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Reactivity of Functionalized Arylcarbenes. 2-Phenylethyl Side Chains and Hetero Analogues

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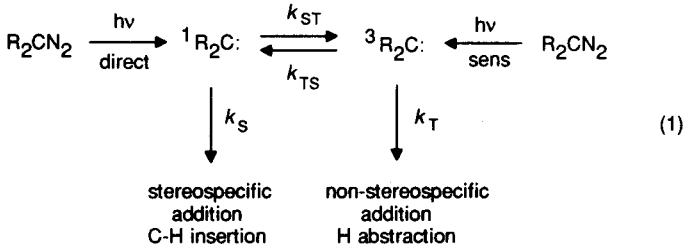
Abstract: Phenylcarbenes with -X-CH_2Ph and -CH_2-X-Ph (X = CH_2, O, $SiMe_2$) groups in the *ortho* position were generated thermally and photolytically from diazo or tosylhydrazone precursors. Stereorandom insertion reactions with β-C-H bonds were observed, pointing to a triplet abstraction-recombination mechanism. Large kinetic and stereochemical deuterium isotope effects support this notion. The ample formation of benzocyclobutenes from 2-CH_2-X-Ph substrates is due to insertion of the carbenes into ArCH_2-X bonds. Addition to the terminal phenyl groups competes with C-H and C-X insertion.The results of benzophenone sensitization and of trapping with methanol suggest that the intramolecular reactions of functionalized arylcarbenes proceed, at best, competitively with spin inversion. © 1997 Elsevier Science Ltd.

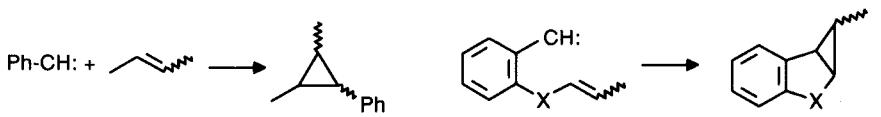
INTRODUCTION

It is widely believed that spin-state-specific mechanisms can be assigned to the reactions of carbenes.[1] Singlet carbenes undergo concerted, stereospecific cycloadditions with alkenes and insertion reactions with C-H bonds. Stepwise, nonstereospecific addition to alkenes and hydrogen abstraction is characteristic of triplet carbenes, Eq.(1). If spin inversion is relatively slow, $k_{ST}<k_S$ and $k_{TS}<k_T$, the mechanism depends on how the carbene is generated. Thus, direct photolysis of diazo precursors induces singlet reactivity whereas sensitized photolysis leads to triplet reactions. Methylene is an eminent example of such behavior.[1] In the case of rapid intersystem crossing, $k_{ST}>k_S$ and $k_{TS}>k_T$, the reaction is channelled through the most favorable transition state, regardless of the spin state in which the carbene is formed. If these conditions prevail, direct and sensitized photolyses of carbene precursors give similar results.



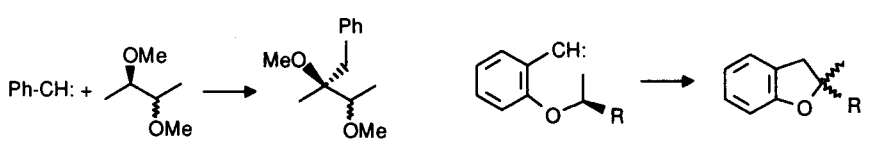
(1)

It appears that arylcarbenes belong to the second category. Although the triplet has been shown to be the ground state of phenylcarbene by low-temperature electron paramagnetic resonance (EPR),[2] the reaction of phenylcarbene with alkenes gives cyclopropanes with greater than 95% retention of configuration.[3,4] The stereospecificity of the addition of phenylcarbene to 2-butene was not affected by dilution with perfluorocyclobutane,[5] nor by benzophenone-sensitized photolysis of phenyldiazomethane.[6] These results clearly indicate that $k_{TS}>k_T$. However, alkenes attached to the *ortho* position of phenylcarbene were found to accept preferentially the triplet carbene.[7] The formation of five-membered rings favors a stepwise process. The rather inefficient *intramolecular* addition of the singlet is attributed to the steric constraints that are associated with a three-center transition state.



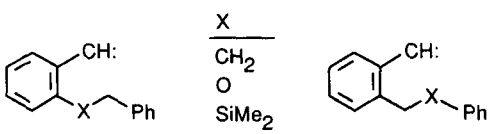
>95% stereospecific non-stereospecific

A similar dichotomy was noted for reactions of arylcarbenes with C-H bonds. The concerted singlet mechanism for *intermolecular* C-H insertion reactions of phenylcarbene is supported by the lack of crossover products,[8] small deuterium isotope effects,[8] and stereoselective insertion into the tertiary C-H bonds of *rac*- and *meso*-2,3-dimethoxybutane.[9] On the other hand, *intramolecular* abstraction of hydrogen was observed for 2-alkoxy substituted phenylcarbenes.[10] Recombination of the intervening 1,5-biradicals leads to non-stereospecific formation of dihydrobenzofurans. The concerted C-H insertion of the singlet carbene becomes competitive if the side chain is lengthened and six-membered rings are created.[10c]



>95% stereospecific non-stereospecific

In the present work, 2-phenylethyl groups in the *ortho* position of phenylcarbene were used to probe the intramolecular reactivity. Competitive reactions with side-chain C-H bonds and phenyl groups are anticipated for these substrates. For mechanistic insight into the C-H "insertion" process, deuterium labels were attached to the side chains (-CHD-CHD-Ph and -X-CHD-Ph) or the diazo groups ($-CDN_2$). Methylene groups of the side chain were replaced with hetero atoms (O, $SiMe_2$) in order to assess substituent effects. In the case of 2-X-CH_2Ph groups, the hetero atom influences the reactivity of the neighboring C-H bonds as well as that of the carbene. Chiral 2-X-CH(R)Ph groups can be employed for stereochemical studies. The hetero atom of 2-CH_2X-Ph groups may be attacked with formation of an ylide and products derived therefrom.[11] Moreover, both the rate and regiochemistry of intramolecular carbene addition to the terminal phenyl group will be affected.



RESULTS AND DISCUSSION

2-(2-Phenylethyl)phenylcarbene (8)

2-(2-Phenylethyl)benzaldehyde (**4**) was obtained from 2-(2-phenylethyl)benzoic acid[12] by way of the analogous benzyl alcohol. Alternative syntheses of **4** were also reported.[12b,13] In order to generate the carbene **8**, the tosylhydrazone **5** was photolyzed in MeOH-NaOMe, and the sodium salt **6** was pyrolyzed. For photolyses in pentane, the diazo compound **7** was prepared from **5** by a standard procedure.[14] Under aprotic conditions, the major reaction of **8** is insertion into the β-C-H bonds of the side chain, leading to 2-phenylindan (**3**). Insertion into α-C-H bonds (→ **2**) and into *ortho*-C-H bonds of the phenyl group (→ **11**) occurs to a minor extent (Scheme 1 and Table 1). Addition to the phenyl group, with formation of the cycloheptatriene **10**, is also observed. In methanol, reaction of **8** with the solvent (→ **9**) predominates. The formal O-H insertion, giving ethers, is thought to be diagnostic of singlet carbenes.[15] Consequently, the fraction of **9** decreases on triplet sensitization, with a concomitant increase of **1** and **3** (Table 1). The increase of **3** suggests that (part of) this product originates from ^{3}**8**. The formation of **1**, on the other hand, does not necessarily involve the carbene **8**. A likely route to **1** is ketyl-mediated electron transfer to **6** or **7**, as discussed elsewhere.[16] (Note that the relative yield of **1** is influenced by [NaOMe] as well as by [Ph_2CO]. These findings point to the intervention of $Ph_2C^{\cdot}O^-$).

Scheme 1

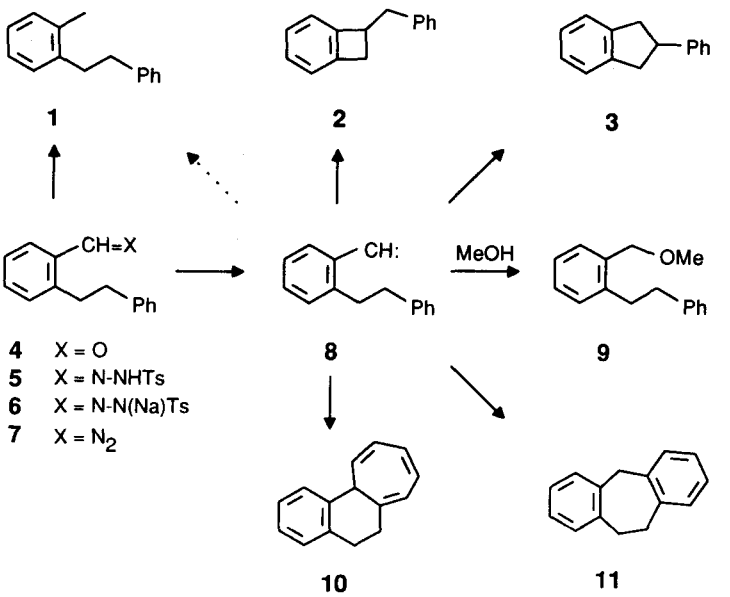


Table 1. Product Distributions (%) Obtained from **5-7**

precursor, conditions	**1**	**2**	**3**	**4**	**9**	**10**	**11**
6, 300 °C, 0.1 mm	0.6	3.1	83.0	0.5	-	9.7	3.1
7, pentane, hν	2.7	5.7	63.0	1.1	-	12.7	14.8
5, MeOH, 0.1 M NaOMe, hν	5.5	1.8	6.4	1.7	82.5	2.1	-
5, MeOH, 0.1 M NaOMe, hν, 0.05 M Ph_2CO	17.2	0.5	22.8	0.7	57.9	0.9	-
5, MeOH, 0.1 M NaOMe, hν, 0.2 M Ph_2CO	23.7	0.4	24.8	0.7	49.5	0.9	-
5, MeOH, 0.2 M NaOMe, hν, 0.2 M Ph_2CO	44.8	0.1	20.2	0.1	34.7	0.1	-
5, MeOH, 0.5 M NaOMe, hν, 0.2 M Ph_2CO	65.8	0.2	9.1	1.1	22.8	1.0	-

For further mechanistic insight, the stereochemistry of the "C-H insertion" reaction, **8** → **3**, was explored by means of deuterium labels. We converted *trans*-stilbene-2-carboxylic acid (**12**)[17] into **7a** as shown in Scheme 2. In order to ensure *cis* addition of deuterium, the double bond was reduced with dideuterodiimide. Photolysis of **7a** in pentane afforded deuterated 2-phenylindan which was analyzed by ^2H NMR to obtain the ratios *cis*-1-D : *trans*-1-D : 2-D = 35 : 27 : 38. The

assignment of *cis*-1-H (δ 3.1), *trans*-1-H (δ 3.4), and 2-H (δ 3.7) in **3** was confirmed by addition of deuterium to 2-phenylindene (**14** → **3b**) since coupling constants ($J_{cis\text{-}1,2}$ = $J_{trans\text{-}1,2}$ = 8.5 Hz) were not helpful. (The orientation of H/D *relative to the phenyl group* is designated as *cis* or *trans*).

