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Cyclopropanation of Vinylidenecyclopropanes. Synthesis of 1-(Dihalomethylene)spiropentanes

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Synthesis of 1-(dihalomethylene)spiropentanes via cyclopropylidenecyclopropanes generated by cyclopropanation of vinylidenecyclopropanes by dihalocarbenes is described. Reaction of diarylvinylidenecyclopropanes with dibromocarbene and dichlorocarbene exclusively gave 1-(dihalomethylene)spiropentanes in high yields. Reaction of monoarylvinylidenecyclopropanes with dihalocarbenes afforded cyclopropylidenecyclopropanes as the major product with the formation of a small amount of 1-(dihalomethylene)spiropentanes. The efficiency of the thermal rearrangement from the cyclopropylidenecyclopropanes to the 1-(dihalomethylene)spiropentane derivatives depended on the substituents and the reaction temperature. Reaction of diarylvinylidenecyclopropanes with diphenylcarbene and phenylthiocarbene gave the corresponding spiropentane derivatives. This type of thermal rearrangement was applicable to the cyclopropanation of 1,1-diarylallenes.

Introduction

Thermal reactions and skeletal conversions of strained small-ring hydrocarbons have been a subject of considerable attention from synthetic and mechanistic viewpoints. Thermolyses of methylenecyclopropanes[1] and cyclopropylidenecyclopropanes[1d,2] have been well investigated to give rearranged products via trimethylenemethane intermediates, but the thermal rearrangement often requires severe conditions at relatively high temperature.[1a−e,g,h,j,k,2] Although addition reaction of carbenes to allenes is one of the straightforward methods for the synthesis of methylenecyclopropanes,[3] it is difficult to control the regiochemistry of products[3h,j,k,m,o,p] and further addition of carbenes to the methylenecyclopropanes to give spiropentane derivatives.[3d,f−h,k,l,p,r,t,w] On the other hand, we and other groups have reported a few examples of thermal[1d,4] and photochemical[5] skeletal conversions of vinylidenecyclopropanes. We then focused our attention on the reactivity of carbenes to allene unit of vinylidenecyclopropanes.[6] We found that the addition of dihalocarbenes to the allenyl bond of vinylidenecyclopropanes proceeds regioselectively and that the subsequent thermal rearrangement of the methylenecyclopropane unit of the initial adducts occurs at ambient temperature to

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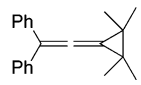
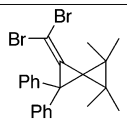
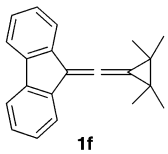
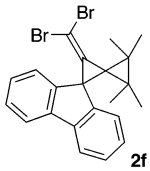
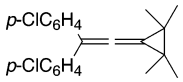
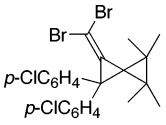
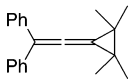
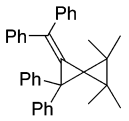
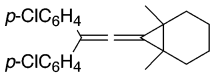
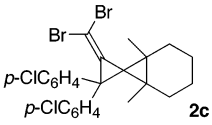
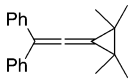
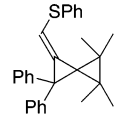
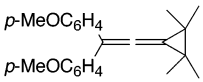
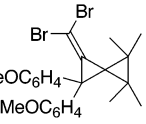
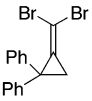
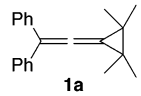
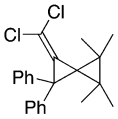
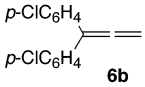
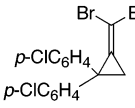
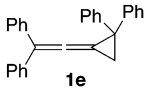
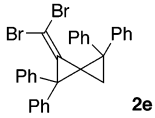
TABLE 1. Reaction of Diarylvinylidenecyclopropanes and Diarylallenes with Carbenes[a]

entry	substrate	precursor of carbene	product	yield[b](%)	entry	substrate	precursor of carbene	product	yield[b](%)
1	 **1a**	$CHBr_3$	 **2a**	73	7	 **1f**	$CHBr_3$	 **2f**	85
2	 **1b**	$CHBr_3$	 **2b**	60	8	 **1a**	Ph_2CHCl [c]	 **4**	41
3	 **1c**	$CHBr_3$	 **2c**	77	9	 **1a**	$PhSCH_2Cl$ [c]	 **(*E*)-5**	10
4	 **1d**	$CHBr_3$	 **2d**	78	10	 **6a**	$CHBr_3$	 **7a**	65
5	 **1a**	$CHCl_3$	 **3a**	99	11	 **6b**	$CHBr_3$	 **7b**	59
6	 **1e**	$CHBr_3$	 **2e**	84					

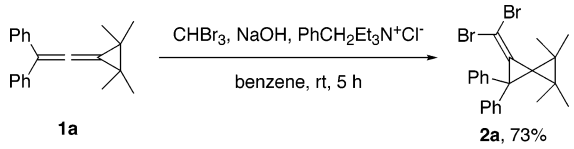
[a] Conditions: substrate (0.06 mol/L), precursor of carbene (5 equiv based on **1** or **6**), NaOH powder (over 20 equiv based on **1** or **6**), $PhCH_2Et_3N^+Cl^-$ (0.1 equiv based on **1** or **6**), benzene, rt, 5 h. [b] Isolated yield. [c] *t*-BuOK (1.2 equiv based on **1a**) and 18-crown-6 (1 equiv based on **1a**) were used instead of NaOH and $PhCH_2Et_3N^+Cl^-$.

give 1-(dihalomethylene)spiropentane derivatives in high yields.

