FLUXIONAL BEHAVIOR OF SUBSTITUTED INDENYL DERIVATIVES OF SILICON AND TIN

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SUMMARY

A series of substituted indenyl compounds of silicon and tin have been prepared and their fluxional behavior investigated by variable temperature proton magnetic resonance spectra. The activation parameters of the exchange process were determined for the four compounds, 1,2-bis(trimethylsilyl)indene, 1-(dimethylphenylsilyl)-indene, 1-(dimethylphenylstannyl)indene, 1-(trimethylstannyl)-1,3-dimethylindene. For the stannanes $E_a = 14$ kcal/mole while for the silanes $E_a \sim 25$ kcal/mole. The molecule 1,2-bis(trimethylsilyl)indene undergoes two processes: (*i*) fluxional behavior which can be interpreted as 1,2-trimethylsilyl migration and, (*ii*) slow hydrogen migration which results in the formation of a mixture of 1,1- and 1,3-bis(trimethylsilyl)indene.

INTRODUCTION

In a previous paper[1] the trimethylindenyl compounds of silicon, germanium, and tin were shown to be fluxional molecules. It was not possible, however, to deduce the mode of rearrangement for those compounds since both the 1,2- and 1,3-shift mechanisms give rise to the same spectral changes in the exchange broadened region. In addition, although a *qualitative* measure of the relative rates of fluxional behavior is apparent from the spectra (*viz.* Sn ≫ Ge > Si), actual values of the rates and activation parameters were not obtained***.

By designing appropriate derivatives of the parent indenyl compounds it was possible to treat the exchange process, using available computing techniques, without recourse to the approximations heretofore required in other studies[2].

The asymmetric site at C(1) gives rise to a magnetic non-equivalence of the two methyl groups in the derivatives $C_6H_5(CH_3)_2MC_9H_7$; M = Si, Sn (I). Exchange of magnetic environments by the fluxional process (whether 1,2-shifts or a suprafacial

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*** The problem, which is one of two site exchange, is complicated by coupling of the two exchanging protons, H(1) and H(3), with the H(2) proton on the five-membered ring. Consequently, the slow exchange spectrum consists of twelve lines and an approximate treatment would be required.
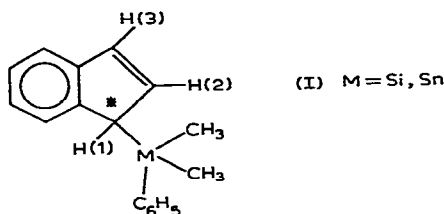
1,3-shift with retention of configuration at the metal atom, *vide infra*) gives rise to a simple two-site exchange between singlet resonances. Replacement of the hydrogens H(1) and H(3) by methyl groups likewise simplifies the calculations.

A variable temperature NMR study of the fluxional molecule 1,2-bis(trimethyl-silyl)indene allows a definite conclusion to be drawn about the rearrangement pathway.

In addition, the process of hydrogen migration observed to occur for the cyclopentadiene compounds[3,4] was noted for 1,2-bis(trimethylsilyl)indene.

EXPERIMENTAL

General data

Unless otherwise indicated, all manipulations were carried out in an atmosphere of dry nitrogen or *in vacuo*. Infrared spectra were recorded using liquid films or on hydrocarbon and fluorocarbon mulls between KBr plates on a Perkin–Elmer 337 spectrometer. NMR spectra were obtained at 60 MHz and 100 MHz utilizing spectrometers (A-60, HA-100) by Varian Associates equipped with variable-temperature probes. Temperature calibrations were made with methanol or ethylene glycol. Spectra were recorded as indicated on the neat liquids or in solution of diphenylether (high temperature kinetic studies), chloroform-*d*, carbon disulfide, or toluene-d_8 (below 0°). Cyclohexane was used as an internal reference. Mass spectra were obtained on a Hitachi Perkin–Elmer RMU6-D spectrometer. Elemental analyses were performed by Mrs. Nancy F. Alvord of the M.I.T. Microanalytical Laboratory and the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Dimethyldiphenylstannane

A solution of phenylmagnesium bromide, prepared from magnesium turnings (5.65 g, 0.23 mole) and bromobenzene (24.2 ml, 0.23 mole) in anhydrous ether (175 ml), was treated dropwise with a solution of dimethyldichlorostannane (21.96 g, 0.10 mole) in ether (350 ml) over 3 h at a rate sufficient to maintain a moderate reflux. The mixture was further refluxed for $1\frac{1}{2}$ h. Upon cooling, it was treated with an aqueous solution (150 ml) buffered to pH 7 and the organic layer was separated, washed (2 × 100 ml) with more buffered solution, separated, and dried (Na$_2$SO$_4$). The ether was removed by distillation at atmospheric pressure and the remainder was vacuum distilled. The small forerun, which crystallized in the condenser, was removed. The product was obtained as a colorless, somewhat viscous liquid at 98°/0.20 mm, $n_D^{26.5}$ 1.5871. The yield was 25.58 g (84% based on dimethyldichlorostannane). (Found: C, 55.54; H, 5.57. C$_{14}$H$_{16}$Sn calcd.: C, 55.50; H, 5.32%.)

The proton NMR spectrum had the following resonances: τ 2.6–2.7 (multiplet, 10); τ 9.56 (singlet, 6), $J(^{117,119}Sn-H)$ 53, 56 Hz. Infrared bands were seen at 3065 s, 3050 m, 3015 m, 2990 m, 2920 m, (br), 2865 w, 1579 w, 1480 m, 1425 vs, 1331

w, 1298 w, 1257 w, 1188 w, 1073 s, 1020 w, 993 m, 746 m, 710 vs, 693 vs, 649 w, 525 m, 510 m, 438 m cm^{-1}.

Dimethylphenyliodostannane

A solution of dimethyldiphenylstannane (12.03 g, 0.04 mole) in CCl_4 (100 ml) was placed in a flask (300 ml) to which was attached a Soxhlet extraction apparatus containing iodine (10.08 g, 0.04 mole). The iodine was extracted into the solution of dimethyldiphenylstannane over a period of 16 h. The solvent was removed at ~30 mm. The remainder was vacuum distilled yielding iodobenzene at 54°/3.8 mm, as identified by its proton NMR spectrum. The product was obtained as a colorless liquid at 100–101°/1.4 mm, n_D^{25} 1.6243. The yield of $(CH_3)_2(C_6H_5)SnI$ was 11.40 g (81% based on dimethyldiphenylstannane). (Found: C, 26.05, 26.06; H, 3.21, 3.03. $C_8H_{11}SnI$ calcd.: C, 27.24; H, 3.14%.)

The NMR spectrum had the following resonances: τ 2.6 (multiplet, 5); τ 9.00 (singlet, 6), $J(^{117,119}Sn-H)$ 56, 58.5 Hz. The infrared spectrum was essentially identical with that reported for dimethyldiphenylstannane in the region 4000–400 cm^{-1}.

1-(Dimethylphenylstannyl)indene

A suspension of indenyllithium (0.02 mole) in hexane (60 ml) was prepared from n-butyllithium (13 ml, 1.6 M) in hexane and indene (2.3 ml). This was treated dropwise with a solution of dimethylphenyliodostannane (7.26 g, 0.02 mole) in hexane (10 ml) and the mixture was refluxed for 1 h. The lithium iodide was removed by filtration and the hexane was distilled at atmospheric pressure. Vacuum distillation yielded the product at 108–100°/0.10 mm. During redistillation a forerun, which solidified in the condenser, was removed and the product was collected at 107°/0.06 mm as a pale yellow liquid, n_D^{23} 1.6242. (Found: C, 59.90; H, 5.57. $C_{17}H_{18}Sn$ calcd.: C, 59.87; H, 5.32%.)

Infrared bands were seen at 3067 s, 3050 w, 3011 m, 2990 w, 2953 w, 2920 m, 1594 w, 1565 w, 1510 w, 1475 m, 1454 s, 1443 vs, 1425 vs, 1355 w, 1331 w, 1313 w, 1296 w, 1224 w, 1195 s, 1153 w, 1141 m, 1105 w, 1070 s, 1014 m, 992 m, 978 w, 935 vs (br), 920 s (br), 855 s, 778 vs, 745 vs (br), 715 vs (br), 690 vs, 650 w, 558 m, 526 s, 508 s, 435 s, 420 s cm^{-1}.