The observed distribution of deuterium can be translated into relative yields of isotopomers **3a-e** (Scheme 2):

cis-1-D = **3a** + 2 x **3d** + **3e** (2)

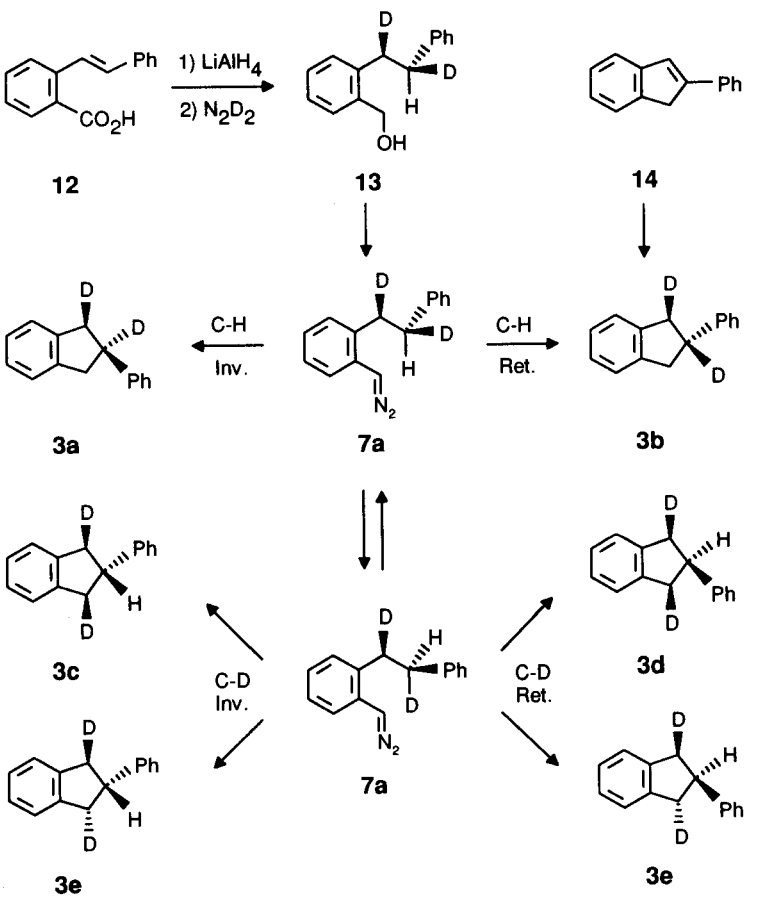
trans-1-D = **3b** + 2 x **3c** + **3e** (3)

2-D = **3a** + **3b** (4)

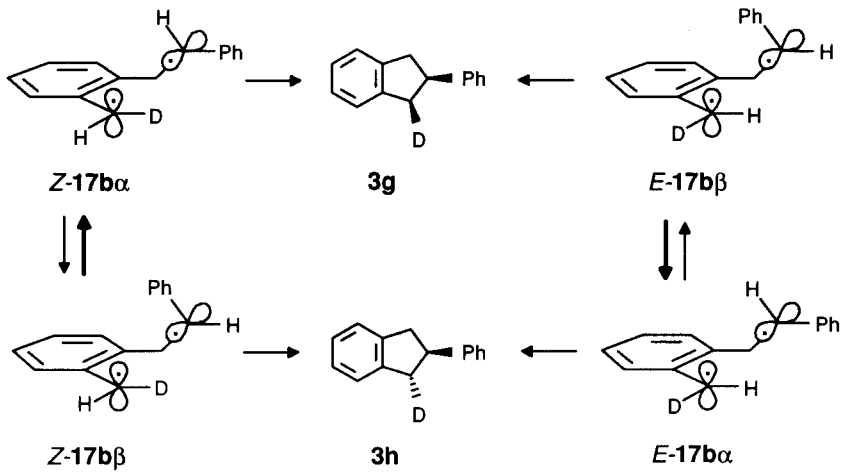
From Eqs. (2)-(4) we obtain

3c + **3d** + **3e** = 0.5(*cis*-1-D + *trans*-1-D - 2-D) (5)

Scheme 2



Scheme 4



2-(Benzyloxy)phenylcarbene (21)

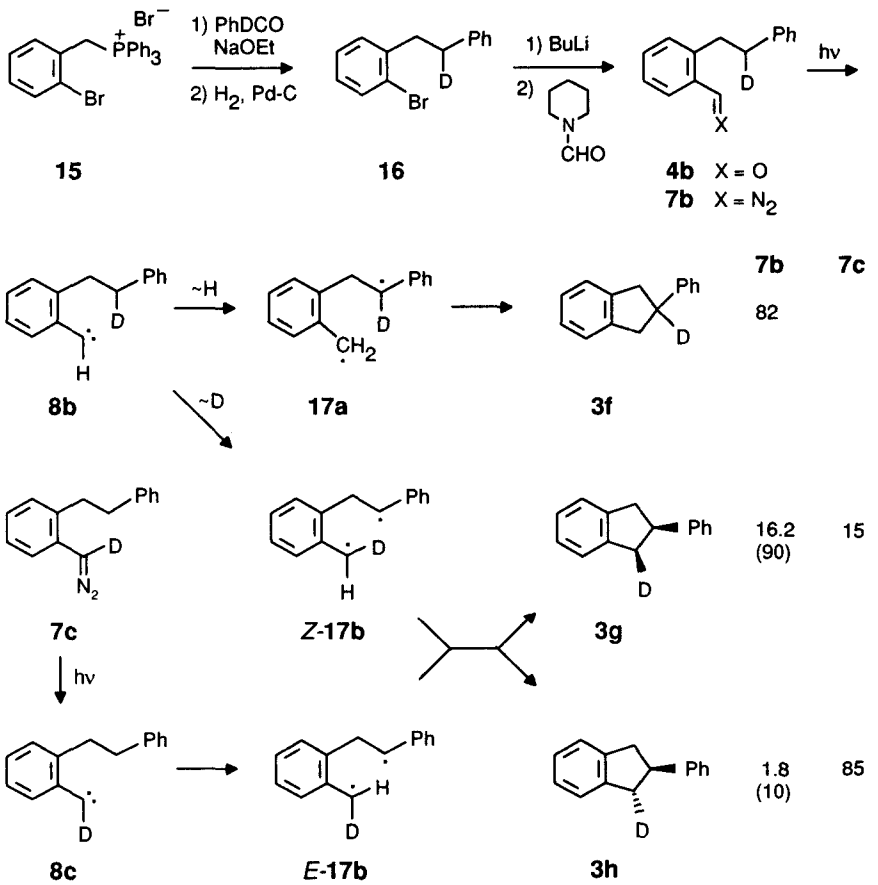
2-Benzyloxybenzaldehyde (**18**)[21] was converted into tosylhydrazone **19** and diazo compound **20** which served to generate the carbene **21** (Scheme 5). With regard to C-H „insertion", the chemistry of **21** parallels that of the carbon analog **8**. Thus, the kinetic isotope effect (k_H/k_D = 4.0) and the stereoselectivity of deuterium transfer, **21a** → *Z*-**22b** + *E*-**22b**, are similar to the data recorded for **8**. In methanol, benzophenone sensitization enhances the ratio of cyclization to O-H insertion for **21** (Table 3) as well as for **8** (Table 1).

Table 3. Product Distributions (%) Obtained by Photolysis of **19** (0.03 M) in MeOH-NaOMe

[NaOMe] (M)	[Ph_2CO] (M)	**22**	**23**	**24**
0.13	-	6.9	3.2	89.9
0.13	0.05	22.1	4.1	73.8
0.13	0.2	33.7	4.7	61.6
0.2	0.2	35.5	10.9	53.6
0.5	0.2	28.9	28.6	42.5

On the other hand, **21** does not react with the β phenyl group, in contrast to **8**. 2,3-Dihydro-2-phenylbenzofuran (**22**) was the only intramolecular product obtained from **20** by pyrolysis or by photolysis in pentane. Analogous reactions of **7** give **10** and **11** in addition to **3** (Scheme 1). Aside from conformational changes, electronic effects can account for the divergent behavior of **8** and **21**: (i) Hydrogen is more readily abstracted from the α position of ethers than from hydrocarbons, as attested by the reaction rates of methyl radicals,[22] phenyl radicals,[23] and carbonyl triplets.[24] Hence

Scheme 3



The stereoselective cyclization of the 1,5-biradicals **17b** is attributed to repulsive interactions between the aryl groups. We suggest that the sterically less congested *anti* conformer α of both *E*- and *Z*-**17b** is favored over the more congested *syn* conformer β. Moreover, cyclization of the α conformers generates a pseudoequatorial orientation of the phenyl group in the incipient indan, in contrast to the pseudoaxial orientation resulting from ring closure of the β conformers. As shown in Scheme 4, *Z*-**17b**α leads eventually to **3g** whereas *Z*-**17b**β affords **3h**, i.e., **3g** > **3h** for *Z*-**17b**. Conversely, *E*-**17b**α produces **3h** while **3g** originates from *E*-**17b**β, i.e., **3h** > **3g** for *E*-**17b**. Analogous diastereoselectivities were observed for 1,5-biradicals arising from ketone triplets by intramolecular hydrogen abstraction, although the substituents involved were sterically more distinct than H and D.[20]

Three factors influence the distribution of **3a-e**: (i) the kinetic deuterium isotope effect, k_H/k_D = (**3a** + **3b**) : (**3c** + **3d** + **3e**) = 3.2, (ii) the ratio of retention to inversion at C-2, and (iii) the stereoselectivity of deuterium transfer, i.e. the ratio of *cis*-1-D to *trans*-1-D resulting from insertion into a β-C-D bond. The latter number, 9.0, was obtained by photolysis of the monodeuterated precursor **7b** (see below). Two mechanistic extremes can be envisioned: (i) C-H (C-D) insertion with complete retention of configuration (**3a** = **3c** = 0; **3d** = 9 x **3e**), and (ii) stereorandom reaction at C-2 (**3a** = **3b**; **3e** = **3c** + **3d**; **3d** = 9 x **3c**). For each case, the expected distribution of deuterium is readily calculated (Table 2). The experimental result is very close to that estimated for the stereorandom process. The deviation is in the order of experimental error and corresponds to 10-12% retention.

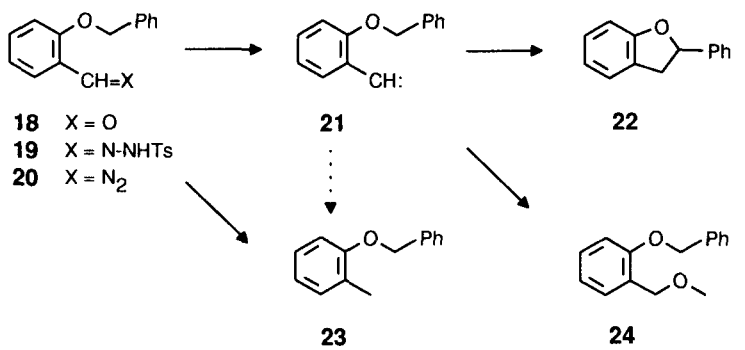
Table 2. Distribution of Deuterium in 2-Phenylindan Obtained from **7a**

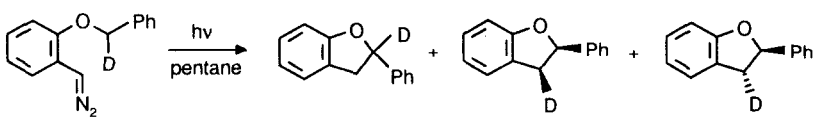
	cis-1-D	*trans*-1-D	2-D
calcd. for retentive insertion	23	39	38
calcd. for stereorandom insertion	36	26	38
observed	**35**	**27**	**38**

The stereorandom formation of **3** points to an abstraction-recombination mechanism involving the 1,5-biradicals **17** (Scheme 3). Some details of this process were elucidated by means of the deuterated precursors **7b** and **7c**. Selective yet complete monodeuteration of the β position was accomplished by the Wittig reaction of deuterobenzaldehyde with the phosphorus ylide derived from **15**. Hydrogenation of the alkene and formylation of **16** were followed by conversion of **4b** into the diazo compound **7b** by way of the tosylhydrazone **5b**. The isotopomeric diazo compound **7c** was obtained by way of H-D exchange when **5** was treated with NaOD-D_2O. Photolyses of **7b** and **7c** in pentane afforded deuterated 2-phenylindans (**3f-3h**) whose relative yields are recorded in Scheme 3. The carbene **8b** abstracts β-H and β-D competitively; k_H/k_D = **3f** : (**3g** + **3h**) = 4.6. The deuterium that is transferred to the carbenic site of **8b** prefers the *cis* orientation relative to phenyl, **3g** : **3h** = 9.0. On the other hand, the deuterium originally attached to the divalent carbon of **8c** is predominatly recovered *trans* to phenyl, **3g** : **3h** = 0.18.[18] The complementary distributions of deuterium obtained with **7b** and **7c** are clearly incompatible with 1,5-biradicals that rotate freely on both ends. Conformationally distinct species, *Z*-**17b** and *E*-**17b**, appear to be involved which, owing to the rotational barrier of benzyl radicals (~ 11 kcal/mol),[19] do not equilibrate prior to ring closure (Scheme 4). Selective formation of *Z*-**17b** from **8b**, and of *E*-**17b** from **8c**, is anticipated if hydrogen is tranferred in the plane of the benzene ring. In fact, the most reactive site of triplet arylcarbenes is the half-filled σ orbital, located in the plane of the arene.

the cyclization of ^{3}**21** (→ **22**) should proceed faster than that of ^{3}**8** (→ **3**). (ii) Owing to the resonance effect of the *ortho* oxygen, the *electrophilic* reactivity of ^{1}**21** toward π systems should be attenuated relative to that of ^{1}**8**. Supporting evidence comes from competitive reactions of 4-methoxyphenylcarbene with alkenes.[25] Both effects concur to favor the formation of **22** from **21**.

