cm^{-1}; ^{1}H NMR δ 1.10–3.30 (br m, 13 H, CH_2 and CH), 7.25–7.90 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{21}H_{23}OP$ 322.1486 (M^+), found 322.1473.

Cycloaddition of 24 to 21. A mixture of **24** (0.40 g, 0.96 mmol) and **21** (1.5 mL) in CH_2Cl_2 (3 mL) was similarly heated at 140 °C for 3 h. Addition of ether to the reaction mixture gave pure **(tricyclo[4.2.1.0^{2,5}]non-7-en-2-yl)triphenylphosphonium perchlorate (25)** (0.34 g, 0.71 mmol, 74%): mp 228–230 °C; IR (KBr) 1610, 1590, 1485, 1100 cm^{-1}; ^{1}H NMR δ 1.0–2.47 (br m, 6 H, CH_2), 2.80–3.60 (br m, 3 H, CH), 6.71 (br s, 2 H, olefinic H), 7.50–7.90 (m, 15 H, phenyl H).

Anal. Calcd for $C_{27}H_{26}O_4PCl$: C, 67.42; H, 5.45. Found: C, 67.27; H, 5.58.

Alkaline Hydrolysis of 25. A solution of **25** (1.40 g, 2.9 mmol) in methanol/H_2O (2:1, 60 mL) containing NaOH (1.40 g, 35 mmol) was heated at reflux for 10 days. After the usual workup, the residue was chromatographed on silica gel to give **22** in 0.12 g (0.38 mmol, 13%) yield together with recovered **25** (0.96 g, 2 mmol, 70%).

Registry No. **1**, 86046-76-6; **2**, 101630-34-6; **3a**, 140-88-5; **3b**, 1896-62-4; **3c**, 614-47-1; **3d**, 123-73-9; **3e**, 97-63-2; **4**, 101630-22-2; **5**, 101630-23-3; **6**, 101630-24-4; **7**, 101630-25-5; **8**, 101630-26-6; **9**, 101630-27-7; **10**, 101630-28-8; **11**, 101630-29-9; **12**, 101630-30-2; **13**, 101630-31-3; **14**, 77-79-2; **15**, 101630-32-4; **16**, 101630-35-7; **17**, 101630-36-8; **18**, 1972-28-7; **19**, 101630-33-5; **20**, 101630-37-9; **21**, 542-92-7; **22**, 101630-38-0; **23**, 101630-39-1; **24**, 86046-73-3; **25**, 101630-41-5.

Supplementary Material Available: ^{13}C NMR data for compounds **4–13, 15, 19, 20, 22, 23,** and **25** (Tables II, III) (2 pages). Ordering information is given on any current masthead page.

Metacyclophanes and Related Compounds. 18. Preparation of *anti*-5,14-Di-*tert*-butyl-8,17-dimethyl[2.3]metacyclophan-1-ene and *anti*-5,15-Di-*tert*-butyl-8,18-dimethyl[2.4]metacyclophan-1-enes with Dichlorocarbene[1,2]

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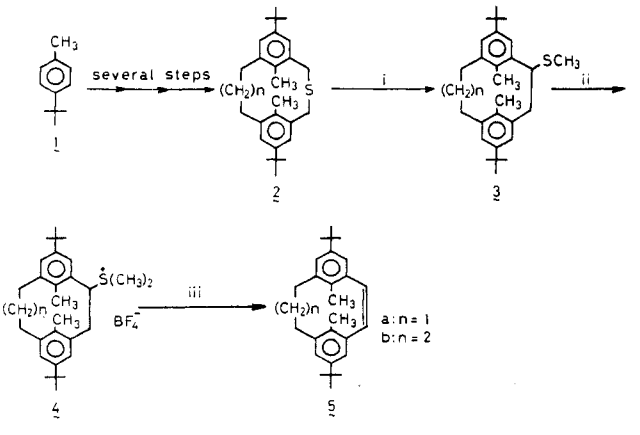
Preparations of *anti*-5,14-di-*tert*-butyl-8,17-dimethyl[2.3]metacyclophan-1-ene (**5a**) and *anti*-5,15-di-*tert*-butyl-8,18-dimethyl[2.4]metacyclophan-1-ene (**5b**) are described. Reaction of *anti*-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophan-1-ene (**5c**) with dichlorocarbene in the presence of phase-transfer catalyst afforded heptafluvenophane (**6**) and cycloheptatrienophane (**7**) in 17% and 24% yield, respectively. It was also found that dichlorocarbene reacted with **6** to provide **7**. Reaction of **5a** with dichlorocarbene gave benzocycloheptatrienophane **12**. Reaction of **5b** with dichlorocarbene afforded only a mixture of isomers **14**. The electronic spectrum of **14** resembles that of **12**.