1-(Trimethylstannyl)-2-bromoindene

The compound $(CH_3)_3SnC_9H_6Br$ was prepared in a similar manner to $(CH_3)_2(C_6H_5)SnC_9H_7$ using chlorotrimethylstannane and the lithium reagent obtained from the reaction of n-butyllithium with 2-bromoindene (see *Results* section). The product, a colorless liquid which turns yellow on standing for several hours or immediately on exposure to air, was distilled at 95–97°/0.10 mm. (Found: C, 40.54; H, 4.42. $C_{12}H_{15}SnBr$ calcd.: C, 40.27; H, 4.23%.)

Infrared bands were seen at 3065 m, 3050 (sh), 2982 m, 2918 s, 2870 (sh), 1604 w, 1552 w, 1520 m, 1450 s, 1440 vs, 1368 m, 1275 s, 1206 m, 1195 s, 1028 w, 1015 m, 940 s, 924 w, 870 s, 857 w, 823 w, 769 vs, 742 vs, 729 (sh), 710 w, 635 w, 590 w, 570 w, 555 w, 525 vs, 501 m, 445 w, 410 m cm^{-1}.

1-(Dimethylphenylsilyl)indene

A suspension of indenyllithium (0.10 mole) in hexane (30 ml) was prepared

from n-butyllithium (62.5 ml, 1.6 M) in hexane and indene (11.6 ml). This was treated dropwise with a solution of dimethylphenylchlorosilane[5] (16.5 ml, 0.10 mole) in hexane (20 ml), and was stirred at reflux for 5 h. The mixture was filtered and the hexane was removed by distillation at atmospheric pressure. Vacuum distillation yielded the product at 112°/0.20 mm as a pale-yellow liquid. The yield was 19.56 g (78% based on dimethylphenylchlorosilane). (Found: C, 81.35; H, 7.26. $C_{17}H_{18}Si$ calcd.: C, 81.54; H, 7.25%.)

Infrared bands were seen at 3070 m, 3050 w, 3010 w, 2958 m, 2922 w, 2900 vw, 2853 w, 1595 w, 1580 w, 1475 w, 1448 m, 1142 s, 1418 s, 1400 w, 1348 w, 1248 s, 1215 m, 1187 m, 1110 s, 1028 (sh), 1020 s, 992 w, 972 m, 929 w, 871 m, 856m, 829 s, 807 s, 798 s, 775 (sh), 767 vs, 751 w, 730 s, 725 s, 710 m, 695 s, 638 (sh), 628 m cm^{-1}.

2-(Trimethylsilyl)indene

Magnesium metal turnings (1.5 g, 0.06 mole) in a three-neck flask equipped with a mechanical stirrer, dropping funnel, and condenser, were treated with ethyl bromide (1 ml) in THF (30 ml) and stirred until the reaction became vigorous. The solution was then removed with a syringe and the magnesium was washed with THF (3 × 20 ml). More THF (40 ml) was added, and a small portion (5 ml) of a solution of 2-bromoindene (12.0 g, 0.06 mole) in THF (30 ml) was introduced with stirring to initiate the reaction at room temperature. The flask was chilled to between −10° and −20° and the remainder of the solution was added dropwise during 1½ h. The mixture was warmed to room temperature and chlorotrimethylsilane (7.9 ml, 0.06 mol) in THF (20 ml) was added dropwise with stirring. It was then refluxed for 1 h and was stirred for an additional 7 h. Water (50 ml) was added followed by ether (50 ml) and the organic layer was separated, dried (MgSO$_4$), and distilled. The ether and THF were removed at atmospheric pressure. After a brief forerun, identified as indene by its NMR spectrum, the product was collected as a colorless liquid at 88–91°/2.7 mm, n_D^{29} 1.5476. The yield was 5.01 g (43% based on 2-bromoindene). It was purified by redistillation at 72–74°/0.8 mm. (Found: C, 76.58; H, 8.05. $C_{12}H_{16}Si$ calcd.: C, 76.53; H, 8.56%.)

The proton NMR spectrum had the following resonances: τ 2.75 (multiplet, 4); τ 2.98 (triplet, 1), J 1.9 Hz; τ 6.71 (doublet, 2) J 1.9 Hz; τ 9.80 (singlet, 9). Infrared bands were seen at 3068 m, 3050 m, 3020 m, 2960 s, 2895 m, 2854 (sh), 1600 w, 1575 w, 1550 m, 1535 s, 1455 s, 1440 (sh), 1385 s, 1295 m, 1262 (sh), 1250 s, 1205 w, 1195 w, 1120 w, 1095 w, 1036 s, 913 m, 879 m, 869 m, 835 vs, 750 s, 712 s, 687 m, 624 m, 590 w, 545 w, 408 m cm^{-1}.

1,2-Bis(trimethylsilyl)indene

A solution of 2-(trimethylsilyl)indene (5.04 g, 0.027 mole) in hexane (20 ml) was treated dropwise with a solution of n-butyllithium (16.8 ml, 1.6 M) in hexane (20 ml), and was stirred for 16 h. The resultant thick, white suspension was treated dropwise with chlorotrimethylsilane (3.5 ml, 0.027 mole) in hexane (10 ml) and was refluxed for 4 h. Water (100 ml) was added and the hexane layer was separated, washed with water, dried (MgSO$_4$), and distilled at atmospheric pressure to remove the hexane. Vacuum distillation gave a yellow liquid at 73°/0.05 mm. The product was distilled at 73°/0.03 mm to give a pale yellow liquid which solidified on standing. This was recrystallized from pentane to give white crystals (m.p. 68–69°). The yield

was 4.2 g [60% based on 2-(trimethylsilyl)indene]. (Found: C, 68.88, 69.16; H, 9.17, 9.06. $C_{15}H_{24}Si_2$ calcd.: C, 69.15; H, 9.29%.)

Infrared bands were seen at 3080 (sh), 3067 w, 3052 w, 3040 w, 2997 w, 2950 m (br), 2891 w, 2875 w, 1926 w, 1896 w, 1505 m, 1445 (sh), 1435 m, 1393 w, 1291 w, 1263 (sh), 1252 s, 1247 (sh), 1185 w, 1154 w, 1145 w, 1102 w, 1036 s, 1018 w, 1008 s, 932 m, 900 m, 855 w, 831 vs (br), 750 s, 731 w, 698 w, 684 w, 630 w, 620 m, 561 w, 466 m, 450 m cm^{-1}. The mass spectrum showed the molecular ion ($C_{15}H_{24}{}^{28}Si_2$) at m/e 280.

1,1- And 1,3-bis(trimethylsilyl)indene

A solution of 1-(trimethylsilyl)indene (18.8 g, 0.10 mole) in hexane (40 ml) was treated dropwise with n-butyllithium (62.5 ml, 1.6 M) in hexane (35 ml) to obtain a thick, white suspension. This was treated dropwise with chlorotrimethylsilane (13 ml, 0.10 mole) in hexane (30 ml), stirred for 16 h, and then refluxed for 8 h. Water (100 ml) was added and the hexane layer was separated, dried (MgSO$_4$), and distilled to remove the hexane at atmospheric pressure. The product was obtained by vacuum distillation at 116°/3.5 mm, n_D^{25} 1.5284 (lit.[6] b.p. 106°/3 mm, n_D^{20} 1.5307; see Results). (Found: C, 69.26; H, 9.52. $C_{15}H_{24}Si_2$ calcd.: C, 69.15; H, 9.29%.)

Infrared bands were seen at 3064 m, 3038 w, 3007 w, 2963 vs, 2930 vw, 2907 w, 1584 w, 1557 vw, 1510 m, 1438 s, 1393 w, 1262 (sh), 1250 vs, 1225 w, 1212 w, 1179 w, 1112 w, 1097 w, 1070 m, 1008 s, 970 m, 915 m, 885 w, 871 w, 830 vvs (br), 770 m, 760 w, 750 w, 729 w, 680 m, 632 m, 610 m, 543 w, 470 s, 428 w cm^{-1}.

1-(Trimethylsilyl)-3-methylindene

The compound $(CH_3)_3SiC_9H_6CH_3$ was prepared in a similar manner to 1-(trimethylsilyl)indene from 1-methylindene[7] (5.0 g, 0.038 mole) and n-butyllithium (24 ml, 1.6 M) in hexane followed by chlorotrimethylsilane (5.36 ml, 0.038 mole). The product was obtained by vacuum distillation at 88°/2.3 mm, and purified by redistillation at 76°/1.05 mm, n_D^{28} 1.5310. The yield was 4.17 g (53% based on 1-methylindene). (Found: C, 76.84; H, 9.03. $C_{13}H_{18}Si$ calcd.: C, 77.15; H, 8.96%.)

