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Intramolecular Reactivity of Arylcarbenes: Derivatives of *o*-Tolylcarbene

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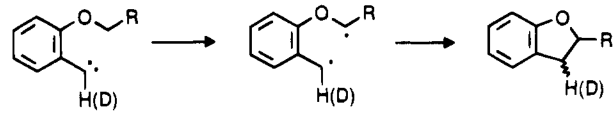
Various CH_2X groups have been attached to the *ortho* position of phenylcarbene. If 2′- or 3′-C—H bonds are present, as in **23** (X = Me), **71** (X = CMe_3), and **58** (X = $SiMe_3$), C—H insertion leading to five- or six-membered rings predominates in the gas phase and competes with intermolecular reactions in solution. The formation of benzocyclobutenes via insertion into 1′-C—H bonds is a very minor reaction path of **23** and **71**. In contrast, **58** produces substantial amounts of the benzocyclobutene **59** by way of C—Si insertion, particularly in the gas phase. Insertion into the Si—Me bonds of **58** also occurs while the C—F bonds of **37** (X = CF_3) and **50** (X = F) are inert. In the gas phase, **37** and **50** give mainly benzocyclobutenes whereas intermolecular reactions prevail in solution. The effects of sensitization and of solvent polarity suggest that benzocyclobutenes arise from singlet arylcarbenes. The amount of carbene—carbene rearrangement decreases in the order **7** (X = H) > **37** (X = CF_3) > **23** (X = Me); no rearrangement was observed with **50** (X = F), **58** (X = $SiMe_3$), and **71** (X = CMe_3).

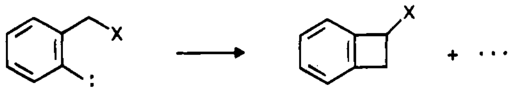
Many *intermolecular* reactions of phenylcarbene proceed from the singlet state, although the ground state is the triplet.[1] Thus the additon of phenylcarbene to alkenes gives cyclopropanes with greater than 95% stereospecificity.[2,3] Neither dilution with perfluorocyclobutane[4] nor benzophenone sensitization[5] has a significant effect on stereoselectivity. These results have been interpreted in terms of rapid singlet–triplet equilibration, with the singlet state being much more reactive than the triplet. Likewise, the concerted singlet mechanism for *intermolecular* C—H insertion reactions of phenylcarbene is supported by the lack of crossover products,[6] small deuterium isotope effects,[6] and stereoselective insertion into the tertiary C—H bonds of *rac*- and *meso*-2,3-dimethoxybutane.[7]

By contrast, we have recently observed nonstereospecific *intramolecular* addition reactions of triplet arylcarbenes to double bonds of an *ortho* side chain.[8] Similarly, (2-alkoxyphenyl)carbenes **1** were found to produce dihydrobenzofurans **3** by way of a triplet abstraction–recombination mechanism.[7] Cyclization of the intervening 1,5-biradicals **2** is subject to conformational control, leading to an unusual steric discrimination between hydrogen and deuterium.[9]



1 **2** **3**

For intramolecular reactions of arylcarbenes, the ring size of the cyclic transititon state appears to be a major factor in determining the multiplicity.[10] In an attempt at elucidating the formation of four-membered rings (benzocyclobutenes), we now report on derivatives of *o*-tolylcarbene (X = CH_3, CF_3, F, and $SiMe_3$). [2-(Alkoxymethyl)phenyl]carbenes (X = OR) were shown previously to give benzocyclobutenes via Stevens rearrangement of oxygen ylides.[10,11]



Results and Discussion

***o*-Tolylcarbene**. The efforts directed to *o*-tolylcarbene (**7**) have focused mainly on the interconversion of **7** with *m*- and *p*-tolylcarbene (**5** and **6**) and with 1-phenylethylidene (**14**) (Scheme 1).[12] The carbene–carbene rearrangements[13] were primarily discussed in terms of transient bicycloheptatrienes **8** and cycloheptatrienylidenes **9** while 1,2,4,6-cycloheptatetraenes **12** were the only intermediates identified spectroscopically in an argon matrix at 10 K.[14] The matrix studies also revealed

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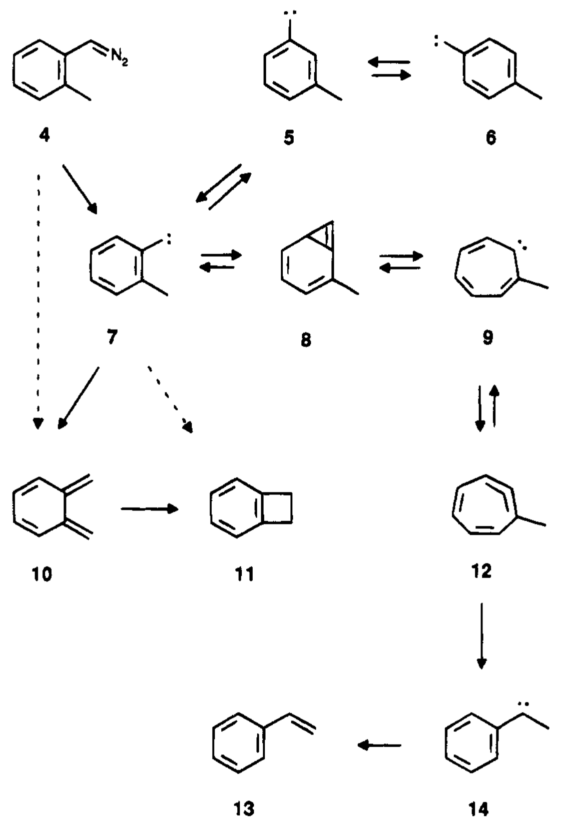
Scheme 1

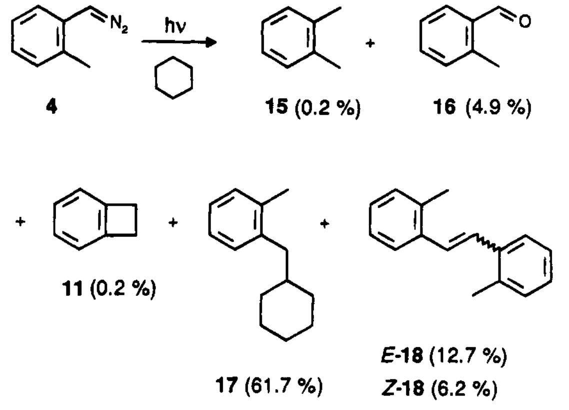


thermally and photochemically induced 1,4-hydrogen shifts in triplet **7** to form singlet *o*-xylylene (**10**). Upon short wavelength irradiation, matrix-isolated **10** cyclized to benzocyclobutene (**11**).[14c] It is not clear whether the two-step migration–cyclization mechanism applies at elevated temperatures. Thermolysis of *o*-tolyldiazomethane (**4**) produces a different **11**:**13** ratio (ca. 3) than the meta and para isomers (ca. 0.8).[12] Conformational effects[12a,d] and norcaradienylidene intermediates[15] have been invoked to explain this anomaly. However, upon trideuteration of the methyl groups, all three isomers of tolylcarbene were found to give the same ratio of **11**-d_3:**13**-d_3.[14c] Therefore, hydrogen migration in the diazo compound **4** was suggested as an alternative route to **11**.

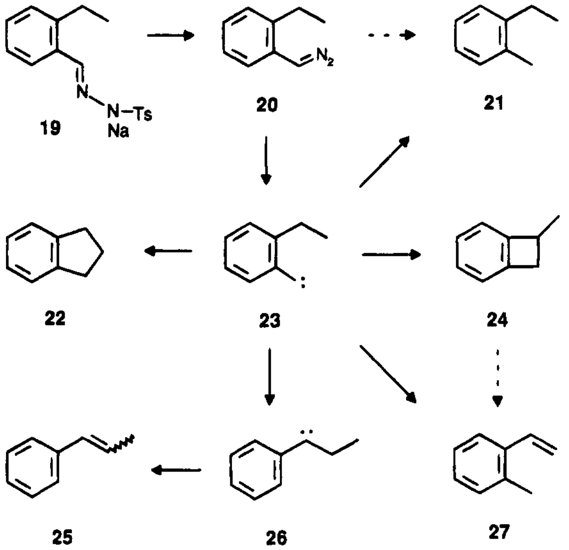
In our hands, photolytic generation of the tolylcarbenes in the gas phase led to similar **11**:**13** ratios from **5** (0.63), **6** (0.59), and **7** (0.70). Our data for **7** deviate from earlier work reporting **11**:**13** = 1.4.[12c] Partial decomposition of **4** during vaporization may explain the discrepancy. It appears that only the thermolysis of **4** is complicated by non-carbenic pathways.