Scheme 5



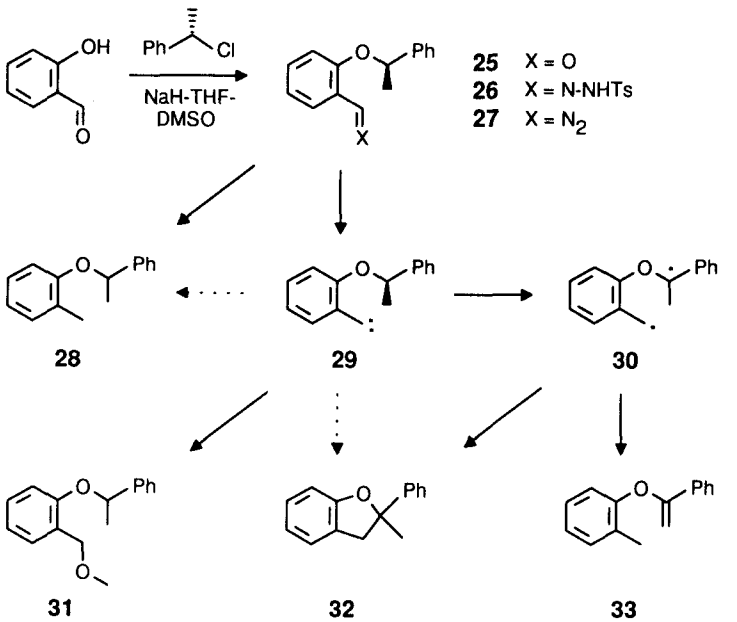


		22a	*Z*-22b	*E*-22b
20a	direct	*80*	13.4 (67)	6.6 (33)
	sens.	79	14.7 (70)	6.3 (30)
20b	direct		34	66
	sens.		31	69

2-(1-Phenylethoxy)phenylcarbene (29)

The stereochemistry of the formal insertion reaction **21** → **22** was not clarified. Although **20a** is a chiral precursor, our attempts to analyze the enantiomers of **22a** by means of nonracemic NMR shift reagents failed. Therefore, we resorted to the carbene **29**. Alkylation of salicylaldehyde with (*S*)-1-chloro-1-phenylethane (82 % *ee*) afforded (*R*)-**25** (67 % *ee*) with some loss of enantiomeric purity, owing to facile ionization of the chloride (Scheme 6). The nonracemic diazo compound **27** was obtained from **25** by way of the tosylhydrazone **26**. Photolysis and thermolysis of **27** gave the dihydrobenzofuran **32** with complete racemization (± 2 %). Hydrogen abstraction leading to the intermediate biradical **30** accounts for the stereorandom „insertion" process.[26] The enantiomers of **25** and **32** were resolved by GC on a chiral stationary phase.[27]

Scheme 6



Product studies were performed with racemic **26** and **27** (Table 4). The enol ether **33**, arising by disproportionation (1,6-hydrogen transfer) from the biradical **30**, was identified by comparison with the product of an unequivocal synthesis (see Experimental). In methanol, the yields of ether **31** from **29** are somewhat lower than those of **24** from **21** (Table 3). Ether formation from ^{1}**29** must compete against the intramolecular abstraction of hydrogen by ^{3}**29** which proceeds more readily than the analogous reaction of ^{3}**21** (tertiary vs. secondary C-H). Intramolecular insertion of **29** into primary C-H bonds of the methyl group, leading to 3,4-dihydro-2-phenyl-2*H*-benzopyran,[28] was not observed.

Table 4. Product Distributions (%) Obtained from **26** and **27**

precursor, conditions	**25**	**28**	**31**	**32**	**33**
27, 300 °C, 0.1 mm	4	trace	-	76	20
27, pentane, hv	trace	-	-	77	23
27, pentane, hv, 0.2 M Ph_2CO[a]	7.6	-	-	88.6	3.8
26, 0.13 M NaOMe-MeOH, hv	-	4.7	82.8	4.7	0.8
26, 0.13 M NaOMe-MeOH, hv, 0.05 M Ph_2CO	-	5.5	62.4	28.6	4.1
26, 0.13 M NaOMe-MeOH, hv, 0.2 M Ph_2CO	-	6.6	48.9	36.5	8.1

[a] Under these conditions, **33** does not persist.

2-(Benzyldimethylsilyl)phenylcarbene (40)

Small and variable effects of silicon on the insertion of carbenes into neighboring C-H bonds have been reported. In the reaction of methylene with 1,1-dimethylsilacyclopentane, the α position is slightly preferred over the β position,[29] but the reverse holds for alkoxycarbonylcarbenes.[30] A silicon α effect was also observed for the copper-catalyzed decomposition of diazomethane in hexamethyldisilane.[31] In the present study, we explore silicon effects on the intramolecular reactivity of **40**. *Ortho* metalation directed by the α-amino alkoxide **34**[32] was used to prepare the aldehyde **35** from which the carbene precursors **36-38** were obtained (Scheme 7).

C-H bonds of the benzyl and methyl groups compete for the divalent carbon of **40**, giving rise to the silaindans **41** and **42**, respectively. As a rule, **41** predominates although **42** is statistically favored by a factor of 3 (Table 5). The smaller **41**: **42** ratio observed on thermolysis (300 °C) of **37** as compared with photolysis (benzene, 25 °C) of **38** conforms with expectation, but the apparent solvent effect of methanol is obscure. The formal insertion reaction, **40** → **41**, is subject to a large deuterium isotope effect (k_H/k_D = 5.1), similar to that of the carbon analog, **8** → **3** (k_H/k_D = 4.6). The data suggest that the abstraction-recombination mechanism applies to **40** as well as to **8**. However, the *E/Z* distribution of deuterium in **41b** is close to unity (Scheme 7), in contrast to the ratio of **3g** : **3h** (Scheme 3). The change is explicable in terms of Scheme 4, if we consider the consequences of replacing CH_2 with $SiMe_2$: (i) The phenyl-aryl repulsion in the β conformers decreases, due to the greater length of C-Si bonds (1.84-1.87 Å), as compared with C-C (1.53-1.54 Å); (ii) vicinal Ph-Me interactions destabilize the α conformers more than the β conformers. Both effects are thought to equalize or even invert the relative stabilities of α and β conformers.

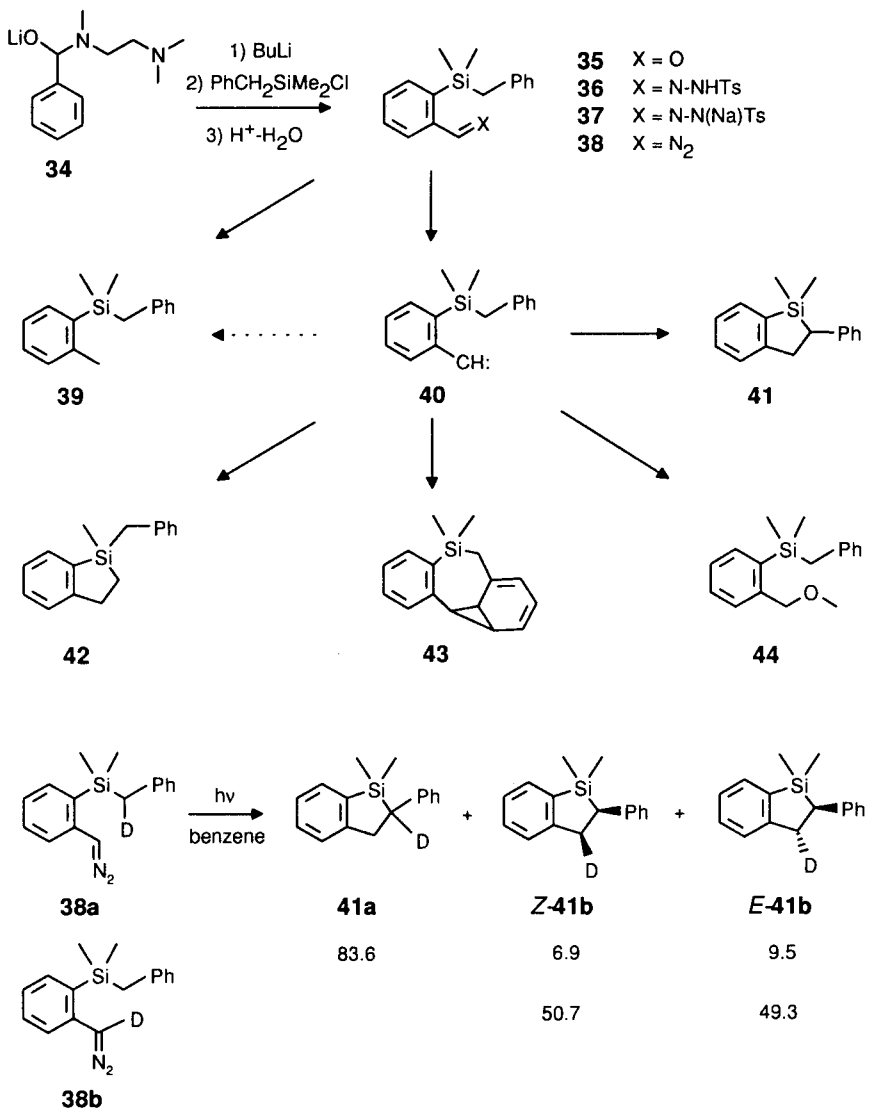
Table 5. Product Distributions (%) Obtained from **36-38**

precursor, conditions	**35**	**39**	**41**	**42**	**43**	**44**
37, 300 °C, 0.1 mm	1.8	0.6	27.6	13.6	56.4	-
38, benzene, hv	2.5	trace	52.5	7.4	37.2	-
38, benzene, hv, 0.46 M Ph_2CO	1.4	trace	66.5	7.5	24.6	-
36, 0.2 M NaOMe-MeOH, hv	0.6	5.5	3.7	4.5	19.1	66.6
36, 0.2 M NaOMe-MeOH, hv, 0.46 M Ph_2CO	0.7	63.8	8.3	3.0	2.6	21.6

The carbenes **3** and **40** also differ in their reactions with the terminal phenyl group. Addition of **3** to the 1'-2' bond leads eventually to the cycloheptatriene **10** (Scheme 1). The analogous product obtained from **40** is clearly a norcaradiene - its ^1H NMR spectrum shows 3 aliphatic protons, in addition to CH_2, and 3 vinylic protons. The spectrum, as well as the stablility of the norcaradiene, indicates addition of **40** to the 2'-3' bond of the terminal phenyl group, with formation of **43**. Valence isomerization of **43** would produce a highly strained bridgehead alkene. Comparison with the isomeric carbene **66** (see below) suggests that the deviating regioselectivity of **3** and **40** should not

be attributed to the relative length of C-C and C-Si bonds. Rather a substituent effect appears to operate. The R_3SiCH_2 group is a potent donor which supplies electrons to the *m*- as well as to the *o*- and *p*-positions (σ_m = -0.16, σ_p = -0.21).[32] Benzyltrimethylsilane, $PhCH_2SiMe_3$, stands out among monosubstituted benzenes in that the chemical shifts of the *o*- and *m*-carbons are the same (δ 127.9).[33] The electron-rich phenyl group of **40** also accounts for the enhanced yield of **43** (Table 5), as compared with that of **10** from **3** (Table 1).

Scheme 7



2-(Phenoxymethyl)phenylcarbene (52)

Formylation of 1-bromo-2-(phenoxymethyl)benzene (**45**)[34] afforded the aldehyde **46** as a source for the carbene precursors **47-49** (Scheme 8). The carbene **52** lacks the β-CH_2 group which was the preferred site of intramolecular attack for **8**, **21**, and **40**. Instead, **52** features a β oxygen which invites formation of an ylide[11] and enhances the nucleophilicity of the terminal phenyl group. Intramolecular addition, leading to **53** and H-shift isomers, predominates in the thermolysis of **48** and makes a major contribution to the photolysis of **49** in benzene (Table 6). 6,11-Dihydrodibenz[*b*,*e*]oxepin (**51**), formally arising by insertion into *o*-C-H bonds, was observed as a minor component in the pyrolysis of **48** but was not detected among the photolysis products of **49**. This result stands in contrast to the formation of **11** from **8** (Table 1); a thermal rearrangement of **53** to give **51** cannot be excluded.

