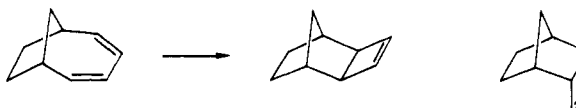


**Table II.** External Heavy Atom Effect by Solvent on Bicyclo[4.2.1]nona-2,4-diene



	solvent : diene (v:v)	exo	endo
hexane	90 : 10 %	28 %	72 %
CH <sub>2</sub> Br <sub>2</sub>	50 : 50	29	71
CH <sub>2</sub> F <sub>2</sub>	90 : 10	27	73
CH <sub>3</sub> CH <sub>2</sub> I	50 : 50	37	63
CH <sub>3</sub> CH <sub>2</sub> Cl	90 : 10	50	50

On the other hand, direct irradiation is undoubtedly a singlet process, especially since intersystem crossing is notoriously inefficient for conjugated dienes.<sup>7</sup> The parent diene **1** typifies the singlet reaction in giving chiefly the endo cyclobutene isomer. However, substitution on the diene system by a moderately heavy atom, chlorine, facilitates intersystem crossing by spin-orbit coupling and as a result the product composition shifts toward that characteristic of the externally sensitized process.<sup>8,9</sup>

This interpretation, a first example of an intramolecular heavy atom effect steering an electrocyclic reaction toward a particular stereochemical outcome, is confirmed by the direct irradiation of **1** in heavy-atom solvent (Table II).<sup>10,11</sup> Surprisingly, the exo-endo ratio is not visibly disturbed in methylene bromide; however, the desired effect is seen to good advantage in ethyl iodide with a significant increase of exo isomer being observed at higher dilution.

For the pair of tricyclo[4.2.1.0<sup>2,5</sup>]non-3-enes, preliminary calculations indicate that the endo is less stable than the exo isomer by a few kilocalories.<sup>13</sup> Thus the less stable isomer is produced preferentially from the more energetic singlet manifold. It appears that this stability order is reversed for tricyclo[4.2.1.0<sup>2,5</sup>]nona-3,7-dienes with the result that the endo isomer is favored in the sensitized and heavy atom reactions.<sup>12,14</sup> These matters are being investigated.

**Acknowledgments.** We are indebted to P. S. Skell for a practical suggestion and K. Schaffner for useful advice. We also appreciate the courteous gesture of R. C. Hahn and R. P. Johnson of informing us of their results prior to publication. Lastly we thank U. Burger and B. May for carrying out impeccable NMR spectral and mass spectroscopic measurements.

## References and Notes

- (1) Part of this research has been submitted as a doctoral dissertation, Thesis No 1638, Faculty of Sciences, University of Geneva, Jan 25, 1974.
- (2) C. W. Jefford and F. Delay, *J. Am. Chem. Soc.*, **94**, 4794 (1972).
- (3) Most theoretical treatments of light-induced electrocyclic reactions usually neglect the multiplicity of the photoexcited states, the energetics of the process, and in general the problem of how the excited reactant passes to ground state product (However, cf. W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am. Chem. Soc.*, **88**, 2742 (1966); W. T. A. M. van der Lugt and L. J. Oosterhoff, *ibid.*, **91**, 6042 (1969); K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971); J. Michl, *Mol. Photochem.*, **4**, 243, 257, 287 (1972); H. Nohira, *Tetrahedron Lett.*, 2573 (1974)).
- (4) C. W. Jefford, U. Burger, and F. Delay, *Helv. Chim. Acta*, **56**, 1083 (1973).
- (5) The dichloro derivative **4** was obtained by chlorinating compound **2** and eliminating a molecule of hydrogen chloride from the trichloro adduct with potassium *tert*-butoxide in dimethylformamide. The trichloro derivative **6** was obtained by similar base treatment of 2,3,4,5-tetrachlorobicyclo[4.2.1]nona-3-ene (ref 4).
- (6) Only reaction to partial conversion (10–50%; 2–4 hr duration) was allowed in order to minimize decomposition by C–Cl bond cleavage and polymerization. The exo-endo isomer ratio was invariant with the reaction time. The cyclobutene isomers were characterized by their NMR spectra and GLC retention times.
- (7) E. Havinga, R. J. deKock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960); E. Havinga and J. L. M. A. Schlatmann, *ibid.*, **16**, 146 (1961); R. S. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 4936 (1967); J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).
- (8) Theoretical and spectroscopic studies of heavy atom effects are plenti-