Photolysis of **4** in cyclohexane afforded mainly 2-(cyclohexylmethyl)toluene (**17**), via insertion of carbene **7** into C—H bonds of the solvent (Scheme 2). Trivial byproducts were *o*-xylene (**15**; H abstraction), *o*-tolualdehyde (**16**; reaction with adventitious traces of oxygen), and 2,2′-dimethylstilbene (**18**; formal dimerization). Benzocyclobutene (**11**) was formed in trace amounts (0.2%) whereas styrene (**13**) was not detected. The **17**:**11** ratio of ca. 300 attests to the inefficient intramolecular C—H insertion of *o*-tolylcarbene.

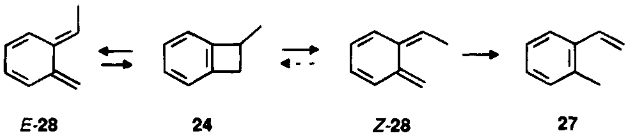
Scheme 2



Scheme 3



(2-Ethylphenyl)carbene (23). In an exploratory study, the tosylhydrazone sodium salt **19** was pyrolyzed to give indan (**22**) and 2-methylstyrene (**27**) (96:4, 72% yield).[16] From an analogous experiment, we obtained 3-methylbenzocyclobutene (**24**, 1.1%) in addition to **22** (97.2%) and **27** (1.7%) (Scheme 3). The origin of **27** in thermal reactions is not clear since **24** ring opens at elevated temperatures with formation of the *o*-xylylene **28**. While (*E*)-**28** has been trapped in the presence of dienophiles,[17a] the reaction is otherwise channeled through (*Z*)-**28** which gives **27** by way of 1,5-H shift.[17b] However, photolysis of (2-ethylphenyl)diazomethane (**20**) also affords **27**, pointing to intramolecular abstraction of vicinal hydrogen by carbene **23** (Table 1).



Evidence for the carbene–carbene rearrangement **23** → **26** was obtained only upon photolysis of **20** in the gas phase. The formation of (*E*)- and (*Z*)-1-phenylpropene (**25**; 4.8 and 4.1%, respectively) is reasonably attributed to 1,2-H shifts of **26**. Recently, gas phase pyrolyses of

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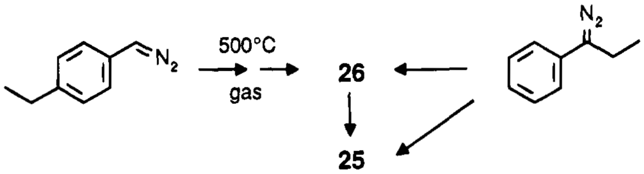
Table 1. C_9 Products from Photolyses[a] of (2-Ethylphenyl)diazomethane (20)

conditions	21	22	24	27	yield (%)[b]
gas phase[c]	6.7	69.1	1.0	14.3	
2,2,3-trimethylpentane	2.7	88.2	7.3	1.8	12.8
>400 nm	1.4	88.8	8.9	0.9	10.7
254 nm, quartz	7.2	84.6	7.3	0.9	9.6
pentane	7.6	81.3	9.6	1.5	
hexafluorobenzene	1.0	86.2	11.9	0.9	2.5
benzene	0.8	82.5	14.5	2.2	5.5
saturated with O_2	0.7	82.7	14.9	1.7	4.9
0.1 M Ph_2CO	0.9	90.1	7.5	1.5	4.1
0.3 M Ph_2CO	1.0	92.6	5.3	1.1	3.4
acetonitrile	1.7	74.9	18.7	0.1	2.2
diethyl ether	8.0	67.2	21.5	3.3	3.3
1,2-dimethoxyethane	6.0	66.9	25.6	1.5	3.3
1,4-dioxane	3.3	66.5	29.1	1.1	2.7
t-butyl alcohol	1.1	61.9	34.7	2.3	3.6
pyridine	4.1	58.5	32.4	4.9	0.9
tetrahydrofuran	8.2	53.8	37.0	1.0	1.9
methanol, 0.2 M NaOMe	55.5	19.8	19.8	4.9	5.1

[a] Pyrex vessel, medium pressure mercury arc, 20 °C, unless specified otherwise. [b] Based on tosylhydrazone; not corrected for the preparation of **20** (60–70% yield). [c] 4.8% of *E*-**25** and 4.1% of *Z*-**25** were also obtained.

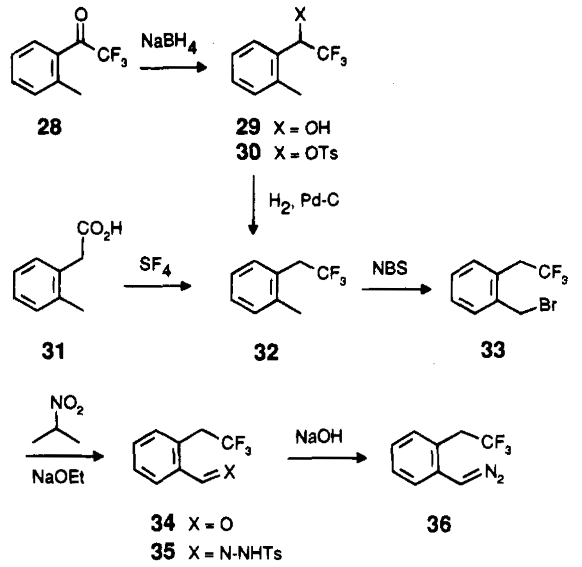
both (4-ethylphenyl)diazomethane and 1-phenyldiazopropane were found to give **25** with different *E*:*Z* ratios (63:37 and 76:24, respectively).[18] These results suggest substantial direct formation of **25** from 1-phenyldiazopropane, without intervention of the carbene **26**. Our *E*:*Z* ratio (54:46) is somewhat lower than that reported by Jones et al., probably due to light-induced *E* → *Z* isomerization of **25** (for an analogous case, see Scheme 5).



The **22**:**24** ratios obtained in photolyses of **20** vary widely, ranging from 69 in the gas phase to ca. 1 in methanol (Table 1). The absence of a significant wavelength effect excludes formation of **22** or **24** from an excited state of **20**. Triplet sensitization with benzophenone was found to enhance the **22**:**24** ratio. In some contrast, the relative amounts of **22** and **24** were not affected by the presence of oxygen, although the yield of 2-ethylbenzaldehyde increased from 1.2% in "degassed" benzene to 11.4% in oxygen-saturated benzene. The **22**:**24** ratio tends to decrease in more polar solvents, but there is no smooth correlation with established parameters of solvent polarity (e.g., compare acetonitrile, E_T = 45.6, with THF, E_T = 37.4). Hydrogen abstraction from the solvent appears to be the source of 1-ethyl-2-methylbenzene (**21**), ethers giving more **21** than hydrocarbons. The exceptional yield of **21** in methanol is due to the presence of the potent hydrogen donor methoxide, as discussed elsewhere.[19]

Our data suggest that **22** arises from the triplet state of **23**, in accordance with previous results on the formation of five-membered rings from functionalized arylcarbenes.[7,9] On the other hand, **24** appears to originate from singlet **23**. The response of **22**:**24** ratios to benzophenone sensitization and the influence of the solvent support this interpretation. An analogous effect of solvent polarity on the ratio of triplet to singlet products from 1,2-diphenyl-1-butylidene has been reported.[20] Measurements of k_{ST} for diarylcarbenes also point to stabilization of the zwitterionic singlet state in polar solvents.[21] As for **23**, our analysis suffers from low yields of intramolecular products. Although the reactivity of the ethyl group in **23** greatly exceeds that of the methyl group in **7**, intermolecular reactions remain predominant. Low susceptibility of the solvent to carbene attack tends to raise the yield of intramolecular products (thus, 2,2,3-trimethylpentane provides mainly primary C—H bonds for carbene insertion). Unfortunately, insufficient solubility of **20** in perfluorinated (cyclo)alkanes precludes application of these inert solvents.

Scheme 4



[2-(2′,2′,2′-Trifluoroethyl)phenyl]carbene (37). The trifluoromethyl group was of interest to us as a strongly electron-withdrawing substituent (σ_I = 0.42) which is unreactive toward carbenes. Hopefully, comparison of **37** with **23** might give some clue to the mechanism of benzocyclobutene formation.

1-Methyl-2-(2′,2′,2′-trifluoroethyl)benzene (**32**) was a key intermediate on the route to diazo compound **36** (Scheme 4). In analogy to a synthesis of the *meta* and *para* isomers,[22] **36** was approached by sodium borohydride reduction of ketone **28** (99%), tosylation of alcohol **29** (89%), and catalytic hydrogenation of tosylate **30** (93%). We also tried the fluorination of **31** with SF_4[23] but obtained a mixture of **32** and acyl fluoride (85:15) which was not readily separated. Bromination of **32** with NBS (65%), followed by treatment of **33** with the sodium salt of 2-nitropropane, led to aldehyde **34** (88%) whose tosylhydrazone **35** (74%) was converted into diazo compound **36** (60–70%).

