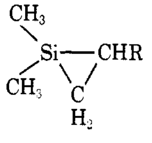
Acknowledgment. This work was supported by the National Research Council of Canada.

D. G. Cooper, R. P. Hughes, J. Powell*
Lash Miller Chemical Laboratories, University of Toronto
Toronto, 181, Ontario, Canada
Received September 27, 1972

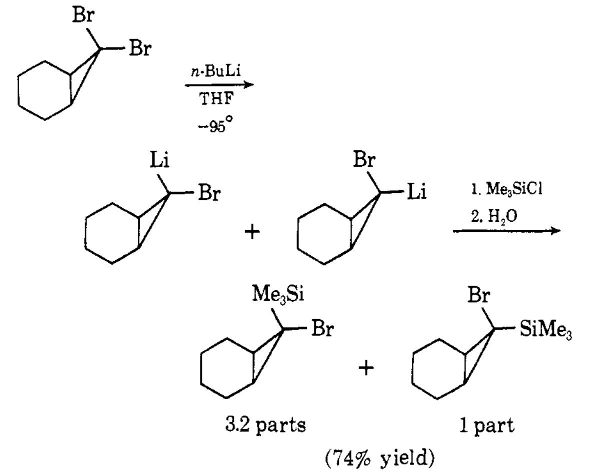
Substituted 7-Siladispiro[2.0.2.1]heptanes. The First Stable Silacyclopropanes

Sir:

Various attempts have been made to prepare silacyclopropanes, but all reactions designed to produce this ring system have been reported to give acyclic or larger (>3) cyclic organosilicon compounds.[1] No evidence is available which could distinguish between thermodynamic and kinetic instability as the explanation for the apparent nonexistence of any compounds containing an SiC_2 ring.[2] Most of such published attempts were directed toward relatively lightly substituted silacyclopropanes of type I. If kinetic factors dominate, then a stabilization of such a ring system might be achieved by significantly increasing the degree of substitution of the ring carbon atoms, preferably with rather bulky groups.[3] We have tested this approach and have found that it does indeed permit the preparation of stable compounds containing the silacyclopropane system.

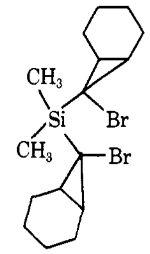


I. R = H or alkyl



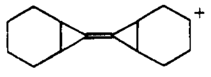
3.2 parts 1 part
(74% yield)

(1)



II

Our synthesis of such silacyclopropanes is based on our studies of the chemistry of *gem*-lithiobromocyclopropanes.[4] These have been found to alkylate trimethylchlorosilane and trimethyltin chloride. For instance, the reaction sequence shown in eq 1 could be carried out. When this lithium reagent was treated with dimethyldichlorosilane in place of Me_3SiCl, silane II, mp 114–116°, could be isolated by crystallization from methanol. Treatment of a THF solution of II with an excess of magnesium at room temperature during 1.5 hr resulted in consumption of about 1 g-atom of Mg/mol of II. The organic layer was decanted under nitrogen and the solid remaining extracted with pentane. Distillation of the combined organic solutions gave a white, crystalline solid, III, bp 95–97° (0.01 mm), mp 72–74°, in 75–80% yield. This product was air sensitive and had to be handled under an inert atmosphere.[5] Combustion analysis (Alfred Bernhardt Mikroanalytisches Laboratorium) established the empirical formula $C_{16}H_{26}Si$ (*Anal.* Calcd: C, 77.97; H, 10.63; Si, 11.40. Found: C, 77.91; H, 10.59; Si, 11.17). A high-resolution mass spectrum of III (modified CEC-21-110B at 70 eV) showed *inter alia* the molecular ion $C_{16}H_{26}Si^+$ (*m/e* found, 246.1807; calcd, 246.1804), a $[C_{16}H_{26}Si-CH_3]^+$ ion (*m/e* found, 231.1570; calcd, 231.1569), and a fragment ion $C_{14}H_{20}^+$ *m/e* found, 188.1564; calcd, 188.1565). The latter very likely is IV. No ions corresponding to a dimeric species, $C_{32}H_{52}Si_2$, or its fragments resulting from CH_3 fission, were observed.[6] The product III reacted exothermally with CCl_4 at room temperature when solutions were prepared for spectroscopic studies. Solution of III in anhydrous methanol also resulted in an exothermic reaction which gave a product, bp 94–96° (0.01 mm), whose combustion analysis indicated the formula $C_{17}H_{30}OSi$. Nmr and ir data showed it to be a methoxysilane. The volatility of III, its mass spectrum, and its anomalously high reactivity (for a tetraorganosilane) suggested that it was a highly strained silacyclopropane derivative, dispiro[bicyclo[4.1.0]heptane-7-2′-silacyclopropane-3′,7′′-bicyclo[4.1.0]heptane. Its methanolysis product then would be IIIa.



