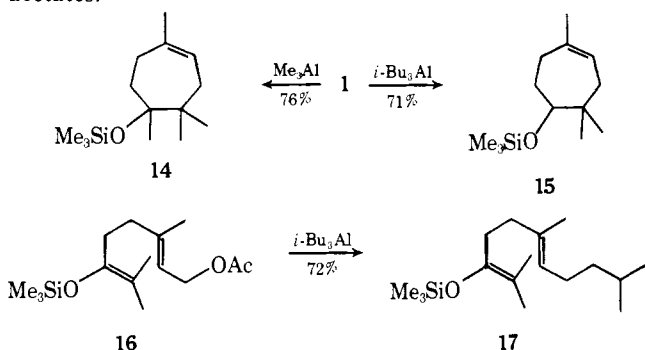


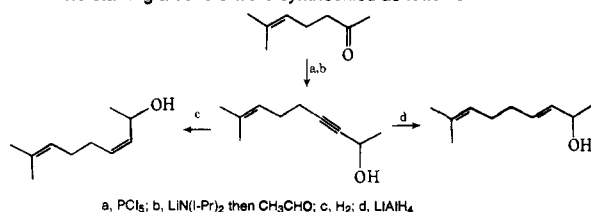
the acyclic silyl ether **17** in 72% yield:<sup>8</sup> NMR (CDCl<sub>3</sub>) δ 0.16 (s, 9 H), 0.87 (d, 6 H, *J* = 6 Hz), 1.60 (br s, 9 H), 5.10 (t, 1 H, *J* = 7 Hz); mass *m/e* 282 (M<sup>+</sup>). Thus, again, the fate of cyclization is markedly affected by steric integrities of the allylic acetates.



The success of the approach illustrated in this communication has made it possible to consider several new biomimetic routes to terpenes as well as a fairly general route to various cycloheptenone derivatives.

## References and Notes

- Y. Naya and M. Kotake, *Tetrahedron Lett.*, 1645 (1968).
- A. T. McPhail, R. I. Reed, and G. A. Sim, *Chem. Ind. (London)*, 976 (1964); J. A. Hartsuck and I. C. Paul, *ibid.*, 977 (1964). Recently, Faulkner et al. reported the structure of a new diterpene from *Dollabella carifornica* as a member of the similar class: C. Ireland, D. J. Faulkner, J. Finer, J. Clardy, *J. Am. Chem. Soc.*, **98**, 4664 (1976).
- For a stimulating discussion for squalene cyclization, see E. E. van Tamelen, *Acc. Chem. Res.*, **1**, 111 (1968), see also J. W. Cornforth, *Angew. Chem., Int. Ed. Engl.*, **7**, 903 (1968).
- Indirect synthesis of karahanaenone: E. Demole and P. Enggist, *J. Chem. Soc., Chem. Commun.*, 264 (1969); *Helv. Chim. Acta*, **54**, 456 (1971). Lanosterol synthesis from squalene analogs having preformed ring: E. E. van Tamelen and R. J. Anderson, *J. Am. Chem. Soc.*, **94**, 8225 (1972), and references cited therein.
- Y. Kitagawa, S. Hashimoto, S. Iemura, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **98**, 5030 (1976).
- Regiospecific formation of an enolate ion from the bromo ketone; see for other method G. Stork and M. Isobe, *J. Am. Chem. Soc.*, **97**, 4745 (1975).
- m*-Chloroperbenzoic acid was added portionwise to a solution of neryl acetate (molar ratio, 1.05:1) in methylene chloride at 0 °C (80% yield); for a similar oxidation, see E. E. van Tamelen and J. P. McCormick, *J. Am. Chem. Soc.*, **92**, 737 (1970).
- Purification by chromatography on silica gel with ether-hexane.
- In polar ether solvents, the regioisomeric *tert*-alcohol was obtained as the major product.
- E. J. Corey and C. U. Kim, *J. Am. Chem. Soc.*, **94**, 7586 (1972); E. J. Corey and C. U. Kim, *J. Org. Chem.*, **38**, 1233 (1973).
- G. C. Joshi and L. M. Pande, *Synthesis*, 450 (1975).
- Because of the acid sensitivity of the product, pyridine should be added to quench the reaction; for the similar example, see J. M. Denis, C. Girard, and J. M. Conia, *Synthesis*, 549 (1972).
- All operations involving organoaluminum reagents were conducted in an atmosphere of dry argon or nitrogen. In a typical preparation of this reagent, 4 mL of cooled solution of trimethylaluminum (1 M in hexane) was treated with trifluoroacetic acid (8 mmol) dropwise at 0 °C (exothermic reaction) (8 mmol of methane was evolved during this operation). After warming to 25 °C over ~10 min, the partially soluble reagent is ready for use in situ.
- The IR, NMR, and mass spectra of synthetic karahanaenone are identical with those of the natural ketone; see ref 1 and 4.
- None of the cyclopentanone derivative was detected by GLC and NMR analysis.
- The reaction should be quenched immediately after the disappearance of the starting acetate, since the product **5** was not sufficiently stable to survive in the presence of these Lewis acids.
- Using the same sequence of reactions for the preparation of **1**, the oily acetate **7** was obtained from 8,2-dimethyl-2,7-nonadien-4-ol which in turn was prepared from 6-methyl-5-hepten-2-one by the aldol condensation with acetone followed by NaBH<sub>4</sub> reduction.
- The acetate **9** and **10** were prepared according to the general route as nerol → **1**. The starting alcohols were synthesized as follows:



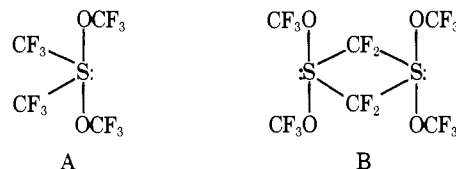
- The starting alcohol was prepared by the aldol condensation of 6-methyl-5-hepten-2-one with acetaldehyde followed by NaBH<sub>4</sub> reduction.
- Reductive termination of cationic cyclization appears to be unique in squalene biosynthesis; see L. J. Mulheirn and P. J. Ramm, *Chem. Soc. Rev.*, **1**, 259 (1972).
- Prepared from geraniol.

Shinsuke Hashimoto, Akira Itoh, Yoshizo Kitagawa  
Hisashi Yamamoto,\* Hitosi Nozaki  
Department of Industrial Chemistry, Kyoto University  
Yoshida, Kyoto 606, Japan  
Received November 29, 1976

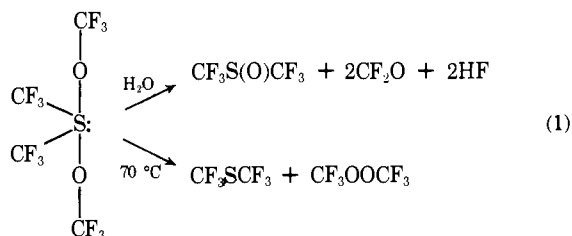
## Two Stable Sulfuranes, (CF<sub>3</sub>)<sub>2</sub>S(OCF<sub>3</sub>)<sub>2</sub> and (CF<sub>3</sub>O)<sub>2</sub>SCF<sub>2</sub>S(OCF<sub>3</sub>)<sub>2</sub>CF<sub>2</sub>

Sir:

Recently we have reported the synthesis of thermally stable chlorobis(dialkylamino)trifluoromethylsulfuranes<sup>1</sup> which are hydrolyzed slowly by water to form the trifluoromethyl(dialkylamino) sulfoxides. In our continuing studies of tri- and tetracoordinated sulfur(IV) compounds, it now has been possible to prepare bis(trifluoromethyl)bis(trifluoromethoxy)sulfurane (A), the first stable member of a new family of tetracoordinated sulfur(IV) compounds, by photolysis of a mixture of bis(trifluoromethyl) sulfide and trifluoromethyl hypochlorite. There is considerable interest in aryl sulfuranes based on reports concerned with the preparation,<sup>2-6</sup> the geometry at sulfur,<sup>7</sup> and the synthetic utility<sup>8-11</sup> of these compounds. Dialkyldialkoxysulfuranes have been suggested as intermediates in the chemistry of sulfonium salts.<sup>12</sup> Compounds which are formal derivatives of sulfur tetrafluoride and sulfur hexafluoride are stable and their geometries and reactivities have been well studied.<sup>13,14</sup>



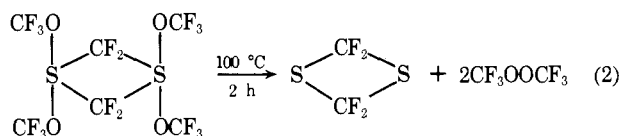
Bis(trifluoromethyl) sulfide<sup>15</sup> and trifluoromethyl hypochlorite<sup>16</sup> are condensed into a 100-mL quartz vessel and photolyzed for 20 h with a Hanovia utility ultraviolet quartz lamp. Bis(trifluoromethyl)bis(trifluoromethoxy)sulfurane (A) is retained in a trap at -78 °C by using trap-to-trap separation techniques. This sulfurane is a pale yellow liquid with an extrapolated boiling point of 72 °C from the equation  $\log P_{\text{Torrr}} = 7.32 + 1532/T$  (valid between 0 and 52 °C). The molar heat of vaporization is 7.0 kcal and the Trouton constant is 20.3 eu. It is stable in Pyrex glass at 25 °C for periods of a few days. However, in the presence of water, hydrolysis occurs to form bis(trifluoromethyl) sulfoxide<sup>15</sup> (86%) and carbonyl fluoride (83%). When heated at 70 °C for 1 h in a stainless steel Hoke vessel, bis(trifluoromethyl) sulfide and bis(trifluoromethyl) peroxide<sup>17</sup> are generated quantitatively (eq 1).



Spectroscopic data further support the existence of this new sulfurane (A). The <sup>19</sup>F NMR spectrum shows resonances at

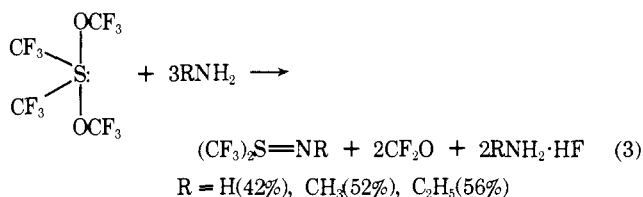
$\phi$  56.2 and 73.6 in the ratio 1:1. The former is assigned to the trifluoromethyl group and is a septet ( $J = 7.4$  Hz) split by the  $\text{OCF}_3$  groups. Also, the infrared spectrum has absorption bands at 1320 (m), 1263 (vs), 1220 (s), 1198 (m), 1104 (vs), 841 (m), 755 (w),  $581\text{ cm}^{-1}$  (w). When the mass spectral data are measured at  $100^\circ\text{C}$  and 17 eV, the molecular ion is absent; however, other fragment peaks, such as  $m/e$  255 ( $\text{C}_3\text{OSF}_9$ ,  $M - \text{OCF}_3$ ), 170 ( $\text{C}_2\text{SF}_6$ ,  $\text{C}_2\text{O}_2\text{F}_6$ ), 138 ( $\text{C}_2\text{F}_6$ ), 117 ( $\text{COSF}_3$ ), 101 ( $\text{CSF}_3$ ), 85 ( $\text{COF}_3$ ), and 69 ( $\text{CF}_3$ ) appeared appropriately. Anal. Calcd for  $\text{C}_4\text{O}_2\text{SF}_{12}$ : C, 14.13. Found: C, 14.06.