ful, cf. S. K. Lower and M. A. El-Sayed, *Chem. Rev.* **66**, 208 (1966); S. P. McGlynn, C. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, pp 40, 183, 261, 307, and 371; G. G. Giachino and D. R. Kearns, *J. Chem. Phys.*, **52**, 2964 (1970); G. Kavarnos, T. Cole, P. Scribe, J. C. Dalton, and N. J. Turro, *J. Am. Chem. Soc.*, **93**, 1032 (1971), and references therein.

- (9) In an attempt to exploit a greater heavy atom effect, some bromobicyclo[4.2.1]nona-2,4-dienes were irradiated in trial experiments. Unfortunately, extensive decomposition to inseparable complex mixtures occurred, presumably as a result of easy C–Br bond cleavage.
- (10) Chemical examples of heavy atom effects are not numerous: (a) conversion of singlet to triplet carbene, A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966); P. S. Skell, S. J. Valenty, and P. W. Humer, *ibid.*, **95**, 5041 (1973); (b) dimerization of acenaphthylene, D. O. Cowan and R. L. E. Drisko, *ibid.*, **92**, 6281, 6286 (1970); (c) addition of acenaphthylene to acrylonitrile (B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970)), to maleic anhydride (W. Hartmann and H. G. Heine, *Angew. Chem.*, **83**, 291 (1971)), and to cyclopentadiene (W. I. Ferree and B. F. Plummer, *J. Am. Chem. Soc.*, **95**, 6709 (1973)); (d) isomerization of bromostilbene: J. Saltiel, D. W. L. Chang, and E. D. Megarity, *J. Am. Chem. Soc.*, **96**, 6521 (1974).
- (11) Other examples, in which di- $\pi$ -methane rearrangements are potentially competitive, but suppressed when a heavy atom is present, are provided by benzo[7,8]bicyclo[4.2.1]nona-2,4,6-triene and its derivatives (ref 12).
- (12) R. C. Hahn and R. P. Johnson, *J. Am. Chem. Soc.*, **97**, 212 (1975).
- (13) P. Gund and J. C. Perleberger, unpublished observations.
- (14) L. G. Cannell, *Tetrahedron Lett.*, 5967 (1966); H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970).

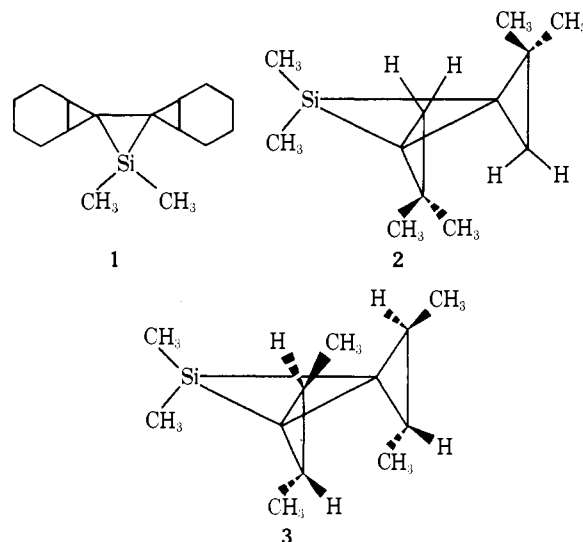
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## Hexamethylsilirane. A Simple, Isolable Silacyclopropane