Scheme 8

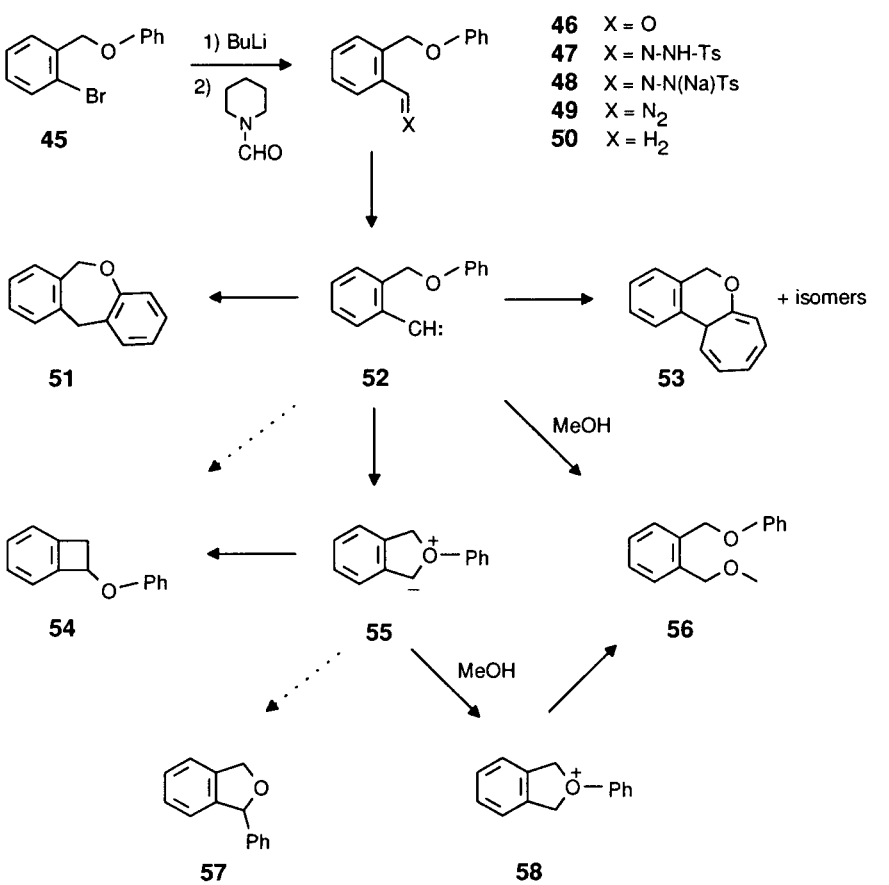
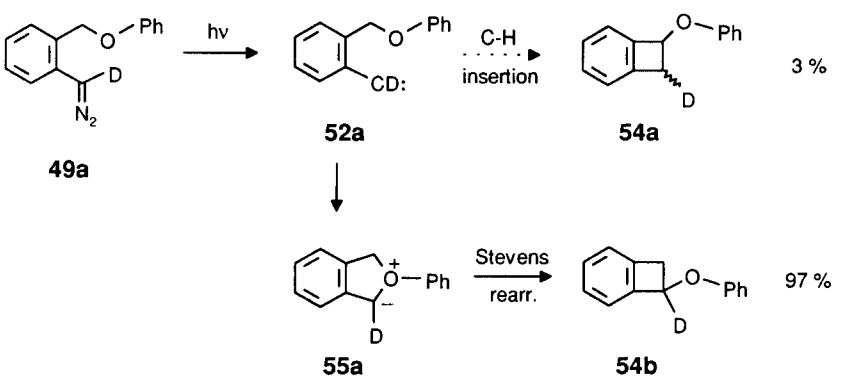


Table 6. Product Distributions (%) Obtained from **47-49**

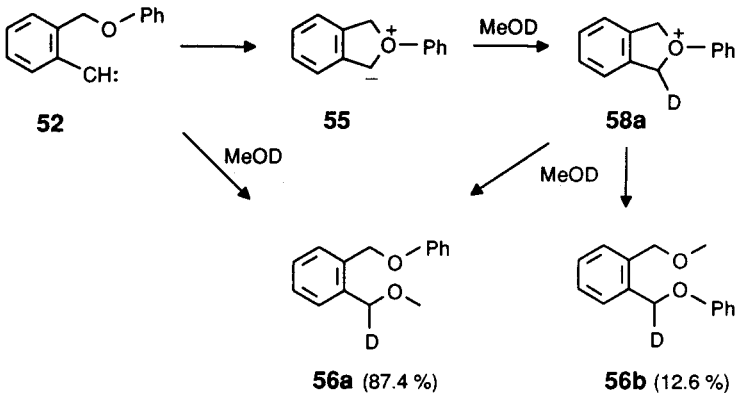
precursor, conditions	**46**	**50**	**51**	**53**	**54**	**56**	**57**
48, 300 °C, 0.1 mm	trace	trace	4.0	86.5	6.2	-	3.3
49, benzene, hv	8.4	0.9	-	38.6	52.1	-	trace
49, benzene, hv, 0.46 M Ph_2CO	19.7	trace	-	59.2	21.1	-	trace
47, 0.2 M NaOMe-MeOH, hv	4.5	2.7	-	1.7	0.4	90.7	trace
47, 0.2 M NaOMe-MeOH, hv, 0.46 M Ph_2CO	trace	64.3	-	trace	trace	35.7	trace

The formation of **54** as a major product in photolyses of **49** might suggest that insertion into α-C-H bonds prevails with **52** (Table 6). However, photolysis of the deuterated diazo compound **49a** reveals that **54** arises almost completely by insertion into the O-CH_2 bond, i.e., by Stevens rearrangement of the ylide **55**. Phenyl migration occurs to a very minor extent although the resulting product **57** is less strained than **54**. The observed migratory aptitudes are in accordance with the radical pair mechanism of the Stevens rearrangement.[35] When **52** is generated at 300 °C, the intervening **55** appears to be less discriminant (**54** : **57** ≅ 2). The results of the pyrolysis could be blurred by partial decomposition of **54** even though additional products were not detected. Alkoxybenzocyclobutenes have been reported to rearrange under similar conditions.[11,36]



49a **52a** **54a** **55a** **54b**

Generation of the ylide **55** competes with capture of the carbene **52** by methanol. When **47** was photolyzed in MeOD-NaOMe, deuterium was incorporated into both α-CH_2 groups of the resulting ether, **56a** : **56b** = 87.4 : 12.6. Obviously, ca. 25% of **56** arise by way of the ylide **55** and oxonium ion **58a**, the latter undergoing nucleophilc displacement by methanol to give **56a,b**. Aside from a small secondary isotope effect, the benzyl positions of **58a** are equivalent.



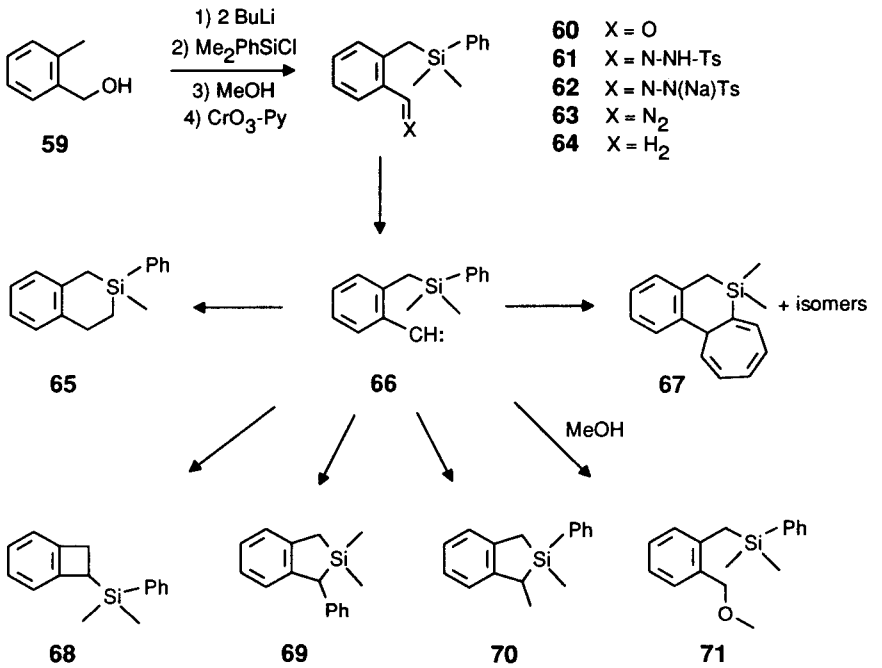
2-(Dimethylphenylsilylmethyl)phenylcarbene (66)

2-Methylbenzyl alcohol (**59**) was bis-metalated and then bis-silylated as described,[37] using $Me_2PhSiCl$ rather than Me_3SiCl. Hydrolysis of the silyl ether was followed by oxidation to give the aldehyde **60**[38] from which the carbene precursors **61-63** were prepared (Scheme 9). Insertion into C-H bonds of the methyl groups (→ **65**) and addition to the phenyl ring (→ **67**) are major reactions of the carbene **66** (Table 7). As was observed for the carbon analog **8**, the addition of **66** proceeds to the 1'-2' bond of the phenyl group, with eventual formation of a cycloheptatriene. It appears that the relative length of C-Si and C-C bonds does not influence the attack of these carbenes on remote arenes. The exceptional regioselectivity of the isomeric carbene **40** (see above) should, therefore, be attributed to a substituent effect. As compared with Me_3SiCH_2, Me_3Si is a poor electron donor (σ_m = -0.04, σ_p = -0.07)[32] which discriminates strongly between the *o*- (δ 133.3) and *m*-positions (δ 127.8) of Me_3SiPh.[39]

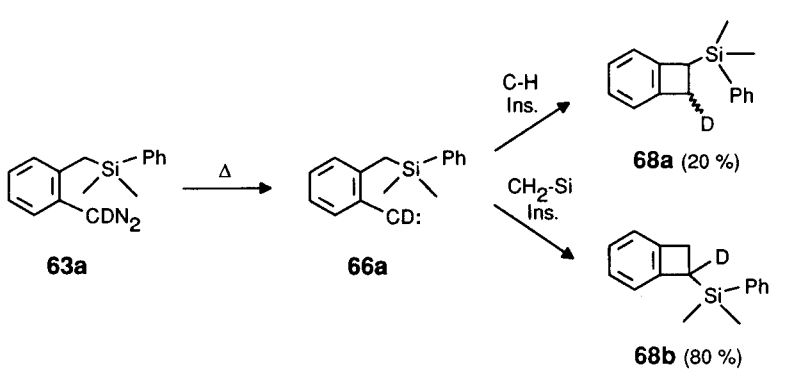
Table 7. Product Distributions (%) Obtained from **61-63**

precursor, conditions	**64**	**65**	**67**	**68**	**69**	**70**	**71**
62, 300 °C, 0.1 mm	0.3	20.7	31.6	19.8	22.5	5.1	-
63, benzene, hv	0.2	30.8	46.5	6.4	10.8	5.3	-
63, benzene, hv, 0.46 M Ph_2CO	2.0	29.0	55.4	2.0	7.4	4.2	-
61, 0.2 M NaOMe-MeOH, hv	4.4	1.1	1.9	3.0	0.1	0.6	88.9
61, 0.2 M NaOMe-MeOH, hv, 0.46 M Ph_2CO	19.6	2.6	trace	0.5	trace	trace	77.2

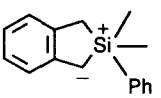
Scheme 9



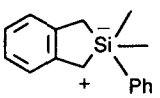
The most remarkable feature of of **66** is insertion into *all* carbon-silicon bonds.[40] Whereas the structures of **69** and **70** leave no doubt as to their mode of formation, **68** can (and does, in part) arise by C-H insertion. Thermolysis of the deuterated precursor **63a** revealed, however, that ca. 80% of **68** originates by insertion into the Si-CH_2- bond.



A contrast similar to that of **66** and **8** was observed for phenylcarbenes with CH_2SiMe_3[40] and $CH_2C(CH_3)_3$[41] side chains in the *ortho* position. The former species undergoes C-H and C-Si insertion reactions competitively whereas the latter shows C-H insertion only. On the other hand, no C-Si insertion was found with **40** where intramolecular attack *at silicon* is unlikely. The question arises whether intermediates are involved in the C-Si insertion reactions of **66**. Pentacovalent silicon can accomodate a positive charge (**72a**) as well as an extra electron pair (**72b**).



72a



72b

According to a recent report, complexes of the general type $R_{3-n}H_nSi(S)_2^+$ can only be found with $n \geq 1$[42] whereas ample precedent for pentaorganosilicates exists.[43] Moreover, the apparent migratory aptitudes, Ph > $PhCH_2$ > Me, are inconsistent with Stevens-type rearrangements of **72a** but conform with 1,2-shifts to the cationic center of **72b**. On the basis of the available data, we prefer **72b** to **72a**. However, **72** has not been intercepted, in contrast to the oxygen ylide **55**. Therefore, the intermediacy of species such as **72** remains speculative.

SUMMARY AND CONCLUSION

Phenylcarbenes insert into the β-C-H bonds of -X-CH_2Ph side chains attached to the *ortho* position (**8**, X = CH_2; **21**, X = O; **40**, X = $SiMe_2$). Stereorandom formation of five-membered rings and large kinetic deuterium isotope effects point to a triplet abstraction-recombination mechanism. Deuterated precursors (-X-CHD-Ph and -CDN_2) lead to *E/Z* distributions of the label which indicate that the intervening 1,5-biradicals rotate freely about the X-C bond. However, the intermediates are conformationally distinct with regard to the benzyl radical that originates from the carbene carbon. α-C-H insertion plays a minor role even with -CH_2-X-Ph substituted phenylcarbenes (**52**, X = O; **66**, X = $SiMe_2$). The carbene **52** inserts selectively into the $ArCH_2$-O bond whereas **66** discriminates moderately between the various C-Si bonds (Ph > $ArCH_2$ > Me). The intermediacy of ylides was confirmed by trapping experiments for X = O but remains speculative for X = $SiMe_2$.