Results and Discussion

To a benzene solution containing 1-diphenylvinylidene-2,2,3,3-tetramethylcyclopropane **1a**[7] were added a large excess of tribromomethane, NaOH powder, and a catalytic amount of $PhCH_2Et_3N^+Cl^-$ (BTEAC), and the mixture was vigorously stirred for 5 h at room temperature. Purification of the resulting mixture afforded a spiropentane derivative **2a** in 73% isolated yield (Scheme 1). Structure of **2a** was determined by its spectral and analytical data and confirmed by X-ray analysis (Figure 1).

SCHEME 1



To survey the generality of this reaction, we investigated the reactions of vinylidenecyclopropanes **1a**−**f** with dibromocarbene and dichlorocarbene (Table 1).[8] Reactions of *p*-chloro and *p*-methoxy derivatives **1b**−**d** with dibromocarbene proceeded efficiently to give spiropentane derivatives **2b**−**d** in high yields. Reaction of **1a** with dichlorocarbene gave the corresponding 1-(dichloromethylene)spiropentane **3a** in a nearly quantitative yield. 2,2-Diphenyl-substituted vinylidenecyclopropane **1e** and fluorene derivative **1f** also reacted with dibromocarbene to give **2e**,**f**, respectively. Reactivity of other carbenes was also investigated. Vinylidenecyclopropane **1a** reacted with diphenylcarbene to give a spiropentane derivative **4** in 41% isolated yield. Reaction of **1a** with phenylthiocarbene also gave spiropentane derivative **(*E*)-5** stereoselectively. The structures of **4** and **(*E*)-5** were confirmed by X-ray analysis (see the Supporting Information). This rearrangement is applicable to regioselective cyclopropanation of 1,1-diarylallenes. It is noteworthy that the

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(7) We have developed a convenient method for the synthesis of vinylidenecyclopropanes: Isagawa, K.; Mizuno, K.; Sugita, H.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2283−2285.

(8) We attempted the reactions in concentrations of diarylvinylidenecyclopropanes from 0.025 to 0.22 mol/L and changed equivalents of haloform from 2.5 to 100 equiv, but the yields did not change appreciably. Progress of the reaction was monitored by TLC, and the reaction was continued until the substrates disappeared.

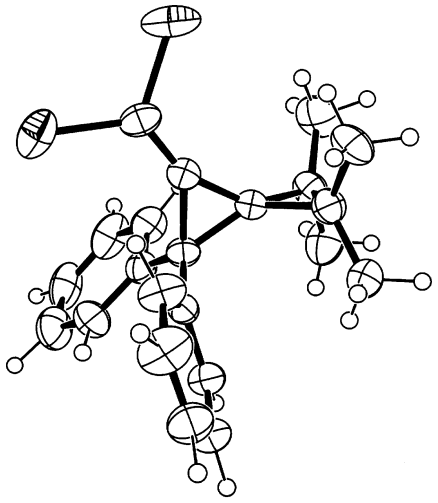
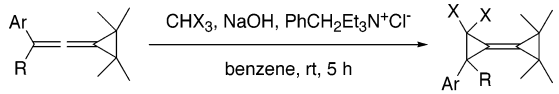


FIGURE 1. ORTEP drawing of **2a**: triclinic, $P\bar{1}$(#2), $Z = 2$, $R = 0.047$, $R_w = 0.079$, $a = 10.2519(8)$ Å, $b = 10.855(1)$ Å, $c = 10.068(2)$ Å, $a = 95.415(3)°$, $\beta = 94.831(2)°$, $\gamma = 117.804(7)°$, $V = 976.1(2)$ Å^3, $D_{calcd} = 1.52$ g/cm^3.

SCHEME 2



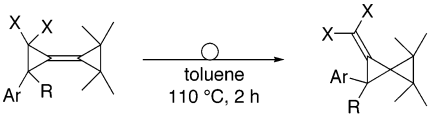
1g-k **8g-k, 9g**

TABLE 2. Synthesis of Cyclopropylidenecyclopropanes[a]

run	substrate	Ar	R	X	product	yield[b] (%)
1	**1g**	1-naphthyl	Me	Br	**8g**	68
2	**1g**	1-naphthyl	Me	Cl	**9g**	79
3	**1h**	Ph	cyclohexyl	Br	**8h**	48
4	**1i**	Ph	Me	Br	**8i**	40
5	**1j**	*p*-ClC_6H_4	Me	Br	**8j**	69
6	**1k**	2-naphthyl	Me	Br	**8k**	65

[a] Conditions: **1** (0.06 mol/L), CHX_3 (5 equiv based on **1**), NaOH powder (over 20 equiv based on **1**), $PhCH_2Et_3N^+Cl^-$ (0.1 equiv based on **1**), benzene, rt, 5 h. [b] Isolated yield.

SCHEME 3



8g-k, 9g **2g-k, 3g, >99%**

reaction of diarylallenes **6a**,**b** with dibromocarbene gave the rearranged products **7a**,**b** exclusively.

