action of **4** with $LiAlH_4$. It was estimated by vpc to be present to the extent of 50% of the reaction mixture.

The Nmr Spectrum of 2,5-Diazabicyclo[2.2.2]octane (13).—2,5-Diazabicyclo[2.2.2]octane dihydrochloride was obtained from Merck.[6] This sample was dissolved in D_2O and the nmr spectrum showed the following signals: δ 2.20 (4 H, m, 80-Hz width), 3.69 (4 H, octet), and 4.05 (2 H, m). To this sample was added concentrated ammonium hydroxide such that the solution was just basic to litmus. The nmr spectrum of this sample had the following signals: δ 2.25 (4 H, m, 80 Hz width) and 3.53 (6 H, m). In the dihydrochloride salt the signal at δ 3.69 represented an AB portion of an ABX system where $J_{AX} = 2.3$, J_{BX} and $J_{AB} = 11$ Hz.

The Nmr Spectrum of 3,8-Dibenzyl-3,8-diazabicyclo[3.2.1]-octane (12).—The sample used here was supplied by Gallo,[5] who prepared the sample by a procedure described by Blackman.[10] The nmr of this sample had the following signals: δ 7.25 (10 H, m), 3.45 (4 H, d), 3.0 (2 H, m), 2.35 (4 H, octet), 1.85 (4 H, m). The signal at δ 2.35 represented the AB portion of an ABX pattern in which $J_{AX} = 3$, $J_{BX} = 2$, and $J_{AB} = 10$ Hz.

Conversion of 4 to 5.—A 1-g sample of **4** was placed in a vacuum sublimator and was heated gradually from 50 to 170° over a 3-hr period at 4 mm. No visual sublimation occurred. The resulting material appeared as a slightly darkened melt. This was taken up in methanol–ethyl acetate. A minimum amount was used such that only the dark impurities dissolved. The remaining white, crystalline solid was recrystallized from ethanol–ethyl acetate to give a solid, mp 117–119°, whose infrared and nmr spectra were identical with those of a sample of **5**. The above conversion also occurred on recrystallization. A 1-g sample of **4** was recrystallized from ethanol–ethyl acetate to give 0.80 g of pure material. Evaporation of the mother liquor gave 0.15 g of a material whose melting point and nmr spectrum were identical with those of a sample of **5**.

Registry No.—**1**, 30715-42-5; **3**, 30715-43-6; **4**, 30788-18-2; **5**, 30715-44-7; **6**, 30715-45-8; **7**, 24425-88-5; **8**, 30715-47-0; **12**, 17740-42-0; **13**, 658-24-2.

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(10) S. W. Blackman and R. Blatzly, *J. Org. Chem.*, **26**, 2750 (1961).

1,1-Dimethyl-1-sila-2,3:6,7-dibenzocycloheptatriene. A Dibenzosilepin

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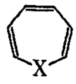
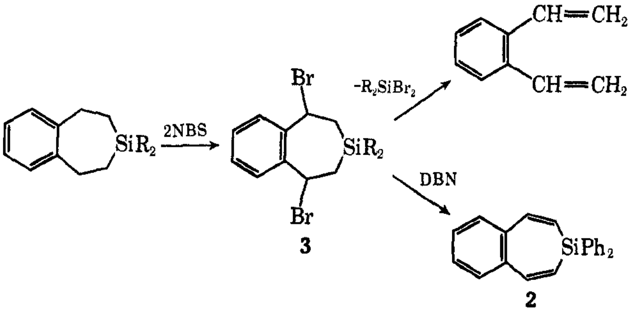
The first example of the dibenzosilepin ring system has been synthesized. 1,1-Dimethyl-1-sila-2,3:6,7-dibenzocycloheptatriene (**6**) was prepared through cyclization of *o,o'*-dilithiobibenzyl and dichlorodimethylsilane followed by free-radical (NBS) dibromination and finally debromination with metallic zinc. The nonplanarity of **6** could not be established through low-temperature nmr studies. The uv spectrum of **6** revealed no evidence of ($\pi \rightarrow d$) π bonding.

