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SYNTHESIS AND CHARACTERIZATION OF 10,11-DIHYDRO-5*H*-DIBENZO[*b*,*f*]METALLEPINS OF GROUP IV*

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SUMMARY

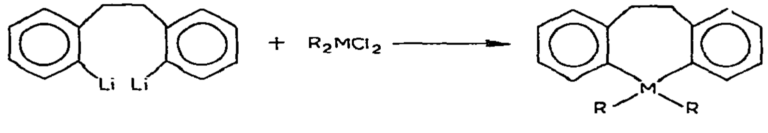
Direct reaction of 2,2'-dilithiobibenzyl with $(CH_3)_2MCl_2$ or $(C_6H_5)_2MCl_2$ where M = Si, Ge, Sn, or Pb results in the formation of 10,11-dihydro-5*H*-dibenzo-[*b*,*f*]metallepins. The germanium derivatives were successfully converted to 5,5-dimethyl- and 5,5-diphenyl-5*H*-dibenzo[*b*,*f*]germepin by bromination followed by dehydrobromination with 1,5-diazabicyclo[4.3.0]non-5-ene. Reactions of dihydrodibenzo[*b*,*f*]stannepins uniformly gave ring cleavage products. The abundances of the metal fragments produced in the mass spectrum of the dihydrodibenzometallepins are recorded and a fragmentation pattern common to the system is given.

INTRODUCTION

We recently reported the synthesis of dihydrodibenzo[*b*,*f*]silepins and their conversion to dibenzo[*b*,*f*]silepins by reaction with *N*-bromosuccinimide followed by dehydrobromination with 1,5-diazabicyclo[4.3.0]non-5-ene[1]. We have extended our studies of metallepins to include the synthesis and characterization of the corresponding derivatives of germanium, tin and lead.

RESULTS AND DISCUSSION

The dihydrodibenzo[*b*,*f*]metallepin derivatives are prepared by the reaction 2,2'-dilithiobibenzyl with an appropriate Group IV halide:



M = Si, Ge, Sn, Pb

(I) R = CH_3
(II) R = C_6H_5

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TABLE 1

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

Compound			Yield (%)[a]	B.p. [°C(mm)] or m.p. (°C)	Analysis found (calcd.) (%)		m/e[b]
No.	M	R			C	H	
(Ia)[c]	Si	CH_3	48	115–118 (0.03)	80.80 (80.67)	7.72 (7.56)	238
(Ib)	Ge	CH_3	35	110–116 (0.03)	68.32 (67.94)	6.45 (6.37)	286
(Ic)	Sn	CH_3	33	109–120 (0.02)[d]	58.49 (58.42)	5.51 (5.51)	330
(Id)	Pb	CH_3	(25)[e]	163–165 (0.30)	— (45.93)	— (4.31)	418
(IIa)[c]	Si	C_6H_5	5	170–172	86.23 (86.14)	6.11 (6.12)	362
(IIb)	Ge	C_6H_5	33	165–168	76.84 (76.63)	5.24 (5.40)	408
(IIc)	Sn	C_6H_5	23	138–141[f]	69.27 (69.32)	5.07 (4.83)	454
(IId)	Pb	C_6H_5	1.4	163–164	57.42 (57.56)	4.30 (4.06)	542

[a] Based on purified material. [b] Based on the principal isotope of the metal heteroatom. [c] See ref. 1. [d] Reported[2]: 130–135°/0.2 mm [e] Based on crude product. [f] Reported[2]: 136–137°.

Yields, physical constants and analytical data for these compounds are recorded in Table 1.

The direct reaction of 2,2′-dilithiobibenzyl with diphenyltin dichloride has been reported by Kuivila[2] to give very low yields of 5,5-diphenyl-5*H*-dihydrodibenzo[*b*,*f*]stannepin (IIc) and the preferred route to stannepins (Ic) and (IIc) was by reaction of methyllithium or phenyllithium with 5,5-dichloro-10,11-dihydrodibenzo[*b*, *f*]stannepin. We obtained satisfactory yields of stannepins by the direct reaction of the organotin halide with 2,2′-dilithiobibenzyl. These are the first seven-membered ring systems reported containing one germanium or lead heteroatom.

Our attempts to prepare 5,5-dimethyl-5*H*-dihydrodibenzo[*b*, *f*]plumbepin in the pure state by distillation, elution over alumina or silica gel, or low temperature recrystallization from ether, heptane or absolute ethanol have thus far been unsuccessful. The crude oil obtained by distillation of the reaction product of 2,2′-dilithiobibenzyl with dimethyllead dichloride shows a proton NMR spectrum that is typical of the other dimethylmetallepins, and a mass spectrum with the expected parent ion, but chemical analyses have consistently shown the material to have a carbon content higher than that calculated for (Id).

