

## NEW PRECURSORS TO SILAFLUORENES

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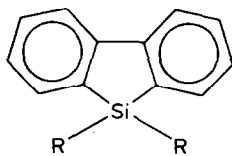
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### Summary

Conversion of 2,2'-dibromo-4,4'-di-*t*-butylbiphenyl and *o*-bromo-*o*'-chlorobiphenyl to organometallic reagents suitable for reaction with  $\text{Me}_2\text{SiCl}_2$  to produce silafluorene has been developed.

### Introduction

Silafluorene or 5-dibenzosilole derivatives (I) were first reported in the 1950's [1]. Although this tricyclic ring system can be generated by thermolytic methods [2] the synthetic route of choice is the condensation of *o,o'*-dilithiobiphenyl with a dichlorosilane [3] where yields of I up to 96% have been claimed [4].



(I)

Recently, nucleophilic substitution at the silicon center in silafluorene and formation of the silafluorenyl anion have been described [5]. We are interested in the silafluorene framework as a rigid analog of diarylsilanes in both monosilane and polysilane derivatives. Although silafluorenes are conveniently prepared from *o*- $\text{BrC}_6\text{H}_4\text{C}_6\text{H}_4\text{Br}$ , we wished to develop less expensive precursors to I. In this report we describe two *o,o'*-dihalobiphenyl precursors to silafluorenes and conditions required to generate the diorganometallic necessary for condensation with a chlorosilane.

## Results and discussion

Two possible alternatives to *o,o'*-dibromobiphenyl as precursors to silafluorenes are *o,o'*-dichlorobiphenyl and 2,2'-dibromo-4,4'-di-*t*-butylbiphenyl (II). The reaction of biphenyl and 2,6-di-*t*-butyl-4-methylphenol (BHT) provides 4,4'-di-*t*-butylbiphenyl (III) (70%) [6]. The bromination of III to give II has been published but the stoichiometry is incorrectly reported with a ratio of Br<sub>2</sub>/III of 3/1 or 7.5/1 [7]. When a ratio of Br<sub>2</sub>/III in excess of 2/1 is employed, tri-, tetra- and penta-brominated derivatives are formed. The best conditions for the maximum yield of II from bromination of III are given in the experimental section.

The low temperature condensation of *o*-Br<sub>2</sub>C<sub>6</sub>H<sub>4</sub> with one-half of an equivalent of *n*-BuLi in THF to give *o,o'*-dibromobiphenyl probably proceeds through an intermediate organolithium reagent, *o*-LiBrC<sub>6</sub>H<sub>4</sub> [8]. Although the less expensive dihalide, *o*-BrC<sub>6</sub>H<sub>4</sub>Cl can be converted with one equivalent of *n*-BuLi (−60°C) to *o*-LiClC<sub>6</sub>H<sub>4</sub> [9], when the reaction is performed with one-half of an equivalent of *n*-BuLi at low temperature the actual product isolated is *o*-ClC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Br-*o* (IV) and not *o*-ClC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Cl-*o*.

The best yields of silafluorenes are obtained when the lithium exchange of the dibromide is performed at −78°C followed by warming to room temperature before addition of the dichlorosilane [4]. When these conditions are employed for the generation of the diorganometallic of II, 60% of the starting material is recovered. The conversion of II to a diorganometallic with *n*-BuLi, Mg or Li proved to be surprisingly difficult. Representative examples of the conditions that were employed in these reactions are shown in Table 1. To test the conversion of II to the diorganometallic compound (or equivalent), solutions were hydrolyzed with water, and the composition of the product mixture was determined by gas chromatography. It was assumed that the *p,p'*-di-*t*-butylbiphenyl (III) which resulted represented conversion of II to a diorganometallic. As can be seen from Table 1, the reaction of II with magnesium mesh or lithium metal is slow in ether and occurs in THF only above room temperature with either metal. With magnesium, activation by EDB is required even with sonication. When the exchange reaction of II with *n*-BuLi in ether is performed at room temperature for 4.5 h, aqueous quench indicated a 95% yield of III. Conditions were found for what appeared to be reasonable conversion of II to the diorganometallic on the basis of the biphenyl III produced (entries 3, 6 and 12 in Table 1); however, quenching with Me<sub>2</sub>SiCl<sub>2</sub> gave not only the expected silafluorene, V, but also significant amounts of III. Although yields of V are the highest with Mg mesh in THF (entry 6), the best compromise to avoid contamination of the silafluorene with biphenyl appears to be the combination of *n*-BuLi in THF/Et<sub>2</sub>O solvent mixture at 0°C (entry 2). Although the origin of III in runs that were quenched with Me<sub>2</sub>SiCl<sub>2</sub> could be attributed to hydrolysis of unreacted diorganometallic reagent, a more likely explanation is deprotonation of the solvent or reaction with adventitious water. To exclude the first possibility a sample of II was allowed to react with *n*-BuLi and quenched with D<sub>2</sub>O. The biphenyl, III, produced was a mixture of C<sub>20</sub>H<sub>24</sub>D<sub>2</sub>, C<sub>20</sub>H<sub>25</sub>D and C<sub>20</sub>H<sub>26</sub> in an approximate ratio of 3/1/2 as determined from the parent cluster in the mass spectrum. Similarly, reaction of II with lithium in THF followed by D<sub>2</sub>O quench gave a mixture of substituted biphenyls in the approximate ratio of 3/2/9. Clearly, III is present before the quenching agent is added. Although slow reaction with