The proton NMR spectrum had the following resonances: τ 2.8 (multiplet, 4); τ 3.83 (quintet, 1), J 1.5 Hz; τ 6.77 (quintet, 1), J 2 Hz; τ 7.86 (triplet, 3), J 1.7 Hz; τ 10.10 (singlet, 9). Infrared bands were seen at 3063 m, 3029 w, 3004 m, 2953 s, 2908 w, 2893 (sh), 2843 w, 1898 w, 1859 w, 1825 w, 1583 m, 1458 (sh), 1448 s, 1438 (sh), 1378 m, 1348 w, 1338 w, 1311 w, 1252 vs, 1178 w, 1109 w, 1070 w, 1040 m, 1028 m, 1006 s, 930 w, 876 vs, 840 vvs (br), 810 m, 765 (sh) 757 vs, 730 m, 707 w, 692 m, 612 s, 555 w, 485 m, 449 w, 408 w cm^{-1}.

1-(Trimethylstannyl)-3-methylindene

Methylindenyllithium was prepared as a suspension in hexane from 1-methylindene[7] (5.0 g, 0.038 mole) in hexane (20 ml) and n-butyllithium (24 ml, 1.6 M) in hexane (40 ml) as in the synthesis of the corresponding silane. To this was added dropwise with stirring a solution of chlorotrimethylstannane (7.65 g, 0.038 mole) in hexane (50 ml) and the mixture was refluxed for 2 h and stirred for 12 h. The lithium chloride was removed by filtration and the filtrate was distilled at atmospheric pressure to remove the hexane. Vacuum distillation gave the product, a pale yellow liquid, at 76°/0.12 mm, which was purified by redistillation at 74.5–75°/0.10

mm, n_D^{28} 1.5817. The yield was 8.10 g (72% based on 1-methylindene). As with the other stannanes, 1-(trimethylstannyl)-3-methylindene is quite water sensitive. (Found: C, 53.13; H, 6.25. $C_{13}H_{18}Sn$ calcd.: C, 53.29; H, 6.19%.)

The proton NMR spectrum had the following resonances: τ 2.75 (multiplet, 4); τ 3.74 (quintet, 1), J(H–H) 1.5 Hz, J(^{117,119}Sn–H) 13 Hz; τ 6.28 (quintet, 1), J(H–H) 1.7 Hz, J(^{117,119}Sn–H) 91 Hz; τ 7.80 (triplet, 3), J(H–H) 1.6 Hz, J(^{117,119}Sn–H) 20.0 Hz; τ 10.14 (singlet, 9), J(^{117,119}Sn–H) 53.0, 55.3 Hz. Infrared bands were seen at 3066 m, 3045 w, 3038 (sh), 3005 w, 2975 w, 2930 (sh), 2914 s, 2852 w, 1608 w, 1592 w, 1577 w, 1453 (sh), 1446 vs, 1438 (sh), 1370 m, 1340 m, 1335 (sh), 1288 w, 1246 m, 1190 s, 1162 w, 1145 w, 1110 w, 1021 w, 1008 m, 961 m, 942 vs, 922 m, 858 s, 805 w, 760 vvs (br), 552 w, 525 vs, 504 s, 470 m, 428 m cm^{-1}.

1-(Trimethylstannyl)-1,3-dimethylindene

Dimethylindenyllithium was prepared as a suspension by adding dropwise, at room temperature, a solution of n-butyllithium (39 ml, 1.6 M) in hexane and hexane (55 ml) to 1,3-dimethylindene[7] (6.0 g, 0.042 mole) in hexane (40 ml) with stirring. The suspension was refluxed for $1\frac{1}{2}$ h and then cooled to room temperature. Chlorotrimethylstannane (8.25 g, 0.041 mole) in hexane (50 ml) was then added dropwise and the resulting mixture stirred overnight. It was then refluxed for 4 h, cooled, and filtered to remove the lithium chloride. The hexane was distilled from the filtrate at atmospheric pressure. Vacuum distillation of the remainder yielded 4.36 g of product at 69°/0.17 mm (34% based on chlorotrimethylstannane). The proton NMR spectrum revealed a small amount ($\sim$15%) of 1,3-dimethylindene, as identified by the characteristic doublet (J 7.5 Hz) at $\sim\tau$ 8.8 and triplet (J 2 Hz) at $\sim\tau$ 8.0 in the proton NMR spectrum. A sample of the desired stannane was obtained after two careful fractionations, distilling at 64°/0.04 mm (n_D^{26} 1.5713). (Found: C, 54.51; H, 6.68. $C_{14}H_{20}Sn$ calcd.: C, 54.77; H, 6.57%.)

Infrared bands were seen at 3065 w, 3043 w, 3005 vw, 2960 (sh, br), 2930 (sh, br), 2915 m (br), 2858 m, 1448 m, 1440 s, 1375 w, 1342 w, 1282 w, 1272 w, 1192 w, 1185 w, 1137 w, 1110 w, 1088 w, 1050 w, 1016 w, 931 w, 816 w, 758 s (br), 743 vs, 566 w, 523 s, 500 m, 430 w cm^{-1}.

Attempted synthesis of 1-(trimethylsilyl)-1,3-dimethylindene

A suspension of 1,3-dimethylindenyllithium was prepared in hexane (50 ml) by adding dropwise n-butyllithium (36.5 ml, 1.6 M) in hexane to 1,3-dimethylindene[7] (5.81 g, 0.04 mole) and refluxing for 7 h. After standing overnight, this was treated with a solution of chlorotrimethylsilane (5.2 ml, 0.04 mole) in hexane (30 ml) and the mixture was stirred for 12 h and then refluxed for 3 h. The mixture was cooled and deuterium oxide (D_2O, 2 ml) added with stirring. A noticeable warming of the reaction mixture occurred. Water was added ($\sim$ 50 ml) and the suspension was stirred until it clarified and separated ($\sim$5 min). The hexane layer was separated, dried ($MgSO_4$), and distilled at atmospheric pressure. Vacuum distillation gave 4.95 g of a colorless liquid at 36°/0.15 mm. The proton NMR spectrum showed an extremely weak peak in the trimethylsilyl region and was consistent with 1-deutero-1,3-dimethylindene (see Results). The material was purified by redistillation at 61°/2.8 mm. The yield was 85% (based on 1,3-dimethylindene). (Found: C, 91.21; H, 8.69. $C_{11}H_{11}D$ calcd.: C, 90.97; H, 9.03%.)

The infrared spectrum showed several differences from that reported[7] for 1,3-dimethylindene. Notably, a weak band occurs at 2118 cm^{-1} in the deutero compound as well as peaks at 1250 w cm^{-1} and 869 m cm^{-1} not present in the non-deuterated hydrocarbon. The band at 1070 cm^{-1} in the hydrogen compound is considerably diminished in intensity as is the band at 926 cm^{-1}. A peak at 912 cm^{-1} in the hydrogen compound is not present in the deuterated form. The 700–800 cm^{-1} regions are considerably different: $C_{11}H_{12}$: 804 s, 778 m, 753 vs, 740 vs, 727 s cm^{-1}. $C_{11}H_{11}D$: 755 s, 747 vs, 733 s, 711 cm^{-1}.

RESULTS

Preparation of compounds

A previous synthesis of dimethyldiphenylstannane has appeared in the literature[8]. Diphenylstannyldisodium, prepared from diphenyldiiodostannane and sodium in liquid ammonia, was reacted with excess methyl iodide to give the product in 84% yield. (The reverse reaction involving dimethylstannyldisodium and bromobenzene failed to give the desired product.) The compound was observed to distill with decomposition (127–140°/3 mm) and showed no well-defined freezing point, becoming more viscous at temperatures down to $-55°$. The authors[8] erroneously concluded that their inability to purify the compound "by either crystallization or distillation renders the Grignard method of preparation impracticable." In fact, the Grignard synthesis utilizing dimethyldichlorostannane and phenylmagnesiumbromide is a singularly straight forward route, giving the desired compound in high yield. Purification is readily obtained by high-vacuum distillation.

