

## Preliminary communication

### Fluxional behavior and isomerization of 1,2-bis(trimethylsilyl)indene: evidence for 1,2-shifts

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A number of studies have demonstrated the fluxional character of  $\sigma$ -indenyl organometallic compounds<sup>1-3</sup>. We report here the synthesis and variable temperature NMR studies of 1,2-bis(trimethylsilyl)indene,  $[(\text{CH}_3)_3\text{Si}]_2\text{C}_9\text{H}_6$ , (I), a fluxional molecule which appears to rearrange by a series of 1,2-shifts. In addition, we have studied its isomerization (via hydrogen migration) to the more stable 1,1- and 1,3-isomers.

The intermediate, 2-trimethylsilylindene, was prepared by treating chlorotrimethylsilane with the Grignard reagent obtained from 2-bromoindene. Reaction of the 2-trimethylsilylindene with *n*-butyllithium followed by chlorotrimethylsilane addition yielded 1,2-bis(trimethylsilyl)indene in 60% yield (based on 2-trimethylsilylindene). The compound is a white crystalline solid (m.p. 68–69°) which can be purified by distillation (73°/0.03 mm) followed by recrystallization from pentane (*Anal.*: Found: C, 68.88; H, 9.17.  $\text{C}_{15}\text{H}_{24}\text{Si}_2$ . Calcd.: C, 69.15; H, 9.29%). The mass spectrum showed the molecular ion  $\text{C}_{15}\text{H}_{24}^{28}\text{Si}_2$  at *m/e* 280. In  $\text{CDCl}_3$  solution the proton NMR spectrum (Fig. 1a) showed resonances at  $\tau$  2.7–2.8 aromatic and olefin(5);  $\tau$  6.30 tertiary (1);  $\tau$  9.74 vinyl-trimethylsilyl (9);  $\tau$  10.05 tertiary trimethylsilyl (9), consistent with the proposed structure. The results of the variable temperature NMR study are shown in Fig. 1b. At temperatures above  $\sim 100^\circ$  a significant broadening of the resonances at  $\tau$  6.30, 9.74 and 10.05 is observed. The complete collapse of the proton signal at  $\tau$  6.30 is obtained at 175°. Changes take place simultaneously in the region  $\tau$  2.7–2.8. The olefinic resonance at  $\tau$  2.8 first broadens and then collapses. The complex aromatic pattern undergoes changes and eventually (*ca.* 175°) simplifies to an AA'BB' pattern. At 150° the two trimethylsilyl signals have merged and at higher temperatures they sharpen to a single line. Additional resonances appear irreversibly in the spectra as indicated in the figure. Their intensity increases on standing and does so rapidly during prolonged heating. Nearly complete conversion could be obtained by heating the sample to 180° for 16 hours (Fig. 1c). The

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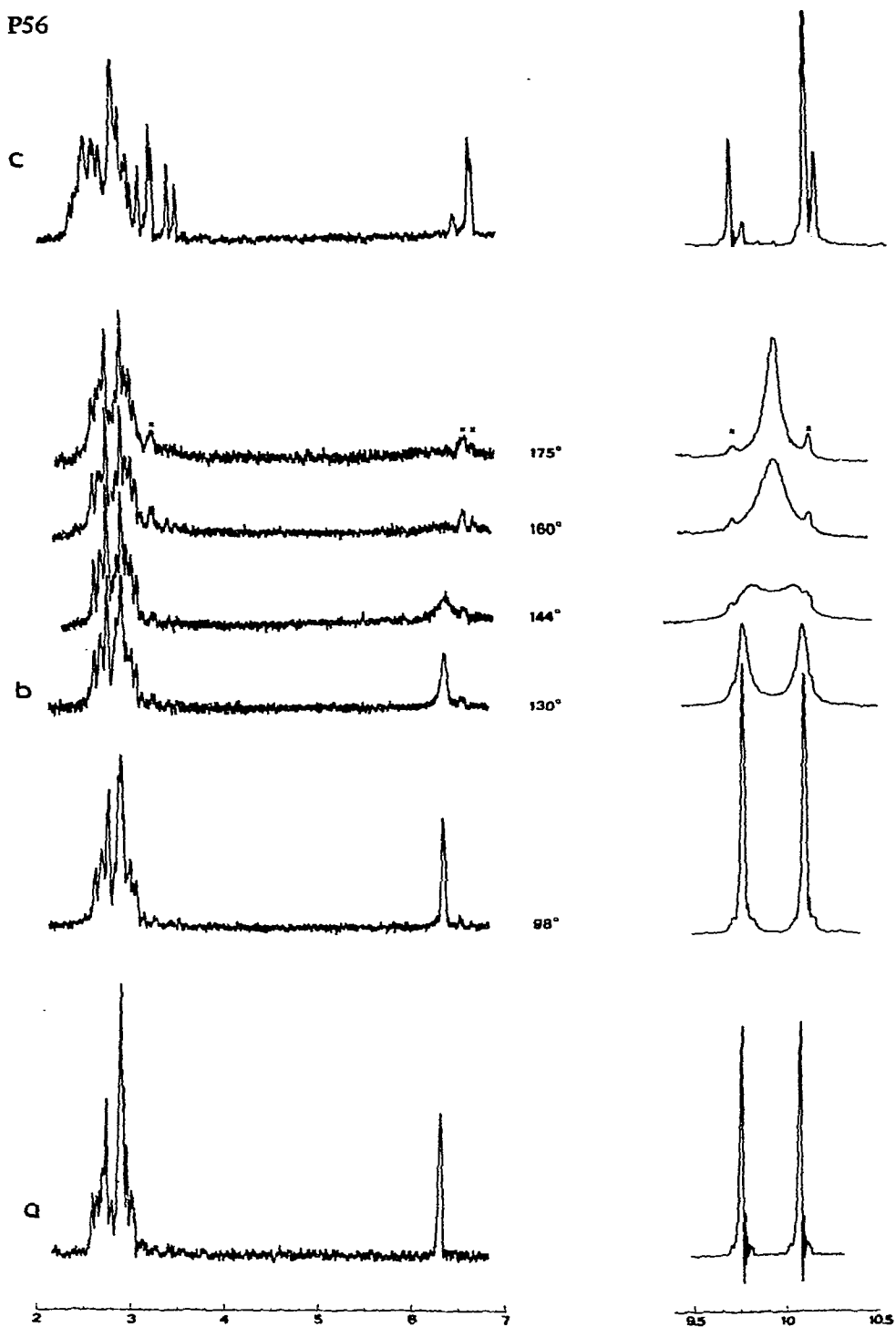
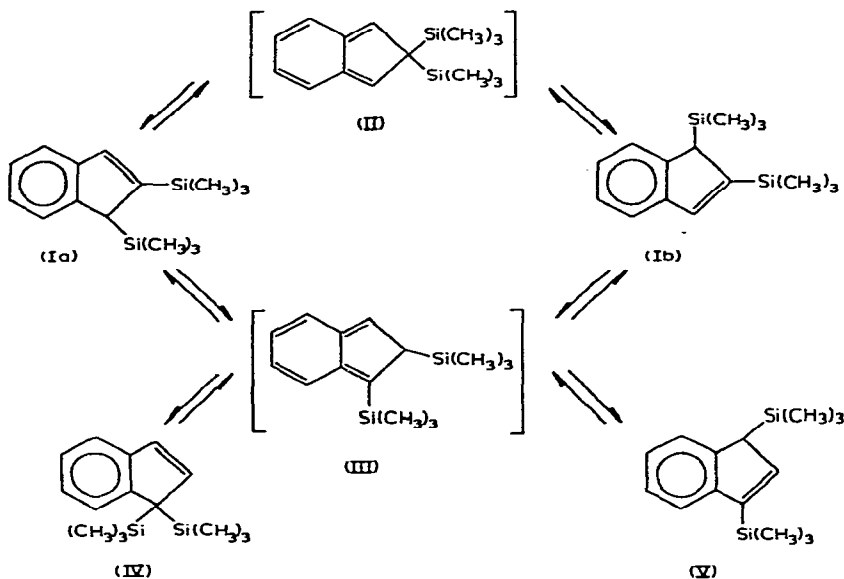


