Chromel–Alumel thermocouple in conjunction with a Tinsley Model 3387F potentiometer. Temperatures were constant to ±0.1 °C. The measured values of the rate constants were [units of 10^{-2} s^{-1}, temperature (°C) in parentheses] 8.99 ± 0.02 (12.3), 5.33 ± 0.02 (7.8), 3.41 ± 0.02 (4.25), 2.10 ± 0.003 (0.0), 1.19 ± 0.004 (−4.1), 0.642 ± 0.002 (−8.55). An Arrhenius plot of this data gave a good straight line with the frequency factor and energy of activation being calculated by the method of least squares, $\log A = 11.46 \pm 0.2$; $E_A = 18.9 \pm 0.2$ kcal/mol; at 275.1 K, $\Delta H^{\ddagger} = 18.4$ kcal/mol, $\Delta S^{\ddagger} = -8.0$ cal deg^{-1}, $\Delta G^{\ddagger} = 20.6$ kcal/mol.

References and Notes

(1) (a) University of Florida; (b) University of Utah; (c) Summer Undergraduate Scholar, University of Utah.
(2) C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, **96**, 3280–3288 (1974).
(3) E. Migirdicyan and J. Baudet, *J. Am. Chem. Soc.*, **97**, 7400–7404 (1975); K. L. Tseng and J. Michl, *ibid.*, **99**, 4840–4842 (1977).
(4) G. Quinkert, J. Palmowski, H.-P. Lorenz, W.-W. Wiersdorff, and M. Finke, *Angew. Chem., Int. Ed. Engl.*, **10**, 198–199 (1971).
(5) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **98**, 8510–8514 (1976).
(6) R. N. Warrener, R. A. Russell, and T. S. Lee, *Tetrahedron Lett.*, 49–52 (1977).
(7) W. R. Dolbier, Jr., L. McCullagh, D. Rolison, and K. E. Anapolle, *J. Am. Chem. Soc.*, **97**, 934–935 (1975).
(8) W. J. Feast and W. E. Preston, *J. Chem. Soc., Chem. Commun.*, 985–986 (1974), have described perfluoroisoindene.
(9) W. R. Dolbier, Jr., K. Matsui, J. Michl, and D. V. Horák, *J. Am. Chem. Soc.*, **99**, 3876–3877 (1977).
(10) F. J. Palensky and H. A. Morrison, *J. Am. Chem. Soc.*, **99**, 3507–3508 (1977).
(11) K. Kamal de Fonseka, C. Manning, J. J. McCullough, and A. J. Yarwood, *J. Am. Chem. Soc.*, **99**, 8257–8261 (1977).
(12) J. A. Berson and M. Pomerantz, *J. Am. Chem. Soc.*, **86**, 3896–3897 (1964).
(13) S. S. Hecht and F. D. Greene, *J. Am. Chem. Soc.*, **89**, 6761–6762 (1967).
(14) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012–7023 (1969).
(15) R. Bonnett and R. F. C. Brown, *J. Chem. Soc., Chem. Commun.*, 393–395 (1972).
(16) U. E. Wiersum and W. J. Mijs, *J. Chem. Soc., Chem. Commun.*, 347–348 (1972).
(17) D. S. Matteson and R. A. Davis, *Inorg. Chem.*, **13**, 859–862 (1974).
(18) D. J. Williams, J. M. Pearson, and M. Levy, *J. Am. Chem. Soc.*, **92**, 1436–1438 (1970).
(19) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179–1184 (1964).
(20) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226–1230 (1961).
(21) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846–848 (1966).
(22) J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920–1921 (1968).
(23) (a) N. L. Bauld, F. R. Farr, and C. S. Chang, *Tetrahedron Lett.*, 2443–2446 (1972). (b) A similarly facile "forbidden" disrotatory electrocyclic closure of a polycyclic butadiene was reported by R. P. Steiner and J. Michl, *J. Am. Chem. Soc.*, **100**, 6413 (1978): $E_{act} = 21.3 \pm 0.6$ kcal/mol, $\log A = 16.3 \pm 0.5$ (s^{-1}); the published value 15.6 ± 0.5 is incorrect, cf. *ibid.* **101**, 512 (1979).
(24) C. F. Wilcox, Jr., B. K. Carpenter, and W. R. Dolbier, Jr., *Tetrahedron*, in press.
(25) G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **99**, 4853–4854 (1977), and personal communication.
(26) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **91**, 6042–6049 (1969).
(27) J. Kolc, J. W. Downing, A. P. Manzara, and J. Michl, *J. Am. Chem. Soc.*, **98**, 930–937 (1976).
(28) R. P. Steiner, R. D. Miller, H. J. Dewey, and J. Michl, *J. Am. Chem. Soc.*, **101**, 1820 (1979).
(29) B. Hudson and B. Kohler, *Annu. Rev. Phys. Chem.*, **25**, 437–460 (1974).
(30) E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **98**, 4533–4540 (1976).
(31) W. Gerhartz and J. Michl, *J. Am. Chem. Soc.*, **100**, 6877–6881 (1978).
(32) H. J. Dewey, M. A. Souto, J. Michl, and K. Nakanishi, to be submitted for publication.
(33) A. Castellan and J. Michl, *J. Am. Chem. Soc.*, **100**, 6824–6827 (1978).
(34) J. W. Downing, J. Michl, P. Jørgensen, and E. W. Thulstrup, *Theor. Chim. Acta*, **32**, 203–216 (1974).
(35) P. Lindner and O. Mårtensson, *Theor. Chim. Acta*, **7**, 352–355 (1967).
(36) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190–200 (1961).
(37) W. R. Dolbier, Jr., L. McCullagh, D. Rolison, and K. E. Anapolle, *J. Am. Chem. Soc.*, **97**, 934–935 (1975).