IV

---

[1] *Inter alia:* (a) J. D. Roberts and S. Dev, *J. Amer. Chem. Soc.*, 73, 1879 (1951); (b) P. S. Skell and E. J. Goldstein, *ibid.*, 86, 1442 (1964); (c) O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, 78, 1039 (1966); (d) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, 90, 3438 (1968); (e) J. W. Connolly, *J. Organometal. Chem.*, 11, 429 (1968); (f) Y.-N. Tang, G. P. Gennaro, and Y. Y. Su, *J. Amer. Chem. Soc.*, 94, 4357 (1972).

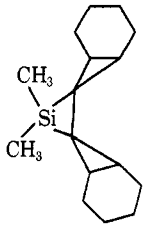
[2] Skell and Goldstein[1b] have suggested that the SiC_2 ring is thermally unstable due to excessive ring strain introduced by the presence of the silicon atom, and this explanation has again been cited by others[1f] more recently.

[3] This approach has served well in the stabilization of small organic ring systems, the least substituted of which were not very stable toward ring opening or other reactions; *cf.* F. D. Greene and S. S. Hecht, *J. Org. Chem.*, 35, 2482 (1970), and references therein.

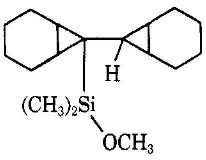
[4] (a) R. L. Lambert, Jr., Ph.D. Thesis, Massachusetts Institute of Technology, 1972; (b) D. Seyferth and R. L. Lambert, Jr., report in preparation.

[5] The melting point, in fact, was dependent on the care which was taken to exclude air during the isolation and purification of the product. The highest melting point observed was that cited.

[6] Species corresponding to $C_{16}H_{26}SiO^+$ and $C_{15}H_{23}SiO^+$ were observed in all mass spectra of III in variable intensity. In low-resolution mass spectra, the intensity of these ions was observed to depend on the care with which air had been excluded from the samples, being lowest for the samples with the highest melting points. These peaks are believed to be due to the presence of an oxidation product, either present initially or formed during introduction of the samples into the mass spectrometer.



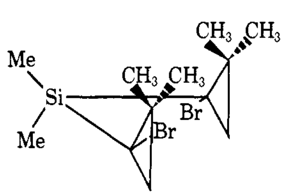
III



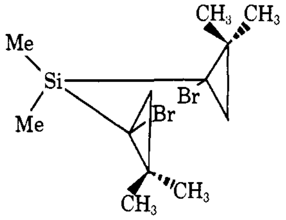
IIIa

The spectral properties of III provided little information concerning its structure. In its ir spectrum (Nujol mull), the absence of bands due to C–O, Si–O, C=C, and Si–H was noted. Its ^1H nmr spectrum (C_6D_6) showed a singlet CH_3–Si resonance at δ 0.33 ppm and its ^{29}Si nmr spectrum showed a singlet at −25.29 ppm (*vs.* $(MeO)_4Si$ = 0),[7] which suggests the presence of a single isomer.

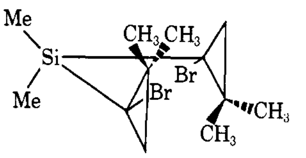
In order to obtain a compound whose spectral properties would be simpler, the lithium reagent from 1,1-dibromo-2,2-dimethylcyclopropane was allowed to react with Me_2SiCl_2 under the same conditions. In principle, one could obtain three isomeric products, V, VI, and VII, and the formation of more than one isomer was suggested by the nmr spectrum of the product which showed three CH_3–Si resonances of approximately equal intensity. Treatment of this product with Mg in THF at room temperature produced a liquid, VIII, bp 50–51° (3.5 mm), in 45% yield. Analysis established the empirical formula $C_{12}H_{22}Si$ and a high-resolution mass spectrum indicated the presence of a monomer species which we believe to be the silacyclopropane VIII. Its proton nmr spectrum showed the $(CH_3)_2Si$ protons as a singlet at δ 0.32, the C–CH_3 groups as singlets at δ 1.24 and 1.27, and the cyclopropyl protons as doublets (*J* = 3.0 Hz) at δ 0.80 and 1.11 ppm. The ^{29}Si nmr spectrum of VIII showed a singlet at −26.72 ppm (*vs.* $(MeO)_4Si$ = 0). ^{13}C nmr spectra of VIII also were obtained.[8] The proton-decoupled spectrum showed six singlets of comparable intensity, consistent with the expectation that VIII has six pairs of chemically different carbon atoms. The partially proton decoupled ^{13}C nmr spectrum showed δ (*vs.* C_6H_6 = 0) +99.529 (q, 2 C, CH_3C), +105.927 (q, 2 C, CH_3C), +106.096 (s, 2 C, quaternary C), +106.376 (s, 2 C, quaternary C), +107.976 (t, 2 C, CH_2), and +134.885 ppm (q, 2 C, $J(^{29}Si-^{13}C)$ = 58 Hz, $(CH_3)_2Si$). Thus proton, silicon, and carbon nmr spectra are fully in agreement with the structure indicated.