The preliminary X-ray crystallographic studies of 5,5-diphenyl-10,11-dihydrodibenzo[*b*,*f*]germepin (IIb) show that the conformation of the seven-membered ring is that of a twisted boat and models indicate that the methylene protons are in nonequivalent environments[3]. However, the proton NMR spectra of all the dihydrodibenzometallepins recorded at ambient temperatures show a singlet in the methylene-proton region which implies rapid conformational isomerization of the seven-membered ring. A study of the variable temperature proton NMR spectra of 5,5-dimethyl-10,11-dihydro-5*H*-dibenzo[*b,f*]silepin from +35 to −94° failed to give evidence for splitting of the methylene singlet[4]. The low barriers to inversion observed for 1,1,4,4-tetramethyl-1,4,-disilacyclohexane and for 1,1-dimethylsilacyclohexane have been attributed to greater carbon–silicon bond distances which result in smaller force constants for bond deformation[5]. Since the carbon–metal bond distances increase from silicon to lead it would be expected that the barriers to rotation would be even lower for the heavier members of Group IV and a singlet-methylene in the dihydrodibenzo[*b, f*]metallepins is therefore reasonable.

Conversion of the dihydrodibenzo[*b, f*]metallepins to dibenzometallepins has been successful only for the germepin and silepin systems. Both 5,5-dimethyl- and 5,5-diphenyl-5*H*-dibenzo[*b, f*]germepin were prepared by bromination of (Ib) and (IIb) respectively with *N*-bromosuccinimide followed by dehydrobromination with 1,5-diazabicyclo[4.3.0]non-5-ene. Yields, physical constants and analytical data for these new compounds are recorded in Table 2. Yields of germepins were lower than the previously reported silepins[1] and germanium products resulting from ring cleavage were extracted from the aqueous layer.

TABLE 2

DIBENZO[*b,f*]GERMEPINS

Compound		Yield (%)[a]	M.p. (°C)	Analyses found (calcd.) (%)		m/e[b]
No.	R			C	H	
(IIIa)	CH_3	16		68.69 (68.41)	5.87 (5.74)	282
(IIIb)	C_6H_5	6.3	193–194.5°	76.75 (77.11)	4.91 (4.94)	406

[a] Based on purified material. [b] Based on ^{74}Ge.

Bromination of dimethylstannepin (Ic) with *N*-bromosuccinimide resulted in ring cleavage and the formation of 2,2′-dibromobibenzyl. The cleavage of two phenyl groups from tetraphenyltin by *N*-bromosuccinimide has also been reported[7]. In the stannepin system, (IIc), the phenyl–tin bonds preferentially cleaved by *N*-bromosuccinimide are those that form the seven-membered ring. Direct attemps to dehydrogenate (Ic) by reaction with dichlorodicyanoquinone in boiling toluene for three days gave 77% yields of 1,2-diphenylethane as the only isolated product. This dehydrogenation method has been successfully utilized for the synthesis of 5,5-dimethyl-5*H*-dibenzo[*b, f*]silepin[4].

It has been demonstrated that both 9,9-dimethyl-9,10-dihydro-9-stannaanthracene and 3,3-dimethyl-3*H*-benzo[*d*]stannepin undergo exchange with boron halides to give good yields of the corresponding boron heterocycles. An exchange reaction of (Ic) with dimethyldichlorosilane was attempted by heating a mixture of the two reagents neat or in anhydrous benzene. In both cases no metallepin derivatives were recovered and an oil was obtained which was tentatively identified as 10,11-dihydrophenanthrene on the basis of its proton NMR spectrum.

TABLE 3

ABUNDANCE OF THE PRINCIPAL METAL CONTAINING FRAGMENTS GENERATED FROM 5,5-DIPHENYL-10,11-DIHYDRODIBENZO[*b*,*f*]METALLEPINS[a,b]