Synthesis of Cyclopropane Derivatives from Olefins by the Reaction with Organic *gem*-Dihalides and Copper[1]
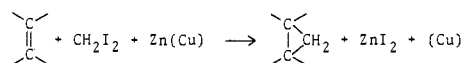
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Abstract: A new, versatile, and convenient method for the synthesis of cyclopropane derivatives is reported and involves the reaction of olefins with organic *gem*-dihalides and copper powder in an aromatic hydrocarbon. The reaction is electrophilic and proceeds stereospecifically, i.e., cis and trans olefins afford cyclopropane derivatives whose configurations with respect to the olefin substituents are cis and trans, respectively. Moreover, ether functions controlled the stereochemistry of the cycloaddition; for example, *cis*-2-methoxybicyclo[4.1.0]heptane was exclusively obtained from 3-methoxycyclohexene. Isomeric olefins, which would be expected from the insertion of the corresponding free carbenes into C–H bonds, were generally not detected in the reaction mixture. The reaction appears to proceed via organocopper intermediates rather than free carbenes. The reaction with diiodomethane gave cyclopropane derivatives in good yields similar to the corresponding Simmons–Smith reaction. The reaction with trihalomethanes gave the corresponding monohalocyclopropane derivatives, and showed the syn stereoselectivity. The reaction with dibromoacetic esters, contrary to the reaction of diazoacetic esters with olefins, gave the corresponding alkoxycarbonylcyclopropane derivatives and showed syn stereoselectivity when steric repulsion between the alkoxycarbonyl group and the olefin substituents was not significant.

Introduction

The reaction of olefins with organozinc reagent prepared from diiodomethane and zinc–copper couple is known as the Simmons–Smith reaction, and has proved to be a versatile and

$$\begin{array}{c} \diagdown C \diagup \\ \| \\ \diagup C \diagdown \end{array} + CH_2I_2 + Zn(Cu) \longrightarrow \begin{array}{c} \diagdown C \diagup \\ | \diagup CH_2 \\ \diagup C \diagdown \end{array} + ZnI_2 + (Cu)$$
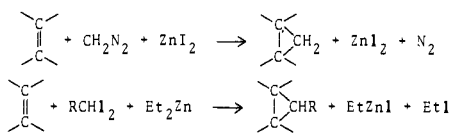
convenient method for the synthesis of cyclopropane derivatives.[2] The copper was reported to play no role other than ac-

Table I. Synthesis of Cyclopropane Derivatives from Olefins, Dihalomethanes, and Copper[a]