Pyrolysis and photolysis of **36** in the gas phase afforded as the major product 3-(trifluoromethyl)benzocyclobutene

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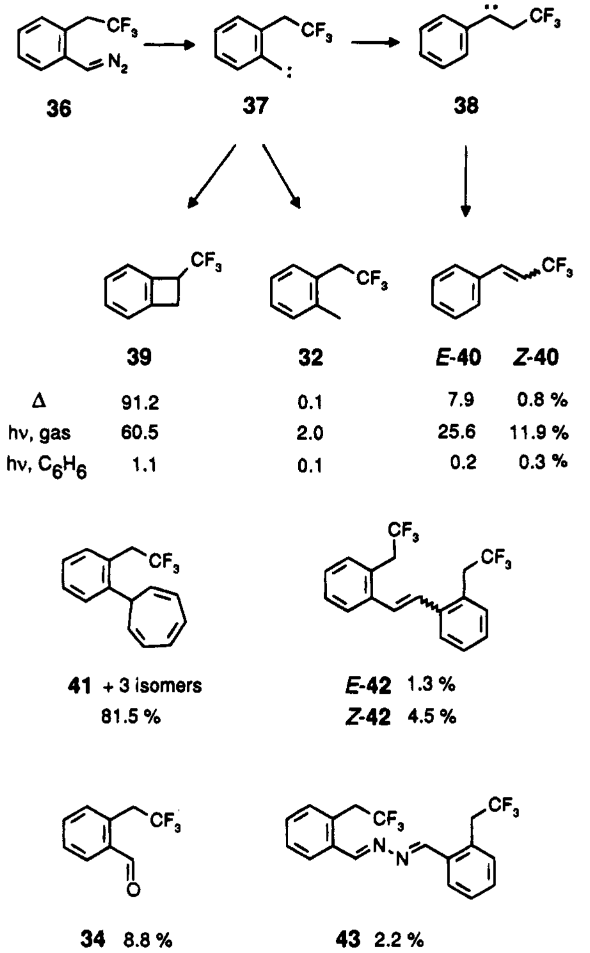
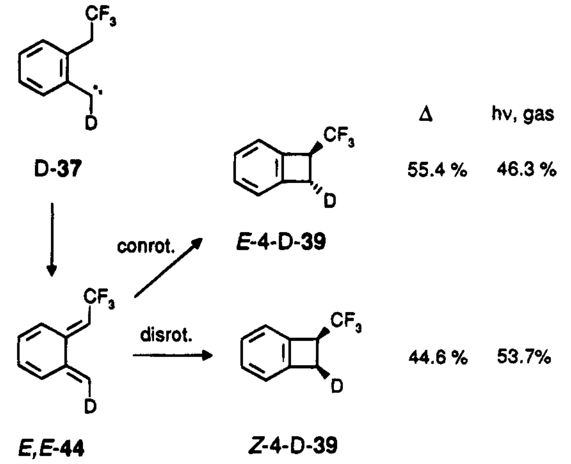
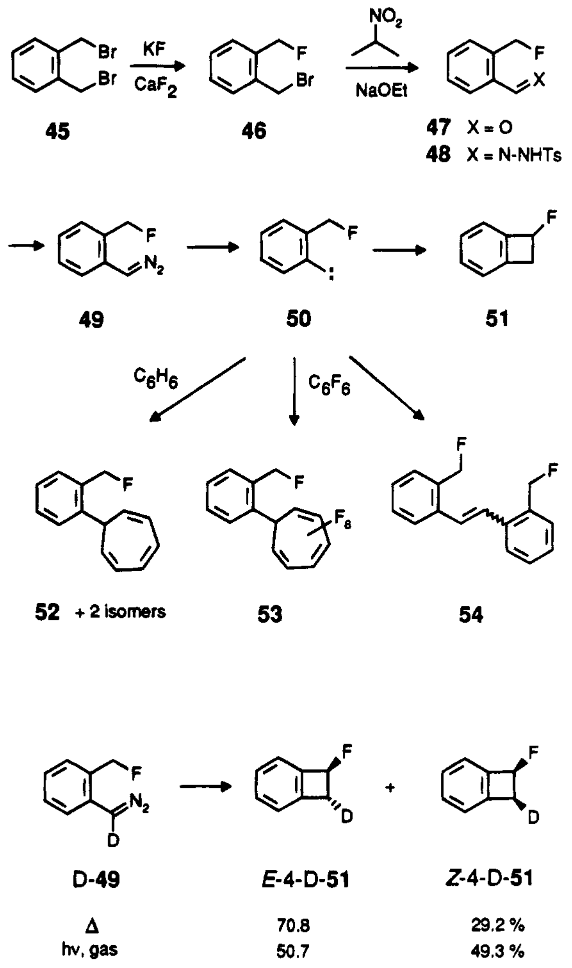
Scheme 5



Scheme 6



Scheme 7



(**39**). 1-Phenyl-3,3,3-trifluoropropene (**40**), resulting from the carbene–carbene rearrangement **37** → **38**, was more prominent in the photolysis than in the pyrolysis of **36** (Scheme 5). Only small amounts of **39** and **40** were produced upon photolysis of **36** in benzene. Under these conditions, intermolecular addition of **37** to benzene prevailed, giving **41** and isomers derived therefrom by H shifts. Aldehyde **34**, stilbene **42**, and azine **43** were obtained as byproducts. The predominance of (*Z*)-**42** is attributed to photoisomerization of (*E*)-**42**.

The apparent gas-phase reactivities of carbenes **23** and **37** differ substantially. Since **37** cannot undergo δ-C–H insertion leading to five-membered rings, the benzocyclobutene **39** emerges as the major product, and carbene–carbene rearrangement is significantly enhanced. In benzene, with intermolecular addition of the carbene as the reference, the yields of benzocyclobutenes from **23** and **37** are similar. Thus, inductive effects play a minor role in the 1,4 ring closure of *o*-tolylcarbenes.

The deuterated carbene D-**37** was generated in order to explore the stereochemistry of benzocyclobutene formation. With 1,4-H shift as the first step, the (*E,E*) isomer of the *o*-quinodimethane D-**44** is expected to predominate. Conrotatory cyclization in thermal reactions, or photochemically induced disrotatory cyclization, would then lead to specific geometries of D-**39** (Scheme 6). Our experimental data deviate but slightly from random distributions of deuterium. The deviations, although correct in sign, are too small to support the suggested mechanism.

[2-(Fluoromethyl)phenyl]carbene (50). Partial exchange of bromine for fluorine in 1,2-bis(bromomethyl)benzene (**45**) afforded 1-(bromomethyl)-2-(fluoromethyl)benzene (**46**) (31%), from which aldehyde **47**, tosylhydrazone **48** (38% overall), and diazo compound **49** were prepared (Scheme 7). Pyrolysis and photolysis of **49** in the gas phase produced 3-fluorobenzocyclobutene (**51**) almost exclusively, with ≤2% of **47** as a byproduct. No evidence for carbene–carbene rearrangement was found. When D-**49** was subjected to gas phase pyrolysis, the (*E*) isomer of 4-D-**51** was formed preferentially. As was pointed out in the preceeding Section (Scheme 6), this result can be interpreted in terms of an *o*-xylylene intermediate. By contrast, gas phase photolysis of **49** led to a 1:1 ratio of (*E*)- and (*Z*)-4-D-**51**. Photolysis of **49** in

Scheme 8

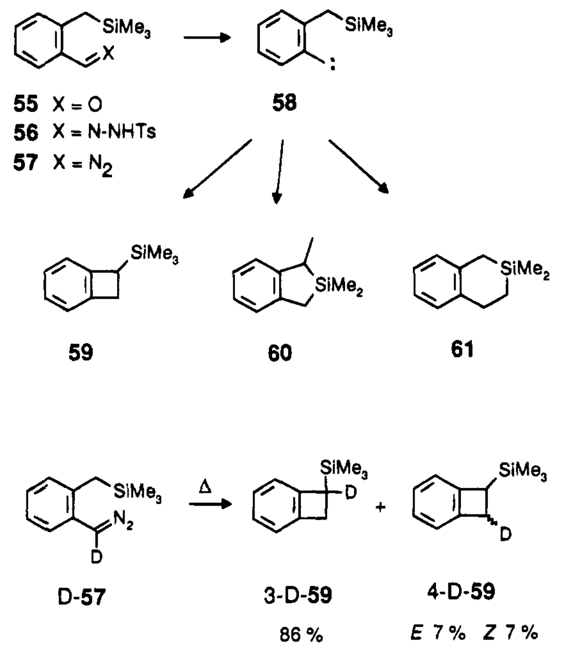


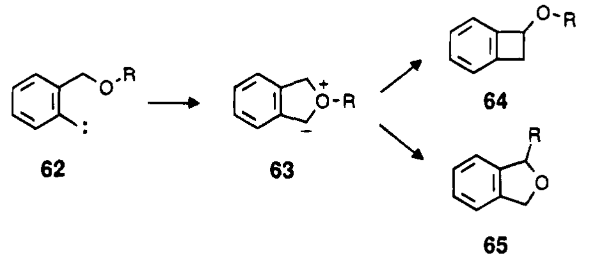
Table 2. Products from [2-[(Trimethylsilyl)methyl]phenyl]diazomethane (57)

conditions	59	60	61	59−61 (%)	55 (%)
Δ, gas	39.7	7.0	53.3	98.3	
hν, C_6H_6	4.8	1.7	93.5	66.5	7.8
hν, C_6H_6, Ph_2CO	2.0	0.2	97.9	38.2	0.8
hν, MeCN	6.1	0.7	93.2	19.5	11.1
hν, Me_2SO	22.5	0.4	77.1	9.3	27.7

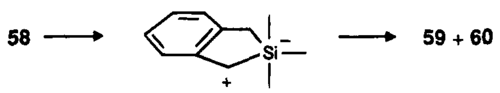
benzene proceeded mainly via addition of **50** to the arene, giving **52** (55%) and two isomers (22 and 23%) resulting from H shifts in **52**. Only traces ($\leq$0.2%) of **51** and **47** were observed. In hexafluorobenzene, formation of the stilbenes **54** (35.5% *Z* and 22.8% *E*) in addition to **53** (41.7%) indicates diminished attack of **50** on the perfluorinated arene. Nevertheless, no significant amounts of **51** were obtained.