Then the monoaryl derivatives **1g**−**k** were allowed to react with dihalocarbenes under the same conditions (Scheme 2, Table 2). Surprisingly the major product in the reactions of monoaryl derivatives **1g**−**k** with dihalocarbenes were changed to the cyclopropylidenecyclopropanes **8g**−**k** and **9g**. The corresponding 1-(dihalomethylene)spiropentanes **2g**−**k** and **3g** were produced as minor components (<5%), and they can be easily separated by HPLC. The isolated cyclopropylidenecyclopropanes **8g**−**k** and **9g** were converted to spiropentane derivatives **2g**−**k** and **3g** quantitatively in refluxing toluene for 2 h, respectively (Scheme 3). These results clearly demonstrate that the reaction of monoarylvinylidenecyclopropanes with dihalocarbenes to give 1-(dihalomethylene)spiropentanes proceeds via the cyclopropylidenecyclopropanes **8** (X = Br) and **9** (X = Cl) as an intermediate. The structures of compounds before and after the thermal rearrangement were confirmed by spectral and analytical data, especially for the X-ray analysis of **9g** and **3g** (Figures 2 and 3).

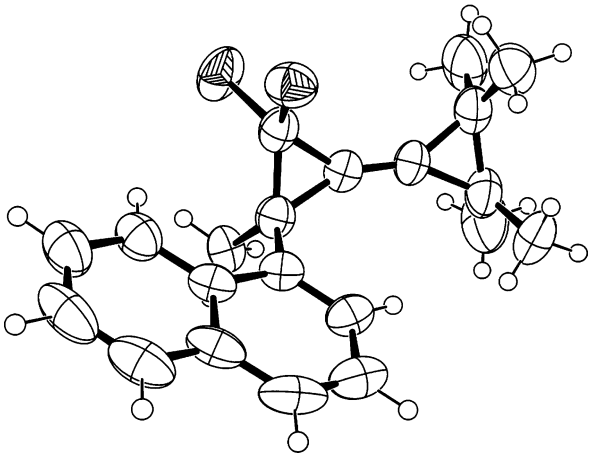


FIGURE 2. ORTEP drawing of **9g**: monoclinic, $P2_1/a$(#14), $Z = 4$, $R = 0.064$, $R_w = 0.077$, $a = 16.4629(7)$ Å, $b = 7.0161(3)$ Å, $c = 16.997(1)$ Å, $\beta = 104.488(3)°$, $V = 1900.8(1)$ Å^3, $D_{calcd} = 1.207$ g/cm^3.

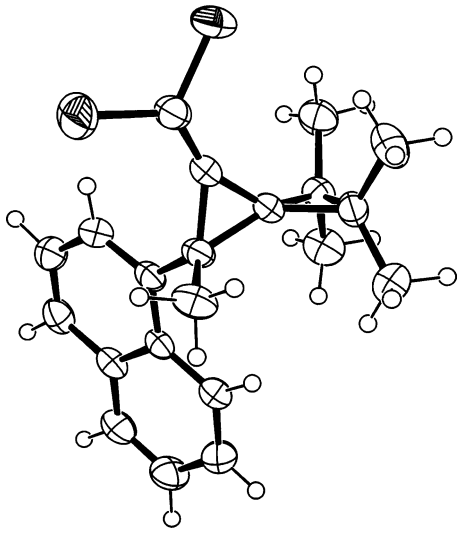
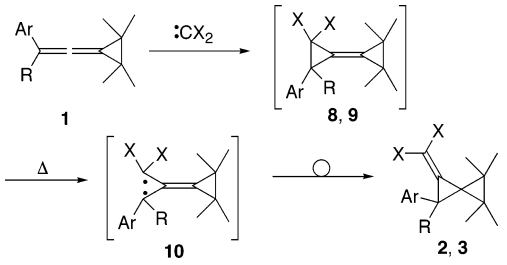


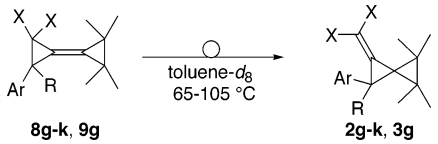
FIGURE 3. ORTEP drawing of **3g**: monoclinic, $C2/c$(#15), $Z = 8$, $R = 0.040$, $R_w = 0.031$, $a = 36.678(1)$ Å, $b = 7.0562(2)$ Å, $c = 14.5444(3)$ Å, $\beta = 104.654(1)°$, $V = 3641.7(2)$ Å^3, $D_{calcd} = 1.260$ g/cm^3.

On the basis of these results, we propose a possible pathway for the formation of **2** and **3** as shown in Scheme 4. The first step is the regioselective addition of dihalocarbene to the allenyl bond of **1** to give the cyclopropylidenecyclopropanes **8** and **9**. Then, **8** and **9** rearrange to the spiropentane derivatives **2** and **3** via trimethylenemethane intermediates **10** generated by homolytic C−C bond cleavage of the cyclopropylidenecyclopropanes. The difference of the products between diaryl derivatives **1a**−**f** and monoaryl derivatives **1g**−**k** clearly indicates that the rearrangement from **8a**−**f** to **2a**−**f** proceeds efficiently at room temperature, whereas the rearrange-

SCHEME 4



SCHEME 5



ment from **8g**−**k** to **2g**−**k** requires more elevated temperature.

