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Cationic Carbenoid Rearrangement of 2-Phenyl Substituted *gem*-Dihalogenospiropentanes

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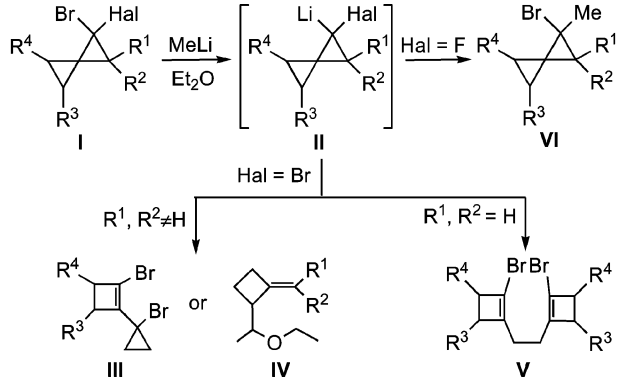
The series of 2-phenyl- and 2,2-diphenyl *gem*-dihalogenospiropentanes were employed as model compounds to study the carbenoid rearrangement with the use of methyllithium. The scope and limitations of this skeletal rearrangement are outlined and its mechanism is discussed.

Introduction

Reaction of *gem*-dihalogenocyclopropanes with alkyllithium reagents is known as a traditional way to obtain substituted allenes (Doering–Skattebol–Moore reaction).[1] However, we have recently reported that some *gem*-dihalogenospiropentanes react with methyllithium in an unusual way: lowering the reaction temperature prevents the formation of allenes and leads to carbenoid skeletal rearrangement.[2] The final steps of this reaction are quite variable and may include halogenophilic processes,[3] insertion into a C–H bond of the solvent,[4] and substitution of the halogen atom for a methyl group.[5] The preferable reaction path is determined by the substituents in the spiropentane moiety as well as by the nature of the halogen atoms (Scheme 1).



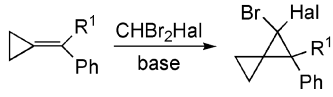
Scheme 1. Reaction of *gem*-dihalogenospiropentanes with methyllithium.

While studying a series of model *gem*-dihalogeno-substituted spiropentanes in the reaction with methyllithium, we had to accept the carbocationic transformation of lithium carbenoid intermediate as the only possible pathway of the rearrangement of **I** into **III**–**V**. Aiming to find out the mechanistic reasons laying beyond this fact and taking into account the ability of phenyl substituents to stabilize the neighboring carbocationic center, we synthesized a series of 2-phenyl-substituted *gem*-dihalogenospiropentanes and studied their reactions with methyllithium.

Results and Discussion

Model *gem*-dihalogenospiropentanes **1**–**9** were obtained by cycloaddition of dihalogenocarbenes to alkylidenecyclopropanes, which were synthesized by a Wittig reaction[6] (Table 1). We chose Makosza conditions[7] for the cycloaddition of mixed dihalogenocarbenes and Doering–Hoffmann conditions[8] for the cycloaddition of dibromocarbene. In the synthesis of mixed bromochloro-substituted

Table 1. Synthesis of model *gem*-dihalogenospiropentanes.



Entry	*gem*-Dihalogenospiropentane	Isolated yields [%]
1	R^1 = Ph, Hal = F	35[a]
2	R^1 = Ph, Hal = Cl	61[b]
3	R^1 = Ph, Hal = Br	58[c]
4	R^1 = Me, Hal = F	39[a]
5	R^1 = Me, Hal = Cl	60[b]
6	R^1 = Me, Hal = Br	53[c]
7	R^1 = H, Hal = F	51[a]
8	R^1 = H, Hal = Cl	53[b]
9	R^1 = H, Hal = Br	55[c]

[a] Conditions: $CHBr_2F$, dibenzo-18-crown-6, NaOH 50%, CH_2Cl_2. [b] Conditions: $CHBr_2Cl$, TEBAC (triethylbenzylammonium chloride), NaOH 50%, CH_2Cl_2. [c] Conditions: $CHBr_3$, *t*BuOK, petroleum ether.

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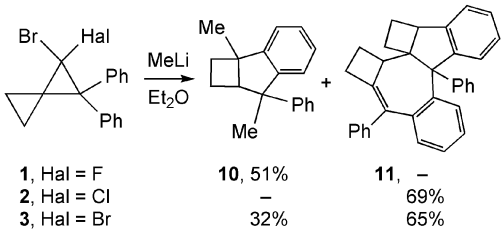
spiropentanes, we used dibenzo-18-crown-6 as a phase-transfer catalyst[9] to avoid a mixture of products.

gem-Dihalogenospiropentanes **1**–**9** were studied in the reaction with methyllithium under appropriate conditions depending on the halogen atoms. Previously, we showed that the most favorable conditions for the rearrangement of *gem*-dibromospiropentanes were –55 °C,[2,3] whereas bromofluorospiropentanes reacted with methyllithium at 0 °C or higher temperatures.[5] Bromochloro-substituted spiropentanes **2**, **5**, and **8** were treated with methyllithium at –65 °C.

We found that the reaction of 2,2-diphenylspiropentanes **1**–**3** with methyllithium led to monomeric (**10**) or dimeric (**11**) products resulting from isomerization of the spiropentane moiety into a four-membered ring followed by S_E substitution and fusion of the cycles (Scheme 2). Their ratio was found to depend dramatically on the nature of the halogen atoms in the starting spiropentane. Treatment of bromofluoride **1** with methyllithium afforded only monomeric product **10**, whereas the reaction of bromochloride **2** led to dimeric product **11** exclusively, and dibromospiropentane **3** gave a mixture of both products in high total yield.