The cyclic sulfide, tetrafluoro-1,3-dithietane, forms the sulfurane B with  $\text{CF}_3\text{OCl}$ . This sulfurane (B) is also a stable liquid with a boiling point of  $131^\circ\text{C}$  from the equation  $\log P_{\text{Torr}} = 7.67 + 1935/T$  ( $\Delta H_v = 8.9$  kcal;  $\Delta S_v = 21.9$  eu). Heating at  $100^\circ\text{C}$  for 2 h in a stainless steel Hoke vessel, sulfurane B decomposes to the tetrafluoro-1,2-dithietane and bis(trifluoromethyl) peroxide quantitatively (eq 2). Further

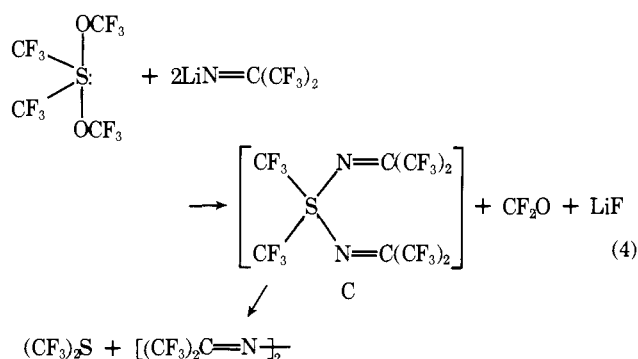


evidence supporting the structure of the new sulfurane B is the spectral data. The  $^{19}\text{F}$  NMR resonances appear at  $\phi$  72.1 and 96.2. The latter resonance is assigned to the  $\text{CF}_2$  groups which are a multiplet split by the  $\text{OCF}_3$  groups ( $J = 12.1$  Hz). The infrared spectrum has absorption bands at 1290 (m), 1233 (ms), 1184 (s), 1120 (s), 1071 (s), 1025 (m), 992 (ms), 755 (m), 733 (m),  $528\text{ cm}^{-1}$  (w). In the mass spectrum, the fragment peaks,  $m/e$  419 ( $\text{C}_5\text{O}_3\text{S}_2\text{F}_{13}$ ,  $M - \text{OCF}_3$ ), 334 ( $\text{C}_4\text{O}_2\text{S}_2\text{F}_{10}$ ), 249 ( $\text{C}_3\text{OS}_2\text{F}_7$ ), 170 ( $\text{C}_2\text{O}_2\text{F}_6$ ), 164 ( $\text{C}_2\text{S}_2\text{F}_4$ ), 85 ( $\text{COF}_3$ ), 82 ( $\text{CSF}_2$ ), and 69 ( $\text{CF}_3$ ) appeared appropriately. Anal. Calcd for  $\text{C}_6\text{O}_4\text{S}_2\text{F}_{16}$ : C, 14.29. Found: C, 14.31.

**Reactions of A.** Bis(trifluoromethyl)bis(trifluoromethoxy)sulfurane (A) is a useful precursor to bis(trifluoromethyl)-*N*-alkylsulfimides when it is reacted with primary amines. In a typical reaction, 1 mmol of A and 3 mmol of ammonia are condensed into a 50-mL Pyrex vessel with a Teflon stopcock. The mixture is allowed to warm slowly to  $-78^\circ\text{C}$  and to remain for 30 min. After this period, it is vacuum distilled at low temperature to give the bis(trifluoromethyl) sulfimide (eq 3).<sup>18</sup> Primary amines can be reacted in the same manner.<sup>10</sup>