olefin	halide	temp, °C	time, h	product	yield,[b] %
cyclohexene	CH_2I_2	70	50	bicyclo[4.1.0]heptane[h]	85–87
cyclohexene	CH_2BrI	70	50	bicyclo[4.1.0]heptane[h]	69
cyclohexene	CH_2ClI	75	96	bicyclo[4.1.0]heptane[h]	5
cis-cyclooctene	CH_2I_2	100[c]	50	cis-bicyclo[6.1.0]nonane[h]	77
1-octene	CH_2I_2	70	47	hexylcyclopropane[h]	86
styrene	CH_2I_2	70	92	phenylcyclopropane[h]	90
styrene	CH_2I_2	75	50	phenylcyclopropane[h]	81
styrene	CH_2I_2	110[c]	16	phenylcyclopropane[h]	90
m-chlorostyrene	CH_2I_2	75	70	m-chlorophenylcyclopropane[i]	75
p-chlorostyrene	CH_2I_2	75	50	p-chlorophenylcyclopropane[h]	80
p-bromostyrene	CH_2I_2	72	50	p-bromophenylcyclopropane[h]	82
p-methylstyrene	CH_2I_2	75	50	p-methylphenylcyclopropane[h]	77
m-trifluoromethylstyrene	CH_2I_2	75	70	m-trifluoromethylphenylcyclopropane[h]	77
m-trifluoromethylstyrene	CH_2I_2[d]	75	50	m-trifluoromethylphenylcyclopropane[h]	89
α-methylstyrene	CH_2I_2	75	50	1-methyl-1-phenylcyclopropane[h]	75
cis-β-methylstyrene	CH_2I_2	75	50	cis-1-methyl-2-phenylcyclopropane[h]	66
trans-β-methylstyrene	CH_2I_2	75	50	trans-1-methyl-2-phenylcyclopropane[h]	66
1,1-diphenylethylene	CH_2I_2	75	50	1,1-diphenylcyclopropane[h]	72
cis-stilbene	CH_2I_2	125[f]	50	cis-1,2-diphenylcyclopropane[i]	22[j]
cis-stilbene	CH_2I_2	150[g]	50	cis-1,2-diphenylcyclopropane[i]	20[k]
cis-stilbene	CH_2BrI	125[f]	50	cis-1,2-diphenylcyclopropane[i]	16[l]
trans-stilbene	CH_2I_2	125[f]	50	trans-1,2-diphenylcyclopropane[h]	27
trans-stilbene	CH_2I_2	150[g]	50	trans-1,2-diphenylcyclopropane[h]	26
allylbenzene	CH_2I_2	75	50	benzylcyclopropane[h]	41
3,4-dihydro-2H-pyran	CH_2I_2	75	50	2-oxabicyclo[4.1.0]heptane[h]	46
isobutyl vinyl ether	CH_2I_2	75	50	isobutyl cyclopropyl ether[h]	18
isobutyl vinyl ether	CH_2I_2[e]	75	50	isobutyl cyclopropyl ether[h]	64
3-methoxycyclohexene	CH_2I_2	75	45	cis-2-methoxybicyclo[4.1.0]heptane[h]	72

[a] Reactions were carried out with 4.0 mmol of olefin, 8.0 mmol of dihalomethane, 18.0 mmol of copper, and 0.2 mmol of iodine in 3.0 mL of benzene. [b] Determined by VPC analysis of the reaction mixture, and were based on the olefin. [c] Toluene was used instead of benzene. [d] 54.0 mmol of copper was used. [e] 9.0 mL of ethylbenzene was used as the solvent. [f] Ethylbenzene was used instead of benzene. [g] Cumene was used instead of benzene. [h] These products were identified by comparison of their ^{1}H NMR and IR spectra with those of authentic samples. [i] These products showed satisfactory analytical data and expected spectra. [j] A 97.1:2.9 mixture of cis and trans isomers was obtained. [k] A 73.7:26.3 mixture of cis and trans isomers was obtained. [l] A 73.4:26.6 mixture of cis and trans isomers was obtained.

tivating the zinc surface for reaction.[3,4] Two useful variations of the reaction have subsequently appeared: diazomethane reacts with zinc iodide in ether to form a reagent which converts olefins to cyclopropane derivatives,[5] and reaction of olefins with diethylzinc and organic *gem*-dihalides gives the corresponding cyclopropane derivatives.[6] Copper is not used

$$\underset{C}{\overset{C}{\diagup}} + CH_2N_2 + ZnI_2 \longrightarrow \underset{C}{\overset{C}{\diagup}} CH_2 + ZnI_2 + N_2$$

$$\underset{C}{\overset{C}{\diagup}} + RCHI_2 + Et_2Zn \longrightarrow \underset{C}{\overset{C}{\diagup}} CHR + EtZnI + EtI$$

in these two variations, but essentially these reactions are similar to the Simmons–Smith reaction.

On the other hand, more than 100 years ago, Butlerow[7] reported that diiodomethane reacted with copper. Some chemical observations seemed to suggest the generation of carbene or carbenoid intermediates. We carried out the reaction in the presence of olefins and found a new, versatile, and useful route to cyclopropane derivatives from olefins.[8]

Results and Discussion

Synthesis of Cyclopropane Derivatives from Olefins by Reaction with Diiodomethane and Copper. The reaction of diiodomethane with copper powder was very slow in benzene in the absence of olefins, and gave ethylene and cyclopropane in 6 and 3% yields, respectively, after 50 h at 70 °C. Ethane, propylene, propane, and C_4 hydrocarbons were not detected in the gaseous products. The formation of ethylene and cyclopropane supports the hypothesis that the reaction of diiodomethane with copper involves carbene or carbenoid intermediates.

The reaction of diiodomethane with copper was found to be much faster in the presence of olefins. The reaction proceeded

$$\underset{C}{\overset{C}{\diagup}} + CH_2I_2 + 2Cu \longrightarrow \underset{C}{\overset{C}{\diagup}} CH_2 + Cu_2I_2$$
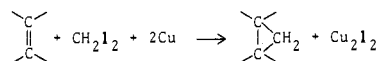
smoothly at moderate temperature and gave the corresponding cyclopropane derivatives in good yields. Some experimental results are given in Table I.