Metal	$C_{26}H_{22}M$	$C_{20}H_{17}M$	$C_{20}H_{16}M$	$C_{14}H_{11}M$	$C_{14}H_{10}M$	$C_{12}H_{10}M$	$C_{12}H_{9}M$	$C_{6}H_{5}M$	M	Other fragments[d]
Si (IIa)	8.5	4.5	100	18	11	24	6.8	18	×	$C_{20}H_{15}Si$(5.7), $C_{19}H_{15}Si$(3.0), $C_{14}H_{9}Si$(6.6), $C_{12}H_{11}Si$(0.5)
Ge (IIb)	23	59	67	22	5	100	21	59	×	
Sn[c] (IIc)	8.6	100	30	11.6	9	86	×	90	×	$C_{12}H_{11}Sn$(9.5)
Pb (IId)	1	1.5	47	2.6	×	×	×	100	100	$C_{20}H_{14}Pb$(4.2), $C_{18}H_{14}Pb$(3.0), $C_{15}H_{14}Pb$(1.6), $C_{14}H_{12}Pb$(4.8)

[a] Data collected at 70 eV. [b] Abundances are recorded relative to the principal metal isotope of the most abundant metal fragment and corrected for ^{13}C. See ref. 6. [c] Data collected at 50 eV. [d] All metal fragments greater than 1% of the most abundant metal fragment are recorded.

TABLE 4

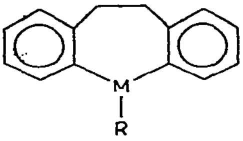
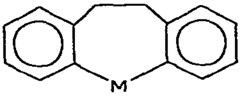
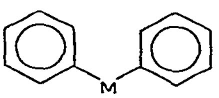
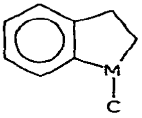
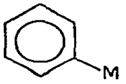
ABUNDANCE OF THE PRINCIPAL METAL CONTAINING FRAGMENTS GENERATED FROM 5,5-DIMETHYL-10,11-DIHYDRODIBENZO[*b*,*f*]METALLEPINS[a,b]

Metal	$C_{16}H_{18}M$	$C_{15}H_{15}M$	$C_{15}H_{13}M$	$C_{14}H_{11}M$	$C_{9}H_{9}M$	$C_{6}H_{5}M$	$CH_{3}M$	M	Other fragments[d]
Si (Ia)	22	100	33	2.9	12	5.1	14	×	$C_{14}H_{12}Si$(1.7), $C_{14}H_{9}Si$(2.4), $C_{6}H_{4}Si$(6.5)[e]
Ge (Ib)	5	100	23.5	×	2.8[e]	6.3	16.7	×	$C_{14}H_{9}Ge$(1.1), $C_{14}H_{7}Ge$(1.9)
Sn (Ic)	1	100	7.5	3.5	×	3.6	29	21	$C_{14}H_{10}Sn$(1.5), $C_{7}H_{5}Sn$(7.6), SnH(6.9)
Pb[f] (Id)	5	100	×	×	×	×	54	100	$C_{14}H_{13}Pb$(3.7), $C_{14}H_{9}Pb$(4.1), $C_{8}H_{14}Pb$(19), $C_{6}H_{9}Pb$(12), $C_{6}H_{7}Pb$(11), PbH(11)

[a] Data collected at 70 eV. [b] Abundances are recorded relative to the principal metal isotope of the most abundant metal fragment and corrected for ^{13}C. See ref. 6. [c] Data collected at 50 eV. [d] All metal fragments greater than 1% of the most abundant metal fragment are recorded. [e] Overlap with organic fragments from dihydrophenanthrene. [f] Base peak is at *m/e* 180 at 70 eV.

TABLE 5

CARBON-ATOM FRAMEWORK FOR FRAGMENTS GENERATED FROM DIHYDROMETALLEPINS UPON ELECTRON IMPACT

No.	No. C atoms in framework	Suggested structure	Ox. No. assignment
(VIa) (VIb)	20 15		M^{IV}
(VIc)	14		M^{III}
(VId)	12		M^{III}
(VIe)	9		M^{IV}
(VIf)	6		M^{II}