[2-[(Trimethylsilyl)methyl]phenyl]carbene (58). 2-[(Trimethylsilyl)methyl]benzaldehyde (**55**)[24] was converted into tosylhydrazone **56** and diazo compound **57**. When **57** was generated from the sodium salt of **56** and subsequently pyrolyzed at 280−300 °C, the products **59**-**61** of intramolecular carbene reactions were formed almost quantitatively (Scheme 8, Table 2). 2,2-Dimethyl-2-sila-1,2,3,4-tetrahydronaphthalene (**61**) clearly arises by insertion of **58** into C−H bonds of the Si-Me groups. The structure of 2-sila-1,2,2-trimethylindan (**60**), confirmed by an unequivocal synthesis, points to insertion of **58** into Si−Me bonds. This observation suggests that 3-(trimethylsilyl)benzocyclobutene (**59**) might result from insertion into C−Si as well as C−H bonds. Analysis of the reaction path(s) by means of deuterium labels was hampered by the small difference in chemical shift between 3-H (δ 2.98) and (*Z*)-4-H (δ 2.91). Consequently, the signals of 3-D and (*Z*)-4-D overlapped in ^{2}H-NMR spectra (61.4 MHz) of D-**59**, only the signal of (*E*)-4-D (δ 3.24) being resolved. ^{2}H-NMR spectroscopy can, of course, deal with incompletely deuterated samples which were routinely obtained by H−D exchange (D_2O/NaOD) during the preparation of aryldiazomethanes from tosylhydrazones. In order to apply ^{1}H-NMR spectroscopy (400 MHz), the completely (98%) labeled carbene precursor D-**57** was synthesized, starting from methyl 2-methylbenzoate and $LiAlD_4$. As a result of these efforts, **59** was found to arise predominantly (86%) via C−Si insertion, only a minor fraction (14%) being due to C−H insertion (Scheme 8).

These findings are reminiscent of [2-(alkoxymethyl)phenyl]carbenes (**62**) which give alkoxybenzocyclobutenes **64** via Stevens rearrangement of oxygen ylides **63**.[10] In the case of R = Me, the "internal" benzyl group migrates exclusively, but with increasing migratory aptitude of R, the formation of dihydroisobenzofurans **65** becomes competitive or even predominant.[10,11]



While ylides **63** have ample intermolecular precedent, the intramolecular insertion of **58** into C−Si bonds is rather unusual. Phenylcarbene is known to attack only the C−H and C=C bonds of benzyltrimethylsilane.[25] Even methylene was found to insert only into C−Si bonds of strained rings.[26] If intermediates with pentacoordinated silicon ("inverse ylides") actually intervene in C−Si insertion reactions, the position of the ylidic site (equatorial rather than apical) may determine the ease of rearrangement.[25]



In solution, the distribution of products **59**−**61** is influenced by the nature of the solvent and by sensitization in a manner similar to that observed with **23**. The strongly enhanced yields of intramolecular products from **58** are largely due to the formation of **61**, i.e., to the large number of 3′-C−H bonds available in **58**. The formation of **60** indicates that C−Si insertion does occur on photolytic generation of **58** in benzene but it is not clear how much of **59** arises by way of C−Si insertion (owing to the low yield of **59**, labeling experiments were not practical). In any event, the enhanced ratios of **61**:**59** and **61**:**60** point to less C−Si insertion in photolysis as compared to pyrolysis of **57**. As a tentative explanation of these observations, we postulate reversible formation of a pentacoordinate silicon intermediate whose rearrangement involves an activation barrier.[25]

[2-(2,2-Dimethylpropyl)phenyl]carbene (71). This carbene was of interest as the carbon analogue of **58**. Alkaline hydrolysis of 3-*tert*-butylphthalide (**66**),[27] followed by hydrogenation, afforded 79% of 2-(2,2-dimethylpropyl)benzoic acid (**67**). Reduction of **67** with $LiAlH_4$ (86%) and oxidation of the resulting benzyl alcohol with

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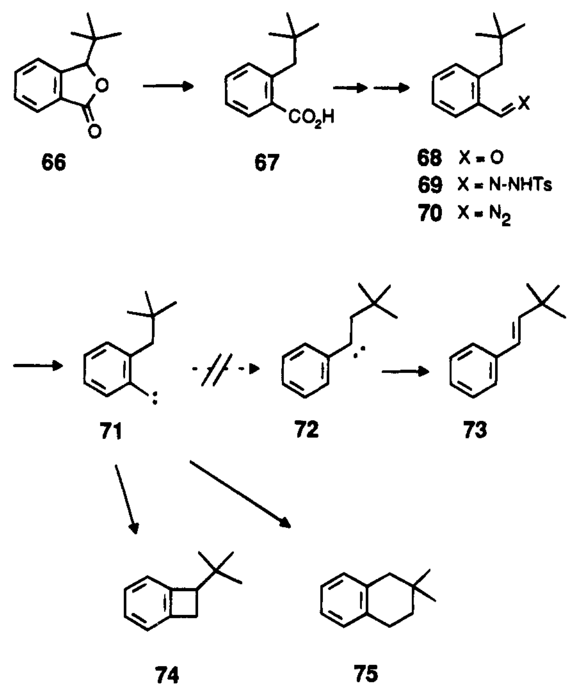
Scheme 9



	74	75	
Δ	1.3	98.7	Σ 69.2 %
hν, C_6H_6	2.8	97.2	Σ 40.2 %
hν, C_6H_6, Ph_2CO	0.7	99.3	Σ 24.7 %

CrO_3–pyridine complex led to aldehyde **68** (81%), from which tosylhydrazone **69** (84%) and diazo compound **70** were prepared (Scheme 9).

Decomposition of **70** produced mainly 2,2-dimethyltetralin (**75**), together with small amounts of 3-*tert*-butylbenzocyclobutene (**74**). Upon photolysis in benzene, the **74**:**75** ratio from **71** is smaller than the **24**:**22** ratio from **23** since the yield of **75** (39%) exceeds that of **22** (4.5%) almost 10-fold. The yields of benzocylobutenes from both precursors are similar (1.1 vs 0.8%). As compared with the silicon analogue **58**, benzocyclobutene formation from **71** is diminished by factors of 30–40 (pyrolysis, gas phase) and 2.5–3 (photolysis, benzene). However, the apparent superiority of **58** is mainly due to the C–Si insertion reaction, as demonstrated by the predominant formation of 3-D-**59** from D-**57**. If only the fraction of 4-D-**59** is taken into account, a factor of 2 remains (pyrolysis, gas phase). Obviously, insertion into the 1′-C–H bonds of *ortho*-functionalized arylcarbenes is not sensitive to steric effects. In accordance with precedent from previous sections, the fraction of **74** decreases on triplet sensitization.

The carbene–carbene rearrangement **71** → **72** should eventually lead to **73**. This reaction sequence was definitively excluded by calibration of the GC trace with an authentic sample of **73**. 1,2,2-Trimethylindan, the carbon analogue of **60**, was also absent. In contrast to the Si–Me bonds of **58**, the C–Me bonds of **71** are not susceptible to intramolecular attack of the arylcarbene.

Summary and Conclusion

Among the 2-CH_2X substituents we have attached to phenylcarbene, two categories can be distinguished. If 2′- or 3′-C–H bonds are present, as in **23** (X = CH_3), **71** (X = $C(CH_3)_3$), and **58** (X = $Si(CH_3)_3$), C–H insertion with formation of five- or six-membered rings predominates in the gas phase. Upon photolytic generation of these carbenes in benzene, the yields of intramolecular C–H insertion products (per C–H bond) increase in the order $CH_3 < C(CH_3)_3 < Si(CH_3)_3$ by factors of 2.9 and 1.6, respectively. The enhanced reactivity of $C(CH_3)_3$ relative to CH_3 is probably due to conformational rather than to the ring size effects ((2-butylphenyl)carbene is known to give more 2-ethylindan than 2-methyltetralin).[28] Although the average lengths of C–C and C–Si bonds differ by ca. 0.33 Å, the reactivities of $C(CH_3)_3$ and $Si(CH_3)_3$ are surprisingly similar.