It was shown that 1 mol of diiodomethane consumed 2 mol of copper. The reaction of diiodomethane with copper in the presence of olefins gave the corresponding copper(I) iodide, which was identified by its X-ray powder patterns. The reaction was usually free from serious side reactions, and did not give isomeric olefins difficult to separate, which would be expected from the insertion of free carbene into C–H bonds. The new reaction seems to proceed via an organocopper intermediate rather than free carbene.

The new reaction gave cyclopropane derivatives in good yields similar to the corresponding Simmons–Smith reaction. However, styrene derivatives gave higher yields of the subsequent phenylcyclopropane derivatives. The result suggests that the new cyclopropanation system is much less sensitive to Lewis acids which interfere with similar cyclopropanation reactions. Presumably copper(I) iodide is a weaker Lewis acid than zinc iodide. On the other hand, in the reaction with vinyl ether, the yield of cyclopropyl ether was low and the principal side reaction was polymerization. Probably vinyl ether is more sensitive than styrene to a Lewis acid. In this case, however, the use of an increased amount of hydrocarbon solvent remarkably improved the yield of cyclopropyl ether. The polymerization may be controlled by the nonpolar solvent.

An aromatic hydrocarbon was found to be the most suitable solvent for the reaction. Copper powder did not react with diiodomethane in aliphatic hydrocarbons such as hexane and cyclohexane. Aromatic hydrocarbons appear to play an im-

Table II. Relative Reactivity of Olefins in the Reaction with Diiodomethane and Copper[a]

olefin	k_x/k_y[b]	k_x/k_y[c]
cyclohexene		1.00
1-octene		1.80 ± 0.09
styrene	1.00	3.89 ± 0.09
p-methylstyrene	1.90 ± 0.08	
p-chlorostyrene	0.499 ± 0.026	
p-bromostyrene	0.505 ± 0.011	
m-chlorostyrene	0.185 ± 0.004	
m-trifluoromethylstyrene	0.040 ± 0.001	
α-methylstyrene		3.12 ± 0.04
cis-β-methylstyrene		0.315 ± 0.002
trans-β-methylstyrene		0.307 ± 0.008
1,1-diphenylethylene		0.773 ± 0.005
cis-stilbene		0.042 ± 0.002
trans-stilbene		0.058 ± 0.002
allylbenzene		1.03 ± 0.02

[a] Reactions were carried out with 1.33 mmol in all of olefins, 2.66 mmol of diiodomethane, 0.06 mmol of iodine, and 6.00 mmol of copper in 2.0 mL of benzene at 75 ± 1 °C. [b] Styrene was the standard olefin. [c] Cyclohexene was the standard olefin.

portant role in the formation of organocopper intermediates from diiodomethane and copper powder. Probably the organocopper intermediates complex with aromatic hydrocarbons as the benzene complex of copper(I) triflate.[10] In ethereal solvents such as diethyl ether and tetrahydrofuran, the reaction of diiodomethane with copper was much faster than in aromatic hydrocarbons, but the yields of cyclopropane derivatives were much lower. Ethereal solvents are known to form coordination compounds with metal alkyls. Coordination of ethereal solvents may enhance the nucleophilic reactivity of the organocopper intermediates, and the carbenoid reaction may be restrained.

Diiodomethane was the most suitable dihalomethane for the reaction. Bromoiodomethane and chloroiodomethane gave cyclopropane derivatives in lower yields, but dibromomethane and dichloromethane did not react with copper under these conditions.

