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SYNTHESIS OF MONOHALOCYCLOPROPANE DERIVATIVES FROM OLEFINS BY THE REACTION WITH TRIHALOMETHANES AND COPPER

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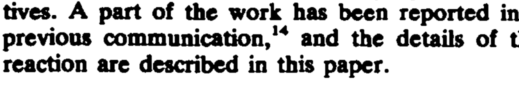
Abstract—Fluoro-, chloro-, bromo-, and iodocyclopropane derivatives were obtained in 10–80% yields by the reaction of $FCHI_2$, $ClCHI_2$, $BrCHI_2$, and CHI_3, respectively, with Cu in the presence of olefins. The reaction was electrophilic, and proceeded stereospecifically, i.e., *cis* and *trans* olefins afforded cyclopropane derivatives whose configurations with respect to the substituents from original olefins were *cis* and *trans*, respectively. Since isomeric olefins were not detected in the reaction mixture which would be expected from the insertion of the corresponding free monohalocarbenes into C—H bonds, the reaction seemed to proceed via organocopper intermediates rather than free monohalocarbenes. With respect to the configuration of the halogen introduced by the new reaction, the *cis* or *endo* isomers were generally obtained predominantly over the corresponding *trans* or *exo* isomers.

Monohalocyclopropane derivatives have often been synthesized by the cycloaddition of monohalocarbenes or carbenoids to olefins, and a considerable information has accumulated on this subject.[1] α-Elimination has been the most promising route to monohalocarbenes or carbenoids. Reaction of alkyllithium with CH_2Cl_2 in the presence of olefins produces monochlorocyclopropane derivatives,[1] but this method is not very useful for the synthesis of the other monohalocyclopropane derivatives. Reaction of Et_2Zn with trihalomethanes in the presence of olefins produces monofluoro-,[2] monochloro-,[2] monobromo-,[2,3] and monoiodocyclopropane derivatives.[4] However, this Zn route is not very convenient since Et_2Zn is flammable in air and precautions must be made to exclude the atmosphere during the reaction. Reaction of olefins with dihalomethylmercury compounds gives the corresponding monohalocyclopropane derivatives in good yields.[5] But the use of organomercury compounds is not desirable because of their toxicity. Photochemical decomposition of $FCHI_2$ in the presence of olefins gives the corresponding monofluorocyclopropane derivatives,[6] and the reaction of olefins with sodium bis(trimethylsilyl)amide and dihalomethane gives the corresponding monohalocyclopropane derivatives.[7] Monohalocyclopropane derivatives can be obtained from olefins and halodiazomethanes.[8,9] Nevertheless, these procedures are not always useful for the synthesis of monohalocyclopropane derivatives, and a convenient route to monofluoro- and monobromocyclopropane derivatives is the partial reduction of the corresponding chlorofluoro-[10,11] and dibromocyclopropane derivatives,[12] respectively. Another convenient route to monobromocyclopropane derivatives is a bromination of cyclopropanecarboxylic acid.[13]

Recently, we found that the reaction of CH_2I_2 with Cu in the presence of olefins gave the corresponding cyclopropane derivatives in good yields.[14] This reaction proceeded stereospecifically and did not give isomeric olefins, which are generally difficult to separate and which would be expected from the insertion of free carbene into C—H bonds. Inorganic materials were eliminated from the reaction mixture by a simple filtration, and distillation of the filtrate gave the isolated products. The simplicity of this procedure compares well with the advantage obtained by the use of insoluble polymer supports in organic synthesis.[15]



As an extension of this work, we have investigated the reaction of trihalomethanes with Cu in the presence of olefins, and found a useful method for the synthesis of monohalocyclopropane derivatives. A part of the work has been reported in a previous communication,[14] and the details of the reaction are described in this paper.