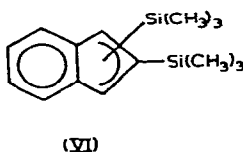
Fig.1. NMR spectra of (a) 1,2-bis(trimethylsilyl)indene in  $\text{CDCl}_3$  solution at  $31^\circ$ , (b) neat 1,2-bis(trimethylsilyl)indene at  $98$ ,  $130$ ,  $144$ ,  $160$  and  $175^\circ$ , and (c) sample used in (b) after 16 hours at  $180^\circ$ . The changes with temperature indicated in (b) are reversible except for the appearance of the addition signals noted by (x).

product was identified as a mixture of the isomers 1,1- and 1,3-bis(trimethylsilyl)indene by comparison with the NMR spectrum of an authentic sample<sup>★</sup>.

We interpret the spectral results in the following manner. The molecule 1,2-[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>C<sub>9</sub>H<sub>6</sub> undergoes an intramolecular<sup>★★</sup> rearrangement which has the effect of averaging the magnetic environments of the two trimethylsilyl groups. A plausible mechanism is given by the reaction sequence Ia ⇌ II ⇌ Ib.



While the experimental data do not prove the intermediacy of structure II in the rearrangement, they do rule out simple 1,3-shifts of a  $\pi$ -bonded structure like VI since in both cases the trimethylsilyl groups are not interchanged<sup>★★★</sup>.



The observed rearrangement to the 1,1- and 1,3-isomers strongly suggests that the sequences I ⇌ III, III ⇌ IV and III ⇌ V occur, involving first hydrogen migration followed by the shift of a trimethylsilyl group. While the process IV ⇌ V does not occur

<sup>★</sup>The mixture of 1,1- and 1,3-[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>C<sub>9</sub>H<sub>6</sub> was prepared in 77% yield by treating 1-trimethylsilylindene with *n*-butyllithium followed by chlorotrimethylsilane. The properties of this mixture are identical with those previously reported for 1,1-bis(trimethylsilyl)indene<sup>4</sup>.

<sup>★★</sup>Intramolecular rearrangement is not proved per se by the available data, but is strongly suggested by the concentration independence of the spectra, the lack of exchange of groups between molecules, and the intramolecular character of the rearrangements in the related cyclopentadienyl compounds<sup>5</sup>.

<sup>★★★</sup>A concerted reaction in which the trimethylsilyl group at position 2 moves to position 3 while the trimethylsilyl group at position 1 migrates to position 2 is in accord with the data.

sufficiently rapidly at temperatures below 200° to cause any averaging of the separate resonances due to the two isomers, the ratio of IV to V is temperature dependent.  $\Delta H$  for the equilibrium  $IV \rightleftharpoons V$  was found to be +2.5 kcal·mole<sup>-1</sup> and independent of concentration in the range 30–130°.

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