When the vast research effort which has been exerted toward the synthesis and study of heterocycloheptatrienes [*e.g.*, oxepines (**1a**), azepines (**1b**), thiepins (**1c**), and diazepines][2] is considered, it is rather surprising to note that only one proven[3] and two possible[4,5] examples of a silicon-containing cycloheptatriene (silacycloheptatriene or silepin, **1d**) have been reported. This dearth of information in the chemical body of knowledge is particularly glaring in view of the unique situation for the possible observation of ($\pi \rightarrow d$) π bonding[6] in the silepin ring system. It could be hoped that the aromatic character derived from cyclic delocalization of the six π electrons would put this type of valence expansion to a stern test.



1a, X = O
b, X = NR
c, X = S
d, X = SiR_2

A search of the literature revealed a single unambiguous example of an intentional silepin synthesis, the benzosilepin **2**, which originally failed[7] due to the extreme lability of the synthetic intermediate, 1,5-dibromo-3,3-dimethyl-1,2,4,5-tetrahydro-3*H*-3-benzosilepin (**3**), which was due to operation of that persistent stumbling block of organosilicon chemistry, the β effect.[8] Birkofer[3] was finally able to prepare **2**, in low yield, through the use of 1,5-diazabicyclo[4.3.0]nonene (DBN) as a dehydrobromination agent. Examination of the carbon–carbon double bond stretching frequencies in the infrared spectrum of **2** led Birkofer to conclude that there was interaction between the π electrons of the olefinic system and the vacant d orbitals of silicon. However, it should be noted that these ir bands (1592 and 1550 cm^{-1}) were not significantly different from the double-bond stretches of other vinylsilanes (*e.g.*,



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[1] National Science Foundation Undergraduate Research Participant, summers of 1969 and 1970.

[2] For an excellent review of the syntheses and chemistry of azepines, oxepines, and thiepins, see L. A. Paquette in "Nonbenzenoid Aromatics," Vol. 1, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1970, pp 249–310.

[3] L. Birkofer and H. Haddad, *Chem. Ber.*, **102**, 432 (1969).

[4] H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 5584 (1964).

[5] K. A. Andrianov, L. M. Vokova, N. V. Delazari, and N. A. Chumaevskii, *Akad. Nauk Latv. SSR*, 435 (1967), report that dimethylmethoxychlorosilane and *o*-dichlorobenzene react with sodium to afford 1,1-dimethyltribenzosilepin in <0.02% yield.

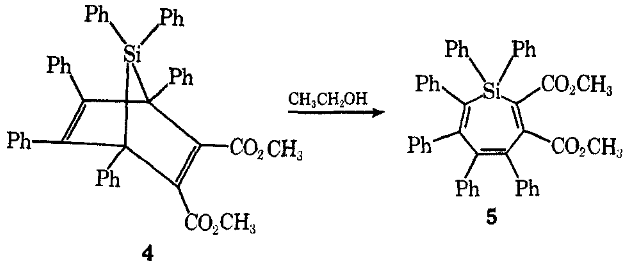
[6] For a summary of the evidence relating to ($p \rightarrow d$) π and ($\pi \rightarrow d$) π bonding to silicon, see E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, part 1, Chapter 1.

[7] L. Birkofer and E. Kramer, *Chem. Ber.*, **102**, 427 (1969).

[8] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960.

cis-β-trimethylsilylstyrene, 1590 and 1570 cm^{-1})[9] which do *not* have the possibility for cyclic conjugation that is present in the silepin ring system. The nmr of **2** was quite similar to that of the analogous benzostannepin,[10] but quite different from that of the tropylium analog, 3-phenyl-3-benzoborepin[11] (*e.g.*, =SiCH=C, δ 6.28, for **2** *vs.* -BCH=C, δ 7.72).

Gilman[4] has tentatively suggested structure **5** for the product from decomposition of the 7-silanorbornadiene (**4**) in ethanol. Obviously the extensive ring substitution of **5** makes structural assignment a virtually impossible task without the use of X-ray diffraction techniques.



4 **5**

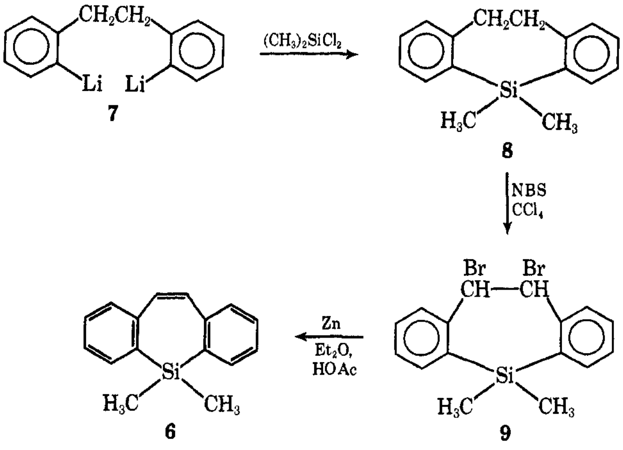
We now report the synthesis of the first dibenzosilepin derivative, 1,1-dimethyl-1-sila-2,3:6,7-dibenzocycloheptatriene (**6**).[12]