Although few [2.2]metacyclophan-1-enes[3,4] have been prepared, there is very little information about their chemical nature and reactivity.[4,5] In addition, the compounds of the [2.3]- and [2.4]metacyclophan-1-ene series are still unknown.

It is well recognized that dichlorocarbene reacts with various olefins to afford the corresponding dichlorocyclopropane derivatives.[6] Weyerstahl and Blüme have shown[7] that dichlorocarbene reacts with aromatic compounds like methylnaphthalenes and toluene in the presence of a phase-transfer catalyst to provide the corresponding cycloheptatriene in very poor yields. So far there is no report on the reaction of dichlorocarbene with dimethyl[2.*n*]-metacyclophan-1-enes, which possess both an olefinic bond as well as methylarene moities.

We now report the preparation of title compounds as well as the behavior of various dimethyl[2.*n*]metacyclophan-1-enes with dichlorocarbene in the presence or ab-

Scheme I[a]



[a] (i) *n*-BuLi, MeI; (ii) $(CH_3O)_2C^+HBF_4^-$; (iii) *t*-BuOK, THF.

(1) A part of this paper was published as a preliminary communication: Tashiro, M.; Kobayashi, K.; Yamato, T.; Yoshihira, K.; Kawazoe, K.; Sato, S.; Tamura, C. *Chem. Pharm. Bull.* **1984**, *32*, 4220.

(2) Part 17. Yamato, T.; Arimura, T.; Tashiro, M., submitted for publication.

(3) Blaschke, H.; Ramey, C. E.; Calder, I.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3675.

(4) Tashiro, M.; Yamato, T. *J. Am. Chem. Soc.* **1982**, *104*, 3701.

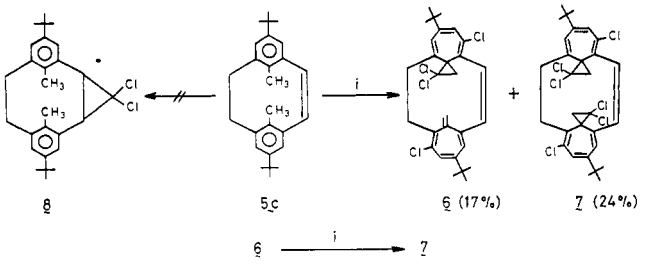
(5) Ramey, C. E.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3681.

(6) Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., John Willy Sons: New York, 1973; Chapter 2.

(7) Wyerstahl, P.; Blume, G. *Tetrahedron* **1972**, *28*, 5281.

0022-3263/86/1951-2214$01.50/0

Scheme II[a]



[a] (i) 50% KOH, $CHCl_3$, n-$(C_4H_9)_4N^+Cl^-$ in benzene at 5 °C for 6 h.

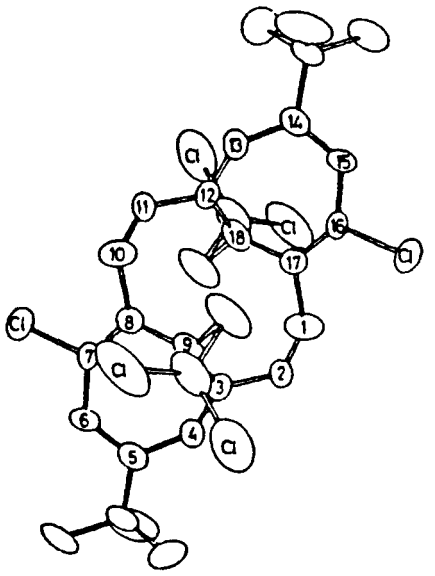


Figure 1. Ortep drawming of 7.

sence of a phase-transfer catalyst.

Results and Discussion

Preparation of Title Compounds 5a and 5b. The compounds **5a** and **5b** were prepared according to the routes shown in Scheme I.

The intermediate thio compounds **2a** and **2b** were prepared in a previous work.[8] The conversion of **2a** and **2b** to **5a** and **5b** were carried out by using standard procedures.[4] The structures of **5a** and **5b** were ascertained by their elemental analyses and spectroscopic data.

Reactions of Dimethyl[2.2]metacyclophan-1-enes 5c–e with Dichlorocarbene. Treatment of the previously known 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophan-1-ene (**5c**)[4] with 50% aqueous KOH solution in a mixture of chloroform and benzene in the presence of tetrabutylammonium chloride as a phase-transfer catalyst at 5 °C following the procedure of Weyerstahl provided heptafluvenophane **6** and cycloheptatrienophane **7** in 17% and 24% yield, respectively (Scheme II). However, no dichlorocyclopropane derivative **8** was detected. In the absence of the phase-transfer catalyst, the starting material **5c** was recovered intact. It was also found that similar dichlorocarbene treatment of **6** yielded **7**, indicating the intermediacy of **6** in the formation of **7** from **5c**. The structure of **7** was determined by X-ray analysis (Figure 1).