Synthesis of monohalocyclopropane derivatives from olefins

The reaction of olefins with trihalomethane and Cu proceeded smoothly at moderate temperature, and gave the corresponding monohalocyclopropane derivatives often in good yields. Some experimental results are given in Table 1. All products were identified by comparison of their ^1H NMR and IR

Table 1. Synthesis of monohalocyclopropane derivatives from olefins, trihalomethanes, and copper[a]

Olefin	Trihalo-methane	Temp. (°C)	Time (h)	Product	Yield[b] (%)	Isomer ratio
Cyclohexene	$FCHI_2$	75	70	*endo*/*exo*-7-Fluorobicyclo[4.1.0]heptane	80	2.4
1-Heptene	$FCHI_2$	85[c]	65	*cis*/*trans*-1-Fluoro-2-pentylcyclopropane	61	2.1
Styrene	$FCHI_2$	90[c]	50	*cis*/*trans*-1-Fluoro-2-phenylcyclopropane	59	2.0
Cyclohexene	$ClCHI_2$	70	25	*endo*/*exo*-7-Chlorobicyclo[4.1.0]heptane	48	2.1
Cyclohexene	Cl_2CHI	70	50	*endo*/*exo*-7-Chlorobicyclo[4.1.0]heptane	14	2.2
cis-Cyclooctene	$ClCHI_2$	83	22	*endo*/*exo*-9-Chloro-*cis*-bicyclo[6.1.0]nonane	50	6.2
1-Octene	$ClCHI_2$	80	22	*cis*/*trans*-1-Chloro-2-hexylcyclopropane	36	3.9
cis-4-Octene	$ClCHI_2$	80	22	*cis*,*cis*/*trans*,*trans*-1-Chloro-2,3-dipropylcyclopropane	48	8.2
trans-4-Octene	$ClCHI_2$	80	22	*cis*,*trans*-1-Chloro-2,3-dipropylcyclopropane	45	—
Styrene	$ClCHI_2$	80	22	*cis*/*trans*-1-Chloro-2-phenylcyclopropane	41	3.7
p-Methylstyrene[d]	$ClCHI_2$	74	21	*cis*/*trans*-1-Chloro-2-*p*-methylphenylcyclopropane	56	7.0
p-Chlorostyrene[d]	$ClCHI_2$	72	20	*cis*/*trans*-1-Chloro-2-*p*-chlorophenylcyclopropane	50	9.1
p-Bromostyrene[d]	$ClCHI_2$	75	28	*cis*/*trans*-1-Chloro-2-*p*-bromophenylcyclopropane	53	7.7
m-Trifluoro-methylstyrene[d]	$ClCHI_2$	75	30	*cis*/*trans*-1-Chloro-2-*m*-trifluoromethylphenyl-cyclopropane	36	4.9
m-Chlorostyrene[d]	$ClCHI_2$	72	42	*cis*/*trans*-1-Chloro-2-*m*-chlorophenylcyclopropane	47	4.7
Cyclohexene	$BrCHI_2$	72	12	*endo*/*exo*-7-Bromobicyclo[4.1.0]heptane	40	1.5
1-Octene	$BrCHI_2$	74	14	*cis*/*trans*-1-Bromo-2-hexylcyclopropane	20	2.7
Styrene	$BrCHI_2$	74	15	*cis*/*trans*-1-Bromo-2-phenylcyclopropane	11	5.7
Cyclohexene	CHI_3	75	8	*endo*/*exo*-7-Iodobicyclo[4.1.0]heptane	10	0.5

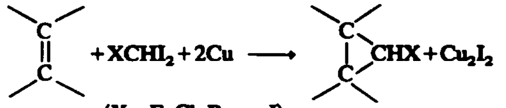
[a] Reactions were carried out with 4.0 mmol of olefin, 8.0 mmol of trihalomethane, 18.0 mmol of Cu powder, and 0.2 mmol of I_2 in 3.0 ml of C_6H_6.

[b] Determined by VPC analysis of the reaction mixture, and were based on the olefin.

[c] $C_6H_5CH_3$ was used instead of C_6H_6 as the solvent.

[d] These reactions were carried out in 4.5 ml of C_6H_6.

spectra with those of authentic samples, or showed satisfactory analytical data and expected spectra.



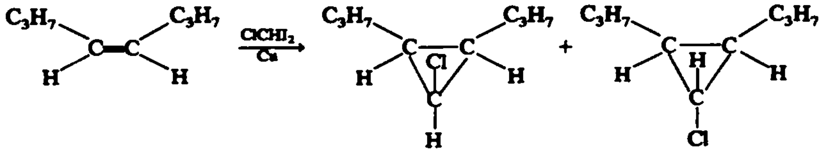
(X = F, Cl, Br, or I)

The reaction did not give isomeric olefins, which would be expected from the insertion of the corresponding free monohalocarbenes into C—H bonds. The reaction seems to proceed via organocopper intermediate rather than free monohalocarbenes.