The reactions of 2-bromoindene were investigated as a method of preparing fluxional molecules of the type:
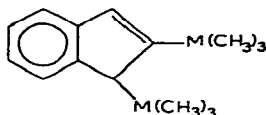
There was no apparent reaction between 2-bromoindene and lithium metal in diethyl ether. Treatment with n-butyllithium gave the intermediate 2-bromo-indenyllithium as identified by the product of its reaction with chlorotrimethylstannane. The Grignard reagent, from 2-bromoindene, had been obtained previously[9] in ether solution, the reaction being initiated with ethylmagnesium bromide. The authors reported a 15% yield of 2-indenecarboxylic acid upon treatment with carbon dioxide and water. They also noted the formation of indene as a byproduct. Improved yields of the desired product, 2-(trimethylsilyl)indene, via the Grignard route, could be obtained by (*i*) using THF in place of diethylether, (*ii*) activating the magnesium by briefly reacting it with ethyl bromide, (*iii*) freeing the 2-bromoindene from any methanol occluded during recrystallization[9] by drying it *in vacuo*, and (*iv*) cooling the reaction once it is initiated.

The literature contains a report[6] of the synthesis of 1,1-bis(trimethylsilyl)-indene in low yield ($\sim 17\%$) from the dimetalated indene obtained by reacting one equivalent of indene with two equivalents of sodium or n-butyllithium. The compound

(prepared in this study by stepwise reaction), which agrees with the literature data, is shown to be a mixture of the isomers 1,1- and 1,3-bis(trimethylsilyl)indene.

Proton magnetic resonance data

The variable temperature proton magnetic resonance spectra of $(CH_3)_2$-$(C_6H_5)SnC_9H_7$ in the region τ 9.4–10.2 are shown in Fig. 1. The two signals which
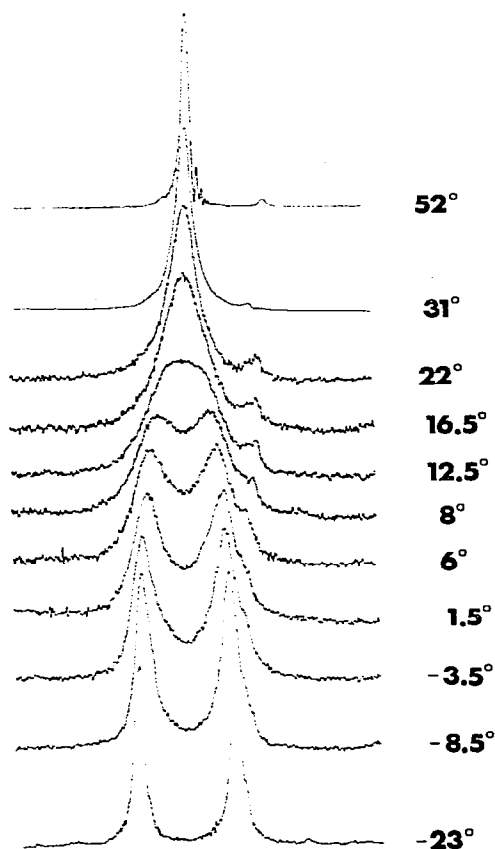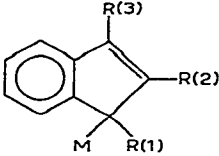

Fig. 1. Variable temperature proton NMR spectra of $(CH_3)_2(C_6H_5)SnC_9H_7$ in the region τ 9.4–10.2 at several temperatures. The peak separation at $-8.5°$ is 9.3 Hz.

can be assigned to the magnetically non-equivalent methyl groups broaden above $-23°$ and coalesce to a single resonance above 12.5°. Changes take place concurrently in the resonances due to the indenyl group. At $-33°$ that portion of the spectrum consists of a complex pattern for the aromatic indenyl and phenyl protons, of relative area 9 at τ 2.5. The AB portion of an ABX patterns occurs at τ 2.98 and τ 3.19 ($J_{AB} \sim 5$ Hz). The X proton is a poorly resolved multiplet at τ 5.76 $[|J(^{117,119}Sn-H)|$ 95 Hz]. Decoupling studies show that the X proton is resolvably coupled to the A proton at τ 3.19 with $J_{AX} \sim 1.5$ Hz. Above $-33°$ the changes which occur in the ABX pattern parallel those observed[1] for $(CH_3)_3SnC_9H_7$. At 148° the doublet at τ 4.44 (2), J 3.8 Hz, with tin satellites $[|J(^{117,119}Sn-H)|57.4$ Hz] is coupled to the triplet (1, J 3.8

TABLE 1

PROTON MAGNETIC RESONANCE DATA[a]

	Aromatic	R(3)[b]	R(2)	R(1)	M(CH₃)_{2,3}	Temp. (°C)
$Me_2PhSiC_9H_7$[b]	~2.4	3.16	3.51	6.37	9.91 }[c] 9.97 }	31, 101[h]
	~2.4	d	3.51	d	9.94	188[h]
$Me_2PhSnC_9H_7$	~2.5	2.98	3.19	5.76	9.71 }[c] 9.89 }	−33[i]
	~2.5	4.44	3.22	4.44	9.81	148[h]
$Me_3SnC_9H_6Br$	~2.8	3.24	—	6.10	9.95	31[h]
	~2.8	4.64	—	4.64	9.95	186[h]
$1,2\text{-}(Me_3Si)_2C_9H_6$	~2.75	2.8	9.74	6.30	10.05	31[j]
	~2.75	d	9.89	d	9.89	175[h]
$1,1+1,3\text{-}(Me_3Si)_2C_9H_6$	~2.7[e,f]	3.01[e] 9.69[f]	3.19[e] 3.36[f]	10.10[e] 6.46[f]	10.10[e] 10.14[f]	31[h]
$Me_3SiC_9H_6CH_3$	~2.8	7.86	3.83	6.77	10.10	31 }[g,h,i] 160 }
$Me_3SnC_9H_6CH_3$	~2.75	7.80	3.74	6.28	10.14	31 }[g,h] 160 }
$Me_3SnC_9H_5(CH_3)_2$	~2.8	7.81	3.79	8.40	10.15	−41[k]
	~2.8	8.10	3.79	8.10	10.15	84[h]

[a] Chemical shift in τ units. [b] Me=CH_3, Ph=C_6H_5; R(1), R(2), and R(3) refer to substituents on the C_5 ring. [c] Magnetically non-equivalent CH_3 groups. [d] Fast exchange limit not achieved. [e] 1,1-Isomer. [f] 1,3-Isomer. [g] Non-fluxional. [h] Neat sample. [i] In CS_2 solution. [j] In $CDCl_3$ solution. [k] In toluene-d_8 solution.

Hz) at τ 3.22. The chemical shift and tin coupling data are summarized in Tables 1 and 2.

The corresponding silane, $(CH_3)_2(C_6H_5)SiC_9H_7$, shows the same behavior as the tin compound, but the onset of spectral changes is ~150° higher. Consequently, the complete range of fluxional behavior is not observed. This closely parallels the results obtained with the trimethyl analogs[1].

The derivative 1-(trimethylstannyl)-2-bromoindene displays the fluxional behavior characteristic of the other indenyltin compounds. In this case, however, the onset of dynamic behavior is ~55° higher than in the compound with a hydrogen in the 2-position.

The proton NMR spectrum of 1,2-bis(trimethylsilyl)indene (Fig. 2A) shows resonances at τ 2.7–2.8 aromatic and olefin (5); τ 6.30 tertiary (1); τ 9.74 vinyltrimethylsilyl (9); τ 10.05 tertiary trimethylsilyl (9), consistent with the proposed structure. The results of the variable temperature NMR study are shown in Fig. 2B. At temperatures above ~100° a significant broadening of the resonances at τ 6.30, 9.74, and 10.05 is observed. The complete collapse of the proton signal at τ 6.30 is obtained at 175°. Changes take place simultaneously in the region τ 2.7–2.8. The olefinic resonance at τ 2.8 first broadens and then collapses. The complex aromatic pattern undergoes changes and eventually (~175°) simplifies to an AA'BB' pattern. At 150° the two

TABLE 2

^{117,119}Sn–H COUPLING CONSTANTS[a]

(structure)	R(1)[b]	R(2)	R(3)	R(1+3)$_{av.}$	Sn(CH$_3$)$_{2,3}$
indenyl, SnMe₃, R(3)=H	±91[c,f]	12	(±18, ∓200)[c]	54.5[d]	51.5, 54
indenyl, SnMe₃, R(3)=Br	±80		±14.5	48	53, 55.5
indenyl, SnMe₂Ph, R(3)=H	±95.2	12	(±19.6, ∓210)	57.4	53, 54
indenyl CH₃, SnMe₃	91	13	20	[e]	53, 55.3
indenyl CH₃, CH₃ SnMe₃	±58.0	13	±19.2	38.6	49.7, 51.8

[a] Values in Hertz. [b] R(1), R(2), and R(3) refer to the substituents (H, CH$_3$, Br) on the C$_5$ ring. [c] Relative signs are indicated in those cases where they have been determined; calculated values are given in parentheses. [d] Average values for ^{117,119}Sn–R(1) and –R(3) obtained from fast exchange spectra. [e] Non-fluxional below 160°. [f] Data from ref. 1.

trimethylsilyl signals have merged and at higher temperatures they sharpen to a single line. Additional resonances appear irreversibly in the spectra as indicated in Fig. 2. Their intensity increases on standing and does so rapidly during prolonged heating. Nearly complete conversion could be obtained by heating the sample at 180° for 16 hours (Fig. 2C). The 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.