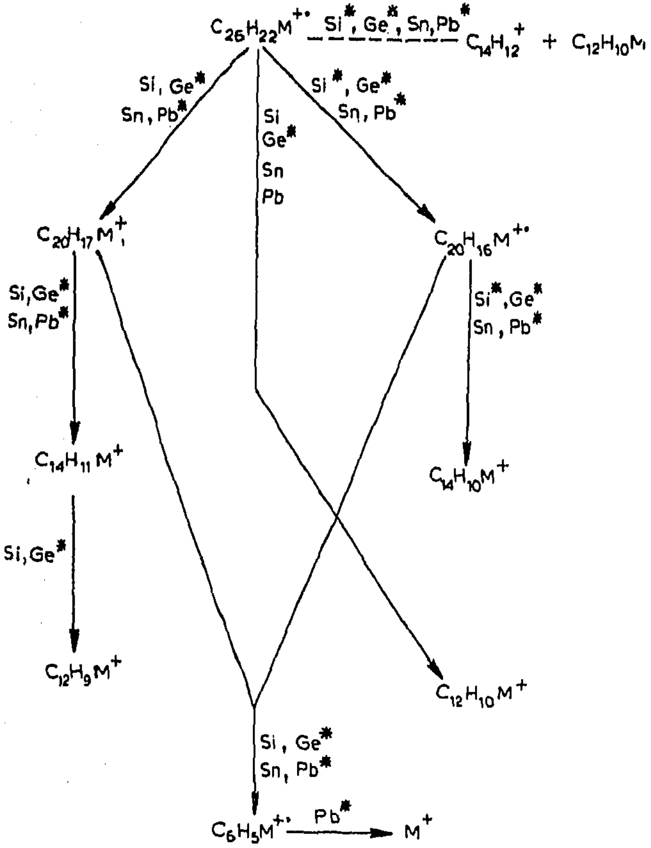
Mass spectra of 10,11-dihydrodibenzo[b, f]metallepins

The abundances of the metal ion fragments produced in the mass spectrum of 5,5-diphenyl-10,11-dihydrodibenzo[*b*, *f*]metallepins and of 5,5-dimethyl-10,11-dihydrodibenzo[*b*,*f*]metallepins are recorded in Tables 3 and 4. The data have been corrected for ^{13}C. In all cases except for (Id) (base peak at 180 at 70eV) the most abundant metal fragment also corresponds to the base peak in the spectrum. The major portion of the ion current is carried by the metal fragments, as has been previously observed for nonheterocyclic organic derivatives of Ge, Sn, and Pb[8-13]. The parent heterocyclic ion generates the dihydrophenanthrene cation, *m/e* 180 and subsequent fragmentation of this cation yields non-metal fragments of minor abundance. The fragmentation pattern that is common to the entire series, and for which there is meta-stable support, is recorded for (IIa-d) in Scheme 1 and that for (Ia-d) in Scheme 2. Structural assignments for the carbon-atom framework (including the heterocycle) for the important fragments are suggested in Table 5 and an oxidation number assignment for the structure is included. Unequivocal assignments for the hydrogen atoms in fragments that differ by one or two mass units cannot be made due to the possible formation of M–H bonds. The MH^+ fragment has been observed

SCHEME 1

META-STABLE SUPPORTED COMMON FRAGMENTATION PATTERN FOR 5,5-DIPHENYL-10,11-DIHYDRODIBENZO-[*b,f*]METALLEPINS

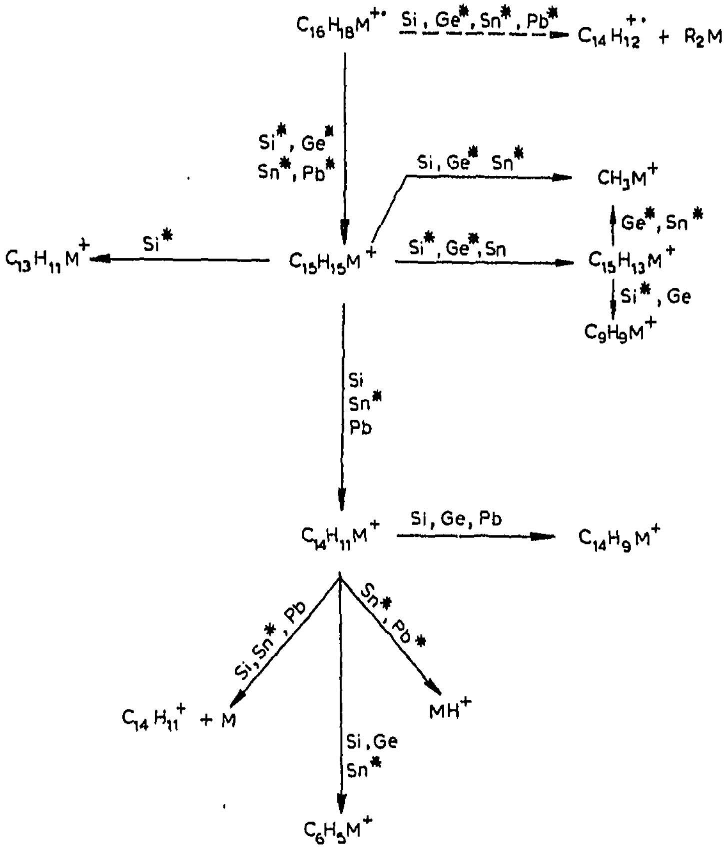
The symbol M* refers to those transitions for which there is meta-stable support. Meta-stables were calculated from the principal metal isotope.