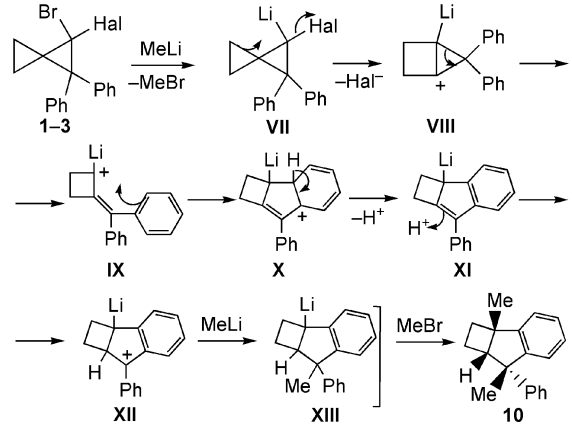


Scheme 2. Reaction of 2,2-diphenyl *gem*-dihalogeno-substituted spiropentanes with methyllithium.

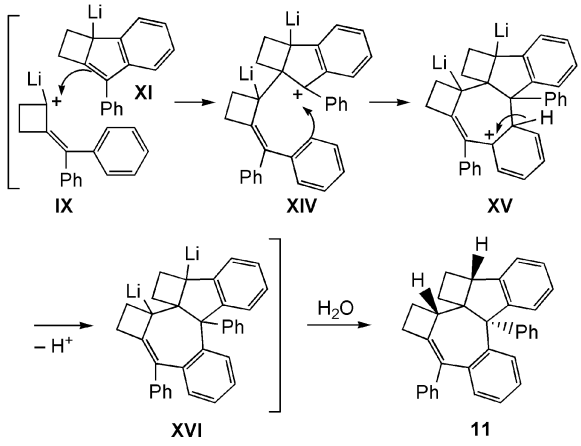
Obviously, the formation of products **10** and **11** is a result of intra- or intermolecular carbocationic cyclization with the participation of the phenyl ring. The presence of two phenyl rings at the 2-position to the carbenoid center is essential for the formation of polycycles **10** and **11**. We can suppose that this cyclization proceeds by *ortho*-electrophilic substitution in the phenyl ring, where the carbocationic center of intermediate **IX** acts as the intramolecular electrophile. Double methylation of intermediate **XI** with methyllithium (acting as nucleophilic methyl source) and methyl bromide (as electrophilic methyl source) leads to compound **10** (Scheme 3).

The structure of compound **10** was determined by using NMR spectroscopy (for NMR spectroscopic data see the Experimental Section). In particular, NOE experiments indicate the relative positions of the H atom and the methyl groups in the internal five-membered cycle. NOE enhancements for the H atom were observed after irradiation of both methyl groups.

Interaction of intermediate **XI** with carbocation **IX** results in the second act of electrophilic substitution, leading to a seven-membered ring (Scheme 4). The structure of hexocyclic compound **11** was proven by single crystal X-ray analysis[10,11] (Figure 1).



Scheme 3. Formation of tricyclic product **10**.



Scheme 4. Formation of fused hexocyclic system **11**.

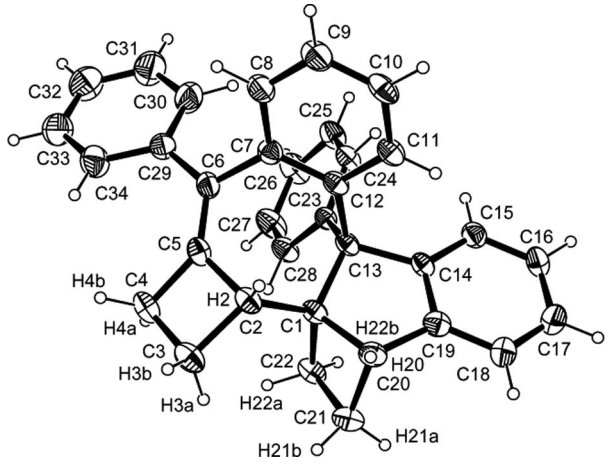


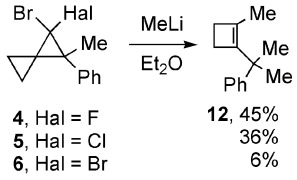
Figure 1. ORTEP-3[12] view of the molecular structure of **11** with the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level. The hydrogen atoms are presented as small circles of arbitrary radius.

The NMR spectra also confirm the structure of compound **11**. The protons of the four-membered cycles give two superimposed ABCDE spin systems. In accordance with known data,[13] cyclobutane and methylenecyclobutane fragments have characteristic differences in the values

of the ^2J and ^4J coupling constants (see the Experimental Section). The sign of long-range coupling constants was determined by using the tickling double resonance technique.

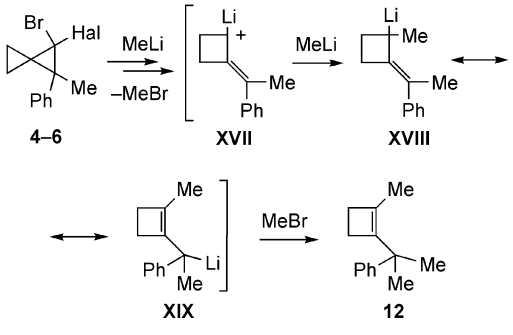
As a whole, the scheme of the reactions of 2,2-diphenyl-*gem*-dihalogenospiropentanes described above involves a number of cationic intermediates, some of them participating in electrophilic *ortho*-substitution processes leading to unique polycyclic structures.

The replacement of one of the phenyl substituents for a methyl group significantly changes the reaction pathway. Thus, 2-methyl-2-phenyl-substituted spiropentanes **4**–**6** reacted with methyllithium in quite a different way. For all the halogenides, no electrophilic substitution pathway was observed, and the main product of the reaction was cyclobutene **12**, a usual product of dihalogenospiropentane–cyclobutene rearrangement (compare **III**, Scheme 1), with the exception of two methyl groups replacing halogen atoms (Scheme 5). In the case of dibromide **6**, product **12** was obtained as a complex mixture of unidentified compounds that made the product difficult to isolate. For dihalogenides **4** and **5**, the yields of product **12** were high enough (over 70% in the case of dibromide **4**) before purification, but we observed partial decomposition of **12** during purification by column chromatography.



Scheme 5. Reaction of 2-methyl-2-phenyl-substituted *gem*-dihalogenospiropentanes with methyllithium. Yields of **12** refer to isolated product.