water cannot be precluded, the origin of III is more likely due to deprotonation of the solvent by the organometallic reagents.

Conversion of *o,o'*-bromochlorobiphenyl to the diGrignard reagent also proved somewhat difficult. In this case the two aryl halide bonds react with magnesium at different rates. Conversion of ArBr to ArMgBr occurred as expected for an aryl bromide but transformation of the ArCl bond required much more vigorous conditions. Since reactions carried out in ether were very slow, the studies were performed in THF and the various attempts are summarized in Table 2. To monitor the reaction of IV with magnesium, aliquots were hydrolyzed and the presence of biphenyl (VI) was used as an indicator of the formation of the diorganometallic. The factors that were varied included the scale, ratio of Mg to IV, presence or absence of additive, heat, time and form of magnesium. The best conversions were achieved with excess magnesium powder and iodine as an additive. Sonication is necessary to reduce the time required for > 90% conversion of IV. Yields of isolated I of up to 87% were obtained when the ratio of Mg to IV was about 8.7. Decreasing the ratio increased the time required for conversion to the organometallic. Although the sonication results were difficult to duplicate with Mg mesh (see runs 3 and 4 in Table 2) these difficulties were not as apparent when Mg powder was employed.

In summary, it has been shown that two other organic halides are suitable precursors to the silafluorene ring system and that yields in excess of 50% and up to about 90% can be realized. We are presently attempting to prepare silafluorenes from condensation of the diorganometallic reagents generated from II and IV with trichlorosilanes and silicon tetrachloride.

## Experimental

### General

Organometallic reactions were carried out in oven-dried glassware. Grignard preparations were carried out under argon and N<sub>2</sub> was used for organolithium reagents.

Dimethyldichlorosilane, n-butyllithium in hexane and 2-bromochlorobenzene were used as supplied. Magnesium, 100 mesh (Alfa), magnesium powder (Strem) and lithium ribbon (0.75 mm) (Aldrich) were stored in dessicators.

The following compounds were prepared by literature methods: 4,4'-di-*t*-butylbiphenyl [6], 2-bromo-4,4'-di-*t*-butylbiphenyl [7], and 5,5-dimethylsilafluorene [1b].

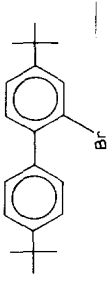
Tetrahydrofuran and ether were dried and purified by distillation from sodium metal benzophenone ketal.

Proton NMR data were recorded on a Varian T-60 spectrometer and a JEOL FX-100 Multinuclear spectrometer. Unless specified otherwise spectra are recorded in CDCl<sub>3</sub> solution and chemical shifts are reported relative to TMS as an internal standard. Mass spectral data were collected on an AEI MS-1201B Mass Spectrometer. Only major ions are included. Melting points were uncorrected and were obtained on a Thomas Hoover capillary melting point apparatus. Analytical GC was carried out using a Varian Aerograph Model 920 instrument equipped with a 2 m × 31.7 mm stainless column packed with OV-17 (2%) on CHROM G 6H/P (80–100 mesh), column temperatures (195–250°C).

Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

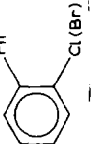
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TABLE I  
REACTION OF II WITH *n*-BuLi, Mg AND Li

Entry	II (g)	<i>n</i> -BuLi Mg or Li	Solvent THF/Et <sub>2</sub> O (ml)	Time/Temp. (h/°C)	H <sub>2</sub> O Quench <sup>a,b</sup> III	II		Mg <sub>2</sub> SiCl <sub>2</sub> Isolated solid (g)	Ratio V/III	% V <sup>c</sup>
										
1	4.0	<i>n</i> -BuLi (13 ml) <sup>d</sup>	17/17	5/0 0.5/25	57	10 <sup>e</sup>	6	1.6		53
2	4.7	<i>n</i> -BuLi (15 ml) <sup>d</sup>	20/20	5/0 0.7/25	71	9 <sup>f</sup>	5	1.95		55
3	4.0	<i>n</i> -BuLi (13 ml) <sup>d</sup>	0.34	4.5/25	95	5	0	1.83 <sup>g</sup>	1/1 <sup>h</sup>	39
4	0.8 (+EDB) <sup>i</sup>	Mg (mesh) 0.26 g	10/0	6/65	85	11	4	0.20 <sup>g</sup>	3/7	32
5	3.0 (+EDB) <sup>i</sup>	Mg (mesh) 2.43 g	25/0	16/65	80	14	6	1.04 <sup>g</sup>	1.3/1	28
6	3.0 (+EDB) <sup>i</sup>	Mg (mesh) 2.4 g	25/0	7/65	86	12	2	1.8 <sup>g</sup>	5.6/1	69
7	0.5 (+EDB) <sup>i</sup>	Mg (mesh) 0.16 g	0/8	5/35	2.3	40	58			
8	3.0 (+EDB) <sup>i</sup>	Mg (powder) 0.7 g	16/0	7/65 <sup>j</sup>	59	8	32			
9	3.0	Mg (powder) 1.18 g	26/0	28/25 <sup>k</sup>			100			
10	1.0	Li (0.08 g)	12/0	3.5/30 8.8/30-50	35 96	32 4	33	0.22 <sup>g</sup>	0/1	0
11	0.99	Li (0.08 g)	0/12	27/35	20	30	50			
12	3.0	Li (0.25 g)	26/0	6.3/54	96	4	4	0.9 <sup>g</sup>	1/3	11

<sup>a</sup> Integration of GLC trace. <sup>b</sup> Aliquot removed and hydrolyzed at time indicated. <sup>c</sup> Yield of V in isolated solid. <sup>d</sup> 1.55 M. <sup>e</sup> An additional component also present (28%) believed to be 2-butyl-4,4'-di-*t*-butylbiphenyl. <sup>f</sup> Fourth component (see footnote e) 16%. <sup>g</sup> Obtained after recrystallization of crude product. <sup>h</sup> Filtrate contains same distribution. <sup>i</sup> EDB = ethylenedibromide added to III. <sup>j</sup> EDB added after III. <sup>k</sup> Sonication.

TABLE 2  
REACTION OF *o*-BROMO-*o'*-CHLOROBIPHENYL WITH MAGNESIUM IN THF

Entry	Dihalide (g)	Mg (g)	Mole ratio Mg/dihalide	Method <sup>a</sup>	Additive <sup>b</sup>	Time (h)	H <sub>2</sub> O Quench <sup>c</sup>	Me <sub>2</sub> SiCl <sub>2</sub>	
								wt.	%I (R ≡ Me)
									IV
<i>Mg Mesh</i>									
1	1.0	0.27	3	R	EDB	6	5	70(21)	5
2	0.5	0.26	5.6	E	EDB	22	59	9(18) <sup>d</sup>	-
3	0.5	0.5	10	S	I <sub>2</sub>	20	43	57	-
4	1.11	1.01	10	S	I <sub>2</sub>	22	82	4(14)	-
5	0.5	0.5	10	R	Anth	47	47	5	-
6	1.0	1.0	10	S	Anth	11	42	46	13
7	1.0	0.27	3	R	EDB	7.5	27 <sup>e</sup>	40 <sup>e</sup>	33 <sup>e</sup>
<i>Mg Powder</i>									
8	3.0	0.81	3	R	EDB	2	55	41	3
9	2.0	2.0	11	S	I <sub>2</sub>	6.7	80	20	-
10	3.0	3.0	11	S	I <sub>2</sub>	9	61	39	-
11	6.0	4.8	8.7	S	I <sub>2</sub>	6	97	0.2(3.2)	-
12	4.4	1.2	3	S	I <sub>2</sub>	6	95	(5.5)	40 <sup>f</sup>
									1.3
									4.1
									87 <sup>g</sup>
									2
									7.3(3.3)
									5 <sup>h</sup>
									19 <sup>i</sup>
									92
									7.3
									2.1
									60

<sup>a</sup> R = Reflux; E = EDB (added with dihalide); S = Sonication. <sup>b</sup> EDB = ethylene dibromide. Anth = anthracene. <sup>c</sup> Integration of GLC trace of hydrolyzed aliquot. <sup>d</sup> Additional component. <sup>e</sup> No change in distribution after 20 h. <sup>f</sup> Crystallization of product residue dissolved in EtOH. <sup>g</sup> Kugelrohr distillation of product residue. <sup>h</sup> Additional Mg added after the initial 6 h. <sup>i</sup> Time since the initial 6 h period.