SCHEME 2

META-STABLE SUPPORTED COMMON FRAGMENTATION PATTERN FOR 5,5-DIMETHYL-10,11-DIHYDRODIBENZO-[*b,f*]METALLEPINS

For note see Scheme 1.

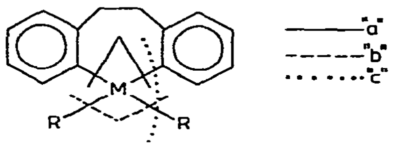


only in the spectrum of (Ic) and (Id).

The parent ion is weak in all systems and except for (Ia) and (IIb) is less than 10% of the most abundant metal fragment, as has also been demonstrated for Ph_4M and Me_4M[8,9,11,12]. The parent cation shows loss of a neutral radical in both system (I) and system (II) [as well as loss of neutral C_6H_6 from (II)] to form the most abundant fragments, (VIa, b) [for all but (IId)]. The source of the proton for elimination of benzene is unclear at this time. Abstraction by the phenyl group can occur from an adjacent phenyl or from the methylene bridge. The latter route is claimed for the silaanthracenes[18], but deuterated benzene is not lost from 1,1-diphenylgermacyclopentane-3,3,4,4-d_4[15]. We are currently attempting to synthesize metallepins labelled with deuterium in the methylene positions in an effort to solve this question and to test the occurrence of hydrogen migration to the metal atom.

For system (IIa, b, c) the order of abundance of the fragments is $R_3M^+ > R_2M^+ > RM^+$ and the ratio of R_2M^+/RM^+ is approximately two for (IIb) and approximately one for (IIc). These observations were also reported for Ph_4Ge and Ph_4Sn[8,9], and probably for Ph_4Si but structural assignments were not made for all fragments[20]. The observed order of abundance for (IId) is $RM^+ = 2R_3M^+ \gg R_2M^+$ whereas the abundance order observed for Ph_4Pb[8] was $R_3M^+ \approx RM^+ \gg R_2M^+$. In both systems the apparent contribution of fragments due to Pb^{III} is small. For the dimethylmetallepins (Ia-d) the observed order of abundance was $R_3M^+ > RM^+ > R_2M^+$ with an increasing abundance of RM^+ as one proceeds from silicon through lead. The substitution of methyl for phenyl results in the suppression of the formation of R_2M^+ fragments and is also observed for mixed phenyl methyl derivatives of Group IV[9,12]. No $Me_2M^{+\cdot}$ is observed in the metallepin systems although there is meta-stable support for the production of Me_2M^0, whereas $Ph_2M^{+\cdot}$ is prominent in the spectra of (IIa-c).

It has been suggested by Glockling *et al.* that the major process leading to the formation of $[Ph_2Sn]^+$, (Sn^{III}), in the spectrum of Ph_4Sn is elimination of Ph_2 from the cation $Ph_4Sn^{+\cdot}$. Three such cleavage processes may be envisioned for heterocyclic compounds as depicted in (VIII).



(VIII)

Cleavage by route "a" generates either $R_2M^{+\cdot}$ or $C_{14}H_{12}^{+\cdot}$ both of which fragments are observed for (IIa-d) and for which transitions there is meta-stable support. Only generation of $C_{14}H_{12}^{+\cdot}$ is observed for (Ia-d). The cleavage route of type "a" from (VIa) is probably the major process generating $C_6H_5M^{+\cdot}$. Cleavage by route "b" generates either $C_{14}H_{12}M^{+\cdot}$ or $C_{12}H_{10}^{+\cdot}$ from (IIa-d). None of the latter is present in the spectra of (IIa-d) and the fragment $C_{14}H_{12}M^{+\cdot}$ is found only in the spectrum of (Id). Alternate routes to $C_{14}H_xM^{+\cdot}$ are possible (Schemes 1 and 2).

Cleavage by route "c" generates a trivalent $R_3M^{+\cdot}$ indistinguishable from the parent ion but which can fragment to generate $C_6H_5M^{+\cdot}$ or $[C_{20}H_{17}]^{+\cdot}$ from (IIa-d).

Although there is no metastable support for this type of cleavage a peak of low abundance at *m/e* 257 appears in the spectrum of (IIa) and (IId). The cation, $[C_{20}H_{17}]^{+\cdot}$, could also be produced by a "c-type" cleavage of the trivalent cation, (VIa). The dimethylmetallepins would generate $CH_3M^{+\cdot}$ or $C_{15}H_{15}{}^{+\cdot}$ by this route. A peak at *m/e* 195 is present in the spectrum of (Ia) and is present in low abundance in the spectrum of (Ib) and (Ic) where it overlaps with metal-containing fragments and also in (Id) at *m/e* 193 with the loss of two protons.