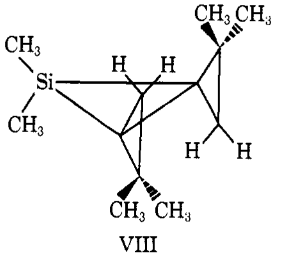
V



VI

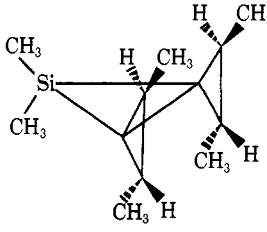


VII



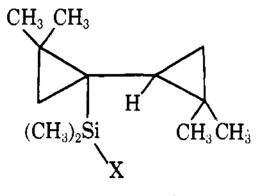
VIII

A third compound, IX, was prepared by the procedure indicated for III and VIII, starting from 1,1-dibromo-*trans*-2,3-dimethylcyclopropane, and for this product the ^1H and ^{13}C nmr spectra, the high resolution mass spectrum, and the combustion analysis were also in agreement with the silacyclopropane structure.



IX

The chemistry of VIII has been investigated in a preliminary manner. It, like III and IX, is oxidatively unstable. In all three cases, the oxidation products were polymeric, which is not surprising in view of the facile moisture-induced ring-opening polymerization of 1-sila-2-oxacyclopentane systems.[9] The methanolysis of VIII at room temperature, an exothermic reaction, gave Xa. This methoxysilane also was obtained by treatment of VIII in pentane with gaseous HCl at −78° and subsequent reaction of the chlorosilane formed (Xb) with MeONa. The action of methyllithium on Xb produced the trimethylsilyl derivative Xc. Cleavage of VIII with methyllithium at −70°, followed by hydrolysis of the bright orange-yellow lithium intermediate, also gave a trimethylsilyl derivative, which, however was different from Xc (by nmr spectra, glc retention times, and $n^{25}D$). One may speculate that HCl cleavage of VIII occurs with retention of configuration but that MeLi cleavage proceeds with inversion at carbon.



Xa. X = OCH_3
Xb. X = Cl
Xc. X = CH_3

---

[7] This ^{29}Si chemical shift is indicative of a silicon atom in an SiC_2 system in an unusual environment. The chemical shifts of acyclic and silacyclic tetraalkylsilanes usually are found at −75 to −97 ppm relative to tetramethoxysilane: R. L. Scholl, G. E. Maciel, and W. K. Musker, *J. Amer. Chem. Soc.*, **94**, 6376 (1972).

[8] Obtained using a Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 Fourier transform data system in a benzene (internal standard)–hexafluorobenzene (internal lock) solvent system. Shift values were obtained with proton decoupling and assignment of structural position was accomplished by varying the degree of proton decoupling, permitting coupling of the ^1H nuclei bonded to the ^{13}C nucleus being observed.

[9] J. L. Speier, M. P. David, and B. A. Eynon, *J. Org. Chem.*, **25**, 1637 (1960).

While the physical, spectroscopic, and chemical evidence presented suggests strongly that the compounds which we report here do indeed contain the silacyclopropane ring, ultimate proof of this will be given only by an X-ray crystal-structure determination. We are continuing work in this area. The ring cleavage and ring insertion reactions of III, VIII, and IX are under investigation. Other bulky substituents are being examined for their application in the stabilization of the SiC_2 ring and extension of this new chemistry to other metallacyclopropanes also is in progress. Prelimiary results suggest that the germacyclopropane ring can be stabilized in similar fashion.[10]

Acknowledgments. The authors are grateful to the U. S. Air Force Office of Scientific Research (NC)-OAR for generous support of this work (Grant No. AF-AFOSR-72-2204), to Dr. D. D. Traficante for the ^{13}C nmr spectra, Professor G. E. Maciel for the ^{29}Si nmr spectra, Dr. C. Hignite for the high-resolution mass spectra, and Dr. Kurt L. Loening for advice on nomenclature.

(10) D. Seyferth and M. Massol, unpublished work.