*2,2'-Dibromo-4,4'-di-t-butylbiphenyl (II)*

A solution of Br<sub>2</sub> (10.8 ml, 0.21 mol) in CCl<sub>4</sub> (18 ml) was added dropwise to a solution of 4,4'-di-t-butylbiphenyl (26.6 g, 0.10 mol) in CCl<sub>4</sub> (100 ml) containing a small amount of iron powder. After completion of addition the reaction mixture was stirred at 29–30°C for 3.3 h and poured into 400 ml of water. The organic layer was washed with 40 ml of 10% NaOH solution and 40 ml of water, dried over Na<sub>2</sub>SO<sub>4</sub> (anhyd). After removal of the solvent, 44.4 g of solid remained. Recrystallization from absolute ethanol (150 ml) gave II (25.8 g, 60.8%), m.p. 156–158°C (ref. 7, 157–158°C). <sup>1</sup>H NMR δ (ppm): 1.36 (s, 18H, t-Bu); 7.12–7.78 (m, 6H, Ar).

*2-Bromo-2'-chlorobiphenyl (IV)*

To a stirred solution of *o*-bromochlorobenzene (57.4 g, 0.29 mol) was added *n*-butyllithium (97 ml, 1.55 M, 0.15 mol) at such a rate as to maintain the internal temperature between –75 to –78°C. After completion of the addition the mixture was stirred for 2.5 h then warmed to 0 to 5°C for 3 h followed by hydrolysis with 150 ml of 5% hydrochloric acid. The organic layer was separated and the aqueous layer extracted with four 30-ml portions of ether. The ether washings were combined with the original organic layer and dried over sodium sulfate, filtered and stripped to give an oily residue (39.3 g). The oil was dissolved in absolute ethanol (25 ml) and cooled to give IV (28.6 g, 71%), m.p. 53–55°C. The analytical sample, m.p. 55°C, was obtained by recrystallization from absolute ethanol. <sup>13</sup>C NMR δ (ppm): 140.30, 139.91, 133.24, 132.51, 131.01, 131.00, 129.35, 129.32, 129.19, 127.05, 126.41, 123.54. <sup>1</sup>H NMR δ (ppm): 7.07–7.93 (m). *m/e* 266 (*M*<sup>+</sup> based on <sup>79</sup>Br, <sup>35</sup>Cl), 231 (*M*<sup>+</sup> – 35), 187 (*M*<sup>+</sup> – 79), 152 (*M*<sup>+</sup> – 114). Anal. Found: C, 53.83; H, 3.24. C<sub>12</sub>H<sub>8</sub>BrCl calcd.: C, 53.87; H, 3.01%.

*3,7-Di-t-butyl-5,5-dimethyl-dibenzosilole (V)*

To a stirred solution of II (4.68 g, 11 mmol) in a mixture of dry tetrahydrofuran (20 ml) and dry ether (20 ml) which was cooled with an ice bath was added dropwise, *n*-butyllithium (15.4 ml, 1.55 M, 24 mmol). The mixture was stirred for 5 h and then allowed to warm to room temperature before dropwise addition of a solution of dimethyldichlorosilane (1.3 ml, 11 mmol) in tetrahydrofuran/ether (6 ml, 1/1). After 13 h at room temperature the reaction mixture was hydrolyzed with water (6 ml). The organic layer was separated and the aqueous layer was extracted with ether (15 ml). The combined organic layers were dried over sodium sulfate and filtered. Removal of the solvent from the filtrate gave an oily solid (4.5 g). Recrystallization of the residue with absolute ethanol (5 ml) gave V (1.95 g, 55%), m.p. 167°C. <sup>1</sup>H NMR δ (ppm): 0.42 (s, 6, SiCH<sub>3</sub>); 1.35 (s, 18, t-Bu); 7.3–7.8 (m, 6, Ar). <sup>13</sup>C NMR δ (ppm): –2.8, 31.4, 34.6, 120.1, 127.2, 129.1, 138.0, 145.1, 149.5. *m/e*: 322 (*M*<sup>+</sup>); 307 (*M*<sup>+</sup> – 15); 147; 119. Anal. Found: C, 81.84; H, 9.39. C<sub>22</sub>H<sub>30</sub>Si calcd.: C, 81.92; H, 9.38%.