The NMR spectrum of the mixture of isomers 1,1- and 1,3-bis(trimethylsilyl)-indene (Fig. 2C) is interpreted as follows. Signals for the 1,1-isomer occur at τ 2.7 (multiplet, 4), aromatic; τ 3.01 (doublet, 1), $J \sim 5.0$ Hz, olefin H(3); τ 3.36 (doublet, 1), $J \sim 5.0$ Hz, olefin H(2); and τ 10.10 (singlet, 18), trimethylsilyl. Resonances for the
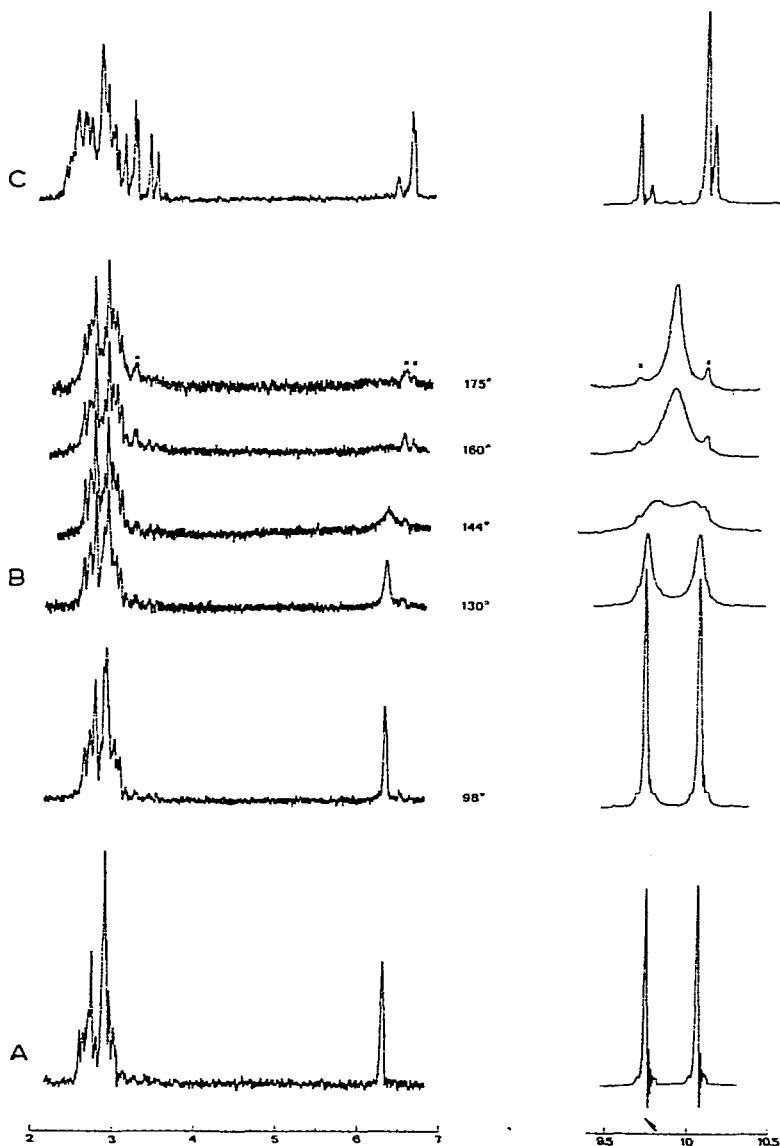
Fig. 2. NMR spectra of (A) 1,2-bis(trimethylsilyl)indene in CDCl₃ solution at 31°, (B) neat 1,2-bis(trimethyl-silyl)indene at 98, 130, 144, 160, and 175°, and (C) sample used in (B) after 16 h at 180°C. The changes with temperature indicated in (B) are reversible except for the appearance of the additional signals noted by (×).

1,3-isomer appear at τ 2.7 (multiplet, 4), aromatic; τ 3.19 (doublet, 1), J 1.8 Hz, olefin; τ 6.46 (doublet, 1), J 1.8 Hz, tertiary; τ 9.69 (singlet, 9), vinyltrimethylsilyl; and τ 10.14 (singlet, 9), tertiary trimethylsilyl. In the spectrum of the neat liquid, the signal at τ 10.10 assigned to the 1,1-isomer is separated from the signal at τ 10.14 assigned to the 1,3-isomer. In CS₂ or CDCl₃ solution these two resonances are not resolved. The relative intensity of the signals due to the two isomers is temperature

dependent. At ambient probe temperature ($\sim 31°$) the ratio of 1,3 to 1,1 is approximately 1/1. At higher temperatures the 1,3-isomer predominates. The temperature dependence of the ratio was studied in the range 31° to 138° on two samples, the neat liquid and a 30% v/v solution in toluene-d_8. The results showed no dependence on concentration. The ratio of isomers (1.3/1.1) was determined at a given temperature by permitting the sample to come to thermal equilibrium in the NMR spectrometer probe (~ 5 min) before recording and integrating the spectrum. The ratio of the areas of the signals at τ 9.69 and τ 10.14 to the signal at τ 10.10 was taken as the ratio $K = [1,3]/[1,1]$. A plot of ln K vs. $1/T$ (°K) for both sets of data gave a straight line. From the slopes $\Delta H = 2.1 \pm 0.3$ kcal/mole. At 55° $\Delta G = +130$ cal/mole and $\Delta S = +6.0$ e.u. The NMR spectrum recorded at 100 MHz on a neat sample at 206° failed to show any evidence for the onset of fluxional behavior.

The proton NMR spectra of the molecules $(CH_3)_3MC_9H_6CH_3$, M = Si and Sn, are consistent with structure (IIa) and not with the isomer (IIb). No evidence for

(IIa)   (IIb)
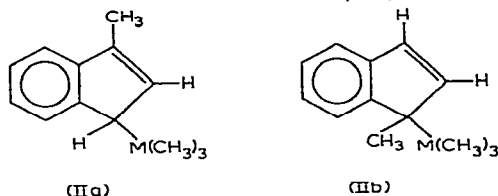
any significant amount of structure (IIb) for either compound was observed in the NMR spectra at temperatures up to 160°.

The molecule $(CH_3)_3SnC_9H_5(CH_3)_2$ has a spectrum at $-41°$ characteristic of a σ-bonded dimethylindenyl group. Resonances occur at $\tau \sim 2.8$ (multiplet, 4), ABCD pattern, aromatic; τ 3.79 (singlet, 1), $J(^{117,119}Sn-H)$ 13 Hz, H(2); τ 7.81 (singlet, 3), $J(^{117,119}Sn-CH_3)$ 19.2 Hz, CH_3(3); τ 8.40 (singlet, 3), $J(^{117,119}Sn-CH_3)$ 58.0 Hz, CH_3(1); and τ 10.15 (singlet, 9), $J(^{117}Sn-CH_3)$ 49.7 Hz, $J(^{119}Sn-CH_3)$ 51.8 Hz. As the temperature is increased changes take place in the region τ 7–9 (Fig. 3). The signals due to the two methyl groups, together with the corresponding tin satellite resonances, broaden and merge to an averaged signal with tin satellites. At 26° the broadened average signal is observed as well as the low-field tin satellite. Only at higher temperatures does the upfield resonance appear. The fast exchange limiting spectrum at 84° has a sharp singlet at τ 8.10 (6), $J(^{117,119}Sn-CH_3)$ 38.6 Hz. Changes also take place in the aromatic proton signals, giving rise to a symmetrical AA'BB' pattern at the fast exchange limit. The signal at τ 3.79 with the tin satellites remains unaltered throughout these changes.