The carbenes **8**, **52**, and **66** add to the 1'-2' bond of the terminal phenyl group with formation of a cycloheptatriene. In contrast, **40** adds to the 2'-3' bond to give a norcaradiene. This anomaly is attributed to the unique electron donating effect of R_3SiCH_2 substituents. Efficient trapping of the carbenes by methanol affords the appropriate ethers. Benzophenone-sensitization exerts a rather small effect on product distributions, enhancing (triplet) C-H "insertion" at the expense of (singlet) O-H insertion. We conclude that even the intramolecular reactions of functionalized arylcarbenes proceed, at best, competitively with spin inversion.

EXPERIMENTAL

General. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were obtained at 80 (Bruker WP 80) and 400 MHz (Bruker AM-400). ^{2}H (61.42 MHz) and ^{13}C (100.61 MHz) NMR spectra were recorded on the Bruker AM-400 spectrometer. Chemical shifts are reported in δ (ppm) relative to tetramethylsilane unless otherwise indicated. Mass spectra (70 eV) were obtained on a Varian MAT CH5 instrument. IR spectra were recorded on a Perkin-Elmer 257 spectrometer. Gas chromatography (GC) was performed by the use of a Siemens Sichromat equipped with glass capillary columns (conditions for the individual mixtures are given below). Varian Aerograph instruments equipped with packed glass columns were used for preparative gas chromatography (PGC). High-pressure liquid chromatography was performed with LDC (Milton Roy) chromatographs and refractometric detection.

Preparation of Tosylhydrazone Sodium Salts. To a solution of the tosylhydrazone (1 mmol) in 5 ml of anhydrous THF was added 1 mmol of sodium hydride (as a suspension in mineral oil). The mixture was stirred for 30 min at room temperature, *n*-pentane (40-50 ml) was added, and stirring was continued for 30 min. The precipitated sodium salt was filtered with suction, washed with *n*-pentane, and dried in *vacuo*. If the sodium salt failed to crystallize, the solvent was removed in *vacuo*, and the residue was triturated with *n*-pentane in an ultrasound bath. Moisture and light should be excluded during these procedures.

Preparation of Diazo Compounds.[14] To a solution of the tosylhydrazone (5 mmol) in 1,4-dioxane (30 ml) was added 5 ml of 50% aqueous sodium hydroxide. The mixture was stirred in the dark at 80 °C for 30 min, diluted with water, and extracted with *n*-pentane. The extracts were dried ($MgSO_4$) and concentrated in *vacuo* to give 60-70% of the diazo compound. Partial deuteration (Ar-CDN_2) was achieved when NaOD-D_2O was employed in this procedure.

Generation of Carbenes. The apparatus used for the flash vacuum pyrolysis of tosylhydrazone sodium salts has been described elsewhere.[44] Photolyses of diazo compounds in aprotic solvents and of of tosylhydrazones in MeOH-NaOMe were performed under nitrogen in pyrex vessels with a water-cooled medium-pressure mercury arc (150 W).

2-(2-Phenylethyl)benzaldehyde Tosylhydrazone (5). Reduction of 2-(2-phenylethyl)benzoic acid[12] with $LiAlH_4$ afforded 2-(2-phenylethyl)benzyl alcohol[45] (96%, m.p. 56 °C) which was oxidized with CrO_3-pyridine-HOAc[46] to give 97% of crude 2-(2-phenylethyl)benzaldehyde (**4**).[13] A solution of **4** (2.1 g, 10 mmol) in methanol (5 ml) was added to a hot concentrated solution of *p*-toluenesulfonylhydrazine (1.86 g, 10 mmol) in methanol. After having been heated at reflux for 30 min, the mixture was allowed to cool to room temp. overnight. The precipitate was filtered off and recrystallized from methanol to give 2.48 g (66%) of **5**; m.p. 136-137 °C; IR (KBr): 3190, 3060 (NH), 1325, 1160 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.4 (s, 3 H), 2.7-3.2 (m, 4 H), 7.0-7.9 (m, 14 H). Anal. Calcd for $C_{22}H_{22}N_2O_2S$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.80; H, 5.88; N, 7.47.

For the preparation of **5a** (= *cis*-α,β-d_2-**5**), *trans*-stilbene-2-carboxylic acid (**12**)[17] was reduced with $LiAlH_4$ to give 2-(*trans*-2-phenylethenyl)benzyl alcohol[17] (89%, m.p. 97-98 °C). A flask was charged with the alcohol (1.56 g, 7 mmol), potassium azodicarboxylate (94 g, 0.48 mol), and MeOD (95 ml). While nitrogen was passed through the mixture, AcOD (41 ml) was added slowly with stirring. After 2 h, water (60 ml) and ether (60 ml) were added. The organic phase was washed with an aqueous solution of $NaHCO_3$, and the aqueous phase was extracted with ether. The combined ether solutions were dried ($MgSO_4$) and

concentrated in *vacuo*. The residue was purified by HPLC to give 1.15 g (72%) of **13**, ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 1 H), 2.95 (m, 2 H), 4.6 (s, 2 H), 7.1-7.5 (m, 9 H). Following the methods used for the preparation of **5**, **13** was converted into **5a**, m.p. 136-137 °C, ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 3 H), 2.75 (d, J = 6 Hz, 1 H), 3.0 (d, J = 6 Hz, 1 H), 7.0-8.0 (m, 14 H).

The synthesis of **5b** (= β-d-**5**) started with 2-bromobenzyltriphenylphosphonium bromide (**15**) which was condensed with PhCDO in 86% yield according to the procedure reported for PhCHO.[47] To a solution of the resulting 2-bromostilbene (8.7 g, 33 mmol, *cis*:*trans* = 64:36) in ethyl acetate (200 ml) was added Pd-C (10%, 200 mg). The mixture was hydrogenated for 6 h at ambient temperature and pressure to give 7.4 g (86%) of 2-d-1-(2-bromophenyl)-2-phenylethane (**16**). Reported methods[48] were adapted to the formylation of **16**: To a mixture of **16** (7.34 g, 28 mmol), anhydrous THF (50 ml), and TMEDA (9.78 g = 12.7 ml, 84 mmol) cooled to -78 °C under nitrogen was added dropwise *n*-butyl lithium (1.6 M in hexane, 53 ml, 85 mmol). After the resulting solution was stirred for 1 h at -78 °C and for 1 h at 0 °C, N-formylpiperidine (19.1 g, 0.17 mol) was added and stirring was continued for 30 min. The reaction mixture was then acidified (pH 2-3) with 2 N HCl and extracted with ether. The combined extracts were washed with water and saturated $NaHCO_3$, dried (Na_2SO_4), and concentrated in *vacuo*. The residue was distilled at 100-120 °C (0.002 Torr), and the distillate was purified by HPLC (Si 60-5, hexane-ether, 7:3) to give 2.73 g (46%) of **4b**; ^{1}H NMR ($CDCl_3$): δ 2.9 (tm, J = 8 Hz, 1 H), 3.3 (d, J = 8 Hz, 1 H), 7.2-7.3 (m, 6 H), 7.42 (td, J = 7.5 and 1.5 Hz, 1 H), 7.50 (td, J = 7.5 and 1.5 Hz, 1 H), 7.82 (dd, J = 7.5 and 1.5 Hz, 1 H), 10.2 (s, 1 H); ^{2}H NMR ($CHCl_3$): δ 2.9. As described for **4**, **4b** afforded the tosylhydrazone **5b** in 71% yield; ^{1}H NMR ($CDCl_3$): δ 2.47 (s, 3 H), 2.75 (tm, J = 8 Hz, 1 H), 2.98 (d, J = 8 Hz, 1 H), 7.0-7.3 (m, 10 H), 7.7 (dd, J = 8 and 1.5 Hz, 1 H), 7.8-7.9 (m, 2 H), 7.92 (s, 1 H).

Reaction Products of 2-(2-Phenylethyl)phenylcarbene (8). The product mixtures obtained from **5**, **6**, and **7** were analyzed by GC (18 m OV1, 170 °C) (Table 1). The minor products 1-methyl-2-(2-phenylethyl)-benzene (**1**),[49] 7-(phenylmethyl)bicyclo[4.2.0]octa-1,3,5-triene (**2**),[50] and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (**11**)[51] were identified by comparison with authentic samples. HPLC (Si 60-5-NO_2, hexane) of the photolysis mixtures obtained from **5** and **7** afforded the major products **3**, **9**, and **10**. 5*H*-Cyclohepta-6,11a-dihydro[*a*]naphthalene (**10**): ^{1}H NMR ($CDCl_3$): δ 2.4 (t, J = 6.5 Hz, 2 H), 2.65 (t, J = 6.5 Hz, 2 H), 2.9 (d, J = 5.5 Hz, 1 H), 5.15 (dd, J = 9 and 5.5 Hz, 1 H), 6.05 (m, 1 H), 6.15 (m, 1 H), 6.6 (m, 2 H), 7.0-7.25 (m, 4 H). 1-(Methoxymethyl)-2-(2-phenylethyl)benzene (**9**): ^{1}H NMR ($CDCl_3$): δ 2.9-3.1 (m, 4 H), 3.5 (s, 3 H), 4.55 (s, 2 H), 7.2-7.6 (m, 9 H). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.91; H, 8.19. 2-Phenylindan (**3**)[52]: ^{1}H NMR ($CDCl_3$): δ 3.1 (dd, J = 15.5 and 8.5 Hz, 2 H), 3.4 (dd, J = 15.5 and 8.5 Hz, 2 H), 3.7 (q, J = 8.5 Hz, 1 H), 7.2-7.4 (m, 9 H); ^{13}C NMR ($CDCl_3$): δ 40.9 (CH_2), 45.5 (CH), 124.3 (CH), 126.1 (CH), 126.4 (CH), 127.0 (CH), 128.4 (CH), 142.9 (C), 145.5 (C). A solution of 2-phenylindene[53] (100 mg, 0.52 mmol) in ethyl acetate (20 ml) was treated with Pd-C (10%, 200 mg) and D_2 (3 atm.) for 1 h to give **3b**, ^{2}H NMR ($CHCl_3$): δ 3.4 (*E*-1-D) and 3.7 (2-D).

2-Benzyloxybenzaldehyde Tosylhydrazone (19). The reaction of 2-benzyloxybenzaldehyde (**18**)[21] (m.p. 46-47 °C, 20.0 g, 94.2 mmol) with *p*-toluenesulfonylhydrazine (17.5 g, 93.8 mmol) in methanol (100 ml), as decribed for **5**, afforded 33.4 g (93%) of **19**; m.p. 120 °C; ^{1}H NMR (CD_3SOCD_3): δ 2.45 (s, 3 H), 5.25 (s, 2 H), 7.2-8.0 (m, 13 H), 8.50 (s, 1 H), 11.55 (s, 1 H). Anal. Calcd for $C_{21}H_{20}N_2O_3S$: C, 66.30; H, 5.30; N, 7.36. Found: C, 66.30; H 5.29; N, 7.31. For deuteration of the side chain, α-d-benzyl chloride[54] was used in the benzylation of salicylaldehyde, followed by conversion of **18a** into **19a** (= β-d-**19**) and **20a**.

Reaction Products of 2-Benzyloxyphenylcarbene (21). The product mixtures obtained from **19** and **20** were analyzed by GC (8 m Carbowax, 180 °C, and 18 m OV17, 170 °C) (Table 3). 1-Benzyloxy-2-methylbenzene (**23**) was prepared for comparison by benzylation of *o*-cresol,[55] ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 3 H), 5.10 (s, 2 H), 6.8-7.6 (m, 9 H). Photolysis of **19** in MeOH-NaOMe as well as methylation (NaH-MeI, THF, reflux, 16 h) of 2-benzyloxybenzyl alcohol[56] afforded 1-benzyloxy-2-methoxymethylbenzene (**24**) b.p. 118 °C (0.2 Torr); ^{1}H NMR ($CDCl_3$): δ 3.4 (s, 3 H), 4.6 (s, 2 H), 5.1 (s, 2 H), 6.8-7.5 (m, 9 H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.98; H, 7.18. The photolysis mixture obtained from **20** (pentane, pyrex) was purified by HPLC (Si 60-5-NO_2, hexane) to give 2,3-dihydro-2-phenylbenzofuran (**22**),[57] ^{1}H NMR ($CDCl_3$): δ 3.2 (dd, J = 16 and 8 Hz, 1 H), 3.8 (dd, J = 16 and 9 Hz, 1 H), 5.8 (dd, J = 9 and 8 Hz, 1 H), 6.8-7.6 (m, 9 H). A solution of 2-phenylbenzofuran[58] (100 mg, 0.52 mmol) in ethyl acetate (20 ml) was treated with Pd-C (10%, 200 mg) and D_2 (3 atm.) for 1 h to give *cis*-2,3-d-**22**, ^{2}H NMR ($CHCl_3$): δ 3.8 and 5.8. Thus the signal of **22** at δ 3.2 is assigned to *Z*-3-H and the signal at δ 3.8 to *E*-3-H.