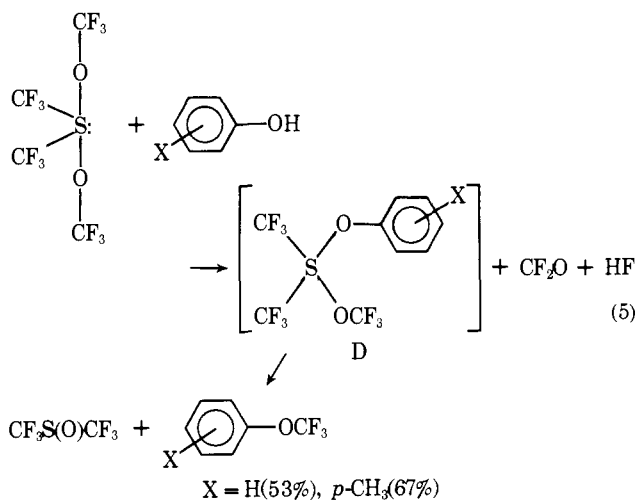


Sulfurane A apparently undergoes a ligand exchange reaction with lithium hexafluoroisopropylideneimine to form a new type of sulfurane (C); however, the latter is unstable de-

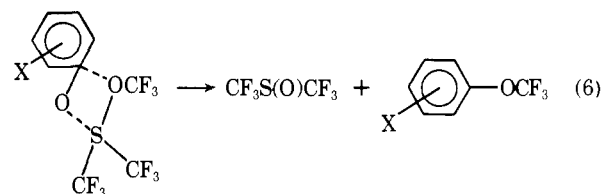


composing to bis(trifluoromethyl) sulfide (85%) and hexafluoroacetone azine<sup>19</sup> (93%) (eq 4).

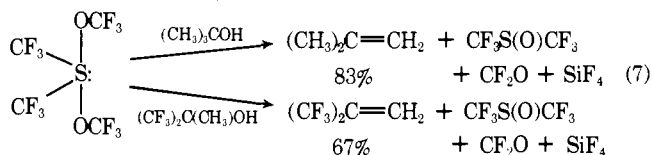
Further evidence of the versatility of sulfurane A is in its reactions which result in trifluoromethylanisole derivatives (eq 5). The formation of trifluoromethylanisole<sup>20-22</sup> by sulfurane



A in ether at  $25^\circ\text{C}$  is complete within 30 min. This product could result from an intramolecular decomposition of sulfurane D, and, in particular, the formation of *p*-trifluoromethoxytoluene supports the contribution of the electrocyclic<sup>7</sup> mechanism 6.



Tertiary alcohols are dehydrated by sulfurane A to give olefins<sup>4</sup> (eq 7).



**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research.

## References and Notes

- T. Kitazume and J. M. Shreeve, *J. Fluorine Chem.*, **9**, 175 (1977).
- W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 5597 (1971).
- R. J. Arhart and J. C. Martin, *J. Am. Chem. Soc.*, **94**, 4997 (1972).
- L. J. Kaplan and J. C. Martin, *J. Am. Chem. Soc.*, **95**, 793 (1973).
- J. C. Martin and T. M. Balthazor, *J. Am. Chem. Soc.*, **99**, 152 (1977).
- I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).
- I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Am. Chem. Soc.*, **94**, 5010 (1972).
- R. J. Arhart and J. C. Martin, *J. Am. Chem. Soc.*, **94**, 5003 (1972).
- J. C. Martin, J. A. Franz, and R. J. Arhart, *J. Am. Chem. Soc.*, **96**, 4604 (1974).
- J. A. Franz and J. C. Martin, *J. Am. Chem. Soc.*, **97**, 583 (1975).
- J. C. Martin and J. A. Franz, *J. Am. Chem. Soc.*, **97**, 6137 (1975).
- K. Mislow, *Acc. Chem. Res.*, **3**, 321 (1970).
- (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev. Chem. Soc.*, **20**, 245 (1966); E. L. Muetterties, *Acc. Chem. Res.*, **3**, 266 (1970), and references cited therein.
- J. M. Shreeve, *Acc. Chem. Res.*, **6**, 387 (1973).
- D. T. Sauer and J. M. Shreeve, *J. Fluorine Chem.*, **1**, 1 (1971).
- C. J. Schack and W. Maya, *J. Am. Chem. Soc.*, **91**, 2902 (1969).
- A. J. Arvia and P. J. Aymomino, *Spectrochim. Acta*, **18**, 1299 (1962).
- S. D. Morse and J. M. Shreeve, *Inorg. Chem.*, **16**, 33 (1977).
- W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

(20) L. M. Yagupol'skii and M. S. Marenets, *Zh. Obshch. Khim. SSSR*, **24**, 885 (1954); **26**, 99 (1956).