From consideration of the fragmentation patterns outlined in Schemes 1 and 2 it can be seen that loss of both neutral phenyl or benzene from cation (VIa) also generates C_{14} metal-containing fragments. The fate of (VIb) is more varied as fragments due to loss of CH_4, H_2 and C_2H_4 are all observed. Loss of neutral fragments is also observed from the trivalent cations, $C_{20}H_{16}M^{+\cdot}$ and $C_{15}H_{13}M^{+}$. We attribute formation of $C_{13}M$ and C_9M fragments to the result of ring reduction as has been observed both for 1,1-diphenylgermacyclopentane[15] and 9-oxo-10-stanna-9,10-dihydroanthracene[17].

We have tried to point out the similarities of the mass-spectral data for the metallepin derivatives as a class and to show that the relationships observed are similar to those observed for the corresponding non-heterocyclic systems of Group IV. From the very limited amount of data currently available it appears that one of the main differences between the mass spectra of heterocyclic compounds and their non-heterocyclic analogs is related to ease of elimination of the metal fragment by rupture of the ring bonds, either to form $R_2M^{+\cdot}$ from the parent cation or RM^+ from R_3M^+. Chemical reactions also show that rupture of the ring bonds occurs with ease. The main difference in the fragmentation patterns of the diphenylmetallepins and the dimethylmetallepins is related to the low abundance of M^{III} fragments in the latter compounds. This phenomenon is also observed for the corresponding non-heterocyclic compounds[8-13].

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 or on a Varian T-60 spectrophotometer. Mass spectral data were collected at 70 eV on an AEI MS-1201B mass spectrometer.

All organometallic halides except diphenyltin dichloride and dimethyllead dichloride were obtained commercially and used without further purification. n-Butyllithium, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and tetraphenyltin were used as supplied.

Dichlorodicyanoquinone (DDQ) was prepared by oxidation of 2,3-dicyanohydroquinone by nitric acid in hydrochloric acid solution[21].

The 2,2′-dibromobibenzyl was prepared by a reported route, purified by recrystallization from absolute ethanol and dried under a vacuum before use in reactions[22].

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

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

The procedure has been previously described in detail[1]. A solution of 5.2 g (0.029 mole) of dimethylgermanium dichloride dissolved in 30 ml anhydrous ether was added to a solution of 2,2'-dilithiobibenzyl prepared from 9.8 g (0.029 mole) of 2,2'-dibromobibenzyl and 0.058 mole of n-butyllithium. After hydrolysis and workup, distillation at reduced pressure yielded 2.9 g of product, b.p. 108–116°/0.03 mm. ν_{max} (thin film): 1504(m), 1475(s), 1460(sh), 1302(w), 1269(m), 1261(s), 1245(m), 1122(s), 1115(m), 1068(w), 1021(w), 945(w), 829(s), 797(s), 788(s), 755(s), 727(s), 699(w), 657(w), 599(s), 579(s), 539(m), 469(s). NMR (CCl_4, TMS as external standard) τ: 2.2–3.2 (m, 8.4, aromatic), 6.85 (s, 3.8, CH_2), 9.38 (s, 5.8, $GeCH_3$).

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

A slurry of 12 g (0.055 mole) dimethyltin dichloride was added to a solution of 2,2'-dilithiobibenzyl prepared from 18.6 g (0.055 mole) of 2,2'-dibromobibenzyl and 0.122 mole of butyllithium. The reaction mixture was heated at reflux overnight. After hydrolysis distillation of the crude product gave 6.1 g of (Ib), b.p. 109–120°/0.020 mm. Alternatively the crude residue could be eluted with heptane over 50 g alumina. Partial decomposition of the product occurs during chromatography. ν_{max} (thin film): 1602(w), 1585(m), 1570(w), 1465(s), 1440(s), 1490(sh), 1298(w), 1266(sh), 1260(m), 1160(w), 1116(m), 1106(m), 1046(w), 1026(s), 948(w), 755(s-brd), 728(sh), 698(m), 560(w), 528(s), 518(sh), 450(s). NMR (CCl_4, TMS as external standard)τ: 2.4–3.2 (m, 8.5, aromatic), 6.9 (s, 4.2, CH_2), 9.50 (s, 5.3, $SnCH_3$).