The NMR spectrum of 1-deutero-1,3-dimethylindene consists of resonances at τ 2.83 (multiplet, 4, aromatic), τ 4.04 (quartet, 1) J 1.5 Hz, olefin H (2); τ 7.96 (doublet, 3), J 1.5 Hz, vinylmethyl; and τ 8.83 (singlet, 3), tertiary methyl, consistent with structure (III).
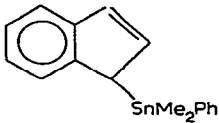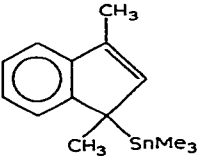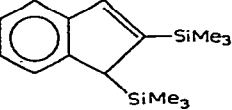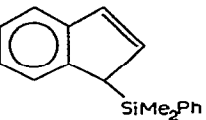

(III)
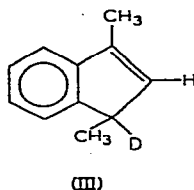
Rates and activation parameters

Using the chemical shift and the spin coupling parameters taken from the observed spectra, the computer program EXCNMR, obtained from Professor G. M. Whitesides based on the method of Kubo[10] and Sack[11], was used to simulate the observed spectra for a number of mean pre-exchange lifetimes. The calculated and observed spectra were matched for the best fit, with particular attention to the peak width at half-heigth.

For two systems, $(CH_3)_2(C_6H_5)MC_9H_7$ (M=Si, Sn), the chemical shift separation of the magnetically non-equivalent methyl groups at the slow-exchange limit was observed to be temperature dependent and approximately linear with temperature in the absence of exchange. Values for the slow-exchange peak separation used to calculate the exchange broadened spectra were obtained by extrapolation of the peak separation shift in the absence of exchange. Figs. 1 and 4 give the observed and calculated spectra for $(CH_3)_2(C_6H_5)SnC_9H_7$, respectively.

It was possible to include in the calculations for $(CH_3)_3SnC_9H_5(CH_3)_2$ the resonances due to the coupling between $^{117,119}Sn$ isotopes and the methyl groups on the indene. The coupling constants $J(^{117,119}Sn-CH_3)$ were taken from the observed spectra at both the slow- and fast-exchange limits. It was found that $J[^{117,119}Sn-CH_3(1)]$ was of the same relative sign as $J[^{117,119}Sn-CH_3(3)]$ (see *Discussion*) and

TABLE 3

ACTIVATION PARAMETERS

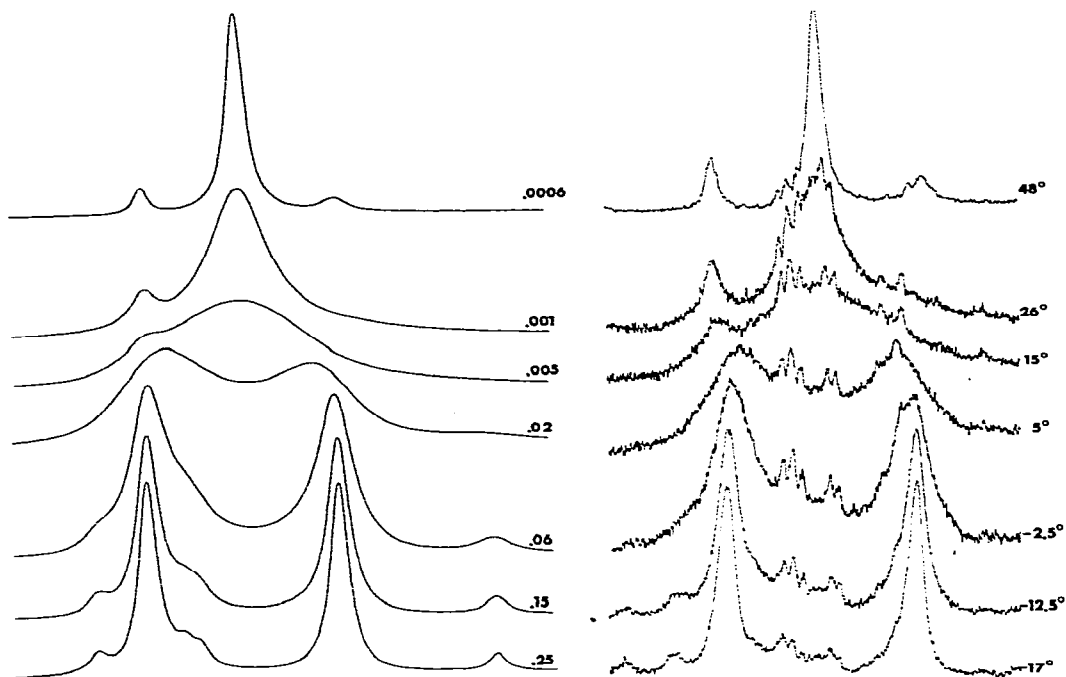|	E_a (kcal/mole)	Log A
(indenyl SnMe$_2$Ph)	14.1±0.4	11.9±0.3
(indenyl CH$_3$, CH$_3$ SnMe$_3$)	14.2±0.7	12.5±0.6
(indenyl —SiMe$_3$, SiMe$_3$)	26.1±1.4	14.4±0.7
(indenyl SiMe$_2$Ph)	23.0±1.6	11.5±0.8

Fig. 3. Detail of the variable temperature NMR spectra of $(CH_3)_3SnC_9H_5(CH_3)_2$ in the region τ 7–9 at several temperatures. The small extraneous signals are due to a trace amount of the hydrocarbon 1,3-dimethylindene (see *Experimental* section). The corresponding computer-simulated spectra with the indicated mean pre-exchange lifetimes τ (in seconds) appear to the left. These spectra include the effect of spin–spin coupling with the isotopes [117,119]Sn (total abundance 16.2%).

the spectra were calculated as three simultaneous 2-site exchanges occurring with the same mean pre-exchange lifetime. The inherent relaxation times of the central methyl resonances in the absence of exchange were adjusted to match the limiting slow-exchange spectra. The observed and calculated spectra are presented in Fig. 3.

The observed and calculated spectra for the coalescence of the two trimethylsilyl resonances in 1,2-$[(CH_3)_3Si]_2C_9H_5$ are given in Fig. 5.

For all four systems the data were fitted by the least-squares method to a linear Arrhenius plot. The activation parameters E_a and log A are presented in Table 3.

DISCUSSION

The variable temperature proton NMR spectra of $(CH_3)_2(C_6H_5)SnC_9H_7$ in the region τ 2–7 resemble in every significant respect those obtained[1] for the analogous molecule $(CH_3)_3SnC_9H_7$. It is quite clear, therefore, that as in the former case the tin atom with its attached groups is executing a series of 1,2- or 1,3-shifts between the enantiamorphous positions 1 and 3 on the indene ring*. The spectra of the dimethyl-