Sir:

Recently, we have prepared the first silacyclopropanes, **1**, **2**, and **3**.<sup>1</sup> All were found to be quite stable thermally but

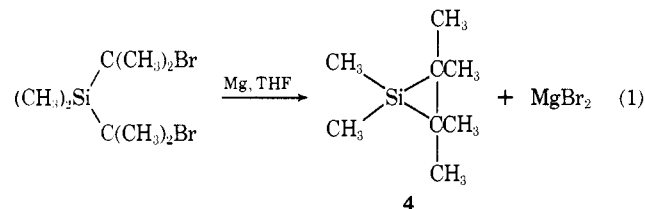


exceptionally reactive. Thus **2**, whose chemistry has been studied in some detail, reacts exothermally at room temperature with reagents which do not attack the Si–C bonds of larger silacycloalkanes, such as atmospheric oxygen, water, alcohols, ammonia, hydrogen sulfide, and carbon tetrachloride.<sup>1,2</sup> This high reactivity of the Si–C bonds of the silacyclopropane rings of **1**, **2**, and **3** no doubt is a result of the great angle strain in the SiC<sub>2</sub> ring.<sup>3</sup>

The various attempts to prepare silacyclopropanes (siliranes) previous to our synthesis of **1**, **2**, and **3**, in retrospect, do not provide useful information concerning the stability of this ring system since the reaction and work-up conditions used did not anticipate the high reactivity of the silirane

ring.<sup>4</sup> Therefore, our preparation of **1**, **2**, and **3** raised several questions. Was the preparation of these compounds successful merely because we had carried out all operations under an inert atmosphere; i.e., are all siliranes stable, provided atmospheric oxygen and moisture are excluded, or was there some important stabilizing factor associated with the dispiro structure common to **1**, **2**, and **3**? If so, was it merely a matter of the steric bulk of the spiroannulated substituted cyclopropane rings which provided some measure of kinetic stability with respect to possible decomposition pathways, or was there some special electronic factor associated with these silicon-containing dispiro systems? In order to provide an answer to these questions, we have prepared and assessed the stability of hexamethylsilirane (**4**). This compound was chosen because it would provide information concerning the question of steric vs. electronic effects since it was highly substituted but not part of a dispiro system.

The preparation of hexamethylsilirane was patterned straightforwardly after our synthesis of **1**, **2**, and **3**. The known dimethyldiisopropylsilane<sup>5</sup> was treated with 2 molar equiv of bromine at 65° to give dimethylbis( $\alpha$ -bromoisopropyl)silane, mp 84–86°, in good yield (>60%).<sup>6</sup> The reaction of this compound with magnesium chips in dry THF under a nitrogen atmosphere produced hexamethylsilirane in yields of up to 76% (eq 1). Trap-to-trap distillation of the

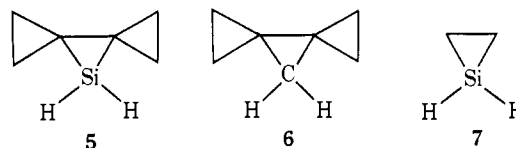


reaction mixture (25° (0.02 mm Hg)) into a receiver at -196° removed the volatile components. Distillation of the THF from the latter at 25° (70 mm Hg) left behind the silirane, but we have not been able to obtain it as an analytically pure compound. Three minor impurities invariably are present:  $\text{Me}_2\text{Si}(\text{CHMe}_2)_2$ ,  $\text{Me}_2\text{Si}(\text{CMe}=\text{CH}_2)_2$ , and  $\text{Me}_2\text{Si}(\text{CHMe}_2)(\text{CMe}=\text{CH}_2)$ ; all probably are by-products of the reaction of the dibromo precursor with magnesium. These have boiling points close to that of **4** and cannot be separated since **4** does not survive attempted fractional distillation or purification by gas chromatography. Nevertheless, the spectroscopy, stability, and chemistry of hexamethylsilirane can readily be studied in the presence of these impurities.