(21) L. M. Yagupol'skii, *Dokl. Akad. Nauk SSSR*, **105**, 100 (1955).

(22) W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964).

Tomoya Kitazume, Jean'ne M. Shreeve\*

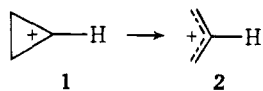
Department of Chemistry, University of Idaho  
Moscow, Idaho 83843

Received March 4, 1977

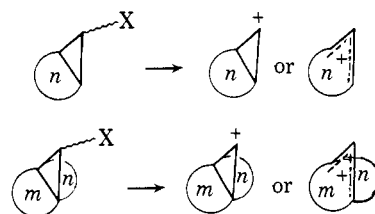
### 11-Methyl-11-tricyclo[4.4.1.0<sup>1,6</sup>]undecyl Cation. First Long-Lived, Distinct Cyclopropyl Cation Showing Significant 2 $\pi$ -Homoaromatic Nature<sup>1</sup>

Sir:

The direct observation of the cyclopropyl cation **1** thus far has evaded all attempts owing to its facile ring opening to the energetically more favorable allyl cation **2**.<sup>2</sup> The former has been shown to be some 39 kcal/mol higher in energy than the latter, and the rearrangement takes place with little or no energy barrier.<sup>3</sup>



Evidence has been presented for the intermediacy of cyclopropyl cations under solvolytic conditions in geometrically constrained bicyclic and tricyclic systems where the cyclopropyl ring is "locked in" so that the ring-opening process is forbidden or at least is minimized.<sup>4,5</sup> In the solvolytic reactions, indeed, the unrearranged cyclopropyl products were obtained with retention of configuration. According to an interpretation



first advanced by Schleyer and Schöllkopf, the intermediate carbocationic species in such reactions are partially opened ("half-opened" cyclopropyl cations).<sup>3a,4</sup> We wish to report now the direct observation under stable ion conditions of the first stable, distinct cyclopropyl cation showing significant 2 $\pi$ -homoaromatic nature.

The highly strained 11-methyl-11-bromotricyclo[4.4.1.0<sup>1,6</sup>]undecane **3**<sup>5,6</sup> in surfuryl chloride fluoride (SO<sub>2</sub>ClF) solution at -60 °C displays in the <sup>1</sup>H NMR spectrum (60 MHz, Figure 1a) a methyl singlet at  $\delta$  1.83 and methylene multiplets at 1.2–1.8. When this solution is slowly added into a well-stirred solution of antimony pentafluoride (SbF<sub>5</sub>) in SO<sub>2</sub>ClF at -120 °C, a light yellow solution is obtained which is stable up to -60 °C.<sup>7</sup> The 60-MHz <sup>1</sup>H NMR spectrum (Figure 1b) of the solution at -90 °C displays three proton resonances centered at  $\delta$  3.18 (m, 4 H), 3.03 (s, 3 H), and 1.90 (m, 4 H). The substantial deshielding of both the methyl and methylene protons points to the formation of a discrete carbocation **4**.