The most obvious route into the dibenzosilepin ring system is through cyclization of *o,o'*-dilithiobibenzyl (**7**)[13] and some dihalosilane, followed by introduction of the final double bond. Indeed a dihydrodibenzosilepin has been reported by Gilman from this very route when dichlorodiphenylsilane was employed.[14]

Addition of a solution of dichlorodimethylsilane in ether to an equimolar solution of *o,o'*-dilithiobibenzyl under nitrogen at room temperature afforded, upon work-up, 1,1-dimethyl-1-sila-2,3:6,7-dibenzocycloheptadiene (**8**) as a colorless liquid in 56% yield. Dihydrosilepin **8** analyzed correctly upon combustion analysis and exhibited a strong parent ion at *m/e* 238 in its mass spectrum. The nmr spectrum was consistent with this structure: $\delta_{TMS}^{CCl_4}$ 0.50 (s, 6 H, =Si-Me$_2$), 3.13 (s, 4 H, -CH$_2$CH$_2$-), 6.82–7.68 (m, 8 H, Ar).

In our hands bromination of **8** with NBS at 50° allowed isolation of 1,1-dimethyl-1-sila-2,3:6,7-dibenzo-4,5-dibromocycloheptadiene (**9**) in *ca.* 30% yield.

Dibromide **9** was converted into the title compound (**6**) through treatment with zinc metal in refluxing ether. Dibenzosilepin (**6**) was obtained in 82% yield as a colorless, viscous liquid. The nmr spectrum consisted of a singlet of area 6 at δ 0.46 (=SiMe$_2$), a singlet of area 2 at δ 6.88 (-CH=CN-), and a multiplet of area 8 centered at δ 7.41 (aromatic). The conversion of **8** to **6** was performed by Corey[12] through monobromination (NBS) and dehydrohalogenation (potassium acetate or DBN) while Cartledge[12] reports dehydrogenation of **8** with DDQ.



7 **8** **9** **6**

It is of considerable interest to determine the effects of introduction of a silicon atom into this well-examined ring system. A number of 2,3:6,7-dibenzo derivatives of seven-membered cyclic conjugated systems (thiepin, azepin, oxepin, tropilidene, tropone, and heptafulvene)[15] have been examined by physical and chemical means. In each case these molecules were found to be nonplanar. Certainly the dibenzosilepin is not the ideal silepin in which to search for cyclic ($\pi \rightarrow$ d) π delocalization in view of the markedly decreased stability of the 1,2:5,6-dibenzotropylium cation in comparison to the parent tropylium cation.[16]

The room temperature nmr spectrum of **6** reveals the SiCH$_3$ groups as a clean singlet which can arise either from a rapidly inverting boat form or a planar system. In a low-temperature nmr study, the Si(CH$_3$)$_2$ resonance remains a sharp singlet until *ca.* −80°. Slight broadening commences at this temperature, but, since olefinic and aromatic signals also begin to broaden, this effect must be ascribed to increased viscosity. It is therefore not possible to state whether **6** is inverting or planar, although the latter situation is considered highly unlikely. Work is presently in progress to resolve that question through X-ray crystallography.

The most telling evidence against any significant cyclic delocalization *via* ($\pi \rightarrow$ d) π bonding comes from the uv spectrum of **6**. Dihydrosilepin **8** exhibits a uv spectrum [λ_{max}^{EtOH} 278 mμ (log ϵ 2.65), 271 (2.70), 265 infl (2.58)] which is extremely similar to that of the all-carbon analog, 1,2:4,5-dibenzocycloheptadiene [λ_{max}^{EtOH} 274 mμ (log ϵ 2.84), 271 (2.91), 265 (2.94)][17] while **6** possesses a simple spectrum [λ_{max}^{EtOH} 294 mμ (log ϵ 4.1)] which does not exhibit a bathochromic shift of a magnitude required to postulate any significant involvement of silicon d orbitals in cyclic conjugation. This conclusion becomes evident upon examination of the uv spectrum of several pertinent model compounds:[18] dibenzo[*a,e*]cycloheptatriene [λ_{max}^{EtOH} 288 mμ (log ϵ 4.19)],[19] dibenzo[*b,f*]thiepin [λ_{max}^{EtOH} 295 mμ (log ϵ

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[9] D. Seyferth, L. G. Vaughan, and R. Suziki, *J. Organometal. Chem.*, **1**, 437 (1964).