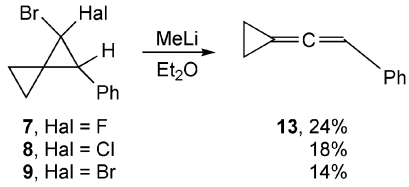
The presence of methyl groups in cyclobutene **12** should be the result of two subsequent acts of substitution, the first one being the electrophilic substitution at the saturated carbon atom in methyllithium (intermediate **XVII** as the electrophilic reagent, Scheme 6) and the second step being nucleophilic substitution reaction in methyl bromide (intermediate **XIX** as nucleophilic reagent).



Scheme 6. Formation of product **12**.

The ability of intermediates **IX** and **XVII** to act as electrophiles can be explained by their comparatively long lifetimes resulting from the additional stabilization of the cationic center by the conjugated phenyl groups.

In the case of monophenylspiropentanes **7**–**9** (the substrates containing a phenyl group as the only 2-substituent), the sole isolated product was allene **13**, that is, the product of the Doering–Skattebol–Moore reaction[1] (Scheme 7). Though compound **13** was the main product of the reaction of bromofluoride **7** with methyllithium, the yield was quite low, which was probably caused by the instability of the resulting allene, which smoothly decomposes even when stored at low temperature. For dihalogenides **8** and **9** we observed NMR signals of some rearrangement products and the mixture of unidentified compounds, which could be a result of their further transformation. We did not isolate any rearrangement products and only allene **13** was obtained in low yields in these reactions. The lower stability of the rearrangement products may be related to the possibility of side reactions of the intermediates, containing a proton in the 2-position, in the presence of methyllithium.



Scheme 7. Reaction of 2-phenyl-substituted *gem*-dihalogenospiropentanes with methyllithium.

Conclusions

Thus, significant progress was made in our studying of the unusual dihalogenospiropentane rearrangement. We have shown that the incorporation of two phenyl rings in the 2-position of the starting *gem*-dihalogenospiropentanes led to the formation of polycyclic fused compounds in the reactions with methyllithium. The products obtained by this route unambiguously confirmed the electrophilic nature of the spiropentyllithium carbenoids and a carbocationic-like mechanism of the studied rearrangement.

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker Avance-400 spectrometer; chemical shifts δ were measured with reference to the solvent (^{1}H: $CDCl_3$, δ = 7.24 ppm; ^{13}C: NMR $CDCl_3$, δ = 77.13 ppm). Mass spectra were recorded with a Finnigan MAT 95 XL spectrometer (70 eV) by using electron impact ionization (EI) and GC–MS coupling. MALDI-TOF spectra were recorded in positive mode by using a Bruker Ultraflex mass spectrometer with dithranol as a matrix. Accurate mass measurements (HRMS) were carried out by using a Jeol GCMate II mass spectrometer (70 eV). Microanalyses were performed with a Carlo Erba 1106 instrument. Infrared spectra were recorded with a Thermo Nicolet FTIR-200 spectrometer. Analytical thin-layer chromatography was carried out with Silufol silica gel plates (supported on aluminum); detection was done by UV lamp (254 and 365 nm) and chemical staining (iodine vapor). Column chromatography was performed on silica gel 60 (230–400 mesh, Merck). Starting compounds 1,1′-(cyclopropylidenemethylene)dibenzene, (1-cyclopropylideneethyl)-

benzene, and (cyclopropylidenemethyl)benzene were synthesized by a known procedure.[6] All other starting materials were commercially available. All reagents except commercial products of satisfactory quality were purified by literature procedures prior to use.

General Procedure for the Addition of Bromofluorocarbene to Alkenes: A 50% aqueous solution of NaOH (22 mL) was added dropwise to a stirred mixture of the corresponding alkene (11.0 mmol), $CHBr_2F$ (2.53 g, 13.2 mmol), and TEBAC (0.1 g, 0.3 mmol) in dichloromethane (22 mL) at 0 °C under an atmosphere of argon. The reaction mixture was warmed up to room temperature and stirred for 24 h. Then, it was treated with ice (20 g). The organic phase was separated, and the water phase was extracted with dichloromethane (3 × 10 mL). The combined organic fractions were washed with water (50 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo; the residue was purified by preparative column chromatography.

1-Bromo-1-fluoro-2,2-diphenylspiro[2.2]pentane (1):[5] Yield: 35% (1.22 g), colorless solid, m.p. 106–108 °C, R_f = 0.2 (petroleum ether). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.30 (ddd, $^2J_{H,H}$ = 5.1 Hz, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 9.5 Hz, 1 H, CH_2), 1.45 (ddd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 6.4 Hz, $^3J_{H,H}$ = 9.5 Hz, 1 H, CH_2), 1.52 (dddd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 9.1 Hz, $^3J_{H,F}$ = 0.9 Hz, 1 H, CH_2), 1.72 (dddd, $^2J_{H,H}$ = 5.1 Hz, $^3J_{H,H}$ = 6.4 Hz, $^3J_{H,H}$ = 9.1 Hz, $^3J_{H,F}$ = 9.0 Hz, 1 H, CH_2), 7.24–7.38 (m, 10 H, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 8.3 ($^3J_{C,F}$ = 4 Hz, CH_2), 11.3 (CH_2), 32.0 ($^2J_{C,F}$ = 9 Hz, C_{spiro}), 43.0 ($^2J_{C,F}$ = 10 Hz, 1 C), 93.3 ($^1J_{C,F}$ = 312 Hz, CBrF), 127.2 (CH, Ph), 127.2 (CH, Ph), 128.2 (2 CH, Ph), 128.5 (2 CH, Ph), 129.3 (2 CH, Ph), 129.5 (2 CH, Ph), 139.0 (C, Ph), 141.0 ($^3J_{C,F}$ = 4 Hz, 1 C, Ph) ppm. IR (nujol): $\tilde{\nu}$ = 3068, 3040, 2970, 2940, 2860, 1600, 1500, 1470, 1390, 1180, 1060, 715, 650, 605 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 318 (12) $[M]^+$, 316 (12) $[M]^+$, 237 (100) $[M - Br]^+$, 222 (29), 203 (35), 159 (32), 115 (19), 109 (21), 91 (43). $C_{17}H_{14}BrF$ (317.20): calcd. C 64.37, H 4.45; found C 64.52, H 4.60.