The formation of benzocyclobutenes via insertion into 1′-C–H bonds is a very minor reaction path of carbenes **23** and **71**. Upon pyrolytic generation in the gas phase, **58** produces substantial amounts of 3-(trimethylsilyl)benzocyclobutene (**59**) by way of C–Si insertion. On the other hand, 1′-C–H insertion is but slightly promoted by $Si(CH_3)_3$, both in the gas phase and in solution. Owing to the absence of 2′-C–H and 3′-C–H bonds, carbenes **37** (X = CF_3) and **50** (X = F) give benzocyclobutene derivatives as the major products of gas phase reactions. In solution, however, intermolecular processes prevail. In all cases we have studied, benzocyclobutene formation decreases upon benzophenone sensitization and increases in polar relative to nonpolar solvents. These data suggest that benzocyclobutenes arise from singlet arylcarbenes. The stereoselective formation of 4-D-**51** from D-**50** can be interpreted in terms of 1,4-hydrogen transfer followed by cyclization of an *o*-quinodimethane. However, in view of the nearly stereorandom reaction of D-**37**, the two-step mechanism remains questionable.

Carbene–carbene rearrangement was observed when **37** (X = CF_3) was generated thermally or photolytically in the gas phase (8.7 and 37.5%, respectively). Only the photochemical approach was successful with **23** (X = CH_3, 8.9% rearrangement). Tentative explanations for this behavior have been reviewed in the section on *o*-tolylcarbene which undergoes carbene–carbene rearrangement more readily (Δ, 25%; hν, 58%) than **21** and **37**. It is reasonable that rearrangement cannot compete with insertion into the abundant 3′-C–H bonds of **58** (X = $Si(CH_3)_3$) and **71** (X = $C(CH_3)_3$) but the reluctance of **50** (X = F) to rearrange is not yet understood.

Experimental Section

General. ^1H NMR and ^2H NMR spectra were obtained at ambient temperature at 80 and 400 MHz for ^1H and 61.42 MHz for ^2H (Bruker AM-400). Chemical shifts are reported in δ relative to tetramethylsilane as an internal standard, unless otherwise indicated. ^{19}F NMR spectra were recorded on a Bruker WP-80 (75.4 MHz) spectrometer; chemical shifts (δ) are relative to $CFCl_3$. IR spectra were recorded on a Perkin-Elmer 257 instrument. GC analyses were run on a Siemens Sichromat equipped with glas capillary columns. Preparative GC utilized Varian Aerograph 920 instruments equipped with packed glass columns. HPLC 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

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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 pentane in an ultrasound bath. Moisture and light should be excluded during these procedures.

Preparation of Diazo Compounds.[29] 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 ($ArCDN_2$) was achieved when $NaOD-D_2O$ was employed in this procedure.

Dediazoniation of Diazo Compounds. The apparatus used for the flash vacuum pyrolysis of tosylhydrazone sodium salts (280–300 °C, 10^{-3} Torr) has been described elsewhere.[30] For the pyrolysis of diazo compounds (e.g., $ArCDN_2$), the apparatus was adapted to injection of small liquid samples through a septum. Gas phase photolysis of diazo compounds was achieved by slowly evaporating the sample (0.5 g) at 10^{-3} Torr into a 2 L flask equipped with an immersion well (Pyrex) in which a medium-pressure mercury arc (Hannovia 150 W) was located. A cold trap cooled by liquid nitrogen was connected to the outlet of the reaction vessel on one side and to the vacuum pump on the other side. The rate of evaporation was adjusted by the temperature of the sample (0–30 °C, water bath) to ensure complete photolysis. If unreacted diazo compound was found in the cold trap, the condensate was returned to the sample flask and passed through the reactor for a second time. Diazo compounds **57** and **70** were not sufficiently volatile for photolysis by this technique. With few exceptions noted in Table 1, photolyses in solution were performed by means of a medium-pressure mercury arc (Pyrex, N_2, 20 °C).

(2-Methylphenyl)diazomethane (4). Photolysis of **4** in the gas phase, according to the standard procedure, afforded bicyclo[4.2.0]octa-1,3,5-triene (**11**, 38.5%), ethenylbenzene (**13**, 54.7%), 1,2-dimethylbenzene (**15**, 1.1%), and 2-methylbenzaldehyde (**16**, 5.7%) in a combined yield of 21.2% (GC). Nonvolatile materials accumulating on the walls of the photoreactor were not analyzed.

Photolysis of **4** (0.04 M) in cyclohexane gave the results specified in Scheme 2 (GC, tetralin as an internal standard). After the solution was concentrated in vacuo, **17** and **18** were isolated by HPLC (SiO_2, hexane:ether = 9:1). 1-(Cyclohexylmethyl)-2-methylbenzene (**17**): ^1H NMR ($CDCl_3$) δ 0.83–1.8 (11 H, m), 2.25 (3 H, s), 2.38 (2 H, d, $J = 6.5$ Hz), 7.0–7.2 (4 H, m). The 2,2′-dimethylstilbenes (*E*)-**18** and (*Z*)-**18** were identified by comparing their NMR spectra with those recorded in the literature.[31] 2-Methylbenzaldehyde azine[32] was not detected in the reaction mixture, although an authentic sample was readily recovered in both GC and HPLC.

(2-Ethylphenyl)diazomethane (20). The diazo compound **20** (λ_{max} 280 and 485 nm) was prepared from tosylhydrazone **19**[16] and photolyzed according to the standard procedure. A low-pressure mercury arc and quartz vessels were used for photolysis at 254 nm. In order to cut off UV light (<400 nm), a 0.1 M solution of sodium nitrite was circulated through the cooling jacket of the medium-pressure mercury arc. Products **21**, **22** (both available from Aldrich), **24**,[33,34] **25**,[35] and **27**[36] were analyzed by GC (79 m OV 17, 90–110 °C), with tetralin as an internal standard for estimating the yields (Table 1). No attempt was made to identify the products resulting from reactions with the solvents.

1-Methyl-2-(2,2,2-trifluoroethyl)benzene (32). In close analogy to a published procedure,[22] 1-(2-methylphenyl)-2,2,2-trifluoroethanone (**28**)[37] (7.1 g, 37.7 mmol) was reduced with $NaBH_4$ (0.46 g, 12 mmol) in 20 mL of 90% dioxane to give 7.1 g (99%) of crude (98%, GC) 1-(2-methylphenyl)-2,2,2-trifluoroethanol (**29**): ^1H NMR ($CDCl_3$) δ 2.02 (3 H, s), 2.70 (1 H, d, $J = 5.0$ Hz), 4.92 (1 H, qd, $J_{HF} = 6.7$ Hz, $J_{HH} = 5.0$ Hz), 6.8–7.2 (3 H, m), 7.4–7.7 (1 H, m); ^{19}F NMR (C_6D_6) δ −77.59 (d, $J = 6.7$ Hz).

Following the procedure reported for 1-phenyl-2,2,2-trifluoroethyl tosylate,[38] **29** was treated with NaH in ether and then with *p*-toluenesulfonyl chloride, yielding 89% of the tosylate **30**, mp 66–67 °C: ^1H NMR ($CDCl_3$) δ 2.4 (6 H, br s), 6.0 (1 H, q, $J = 6.0$ Hz), 7.0–7.4 (6 H, m), 7.4–7.7 (2 H, m); ^{19}F NMR ($CDCl_3$) δ −77.1 (d, $J = 6.0$ Hz). Hydrogenolysis of **30** over 10% Pd–C in 95% ethanol, at room temperature and atmospheric pressure, gave **32** in 93% yield (GC). The solution was concentrated by distillation through a 20 cm Vigreux column. PGC (2 m SE 30, 100 °C) afforded pure **32**: ^1H NMR ($CDCl_3$) δ 2.32 (3 H, s), 3.35 (2 H, q, $J = 10.7$ Hz), 7.1–7.2 (4 H, m); ^{19}F NMR δ −66.3 (t, $J = 10.7$ Hz). Anal. Calcd for $C_9H_9F_3$: C, 62.07; H, 5.21. Found: C, 61.89; H, 5.30.