Synthesis of 5,5-*dimethyl*-10,11-*dihydro-5H-dibenzo[b, f]plumbepin (Id).*

A slurry of 6.7 g (0.022 mole) of dimethyllead dichloride[24] was added to a solution of 2,2'-dilithiobibenzyl prepared from 7.37 g. 2,2'-dibromobibenzyl and 0.043 mole of butyllithium. The mixture was heated to reflux for 4 h. After hydrolysis and removal of the ether 8.3 g of oil was obtained. Distillation gave 2.3 g of (Ic), b.p. 163–65°/0.3 mm. ν_{max} (thin film): 1601(w), 1580(w), 1499(sh), 1450(s), 1295(w), 1269(s), 1261(s), 1205(w), 1160(m), 1112(m), 1100(m), 1071(w), 1032(sh), 1024(m), 940(w), 907(w), 870(w), 750(s-brd), 725(s), 700(s), 532(m), 478(s), 442(s). NMR (CCl_4, TMS as internal standard)τ: 2.3–3.4 (m, 8.0, aromatic), 7.0 (s, 4.0, CH_2), 8.95 (s, 9.0, $PbCH_3$).

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

A solution of 5.0 g (0.017 mole) of diphenylgermanium dichloride was added to a solution of 2,2'-dilithiobibenzyl prepared from 5.72 g (0.017 mole) of 2,2'-dibromobibenzyl and 0.0368 mole of butyllithium. After hydrolysis and removal of the solvent, 2.25 g of crude product separated from the oil produced. Recrystallization from ethanol afforded 2.0 g of (IIa), m.p. 165–168°. A further 0.3 g of product was obtained by elution of the oil with 4/1 heptane/benzene over 70 g silica gel. ν_{max} (KBr disk): 1480(w), 1435(s), 1260(m), 1112(w), 1090(s), 1062(w), 1022(w), 997(w), 785(w), 767(m), 756(m), 737(s), 697(s), 572(w), 535(w), 475(m-brd), NMR (CCl_4, TMS as internal standard) τ: 2.5–3.1 (m, 17.9, aromatic), 6.87 (s, 4.1, CH_2).

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

A solution of 8.0 g (0.023 mole) of diphenyltin dichloride[23] was added to a solution of 2,2'-dilithiobibenzyl prepared from 7.9 g (0.023 mole) of 2,2'-dibromobibenzyl and 0.047 mole of butyllithium. The reaction mixture was stirred at room temperature overnight. After hydrolysis and removal of the solvent the residue was dissolved in a minimal amount of benzene and eluted over 50 g alumina with heptane to yield 4.4 g of crude product. Elution of 1.9 g of crude product over 29 g of alumina gave 1.05 g of product, (IIb), m.p. 138–141°, from a 3/1 heptane/benzene mixture. ν_{max} (nujol mull): 1260(m), 1118(w), 1105(w), 1075(m), 1021(w), 998(w), 808(w), 790(w), 760(s), 730(s), 700(s), 658(w), 560(w), 450(m-brd). NMR (CCl_4, TMS as internal standard) τ: 2.3–3.1 (m, 17.9, aromatic), 6.83 (s, 4.1, CH_2).

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

A slurry of 4.8 g (0.011 mole) of diphenyllead dichloride was added to a solution of 2,2'-dilithiobibenzyl prepared from 3.76 g of 2,2'-dibromobibenzyl and 0.022 mole of butyllithium. After hydrolysis and evaporation of the solvent an oil was obtained. Elution of 0.75 g of the oil over 25 g of alumina with 2/1 benzene/heptane gave 0.17 g of crude product. Recrystallization of the crude material gave 0.08 g of (IIc), m.p. 163–164°. ν_{max} (nujol mull): 1300(w), 1260(w), 1097(w), 1062(w), 1017(m), 997(m), 905(w), 760(s), 730(sh), 723(s), 697(s), 557(w), 530(w), 442(m), 432(sh). NMR (CCl_4, TMS as external standard) τ: 2.3–3.3 (m, 17.9, aromatic), 6.87 (s, 4.1, CH_2).