Crystal data: monoclinic $P2_1/c$, a = 11.852 (5), b = 7.343 (1), and c = 18.459 (5) Å, and β = 109.75 (2)°, V = 1512.0 Å^3, ρ_c = 1.33 g·cm^{-3}, and Z = 2. Bond angles and bond lengths of **7** are shown in Figure 2.

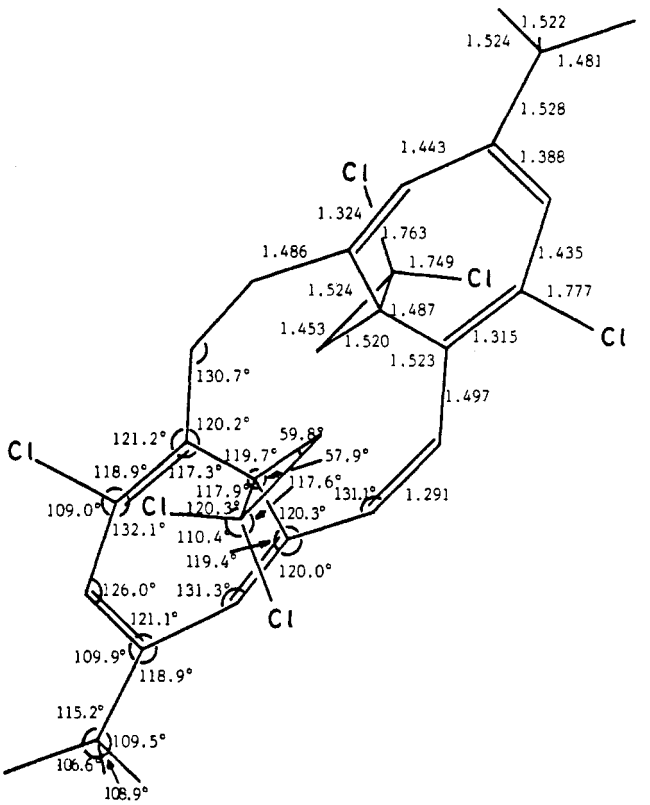
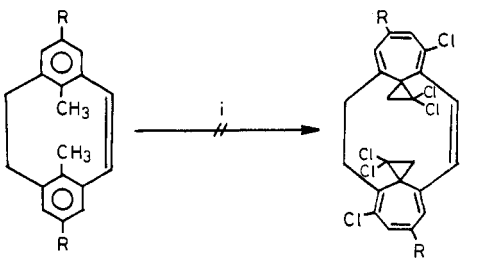


Figure 2. Bond angles and lengths of 7.

Scheme III[a]



[a] (i) 50% KOH, $CHCl_3$, n-$(C_4H_9)_4N^+Cl^-$ in benzene at room temperature.

The structure of **6** was assumed from the above chemical conversion, its elemental analysis, and spectroscopic data.

From the above results it was expected that other 8,16-dimethyl[2.2]metacyclophan-1-enes such as 8,16-dimethyl[2.2]metacyclophan-1-ene (**5d**)[9] and 5,13-dichloro-8,16-dimethyl[2.2]metacyclophan-1-ene (**5e**)[10] to behave similarly with dichlorocarbene (Scheme III). On the other hand, treatment of **5d** and **5e** with dichlorocarbene gave a small amount of a mixture of complex products along with large amounts of the starting materials.

These results seem to indicate that the bulky *tert*-butyl group in **5c** plays an important role in the reaction with dichlorocarbene.

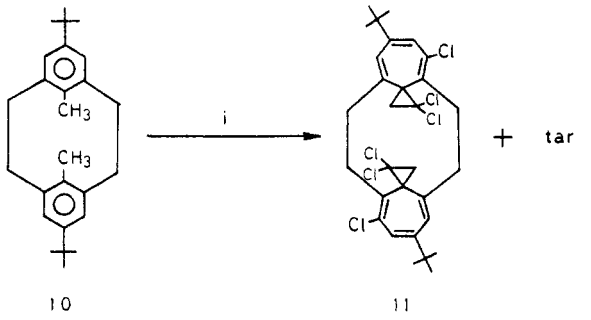
From the reaction of **5c** with dichlorocarbene it is very clear that attack occurs at the benzene rings and not with the isolated olefinic bond. Based on this, we treated

(8) Tashiro, M.; Sakamoto, H.; Kobayashi, K.; Yamato, T., submitted for publication.

(9) Tashiro, M.; Yamato, T.; Kobayashi, K. *J. Org. Chem.* **1984**, *49*, 4724.

(10) Tashiro, M.; Yamato, T.; Kobayashi, K. *J. Org. Chem.* **1984**, *49*, 3380.