The proton, carbon-13, and silicon-29 NMR spectra of hexamethylsilirane prove its structure: <sup>1</sup>H NMR (in THF- $\text{C}_6\text{H}_6$ )  $\delta$  0.133 (s, 6 H, Si-CH<sub>3</sub>) and 1.13 ppm (s, 12 H, C-CH<sub>3</sub>); <sup>13</sup>C FT NMR (in THF) (proton-decoupled spectrum) singlets at 20.97 and 18.16 ppm downfield from TMS and a singlet at 9.67 ppm upfield from TMS; in the off-resonance decoupled spectrum the 20.97 and 9.67 ppm signals appeared as quartets and the 18.16 ppm signal as a singlet; this suggests the assignments C-CH<sub>3</sub> (+20.97), Si-CH<sub>3</sub> (-9.67), cyclopropane C (+18.17 ppm); <sup>29</sup>Si FT NMR (in THF-( $\text{Me}_2\text{SiO}$ )<sub>4</sub>) (off-resonance decoupled spectrum) singlet at 29.19 ppm downfield from tetramethoxysilane. A fully proton-coupled spectrum showed a seven-line resonance centered at 29.19 ppm downfield from tetramethoxysilane. This anomalously high-field position for the <sup>29</sup>Si resonance (49.31 ppm upfield from ( $\text{CH}_3$ )<sub>4</sub>Si) in **4** is characteristic of silacyclopropanes.<sup>1</sup>

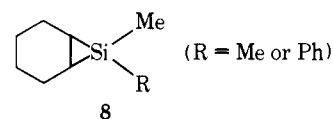
The questions which prompted the present study were answered when we examined the thermal stability of hexamethylsilirane. This compound appears to be stable (under

an inert atmosphere) at 0° for prolonged periods of time; it is stable at room temperature for at least 9 days. At 37°, its half-life in THF solution is 81 hr, at 63°, only 5 hr.<sup>7</sup> In contrast, the dispiro system **2** has a half-life of about 7 days at 65°; it also can be analyzed and isolated by gas chromatography (4 ft 10% UC-W98 silicone column, injection port and detector at 200°, column at temperatures up to 150°). Compound **1** can be distilled at 95–97° (0.01 mm). Thus hexamethylsilirane is considerably less stable than the 7-siladispiro[2.0.2.1]heptane derivatives **1**, **2**, and **3**, and so we suggest that electronic, in addition to steric, factors are important in making the latter class so stable.<sup>8</sup> Support for this experimental finding has been provided by calculations of Mollere and Hoffmann,<sup>9</sup> who found that **5** was stabilized considerably with respect to **6** and **7** by d- $\sigma$  hyperconjugation,



i.e., overlap of filled Walsh orbitals of the spiroannulated cyclopropane rings with vacant silicon 3d orbitals of suitable symmetry.

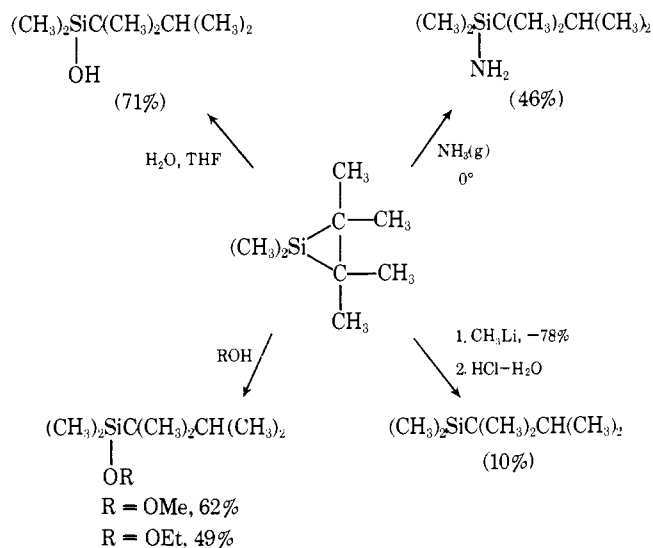
It is likely that steric factors also will be of some importance, and we expect that highly substituted siliranes such as **4** will be more stable than those in which the ring carbon atoms do not bear two alkyl substituents. In this connection, we note that **8**, prepared recently by silylene addition to cy-