The <sup>1</sup>H NMR spectrum of **4** seems to indicate the symmetrical nature of the ion. The proton-decoupled <sup>13</sup>C NMR spectrum (Figure 1c) of the ion obtained at -90 °C, however, shows seven carbon resonances. According to the off-resonance <sup>13</sup>C NMR spectrum, the two most deshielded resonances at  $\delta_{13C}$  210.0 and 168.5 (from external TMS) are singlets, which

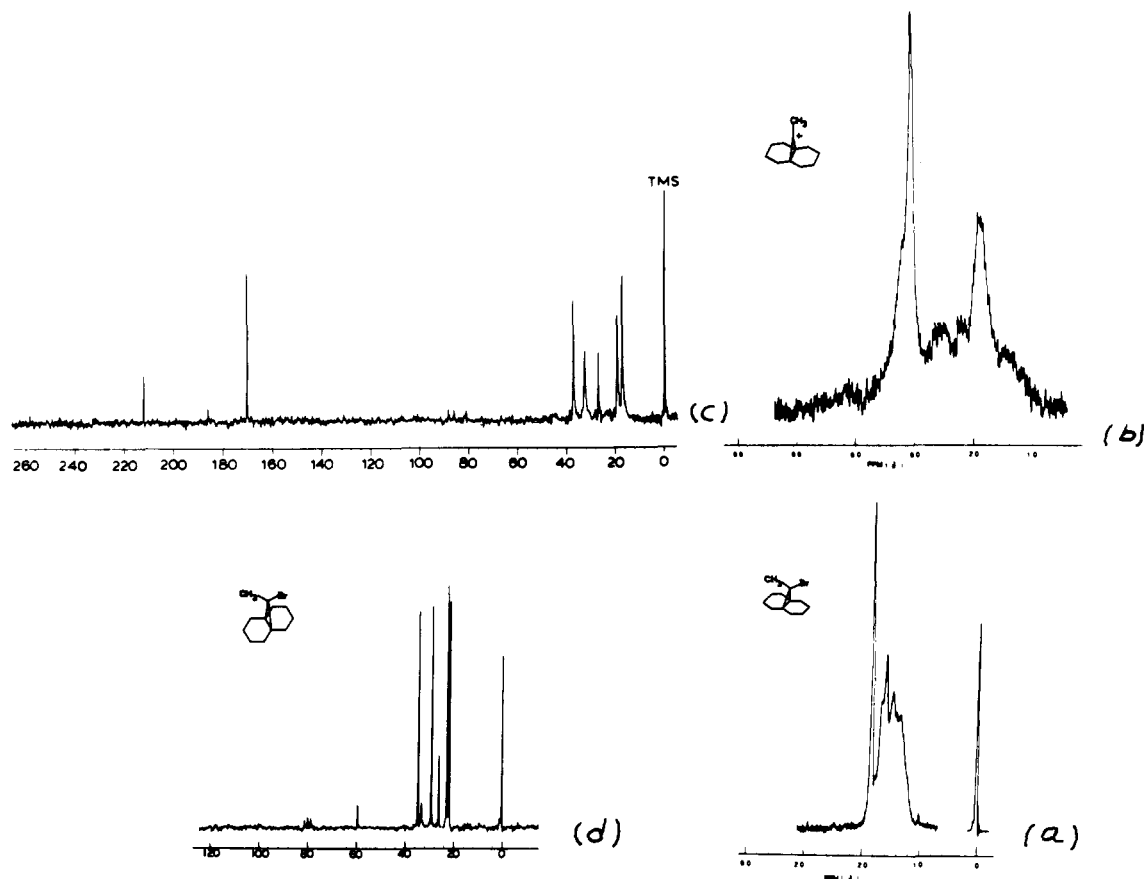


Figure 1. (a) 60-MHz <sup>1</sup>H NMR spectrum of **3** in SO<sub>2</sub>ClF at -60 °C; (b) 60-MHz <sup>1</sup>H NMR spectrum of **4** in SbF<sub>5</sub>-SO<sub>2</sub>ClF at -90 °C; (c) proton decoupled <sup>13</sup>C NMR spectrum of **4**; (d) proton decoupled <sup>13</sup>C NMR spectrum of **3**.