The reaction gave monohalocyclopropane derivatives in a stereospecific way. The reaction of *cis*-4-octene with $ClCHI_2$ and Cu afforded a 8.2:1 mixture of *cis*,*cis*- **1** and *trans*,*trans*-1-chloro-2,3-dipropylcyclopropane **2**, but the *cis*,*trans* isomer **3** was not detected in the reaction mixture. The corresponding reaction with *trans*-4-octene gave **3**, but **1** and **2** were not detected in the reaction mixture in this case.

The ^1H NMR spectra of **1**, **2**, and **3** showed the absorption of the ring proton in the geminal position to Cl at δ 3.15 (triplet, $J = 7.2$ Hz), 2.34 (triplet, $J = 4.0$ Hz) and 2.77 (doublet of doublets, $J_{(cis)} = 6.5$ Hz and $J_{(trans)} = 4.0$ Hz), respectively. These absorptions were assigned to the ring protons of the *cis*,*cis*, *trans*,*trans*, and *cis*,*trans* isomers, respectively.

Experience has shown that electron-donating substituents in olefin increased both yield and rate of the reaction. Consequently the reaction is electrophilic. The relative reactivity of substituted styrenes was investigated in the reaction with $ClCHI_2$ and Cu. Results are given in Table 2. Logarithm of the relative reactivity was plotted against Hammett σ^+-value in Fig. 1. The plot gave a ρ-value of -1.13 ± 0.02, which is more negative than that in the reaction of $C_6H_5HgCCl_2Br$ with substituted styrenes.[16] The result suggests the importance of the inductive effect of the substituents in the new reaction.



1 (8.2:1) **2**

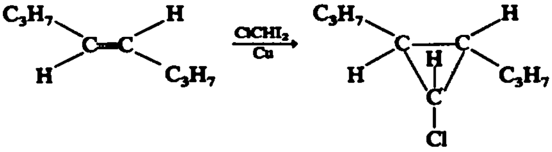


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Table 2. Relative reactivity of substituted styrenes in the reaction with $ClCHI_2$ and Cu[a]

X in $XC_6H_4CH{=}CH_2$	k_X/k_H (av)
p-CH_3	2.53
H	1.00
p-Cl	0.762
p-Br	0.673
m-Cl	0.372
m-CF_3	0.290

[a] Reaction conditions: olefin, 4.0 mmol; $ClCHI_2$, 8.0 mmol; Cu, 18.0 mmol; I_2, 0.2 mmol; C_6H_6 as solvent, 4.5 ml; 75 ± 1°C; 2 h.

As can be seen in Table 1, the new reaction showed essentially the *syn* stereoselectivity. That is, with respect to the configuration of the halogen introduced by the reaction, *endo* or *cis* isomers predominated over the corresponding *exo* or *trans* isomers, respectively. The configuration was determined by the difference in the chemical shift of the proton α to the halogen which allowed the configurational designation, or by the difference in coupling constants of the cyclopropane protons. The stereoselectivity may be determined by a balance of electrostatic interaction and steric repulsion between the halogen of the carbenoid and the substituents of the olefin. In the reaction with cyclohexene, the *endo*/*exo* isomer ratios were 2.4(F), 2.1(Cl), 1.5(Br), and 0.5(I), here the halogen introduced by the new reaction is given in the parentheses. This result suggests that the electrostatic interaction between the halogen of the carbenoid and the substituents of the olefin enhances the *syn*-selectivity, whereas the steric repulsion enhances the *anti*-selectivity. In the reaction of substituted styrenes with $ClCHI_2$ and Cu, electron-donating substituent attached to the phenyl group appears to enhance the *syn*-selectivity of the reaction.