[10] A. J. Leusink, J. G. Noltes, H. A. Budding, and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, **83**, 1036 (1964).

[11] A. J. Leusink, W. Drenth, J. G. Noltes, and G. J. M. van der Kerk, *Tetrahedron Lett.*, 1263 (1967).

[12] After our work was complete and the manuscript submitted, there appeared two reports of the synthesis of **8** and **6**: J. Y. Corey, M. Dueber, and B. Bichlmeir, *J. Organometal. Chem.*, 167 (1971), and F. K. Cartledge and P. D. Mollere, *ibid.*, 175 (1971). The three reports agree with regard to the conclusions about electronic delocalization in the central ring and physical constants. The sole exception is the nmr spectrum of **8** reported by Corey, which is somewhat at odds with that found by Cartledge and this report.

[13] R. L. Letsinger and I. H. Skoog, *J. Amer. Chem. Soc.*, **77**, 5176 (1955).

[14] H. Gilman and W. H. Atwell, *J. Org. Chem.*, **28**, 2906 (1963).

[15] M. Nógrádi, W. D. Ollis, and I. O. Sutherland, *Chem. Commun.*, 158 (1970), and references cited therein.

[16] G. Berti and A. DaSettimo, *Ann. Chim.* (*Rome*), **49**, 1237 (1959).

[17] C. D. Gutsche and H. E. Johnson, *J. Amer. Chem. Soc.*, **77**, 5933 (1955).

[18] Unfortunately, the interesting comparison with the uv spectrum of **2** cannot be made as this spectrum was not reported in ref 3.

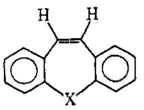
[19] E. D. Bergmann and M. Rabinovitz, *J. Org. Chem.*, **25**, 827 (1960).

3.70), 262 (4.47)],[19] *cis*-stilbene [λ_{max}^{EtOH} 280 mμ (log ϵ 4.02)],[20] 1,2:4,5-dibenzotropylium cation [λ_{max} 540 mμ (log ϵ 3.51), 508 (3.51), 397 (3.94), etc.][21] However, the nagging problem of separation of the inductive effect of the heteroatom from d-orbital stabilization of the π^* orbitals, *i.e.*, that we are observing the results of two counteracting effects (see ref 5, pp 29–35), continues to plague this type of analysis.

A cursory inspection of the chemical shift of the two olefinic protons would appear to indicate some polarization of **6**, if not actual cyclic delocalization. With one exception the comparisons which can be made from Table I indicate a separation of charge in **6** in the direction which would be expected from ($\pi \rightarrow$ d) π bonding. However, without specific knowledge of the effects of the various functional group anisotropies in Table I any conclusions with regard to polarization of **6** must be regarded as tentative, especially in view of the reported position (418 Hz) for the corresponding hydrogens in dibenzo[*a*,*e*]cycloheptatriene.[23]

TABLE I

CHEMICAL SHIFT POSITIONS OF OLEFINIC PROTONS



cis-Stilbene (393 Hz)[a]

X = C=CH$_2$ (402 Hz)[a]
X = C=O (414.5 Hz)[a]
X = C=C(CN)$_2$ (421 Hz)[a]
X = CHCH$_2$OH (390 Hz)[a]
X = CH$_2$ (418 Hz)[b]

6 (413 Hz)[c]

[a] M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron*, **22**, 225 (1966). [b] E. Müller and H. Kessler, *Justus Liebigs Ann. Chem.*, **692**, 58 (1966). [c] This work.

The mass spectrum of **6** (70 eV) is relatively uneventful, revealing a strong parent ion (*m*/*e* 236) and a facile loss of ·CH$_3$ (*m*/*e* 221, M^* 206.6). The intensity of this fragment ion (*m*/*e* 221) is close to that of the parent ion and insufficient to postulate any unusual stability for the silatropylium cation.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer. Routine proton nmr spectra were determined on a Varian A-60 instrument employing tetramethylsilane as the internal standard. Low-temperature nmr spectra were measured on a Perkin-Elmer R20-B instrument. Uv spectra were recorded on a Cary Model 14 spectrophotometer. Analyses were carried out by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany.

