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SYNTHESIS OF DIBENZO[*b*, *f*]SILEPINS*

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SUMMARY

The reaction of *o,o'*-dilithiobibenzyl with substituted silicon halides results in the formation of previously unreported 10,11-dihydro-5*H*-dibenzo[*b,f*]silepins. The bromination of the dihydrodibenzosilepins followed by dehydrobromination with potassium acetate and 1,5-diazabicylo[4.3.0]non-5-ene results in the formation of the symmetrical dibenzosilepin derivatives. The spectral data for these new compounds are discussed.

INTRODUCTION

Attempts to prepare trivalent silicon cations by chemical methods generally used to prepare carbonium ions have been unsuccessful[1]. These previous attempts were mainly directed towards the generation of $(C_6H_5)_3Si^+$ or substituted analogs of the trityl carbonium ion, Ar_3C^+. Experimental results from hydride abstraction data indicate that the triphenylsiliconium ion is less stable than either the trityl carbonium ion or the tert-butylcarbonium ion. A more reasonable model for a stable siliconium ion could be the tropylium ion which has been shown to be more stable than the trityl carbonium ion[2]. We wish to report here the synthesis and characterization of dibenzo-[*b,f*]silepins, potential precursors of the silicon analog of the tropylium ion.

RESULTS AND DISCUSSION

Preliminary investigations were directed to the synthesis of tribenzosilepin derivatives by reaction of *o,o'*-dilithioterphenyl[3] with phenyl dichlorosilane according to the following eqn.:

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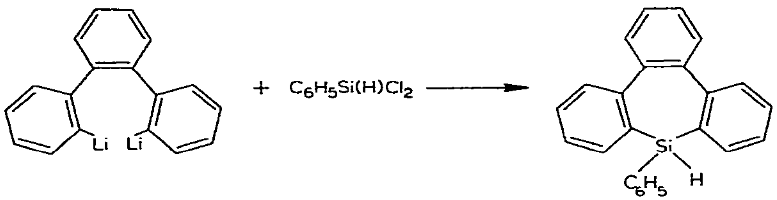
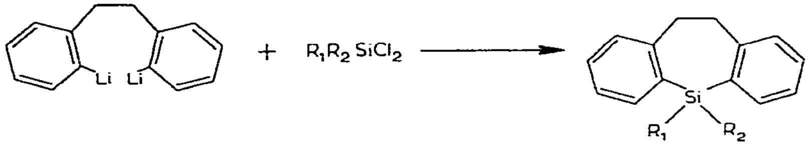


Although a reaction occurs between these reagents, attempts to isolate pure reaction products were unsuccessful[4]. It has since been reported that 1,1-dimethyltribenzosilepin is formed in 0.02 % yield from the reaction of a mixture of *o*-dichlorobenzene and dimethylmethoxychlorosilane with metallic sodium in refluxing toluene[5].

The dihydrodibenzo[*b,f*]silepin derivatives are prepared by the reaction of *o,o'*-dilithiobibenzyl with the appropriate silicon halide:

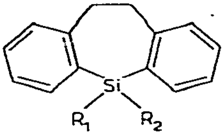


(Ia), $R_1 = R_2 = CH_3$
(Ib), $R_1 = R_2 = C_6H_5$
(Ic), $R_1 = OCH_3$; $R_2 = C_6H_5$

Yields, physical constants and analytical data for these compounds are recorded in Table 1. The variations in yield probably reflect steric hindrance to ring closure when two large phenyl groups are present on silicon *vs.* the two smaller methyl groups. The proton NMR spectra of the dihydrodibenzosilepins recorded at ambient temperatures show a singlet in the methylene-proton region which indicates rapid conformational isomerization of the seven-membered ring system at room temperature.