Robert L. Lambert, Jr., Dietmar Seyferth*
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received October 5, 1972

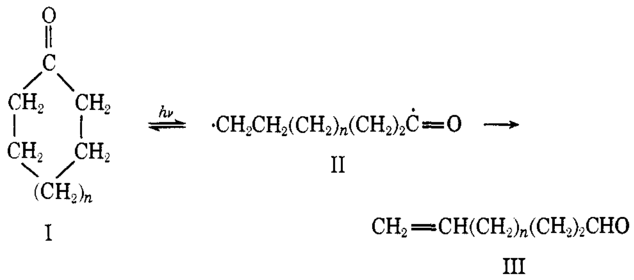
Chemically Induced Dynamic Nuclear Spin Polarization Derived from Biradicals Generated by Photochemical Cleavage of Cyclic Ketones, and the Observation of a Solvent Effect on Signal Intensities[1]

Sir:

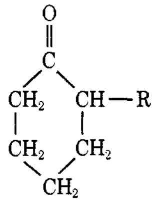
Previously we have given a qualitative discussion of the theory of chemically induced dynamic nuclear spin polarization (CIDNP) applied to reactions proceeding through diradical intermediates.[2] The important difference of CIDNP derived from biradicals and the much more common radical pair based CIDNP is the absence of diffusive separation of the correlated electron spins in the former.[3] To observe CIDNP in either system it is necessary that one of the triplet substates be nearly degenerate with the zero-order singlet state for a time sufficiently long for the wave function to evolve. In radical pairs at high fields the rapidity of diffusive separation assures a vanishing scalar exchange coupling ($2J$) between the components of the pair, leading to degeneracy of T_0 ($|1,0>$) and S ($|0,0>$) states. Mixing between these states *via* the small hyperfine interactions does not involve any change in the z components of the nuclear spin angular momentum. A competitive process such as diffusion is therefore necessary to observe polarization *via* spin selection.

In biradicals, however, it is possible that the mean singlet–triplet splitting, $\langle 2J \rangle$, approaches the electron Zeeman splitting ($g\beta H_0 \sim \langle 2|J| \rangle$) and leads to near degeneracy between the $T_\pm$ ($|1,1\pm>$) and S states. According to the selection rule, $\Delta(m_z)_s = -\Delta(m_z)_I$, $T_\pm$–S mixing leads to net nuclear spin flips and thus does not require diffusion or other competitive processes. Some flexibility to meet the required conditions is given by the possibility of adjusting the magnetic field to the residual exchange coupling in the biradical. However, a further restriction is imposed by the requirement to generate the biradical from a triplet precursor because only then does a net intersystem crossing occur between the biradical and the product ground state. These rather severe limitations are the reasons that only very few biradical reactions have been reported to exhibit CIDNP signals.[2,4]

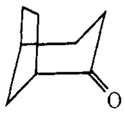
In this communication we wish to give examples of simple biradicals which meet the conditions specified above and give CIDNP spectra in their products.[5] When the cyclic ketones Ib–Ie were irradiated in chloroform, strong emission signals were observed for the reactants (Ib–Ie) and their products (IIIb–IIIe).[6]



a, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$
e, $n = 5$



IVa, R = CH_3
IVb, R = C_6H_5



V

Specifically the signals were assigned to the α and β protons of I and the olefinic and aldehyde protons of III. A typical spectrum, that of irradiated cycloheptanone (Ib), is shown in Figure 1. The fact that all transitions are in emission, regardless of the absolute signs of the hyperfine coupling of the corresponding protons in II, constitutes good evidence for T_-–S

---

(1) Supported by grants from the Petroleum Research Fund (3965-C4), administered by the American Chemical Society, and the National Science Foundation (GP 18719X).

(2) G. L. Closs, *Ind. Chem. Belg.*, **36**, 1064 (1971); see also G. L. Closs, *J. Amer. Chem. Soc.*, **93**, 1546 (1971); J. F. Garst, R. M. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *ibid.*, **92**, 5761 (1970).

(3) For recent reviews on CIDNP see: G. L. Closs, *Proc. Int. Congr. Pure Appl. Chem., XXIIIrd, Spec. Lect.*, **4**, 19 (1971); H. R. Ward, *Accounts Chem. Res.*, **5**, 18 (1972); R. G. Lawler, *ibid.*, **5**, 25, (1972); R. Kaptein, Dissertation, Leiden, 1971; H. Fischer, *Fortschr. Chem. Forsch.*, **24**, 1 (1971).

(4) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **12**, 16 (1971), have observed signals arising from large biradicals. In these cases, however, competing, spin independent, intermolecular reactions were possible and thus the normal T_0-S mixing mechanism can account for the observed spectra.

(5) The ^{13}C CIDNP spectra of an almost identical series of compounds have recently been observed by R. Kaptein (private communication).

(6) The ketones were irradiated inside a modified probe of an HA-60 nmr spectrometer with the condensed beam of a 1000-W xenon-mercury lamp (optics, $f = 1$). Although a quartz insert and nmr tube gave somewhat more intense spectra, the effect was also observable in Pyrex equipment.