In general, rearrangement of alkyl-substituted methylenecyclopropanes via trimethylenemethane intermediate proceeds by photoirradiation[9] or heating at high temperature.[1a−e,g,h,j,k,2,3s,4a−c,6a] Substitution of methylenecyclopropanes by aryl groups or halogen atoms makes the temperature of the rearrangement lower.[1g,l−o,3o,q,4a−c] Thermal rearrangement of alkyl-substituted cyclopropylidenecyclopropanes to spiropentanes also requires high temperature (>170 °C),[1d,2a−c] but the rearrangement of halogenated derivatives proceeds under relatively mild conditions (100−160 °C).[2d] In contrast, to the best of our knowledge, the rearrangement of **1a**−**f** to **2a**−**f** occurring at room temperature is a rare case.[10]

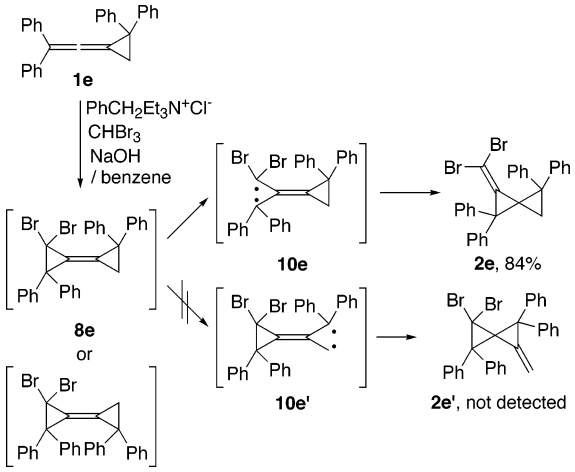
To clarify the mechanism of this rearrangement, the structure−reactivity relationship was evaluated by activation energies calculated by Arrhenius plot of the rearrangement from **8g**−**k**, **9g** to **2g**−**k**, **3g** in toluene-d_8 (Scheme 5, Table 3). Rotation of the aromatic ring of **8**, **9** might be important because the interaction of π-orbitals of the aromatic ring and σ-orbital of the cyclopropane ring seems to accelerate the rearrangement. This assumption is supported by the fact that the activation energy decreased in the order of **8g** > **8h** > **8i** (runs 1−4 in Table 3). The rotation of naphthyl ring of **8g** is suppressed by the interaction between the hydrogen atom on peri-position of the 1-naphthyl ring and the

TABLE 3. Activation Energies for the Rearrangement from 8g-k, 9g to 2g−k, 3g

run	substrate	Ar	R	X	product	E_a[a] (kJ/mol)
1	**8g**	1-naphthyl	Me	Br	**2g**	140.0
2	**9g**	1-naphthyl	Me	Cl	**3g**	119.3
3	**8h**	Ph	cyclohexyl	Br	**2h**	107.6
4	**8i**	Ph	Me	Br	**2i**	105.5
5	**8j**	*p*-ClC_6H_4	Me	Br	**2j**	99.6
6	**8k**	2-naphthyl	Me	Br	**2k**	93.6

[a] Activation energies were calculated by Arrhenius plots of reactions in toluene-d_8 at 65−105 °C.

SCHEME 6



methyl group. Rotation of phenyl ring of **8h** is suppressed by the steric hindrance of cyclohexyl group compared with that of methyl group of **8i**. The fluorene derivative **1f** in which aromatic rings cannot rotate gave only spiropentane derivative **2f** at room temperature (Table 1, entry 7). This result also supports the above assumption.

The second factor related to the efficiency of the rearrangement may be radical stabilization ability of the substituents. Activation energies required for the rearrangement of **8j** and **8k** were lower than that of **8i**. The *p*-chlorophenyl group of **8j** and 2-naphthyl group of **8k** might act to stabilize the intermediate **10** than the stabilization by the phenyl group of **8i**.[11]

The radical stabilization effect on the intermediate in this rearrangement was further supported by the regioselective cyclopropanation of vinylidenecyclopropane **1e** with dibromocarbene (Table 1, run 6, and Scheme 6). When dibromocarbene adds to the allenyl bond of vinylidenecyclopropane **1e**, cyclopropylidenecyclopropane intermediate **8e** should be formed. As the result of this reaction, only spiropentane derivative **2e** was produced without any formation of **2e′**. This result suggests that the C−C bond cleavage of **8e** occurred only at the dibromo-substituted cyclopropane ring; hence, we concluded that effect of halogen atoms to this thermal rearrangement is mainly due to their radical stabilization ability.[2d]

Conclusion

In conclusion, cyclopropanation of diarylvinylidenecyclopropanes by dihalocarbenes gave 1-(dihalomethylene)-

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(10) Creary et al. suggested that the two phenyl groups in an analogous methylenecyclopropane should allow the rearrangement to occur below room temperature. The methylenecyclopropane rearrangement of systems substituted with phenyl and methoxy groups occur readily at room temperature. See refs 1m and 3q.

(11) The radical-stabilizing effect of the 2-naphthyl group and halogen atoms has been discussed in refs 1l−n.

spiropentanes in high yields via cyclopropylidenecyclopropane intermediates. In the case of monoaryl derivatives, the rearrangement can be controlled by the substituents and the reaction temperature. Methylenespiropentane frameworks are important intermediates,[2c,6a,9l,12,13] especially for the synthesis of spiro-condensed cyclopropanes.[3w,14] It is expected that the present study will provide useful information for the synthesis of cyclopropylidenecyclopropanes and spiropentane derivatives.