TABLE 1

10,11-DIHYDRODIBENZO[*b, f*]SILEPIN

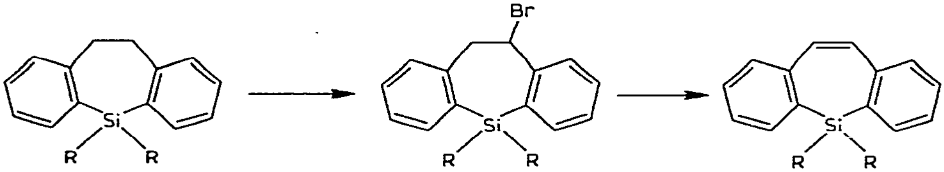


(I)

Compound			Yield (%)[a]	B.p. [°C (mm)] or m.p. (°C)	Analysis found (calcd.) (%)			m/e
No.	R_1	R_2			C	H	Si	
(Ia)	CH_3	CH_3	48	115–118 (0.03)	80.80 (80.67)	7.72 (7.56)	11.68 (11.76)	238
(Ib)	C_6H_5	C_6H_5	5	170–172[b]	86.23 (86.14)	6.11 (6.12)		362
(Ic)	C_6H_5	OCH_3	40	160–165 (0.03) 79–81	80.10 (79.75)	6.51 (6.33)	9.56 (8.86)	316

[a] Based on purified material. [b] Reported[6]: 174–175°.

Our attempts to directly dehydrogenate the dihydrosilepins with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in boiling benzene were unsuccessful and the starting silicon compounds were recovered. The symmetrically substituted silepins [(IIa) and (IIb)] were prepared by a two-step synthesis involving bromination of the benzylic position of the dihydrosilepin with *N*-bromosuccinimide (NBS) followed by dehydrobromination with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or potassium acetate according to the following eqn.:



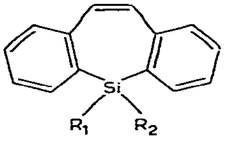
(Ia), R = CH_3
(Ib), R = C_6H_5

(IIa), R = CH_3
(IIb), R = C_6H_5

Yields, physical constants and analytical data for these new compounds are recorded in Table 2. The intermediate brominated dihydrosilepin was not purified before the dehydrobromination step. Birkofer and Kramer[7] reported ring cleavage on reaction of NBS with 3,3-dimethyl-1,2,4,5-tetrahydro-3*H*-3-benzosilepin to give *o*-divinylbenzene. Bromination of (Ia) results in some ring cleavage to give about 5% yields of *trans*-stilbene and not the expected *cis*-stilbene.

TABLE 2

DIBENZO[*b*, *f*]SILEPIN



(II)

Compound			Yield (%)[a]	B.p. [°C (mm)] or m.p (°C)	Analysis found (calcd.) (%)		m/e
No.	R_1	R_2			C	H	
(IIa)	CH_3	CH_3	36	110–123(0.2)[b]	81.76 (81.36)	6.55 (6.78)	236
(IIb)	C_6H_5	C_6H_5	40	195–197	86.69 (86.62)	5.77 (5.61)	360

[a] Based on purified product. [b] Boiling point of crude product.

Reagents such as potassium tert-butoxide, sodium methoxide, potassium acetate and DBN all affected the dehydrobromination reaction. However, for ease of isolation and purification of the resultant silepin species it was found that potassium acetate and DBN were the most effective reagents for (Ia) and (Ib) respectively. The NMR spectrum of the silepins is characterized by loss of methylene proton absorption at τ 7.0 ppm and the presence of vinylic protons at τ 3.1 to τ 3.25 ppm.

Although NBS reacts with silepin (Ic) and dehydrobromination occurs on reaction with potassium tert-butoxide, potassium acetate or DBN as indicated by the presence of vinylic protons in the NMR spectrum of the reaction residues, all attempts to isolate a pure unsymmetrical silepin compound have been unsuccessful. Distillation results in decomposition and elution chromatography of the reaction product over alumina, silicic acid or silica gel gives only ring cleavage products which we have not yet identified. We are currently studying other synthetic methods in an attempt to prepare silepins with a leaving group on silicon.