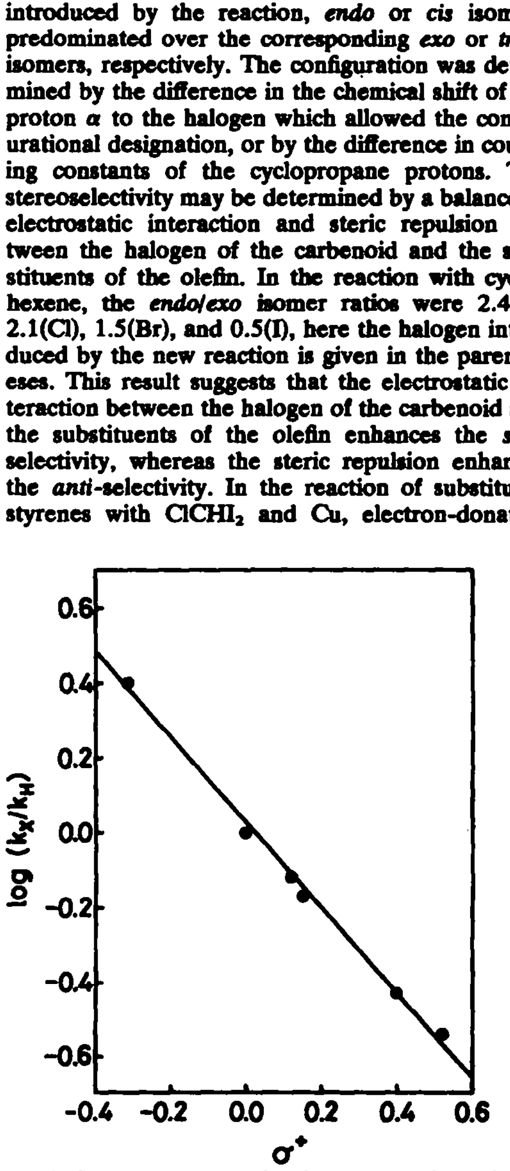
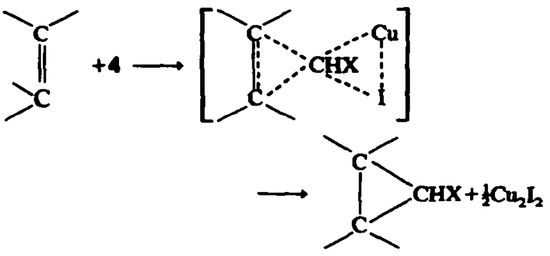


Fig. 1. The Hammett plot for the reaction of substituted styrenes with $ClCHI_2$ and Cu in C_6H_6 at 75°C.

The yield of monohalocyclopropane derivatives decreased when the reaction time was too long. This tendency was in the order I > Br > Cl ≫ F. In Table 1 is shown the results of the reaction carried out under the condition which gave the maximum yield of monohalocyclopropane derivatives. An important side reaction seems to be the coupling of monohalocyclopropane derivatives with the organocopper intermediates derived from trihalomethanes.

Although no detailed investigation of the mechanism of the new reaction has been made, several experimental observations have suggested a reasonable interpretation. We propose the following mechanism for the reaction.

$$XCHI_2 + Cu \longrightarrow \underset{\textbf{4}}{XCHICu} + \tfrac{1}{2}Cu_2I_2$$



The formation of iodohalomethylcopper **4** from halodiiodomethane and Cu would be a reasonable speculation, since CH_3Cu was reported to be detected in the reaction of CH_3Cl and Cu.[17] Perfluoroalkylcopper compounds can be prepared directly from perfluoroalkyl halides and Cu.[18] It would be better to consider that the organocopper intermediate **4** is associated, since the reaction system was heterogeneous and the organocopper intermediates seemed to be insoluble in the aromatic hydrocarbon. Since the aromatic hydrocarbon plays an important role in the new reaction, it would form coordination compounds with the organocopper intermediates. Probably the organocopper intermediates are complexes with aromatic hydrocarbon as the benzene complex of copper(I) triflate.[19]

The subsequent one-step methylene-transfer mechanism is similar to that suggested for the Simmons–Smith reaction.[20] A mechanism involving free monohalocarbenes would be unlikely, since isomeric olefins were not detected in the reaction mixture as was mentioned above. A mechanism involving carbanions would also be unlikely, because the reaction showed an electrophilic nature.

Preparation of dichloroiodo- and chlorodiiodomethane

$FCHI_2$ was prepared by the reaction of $FCHBr_2$ with NaI.[21] $BrCHI_2$ was prepared by the reaction of Br_2 with CHI_3.[22] The reported method for the preparation of Cl_2CHI and $ClCHI_2$ involves the reaction of CHI_3 with $HgCl_2$.[22] Since the use of a large quantity of Hg compound is not desirable, we attempted to find an alternative method for the preparation of Cl_2CHI and $ClCHI_2$ by an application of a literature method for the preparation of CH_3CHI_2,[23] which involves the action of $AlCl_3$ on a mixture of CH_3CHCl_2 and EtI.