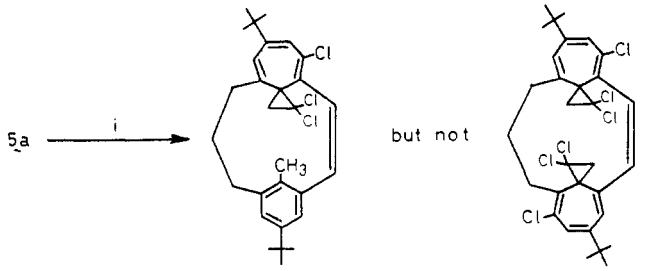
Scheme IV[a]



10 11

[a] (i) 50% KOH, $CHCl_3$, n-$(C_4H_9)_4N^+Cl^-$ in benzene at 35 °C for 8.5 h.

Scheme V[a]



12 13

[a] (i) 50% KOH, $CHCl_3$, n-$(C_4H_9)_4N^+Cl^-$ in benzene at room temperature for 34.5 h.

5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane (**10**) with dichlorocarbene. Indeed, the corresponding cycloheptatrienophane **11** was obtained as expected, but only in very poor yield (0.86%) along with large amounts of resinous materials (Scheme IV).

The structure of **11** was ascertained from the elemental analysis as well as spectroscopic data. The latter compares very well with those of **7**. The above observations seem to indecate that the presence of an isolated olefinic moiety as well as *tert*-butyl groups in **5c** accelerate the reaction with dichlorocarbene.

It was, however, found that **5c** was unreactive toward diphenyldiazomethane and ethyl diazoacetate either photochemically or thermally.

Reactions of [2.3]- and [2.4]Metacyclophan-1-enes 5a and 5b with Dichlorocarbene. Reaction of **5a** with dichlorocarbene under similar conditions led to an unexpected product **12** (Scheme V). The expected product **13** was not obtained. The reaction time, in this case, was longer than that in **5c**. The structure of **12** was confirmed from spectroscopic data as well as elemental analysis. The behavior of **5a** appears to be similar to **5c** with respect to the lack of reactivity of the isolated olefinic bond.

Similarly **5b** with dichlorocarbene under prolonged reaction time gave the product **14** in 14% yield. About 65% of the starting material **5b** was recovered intact. The elemental analysis and spectroscopic data on **14** agrees with the molecular formula, $C_{30}H_{37}Cl_3$. Moreover, the electronic spectrum of **14** closely resembles that of **12**, indicating their similar nature (Figure 3).

Theoretically there could be six possible isomers for the compound **14** and all are shown in Figure 4. However, the ^1H NMR spectrum of **14**, although complex, appears to be due to a mixture of only two isomers. Unfortunately, the individual components could not be isolated by the usual chromatographic techniques (column, TLC, etc.). From the similarity of the electronic spectrum (to **12**) and analysis of the NMR pattern, the main product in the

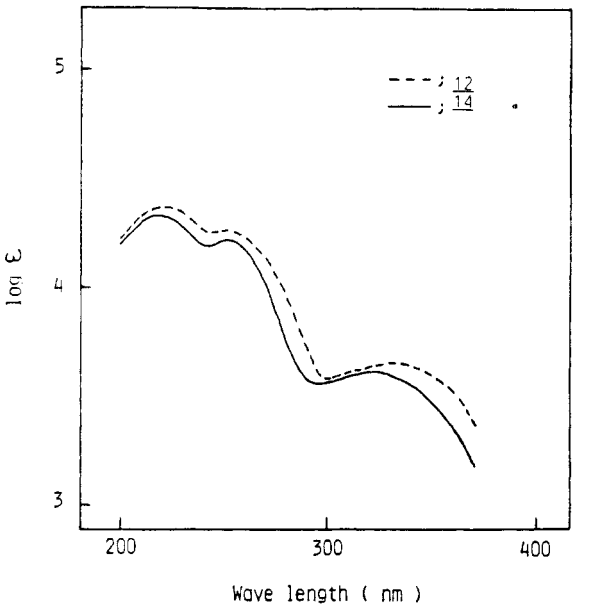


Figure 3. Electronic spectra of **12** and **14** (cyclohexane).

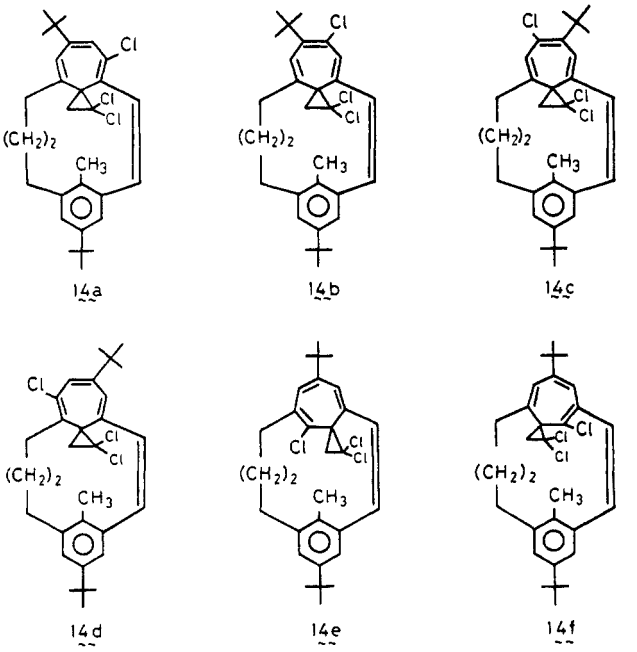


Figure 4.

mixture is assumed to have structure **14a**.