Experimental Section

Cyclopropanation of Vinylidenecyclopropanes. To a benzene solution containing vinylidenecyclopropane **1a** (500 mg) were added a large excess of tribromomethane (0.5 mL), $PhCH_2Et_3N^+Cl^-$ (BTEAC, 0.1 equiv) as a phase-transfer agent, and a large excess of NaOH (powder), and the mixture was stirred for 5 h. Purification of the resulting mixture by use of column chromatography on silica gel followed by recrystallization from methanol afforded methylenespiropentane derivative **2a**. Other compounds were synthesized by a similar method.[8]

1-Dibromomethylene-4,4,5,5-tetramethyl-2,2-diphenylspiro[2.2]pentane (2a): mp 148−149 °C (methanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.22 (m, 10 H), 1.39 (s, 6 H), 0.91 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.40, 138.23, 128.51, 127.83, 126.32, 68.01, 50.57, 46.77, 31.69, 21.48, 20.13; IR (KBr) 2951, 2916, 2863, 1602, 1494, 1443, 1375 cm^{-1}; UV (cyclohexane) λ_{max} 220 nm (shoulder, log ϵ = 4.30). Anal. Calcd for $C_{22}H_{22}Br_2$: C, 59.22; H, 4.97. Found: C, 59.19; H, 5.12.

1,1-Bis(4-chlorophenyl)-2-dibromomethylene-4,4,5,5-tetramethylspiro[2.2]pentane (2b): mp 138.5−139.5 °C (methanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.14 (m, 8 H), 1.38 (s, 6 H), 0.92 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.47, 136.47, 132.40, 129.75, 128.21, 68.79, 50.67, 45.61, 31.94, 21.44, 20.19; IR (KBr) 2998, 2973, 2948, 2917, 2864, 1901, 1490 cm^{-1}; UV (cyclohexane) λ_{max} 229 nm (log ϵ = 4.46). Anal. Calcd for $C_{22}H_{20}Br_2Cl_2$: C, 51.30; H, 3.91. Found: C, 50.95; H, 4.06.

1,6-Dimethylbicyclo[4.1.0]heptane-7-spiro-2′,2′-bis(4-chlorophenyl)-3′-(dibromomethylene)cyclopropane (2c): mp 126−127 °C (methanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.14 (m, 8 H), 1.42−0.87 (m, 14 H); ^{13}C NMR (75 MHz, CDCl3) δ 141.06, 136.23, 132.43, 129.68, 128.28, 68.62, 48.77, 46.06, 32.50, 28.88, 21.77, 21.26; IR (KBr): 2933, 2858, 1735, 1560, 1491, 1396 cm^{-1}; UV (cyclohexane) λ_{max} 229 nm (log ϵ = 4.46). Anal. Calcd for $C_{24}H_{22}Br_2Cl_2$: C, 53.27; H, 4.10. Found: C, 53.04; H, 4.17.

1-Dibromomethylene-2,2-bis(4-methoxyphenyl)-4,4,5,5-tetramethylspiro[2.2]pentane (2d): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18−1.15 (m, 4 H), 6.85−6.82 (m, 4 H), 1.37 (s, 6 H), 0.93 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.96, 142.85, 130.61, 129.56, 113.22, 67.30, 55.24, 50.40, 45.78, 31.66, 21.49, 20.25; IR (KBr) 2996, 2951, 2831, 1609, 1511, 1458, 1248 cm^{-1}; UV (cyclohexane) λ_{max} 236 nm (log ϵ = 4.40).

1-Dibromomethylene-2,2,4,4-tetraphenylspiro[2.2]-pentane (2e): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−6.96 (m, 18 H), 6.79−6.75 (m, 2 H), 2.54 (d, J = 5.13 Hz, 1 H), 2.25 (d, J = 5.13 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.27, 140.41, 140.15, 138.43, 137.35, 130.00, 128.61, 128.28, 128.22, 127.73, 127.01, 126.96, 126.86, 126.59, 125.86, 71.80, 45.48, 44.40, 41.03, 22.34; IR (KBr) 3057, 3024, 1735, 1601, 1493, 1444 cm^{-1}; UV (cyclohexane) λ_{max} 220 nm (shoulder, log ϵ = 4.51). Anal. Calcd for $C_{30}H_{22}Br_2$: C, 66.44; H, 4.09. Found: C, 66.73; H, 3.88.

1-Dibromomethylene-2,4,4,5,5-pentamethyl-2-(1-naphthyl)spiro[2.2]pentane (2g): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16−8.13 (m, 1 H), 7.86−7.73 (m, 2 H), 7.55−7.26 (m, 4 H), 1.87 (s, 3 H), 1.50 (s, 3 H), 1.45 (s, 3 H), 1.15 (s, 3 H), 0.49 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.80, 135.80, 134.00, 132.42, 128.97, 127.81, 125.49, 125.42, 125.04, 124.95, 66.19, 50.35, 38.33, 32.32, 31.97, 29.79, 21.92, 21.44, 20.31, 20.18, 18.38; IR (KBr) 3005, 2921, 2858 cm^{-1}; UV (cyclohexane) λ_{max} 284 (log ϵ = 3.88), 275 (log ϵ = 3.80), 225 nm (log ϵ = 4.80). Anal. Calcd for $C_{21}H_{22}Br_2$: C, 58.09; H, 5.11. Found: C, 57.95; H, 5.28.