The new reaction was found to proceed stereospecifically. Reaction of highly purified samples of *cis-* and *trans-*β-methylstyrene with diiodomethane and copper in benzene at 75 °C for 50 h gave *cis-* and *trans-*1-methyl-2-phenylcyclopropane, respectively. Vapor phase chromatographic analysis of the reaction mixture and the ¹H NMR spectra of the isolated products indicated the absence of the other isomer of the cyclopropane derivatives in both cases. The unreacted olefins were recovered pure. The reaction of pure *trans-*stilbene with diiodomethane and copper in ethylbenzene at 125 °C for
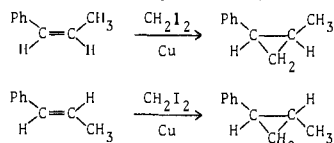
50 h gave *trans-*1,2-diphenylcyclopropane. *cis-*1,2-Diphenylcyclopropane and *cis-*stilbene were not detected in the reaction mixture. On the other hand, the corresponding reaction with pure *cis-*stilbene gave a 97.1:2.9 mixture of *cis-* and *trans-*1,2-diphenylcyclopropane. The recovered stilbene was also a 98.1:1.9 mixture of cis and trans isomers. When the reaction was carried out in cumene at 150 °C for 50 h, *trans-*stilbene gave pure *trans-*1,2-diphenylcyclopropane, and the recovered stilbene was the pure trans isomer. However, *cis-*stilbene gave a 73.7:26.3 mixture of *cis-* and *trans-*1,2-diphenylcyclopropane, and the recovered stilbene was a 93.7:6.3 mixture of cis and trans isomers. These experimental results show that the new cyclopropanation reaction probably loses
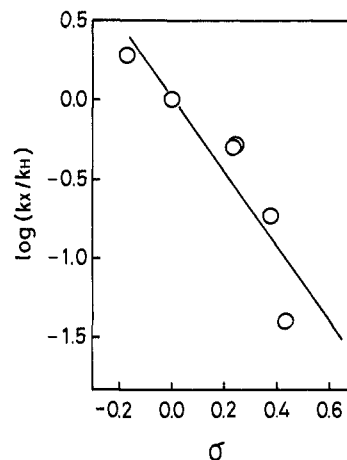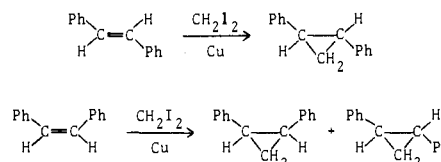

Figure 1. The Hammett correlation of relative reactivity of substituted styrenes in the reaction with diiodomethane and copper in benzene at 75 °C.

stereospecificity to some extent during heating at high temperature for a long time by the action of copper(I) iodide. In fact, *cis-*1,2-diphenylcyclopropane isomerized during heating

in the presence of copper(I) iodide (see Experimental Section for details). Copper(I) halides are known to catalyze cis–trans isomerization of olefins. *cis-*Stilbene isomerized during heating in the presence of copper(I) halides, but *trans-*stilbene did not isomerize under the conditions. (See Experimental Section for details.)

In the Simmons–Smith reaction, oxygen coordination is an important aspect of the stereospecific synthesis of cyclopropane derivatives, and has been used widely in synthesis.[11] This type of stereospecific synthesis was found to be applicable to the new cyclopropanation. For example, reaction of 3-methoxycyclohexene with diiodomethane and copper gave *cis-*2-methoxybicyclo[4.1.0]heptane in 72% yield, and the trans isomer was
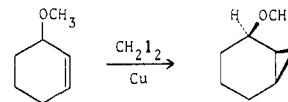
not detected in the reaction mixture, similarly to the corresponding Simmons–Smith reaction.[12]

Experience has shown that electron-withdrawing substituents attached to the olefinic linkage decreased both yields and the rate of cyclopropane formation. The relative reactivity of some olefins was investigated and the results are summarized in Table II. The logarithm of the relative reactivity of substituted styrenes in the new cyclopropanation is plotted against Hammett σ value in Figure 1. The plot gave a ρ value of -2.4 ± 0.3, which is more negative than -1.61 reported for the reaction of zinc carbenoid generated from diethylzinc and diiodomethane with substituted styrenes,[13] and -0.619 reported for the reaction of dichlorocarbene generated from phenyl(bromodichloromethyl)mercury with substituted styrenes.[14] The result suggests the importance of substituent inductive effects in the new reaction. In other words, the cyclopropanation is a more electrophilic reaction than the methylene transfer to olefins by the zinc carbenoid. The new reaction gave unpromising results in the cyclopropanation of acrylic esters and nitriles because of the large spread in relative reactivities.

Relative reactivity of several other olefins in the new cyclopropanation was also determined using cyclohexene as the standard. Styrene might be expected to be especially reactive because of the conjugated double bonds, but it reacted at a rate comparable to those of cyclohexene and 1-octene. Therefore, the conjugative effect appears to be much less important than the inductive effect in the reaction.

As can be seen in Table II, *gem*-disubstituted olefins showed much higher reactivity than the corresponding *vic*-disubstituted olefins. α-Methylstyrene was much more reactive than *cis*- and *trans*-β-methylstyrene, and 1,1-diphenylethylene was much more reactive than *cis*- and *trans*-stilbene. The results indicate that steric effects are important in the new cyclopropanation. The steric repulsion between the substituents of the olefin and the organocopper intermediates in the transition state seems to be more important in the reaction with *vic*-disubstituted olefins than in the reaction with *gem*-disubstituted olefins.