Although, our studies does not shed much light on the mechanism of dichlorocarbene with **5**, a possible mechanistic pathway for the formation of products is shown in Scheme VI.

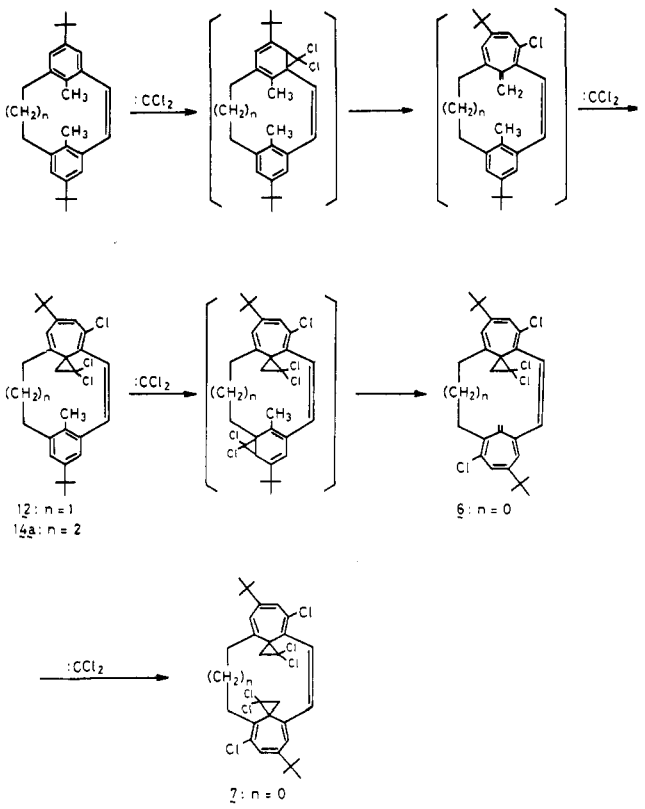
From the observed rate of reactivity of **5a–c** with dichlorocarbene, one could propose the relative reactivity order to be **5c** > **5a** > **5b**. This is in agreement with the relative strains in those molecules. Moreover, compounds **12** and **14** appear to be unreactive toward dichlorocarbene.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were recorded at 100 MHz with a Nippon Denshi JEOL FT-100 NMR spectrometer with Me_4Si as an internal reference. IR spectra were measured on KBr pellets or a liquid film on NaCl plates in a Nippon Bunko IR-A-102 spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct inlet system.

Wittig Rearrangement of 2a To Give 3a. To a stirred solution of 700 mg (1.77 mmol) of **2a** in 25 mL of dry tetrahydrofuran

Scheme VI



under nitrogen was added 1.7 mL of a 15% hexane solution of *n*-butyllithium (3.98 mmol), with ice cooling. After stirring the reaction mixture for 10 min at room temperature, 0.32 mL (5.14 mmol) of methyl iodide was added. The reaction mixture was worked up by addition of H_2O and CH_2Cl_2. The dichloromethane extract was washed with water, dried over Na_2SO_4, and concentrated. The products were purified by filtration through silica gel with 1:1 hexane–benzene to give 673 mg (98%) of **3a**: colorless prisms (hexane); mp 154–156 °C dec; NMR ($CDCl_3$) δ 0.70, 0.71 (each 3 H, s), 1.28, 1.31 (each 9 H, s), 1.88–2.16 (2 H, m), 2.07 (3 H, s), 2.40–2.78 (5 H, m), 3.06 (1 H, dd, J = 11.0 Hz, 3.5 Hz), 3.90 (1 H, dd, J = 11.0 Hz, 3.5 Hz), 6.98 (1 H, d, J = 2.0 Hz), 7.05 (2 H, br s), 7.72 (1 H, d, J = 2.0 Hz); mass spectrum; m/e 408 (M^+). Anal. Calcd for $C_{28}H_{40}S$: C, 82.29; H, 9.86. Found: C, 82.51; H, 9.81.