1-Cyclohexyl-2-dibromomethylene-4,4,5,5-tetramethyl-1-phenylspiro[2.2]pentane (2h): mp 156−156.5 °C (methanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.15 (m, 5 H), 2.33−2.26 (m, 1 H), 1.86−1.63 (m, 5 H), 1.43−1.11 (m, 14 H), 0.43 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.75, 138.99, 127.88, 127.43, 125.91, 66.68, 46.89, 46.85, 39.11, 31.57, 31.49, 30.88, 28.83, 27.18, 26.80, 26.65, 21.54, 20.76, 20.46, 18.88; IR (KBr) 3057, 3005, 2979, 2937, 2849 cm^{-1}; UV (cyclohexane) λ_{max} 222 nm (log ϵ = 4.27). Anal. Calcd for $C_{22}H_{28}Br_2$: C, 58.42; H, 6.24. Found: C, 58.16; H, 6.36.

1-Dibromomethylene-2,4,4,5,5-pentamethyl-2-phenylspiro[2.2]pentane (2i): mp 53.5−54.5 °C (methanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.15 (m, 5 H), 1.63 (s, 3 H), 1.36 (s, 3 H), 1.32 (s, 3 H), 1.22 (s, 3 H), 0.66 (s, 3 H); ^{13}C NMR

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(75 MHz, $CDCl_3$) δ 140.30, 128.00, 125.92, 125.83, 65.51, 50.49, 37.54, 31.59, 31.50, 31.42, 21.54, 21.29, 19.70, 19.28, 17.33; IR (KBr) 2952, 2924, 2866, 1375 cm^{-1}; UV (cyclohexane) λ_{max} 223 nm ($\log \epsilon = 4.36$). Anal. Calcd for $C_{17}H_{20}Br_2$: C, 53.15; H, 5.25. Found: C, 53.53; H, 5.28.

1-(4-Chlorophenyl)-2-dibromomethylene-1,4,4,5,5-pentamethylspiro[2.2]pentane (2j): oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27−7.24 (m, 2 H), 7.10−7.08 (m, 2 H), 1.60 (s, 3 H), 1.36 (s, 3 H), 1.32 (s, 3 H), 1.21 (s, 3 H), 0.68 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.70, 139.05, 131.61, 128.18, 127.30, 65.97, 50.53, 37.00, 31.68, 31.62, 21.52, 21.25, 19.66, 19.41, 17.27; IR (neat) 2987, 2952, 2918, 2866, 1488, 1375 cm^{-1}; UV (cyclohexane) λ_{max} 230 nm ($\log \epsilon = 4.38$). Anal. Calcd for $C_{17}H_{19}Br_2Cl$: C, 48.78; H, 4.58. Found: C, 48.65; H, 4.99.

1-Dibromomethylene-2,4,4,5,5-pentamethyl-2-(2-naphthyl)spiro[2.2]pentane (2k): oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81−7.74 (m, 3 H), 7.66−7.65 (m, 1 H), 7.46−7.42 (m, 2 H), 7.25−7.18 (m, 1 H), 1.74 (s, 3 H), 1.39 (s, 3 H), 1.36 (s, 3 H), 1.24 (s, 3 H), 0.66 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.40, 138.19, 133.22, 131.81, 127.536, 127.532, 127.41, 125.86, 125.31, 124.60, 124.34, 65.76, 50.44, 37.77, 31.67, 31.56, 21.51, 21.33, 19.73, 19.58, 17.39; IR (NaCl) 3056, 2987, 2952, 2920, 2866, 1735, 1601, 1507, 1458, 1411, 1377 cm^{-1}; UV (cyclohexane) λ_{max} 288 ($\log \epsilon = 3.85$), 278 ($\log \epsilon = 4.00$), 268 ($\log \epsilon = 4.01$), 228 nm ($\log \epsilon = 4.88$). Anal. Calcd for $C_{21}H_{22}Br_2$: C, 58.09; H, 5.11. Found: C, 58.26; H, 5.07.

1-Dichloromethylene-4,4,5,5-tetramethyl-2,2-diphenylspiro[2.2]pentane (3a): mp 129−130 °C (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 7.30−7.23 (m, 10 H), 1.34 (s, 6 H), 0.94 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.81, 135.05, 128.87, 128.49, 126.36, 105.14, 48.99, 44.46, 31.26, 21.42, 20.12; IR (KBr) 2999, 2949, 2918, 2866, 1560, 1496, 1379 cm^{-1}; UV (cyclohexane) λ_{max} 223 nm ($\log \epsilon = 4.35$). Anal. Calcd for $C_{22}H_{22}Cl_2$: C, 73.95; H, 6.21. Found: C, 73.84; H, 6.41.