2-(1-Phenylethoxy)benzaldehyde Tosylhydrazone (26). To a solution of salicylaldehyde (13.03 g, 107 mmol) in anhydrous THF (250 ml) was added in portions with stirring sodium hydride (60% dispersion in mineral oil, 5.12 g, 107 mmol). After the evolution of hydrogen had ceased, the THF was removed in *vacuo*, the residue was dissolved in anhydrous DMSO (150 ml), and a solution of 1-chloro-1-phenylethane (13.81 g, 98.2 mmol) in DMSO (10 ml) was added. The mixture was stirred under nitrogen at 100 °C for 17 h and was then diluted with *n*-pentane (100 ml) and water (100 ml). The phases were separated and the aqueous phase was extracted with *n*-pentane (2 x 100 ml). The combined pentane solutions were washed with water (200 ml), dried (K_2CO_3), and concentrated in *vacuo*. The residue was distilled in *vacuo* to give 15.5 g (70%) of 2-(1-phenylethoxy)benzaldehyde (**25**), b.p. 135-136 °C (0.07 Torr); IR (film): 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 1.75 (d, J = 6.5 Hz, 3 H), 5.45 (q, J = 6.5 Hz, 1 H), 6.8-7.7 (m, 8 H), 7.85 (br d, J = 8 Hz, 1 H), 10.70 (s, 1 H). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.63; H, 6.24. Found: C, 79.55; H, 6.35.

When performed with (*S*)(-)-1-chloro-1-phenylethane[59] (α_D^{25} = -83.2°, 81.8 % *ee*), the same procedure afforded (*R*)(+)-**25** (63%, α_D^{25} = 31.0°, 67 % *ee*). The *ee* of these compounds was estimated by GC on a 30 m capillary column coated with heptakis-(3-*O*-acetyl-2,6-di-*O*-methyl)-β-cyclodextrin (18% in OV 1701) at 70 °C and 140 °C, respectively.

The reaction of **25** (1.85 g, 8.2 mmol) with *p*-toluenesulfonylhydrazine (1.60 g, 8.6 mmol) in methanol (20 ml), as described for **5**, gave 2.16 g (67%) of **26**, m.p. 144-145 °C; ^{1}H NMR ($CDCl_3$): δ 1.65 (d, J = 6.5 Hz, 3 H), 2.45 (s, 3 H), 5.30 (q, J = 6.5 Hz, 1 H), 6.6-7.5 (m, 10 H), 7.7-8.1 (m, 3 H), 8.35 (s, 1 H). Anal. Calcd for $C_{22}H_{22}N_2O_3S$: C, 66.98; H, 5.62; N, 7.10. Found: C, 67.14; H, 5.68; N, 7.13.

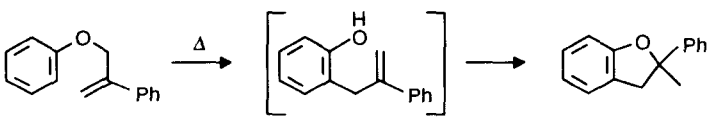
Reaction Products of 2-(1-Phenylethoxy)phenylcarbene (29). The product mixtures obtained from **26** and **27** were analyzed by GC (20 m OV 17, 200 °C, and 8 m Carbowax, 160 °C) (Table 4) and separated by HPLC (Si 60-5, hexane-ether, 99:1). The structural assignments were confirmed by syntheses (see below). 3,4-Dihydro-2-phenyl-2*H*-benzopyran,[28] the product arising by insertion into C-H bonds of the side-chain methyl group, was not detected in significant amounts. Product mixtures from the photolysis and thermolysis of nonracemic **27** were subjected to GC on OV 17, and the peak of **32** was transferred to the cyclodextrin column (see above) where the enantiomers were separated (110.7 and 111.9 min at 140 °C). In each case, **32** was found to be racemic (± 2%).

Alkylation of 2-methylphenol (4.46 g, 41.2 mmol) with 1-chloro-1-phenylethane (5.79 g, 41.2 mmol), according to the procedure given for **25**, afforded 6.05 g (69%) of 1-methyl-2-(1-phenylethoxy)benzene

(**28**), b.p. 96 °C (0.3 Torr); ^{1}H NMR ($CDCl_3$): δ 1.7 (d, J = 7 Hz, 3 H), 2.4 (s, 3 H), 5.4 (q, J = 7 Hz, 1 H), 6.6-7.6 (m, 9 H). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.92; H, 7.68.

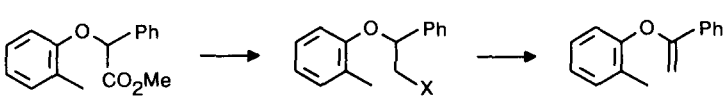
Reduction of **25** (1.0 g, 4.4 mmol) with $LiAlH_4$ (0.38 g, 10 mmol) in ether (40 ml) gave 0.95 g (94%) of 2-(1-phenylethoxy)benzyl alcohol; ^{1}H NMR ($CDCl_3$): δ 1.7 (d, J = 7 Hz, 3 H), 2.7 (s, 1 H), 4.8 (s, 2 H), 5.4 (q, J = 7 Hz, 1 H), 6.7-7.6 (m, 9 H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.85; H, 7.12. To a solution of the alcohol (0.75g, 3.3 mmol) in THF (9 ml) was added sodium hydride (60% dispersion in mineral oil, 0.13 g, 33 mmol). After the evolution of hydrogen had ceased, methyl iodide (0.94 g, 6.6 mmol) was added, and the mixture was heated at reflux for 16 h. Water was added, the phases were separated, and the aqueous phase was extracted with ether (3 x 5 ml). The combined organic phases were washed with brine, dried (K_2CO_3), and concentrated in *vacuo* to give 0.68 g (88%) of 1-methoxymethyl-2-(1-phenylethoxy)benzene (**31**); ^{1}H NMR ($CDCl_3$): δ 1.65 (d, J = 6.5 Hz, 3 H), 3.45 (s, 3 H), 4.6 (s, 2 H), 5.3 (q, J = 6.5 Hz, 1 H), 6.6-7.5 (m, 9 H). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H. 7.49. Found: C, 79.25; H, 7.52.

Alkylation of sodium phenoxide with 3-bromo-2-phenylpropene afforded 3-phenoxy-2-phenylpropene (**73**).[60] When **73** was heated at 290 °C for 2 min, a sequence of Claisen rearrangement and cyclization produced 2,3-dihydro-2-methyl-2-phenylbenzofuran (**32**) (22%, purified by short-path distillation at 100-120 °C, 0.005 Torr). ^{1}H NMR ($CDCl_3$): δ 1.8 (s, 3 H), 3.4 (s, 2 H), 6.8-7.7 (m, 9 H). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.60; H, 6.70.



73 **32**

Using the same procedure for the synthesis of **25**, 2-methylphenol (10.5 g, 97 mmol) was treated with methyl α-chlorophenylacetate (8.9 g, 48 mmol) to give methyl (2-methylphenoxy)phenylacetate (**74**) (7.2 g, 58%); IR (film): 1770 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 2.4 (s, 3 H), 3.7 (s, 3 H), 5.7 (s, 1 H), 6.7-7.7 (m, 9 H). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.99; H, 6.31. Reduction of **74** (7.1 g, 28 mmol) with $LiAlH_4$ (1.05 g, 28 mmol) in ether afforded 5.4 g (85%) of 2-(2-methylphenoxy)-2-phenylethanol (**75**); ^{1}H NMR ($CDCl_3$): δ 1.8 (s, 1 H), 2.4 (s, 3 H), 3.9 (m, 2 H), 5.3 (t, J = 5 Hz, 1 H), 6.6-7.5 (m, 9 H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.88; H, 7.15. According to a standard procedure,[61] **75** (5.3 g, 23 mmol) reacted with *p*-toluenesulfonyl chloride (6.64 g, 35 mmol) and pyridine (3.67 g, 46 mmol) to give 6.5 g (74%) of the tosylate **76**; m.p. 83 °C; ^{1}H NMR ($CDCl_3$): δ 2.2 (s, 3 H), 2.4 (s, 3 H), 4.3 (m, 2 H), 5.3 (t, J = 5 Hz, 1 H), 6.4-7.8 (m, 13 H). Anal. Calcd for $C_{22}H_{22}O_4S$: C, 74.98; H, 5.80. Found: C, 74.99; H, 5.81. To a solution of KOH (0.37 g, 6.5 mmol) in triglyme (2 ml) was added with stirring at 100 °C **76** (1.0 g, 26 mmol). The temperature was slowly raised to 200 °C, and vacuum (0.5-1 Torr) was applied to tranfer volatiles to a cold trap. HPLC (Si 60-5, hexane-ether, 99:1) of the distillate gave 0.39 g (70%) of 1-methyl-2-(1-phenylethenyloxy)benzene (**33**); ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3 H), 4.0 (d, J = 2 Hz, 1 H), 4.8 (d, J = 2 Hz, 1 H), 6.9-7.8 (m, 9 H). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.66; H, 6.78.



74 **75** X = OH **76** X = OTs **33**

2-(Benzyldimethylsilyl)benzaldehyde Tosylhydrazone (36). To a solution of *N,N,N'*-trimethyl-1,2-diaminoethane[62] (2.0 ml, 15.6 mmol) in THF (40 ml) was added dropwise at -20 °C *n*-butyl lithium (1.6 M in hexane, 9.5 ml, 15.2 mmol). After the solution was stirred for 15 min, benzaldehyde (1.55 g, 14.6 mmol) was added and stirring was continued for 15 min. *n*-Butyl lithium (1.6 m in hexane, 27.5 ml, 44 mmol) was then added and the mixture was kept at -20 °C for 24 h. The temperature was then lowered to -42 °C, benzylchlorodimethylsilane[63] (16.2 g, 87.8 mmol) was added and the resulting solution was stirred overnight with gradual warming to room temperature. The mixture was partitioned between 10% HCl and ether. The ether extracts were washed with brine, dried ($MgSO_4$), and concentrated in *vacuo*. HPLC (Si 60-5, hexane-ether, 60:1) afforded 2.9 g (78%) of 2-(benzyldimethylsilyl)benzaldehyde (**35**); IR (film):1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 0.31 (s, 6 H), 2.46 (s, 2 H), 6.85-7.38 (m, 5 H), 7.47-7.66 (m, 3 H), 7.82-7.98 (m, 1 H), 10.07 (s, 1 H). In order to obtain a deuterated sample, α-d-benzyl chloride[54] was used in the preparation of benzylchlorodimethylsilane.

To a concentrated solution of *p*-toluenesulfonylhydrazine (2.1 g, 11.4 mmol) in methanol was added a solution of **35** (2.9 g, 11.4 mmol) in methanol (5 ml). The mixture was stirred under nitrogen at room temperature for 14 h. Even when the solvent was removed in *vacuo*, the tosylhydrazone did not crystallize and was, therefore, submitted to HPLC (Si 60-5-C_{18}, methanol-water, 80:20). The appropriate fraction of the eluate was evaporated to dryness and the residue was dissolved in ether. Slow addition of *n*-pentane to the dry ($MgSO_4$) ether solution precipitated 4.3 g (89%) of **36**; m.p. 102-103 °C; ^1H NMR ($CDCl_3$): δ 0.20 (s, 6 H), 2.20 (s, 2 H), 2.31 (s, 3 H), 6.7-7.1 (m, 5 H), 7.1-7.5 (m, 7 H), 7.70 (s, 1 H), 7.78 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{23}H_{26}N_2O_2SSi$: C, 66.35; H, 6.21; N, 6.63. Found: C, 66.43; H, 6.16; N, 6.74.

Reaction Products of 2-(Benzyldimethylsilyl)phenylcarbene (40). The product mixtures obtained from **36-38** were analyzed by GC (20 m OV 17, 180 °C) (Table 5). For comparison, a sample of **39** was prepared by the following procedure: To a solution of 2-methylphenyl lithium, prepared from 1-iodo-2-methylbenzene (1.0 g, 4.6 mmol) and lithium (64 mg, 9.2 mmol) in ether (10 ml), was added benzylchlorodimethylsilane (0.85 g, 4.6 mmol). The mixture was heated at reflux for 3 h and then partitioned between water and ether. The combined ether solutions were washed with aqueous $Na_2S_2O_3$ and water, dried ($MgSO_4$), and concentrated in *vacuo*. HPLC (Si 60-5-C_{18}, methanol-water, 80:20) of the residue afforded 0.84 g (76%) of 1-(benzyldimethylsilyl)-2-methylbenzene (**39**); ^1H NMR ($CDCl_3$): δ 0.31 (s, 6 H), 2.40 (s, 2 H), 2.46 (s, 3 H), 6.9-7.5 (m, 9 H). Anal. Calcd for $C_{16}H_{20}Si$: C, 79.92; H, 8.40. Found: C, 80.70; H, 8.38.