Compound **3b** was prepared in 88% yield by the same method: colorless prisms (hexane); mp 180–181 °C; NMR ($CDCl_3$) δ 0.80–1.60 (4 H, m), 0.91, 0.96 (each 3 H, s), 1.28, 1.31 (each 9 H, s), 1.89–2.40 (2 H, m), 2.05 (3 H, s), 2.56–2.96 (3 H, m), 3.14 (1 H, dd, J = 11.7 Hz, 3.7 Hz), 4.14 (1 H, dd, J = 11.7 Hz, 3.7 Hz), 6.82 (1 H, d, J = 2.2 Hz), 6.88 (1 H, d, J = 2.2 Hz), 7.13 (1 H, d, J = 2.2 Hz), 7.78 (1 H, d, J = 2.2 Hz); mass spectrum, m/e 422 (M^+). Anal. Calcd for $C_{29}H_{42}S$: C, 82.40; H, 10.01. Found: C, 82.57; H, 10.23.

Preparation of Sulfonium Salt 4a. A solution of 1.91 g (4.67 mmol) of a mixture of isomers **3a** in 10 mL of dichloromethane was added with stirring to a suspension of 6.5 g of dimethoxycarbonium tetrafluoroborate in 5 mL of dichloromethane that was maintained at −30 °C under nitrogen. The mixture was allowed to warm to room temperature and was stirred for an additional 4 h. Then, 150 mL of ethyl acetate was added, the mixture was stirred overnight, and the solvent was decanted. The resulting crystalline precipitate was collected and dried, giving 1.12 g (47%) of **4a**: colorless crystals; mp 280–283 °C dec; NMR (Me_2SO-d_6) δ 0.69, 0.75 (each 3 H, s), 1.27 (18 H, s), 1.84–2.13 (2 H, m), 2.48–3.00 (6 H, m), 2.82, 3.31 (each 3 H, s), 4.30–4.54 (1 H, m), 7.00–7.30 (4 H, m). Anal. Calcd for $C_{29}H_{43}SBF_4$: C, 68.23; H, 8.49. Found: C, 67.98; H, 8.36.

Sulfonium salt **4b** was obtained in 78% yield by the same method: colorless needles; mp 274–277 °C dec; NMR (Me_2SO-d_6) δ 0.80–1.60 (4 H, m), 0.92, 1.01 (each 3 H, s), 1.27 (18 H, s), 1.88–2.34 (2 H, m), 2.56–3.28 (4 H, m), 2.75, 3.31 (each 3 H, s), 4.56–4.80 (1 H, m), 6.88, 7.05, 7.23, 7.41 (each 1 H, d, J = 2.0 Hz). Anal. Calcd for $C_{30}H_{45}SBF_4$: C, 68.69; H, 8.65. Found: C, 68.44; H, 8.52.

Hofmann Elimination of 4a To Give 5,14-Di-*tert*-butyl-8,17-dimethyl[2.3]metacyclophan-1-ene (5a). To a solution of 1.12 g (2.19 mmol) of **4a** in 70 mL of dry tetrahydrofuran was added with stirring 440 mg (3.92 mmol) of potassium *tert*-butoxide. After the mixture was stirred at room temperature under nitrogen for 4 h, benzene was added and the mixture was acidified by the addition of dilute aqueous hydrochloric acid. The organic layer was separated, washed with water, dried, and concentrated. The residue was recrystallized from methyl alcohol to give 639 mg (81%) of **5a**: colorless prisms (MeOH); mp 196–199 °C; NMR ($CDCl_3$) δ 0.84 (6 H, s), 1.28 (18 H, s), 1.80–2.08 (2 H, m), 2.45–2.67 (4 H, m), 6.64 (2 H, s), 6.84, 6.93 (each 2 H, d, J = 2.3 Hz); mass spectrum, m/e 360 (M^+). Anal. Calcd for $C_{27}H_{36}$: C, 89.94; H, 10.06. Found: C, 89.30; H, 10.12.

Compound **5b** was obtained in 92% yield in the same method: colorless prisms (MeOH); mp 176–179 °C; NMR ($CDCl_3$) δ 0.80–1.48 (4 H, m), 1.04 (6 H, s), 1.27 (18 H, s), 1.91–2.36 (2 H, m), 2.58–2.88 (2 H, m), 6.73 (2 H, s), 6.80, 6.95 (each 2 H, d, J = 2.2 Hz); mass spectrum, m/e 374 (M^+). Anal. Calcd for $C_{28}H_{38}$: C, 89.78; H, 10.22. Found: C, 89.73; H, 10.23.

Reaction of 5c with Dichlorocarbene. To a stirred solution of 4.5 g (13.0 mmol) of **5c** and 4.5 g (16.2 mmol) of tetrabutylammonium chloride in 110 mL of chloroform and 450 mL of benzene was added 500 mL of 50% KOH aqueous solution over a period of 2 h at 5 °C. After the solution was stirred vigorously for 4 h at 5 °C, the reaction mixture was poured into a large amount of water. The organic layer was extracted with dichloromethane. The dichloromethane extract was washed with water, dried over Na_2SO_4 and evaporated in vacuo. The residue was chromatographed on silica gel with hexane (5 times) to afford 1.17 g (17.2%) of **6** and 1.76 g (22.4%) of **7**.