From a practical standpoint, the new reaction offers some advantages over the Simmons–Smith reaction and its variations. (1) An ordinary commercial grade of copper powder was used without further purification. Although we dried the solvent with calcium hydride prior to the reaction, the new reaction was not very sensitive to the moisture of the reaction system. Therefore no special precaution associated with purity of reagents was necessary in order to carry out successful cyclopropanations. On the contrary, in the Simmons–Smith reaction, the method of preparation of the zinc–copper couple is an important factor in determining its reactivity toward diiodomethane in ether solvent and in achieving reproducible yields of cyclopropane derivatives. Moreover, reagents must be dried since small quantities of water react with the zinc reagent to foul the couple surface. (2) The new reaction can be carried out in air. The final yields of products and the rate of reaction were not affected when carried out under nitrogen. On the contrary, the variation of the Simmons–Smith reaction using diethylzinc instead of zinc–copper couple must be carried out under nitrogen, since diethylzinc is flammable in air. (3) With the new cyclopropanation, simple filtration was sufficient for the removal of inorganic materials from the reaction mixture, and distillation gave the isolated products. This simple procedure compares well with the advantages obtained when insoluble polymer supports are used in organic synthesis.[15] On the other hand, in the Simmons–Smith reaction, the reaction mixture is normally worked up by washing the ethereal solution with saturated ammonium chloride solution to remove zinc salts, and the product is isolated by appropriate techniques. An excess amount of the solvent is usually used in order to extract organic materials from the aqueous layer, and the organic layer should be dried.

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

$$CH_2I_2 + Cu \longrightarrow ICH_2Cu + \tfrac{1}{2}Cu_2I_2$$
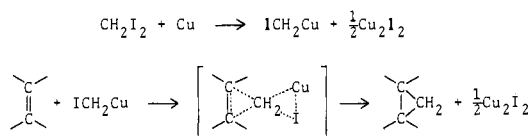
The formation of iodomethylcopper from diiodomethane and copper is reasonable speculation, since methylcopper was reported to be detected in the reaction between methyl chloride and copper.[16] In fact, as was mentioned above, the reaction of diiodomethane with copper gave ethylene and cyclopropane as in the reaction of diiodomethane with zinc–copper couple.[2] The latter reaction is generally considered to give iodomethylzinc compounds.[2] It is more convincing to consider that the iodomethylcopper is associated, since the reaction system was

heterogeneous and the organocopper intermediates seem to be insoluble in the aromatic hydrocarbon. Since an aromatic hydrocarbon plays an important role in the new reaction, it may form coordination compounds with organocopper intermediates.

The subsequent one-step methylene-transfer mechanism is similar to that suggested for the Simmons–Smith reaction.[2] Mechanisms involving free carbene would be unlikely, since isomeric olefins were not detected in the reaction mixture as was mentioned above. Mechanisms involving carbanions would also be unlikely, because the reaction is electrophilic.
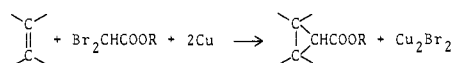
Since the reaction of diiodomethane with copper was extremely slow in the absence of olefins, the following mechanism, which does not involve the formation of iodomethylcopper prior to the reaction with olefins, is proposed.
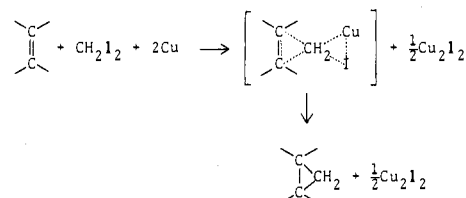
Synthesis of Alkoxycarbonylcyclopropane Derivatives from Olefins by the Reaction with Dibromoacetic Esters and Copper.

The Simmons–Smith reaction is substantially applicable only to diiodomethane. In the reaction with cyclohexene and 1,1-diiodoethane, 7-methylbicyclo[4.1.0]heptane was obtained in 3.6% yield.[17] A single example of the methylene-transfer reaction has been reported that employs ethyl diiodoacetate and zinc–copper couple.[18] The variation of the Simmons–Smith reaction using diethylzinc instead of zinc–copper couple is applicable to diiodomethane, 1,1-diiodoethane, aryldiiodomethane, and trihalomethanes,[6] but is not applicable to dihaloacetic esters.[19]

On the other hand, we have found that the new cyclopropanation is applicable to a variety of organic *gem*-dihalides. The reaction of dibromoacetic esters with copper powder in the presence of olefins gave the corresponding alkoxycarbon-

ylcyclopropane derivatives in fair yields. Some experimental results are given in Table III.

Yields of alkoxycarbonylcyclopropane derivatives are not very good in the new reaction. However, the reaction offers some advantages over the previously described methods. Thermal, photochemical, and catalytic decomposition of diazoacetic esters in the presence of olefins has been most frequently used to prepare alkoxycarbonylcyclopropane derivatives.[20,21] From a practical standpoint, this method is not very convenient since diazoacetic esters are toxic and potentially explosive. The methyl ester of diazoacetic acid has been reported to explode with extreme violence on heating. The new reaction is free of explosion hazards. Introduction of various ester groups is not difficult and many new methyl esters of cyclopropanecarboxylic acids are reported in this work. Preparation of alkoxycarbonylcyclopropane derivatives using organozinc reagents[22] and copper(I) oxide-isocyanide complex[23] were reported to show limited applicability.