The mass spectrum of (Ia) (*m/e* 238, 73%) shows loss of a methyl group to give the base peak [(P − 15), *m/e* 223, 100%]. In contrast to this, (Ib) (*m/e* 362, 5.6%) shows loss of benzene, C_6H_6, to give the base peak [(P − 78), *m/e* 284, 100%] and (Ic) (*m/e* 316, 23.3%) loses both methanol [(P − 32), *m/e* 284, 18.7%] and benzene [(P − 78), *m/e* 238, 79.4%]. All three compounds show loss of the R_1R_2Si moiety to give an ion at *m/e* 178 [23.4% for (Ia), 29% for (Ib), and 100% for (Ic)]. It would be expected that loss of R_1R_2Si by the dihydrodibenzosilepins could lead to the 10,11-dihydrophenanthrene cation (*m/e* 180). The base peak in the mass spectrum of 10,11-dihydrophenanthrene[8] appears at an *m/e* 178 which indicates facile formation of phenanthrene from this system, therefore the peak at *m/e* 178 in the dihydrodibenzosilepins from loss of R_1R_2Si is not unreasonable. Although the $(CH_3)_2Si$ (*m/e* 58) species was not observed for (Ia), $(C_6H_5)_2Si$ (*m/e* 182, 23%) appears in the spectrum of (Ib) and $C_6H_5(OCH_3)Si$ (*m/e* 136, 20%) in the spectrum of (Ic).

Recent reports[9,10] of the mass spectra of derivatives of 9,10-dihydro-9-silaanthracene show loss of an HX fragment where X = Cl, Br or C_6H_6. When both halogen and phenyl are bonded to silicon, loss of benzene is preferred to the elimination of hydrogen halide[10]. The suggested driving force for the elimination of HX is the supposed facile formation of an aromatic silicon-containing system. The saturated silepin derivatives (Ia, b, c) show ready loss of HX (where X = C_6H_5 and OCH_3) also, but the resultant silicon-containing fragment is not aromatic. In both cases loss of HX could be due to the stereochemistry of the system, where models show that the center ring is folded in the boat form with a methylene proton and silicon substituent in close proximity across the ring. This could result in ready loss of an HX fragment. A single crystal determination of (Ic) is in progress to determine the stereochemistry of the dihydrodibenzosilepin ring systems[11].

The silepin derivative (IIa) shows loss of methyl [(P − 15), *m/e* 221, 39%] and a base peak corresponding to loss of the $(CH_3)_2Si$ moiety [(P − 58), *m/e* 178, 100%] whereas (IIb) (*m/e* 360, 1%) shows only the base peak corresponding to $(C_6H_5)_2Si$ (*m/e* 182, 100%). In the case of (IIb) the process of loss of $(C_6H_5)_2Si$ is probably a thermal one as the non-volatility of the solid necessitates a high source temperature to obtain the mass spectrum*.

The dihydrodibenzo[*b,f*]metallepins of other group IV elements have also been prepared and their chemical and physical properties are currently under study.

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* Pyrolysis of the product obtained from bromination and dehydrobromination of (Ic) results in the loss of silicon.

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of dry nitrogen in flame-dried glassware. IR spectra were determined as thin films or as Nujol mulls on a Perkin–Elmer 337 grating spectrophotometer. Proton NMR spectra were recorded in carbon tetrachloride on a Perkin–Elmer R-20 spectrophotometer. Mass spectral data were collected on an AEI MS-1201B mass spectrometer.

The silicon halides, n-butyllithium and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were commercially available and used without further purification. Anhydrous ether and spectral grade carbon tetrachloride were used as supplied. The *o,o'*-dibromobibenzyl was prepared by a reported route, purified by recrystallization from absolute ethanol and dried under a vacuum before use in reactions[12].