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* Only suprafacial migrations are considered to occur. Antarafacial shifts would appear to require significantly more energy.
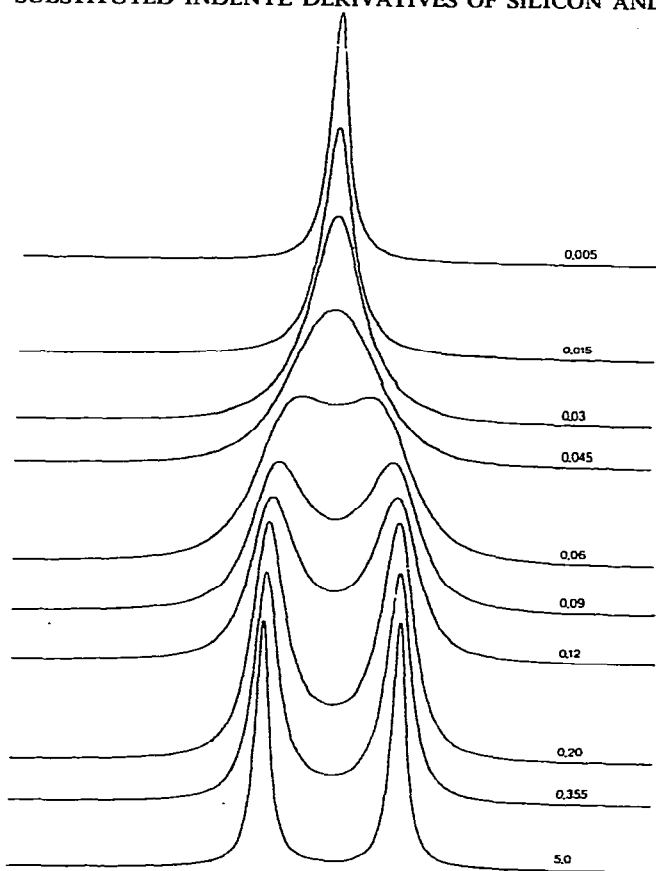
Fig. 4. Calculated line shapes for the methyl resonances of $(CH_3)_2(C_6H_5)SnC_9H_7$ as a function of the mean pre-exchange lifetime τ (in seconds). (Compare Fig. 1.)
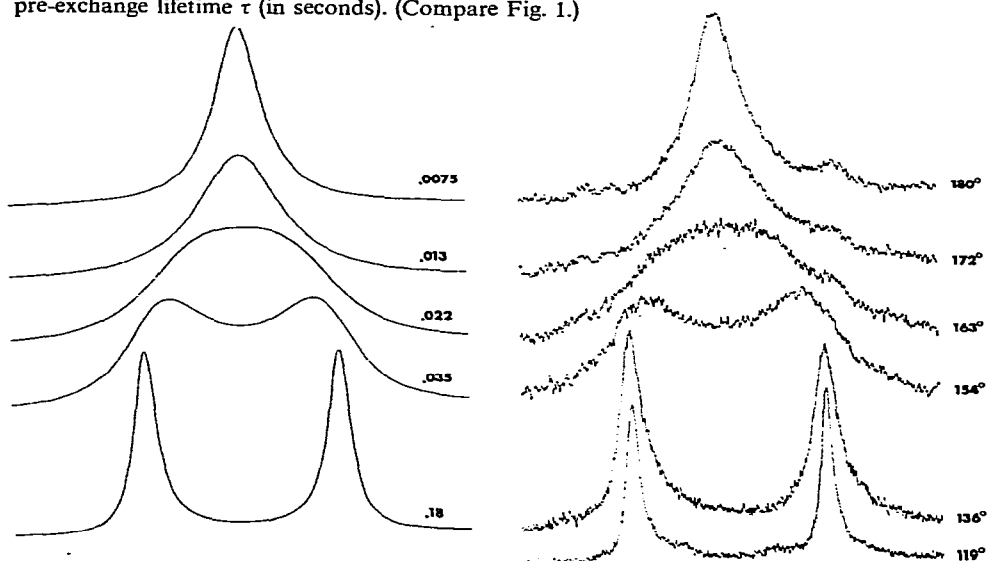
Fig. 5. The observed NMR spectra of 1,2-bis(trimethylsilyl)indene in the region τ 9.5–10.5 at several temperatures (right) and calculated line shapes as a function of the mean pre-exchange lifetime τ (in seconds).

phenylstannyl group allow a further conclusion to be drawn. In the slow exchange limiting spectrum the two methyl groups are magnetically non-equivalent (being separated by 0.18 ppm in CS_2 solution at $-33°$). At temperatures below the slow exchange limit this separation is temperature dependent, decreasing linearly with increasing temperature. Thus it is likely that the observed magnetic non-equivalence is due, at least in part, to restricted rotation about the C(1)–Sn bond or unequal rotamer populations, since differences due to intrinsic asymmetry are generally assumed to be temperature-independent[12]*.

At higher temperatures the two methyl signals broadened and coalesced to a single sharp resonance, a 2-site exchange process which permitted the accurate determination of activation parameters. A 1,2-shift mechanism involving either a discrete isoindenyl intermediate (IV) or a π-bonded intermediate (V) (both of which


(IV)   (V)
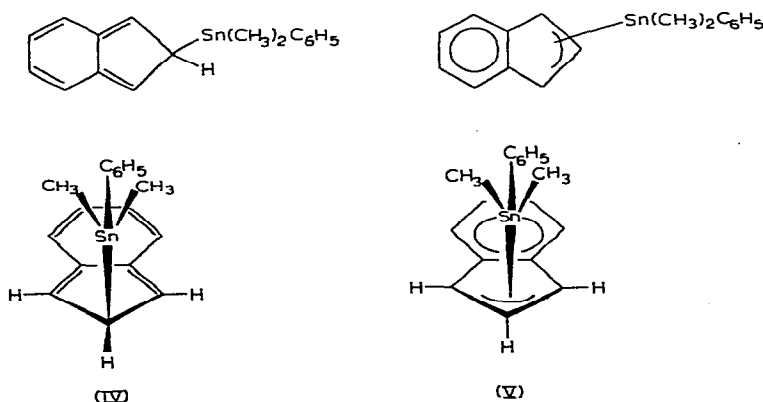
contain a mirror plane of symmetry which relates one CH_3 group to the other) is consistent with the experimental observations. Likewise a 1,3-shift which leaves the configuration at the tin atom unaltered but reverses the configuration at the asymmetric carbon atom interchanges the magnetic environments of the two methyl groups and gives rise to a time-averaged equivalence. What is *not* in agreement with the experimental results is a 1,3-*shift with a simultaneous inversion at the tin atom* (VI). This "internal S_N2 displacement reaction" at the tetrahedral tin atom retains the non-equivalence of the methyl groups which would then be expected to display separate resonances at the fast-exchange limit. Similar conclusions can be drawn regarding the fluxional behavior of the corresponding silane.

Studies of the variable temperature NMR behavior of $(CH_3)_3SnC_9H_5(CH_3)_2$ showed it to be fluxional and the relatively simple spectral pattern in the ring methyl region permitted the activation parameters to be determined.

A number of indenyltin compounds have been studied and the tin–hydrogen

* As this work was nearing completion a communication appeared[13] reporting the first example of the magnetic nonequivalence of methyl groups attached to hetero atoms. The compounds were salts of the type $[(CH_3)_2ECH(CH_3)(C_6H_5)]^+Br^-$ (E $=NC_6H_5$, PC_6H_5, S, Se) and the chemical shift separation of the methyl resonances was found to be strongly solvent dependent.
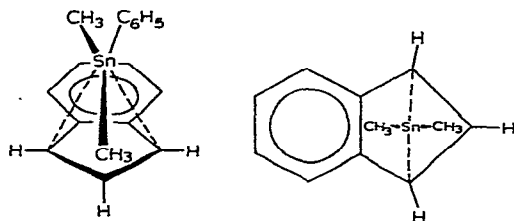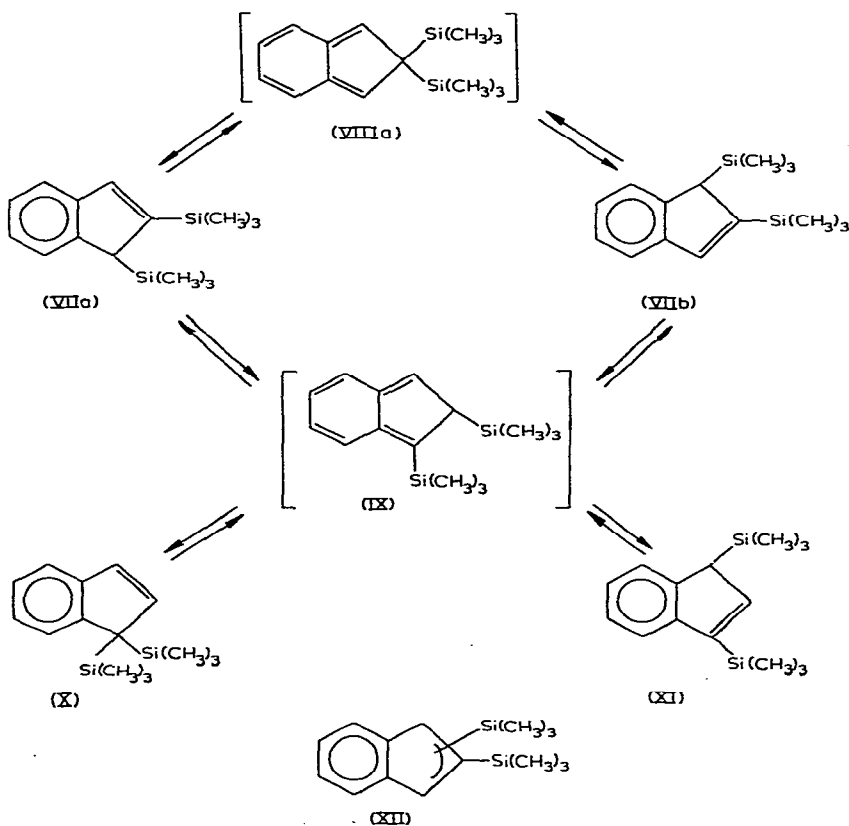
(VI)   (Phenyl group directly
        above Sn omitted for
        clarity)

coupling constants are given in Table 2. Several conclusions can be drawn from the data: (i) $|J[^{117,119}Sn-H(2)]|$ has a value of 12–13 Hz for a variety of substituted molecules; (ii) the value of $|J[^{117,119}Sn-H(1)]|$ is large for tin–hydrogen coupling constants being in the range 80–95 Hz; (iii) $|J[^{117,119}Sn-R(3)]|$ is uniformly 15–20 Hz regardless of whether R(3) is CH_3 or H, and (iv) $J[^{117,119}Sn-R(1)]$ is of the same sign as $J[^{117,119}Sn-R(3)]$ for those molecules which are fluxional and thereby permit the relative signs to be determined.