Alternatively, 3.0 g (20 mmol) of (2-methylphenyl)acetic acid (**31**) and a catalytic amount (ca. 0.1 g) of water were placed in a stainless-steel autoclave, 8.6 g (80 mmol) of SF_4 was introduced on a vacuum line, and the mixture was stirred at 120 °C for 4.5 h. After cooling to room temperature, gases from the autoclave were absorbed in an aqueous solution of calcium chloride, and the residue was triturated with *n*-pentane. The solution was filtered, neutralized with $NaHCO_3$, washed with water, dried with $MgSO_4$, and concentrated by distillation. The liquid product (1.55 g, 50%) consisted of two components (85:15, GC) which were separated by PGC (2 m SE 30, 100 °C). The major component was identical in every respect with the sample of **32** obtained above. The minor product (ν_{co} 1840 cm^{-1}) was tentatively assigned as (2-methylphenyl)acetyl fluoride (ν_{co} 1843 cm^{-1}was reported for phenylacetyl fluoride).[39]

[2-(2,2,2-Trifluoroethyl)phenyl]diazomethane (36). A solution of **32** (5.25 g, 30.1 mmol), NBS (5.36 g, 30.1 mmol), and dibenzoyl peroxide (50 mg, 0.2 mmol) in CCl_4 (100 mL) was refluxed for 1 h. Additional dibenzoyl peroxide (25 mg, 0.1 mmol) was added, and heating was continued for 30 min. The mixture was cooled, filtered, and distilled to give 4.98 g (65%) of 1-(bromomethyl)-2-(2,2,2-trifluoroethyl)benzene (**33**): bp 67–69 °C (0.8 Torr); ^1H NMR ($CDCl_3$) δ 3.57 (2 H, q, $J = 10.6$ Hz), 4.54 (2 H, s), 7.2–7.4 (4 H, m); ^{19}F NMR ($CDCl_3$) δ −66.1 (t, $J = 10.6$ Hz).

Sodium (0.46 g, 20 mmol) was dissolved 20 mL of ethanol. 2-Nitropropane (2.29 g, 25.5 mmol) and **33** (4.90 g, 19.4 mmol) were added to the solution of sodium ethoxide. After being stirred at room temperature for 15 h, the mixture was diluted with water and extracted with ether. The extracts were washed with 10% NaOH and water, dried ($MgSO_4$), and concentrated by distillation. An amount of 3.2 g (88%) of crude 2-(2,2,2-trifluoroethyl)benzaldehyde (**34**) was obtained as a yellow liquid: ^1H NMR ($CDCl_3$) δ 4.01 (2 H, q, $J = 10.3$ Hz), 7.3–7.9 (4 H, m), 10.09 (1 H, s); ^{19}F NMR ($CDCl_3$) δ −66.1 (t, $J = 10.3$ Hz); ν_{co} 1702 cm^{-1}. This material was carried on without purification.

An amount of 3.0 g (15.9 mmol) of crude **34** and 3.1 g (16.7 mmol) of tosylhydrazine, dissolved in 80 mL of methanol, were stirred for 1 h at 60 °C. Crystallization at 5 °C afforded 4.2 g (74%) of the tosylhydrazone **35**: mp 174–175 °C; ^1H NMR ($CDCl_3$) δ 2.42 (3 H, s), 3.65 (2 H, q, $J = 10.3$ Hz), 7.2–7.7 (7 H, m), 7.85 (2 H, d, $J = 8$ Hz), 7.95 (1 H, s); ^{19}F NMR ($CDCl_3$)

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δ −66.1 (t, J = 10.3 Hz). Anal. Calcd for $C_{16}H_{15}F_3N_2O_2S$: C, 53.93; H, 4,24; N, 7.86. Found: C, 53.85; H, 4,33; N, 8.04.

The sodium salt of **35** was prepared and pyrolyzed according to the standard protocol. The product mixture (Scheme 5) was obtained in 50% yield. PGC (5 m DC 200, 105 °C) afforded 7-(trifluoromethyl)bicyclo[4.2.0]octa-1,3,5-triene (**39**): ^{1}H NMR ($CDCl_3$) δ 3.32 (1 H, dd, J = 14.0 and 2.7 Hz), 3.42 (1 H, dd, J = 14.0 and 5.5 Hz), 4.08 (1 H, qdd, J = 8.7, 5.5, and 2.7 Hz), 7.1−7.4 (4 H, m); ^{19}F NMR ($CDCl_3$) δ −72.8 (d, J = 8.7 Hz). Anal. Calcd for $C_9H_7F_3$: C, 62.79; H, 4.10. Found: C, 62.88; H, 4.09. The minor components (*E*)- and (*Z*)-1-phenyl-3,3,3-trifluoropropene (**40**) were identified by comparison with authentic samples.[40]

Similarly, D-**39** was isolated from the gas phase pyrolysis and photolysis of D-**36**. The ^{2}H NMR spectra of these samples revealed that the position α to CF_3 was undeuterated (no signal at δ 4.08, broad peak at δ 3.4). The (*E*):(*Z*) distributions of deuterium (Scheme 6) were obtained from 400 MHz ^{1}H NMR spectra, taking the signal at δ 4.08 as reference (≡ 1.00 H).

Photolyses of **36** in benzene afford mainly arylcycloheptatrienes (Scheme 5). *Four isomers in the ratio 56:29:9:6* were indicated by GC. Separation by HPLC (Polygosil-NO_2, hexane) yielded the major isomer (56%) as the first fraction: 7-[2-(2,2,2-trifluoroethyl)phenyl]cycloheptatriene (**41**): ^{1}H NMR ($CDCl_3$) δ 2.91 (1 H, t, J = 5.5 Hz), 3.32 (2 H, q, J = 10.5 Hz), 5.32 (2 H, dd, J = 9.0 and 5.5 Hz), 6.25 (2 H, dm, J = 9.0 Hz), 6.75 (2 H, m), 7.25−7.35 (2 H, m), 7.43 (1 H, td, J = 6.8 and 2.0 Hz), 7.58 (1 H, dd, J = 7.8 and 1.0 Hz); ^{19}F NMR ($CDCl_3$) δ −66.5 (t, J = 10.5 Hz). The second fraction contained three isomers. The most prominent species, corresponding to 29% of the original mixture, is assigned as 2-[2-(2,2,2-trifluroethyl)-phenyl]cycloheptatriene: ^{1}H NMR ($CDCl_3$) δ 2.38 (2 H, t, J = 7.0 Hz), 3.22 (2 H, q, J = 10.8 Hz), 5.25 (1 H, t, J = 7.0 Hz), 5.58 (1 H, dt, J = 9.3 and 7.0 Hz), 6.20 (1 H, dd, J = 9.3 and 5.4 Hz), 6.55 (1 H, d, J = 11.2 Hz), 6.64 (1 H, dd, J = 11.2 and 5.4 Hz), 7.2−7.4 (4 H, m).

In addition to arylcycloheptatrienes, the photolysis of **36** in benzene produced small amounts of the stilbenes **42** and of the azine **43** (Scheme 5), as indicated by GC. These compounds were more conveniently obtained by keeping neat **36** for 6 h at 30 °C. By means of HPLC (SiO_2, hexane:ether = 20:1), (*E,Z*)-**42** was separated from **43**, the latter being identified by ^{1}H NMR ($CDCl_3$) δ 3.82 (4 H, q, J = 9.9 Hz), 7.2−7.6 (6 H, m), 7.9−8.1 (2 H, m), 8.92 (2 H, s). Less-polar HPLC conditions (SiO_2, hexane) were then employed to separate (*E*)- and (*Z*)-**42**. ^{1}H NMR ($CDCl_3$): (*E*)-**42** δ 3.52 (4 H, q, J = 10.6 Hz), 7.2−7.7 (10 H, m); (*Z*)-**42** δ 3.43 (4 H, q, J = 10.7 Hz), 6.8−7.4 (10 H, m). These spectra do not reveal the configuration of the stereoisomers. In order to identify the "hidden" olefinic protons, the stilbenes obtained from D-**36** were analyzed by ^{2}H NMR ($CHCl_3$): (*E*)-**42** δ 7.20; (*Z*)-**42** δ 6.78. As a rule, the olefinic protons of (*Z*)-stilbenes are more shielded than those of (*E*)-stilbenes.[41]

[2-(Fluoromethyl)phenyl]diazomethane (49). To a solution of potassium fluoride (5.81 g, 0.1 mol) in methanol (160 mL) was added calcium fluoride (7.81 g, 0.1 mol). The solvent was removed, and the residue was dried in vacuo at 100 °C for 1 h. The solid thus obtained was added to a solution of 1,2-bis(bromomethyl)benzene (13.2 g, 50 mmol) in acetonitrile (100 mL). After being refluxed for 90 h, the mixture was partitioned between water and ether. The ether extracts were dried ($MgSO_4$) and concentrated. Fractional distillation of the residue afforded 3.1 g (31%) of 1-(bromomethyl)-2-(fluoromethyl)benzene (**46**): bp 56 °C (0.2 Torr); ^{1}H NMR ($CDCl_3$) δ 4.58 (2 H, d, J = 0.5 Hz), 5.55 (2 H, d, J = 46.8 Hz), 7.3−7.4 (4 H, m).