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

Synthesis of 5,5-*dimethyl*-10,11-*dihydro-5H-dibenzo*[*b,f*]*silepin* (*Ia*)

Into a 500-ml, three-necked flask equipped with a stirrer, reflux condenser, addition funnel, and a nitrogen inlet and outlet was added approximately 100 ml of anhydrous ether. The flask containing the ether was cooled in an ice bath and a solution containing 0.097 mole of n-butyllithium in pentane was added. A solution containing 15 g (0.044 mole) of *o,o'*-dibromobibenzyl in 75 ml of ether was added dropwise to the cold, stirred butyllithium solution. Following the completion of the addition, the reaction mixture was heated at reflux for 45 min, during which time a pale yellow solid precipitates from the reaction mixture. The reaction mixture was cooled to 0° before the dropwise addition of a solution containing 5.7 g (0.044 mole) of dimethyldichlorosilane in about 50 ml of ether. After addition was complete the mixture was heated to reflux for 45 min before hydrolysis with 200 ml of distilled water. The ether layer was separated and dried over sodium sulfate. After removal of the ether, the residue was distilled at reduced pressures yielding 4.1 g of product, b.p. 115–118°/0.03 mm. ν_{max} (thin film): 1599 m, 1480 m, 1280 (sh), 1255 s, 1248 (sh), 1130 s, 1120 m, 835 s, 815 s, 790 w, 775 s, 760 s, 732 s, 688 m, 670 w, 642 m, 575 m, 550 m, 487 m, 430 m cm^{-1}; NMR (CCl_4, TMS as external standard) τ: 2.3–3.1 (m, 8.14, aromatic), 7.0 (s, 4.0, $-CH_2-$), 9.16 ppm (s, 5.6, $-SiCH_3$); λ_{max}(EtOH) 278 (ε 860), 270 (975) and 216 (18,500) nm.

If an excess of n-butyllithium is not used in the generation of *o,o'*-dilithiobibenzyl an impure product is obtained as indicated by broad absorption in the NMR spectrum between τ 7.0 and 9.6 ppm.

The impurity can be removed by eluting 0.50 g of the crude product with heptane over 40 g of neutral activated alumina in a water-jacketed column held at 3°. Partial decomposition of the sample occurs on the alumina column.

Synthesis of 5,5-*diphenyl*-10,11-*dihydro-5H-dibenzo*[*b,f*]*silepin* (*Ib*)

(Ib) was prepared from 15 g (0.044 mole) of *o,o'*-dibromobibenzyl and 11.1 g (0.044 mole) of diphenyldichlorosilane in the same manner as (Ia). The reaction mixture was hydrolyzed with distilled water and the ether layer was separated and dried over sodium sulfate. After removal of the ether, an oil and a solid remained. The solid was eluted with heptane on a column containing 40 g of neutral activated alumina, yielding 1.4 g of solid, melting point 170–172°. ν_{max} (nujol mull): 1600 m, 1580 w, 1440 m, 1270 w, 1260 m, 1131 m, 1120 m, 1108 m, 1079 w, 998 w, 791 w, 779 m, 761 m, 750 m, 740 (sh), 718 w, 702 s, 685 w, 580 w, 560 s, 515 s, 480 m cm^{-1}; NMR (CCl_4, TMS) τ: 2.5–3.1 (m, 17.8, aromatic), 6.9 (s, 4.2, $-CH_2-$) ppm; λ_{max}(EtOH) 277 (ε 880), 271 (1,300) and 217 (46,400) nm.

*Synthesis of 5-methoxy-5-phenyl-*10,11*-dihydro-5H-dibenzo[b,f]silepin (Ic)*

(Ic) was prepared from 15 g (0.044 mole) of *o,o'*-dibromobibenzyl and 9.3 g (0.044 mole) of phenyltrichlorosilane in the same manner as (Ia). After completion of the addition of the phenyltrichlorosilane to the *o,o'*-dilithiobibenzyl and the refluxing period, a three-fold molar excess of sodium methoxide was added and the reaction mixture was heated to reflux for 10 h. The solution was then filtered from the insoluble solid. After removal of the ether the residue was distilled at reduced pressures to give the crude product, b.p., 160–165°/30 μ. The product was further purified by recrystallization from absolute methanol to give 5.5 g of solid, m.p., 79–81°. ν_{max} (thin film): 1600 m, 1580 w, 1480 m, 1440 s, 1260 m, 1190 (br), 1160 w, 1135 s, 1125 s, 1115 s, 1082 s, 1028 m, 1100 w, 788 m, 760 s, 740 s, 704 s, 680 m, 660 m, 580 m, 560 ms, 532 s, 502 m cm^{-1}; NMR (CCl_4, TMS) τ: 2.3–3.1 (m, 13.2, aromatic), 6.5 (s, 2.9, OCH_3), 6.9 (s, 3.9, $-CH_2-$) ppm.