1-Bromo-1-fluoro-2-methyl-2-phenylspiro[2.2]pentane (4):[5] Yield: 39% (1.09 g), colorless liquid, R_f = 0.4 (petroleum ether). Two isomers, A/B = 1:1. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.10 (ddd, $^2J_{H,H}$ = 4.6 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 9.3 Hz, 1 H, CH_2), 1.21–1.44 (m, 4 H, CH_2), 1.54 (ddd, $^2J_{H,H}$ = 5.1 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 9.3 Hz, 1 H, CH_2), 1.59–1.69 (m, 2 H, CH_2), 1.70 (d, $^4J_{H,F}$ = 1.9 Hz, 3 H, CH_3), 1.72 (d, $^4J_{H,F}$ = 2.4 Hz, 3 H, CH_3), 7.35–7.48 (m, 10 H, CH, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 6.21 ($^3J_{C,F}$ = 3.8 Hz, CH_2), 8.91 (CH_3), 9.01 ($^3J_{C,F}$ = 3.5 Hz, CH_2), 10.88 (CH_3), 20.41 ($^3J_{C,F}$ = 5.2 Hz, CH_2), 24.90 ($^3J_{C,F}$ = 3.6 Hz, CH_2), 30.90 ($^2J_{C,F}$ = 8.1 Hz, 1 C), 31.04 ($^2J_{C,F}$ = 9.6 Hz, 1 C), 34.54 ($^2J_{C,F}$ = 9.9 Hz, 1 C), 35.43 ($^2J_{C,F}$ = 10.9 Hz, 1 C), 93.98 ($^1J_{C,F}$ = 314 Hz, CBrF), 94.86 ($^1J_{C,F}$ = 308 Hz, CBrF), 127.07 (2 CH, Ph), 128.25 (2 CH, Ph), 128.32 (2 CH, Ph), 128.36 (2 CH, Ph), 128.42 (2 CH, Ph), 138.89 (C, Ph), 141.90 (C, Ph) ppm. IR (film): $\tilde{\nu}$ = 3070, 3030, 3000, 2930, 2880, 1600, 1500, 1450, 1380, 1190, 1100, 1005, 980, 875, 780, 710, 640 cm^{-1}. $C_{12}H_{12}BrF$ (255.13): calcd. C 56.49, H 4.74; found C 56.70, H 4.73.

1-Bromo-1-fluoro-2-phenylspiro[2.2]pentane (7): Yield: 51% (1.35 g), colorless liquid, R_f = 0.5 (petroleum ether). Two isomers, A/B 1:0.9. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.19–1.30 (m, 3 H, CH_2, A, B), 1.31–1.42 (m, 3 H, CH_2, A, B), 1.48 (dddd, $^2J_{H,H}$ = 3.6 Hz, $^3J_{H,H}$ = 5.6 Hz, $^3J_{H,H}$ = 9.4 Hz, $^4J_{H,F}$ = 0.6 Hz, 1 H, CH_2, B), 1.55 (dddd, $^2J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 6.3 Hz, $^3J_{H,H}$ = 9.2 Hz, $^4J_{H,F}$ = 0.8 Hz, 1 H, CH_2, A), 3.02 (s, 1 H, CH, A), 3.10 (d, $^3J_{H,F}$ = 13.6 Hz, 1 H, CH, B), 7.26–7.38 (m, 10 H, 5 CH, Ph, A, 5 CH, Ph, B) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 7.79 ($^1J_{C,H}$ = 165 Hz, CH_2, A), 8.45 ($^1J_{C,H}$ = 163, $^3J_{C,F}$ = 3.5 Hz, CH_2, B), 8.98 ($^1J_{C,H}$ = 163 Hz, CH_2, B), 11.35 ($^1J_{C,H}$ = 164 Hz, CH_2, A), 26.78 ($^2J_{C,F}$ = 8.6 Hz, C_{spiro}), 26.95 ($^2J_{C,F}$ = 8.7 Hz, C_{spiro}), 34.94 ($^1J_{C,H}$ = 161 Hz, $^2J_{C,F}$ = 11.7 Hz, CH, B), 37.71 ($^1J_{C,H}$ = 163 Hz, $^2J_{C,F}$ = 11.0 Hz, CH, A), 86.29 ($^1J_{C,F}$ = 311 Hz, CBrF, A), 92.43 ($^1J_{C,F}$ = 310 Hz, CBrF, B), 127.16 ($^1J_{C,H}$ = 160 Hz, CH, Ph, A), 127.30 ($^1J_{C,H}$ = 160 Hz, CH, Ph, B), 128.22 ($^1J_{C,H}$ = 160 Hz, 2 CH, Ph), 128.43 ($^1J_{C,H}$ = 160 Hz, 2 CH, Ph), 128.59 ($^1J_{C,H}$ = 159 Hz, 2 CH, Ph), 128.78 ($^1J_{C,H}$ = 159 Hz, 2 CH, Ph), 134.35 (C, Ph, A), 135.79 (C, Ph, B) ppm. IR (film): $\tilde{\nu}$ = 3095, 3072, 3041, 3013, 1609, 1528, 1499, 1459, 1348, 1188, 1136, 1100, 935, 870, 704, 648, 598, 526 cm^{-1}. $C_{11}H_{10}BrF$ (241.10): calcd. C 54.80, H 4.18; found C 54.71, H 4.10.

General Procedure for the Addition of Bromochlorocarbene to Alkenes: A 50% aqueous solution of NaOH (22 mL) was added dropwise to a stirred mixture of the corresponding alkene (11.0 mmol), $CHBr_2Cl$ (2.74 g, 13.1 mmol), and dibenzo-18-crown-6 (0.1 g, 0.3 mmol) in dichloromethane (22 mL) at 0 °C under an atmosphere of argon. The reaction mixture was warmed up to room temperature and stirred for 24 h. Then it was treated with ice (20 g). The organic phase was separated, and the water phase was extracted with dichloromethane (3 × 10 mL). The combined organic fractions were washed with water (50 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo; the residue was purified by preparative column chromatography.