Synthesis of 5,5-*dimethyl*-5*H*-*dibenzo*[*b*, *f*]*germepin* (*IIIa*)

A solution of 0.90 g (3.2 mmole) of (Ib) in 5 ml carbon tetrachloride was added dropwise to a stirred slurry of 0.54 g (3.0 mmole) of *N*-bromosuccinimide and 0.05 g of benzoyl peroxide in 20 ml of refluxing carbon tetrachloride. The reaction was initiated by irradiation with a sunlamp for 15 min after addition of (Ia). After completion of the reaction the succinimide was removed and the carbon tetrachloride evaporated. The reaction residue was dissolved in 15 ml of ether and to this stirred solution was slowly added dropwise a solution of 0.81 g (6.5 mmole) of DBN in 10 ml of ether. After addition was complete the reaction mixture was heated to reflux for 15 min. The solution was decanted from the gummy residue and the ether evaporated to give 1.3 g of a yellow-brown oil. Elution of 0.5 g of oil over 65 g of silica gel with benzene afforded 0.25 g of a colorless oil which proved to be a 70/30 mixture of (IIIa) and starting material (Ia). Further elution of the oil over 50 g of silicic acid with 2/3 benzene/heptane gave 0.08 g of pure (IIIa). ν_{max} (thin film): 1740(m), 1600(w), 1470(m), 1430(m), 1290(w), 1268(m), 1235(w), 1128(m), 1072(w), 1026(w), 950(w), 905(w), 877(w), 832(m), 803(s), 775(m), 758(m), 738(s), 695(w), 608(m), 585(m), 540(w), 498(w), 450(m), 435(m). NMR (CCl_4, TMS as internal standard) τ: 2.3–3.0 (m, 8.0, aromatic), 3.2 (s, 1.9, vinyl), 9.39 (s, 6.1, $GeCH_3$).

Synthesis of 5,5-*diphenyl*-5*H*-*dibenzo*[*b*, *f*]*germepin* (*IIIb*)

A solution of 0.90 g (2.3 mmole) of (IIb) was brominated with 0.39 g (2.2 mmole) of *N*-bromosuccinimide according to the method described for (IIIa). Removal of carbon tetrachloride gave 1.1 g of solid material. To a stirred ether slurry of 0.9 g of the solid in 50 ml of ether was added slowly a solution of 0.42 g (3.6 mmole) DBN. After addition was complete the mixture was heated at reflux for $\frac{1}{2}$ h. The solution was decanted from the gummy residue and the ether evaporated to give 1.1 g of oil plus solid. The residue was extracted with 10% benzene in heptane to leave 0.70 g of insoluble solid. Elution of the 0.70 g of solid over 60 g of silica gel with 3/1 benzene/

heptane gave 0.10 g of crude product. Recrystallization from absolute ethanol gave 0.07 g of pure (IIIb), m.p. 193–194.5°. ν_{max}(KBr): 1458(w), 1435(m), 1268(w), 1258(sh), 1186(w), 1158(w), 1092(s), 1065(w), 1028(w), 999(w), 800(s), 778(m), 759(w), 737(s), 702(s), 674(w), 539(m), 498(w), 454(s), 439(m). NMR (CCl_4, TMS as internal standard) τ: 2.5–3.0 (m, 18.0, aromatic), 3.34 (s, 2.0, vinyl).

Reaction of (Ic) with N-bromosuccinimide

A solution of 0.75 g (2.3 mmole) of (Ic) in 10 ml of carbon tetrachloride was added to a refluxing slurry of 0.46 g (2.6 mmole) of NBS in 15 ml of carbon tetrachloride. Reaction was inititated with a sun lamp. After removal of the succinimide the carbon tetrachloride was removed and the reaction residue eluted over 50 g of alumina with heptane to give 0.45 g of solid identified as 2,2'-dibromobibenzyl.

Reaction of (Ic) with dichlorodicyanoquinone

A solution of 1.5 g (4.6 mmole) of (Ic) and 1.1 g (4.8 mmole) of dichlorodicyanoquinone in 20 ml anhydrous toluene was refluxed for three days. The solution was filtered from the black solid that formed and the solvent removed from the mother liquor to give a red-black oil. The oil was extracted with hot heptane and the heptane soluble portion eluted over 80 g silica gel. The fraction eluted with benzene weighed 0.65 g and was identified as 1,2-diphenylethane by comparison with a known sample. Similar reactivity was observed for (IIc).

Reaction of (Ic) with dimethyldichlorosilane

A mixture of 0.7 g (2.1 mmole) of (Ic) and 0.3 g (2.3 mmole) of dimethyldichlorosilane in 20 ml of anhydrous benzene was refluxed for a total of four days. The benzene was removed and the oil residue was eluted through a $15 \times \frac{1}{2}$ inch column of alumina with heptane. Approximately 0.35 g of oil containing no silicon or tin was obtained. The proton NMR spectrum of the heptane eluant gave an integration ratio for aromatic/methylene of 2/1 and no Me_2M. Heating a mixture of (Ic) and dimethyldichlorosilane neat at either 150° or at 80° produced similar results.

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