6: Reddish brown plates (MeOH); mp 202–204 °C; UV (cyclohexane) λ_{max} 217 nm (log ϵ 4.26, sh), 252 (4.19, sh), 294 (3.93, sh), 415 (4.03); NMR (CCl_4) δ 5.43, 5.51 (each 1 H, d, J = 1.5 Hz, exocyclic methylene protons); mass spectrum, m/e 520, 522, 524 (M^+). Anal. Calcd for $C_{29}H_{32}Cl_4$: C, 66.68; H, 6.17. Found: C, 66.68; H, 6.16.

7: Pale yellow needles (MeOH); mp 196–197 °C; UV (cyclohexane) λ_{max} 218 nm (log ϵ 4.39), 272 (4.31), 350 (3.88, sh); NMR (CCl_4) δ 1.24 (18 H, s), 1.48 (2 H, d, J = 8.0 Hz), 1.58 (2 H, d, J = 8.0 Hz), 1.62–1.76 (2 H, m), 3.10–3.24 (2 H, m), 6.09 (2 H, s), 6.42 (2 H, d, J = 1.5 Hz), 6.64 (2 H, d, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 30.411 (q), 32.349 (t), 32.701 (t), 36.341 (s), 39.218 (s), 64.111 (s), 126.462 (d), 130.511 (s), 130.980 (d), 133.626 (s), 133.799 (d), 134.799 (s), 149.007 (s); mass spectrum, m/e 602, 604, 606, 608 (M^+). Anal. Calcd for $C_{30}H_{32}Cl_6$: C, 59.53; H, 5.33. Found: C, 59.50; H, 5.42.

Reaction of 10 with Dichlorocarbene. To a stirred solution of 400 mg (1.15 mmol) of **10** and 400 mg (1.44 mmol) of tetrabutylammonium chloride in 24 mL of chloroform and 45 mL of benzene was added 40 mL of 50% KOH aqueous solution. After the solution was stirred vigorously for 8.5 h at 35 °C, the reaction mixture was poured into a large amount of water. The organic layer was extracted with dichloromethane. The dichloromethane extract was washed with water, dried over Na_2SO_4, and evaporated under vacuum, and the residue was chromatographed on silica gel. Further purification was done by preparative TLC with hexane as the eluant. The pale yellow crystals isolated were recrystallized from hexane to give 6 mg (0.86%) of **11**: pale yellow prisms (MeOH); mp 218–221 °C; UV (cyclohexane) λ_{max} 213 nm (log ϵ 4.32), 237 (4.33), 283 (3.70); NMR ($CDCl_3$) δ 1.20 (18 H, s), 1.56 (2 H, d, J = 8.0 Hz), 1.66 (2 H, d, J = 8.0 Hz), 1.80–3.16 (8 H, m), 6.35 (2 H, d, J = 1.0 Hz), 6.51 (2 H, d, J = 1.0 Hz); mass spectrum, m/e 604, 606, 608, 610 (M^+). Anal. Calcd for $C_{30}H_{34}Cl_6$: C, 59.33; H, 5.64. Found: C, 59.41; H, 5.71.

Reaction of 5a with Dichlorocarbene. To a stirred solution of 200 mg (0.555 mmol) of **5a** and 200 mg (0.720 mmol) of tetrabutylammonium chloride in 7 mL of chloroform and 16 mL of benzene was added with stirring 10 mL of 50% KOH aqueous solution at room temperature. After the solution was stirred vigorously for 34.5 h at room temperature, the reaction mixture was poured into large amount of water. The organic layer was extracted with dichloromethane. The dichloromethane extract

was washed with water, dried over Na_2SO_4, and evaporated under vacuum, and the residue was chromatographed on silica gel followed by purification by preparative TLC with hexane as the eluant to afford 146 mg (38%) of **12**: pale yellow prisms (MeOH); mp 181–183.5 °C; UV (cyclohexane) λ_{max} 216 nm (log ϵ 4.38), 230 (4.35, sh), 254 (4.28), 277 (4.04, sh), 336 (3.67); NMR ($CDCl_3$) δ 0.67, 1.14 (each 1 H, d, J = 8.5 Hz), 1.19, 1.33 (each 9 H, s), 1.88–2.50 (4 H, m), 2.17 (3 H, s), 3.02–3.34 (2 H, m), 6.17, 6.61 (each 1 H, d, J = 12.0 Hz), 6.24, 6.61 (each 1 H, s), 6.90, 6.97 (each 1 H, d, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 149.06 (s), 147.48 (s), 141.49 (s), 138.79 (s), 137.79 (s), 137.50 (s), 135.09 (s), 133.98 (d), 133.63 (d), 132.45 (s), 130.28 (d), 126.70 (d), 126.35 (d), 121.82 (d), 65.29 (s), 40.57 (s), 36.22 (s), 34.87 (t), 34.11 (s), 32.06 (t), 31.41 (q), 30.18 (q), 29.19 (t), 26.24 (t), 18.44 (q); mass spectrum, m/e 488, 490, 492, 494 (M^+). Anal. Calcd for $C_{29}H_{35}Cl_3$: C, 71.09; H, 7.20. Found: C, 70.92; H, 7.25.