1-Bromo-1-chloro-2,2-diphenylspiro[2.2]pentane (2): Yield: 61% (2.23 g), colorless solid, m.p. 95–96 °C, R_f = 0.2 (petroleum ether). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.35 (ddd, $^2J_{H,H}$ = 4.6 Hz, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 9.2 Hz, 1 H, CH_2), 1.45 (ddd, $^2J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 9.2 Hz, 1 H, CH_2), 1.74 (ddd, $^2J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 9.2 Hz, 1 H, CH_2), 1.80 (ddd, $^2J_{H,H}$ = 4.6 Hz, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 9.2 Hz, 1 H, CH_2), 7.26–7.31 (m, 2 H, 2 CH, Ph), 7.34–7.39 (m, 4 H, 4 CH, Ph), 7.45–7.50 (4 H, 4 CH, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 10.67 (CH_2), 12.41 (CH_2), 36.15 (C_{spiro}), 44.62 (CPh_2), 60.0 (CBrCl), 127.09 (CH, Ph), 127.15 (CH, Ph), 128.16 (2 CH, Ph), 128.24 (2 CH, Ph), 129.34 (2 CH, Ph), 129.46 (2 CH, Ph), 104.44 (C, Ph), 141.87 (C, Ph) ppm. IR (nujol): $\tilde{\nu}$ = 3092, 3061, 3029, 2975, 2947, 2870, 1598, 1582, 1495, 1451, 1382, 1152, 1089, 1040, 818, 720, 622, 546 cm^{-1}. $C_{17}H_{14}BrCl$ (333.65): calcd. C 61.20, H 4.23; found C 61.27, H 4.23.

1-Bromo-1-chloro-2-methyl-2-phenylspiro[2.2]pentane (5): Yield: 60% (1.79 g), colorless liquid, R_f = 0.5 (petroleum ether). Two isomers, A/B = 1:1. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.10 (ddd, $^2J_{H,H}$ = 4.7 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 9.5 Hz, 1 H, CH_2), 1.26–1.34 (m, 3 H, CH_2), 1.34 (ddd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 9.7 Hz, 1 H, CH_2), 1.45 (ddd, $^2J_{H,H}$ = 5.2 Hz, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 9.7 Hz, 1 H, CH_2), 1.74 (s, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 1.74–1.81 (m, 2 H, CH_2), 7.32–7.45 (m, 10 H, CH, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 8.64 ($^1J_{C,H}$ = 164 Hz, CH_2), 10.19 ($^1J_{C,H}$ = 162 Hz, CH_2), 11.23 ($^1J_{C,H}$ = 164 Hz, CH_2), 12.62 ($^1J_{C,H}$ = 164 Hz, CH_2), 23.93 ($^1J_{C,H}$ = 129 Hz, CH_3), 26.58 ($^1J_{C,H}$ = 129 Hz, CH_3), 35.14 (C), 35.30 (C), 36.75 (C), 36.82 (C), 60.97 (CBrCl), 61.46 (CBrCl), 127.09 ($^1J_{C,H}$ = 158 Hz, CH, Ph), 127.12 ($^1J_{C,H}$ = 158 Hz, CH, Ph), 128.19 ($^1J_{C,H}$ = 156 Hz, 2 CH, Ph), 128.23 ($^1J_{C,H}$ = 156 Hz, 2 CH, Ph), 128.41 ($^1J_{C,H}$ = 158 Hz, 2 CH, Ph), 128.50 ($^1J_{C,H}$ = 158 Hz, 2 CH, Ph), 140.86 (C, Ph), 142.61 (C, Ph) ppm. IR (film): $\tilde{\nu}$ = 3065, 3036, 3000, 2971, 2934, 2878, 1605, 1498, 1449, 1381, 1143, 1086, 1034, 1008, 945, 824, 765, 703, 602 cm^{-1}. $C_{12}H_{12}BrCl$ (271.58): calcd. C 53.07, H 4.45; found C 53.24, H 4.58.

1-Bromo-1-chloro-2-phenylspiro[2.2]pentane (8): Yield: 53% (1.50 g), colorless liquid, R_f = 0.5 (petroleum ether). Two isomers,

A/B = 1:0.8. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.30–1.44 (m, 2 H, CH_2, A, 2 H, CH_2, B), 1.46–1.59 (m, 2 H, CH_2, A, 2 H, CH_2, B), 3.15 (s, 1 H, CH, B), 3.30 (s, 1 H, CH, A), 7.35–7.45 (m, 5 H, 5 CH, Ph, A, 5 H, 5 CH, Ph, B) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 9.91 ($^1J_{C,H}$ = 165 Hz, CH_2, A), 10.51 ($^1J_{C,H}$ = 165 Hz, CH_2, B), 10.94 ($^1J_{C,H}$ = 165 Hz, CH_2, B), 12.20 ($^1J_{C,H}$ = 166 Hz, CH_2, A), 31.06 (C_{spiro}, A), 31.19 (C_{spiro}, B), 39.30 ($^1J_{C,H}$ = 164 Hz, CH, B), 39.94 ($^1J_{C,H}$ = 164 Hz, CH, A), 52.97 (CBrCl), 56.13 (CBrCl), 127.41 ($^1J_{C,H}$ = 160 Hz, CH, Ph, A), 127.46 ($^1J_{C,H}$ = 160 Hz, CH, Ph, B), 128.06 ($^1J_{C,H}$ = 160 Hz, 2 CH, Ph, B), 128.12 ($^1J_{C,H}$ = 160 Hz, 2 CH, Ph, A), 129.05 ($^1J_{C,H}$ = 161 Hz, 2 CH, Ph, B), 129.13 ($^1J_{C,H}$ = 165 Hz, 2 CH, Ph, A), 135.09 (C, Ph, A), 136.09 (C, Ph, B) ppm. IR (film): $\tilde{\nu}$ = 3070, 3039, 3008, 2935, 2867, 1604, 1499, 1459, 1158, 1069, 1040, 960, 891, 830, 781, 749, 700, 615, 567, 556 cm^{-1}. $C_{11}H_{10}BrCl$ (257.55): calcd. C 51.30, H 3.91; found C 51.41, H 4.16.