clohexene, could not be isolated, nor, apparently, could either compound be characterized spectroscopically in solution (it was their reactions with methanol which confirmed that they had been formed).<sup>10</sup> This may be a consequence of diminished thermal stability with respect to **4**. The question of "steric stabilization" of the silirane ring is receiving further attention in these laboratories.

As expected, hexamethylsilirane, like **1**, **2**, and **3**, is exceptionally reactive. On exposure to air, exothermic oxidation causes it to fume strongly. Oxidation under controlled conditions gave a nonvolatile peroxidic material which oxi-

#### Scheme I



dizes iodide ion to iodine and triphenylphosphine to triphenylphosphine oxide. Scheme I summarizes some other reactions of **4** which have been studied.<sup>11</sup> All reactions were carried out in THF solution. With the alcohols and with water, exothermic reactions at room temperature were observed. In the case of the reaction with methylolithium, higher oligomers, up to THF-insoluble-polymer, were formed. These must have resulted from attack of the intermediate lithium reagent,  $\text{Me}_3\text{SiC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{Li}$ , at the silacyclopropane ring.

For all new compounds combustion analyses and spectroscopic data were obtained which were in full agreement with the structures indicated.

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- (2) D. Seyferth, C. K. Haas, and D. C. Annarelli, *J. Organomet. Chem.*, **56**, C7 (1973).
- (3) The X-ray crystal structure of one of the isomers of **1** has been determined and the endocyclic C-Si-C angle was found to be  $49^\circ$ : G. D. Stucky, private communication.
- (4) References to previously reported attempts to prepare silacyclopropanes are collected in ref 1. Without doubt, other unsuccessful attempts remain unpublished.
- (5) C. Eaborn, *J. Chem. Soc.*, 2755 (1949).
- (6) This reaction is based on the known bromination of dimethylsopropylchlorosilane: F. K. Cartledge and J. P. Jones, *J. Organomet. Chem.*, **67**, 379 (1974).
- (7) Determined by quenching aliquots of the hexamethylsilirane-THF solution with anhydrous methanol at various times and determining the yield of  $\text{Me}_2\text{CHCMe}_2\text{SiMe}_2\text{OMe}$  formed by GLC. NMR techniques also are applicable. The decomposition products have not yet been isolated.
- (8) NOTE ADDED IN PROOF. A referee has suggested that to assess steric vs. electronic factors 1,1,2,3-tetramethyl-2,3-disopropylsilirane or 1,1-dimethyl-2,2,3,3-tetraethylsilirane would be better compounds than hexamethylsilirane for the comparison with **2**. Although hexamethylsilirane is somewhat less hindered than **2**, we feel it is a reasonably good first approximation for the purpose under discussion. The two compounds suggested are more hindered than **2** since the alkyl substituents on the carbon atoms are not "tied back" as in the dispiro system.
- (9) P. D. Mollere and R. Hoffmann, *J. Am. Chem. Soc.*, submitted.
- (10) M. Ishikawa and M. Kumada, *J. Organomet. Chem.*, **81**, C3 (1974).
- (11) Indicated yields are based on the amount of dibromo precursor used.