Reaction of 5b with Dichlorocarbene. To a stirred solution of 250 mg (0.667 mmol) of **5b** and 250 mg (0.900 mmol) of tetrabutylammonium chloride in 9 mL of chloroform and 12 mL of benzene was added with stirring 12 mL of 50% KOH aqueous solution at room temperature. After the solution was stirred vigorously for 24 h at room temperature, the reaction mixture was poured into a large amount of water. The organic layer was extracted with dichloromethane. The dichloromethane extract was washed, dried over Na_2SO_4, and evaporated under vacuum, and the residue was chromatographed on silica gel, followed by preparative TLC purification with hexane as the eluant to afford 162 mg (65%) of recovered **5b** and 46.5 mg (14%) of **14**: colorless crystals; mass spctrum, m/e 502, 504, 506, 508 (M^+).

X-ray Analysis of 7. Crystal data are as follows: $C_{30}H_{32}Cl_6$, M_r = 605.3, monoclinic; space group $P2_1/C$; a = 11.852 (5), b = 7.343 (1), and c = 18.459 (5) Å; β = 109.75 (2)°; V = 1512.0 Å^3; Z = 2; c = 1.33 g·cm^{-3}. The final R value is 0.133.

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General Syntheses of 6- and 7-Carbomethoxy-*trans*-1-heteradecalins and 6- and 7-Carbomethoxy-*trans*-2-heteradecalins

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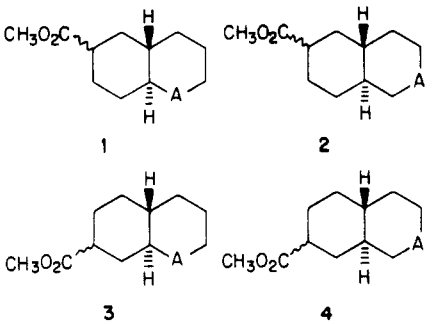
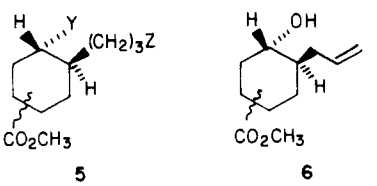
Two routes to all of the title compounds in the oxa and aza series have been studied. The most general path, involving a cyclohexene oxide intermediate, was not successful because of difficulty in separating regioisomers. Allylation of 4-carbomethoxycyclohexanone (**11**) followed by reduction produced the required trans-disubstituted allyl alcohols, which were converted to all of the desired 6-carbomethoxy-*trans*-1-heteradecalins. The allyl ketones were subjected to a homologation–side chain contraction sequence to produce the 6-carbomethoxy-*trans*-2-heteradecalins. Allylation of 3-carbomethoxycyclohexanone (**12**) was not regioselective, but all four product isomers were characterized. The desired 5-carbomethoxy-2-allylcyclohexanone isomers (**27** and **28**) were converted to the 7-carbomethoxy-*trans*-decalins by similar series of reactions.

Syntheses of *trans*-1- and -2-heteradecalin ring systems have been reported starting from acyclic, monocyclic, and bicyclic precursors.[1] When embarking on the syntheses of all of the 6- and 7-carbomethoxy-*trans*-1-heteradecalins and 6- and 7-carbomethoxy-*trans*-2-heteradecalins (**1–4**),[2] as we did several years ago in order to probe a variety of heteratom effects, the hope would be to develop a general synthetic route adaptable to all of the desired targets or, at least, a significant subset of targets. Our earlier attempts utilizing a variety of synthetic approaches[3-7] produced only isolated examples of the target systems, although a Robinson annulation route[5-8] promises to be general for all of the desired 2-heteradecalins.

For a general approach, retrosynthetic analysis suggests that the target compounds could all be obtained from a trans-disubstituted carbomethoxycyclohexane of type **5** provided that group Y could accommodate both a facile interchange between heteroatoms (to produce the 1-heteradecalins) and a homologation (to produce the 2-heteradecalins) and that group Z could be displaced by a variety



of heteroatoms and be easily shortened by one carbon. One such intermediate would be of type **6**, for which two approaches were deemed attractive.



If a 4-substituted cyclohexene formed signficant amounts of epimeric[2] epoxides **7** and **8**, the stereoelectronic requirement for trans-diaxial ring opening[9] of the epoxide by an allyl Grignard reagent, for example, would produce regioisomeric *trans*-2-allylcyclohexanols, one of which

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