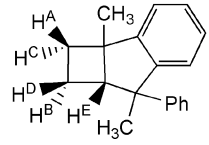
General Procedure for the Addition of Dibromocarbene to Alkenes: A solution of bromoform (3.34 g, 1.16 mL, 13.2 mmol) in petroleum ether (3 mL) was added dropwise to a stirred mixture of the corresponding alkene (11.0 mmol) and *t*BuOK (1.95 g, 26.4 mmol) in petroleum ether (10 mL) at 0 °C under an atmosphere of argon. After 20 min the resulting mixture was slowly warmed up to room temperature and then stirred for 48 h. Then it was quenched with cold water (10 mL). The organic phase was separated, and the water phase was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo; the residue was purified by preparative column chromatography.

1,1-Dibromo-2,2-diphenylspiro[2.2]pentane (3): Yield: 58% (2.41 g), colorless solid, m.p. 126–127 °C (petroleum ether). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.35–1.39 (m, 2 H, CH_2), 1.83–1.86 (m, 2 H, CH_2), 7.23–7.28 (m, 2 H, 2 CH, Ph), 7.30–7.36 (m, 4 H, 4 CH, Ph), 7.43–7.47 (m, 4 H, 4 CH, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 13.02 (2 CH_2), 37.00 (C_{spiro}), 44.51 (CBr_2), 46.29 (CPh_2), 127.17 (2 CH, Ph), 128.24 (4 CH, Ph), 129.39 (4 CH, Ph), 141.78 (2 C, Ph) ppm. IR (nujol): $\tilde{\nu}$ = 3070, 3045, 3014, 2936, 2869, 1601, 1498, 1450, 1382, 1149, 1067, 1039, 978, 845, 780, 716, 626, 611, 542 cm^{-1}. $C_{17}H_{14}Br_2$ (378.10): calcd. C 54.00, H 3.73; found C 54.11, H 3.65.

1,1-Dibromo-2-methyl-2-phenylspiro[2.2]pentane (6): Yield: 53% (1.84 g), colorless solid, m.p. 97 °C, b.p. 63–65 °C/2 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.16 (ddd, $^2J_{H,H}$ = 4.6 Hz, $^3J_{H,H}$ = 6.3 Hz, $^3J_{H,H}$ = 9.4 Hz, 1 H, CH_2), 1.32 (ddd, $^2J_{H,H}$ = 4.6 Hz, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 9.1 Hz, 1 H, CH_2), 1.40 (ddd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 9.4 Hz, 1 H, CH_2), 1.72 (s, 3 H, CH_3), 1.82 (ddd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 6.3 Hz, $^3J_{H,H}$ = 9.1 Hz, 1 H, CH_2), 7.27–7.40 (m, 5 H, CH, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 10.75 (CH_2), 13.18 (CH_2), 26.35 (CH_3), 36.05 (C), 36.58 (C), 47.98 (C), 127.05 (CH, Ph), 128.11 (2 CH, Ph), 128.33 (2 CH, Ph), 142.34 (C, Ph) ppm. $C_{12}H_{12}Br_2$ (316.03): calcd. C 45.61, H 3.83; found C 45.52, H 3.90.

1,1-Dibromo-2-phenylspiro[2.2]pentane (9): Yield: 55% (1.82 g), colorless liquid, R_f = 0.3 (petroleum ether). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.36–1.41 (m, 2 H, CH_2), 1.43–1.49 (m, 1 H, CH_2), 1.56–1.62 (m, 1 H, CH_2), 3.25 (s, 1 H, CH), 7.33–7.41 (m, 5 H, 5 CH, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 11.86 (CH_2), 12.80 (CH_2), 31.97 (C_{spiro}), 39.92 (CH), 39.96 (CBr_2), 127.54 (CH, Ph), 128.16 (2 CH, Ph), 129.15 (2 CH, Ph), 136.27 (C, Ph) ppm. IR (film): $\tilde{\nu}$ = 3068, 3037, 3005, 2968, 2935, 2863, 1604, 1496, 1457, 1381, 1117, 1061, 1030, 953, 822, 770, 746, 731, 699, 675, 620, 609, 550 cm^{-1}. $C_{11}H_{10}Br_2$ (302.01): calcd. C 43.75, H 3.34; found C 43.52, H 3.45.

General Procedure for the Reaction of *gem*-Dihalogenospiropentanes with Methyllithium: A solution of 1.5 N methyllithium (6.0 mmol, 4.0 mL for dibromospiropentanes and bromochlorospiropentanes; 8.0 mol, 5.3 mL for bromofluorospiropentanes) in ether was added dropwise to a solution of dihalogenospiropentane (4.0 mmol) in absolute ether (10 mL) under an atmosphere of argon at low temperature (–65 °C for bromochlorospiropentanes, –55 °C for dibromospiropentanes, 0 °C for bromofluorospiropentanes). The reaction mixture was stirred (1.5 h for dibromospiropentanes, 10 h for bromochlorospiropentanes, 5 h for bromofluorospiropentanes). Then it was warmed up to 0 °C and quenched with an equal amount of cold water. The organic phase was separated, and the water phase was extracted with diethyl ether (3 × 3 mL). The combined organic fractions were washed with water (5 mL) and dried with $MgSO_4$. The solvent was evaporated; the products were isolated by preparative column chromatography.