1-Dichloromethylene-2,4,4,5,5-pentamethyl-2-(1-naphthyl)spiro[2.2]pentane (3g): mp 155−156 °C (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 8.17−8.14 (m, 1 H), 7.85−7.82 (m, 1 H), 7.76−7.73 (m, 1 H), 7.50−7.37 (m, 4 H), 1.85 (s, 3 H), 1.52 (s, 3 H), 1.41 (s, 3 H), 1.11 (s, 3 H), 0.53 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.47, 135.41, 134.08, 132.46, 129.03, 127.90, 125.67, 125.56, 125.16, 125.15, 125.02, 104.22, 48.63, 36.11, 31.75, 31.29, 21.84, 21.24, 20.76, 20.01, 18.26; IR (KBr) 3005, 2987, 2950, 2918, 2866 cm^{-1}; UV (cyclohexane) λ_{max} 295 ($\log \epsilon = 3.75$), 284 ($\log \epsilon = 3.91$), 274 ($\log \epsilon = 3.82$), 224 nm ($\log \epsilon = 4.78$). Anal. Calcd for $C_{21}H_{22}Cl_2$: C, 73.04; H, 6.42. Found: C, 73.00; H, 6.30.

1-Diphenylmethylidene-4,4,5,5-tetramethyl-2,2-diphenylspiro[2.2]pentane (4): mp 176.5−177.5 °C (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 7.41−7.00 (m, 20 H), 0.80 (s, 6 H), 0.75 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.57, 141.45, 140.81, 140.02, 138.91, 137.28, 131.20, 130.85, 128.95, 127.71, 127.64, 127.52, 127.21, 126.92, 126.28, 125.98, 125.70, 125.58, 43.77, 39.08, 30.43, 20.95, 20.47; IR (KBr) 3058, 3031, 2243, 1493 cm^{-1}; UV (cyclohexane) λ_{max} 302 ($\log \epsilon = 3.89$), 238 nm ($\log \epsilon = 4.14$). Anal. Calcd for $C_{34}H_{32}$: C, 92.68; H, 7.32. Found: C, 92.78; H, 6.92.

***(E)*-1,1,2,2-Tetramethyl-4,4-diphenyl-5-(phenylthiomethylene)spiro[2.2]pentane ((*E*)-5):** mp 119−120 °C dec (hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36−7.14 (m, 15 H), 6.62 (s, 1 H), 1.38 (s, 6 H), 0.98 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.15, 140.90, 137.69, 128.81, 128.67, 127.80, 127.70, 125.82, 125.66, 105.44, 46.25, 40.53, 31.02, 21.77, 20.23; IR (KBr) 3057, 3031, 2998, 2913, 2866, 1581, 1492, 1478, 1438, 1375, 1086, 1024 cm^{-1}; UV (cyclohexane) λ_{max} 279 ($\log \epsilon = 4.18$), 258 nm ($\log \epsilon = 4.13$). Anal. Calcd for $C_{28}H_{28}S$: C, 84.80; H, 7.12. Found: C, 84.40; H, 4.14.

1-Dibromomethylene-2,2-diphenylcyclopropane (7a): mp 92.5−93.5 °C (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 7.34−7.26 (m, 10 H), 2.16 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.52, 136.55, 128.44, 127.89, 127.10, 76.04, 43.93, 28.07; IR (KBr) 3057, 3026, 2979, 1957, 1748, 1592, 1494, 1448, 1013 cm^{-1}; UV (cyclohexane) λ_{max} 222 nm ($\log \epsilon = 4.34$). Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32. Found: C, 52.63; H, 3.17.

1,1-Bis(*p*-chlorophenyl)-2-(dibromomethylene)cyclopropane (7b): mp 110−111 °C (methanol); ^1H NMR (300 MHz, C_6D_6) δ 7.16−7.01 (m, 4 H), 6.99−6.80 (m, 4 H), 1.51 (s, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 138.76, 136.33, 133.50, 129.50, 129.00, 77.22, 42.60, 27.91; IR (KBr) 3100, 3057, 2979, 2918, 2849, 1902, 1745, 1493, 1398 cm^{-1}; UV (cyclohexane) λ_{max} 230 nm ($\log \epsilon = 4.47$). Anal. Calcd for $C_{16}H_{10}Br_2Cl_2$: C, 44.39; H, 2.33. Found: C, 44.39; H, 2.24.

2,2-Dibromo-2′,2′,3,3′,3′-pentamethyl-3-(1-naphthyl)-1,1′-bicyclopropylidene (8g): mp 128−131 °C dec (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 8.17−8.12 (m, 1 H), 7.91−7.88 (m, 1 H), 7.79−7.76 (m, 1 H), 7.66−7.60 (m, 1 H), 7.55−7.50 (m, 1 H), 7.38−7.26 (m, 2 H), 1.86 (s, 3 H), 1.51 (s, 3 H), 1.39 (s, 3 H), 1.35 (s, 3 H), 1.34 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.46, 139.15, 134.01, 131.00, 128.59, 127.96, 126.14, 126.05, 125.90, 125.75, 125.19, 121.01, 40.68, 34.91, 26.44, 24.67, 24.33, 21.28, 21.01, 20.59, 20.52; IR (KBr) 3057, 2987, 2923, 2866, 1448, 1370, 1108 cm^{-1}; UV (cyclohexane) λ_{max} 298 ($\log \epsilon = 3.60$), 286 ($\log \epsilon = 3.71$), 276 ($\log \epsilon = 3.63$), 226 nm ($\log \epsilon = 4.63$). Anal. Calcd for $C_{21}H_{22}Br_2$: C, 58.09; H, 5.11. Found: C, 58.43; H, 5.15.