The product mixture obtained on pyrolysis of **37** was separated by HPLC (Si 60-5-NO_2, hexane) to give **41-43**. 1,1-Dimethyl-2-phenyl-1-silaindan (**41**): ^1H NMR ($CDCl_3$): δ -0.03 (s, 3 H), 0.39 (s, 3 H), 2.82 (dd, J = 8.3 and 7.6 Hz, 1 H), 3.37 (dd, J = 16.5 and 7.6 Hz, 1 H), 3.50 (dd, J = 16.5 and 8.3 Hz, 1 H), 7.03-7.4 (m, 8 H), 7.51 (d, J = 7.3 Hz, 1 H). **41a,b** from **38a**: ^2H NMR ($CHCl_3$): δ 2.80 (83.6%), 3.38 (9.5%), 3.52 (6.9%). **41b** from **38b**: ^2H NMR ($CHCl_3$): δ 3.38 (49.3%), 3.52 (50.7%). Anal. Calcd for $C_{16}H_{17}DSi$: C, 80.25; H, 8.01. Found: C, 80.30; H, 7.93. 1-Benzyl-1-methyl-1-silaindan (**42**): ^1H NMR ($CDCl_3$): δ 0.30 (s, 3 H), 0.87-1.14 (m, 2 H), 2.35 (s, 2 H), 2.82-3.11 (m, 2 H), 6.9-7.6 (m, 9 H). Anal. Calcd for $C_{16}H_{18}Si$: C, 80.59; H, 7.62. Found: C, 80.68; H, 7.74. 9,9-Dimethyl-9-silaquadricyclo[9.3.1.0.^{2,15}0^{3,8}]pentadeca-3,5,7,11,13-pentaene (**43**): ^1H NMR ($CDCl_3$): δ 0.29 (s, 3 H), 0.38 (s, 3 H), 1.72-1.84 (m, 3 H), 1.92 (td, J = 8.8 and 5.6 Hz, 1 H), 2.02 (t, J = 8.8 Hz, 1 H), 5.07 (d, J = 5.7 Hz, 1 H), 5.55 (dd, J = 9.5 and 5.7 Hz, 1 H), 5.67 (dd, J = 9.5 and 5.5 Hz, 1 H), 7.1-7.4 (m, 4 H). Anal. Calcd for $C_{16}H_{18}Si$: C, 80.59; H, 7.62. Found: C, 80.50; H, 7.68.

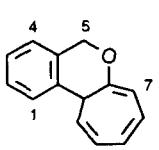
The product mixture obtained on photolysis of **36** in 0.2 M NaOMe-MeOH was separated by HPLC (Si 60-5-NO_2, pentane-ether, 30:1) to give 1-(benzyldimethylsilyl)-2-(methoxymethyl)benzene (**44**); ^1H NMR

($CDCl_3$): δ 0.29 (s, 6 H), 2.38 (s, 2 H), 3.39 (s, 3 H), 4.43 (s, 2 H), 6.85-7.55 (m, 9 H). Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.48; H, 8.22. Found: C, 75.50; H, 8.18.

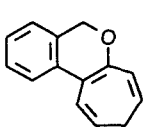
2-(Phenoxymethyl)benzaldehyde Tosylhydrazone (47). Reported methods[48] were adapted to the formylation of 1-bromo-2-(phenoxymethyl)benzene (**45**).[34] To **45** (8.42 g, 32 mmol) dissolved in THF (50 ml) and cooled to -78 °C under nitrogen was added *n*-butyllithium (1.6 M in hexane, 20 ml, 32 mmol). After the mixture was stirred for 30 min at -78 °C, N-formylpiperidine (3.98 g, 35.2 mmol) was added while keeping the internal temperature below -65 °C. The resulting solution was stirred for 6 h with gradual warming to room temperature. The mixture was then acidified (pH 2-3) and extracted with ether. The combined extracts were washed with NH_4Cl and NaCl solutions, dried ($MgSO_4$), and concentrated in *vacuo*. The residue was purified by HPLC (Si 60-5, hexane-ether, 1:1) to give 5.6 g (82%) of 2-(phenoxymethyl)benzaldehyde (**46**); IR (film): 1695 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 5.52 (s, 2 H), 6.8-7.8 (m, 8 H), 7.88 (dd, *J* = 6.5 and 2.4 Hz, 1 H), 10.20 (s, 1 H).

To a solution of **46** (5.0 g, 23.6 mmol) in methanol (5 ml) was added a concentrated solution of *p*-toluenesulfonylhydrazine (4.4 g, 23.6 mmol) in methanol. The mixture was stirred for 4 h at room temperature. The precipitate was filtered off and recrystallized from methanol to give 8.1 g (93%) of **47**; ^1H NMR ($CDCl_3$): δ 2.34 (s, 3 H), 5.15 (s, 2 H), 6.8-7.7 (m, 11 H), 7.86 (d, *J* = 8.4 Hz, 2 H), 8.00 (s, 1 H), 8.18 (br s, 1 H). Anal. Calcd for $C_{21}H_{20}N_2O_3S$: C, 66.28; H, 5.31; N, 7.36. Found: C, 66.39; H, 5.36; N, 7.42.

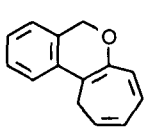
Reaction Products of 2-(Phenoxymethyl)phenylcarbene (52). The product distributions were estimated by GC (20 m OV 17, 180 °C, and 11.5 m OV 225, 190 °C) (Table 6). A mixture of **53** and isomers was isolated by HPLC (Si 60-5, hexane-ether, 30:1) from the pyrolysis products of **48**. Two components were separated by GC, and three components were indicated by ^1H NMR. Anal. Calcd for $C_{14}H_{12}O$: C, 85.67; H, 6.18. Found (mixture): C, 85.63; H, 6.25. 5,11a-Dihydrobenzo[*d*]cyclohepta[*b*]pyran (**53**, 42%): ^1H NMR ($CDCl_3$): δ 2.87 (d, *J* = 5.8 Hz, 1 H), 4.52 (d, *J* = 14.0 Hz, 1 H), 4.63 (d, *J* = 14.0 Hz, 1 H), 5.01 (dd, *J* = 9.0 and 5.8 Hz, 1 H), 5.20 (dd, *J* = 9.0 and 5.3 Hz, 1 H), 6.15 (d, *J* = 6.2 Hz, 1 H), 6.46 (dd, *J* = 11.0 and 5.3 Hz, 1 H), 6.52 (dd, *J* = 11.0 and 6.2 Hz, 1 H), 6.6-7.35 (m, 4 H). 5,9-Dihydrobenzo[*d*]cyclohepta[*b*]pyran (**53a**, 48%): ^1H NMR ($CDCl_3$): δ 2.21 (t, *J* = 7.0 Hz, 2 H), 4.79 (s, 2 H), 5.27 (dt, *J* = 9.5 and 7.0 Hz, 1 H), 5.38 (dt, *J* = 10.0 and 7.0 Hz, 1 H), 6.28 (d, *J* = 10.0 Hz, 1 H), 6.43 (d, *J* = 9.5 Hz, 1 H), 6.6-7.35 (m, 4 H). 5,11-Dihydrobenzo[*d*]cyclohepta[*b*]pyran (**53b**, 10%): ^1H NMR ($CDCl_3$): δ 2.55 (d, *J* = 7.0 Hz, 2 H), 4.55 (s, 2 H), 5.33 (dt, *J* = 9.0 and 7.0 Hz, 1 H), 6.20 (dd, *J* = 9.0 and 5.5 Hz, 1 H), 6.41 (dd, *J* = 11.3 and 5.5 Hz, 1 H), 7.09 (d, *J* = 11.3 Hz, 1 H), 6.6-7.35 (m, 4 H). Hydrogenation (10% Pd-C, ether) of the mixture gave a single product, 5,7,8,9,10,11,11a-octahydrobenzo[*d*]cyclohepta[*b*]pyran (**53c**), ^1H NMR ($CDCl_3$): δ 1.5-2.4 (m, 10 H), 2.58-2.83 (m, 1 H), 3.78-4.04 (m, 1 H), 4.78 (s, 2 H), 6.8-7.3 (m, 4 H).



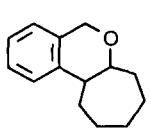
53



53a



53b



53c

The minor products 1-methyl-2-(phenoxymethyl)benzene (**50**)[64] and 1,3-dihydro-2-phenylisobenzofuran (**57**)[65] were identified by comparison with authentic samples. Reduction with $NaBH_4$ of 6,11-dihydrodibenz[*b,e*]oxepin-11-one[66] afforded 86% of 6,11-dihydrodibenz[*b,e*]oxepin-11-ol,[67] m.p. 89 °C, which was

hydrogenated (ether, 10% Pd-C, 2.5 bar, room temperature, 5 h). 6,11-Dihydrodibenz[*b,e*]oxepin (**51**) (10-15%) was separated from unreacted starting material (85-90%) by HPLC (Si 60-5, pentane-ether, 3:2 and pentane-ether, 30:1). ^{1}H NMR ($CDCl_3$) of **51**: δ 4.2 (s, 2 H), 5.2 (s, 2 H), 6.7-7.3 (m, 8 H). Cycloaddition of phenoxyethene[68] with benzyne,[69] generated as described for the synthesis of benzobarrelenes,[70] provided 6% of 7-phenoxybicyclo[4.2.0]octa-1,3,5-triene (**54**); ^{1}H NMR ($CDCl_3$): δ 3.18 (dd, J = 14.0 and 2.0 Hz, 1 H), 3.32 (dd, J = 14.0 and 4.2 Hz, 1 H), 5.40 (dd, J = 4.2 and 2.0 Hz, 1 H), 6.9-7.25 (m, 9 H). Anal. Calcd for $C_{14}H_{12}O$: C, 85.67; H, 6.18. Found: C, 85.79; H, 6.19. The photolysis mixture obtained from **49a** in benzene was separated by HPLC (Si 60-5-C_{18}, methanol-water, 4:1) to give **54a,b**; ^{2}H NMR ($CHCl_3$): δ 3.14-3.3 (3%), 5.4 (97%).

The products obtained on photolysis of **47** in 0.2 M NaOMe-MeOH were partitioned between water and ether. HPLC (Si 60-5, hexane-ether, 10:1) of the organic phase afforded 1-(methoxymethyl)-2-(phenoxymethyl)benzene (**56**); ^{1}H NMR ($CDCl_3$): δ 3.41 (s, 3 H), 4.68 (s, 2 H), 5.16 (s, 2 H), 6.9-7.6 (m, 9 H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.91; H, 7.08. Found: C, 78.79; H, 7.09. An analogous experiment was performed in NaOMe-MeOD to obtain **56a,b**; ^{2}H NMR ($CHCl_3$): δ 4.65 (87.4%), 5.12 (12.6%).

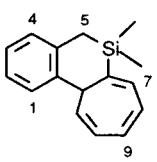
2-(Dimethylphenylsilylmethyl)benzaldehyde Tosylhydrazone (61). The following synthesis is a modification of the procedure of Ito et al.[37] To a stirred, nitrogen-blanketed solution of 2-methylbenzyl alcohol (7.8 g, 64 mmol) in anhydrous diglyme (250 ml) was added *n*-butyllithium (1.6 m in hexane, 80 ml, 126 mmol) at -78 °C over 30 min. On warming to -20 °C, the cream-yellow slurry became a homogeneous dark-red solution. After the mixture was stirred for 30 min at -20 to -10 °C, chlorodimethylphenylsilane (21.9 g, 128 mmol) and triethylamine (5 ml) were added, and stirring was continued at room temperature for 12 h. Ice water was then added, and the mixture was extracted repeatedly with ether. The combined extracts were washed with ice water and brine, dried ($MgSO_4$), and concentrated in *vacuo*. Unreacted and monosilylated alcohol were removed by distillation at 120 °C, 0.2 Torr. The residue [^{1}H NMR ($CDCl_3$): δ 0.20 (s, 6 H), 0.35 (s, 6 H), 2.26 (s, 2 H), 4.40 (s, 2 H), 6.8-7.65 (m, 14 H)] was dissolved in methanol-water (9:1) and heated at reflux until the silyl ether was hydrolyzed (ca. 3 d, monitored by GC). The solvent was removed in *vacuo*, and the residue was extracted with ether. The extracts were dried ($MgSO_4$), concentrated, and distilled to give 7.1 g (43%) of 2-(dimethylphenylsilylmethyl)benzyl alcohol, b.p. 120 °C (0.2 Torr); ^{1}H NMR ($CDCl_3$): δ 0.30 (s, 6 H), 1.40 (br s, 1 H), 2.40 (s, 2 H), 4.38 (s, 2 H), 6.9-7.7 (m, 9 H).