The procedure described for **33** was applied to **46** (3.0 g, 14.8 mmol), yielding 2.0 g (100%) of crude 2-(fluoromethyl)benzaldehyde (**47**): ^{1}H NMR ($CDCl_3$) δ 5.84 (2 H, d, J = 47.6 Hz), 7.45−7.75 (3 H, m), 7.86 (1 H, ddd, J = 7.0, 2.1, and 1.0 Hz), 10.09 (1 H, d, J = 1.6 Hz). A solution of crude **47** (2.0 g, 14.5 *mmol) was added to a concentrated solution of tosylhydrazine* (2.7 g, 14.5 mmol) in methanol. The mixture was stirred for 14 h at room temperature under nitrogen. The precipitate was filtered with suction and recrystallized from methanol to give 1.7 g (38%) of the tosylhydrazone **48**: mp 128−129 °C; ^{1}H NMR ($CDCl_3$) δ 2.44 (3 H, s), 5.53 (2 H, d, J = 46.8 Hz), 7.3−7.7 (6 H, m), 7.90 (2 H, d, J = 8.0 Hz), 7.96 (1 H, s), 8.18 (1 H, br s). Anal. Calcd for $C_{15}H_{15}FN_2O_2S$: C, 58.80; H, 4.95; N, 9.14. Found: C, 58.73; H, 4.91; N, 9.28.

The sodium salt of **48** and the diazo compound **49** were obtained according to the standard procedures. Flash pyrolysis afforded in 30% yield a 2:98 mixture of **47** and 7-fluorobicyclo[4.2.0]octa-1,3,5-triene (**51**): ^{1}H NMR ($CDCl_3$) δ 3.35 (1 H, ddd, J_{HH} = 14.5 and 1.5 Hz, J_{HF} = 10.5 Hz), 3.60 (1 H, ddd, J_{HH} = 14.5 and 4.3 Hz, J_{HF} = 5.2 Hz), 5.92 (1 H, J_{HH} = 4.3 and 1.7 Hz, J_{HF} = 57.2 Hz). ^{2}H NMR (CCl_4) of D-**51** from the pyrolysis and photolysis of D-**49**: δ 3.38 and 3.63 (Scheme 7). Anal. Calcd for C_8H_6DF: C, 78.01; H, 6.56. Found: C, 78.05; H, 6.47.

Photolysis of **49** in benzene afforded in 45% yield (GC) a mixture (55:23:22) of [2-(fluoromethyl)phenyl]cycloheptatrienes. Anal. Calcd for $C_{14}H_{13}F$: C, 83.96; H, 6.56. Found: C, 83.77; H, 6.53. Attempted separation by HPLC (SiO_2, *n*-pentane) gave as the first fraction 7-[2-(fluoromethyl)phenyl]cycloheptatriene (**52**): ^{1}H NMR (C_6D_6) δ 3.10 (1 H, d, J = 5.5 Hz), 5.04 (2 H, d, J = 48.0 Hz), 5.26 (2 H, dd, J = 9.0 and 5.5 Hz), 6.11 (2 H, dm, J = 9.0 Hz), 6.5−6.6 (2 H, m), 7.05−7.25 (3 H, m), 7.34 (1 H, d, J = 7.8 Hz). Two isomers found in the second fraction were assigned as 1-[2-(fluoromethyl)phenyl]cycloheptatriene: ^{1}H NMR (C_6D_6) δ 2.53 (2 H, d, J = 7.0 Hz), 5.12 (2 H, d, J = 48.3 Hz), 5.19 (1 H, dt, J = 9.0 and 7.0 Hz), 6.06 (1 H, dm, J = 6.0 Hz), 6.12 (1 H, dm, J = 9.0 Hz), 6.43−6.47 (2 H, m), 7.0−7.4 (4 H, m), and 2-[2-(fluoromethyl)phenyl]cycloheptatriene: ^{1}H NMR (C_6D_6) δ 2.14 (2 H, t, J = 7.0 Hz), 5.15 (2 H, d, J = 48.3 Hz), 5.13 (1 H, t, J = 7.0 Hz), 5.26 (1 H, dt, J = 9.3 and 7.0 Hz), 6.03 (1 H, dd, J = 9.3 and 5.5 Hz), 6.42 (1 H, dd, J = 11.2 and 5.5 Hz), 6.53 (1 H, d, J = 11.2 Hz), 7.0−7.3 (3 H, m), 7.39 (1 H, d, J = 7.8 Hz). Very minor amounts of 2-(fluoromethyl)toluene, **51**, **47**, and 2-(fluoromethyl)benzaldehyde azine were detected among the photolysis products of **49** by GC and HPLC. For comparison, the azine was prepared from **47** by a standard procedure:[42] ^{1}H NMR ($CDCl_3$) δ 5.80 (4 H, d, J = 47.8), 7.3−7.7 (6 H, m), 7.75−8.0 (2 H, m), 8.83 (2 H, d, J = 1.2 Hz). Anal. Calcd for $C_{16}H_{14}F_2N_2$: C, 70.56; H, 5.19; N, 10.29. Found: C, 70.60; H, 5.28; N, 10.33.

The product mixture obtained on photolysis of **49** in hexafluorobenzene was separated by HPLC (SiO_2, hexane: ether = 99:1). Products are listed in the order of elution (relative yields by GC): 41.7% of 7-[2-(fluoromethyl)phenyl]-1,2,3,4,5,6-hexafluorocycloheptatriene (**53**): ^{1}H NMR (C_6D_6) δ 4.59 (1 H, tt, J = 23.3 and 6.0 Hz), 4.90 (2 H, d, J = 47.7 Hz), 6.7−6.9 (4 H, m). Anal. Calcd for $C_{14}H_7F_7$: C, 54.55; H, 2.29. Found: C, 54.47; H, 2.35. 35.5% of (*Z*)-2,2′-bis(fluoromethyl)-stilbene (*Z*-**54**), ^{1}H NMR (C_6D_6) δ 5.07 (4 H, d, J = 48.1 Hz), 6.57 (2 H, s), 6.75 (2 H, tm, J = 7.5 Hz), 6.88 (2 H, tm, J = 7.5 Hz), 6.95 (2 H, dm, J = 7.5 Hz), 7.14 (2 H, dm, J = 7.5 Hz). 22.8% of (*E*)-2,2′-bis(fluoromethyl)stilbene (*E*-**54**): ^{1}H NMR (C_6D_6) δ 5.11 (4 H, d, J = 48.1), 7.00 (2 H, tm, J = 7.3 Hz), 7.08 (2 H, tm, J = 7.3 Hz), 7.11 (2 H, dm, J = 7.3 Hz), 7.25 (2 H, s), 7.46 (2 H, dm, J = 7.3 Hz). Anal. Calcd for $C_{16}H_{14}F_2$: C, 78.66; H, 5.79. Found (*E,Z* mixture): C, 78.65; H, 5.70.

[2-[(Trimethylsilyl)methyl]phenyl]diazomethane (57). To a solution of tosylhydrazine (3.4 g, 18.2 mmol) in methanol (25 mL) was added 2-[(trimethylsilyl)methyl]benzaldehyde (**55**)[24] (3.5 g, 18.2 mmol). The mixture was stirred for 24 h at room temperature under nitrogen. The precipitate was filtered with suction, recrystallized from methanol, and dried over calcium chloride (35 °C, 10^{-2} Torr, 24 h) to give 4.4 g (67%) of the tosylhydrazone **56**: mp 108−109 °C; ^{1}H NMR ($CDCl_3$) δ −0.10 (9 H, s), 2.24 (2 H, s), 2.39 (3 H, s), 6.94 (1 H, dd, J = 7.8 and 1.3 Hz), 7.06 (1 H, td, J = 7.8 and 1.5 Hz), 7.19 (1 H, td, J = 7.8 and 1.3 Hz), 7.28 (2 H, d, J = 8.2 Hz), 7.63 (1 H, dd, J = 7.8 and 1.5 Hz), 7.85 (2 H, d, J = 8.2 Hz), 7.95 (1 H,

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s), 7.96 (1 H, br s). Anal. Calcd for $C_{18}H_{24}N_2O_2SSi$: C, 59.95; H, 6.72. Found: C, 60.10; H, 6.89. In order to obtain D-**56**, the synthesis started from methyl 2-methylbenzoate (8.0 g, 53.3 mmol) which was reduced with $LiAlD_4$ (1.3 g, 31 mmol) in ether (50 mL) to give 5.3 g (80%) of dideuterated 2-methylbenzyl alcohol. The further steps leading to D-**55** were as reported.[24b]

Flash pyrolysis of the sodium salt of **56** afforded 39.7% of bicyclo[4.2.0]octa-1,3,5-trien-7-yltrimethylsilane (**59**),[33,43] 7.0% of 2,3-dihydro-1,2,2-trimethyl-1*H*-2-silaindene (**60**), and 53.3% of 2,2-dimethyl-1,2,3,4-tetrahydro-2-silanaphthalene (**61**).[44] The components were separated by PGC (2 m Carbowax, 130 °C). ^1H NMR ($CDCl_3$) of **59**: δ −0.03 (9 H, s), 2.91 (1 H, dd, J = 14.0 and 3.0 Hz), 2.98 (1 H, dd, J = 6.0 and 3.0 Hz), 3.24 (1 H, dd, J = 14.0 and 6.0 Hz), 6.92 (1 H, m), 6.99 (1 H, m), 7.09 (1 H, m), 7.14 (1 H, m). The spectrum was previously recorded at low resolution, without distinguishing the aliphatic protons.[43] D-**59**: ^2H NMR (CCl_4) δ 3.0 (93%), 3.3 (7%). ^1H NMR ($CDCl_3$) integration showed 2.02 H at δ 2.8−3.3 (relative to 4 ArH) of which 0.16 H appeared at δ 2.98. By difference, the species contains 0.98 D of which 86% is located α to silicon (Scheme 8).