The non-fluxional molecules $(CH_3)_3MC_9H_6CH_3$ (M=Si, Sn) offer some insight into the factors which govern such processes. A mixture of the isomers 1-(tri-

methylstannyl)-1-methylindene and 1-(trimethylstannyl)-3-methylindene might have been expected from the reaction of chlorotrimethylstannane with methylindenyl-lithium. In fact only the latter (1,3-) isomer is obtained. Any equilibrium between the two isomers (whether rapid on the NMR time scale or not) overwhelmingly favors the 1,3-form even at 160°. The same conclusions apply to the corresponding silane.

A number of examples of fluxional tin compounds are known in which the tin atom is bound to a carbon which is also bonded to a methyl group [viz. $(CH_3)_3$-$SnC_5(CH_3)_5$[3] and $(CH_3)_3SnC_9H_5(CH_3)_2$]. No such fluxional silane is known. Attempts to prepare $(CH_3)_3SiC_5(CH_3)_5$ and $(CH_3)_3SiC_9H_5(CH_3)_2$ were not successful*. It is unlikely that steric effects are responsible since a measurable amount of 1,1-bis(trimethylsilyl)indene exists in equilibrium with the 1,3-isomer even at 140°, and at room temperature the ratio is close to 1/1.

The molecule 1,2-bis(trimethylsilyl)indene undergoes an intramolecular rearrangement which has the effect of averaging the magnetic environments of the two trimethylsilyl groups. A plausible mechanism is given by the reaction sequence (VIIa) ⇌ (VIIIa) ⇌ (VIIb). While the experimental data do not *prove* the intermediacy of structure (VIII) in the rearrangment, *they do rule out simple 1,3-shifts or a π-bonded structure like (XII)* since in both of these cases the trimethylsilyl groups are not interchanged.

An alternative, equally plausible mechanism for the fluxional rearrangement of 1,2-bis(trimethylsilyl)indene is the concerted process in which the trimethylsilyl group in the 1-position migrates to the 2-position while the trimethylsilyl group in the 2-position simultaneously goes to the 3-position. This is indicated schematically in (VIIIb). The rearrangement sequence (VIIa) ⇌ (VIIIb) ⇌ (VIIb), which is equal-

(VIII b)
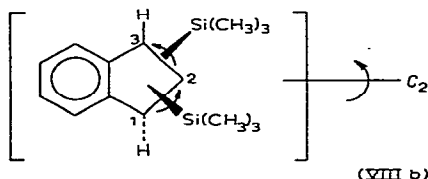
ly consistent with the experimental results, differs in several respects from the sequence (VIIa) ⇌ (VIIIa) ⇌ (VIIb) described above. The intermediate (or transition state) (VIIIa) has C_{2v} symmetry and can rearrange to one of *four* equivalent indenyl structures. In contrast, rearrangement via (VIIIb) introduces only the two-fold axis indicated. The trimethylsilyl group in the 1-position (above the plane of the indenyl group in VIIIb) displaces from the 2-position the other trimethylsilyl group which migrates to the 3-position (below the plane). In this process the configuration of the asymmetric site is retained during the rearrangement in which it is transferred from the 1-position to the 3-position. The configuration at the asymmetric carbon is not retained by rearrangements via structure (VIIIa).

The observed rearrangement to the 1,1- and 1,3-isomers strongly suggests that the sequences (VII) ⇌ (IX), (IX) ⇌ (X), and (IX) ⇌ (XI) occur, involving first

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* This may be due to the inherent instability of such structures or to an enhanced hydrolytic reactivity of the Si–C(1) bond. For comparison tert-butyltrimethylsilane, $(CH_3)_3CSi(CH_3)_3$, is stable to water and heat[14].

hydrogen migration followed by the shift of the trimethylsilyl group. Structure (IX) is also the presumed intermediate or transition state in the equilibrium (X) $\rightleftharpoons$ (XI) which does not occur sufficiently rapidly at temperatures below 200° to cause any averaging of the separate resonances of the two isomers. The energy difference between structures (X) and (XI) ($\Delta H = 2.1$ kcal/mole) is quite small.

The activation parameters are given for four of the fluxional systems in Table 3. The values for the two tin compounds, $(CH_3)_2(C_6H_5)SnC_9H_7$ and $(CH_3)_3SnC_9H_5$-$(CH_3)_2$, are equal within experimental error. For comparison, the only other values reported in the literature for a fluxional σ-indenyl compound are $E_a = 12.9 \pm 0.6$ kcal/mole and log $A = 12.0 \pm 0.5$ for diindenylmercury[2].

The molecule 1-(dimethylphenylsilyl)indene has $E_a = 23.0 \pm 1.6$ kcal/mole and log $A = 11.5 \pm 0.8$. The activation energy for the silane is approximately 9 kcal/mole higher than for the corresponding stannane, in agreement with the observation that the onset of changes in the NMR spectrum occurs $\sim 150°$ higher for the silane.

The activation energy for the molecule $[(CH_3)_3Si]_2C_9H_6$ is 26.1 ± 1.4 kcal/mole in good agreement with the other fluxional silane studied. The value of log $A = 14.4 \pm 0.7$ is significantly higher than for the others (log $A = 11.5$–12.5).

In their study of the non-fluxional molecule π-$C_5H_5Fe(CO)_2$-σ-C_9H_7, Cotton and coworkers[15] calculated that a 1,2-shift for a σ-bonded indenyl group would give rise to an isoindenyl structure, (XIV), which is ~ 9 kcal/mole less stable than the

(XIII)   (XIV)   (XV)
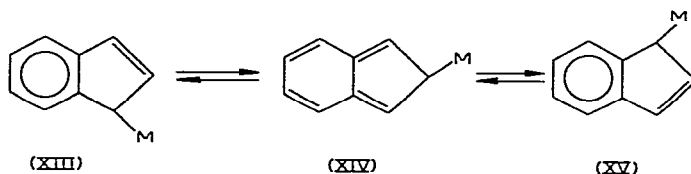
either (XIII) or (XV). Thus any fluxional process involving 1,2-shifts would be energetically less favorable by that amount. In contrast, a 1,2-shift in the corresponding cyclopentadienyl compound occurs between equivalent, low-energy structures.

The experimental data appear to be consistent with these considerations. In the fluxional indenyltin compounds (for which $E_a \sim 14$ kcal/mole), assuming 9 kcal/mole is required for the formation of the less stable isoindenyl structure, the fluxional process requires 5 kcal/mole. For the cyclopentadienyltin compounds an activation energy of 5 kcal/mole is consistent with the observation of dynamic spectra as low as $-80°$. Likewise, for the indenylsilanes ($E_a \sim 25$ kcal/mole) the difference of 9 kcal/mole for the isoindenyl structure leaves ~ 16 kcal/mole for the fluxional process.

It seems likely, therefore, that the 9 kcal/mole barrier for the indenyl systems, rather than preventing 1,2-shifts, serves to separate the fluxional cyclopentadienyl and indenyl molecules into two classes: (i) those for which the cyclopentadienyl derivative is rapidly fluxional even at low temperatures but the indenyl derivative is amenable to study at convenient temperatures (e.g. tin and mercury compounds), and (ii) those for which the cyclopentadienyl derivatives can be studied at readily accessible temperatures but the indenyl derivatives are fluxional only at elevated temperatures, if at all [e.g. silicon, germanium, and π-$C_5H_5Fe(CO)_2$ compounds].

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