To a stirred solution of pyridine (27.6 g, 0.35 mol) in anhydrous acetic acid (130 ml) was added at 10-15 °C chromium trioxide (17.5 g, 0.22 mol) in small portions. The mixture was diluted with anhydrous acetic acid (220 ml) and cooled to 5 °C. A solution of 2-(dimethylphenylsilylmethyl)benzyl alcohol (4.37 g, 17 mmol) in ether (50 ml) was added over 10 min, and stirring was continued for 15 min. The mixture was then partitioned between water and ether. The combined ether solutions were washed with water, neutralized with solid $NaHCO_3$, washed with aqueous Na_2CO_3, dried ($MgSO_4$), and concentrated in *vacuo* to give 3.5 g (79%) of crude 2-(dimethylphenylsilylmethyl)benzaldehyde (**60**);[38] IR (film): 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 0.33 (s, 6 H), 2.96 (s, 2 H), 7.09 (dd, J = 7.4 and 2.1 Hz, 1 H), 7.13-7.67 (m, 7 H), 7.76 09 (dd, J = 7.0 and 2.1 Hz, 1 H), 10.05 (s, 1 H). In order to obtain **60**-d, the same procedure was applied to α,α-d_2-2-methylbenzyl alcohol.

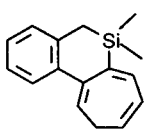
To a concentrated solution of *p*-toluenesulfonylhydrazine (2.6 g, 13.8 mmol) in methanol was added a solution of crude **60** (3.5 g, ~13.8 mmol) in methanol (5 ml). The mixture was stirred under nitrogen at room temperature for 14 h. The precipitate was filtered off and recrystallized from methanol to give 4.5 g (63%) of **61**, m.p. 134 °C; ^{1}H NMR ($CDCl_3$): δ 0.19 (s, 6 H), 2.40 (s, 5 H), 6.87 (dd, J = 7.8 and 1.3 Hz, 1 H), 7.03 (td,

J = 7.8 and 0.9 Hz, 1 H), 7.15 (td, J = 7.8 and 1.3 Hz, 1 H), 7.18-7.35 (m, 8 H), 7.40 (s, 1 H), 7.60 (dd, J = 7.8 and 1.5 Hz, 1 H), 7.79 (d, J = 8.2 Hz, 2 H). Anal. Calcd for $C_{23}H_{26}N_2O_2SSi$: C, 65.35; H, 6.21; N, 6.63. Found: C, 65.47; H, 6.21; N, 6.66.

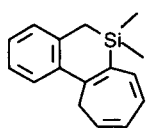
Reaction Products of 2-(Dimethylphenylsilylmethyl)phenylcarbene (66). The product distributions were estimated by GC (20 m OV 17, 180 °C, and 31 m OV 1, 180 °C) (Table 7). The product mixture obtained on pyrolysis of **62** was separated by HPLC (Si 60-5, hexane) to give the following compounds: 2-Methyl-2-phenyl-1,2,3,4-tetrahydro-2-silanaphthalene (**65**); ^{1}H NMR ($CDCl_3$): δ 0.30 (s, 3 H), 1.00 (t, J = 6.8 Hz, 1 H), 1.07 (t, J = 6.8 Hz, 1 H), 2.09 (d, J = 14.5 Hz, 1 H), 2.31 (d, J = 14.5 Hz, 1 H), 2.86 (t, J = 6.8 Hz, 2 H), 7.10 (br s, 4 H), 7.2-7.55 (m, 5 H). 5,6-Dihydro-6,6-dimethyl-6-sila-11a*H*-cyclohepta[*a*]naphthalene (**67**) and isomers (two GC peaks): Calcd for $C_{16}H_{18}Si$: C, 80.59; H, 7.62. Found (mixture): C, 80.47, H, 7.51. ^{1}H NMR (C_6D_6) of **67**: δ 0.02 (s, 6 H), 2.00 (s, 2 H), 2.78 (dt, J = 5.9 and 0.9 Hz, 1 H), 5.12 (ddd, J = 9.1, 5.9, and 0.8 Hz,1 H), 6.08 (ddt, J = 9.1, 5.7, and 0.9 Hz, 1 H), 6.44 (ddd, J = 5.3, 0.9 and 0.8 Hz, 1 H), 6.66 (ddd, J = 11.0, 5.3, and 0.8 Hz, 1 H), 6.77 (ddd, J = 11.0, 5.3, and 0.8 Hz, 1 H), 6.9-7.4 (m, 4 H). ^{1}H NMR (C_6D_6) of **67a**: δ 0.05 (s, 6 H), 1.99 (s, 2 H), 2.25 (t, J = 5.9 Hz, 2 H), 5.28 (dt, J = 9.1 and 6.7 Hz, 1 H), 5.45 (t, J = 6.7 Hz, 1 H), 6.30 (dd, J = 9.1 and 5.9 Hz, 1 H), 6.65 (d, J = 5.9 Hz, 1 H), 6.9-7.4 (m, 4 H). ^{1}H NMR (C_6D_6) of **67b**: δ -0.05 (s, 6 H), 2.04 (s, 2 H), 2.15 (t, J = 6.9 Hz, 2 H), 5.48 (dt, J = 9.6 and 6.9 Hz, 1 H), 5.51 (dt, J = 9.6 and 6.9 Hz, 1 H), 6.27 (d, J = 9.6 Hz, 1 H), 6.42 (d, J = 9.6 Hz, 1 H), 6.9-7.4 (m, 4 H). Hydrogenation (10% Pd-C, C_6D_6) of the mixture gave a single product, **67c**; ^{1}H NMR ($CDCl_3$): δ -0.16-0.20 (m, 7 H), 0.9-2.4 (m, 13 H), 6.9-7.2 (m, 4 H).



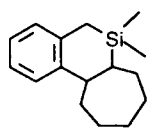
67



67a



67b

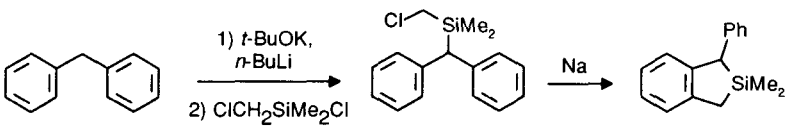


67c

Bicyclo[4.2.0]octa-1,3,5-trien-7-yldimethylphenylsilane (**68**): ^{1}H NMR ($CDCl_3$): δ 0.19 (s, 3 H), 0.26 (s, 3 H), 2.99 (dd, J = 13.5 and 2.0 Hz, 1 H), 3.23 (dd, J = 6.0 and 2.0 Hz, 1 H), 3.28 (dd, J = 13.5 and 6.0 Hz, 1 H), 6.87 (br d, J = 7.5 Hz, 1 H), 6.97 (br d, J = 7.5 Hz, 1 H), 7.10 (br t, J = 7.5 Hz, 1 H), 7.12 (br t, J = 7.5 Hz, 1 H), 7.27-7.41 (m, 3 H), 7.46-7.51 (m, 2 H). Anal. Calcd. for $C_{16}H_{18}Si$: C, 80.59; H, 7.62. Found: C, 80.57; H, 7.59. Thermolysis of **62a** afforded **68a,b**; ^{2}H NMR ($CHCl_3$): δ 3.0 (10%), 3.25 (90%). The signals of 7-D and *E*-8-D are not resolved; it is assumed that the amount of *E*-8-D equals that of *Z*-8-D.

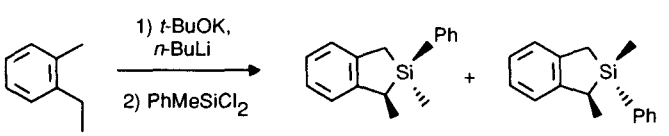
The assignments of minor products were confirmed by synthesis. To a stirred, nitrogen-blanketed solution of *o*-xylene (0.5 g, 4.7 mmol) in hexane (50 ml) was added potassium *t*-butoxide (584 mg, 5.2 mmol) and *n*-butyllithium (1.6 m in hexane, 3.25 ml, 5.2 mmol). The mixture was heated at reflux for 30 min. After a solution of chlorodimethylphenylsilane (802 mg, 4.7 mmol) in hexane (10 ml) was added, heating at reflux was continued for 14 h. The mixture was then poured into ice water and extracted with ether. The combined organic solutions were washed with water, dried ($MgSO_4$), and concentrated in *vacuo*. Fractional distillation of the residue afforded 0.36 g (32%) of dimethyl(2-methylbenzyl)phenylsilane (**64**); b.p. 96 °C (0.2 Torr); ^{1}H NMR ($CDCl_3$): δ 0.29 (s, 6 H), 2.09 (s, 3 H), 2.32 (s, 2 H), 6.8-7.6 (m, 9 H). Anal. Calcd for $C_{16}H_{20}Si$: C, 79.92; H, 8.40. Found: C, 79.80; H, 8.44.

To a stirred, nitrogen-blanketed solution of diphenylmethane (8.7 g, 52 mmol) in ether (100 ml) was added potassium *t*-butoxide (6.4 g, 57 mmol) and *n*-butyllithium (1.6 M in hexane, 35.6 ml, 57mmol). The mixture was heated at reflux for 1 h and was then allowed to cool to room temperature. A solution of chloro(chloromethyl)dimethylsilane (7.4 g, 52 mmol) in ether (10 ml) was added, and stirring was continued for 30 min. The resulting yellow solution was acidified with 10% HCl and extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and concentrated in *vacuo*. Fractional distillation of the residue afforded 8.1 g (57%) of (chloromethyl)dimethyl(diphenylmethyl)silane (**77**); b.p. 103-106 °C (0.1 Torr); ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 6 H), 2.79 (s, 2 H), 3.88 (s, 1 H), 7.15-7.45 (m, 10 H). To a nitrogen-blanketed solution of **77** (1.0 g, 3.6 mmol) in anhydrous benzene (50 ml) was added sodium (0.33 g, 14.4 mmol) in small pieces. The mixture was heated at reflux for 19 h, cooled to room temperature, and filtered. The filtrate was washed with water, dried ($MgSO_4$), and concentrated in *vacuo*. HPLC (Si 60-5, hexane) of the residue afforded 165 mg (19%) of 2,2-dimethyl-1-phenyl-2-silaindan (**69**); ^{1}H NMR ($CDCl_3$): δ -0.08 (s, 3 H), 0.33 (s, 3 H), 2.18 (s, 2 H), 3.74 (s, 1 H), 6.85-7.45 (m, 9 H). Anal. Calcd. for $C_{16}H_{18}Si$: C, 80.59; H, 7.62. Found: C, 80.48; H, 7.71.



77 **69**

To a nitrogen-blanketed solution of 1-ethyl-2-methylbenzene (3.0 g, 25 mmol) in hexane (100 ml) was added potassium *t*-butoxide (6.2 g, 55 mmol) and *n*-butyllithium (1.6 M in hexane, 34.4 ml, 55 mmol). The mixture was heated at reflux for 1 h. After a solution of dichloromethylphenylsilane (4.8 g, 25 mmol) in hexane (10 ml) was added, heating at reflux was continued for 14 h. Conventional workup (see **64**) gave 1.9 g (32%) of 1,2-dimethyl-2-phenyl-2-silaindan (**70**), b.p. 92-94 °C (0.2 Torr). Two diastereomers were obtained by HPLC (Si 60-5-C_{18}, methanol-water, 4:1). ^{1}H NMR ($CDCl_3$) of **70a**: δ 0.56 (s, 3 H), 1.20 (d, J = 7.4 Hz, 3 H), 2.20 (d, J = 16 Hz, 1 H), 2.40 (q, J = 7.4 Hz, 1 H), 2.51 (d, J = 16 Hz, 1 H), 6.98-7.47 (m, 9 H). ^{1}H NMR ($CDCl_3$) of **70b**: δ 0.46 (s, 3 H), 1.44 (d, J = 7.4 Hz, 3 H), 2.20 (d, J = 16 Hz, 1 H), 2.46 (d, J = 16 Hz, 1 H), 2.58 (q, J = 7.4 Hz, 1 H), 7.08-7.70 (m, 9 H). Anal. Calcd. for $C_{16}H_{18}Si$: C, 80.59; H, 7.62. Found for **70a**: C, 80.48; H, 7.61. Found for **70b**: C, 80.43; H, 7.71.



70a **70b**

The products obtained on photolysis of **61** in 0.2 M NaOMe-MeOH were partitioned between water and ether. HPLC (Si 60-5, pentane-ether, 5:1) of the organic phase afforded 1-(dimethylphenylsilylmethyl)-2-(methoxymethyl)benzene (**71**); ^{1}H NMR ($CDCl_3$): δ 0.29 (s, 6 H), 2.39 (s, 2 H), 3.29 (s, 3 H), 4.20 (s, 2 H), 6.86-7.53 (m, 9 H). Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.48; H, 8.22. Found: C, 75.31; H, 8.18.

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