2a,7-Dimethyl-7-phenyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]indene (10):[5] Yield: 51% (0.50 g) from bromofluorospiropentane **4**, 32% (0.31 g) from dibromospiropentane **6**. Colorless oil, R_f = 0.2 (petroleum ether). ^{1}H NMR (400.1 MHz, C_6D_6, 25 °C), cyclobutane protons (ABCDE system): δ = 1.02 (dddd, $^3J_{A,B}$ = 2.2 Hz, $^2J_{A,C}$ = –11.9 Hz, $^3J_{A,D}$ = 9.0 Hz, $^4J_{A,E}$ = 3.5 Hz, 1 H, H^A), 1.35 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.70 (dddd, $^3J_{A,B}$ = 2.2 Hz, $^3J_{B,C}$ = 8.9 Hz, $^2J_{B,D}$ = –11.1 Hz, $^3J_{B,E}$ = 1.6 Hz, 1 H, H^B), 2.15 (m, $^2J_{A,C}$ = –11.2 Hz, $^3J_{B,C}$ = 8.9 Hz, $^3J_{C,D}$ = 10.2 Hz, $^4J_{C,E}$ = 0.5 Hz, 1 H, H^C), 2.32 (m, $J_{A,D}$ = 9.0 Hz, $^2J_{BD}$ = –11.05 Hz, $^3J_{C,D}$ = 10.2 Hz, $^3J_{D,E}$ = 8.0 Hz, 1 H, H^D), 3.24 (m, $^4J_{A,E}$ = 3.5 Hz, $^3J_{B,E}$ = 1.6 Hz, $^4J_{C,E}$ = 0.5 Hz, $^3J_{D,E}$ = 8.0 Hz, 1 H, H^E) ppm; aromatic protons: δ = 7.18–7.24 (m, 1 H, Ph), 7.25–7.38 (m, 6 H, Ph), 7.42–7.48 (m, 2 H, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 18.6 ($^1J_{C,H}$ = 125 Hz, CH_3), 23.0 ($^1J_{C,H}$ = 138 Hz, CH_2), 26.2 ($^1J_{C,H}$ = 128 Hz, CH_3), 28.9 ($^1J_{C,H}$ = 138 Hz, CH_2), 48.4 ($^1J_{C,H}$ = 138 Hz, CH), 52.3 (C), 57.9 (C), 125.5 (CH, Ph), 125.8 (CH, Ph), 125.9 (CH, Ph), 126.5 (CH, Ph), 127.0 (CH, Ph), 127.6 (2 CH, Ph), 127.7 (2 CH, Ph), 143.3 (C, Ph), 146.7 (C, Ph), 151.5 (C, Ph) ppm. IR (film): $\tilde{\nu}$ = 3020, 2985, 2950, 2925, 2870, 1600, 1525, 1500, 1470, 1430, 1380, 1125, 1080, 940, 772, 750, 730, 675 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 248 (26) $[M]^+$, 233 (15), 220 (54), 205 (100), 192 (20), 178 (15), 143 (26), 128 (13), 115 (9), 91 (14), 77 (4). $C_{19}H_{20}$ (248.36): calcd. C 91.88, H 8.12; found C 91.63, H 8.34.

5,13b-Diphenyl-7,7a,8,9,9a,13b-hexahydro-6*H*-dibenzo[*a*,*h*]dicyclobuta[*c*,*e*]azulene (11): Yield: 69% (0.60 g) from bromochlorospiropentane **5**, 65% (0.57 g) from dibromospiropentane **6**, colorless crystals (prism), m.p. 201 °C (MeOH/$CHCl_3$). ^{1}H NMR (400.1 MHz, C_6D_6, 25 °C, cyclobutane protons, ABCDE system): δ = 1.65 (m, $^2J_{A,B}$ = –10.8 Hz, $^3J_{A,C}$ = 1.6 Hz, $^3J_{A,D}$ = 8.2 Hz, $^3J_{A,E}$ = 1.2 Hz, 1 H, A = H^{21A}), 2.14 (m, $^2J_{A,B}$ = –10.8 Hz, $^3J_{B,C}$ = 8.1 Hz, $^3J_{B,D}$ = 10.9 Hz, $^3J_{B,E}$ = 7.7 Hz, 1 H, B = H^{21B}), 2.45 (m, $^3J_{A,C}$ = 1.6 Hz, $^3J_{B,C}$ = 8.1 Hz, $^2J_{C,D}$ = –11.8 Hz, $^4J_{C,E}$ = 4.2 Hz, 1 H, C = H^{22A}), 2.80 (m, $^3J_{A,D}$ = 8.2 Hz, $^3J_{B,D}$ = 10.9 Hz, $^2J_{C,D}$ = –11.8 Hz, $^4J_{D,E}$ = 0.2 Hz, 1 H, D = H^{22B}), 3.41 (m, $^3J_{A,E}$ = 1.2 Hz, $^3J_{B,E}$ = 7.7 Hz, $^4J_{C,E}$ = 4.2 Hz, $^4J_{D,E}$ = 0.2 Hz, 1 H, E = H^{20}) ppm; methylenecyclobutane protons (ABCDE system) δ = 1.65 (m, $^2J_{A,B}$ = –11.8 Hz, $^3J_{A,C}$ = 9.7 Hz, $^3J_{A,D}$ = 3.9 Hz, $^3J_{A,E}$ = 4.0 Hz, 1 H, A = H^{3A}), 2.14 (m, $^2J_{A,B}$ = –11.8 Hz, $^3J_{B,C}$ = 9.1 Hz, $^3J_{B,D}$ = 9.4 Hz, $^3J_{B,E}$ = 9.0 Hz, 1 H, B = H^{3B}), 2.45 (m, $^3J_{A,C}$ = 9.7 Hz,