It was shown that 1 mol of dibromoacetic ester consumed 2 mol of copper and gave a stoichiometric amount of copper(I) bromide, which was identified by X-ray powder patterns. Except for the case with cyclohexene,[24] the reaction did not give isomeric olefins which would be expected from the insertion of free alkoxycarbonylcarbene into C–H bonds. The reaction seems to proceed via organocopper intermediates rather than free alkoxycarbonylcarbene.

Table III. Synthesis of Alkoxycarbonylcyclopropane Derivatives from Olefins, Dibromoacetic Esters, and Copper[a]

olefin	temp, °C	time, h	product	yield,[b] %	isomer ratio
cyclohexene	55	50	*exo-/endo*-7-methoxycarbonylbicyclo[4.1.0]heptane[g]	31	2.4
cyclohexene[c]	60	50	*exo-/endo*-7-ethoxycarbonylbicyclo[4.1.0]heptane[f]	21	1.6
1-hexene	60	98	*cis-/trans*-1-butyl-2-methoxycarbonylcyclopropane[g]	25	2.7
cycloheptene	55	50	*exo-/endo*-8-methoxycarbonylbicyclo[5.1.0]octane[g]	46	1.9
cis-cyclooctene	55	50	*exo-/endo*-9-methoxycarbonyl-*cis*-bicyclo[6.1.0]nonane[g]	71	1.3
1-octene	70	50	*cis-/trans*-1-hexyl-2-methoxycarbonylcyclopropane[g]	21	2.7
styrene	100[d]	48	*cis-/trans*-1-methoxycarbonyl-2-phenylcyclopropane[g]	22	1.6
trans-stilbene	120[e]	50	*cis,trans*-1-methoxycarbonyl-2,3-diphenylcyclopropane[f]	20	

[a] Reactions were carried out with 4.0 mmol of olefin, 8.0 mmol of methyl dibromoacetate, 18.0 mmol of copper, and 0.2 mmol of iodine in 3.0 mL of benzene. [b] Determined by VPC analysis of the reaction mixture, and were based on the olefin. [c] Ethyl dibromoacetate was used instead of methyl dibromoacetate. [d] Toluene was used instead of benzene. [e] Ethylbenzene was used instead of benzene. [f] These products were identified by comparison of their ¹H NMR and IR spectra with those of authentic samples. [g] These products showed satisfactory analytical data and expected spectra.
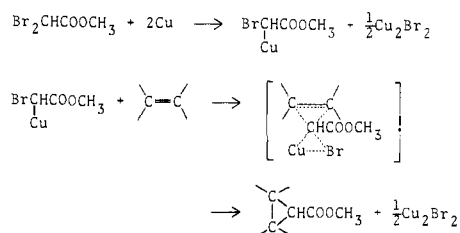
An aromatic hydrocarbon was also the most suitable solvent for the reaction. Copper did not react with dibromoacetic esters in aliphatic hydrocarbons. In ethereal solvents, the yields of cyclopropane derivatives were much lower.

Dibromoacetic esters were found to be the most suitable dihaloacetic esters for the reaction. Dichloroacetic esters did not react with copper under the conditions. Diiodoacetic, bromoiodoacetic, and chloroiodoacetic esters rapidly reacted with copper, but the yields of cyclopropane derivatives were very low.

Experience has shown that electron-withdrawing substituents attached to the olefinic linkage decreased the yields and rate of cyclopropane formation, contrary to the reaction of copper(I) oxide–isocyanide complex of α-halo esters with olefins.[23] Thus a mechanism involving a carbanion seems to be unlikely in the new reaction.

Contrary to the reaction of diazoacetic esters with olefins,[20,21] the new reaction showed syn stereoselectivity when steric repulsion between the alkoxycarbonyl group and the substituents of the olefin was not significant. The cis isomers were obtained predominantly over the corresponding trans isomers from terminal olefins such as 1-hexene, 1-octene, and styrene. Although the exo isomers predominated over the corresponding endo isomers in the reaction with cyclic olefins, the anti selectivity was much lower than that of the corresponding reaction of ethyl diazoacetate. For example, the exo/endo isomer ratios in the reaction of methyl dibromoacetate with copper in the presence of cyclohexene, cycloheptene, and *cis*-cyclooctene were 2.4, 1.9, and 1.3, respectively. On the other hand, the corresponding isomer ratios in the decomposition of ethyl diazoacetate catalyzed by trialkyl phosphite–copper(I) chloride complex in the presence of the above cyclic olefins were reported to be 6.9, 3.3, and 2.1, respectively.[25] This difference between the two reactions in stereoselectivity is ascribable, at least partly, to the difference in steric repulsion between the substituents of olefins and the organometallic intermediates.