2,2-Dibromo-3-cyclohexyl-2′,2′,3′,3′-tetramethyl-2-phenyl-1,1′-bicyclopropylidene (8h): mp 92.5−94 °C dec (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 7.41−7.03 (m, 5 H), 2.19−2.15 (m, 1 H), 1.76−1.53 (m, 5 H), 1.40 (s, 3 H), 1.35 (s, 3 H), 1.33 (s, 3 H), 1.30−0.80 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.39, 137.47, 131.11, 130.23, 127.53, 126.78, 121.79, 48.68, 48.45, 34.01, 30.96, 29.23, 26.84, 26.27, 26.05, 24.21, 23.79, 21.57, 21.30, 20.51, 20.44; IR (KBr) 2985, 2927, 2850, 1491, 1445, 1105 cm^{-1}; UV (cyclohexane) λ_{max} 216 nm ($\log \epsilon = 4.32$). Anal. Calcd for $C_{22}H_{28}Br_2$: C, 58.42; H, 6.24. Found: C, 58.06; H, 6.56.

2,2-Dibromo-2′,2′,3,3′,3′-pentamethyl-3-phenyl-1,1′-bicyclopropylidene (8i): mp 93−94 °C dec (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 7.33−7.25 (m, 5 H), 1.78 (s, 3 H), 1.40 (s, 3 H), 1.36 (s, 3 H), 1.35 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.99, 141.81, 128.15, 128.04, 127.18, 120.38, 40.64, 34.81, 26.43, 24.67, 24.16, 20.86, 20.81, 20.60, 20.53; IR (KBr) 3061, 2991, 2949, 2920, 2864, 1496, 1444 cm^{-1}; UV (cyclohexane) λ_{max} 211 nm (shoulder, $\log \epsilon = 4.39$). Anal. Calcd for $C_{17}H_{20}Br_2$: C, 53.15; H, 5.25. Found: C, 53.35; H, 5.21.

2,2-Dibromo-3-(*p*-chlorophenyl)-2′,2′,3,3′,3′-pentamethyl-1,1′-bicyclopropylidene (8j): mp 69−75 °C dec (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2 H), 7.22−7.19 (m, 2 H), 1.75 (s, 3 H), 1.38 (s, 3 H), 1.35 (s, 3 H), 1.34 (s, 3 H), 1.25 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.43, 140.31, 133.01, 129.54, 128.26, 120.03, 39.93, 34.12, 32.23, 24.79, 24.23, 20.83, 20.77, 20.57, 20.49; IR (KBr) 2987, 2952, 2918, 2866, 1488, 1375, 1088 cm^{-1}; UV (cyclohexane) λ_{max} 223 nm ($\log \epsilon = 4.36$). Anal. Calcd for $C_{17}H_{19}Br_2Cl$: C, 48.78; H, 4.58. Found: C, 48.59; H, 4.48.

2,2-Dibromo-2′,2′,3,3′,3′-pentamethyl-3-(2-naphthyl)-1,1′-bicyclopropylidene (8k): mp 72−81 °C dec (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 7.85−7.66 (m, 4 H), 7.51−7.25 (m, 3 H), 1.86 (s, 3 H), 1.52 (s, 3 H), 1.39 (s, 3 H), 1.38 (s, 3 H), 1.31 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.99, 139.36, 132.97, 132.50, 127.75, 127.72, 127.59, 127.12, 126.12, 125.98, 125.84, 120.54, 40.81, 34.57, 26.40, 24.73, 24.21, 21.01, 20.84, 20.61, 20.57; IR (KBr) 3057, 2987, 2945, 2916, 2861, 1601, 1438, 1371 cm^{-1}; UV (cyclohexane) λ_{max} 276 ($\log \epsilon = 3.87$), 267 nm ($\log \epsilon = 3.90$). Anal. Calcd for $C_{21}H_{22}Br_2$: C, 58.09; H, 5.11. Found: C, 58.00; H, 5.00.

2,2-Dichloro-2′,2′,3,3′,3′-pentamethyl-3-(1-naphthyl)-1,1′-bicyclopropylidene (9g): mp 109−110 °C dec (methanol); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16−7.25 (m, 7 H), 1.83 (s, 3 H), 1.51 (s, 3 H), 1.35 (s, 3 H), 1.34 (s, 3 H), 1.32 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.71, 137.80, 133.95, 131.33, 128.56, 128.02, 126.16, 126.08, 125.71, 125.62, 125.20, 119.00, 63.44, 40.24, 24.48, 24.31, 24.03, 21.31, 21.05, 20.62, 20.57;

IR (KBr) 3065, 2989, 2926, 2866, 1507, 1448, 1371 cm^{-1}; UV (cyclohexane) λ_{max} 296 (log ϵ = 3.81), 285 (log ϵ = 3.96), 275 (log ϵ = 3.85), 227 nm (log ϵ = 4.78). Anal. Calcd for $C_{21}H_{22}Cl_2$: C, 73.04; H, 6.42. Found: C, 73.13; H, 6.36.

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Supporting Information Available: Synthetic procedure, spectral and analytical data of vinylidenecyclopropanes **1a**−**j**, and X-ray reports and ORTEP drawings of **2a**, **3g**, **4**, **(*E*)-5**, and **9g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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