For an unequivocal structural assignment of **60**, 2,3-dihydro-2,2-dimethyl-1*H*-2-silaindene[45] (0.33 g, 2.0 mmol) in *n*-hexane (20 mL) was metalated with KO-*t*-Bu (0.26 g, 2.3 mmol) and *n*-BuLi (2.2 mmol). After 30 min at room temperature, methyl iodide (0.43 g, 3 mmol) was added, and stirring was continued for 4 h. The reaction was then quenched with water. The organic phase was dried ($MgSO_4$) and concentrated by distillation. PGC of the residue afforded pure **60**: ^1H NMR ($CDCl_3$) δ 0.10 (3 H, s), 0.21 (3 H, s), 1.28 (3 H, d, J = 7 Hz), 2.00 (2 H, s), 2.17 (1 H, q, J = 7 Hz), 6.95−7.3 (4 H, m).

[2-(2,2-Dimethylpropyl)phenyl]diazomethane (70). 3-(2,2-Dimethylpropyl)phthalide (**66**)[27] (2.65 g, 13.9 mmol) was added to a solution of sodium hydroxide (0.71 g, 17.8 mmol) in water (2o mL). The mixture was heated at 95 °C for 45 min. After cooling to room temperature, the solution was buffered with 3.1 g of sodium hydrogen phosphate and 0.22 g of phosphoric acid (pH 8−9). Hydrogenolysis was performed over 0.49 g of 10% Pd−C, at 120 °C and 2.8 atm, for 14 h. The solution was filtered, acidified with dilute hydrochloric acid, and extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and evaporated to give 2.1 g (79%) of 2-(2,2-dimethylpropyl)benzoic acid (**67**): mp 79−80 °C; ^1H NMR ($CDCl_3$) δ 0.93 (9 H, s), 3.13 (2 H, s), 7.1−7.6 (3 H, m), 7.99 (1 H, dd, J = 7.2 and 2.0 Hz), 10.7 (1 H, br s).

Reduction of **67** (2.0 g, 10.4 mmol) with $LiAlH_4$ (0.30 g, 7.8 mmol) in ether (60 mL) at reflux for 5 h afforded 1.6 g (86%) of 2-(2,2-dimethylpropyl)benzyl alcohol: bp 61 °C (0.2 Torr); ^1H NMR ($CDCl_3$) δ 0.75 (9 H, s), 1.40 (1 H, s), 2.44 (2 H, s), 4.56 (2 H, s), 6.9−7.4 (4 H, m).

To a solution of 22.2 g (0.28 mol) of pyridine in 110 mL of glacial acetic acid in portions 14.0 g (0.14 mol) of chromium trioxide was added with vigorous stirring while the temperature was kept at 10−15 °C. The solution was diluted with 175 mL of glacial acetic acid and cooled to 5 °C; then 2.5 g (14 mmol) of 2-(2,2-dimethylpropyl)benzyl alcohol in 35 mL of ether was added during 10 min. The mixture was stirred for additional 15 min, poured into water, and extracted with ether. The extract was washed with water and made basic with solid $NaHCO_3$ and then washed with a saturated solution of $NaHCO_3$, dried ($MgSO_4$), and concentrated to give 2.0 g (81%) of 2-(2,2-dimethylpropyl)benzaldehyde (**68**): ^1H NMR ($CDCl_3$) δ 0.73 (9 H, s), 2.82 (2 H, s), 6.9−7.45 (3 H, m), 7.70 (1 H, dd, J = 6.0 and 1.9 Hz), 10.15 (1 H, s); IR (film) ν_{co} 1690 cm^{-1}.

To a solution of 2.1 g (11.3 mmol) of tosylhydrazine in 20 mL of methanol was added 2.0 g (11.3 mmol) of crude **68**. The mixture was stirred at room temperature for 14 h under nitrogen. The precipitate was filtered with suction, recrystallized from methanol, and dried in vacuo to give 3.3 g (84%) of the tosylhydrazone **69**: mp 158 °C; ^1H NMR ($CDCl_3$) δ 0.80 (9 H, s), 2.40 (3 H, s), 2.59 (2 H, s), 6.95−7.4 (6 H, m), 7.7−7.95 (3 H, m), 8.12 (1 H, s). Anal. Calcd for $C_{19}H_{24}N_2O_2S$: C, 66.23; H, 7.04; N, 8.13. Found: C, 66.32; H, 7.11; N, 8.20.

The sodium salt of **69** and the diazo compound **70** were prepared according to the standard procedures. Thermolysis and photolysis of **70** gave mainly 2,2-dimethyltetralin (**75**),[46] together with small amounts of **68** and **74** (Scheme 9). Flash pyrolysis (550 °C, 10^{-2} Torr)[33] of 2-(2,2-dimethylpropyl)benzyl chloride was employed as an alternative approach to 7-(2,2-dimethylpropyl)bicyclo[4.2.0]octa-1,3,5-triene (**74**): ^1H NMR ($CDCl_3$) δ 0.95 (9 H, s), 2.83 (1 H, dd, J = 14.0 and 3.2 Hz), 3.01 (1 H, dd, J = 14.0 and 5.2 Hz), 3.34 (1 H, dd, J = 5.2 and 3.2 Hz), 6.95−7.45 (4 H, m). Anal. Calcd for $C_{12}H_{16}$: C, 89.92; H, 10.08. Found: C, 89.75; H, 10.08.

Addition of 4.3 g (50 mmol) of 2,2-dimethylpropanal in 50 mL of ether to benzylmagnesium chloride, prepared from 6.33 g (50 mmol) of benzyl chloride and 1.22 g (50 mmol) of magnesium turnings in 100 mL of ether, followed by conventional workup, afforded 5.6 g (63%) of 1-phenyl-3,3-dimethylbutan-2-ol: bp 55 °C (0.2 Torr); ^1H NMR ($CDCl_3$) δ 1.07 (9 H, s), 2.09 (1 H, br s), 2.51 (1 H, dd, J = 13.8 and 10.6 Hz), 2.98 (1 H, dd, J = 13.8 and 2.4 Hz), 3.49 (1 H, dd, J = 10.6 and 2.4 Hz), 7.2−7.4 (4 H, m). To a solution of this alcohol (1.0 g, 5.6 mmol) in pyridine (30 mL) was added at 0 °C thionyl chloride (8.9 g, 74.7 mmol) during 1.5 h. After being stirred for additional 5 h, the mixture was poured onto ice and extracted with ether. The extract was washed with water and $NaHCO_3$, dried ($MgSO_4$), and concentrated. The yellow oil (0.78 g, 87%) was purified by HPLC (SiO_2, *n*-hexane) to give (*E*)-1-phenyl-3,3-dimethyl-1-butene (**73**): ^1H NMR ($CDCl_3$) δ 1.11 (9 H, s), 6.24 (1H, d, J = 16.2 Hz), 6.31 (1 H, d, J = 16.2 Hz), 7.17 (1 H, t, J = 7.5 Hz), 7.27 (2 H, t, J = 7.5 Hz), 7.35 (2 H, d, J = 7.5 Hz). **73** was not detected by GC in the product mixtures obtained from **70**.

Methyllithium (18.8 mmol) was added to 2,2-dimethyl-1-indanone[47] (1.5 g, 9.4 mmol) in ether (30 mL). The mixture was refluxed for 14 h and then partitioned between water and ether. The organic phase was dried ($MgSO_4$) and distilled to give 1.2 g (72%) of 1,2,2-trimethylindan-1-ol: ^1H NMR ($CDCl_3$) δ 1.00 (3 H, s), 1.09 (3 H, s), 1.38 (3 H, s), 1.90 (1 H, br s), 2.55 (1 H, d, J = 15 Hz), 2.87 (1 H, d, J = 15 Hz), 7.0−7.4 (4 H, m). Hydrogenolysis of this alcohol (0.30 g, 1.7 mmol) in ether over 10% Pd−C (50 mg), at room temperature and atmospheric pressure, followed by HPLC (SiO_2, *n*-pentane), afforded 0.22 g (81%) of 1,2,2-trimethylindan: ^1H NMR ($CDCl_3$) δ 0.89 (3 H, s), 1.19 (3 H, d, J = 7.2 Hz), 1.20 (3 H, s), 2.71 (2 H, s), 2.84 (1 H, q, J = 7.2 Hz), 7.1−7.3 (4 H, m). 1,2,2-Trimethylindane was not detected by GC in the product mixtures obtained from **70**.

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