We found that the reaction of $CHCl_3$ with a nearly equimolar amount of EtI in the presence of $AlCl_3$ gave Cl_2CHI and $ClCHI_2$ in 32 and 26% yields, respectively, based on EtI. The reaction

$$CHCl_3 + CH_3CH_2I \xrightarrow{AlCl_3} \underset{32\%}{Cl_2CHI} + \underset{26\%}{ClCHI_2}$$

gave a mixture of $CHCl_3$, Cl_2CHI, $ClCHI_2$, and CHI_3. It was difficult to prepare $ClCHI_2$ selectively by this method.

EXPERIMENTAL

Elementary analyses were carried out at the Elementary Analyses Center of Kyoto University. ^1H NMR spectra were taken on a Varian T-60-A spectrometer in CCl_4 using TMS as internal standard. IR spectra were recorded on a Japan Spectroscopic Co. Model 402G spectrometer, or Hitachi Model 215 grating spectrophotometer. Mass spectra were obtained on a Hitachi Model RMU-6 mass spectrometer. VPC analysis was performed on a Shimadzu GC-4A, GC-4B or GC-4C gas chromatograph.

Materials. $FCHBr_2$ was prepared according to a literature method.[24] $FCHI_2$ was prepared by the reaction of $FCHBr_2$ with NaI in Me_2CO[21] or in water using Bu_4NBr as a phase-transfer catalyst.[25] $BrCHI_2$ was prepared according to the procedure of Auger.[22] Commercial products of EtI and $CHCl_3$ were used without further purification. Olefins and solvents were purified by distillation and drying with CaH_2. The ordinary commercial grade of Cu powder (particle size was 5–15 μ) was used without further purification. I_2, anhydrous $AlCl_3$, and other chemicals were used without further purification.

Preparation of $ClCHI_2$ and Cl_2CHI. A mixture of 400 ml (5.0 mol) of $CHCl_3$ and 400 ml (5.2 mol) of EtI was heated with 24 g of anhydrous $AlCl_3$ on a water bath at room temperature for 1 h with stirring. During this time EtCl, which was formed by the reaction, bubbled out of the solution. The mixture was then allowed to react at 45–50°C for 2 h with stirring, and was poured into water, washed with an aqueous $NaHSO_3$ solution, and dried over $CaCl_2$. Yields were determined by VPC analysis of the reaction mixture. Products were separated by distillation, and were identified by comparison of their spectral data with those of authentic samples.[22]

Synthesis of monohalocyclopropane derivatives from olefins (general procedure). The reaction vessel was a two-necked flask equipped with a reflux condenser and a magnetic stirrer. Cu powder was allowed to react with a small amount of I_2 in a solvent at room temperature. After the brown color of I_2 disappeared, olefin and trihalomethane were added, and the mixture was heated at the prescribed temperature with stirring. After the reaction, the inorganic materials were separated by filtration. A fine glass-fibre paper was suitable for this purpose. Yields were determined by VPC analysis of the reaction mixture. Results are summarized in Table 1. Products were isolated by collection from the reaction mixture by VPC, and were analyzed. ^1H NMR and IR spectra of *endo-* and *exo*-7-fluorobicyclo[4.1.0]heptane,[26] *cis-* and *trans*-1-fluoro-2-pentylcyclopropane,[10] *cis-* and *trans*-1-fluoro-2-phenylcyclopropane,[26] *endo-* and *exo*-7-chlorobicyclo[4.1.0]heptane,[27] *cis,cis-* and *trans,trans*-1-chloro-2,3-dipropylcyclopropane,[28] *endo-* and *exo*-7-bromobicyclo[4.1.0]heptane,[2,29] *cis-* and *trans*-1-bromo-2-hexylcyclopropane,[30] *cis-* and *trans*-1-bromo-2-phenylcyclopropane,[31] and *endo-* and *exo*-7-iodobicyclo[4.1.0]heptane[4] were respectively identical with those of authentic materials. Spectral and elementary analyses of the other monohalocyclopropane derivatives are given below.

endo-9-*Chloro*-cis-*bicyclo*[6.1.0]*nonane*. $n_D^{30} = 1.4928$; ^1H NMR (CCl_4) δ 0.3–2.3 (m, 14H), 3.17 (t, $J = 7.0$ Hz, 1H). (Found: C, 67.85; H, 9.46; Cl, 22.57%. $C_9H_{15}Cl$ requires: C, 68.13; H, 9.53; Cl, 22.34%.)