*Preparation of 9,9-dimethylsilafluorene from IV*

A slurry magnesium (powder, 4.76 g, 196 mmol), IV (6.0 g, 22.4 mmol) and a few crystals of iodine in THF (66 ml) was sonicated for 6 h. The Grignard reagent was cannulated to a fresh dry three-necked flask and cooled with an ice bath. A solution of dimethyldichlorosilane (2.7 ml, 22 mmol) in THF (12 ml) was added dropwise to the Grignard reagent and the solution stirred overnight with gradual warming to

room temperature. The reaction mixture was hydrolyzed with water, the organic layer separated and the aqueous layer extracted with ether. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered and solvent removed to give an oil. Kugelrohr distillation provided a fraction, b.p.  $89\text{--}110^\circ\text{C}/0.4\text{--}0.8$  mmHg which solidified to give I ( $\text{R} = \text{Me}$ ) (4.1 g, 87%), m.p.  $55\text{--}58^\circ\text{C}$  (ref. 1b,  $58\text{--}59^\circ\text{C}$ ).  $^1\text{H}$  NMR  $\delta$  (ppm): 0.41 (s, 5.5H, Si- $\text{CH}_3$ ); 7.1-7.9 (m, 8.5H, Ar).

#### *Reaction of II with n-BuLi, Mg and Li*

Samples of II were stirred in dry THF or  $\text{Et}_2\text{O}$  or a mixture of these two solvents with magnesium (mesh or powder), Li (ribbon) or n-BuLi (in hexane) under argon. The conditions and times are given in Table 1. The presence of the diorganometallic reagent was determined by addition of water or dimethyldichlorosilane.

a. *Water.* An aliquot was added to water and the organic layer analyzed by GLC (column temperature  $245^\circ\text{C}$ ) and results compared to authentic samples (4,4'-di-t-butylbiphenyl, 2-bromo-4,4'-di-t-butylbiphenyl and II).

b.  *$\text{Me}_2\text{SiCl}_2$ .* After workup as described for the synthesis of V, removal of the solvent gave an oily solid. Recrystallization of the sample from absolute ethanol at  $0^\circ\text{C}$  gave V. The ratio of V to 4,4'-di-t-butylbiphenyl in the sample was determined by GLC and  $^1\text{H}$  NMR. The yields of V are calculated on the basis of starting II.

#### *Reaction of IV with Mg*

Compound IV was stirred in dry THF with magnesium (mesh or powder) and additives under argon. The conditions and times are shown in Table 2. Aliquots were added to water and the organic layer was analyzed by GLC (column temperature  $195^\circ\text{C}$ ) and the results compared to authentic samples (biphenyl, 2-bromo-biphenyl and IV).

#### *Reaction of 2,2'-dibromo-4,4'-di-t-butylbiphenyl with n-BuLi followed by $\text{D}_2\text{O}$*

A solution of n-BuLi (1.9 ml, 1.55 M) was added dropwise to II (0.62 g, 1.5 mmol) in 11 ml of anhydrous ether at room temperature and the mixture stirred for 4 h. After addition of  $\text{D}_2\text{O}$  (2 ml) the organic layer was separated and extracted with ether. The combined organic solutions were dried over  $\text{Na}_2\text{SO}_4$ , filtered and evaporated to give 0.23 g of solid. GLC analysis of the solid indicated a minor impurity of 2-bromo-4,4'-di-t-butylbiphenyl and after one recrystallization from ethanol gave a white solid, m.p.  $113\text{--}118^\circ\text{C}$  (lit. 7,  $128\text{--}129^\circ\text{C}$ ). Mass spectral analysis of the molecular ion cluster,  $m/e = 266$  through 269, indicated that the ratio of dideuterated to monodeuterated to undeuterated material was 2.9/1.0/2.1.  $^{13}\text{C}$  NMR: 149.7, 138.0, 126.5, 125.6, 118.7, 34.3, 31.4.

#### *Reaction of 2,2'-dibromo-4,4'-di-t-butylbiphenyl with Li metal followed by $\text{D}_2\text{O}$*

A solution of II (1.0 g, 2.4 mmol) in anhydrous THF (12 ml) was heated at  $48\text{--}50^\circ\text{C}$  for 4.5 h in the presence of Li (0.09 g, 13 mmol). The reaction mixture was quenched by  $\text{D}_2\text{O}$  (2 ml). After workup, mass spectral analysis of the molecular ion cluster,  $m/e = 266$  through 269, indicated that the ratio of dideuterated to monodeuterated to undeuterated material was 3/2/9.  $^{13}\text{C}$  NMR  $\delta$  (ppm): 149.7, 138.0, 126.5, 125.6, 34.3, 31.4, which is identical to that of an authentic sample of III.

## Acknowledgement

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