***o*,*o*′-Dilithiobibenzyl** (**7**).—This material was prepared by the method of Letsinger and Skogg.[13] A solution consisting of 80 ml (1.6 *M* in hexane) of *n*-butyllithium and 150 ml of anhydrous ether was slowly added under argon to a stirred solution of 20 g (59 mmol) of *o*,*o*′-dibromobibenzyl in 300 ml of ether kept at 5°. After completion of addition, the reaction mixture was refluxed for 1 hr.

1,1-Dimethyl-1-sila-2,3:6,7-dibenzocyclohepta-2,6-diene (**8**).—A solution of 7.7 g (60 mmol) of dry dimethyldichlorosilane in 200 ml of anhydrous ether was slowly added under argon to the uncooled solution described above. The reaction mixture was allowed to stir for an additional 3 hr and then hydrolyzed with 1 *N* HCl. The ether layer was separated, washed with water, and dried over magnesium sulfate. Evaporation of the ether *in vacuo* afforded a yellow oil which upon distillation yielded 7.9 g (56%) of colorless **8**. Analytically pure **8** was obtained by careful distillation on a Nester–Faust annular Teflon spinning-band column: bp 112° (0.1 mm); ν_{max}^{neat} 2930, 1590, 1480, 1400, 1265, 1255, 1138, 1117, 1074 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 0.50 (s, 6 H), 3.13 (s, 4 H), 6.82–7.68 (m, 8 H); mass spectrum *m*/*e* 238 (parent ion).

Anal. Calcd for C$_{16}$H$_{18}$Si: C, 80.61; H, 7.61; Si, 11.83. Found: C, 80.57; H, 7.47; Si, 11.76.

1,1-Dimethyl-1-sila-2,3:6,7-dibenzo-4,5-dibromocyclohepta-2,6-diene (**9**).—To a stirred solution of **7** (18.0 g, 75.5 mmol) and a catalytic amount of benzoyl peroxide in carbon tetrachloride (1 l.) under a nitrogen atmosphere at 50° was added *N*-bromosuccinimide (27.0 g, 152 mmol). The reaction mixture was allowed to stir at 50° overnight and cooled, and the succinimide was removed by filtration. Evaporation of solvent, percolation through a silica gel column (hexane), and recrystallization from methanol afforded white, crystalline **9**: yield 9.0 g (30%); mp 178.0–178.5°; ν_{max}^{KBr} 2930, 1420, 1385, 1287, 1251, 1241, 1229, 1148, 1128, 1084, 1073 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 0.53 (s, 6 H), 5.68 (s, 2 H), 7.25 (m, 8 H).

Anal. Calcd for C$_{16}$H$_{16}$Br$_2$Si: C, 48.50; H, 4.07. Found: C, 48.56; H, 4.05.

1,1-Dimethyl-1-sila-2,3:6,7-dibenzocycloheptatriene (**6**).—A solution of dibromide **9** (10.0 g, 25 mmol) in ether (250 ml) was added, at a rate sufficient to maintain gentle refluxing, to a stirred mixture of activated zinc (2 g), ether (500 ml), and a few drops of acetic acid. After addition was completed the mixture was stirred for 2 hr, filtered, and washed with water. Removal of solvent *in vacuo* afforded a light yellow oil which was distilled to yield colorless **6**: 5.0 g (82%); bp 116.5–117.5° (0.2 mm); mass spectrum *m*/*e* 236; $\delta_{TMS}^{CCl_4}$ 0.46 (s, 6 H), 6.88 (s, 2 H), 7.41 (m, 8 H).

Anal. Calcd for C$_{16}$H$_{16}$Si: C, 81.29; H, 6.82; Si, 11.88. Found: C, 81.26; H, 6.73; Si, 11.83.

Registry No.—**6**, 29668-89-1; **8**, 29784-73-4; **9**, 29668-90-4.

Acknowledgment.—The authors are indebted to the Public Health Service (Grant No. GM 16689-02 from the National Institutes of Health) for generous support of this work.

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(20) R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 2755 (1953).

(21) G. Naville, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **43**, 1225 (1960).