exo-9-*Chloro*-cis-bicyclo[6.1.0]*nonane*. $n_D^{30} = 1.4935$; ^1H NMR (CCl_4) δ 0.3–2.7 (m, 15H). (Found: C, 67.84; H, 9.34; Cl, 22.53%. $C_9H_{15}Cl$ requires: C, 68.13; H, 9.53; Cl, 22.34%.)

cis-1-*Chloro-2-hexylcyclopropane*. $n_D^{30} = 1.4424$; ^1H NMR (CCl_4) δ 0.1–1.7 (m, 16H), 3.06 (m, 1H). (Found: C, 67.17; H, 10.80; Cl, 22.17%. $C_9H_{17}Cl$ requires: C, 67.27; H, 10.66; Cl, 22.06%.)

trans-1-*Chloro-2-hexylcyclopropane*. $n_D^{30} = 1.4369$; ^1H NMR (CCl_4) δ 0.4–1.7 (m, 16H), 2.62 (m, 1H). (Found: C, 66.99; H, 10.48; Cl, 22.12%. $C_9H_{17}Cl$ requires: C, 67.27; H, 10.66; Cl, 22.06%.)

cis,trans-1-*Chloro*-2,3-*dipropylcyclopropane*. $n_D^{30} = 1.4350$; ^1H NMR (CCl_4) δ 0.95 (t, $J = 6.0$ Hz, 6H), 0.3–1.8 (m, 10H), 2.77 (d of d, $J_{(cis)} = 6.5$ Hz and $J_{(trans)} = 4.0$ Hz, 1H). (Found: C, 67.57; H, 10.86; Cl, 22.03%. $C_9H_{17}Cl$ requires: C, 67.27; H, 10.66; Cl, 22.06%.)

cis-1-*Chloro-2-phenylcyclopropane*. $n_D^{30} = 1.5487$; ^1H NMR (CCl_4) δ 1.3 (m, 2H), 2.3 (m, 1H), 3.3 (m, 1H), 7.22 (m, 5H). (Found: C, 70.72; H, 6.13; Cl, 23.15%. C_9H_9Cl requires: C, 70.83; H, 5.94; Cl, 23.23%.)

trans-1-*Chloro-2-phenylcyclopropane*. $n_D^{30} = 1.5448$; ^1H NMR (CCl_4) δ 1.3 (m, 2H), 2.3 (m, 1H), 3.0 (m, 1H), 7.1 (m, 5H). (Found: C, 70.55; H, 6.23; Cl, 22.98%. C_9H_9Cl requires: C, 70.83; H, 5.94; Cl, 23.23%).

cis-1-*Chloro*-2-p-*methylphenylcyclopropane*. $n_D^{30} = 1.5414$; ^1H NMR (CCl_4) δ 1.2 (m, 2H), 2.17 (m, 1H), 2.29 (s, 3H), 3.2 (m, 1H), 7.01 (s, 4H); MS *m/e* (rel %) 168 (1.86), 166 (4.84 M^+), 131 (100), 115 (20), 91 (20). (Found: C, 71.89; H, 6.84; Cl, 21.29%. $C_{10}H_{11}Cl$ requires: C, 72.07; H, 6.65; Cl, 21.27%.)

trans-1-*Chloro*-2-p-*methylphenylcyclopropane*. $n_D^{30} = 1.5375$; ^1H NMR(CCl_4) δ 1.2 (m, 2H), 2.2 (m, 1H), 2.29 (s, 3H), 3.0 (m, 1H), 6.9 (m, 4H); MS *m/e* (rel %) 168 (3.03), 166 (8.63 M^+), 131 (100), 115 (58), 91 (39).

cis-1-*Chloro*-2-p-*chlorophenylcyclopropane*. $n_D^{30} = 1.5611$; ^1H NMR (CCl_4) δ 1.2 (m, 2H), 2.2 (m, 1H), 3.3 (m, 1H), 7.13 (q(AB), $J = 9.3$ Hz, 4H); MS *m/e* (rel %) 190 (1.55), 188 (9.01), 186 (15.28 M^+), 151 (100), 116 (48), 115 (64). (Found: C, 57.95; H, 4.37; Cl, 37.85%. $C_9H_8Cl_2$ requires: C, 57.79; H, 4.31; Cl, 37.90%.)