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## Nuclear Magnetic Resonance Studies of Metal Complexes Using Lanthanide Shift Reagents. Lanthanide Induced Shifts in the Spectra of Oxygen-Donor Ligands Coordinated to Nickel(II)

Sir:

Since the introduction of lanthanide shift reagents (LSR) in 1969,<sup>1</sup> these reagents have been widely used to simplify the NMR spectra of organic compounds and examples of their use with organometallic compounds have also recently appeared.<sup>2</sup> We now report the successful use of these reagents to induce shifts in the spectra of coordinated ligands in coordination complexes containing oxygen donors. The effect of added shift reagent on the  $^1\text{H}$  NMR spectra of a range of diamagnetic nickel complexes of type I has been studied.

The spectrum of *N,N'*-ethylenebis(acetylacetonato)nickel(II) (**1**,  $\text{R} = \text{CH}_3$ ) in deuteriochloroform has been pre-

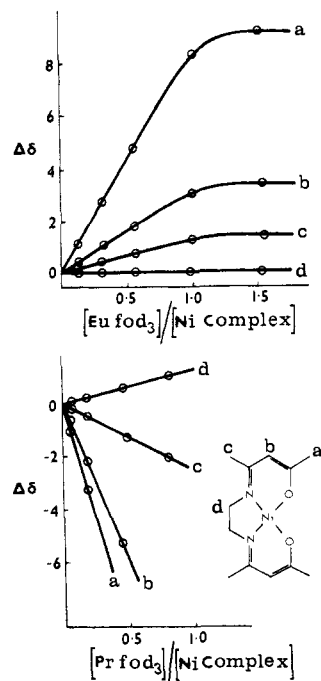
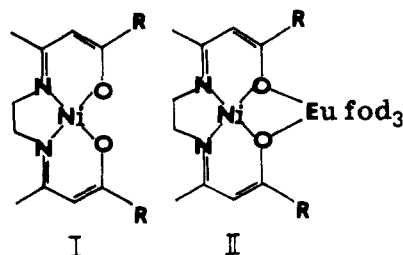


Figure 1. Comparison of the relative chemical shifts ( $\Delta\delta$ ) induced by  $\text{Eu}(\text{fod})_3$  and  $\text{Pr}(\text{fod})_3$  in the NMR spectrum of (**1**,  $\text{R} = \text{CH}_3$ ).



viously described<sup>3</sup> and contains single peaks ( $\delta$  values) at 1.87 ( $-\text{CH}_3$ ), 3.07 ( $-\text{CH}_2-$ ), and 4.89 ( $=\text{CH}-$ ) ppm. On successive additions of  $\text{Eu}(\text{fod})_3$  or  $\text{Pr}(\text{fod})_3$  to this compound, the proton resonance shifts illustrated in Figure 1 are observed.

As is usually the case with organic compounds,  $\text{Eu}(\text{fod})_3$  and  $\text{Pr}(\text{fod})_3$  cause a particular proton resonance to shift in opposite directions. The relative orders of the shifts in Figure 1 are in accord with the LSR interacting with the cis oxygen atoms of the nickel complex as shown by II; however, the possibility that the interaction is monodentate in nature and is associated with a rapid equilibrium between oxygen donor sites on the nickel complex cannot be dismissed on the present evidence. Nevertheless, the ability of europium and praseodymium to expand their coordination numbers from six to eight has been well documented,<sup>4</sup> and the electron lone pairs associated with such cis oxygen donors in related complexes have been shown to be capable of coordinating simultaneously to a second metal ion.<sup>5</sup> Examples of difunctional organic molecules acting as bidentate ligands toward LSR's are also known.<sup>6,7</sup>

It is pertinent that both  $\text{Eu}(\text{fod})_3$  and  $\text{Pr}(\text{fod})_3$  have been shown to self-associate (in  $\text{CCl}_4$ ) via bridging  $\beta$ -diketone oxygen donors in a manner which appears analogous to the interactions reported here.<sup>8</sup>

Although a general trend of diminution of shift with distance from LSR is apparent (Figure 1), clearly a detailed analysis of the magnitude of the shifts associated with bidentate systems of the present type is inappropriate in terms of the McConnell-Robertson equation.<sup>7</sup>