Synthesis of 5,5-dimethyl-5H-dibenzo[b,f]silepin (IIa)

To a dry, nitrogen-filled, 100 ml, three-necked flask equipped with a stirrer, nitrogen inlet and outlet, and a reflux condenser were added 6.2 g (0.026 mole) of the dihydrodibenzosilepin (Ia), 4.4 g of *N*-bromosuccinimide, 0.1 g benzoyl peroxide and 25 ml of carbon tetrachloride. The mixture was heated to reflux. If reaction had not occurred after 1 h a sun lamp was used to initiate reaction. After completion of the reaction as indicated by the formation of succinimide (which is less dense than CCl_4) the solvent was removed. The residue was dissolved in ether and a mixture of 4.5 g potassium acetate and 1.5 ml of glacial acetic acid were added, and the solution heated to reflux for ½ h. The mixture was then poured onto ice containing 3.0 g of sodium hydroxide. The aqueous layer was extracted with ether and the ether layer dried over sodium sulfate. After removal of the ether the residue was distilled under vacuum yielding 3.0 g of crude product, b.p. 110–123°/0.2 mm. Attempted low temperature recrystallization of the crude product from ether yielded 0.22 g of a solid identified as *trans*-stilbene by comparison with a known sample. The crude silepin was purified by elution with 20% benzene in heptane over 80 g of silicic acid, giving 2.2 g of oil. ν_{max} (thin film): 1580 w, 1470 w, 1410 w, 1267 s, 1255 (sh), 1245 m, 1160 w, 1132 s, 1075 m, 878 w, 840 s, 815 s, 805 s, 785 s, 772 w, 740 s, 790 (br), 645 m, 552 w, 440 m cm^{-1}; NMR (CCl_4, TMS) τ: 2.2–2.9 (m, 8.3 aromatic), 3.1 (s, 1.6, vinylic), 9.6 (s, [illegible].8, $-SiCH_3$) ppm; λ_{max}(EtOH) 293 (ε 8,500) and 215 (39,100) nm.

5,5-diphenyl-5H-dibenzo[b,f]silepin (IIb)

To a dry, nitrogen-filled, three-necked flask equipped with a nitrogen inlet and outlet and a reflux condenser was added 1.0 g (2.8×10^{-3} mole) of (Ib) and 0.49 g (2.8×10^{-3} mole) of *N*-bromosuccinimide. The mixture was heated to reflux with stirring and irradiated with a sun lamp. After the reaction was complete as indicated by the formation of the succinimide (0.23 g or 2.3×10^{-3} mole) the CCl_4 was removed and the residue dissolved in 15 ml of anhydrous ether. To this stirred ether solution was added dropwise a solution of 0.69 g (5.5×10^{-3} mole) of DBN dissolved in 15 ml of ether. After addition was complete the solution was heated to reflux for 1 h. The solution was then decanted from the gummy residue and the ether removed. The residue remaining after evaporation of the ether was eluted over 50 g of silicic acid with 25% benzene in heptane, yielding 0.40 g of solid, m.p. 195–197°. ν_{max} (nujol mull): 1131 m, 1110 m, 1105 m, 798 s, 775 s, 740 s, 698 s, 678 m, 562 m, 546 m, 530 s, 508 s, 498 m, 450 w cm^{-1}; NMR (CCl_4, TMS) τ: 2.55–2.85 (m, 18.1, aromatic), 3.25 (s, 1.9, vinylic) ppm; λ_{max}(EtOH) 299 (ε 10,000) and 222 (36,000) nm.

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