trans-1-*Chloro*-2-p-*chlorophenylcyclopropane*. $n_D^{30} = 1.5599$; ^1H NMR (CCl_4) δ 1.3 (m, 2H), 2.2 (m, 1H), 3.0 (m, 1H), 7.03 (q(AB), $J = 7.6$ Hz, 4H); MS *m/e* (rel %) 190 (1.56), 188 (11. 51), 186 (16.93 M^+), 151 (100), 116 (54), 115 (70).

cis-1-*Chloro*-2-p-*bromophenylcyclopropane*. $n_D^{30} = 1.5848$; ^1H NMR (CCl_4) δ 1.3 (m, 2H), 2.2 (m, 1H), 3.3 (m, 1H), 7.22 (q(AB), $J = 8.6$ Hz, 4H). (Found: C, 46.94; H, 3.35; Cl, 15.36; Br, 34.62%. C_9H_8ClBr requires: C, 46.69; H, 3.48; Cl, 15.31; Br, 34.51%.)

trans-1-*Chloro*-2-p-*bromophenylcyclopropane*. $n_D^{30} = 1.5820$; ^1H NMR (CCl_4) δ 1.3 (m, 2H), 2.2 (m, 1H), 3.0 (m, 1H), 7.13 (q(AB), $J = 8.6$ Hz, 4H); MS *m/e* (rel %) 234 (2.70), 232 (8.71), 230 (6.02 M^+), 116 (72), 115 (100).

cis-1-*Chloro*-2-m-*trifluoromethylphenylcyclopropane*. $n_D^{30} = 1.4782$; ^1H NMR (CCl_4) δ 1.4 (m, 2H), 2.3 (m, 1H), 3.3 (m, 1H), 7.4 (m, 4H); MS *m/e* (rel %) 222 (4.48), 220 (13,96 M^+), 185 (100), 165 (29), 115 (24). (Found: C, 54.54; H, 3.89; Cl, 16.12; F, 26.08%. $C_{10}H_8ClF$ requires: C, 54.44; H, 3.65; Cl, 16.07; F, 25.83%.)

trans-1-*Chloro*-2-m-*trifluoromethylphenylcyclopropane*. $n_D^{30} = 1.4797$; ^1H NMR (CCl_4) δ 1.5 (m, 2H), 2.3 (m, 1H), 3.1 (m, 1H), 7.3 (m, 4H); MS *m/e* (rel %) 222 (4.72), 220 (14.19 M^+), 185 (100), 165 (25), 115 (21).

cis-1-*Chloro*-2-m-*chlorophenylcyclopropane.* n_D^{30} = 1.5604; ^{1}H NMR (CCl_4) δ 1.3 (m, 2H), 2.2 (m, 1H), 3.3 (m, 1H), 7.1 (m, 4H); MS *m/e* (rel %) 190 (0.62), 188 (4.99), 186 (6.94 M^+), 151 (100), 116 (52), 115 (83). (Found: C, 57.96; H, 4.51; Cl, 37.93%. $C_9H_8Cl_2$ requires: C, 57.79; H, 4.31; Cl, 37.90%.)

trans-1-*Chloro*-2-m-*chlorophenylcyclopropane.* n_D^{30} = 1.5579; ^{1}H NMR (CCl_4) δ 1.4 (m, 2H), 2.3 (m, 1H), 3.1 (m, 1H), 7.1 (m, 4H); MS *m/e* (rel %) 190 (0.56), 188 (2.40), 186 (3.04 M^+), 151 (100), 116 (49), 115 (86).

Competitive reactions. In a two-necked flask equipped with a reflux condenser and a magnetic stirrer, 4.0 mmol in all of two olefins, 8.0 mmol of $ClCHI_2$, 18.0 mmol of Cu powder, and 0.2 mmol of I_2 were allowed to react in 4.0 ml of C_6H_6 at 75 ± 1° for 2 h. After the reaction, inorganic materials were removed by filtration, and the organic layer was analyzed by VPC. Total yields of chlorocyclopropane derivatives did not exceed 10% under these conditions. The relative reactivity was calculated by the following equation:[32] $k_X/k_H = (P_X/P_H)(O_H/O_X)$, where P is the mole of product and O is that of reactant. The quasi-first order kinetics with respect to reactants was ascertained in each reactions as are illustrated in Table 3.

Table 3. Competitive reaction of styrene and *p*-chlorostyrene with varied molar ratio

p-Chlorostyrene (mole fraction)	k_X/k_H
0.216	0.801
0.357	0.670
0.482	0.810
0.672	0.769
0.815	0.762

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