$^3J_{B,C}$ = 9.1 Hz, $^2J_{C,D}$ = –17.0 Hz, $^4J_{C,E}$ = –4.5 Hz, 1 H, C = H^{4A}), 2.80 (m, $^3J_{A,D}$ = 3.9 Hz, $^3J_{B,D}$ = 9.4 Hz, $^2J_{C,D}$ = –17.0 Hz, $^4J_{D,E}$ = 1.6 Hz, 1 H, D = H^{4B}), 3.41 (m, $^3J_{A,E}$ = 4.0 Hz, $^3J_{B,E}$ = 9.0 Hz, $^4J_{C,E}$ = –4.5 Hz, $^4J_{D,E}$ = 1.6 Hz, 1 H, E = H^2) ppm; phenyl groups: δ = 6.51–6.56 (m, 2 H), 7.04–7.07 (m, 3 H), 6.96 (tt, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, *p*-H), 7.08–7.13 (m, 2 H, *m*-H), 7.19–7.23 (2 H, *o*-H); benzyl groups: 6.49 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H), 6.77 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H), 6.91 (ddd, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.04 (ddd, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.28–7.30 (m, 1 H), 7.32–7.35 (m, 2 H), 7.42 (br. d, $^3J_{H,H}$ = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 20.96 ($^1J_{C,H}$ = 136 Hz, CH_2, C^3), 20.96 ($^1J_{C,H}$ = 136 Hz, 1 C, CH_2, C^3), 25.82 ($^1J_{C,H}$ = 135 Hz, 1 C, CH_2, C^{21}), 28.97 ($^1J_{C,H}$ = 136 Hz, 1 C, CH_2, C^4), 29.75 ($^1J_{C,H}$ = 135 Hz, 1 C, CH_2, C^{22}), 48.0 ($^1J_{C,H}$ = 138 Hz, 1 C, CH, C^2), 52.49 ($^1J_{C,H}$ = 140 Hz, 1 C, CH_2 C^{20}), 67.64 (1 C, C^1), 67.79 (1 C, C^{13}), 124.90 (2 C, CH=), 125.18 (1 C, CH=), 125.85 (1 C, CH=), 126.07 (1 C, CH=), 126.61 (1 C, CH=), 126.72 (1 C, CH=), 126.85 (2 C, CH=), 127.45 (2 C, CH=), 127.60 (1 C, CH=), 128.21 (2 C, CH=), 128.73 (1 C, CH=), 129.38 (1 C, CH=), 129.55 (2 C, CH=), 133.95 (1 C, C=), 138.63 (1 C, C=), 141.55 (1 C, C=), 143.85 (1 C, C=), 146.74 (1 C, C=), 147.41 (1 C, C=), 148.11 (1 C, C=), 148.84 (1 C, C=) ppm. IR (nujol): $\tilde{\nu}$ = 3060, 2963, 2946, 2865, 1600, 1497, 1468, 1379, 1116, 762, 745, 717 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 438 (7), 437 (37), 436 (100) $[M]^+$, 409 (11), 408 (41), 407 (29), 391 (10), 380 (16), 379 (11), 359 (10), 332 (22), 331 (86), 330 (49), 329 (27), 317 (17), 316 (15), 315 (31), 304 (14), 303 (22), 302 (25), 291 (20), 289 (15), 253 (21), 252 (15), 228 (11), 217 (15), 215 (25), 204 (14), 203 (14), 202 (16). MS (MALDI-TOF): *m*/*z* (%) = 436 (23). $C_{34}H_{28}$ (436.59): calcd. C 93.54, H 6.46; found C 93.40, H 6.55.

[1-Methyl-1-(2-methylcyclobut-1-en-1-yl)ethyl]benzene (12):[5] Yield: 45% (0.33 g) from bromofluorospiropentane **1**, 36% (0.26 g) from bromochlorospiropentane **2**, 6% (0.04 g) from dibromospiropentane **3**. Colorless solid, R_f = 0.3 (petroleum ether). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.48 (s, 6 H, 2 CH_3), 1.57 (s, 3 H, CH_3), 2.20–2.28 (m, 4 H, 2 CH_2), 7.18–7.24 (m, 1 H, CH, Ph), 7.32–7.43 (m, 4 H, 4 CH, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 15.4 ($^1J_{C,H}$ = 126 Hz, CH_3), 25.8 ($^1J_{C,H}$ = 137 Hz, CH_2), 28.1 ($^1J_{C,H}$ = 127 Hz, 2 CH_3), 28.9 ($^1J_{C,H}$ = 137 Hz, CH_2), 29.8 (C), 125.6 (CH, Ph), 126.3 (2 CH, Ph), 128.0 (2 CH, Ph), 135.1 (C, Ph), 146.6 (C=), 148.7 (C=) ppm. IR (nujol): $\tilde{\nu}$ = 3030, 3000, 2970, 2875, 1665, 1600, 1475, 1430, 1372, 1250, 1170, 772, 715, 685 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 186 (12) $[M]^+$, 171 (100), 156 (12), 143 (48), 129 (21), 115 (11), 91 (23), 77 (9), 41 (10), 39 (5). $C_{14}H_{18}$ (186.29): calcd. C 90.26, H 9.74; found C 90.32, H 9.71.

(2-Cyclopropylidenevinyl)benzene (13):[14] Yield: 24% (0.14 g) from bromofluorospiropentane **7**, 18% (0.10 g) from bromochlorospiropentane **8**, 14% (0.08 g) from dibromospiropentane **9**. Colorless oil, R_f = 0.5 (petroleum ether). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 1.68–1.74 (m, 2 H, CH_2), 1.74–1.79 (m, 2 H, CH_2), 6.33 (dt, $^5J_{H,H}$ = 3.6 Hz, $^5J_{H,H}$ = 7.1 Hz, 1 H, CH), 7.17–7.22 (m, 1 H, CH, Ph), 7.31–7.35 (m, 4 H, 4 CH, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 8.70 (2 CH_2), 79.99 (C=), 96.62 (CH), 126.49 (CH, Ph), 126.55 (2 CH, Ph), 128.52 (2 CH, Ph), 131.62 (C, Ph), 189.98 (=C=) ppm. IR (film): $\tilde{\nu}$ = 3092, 3060, 3035, 2938, 2880, 2863, 2026, 1960, 1602, 1498, 1455, 1265, 1168, 802, 755, 710 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 143 (8), 142 (85) $[M]^+$, 141 (100), 140 (3), 139 (10), 116 (5), 115 (40), 139 (10), 116 (5), 115 (40), 114 (2), 103 (5), 102 (22), 91 (3), 89 (4), 77 (3), 76 (3), 63 (6), 51 (4). HRMS (EI): calcd. for $C_{11}H_{10}$ 142.0783; found 142.0758.

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