Reaction of methyl dibromoacetate in the absence of olefin in benzene at 75 °C for 88 h gave methyl monobromoacetate (5–7%), dimethyl maleate (trace), and dimethyl fumarate (trace), together with a large amount of an unidentified product. Under these conditions, 21–25% of methyl dibro-

moacetate remained unchanged in the reaction mixture. Although a detailed investigation was not made, we propose the following mechanism for the new reaction.

The formation of methyl monobromoacetate, dimethyl maleate, and dimethyl fumarate may support the formation of an intermediate organocopper compound, bromo(methoxycarbonyl)methylcopper; however, a better explanation is that the organocopper compound is associated and coordinated with the aromatic hydrocarbon.

Synthesis of Other Cyclopropane Derivatives from Olefins. The reaction of olefins with trihalomethanes and copper gave the corresponding monohalocyclopropane derivatives in fair yields, and showed syn stereoselectivity. For example, the reaction of chlorodiiodomethane, copper, and cyclohexene gave a 2.1:1 mixture of *endo*- and *exo*-7-chlorobicyclo[4.1.0]-heptane in 48% yield.[1] Full details of these and other experiments will be reported in the near future.

The reaction of olefins, 1,1-diiodoethane, and copper gave the corresponding methylcyclopropane derivatives in 11–32% yields.[26] Intramolecular reactions leading to olefins[17,28] appeared to predominate over the cyclopropanation of olefins. The reaction of olefins, ω,ω-dibromoacetophenone, and copper gave the corresponding benzoylcyclopropane derivatives in 2–12% yields.[27] This is the first example of acylcyclopropanation of olefins by formally divalent carbon intermediate without use of diazoketones. The reaction of phenyldiiodomethane with copper and cyclohexene gave *exo*- and *endo*-7-phenylbicyclo[4.1.0]heptane in low yield. The major products were *cis*- and *trans*-stilbene in this case.[29]

Experimental Section

Elemental analyses were performed at the Elementary Analysis Center of Kyoto University. ¹H NMR spectra were taken on a Varian T-60-A or Japan Electron Optics Laboratory Model 4H-100 spectrometer in carbon tetrachloride using tetramethylsilane as internal standard. IR spectra were recorded on a Japan Spectroscopic Co. Model 402G spectrometer or Hitachi 215 grating spectrophotometer. Mass spectra were obtained on a Hitachi Model RMU-6 mass spectrometer. VPC analyses were performed on a Shimadzu GC-4A or GC-4B gas chromatograph. X-ray powder data were obtained on a Rigaku Denki Co. X-ray diffractometer with Fe Kα radiation.

Materials. Bromoiodomethane,[30] chloroiodomethane,[30] chlorodiiodomethane,[31] dichloroiodomethane,[31] methyl dibromoacetate,[32] ethyl dibromoacetate,[32] methyl chloroiodoacetate,[30] methyl bromoiodoacetate,[30] and methyl diiodoacetate[30] were prepared by minor modification of literature methods. Diiodomethane was purified by distillation. *p*-Chlorostyrene,[33] *p*-bromostyrene,[33] *p*-methylstyrene,[33] *p*-methoxystyrene,[33] *m*-chlorostyrene,[33] *m*-trifluoromethylstyrene,[33] 3-methoxycyclohexene,[34] and *cis*-stilbene[35] were prepared by conventional methods. *cis*-β-Methylstyrene[36] and *trans*-β-methylstyrene[33] were prepared by literature methods and purified by collection using VPC. Other olefins were commercially available and were purified by distillation. The ordinary commercial grade of copper powder

$$Br_2CHCOOCH_3 + 2Cu \longrightarrow Br\underset{Cu}{C}HCOOCH_3 + \tfrac{1}{2}Cu_2Br_2$$

$$Br\underset{Cu}{C}HCOOCH_3 + \overset{}{\underset{}{C}}=\overset{}{\underset{}{C}} \longrightarrow \left[\begin{array}{c} C-\!\!-\!\!-C \\ CHCOOCH_3 \\ Cu-\!\!-\!\!Br \end{array} \right]$$

$$\longrightarrow \overset{C}{\underset{C}{\diagup}}CHCOOCH_3 + \tfrac{1}{2}Cu_2Br_2$$

Table IV. Isomerization of *cis*-Stilbene to *trans*-Stilbene in the Presence of Copper(I) Halides[a]

cis-stilbene		copper(I) halide			recovered stilbene
mg	mmol	halogen	mg	mmol	cis:trans
53.6	0.297	I	43.9	0.116	25.0:75.0
39.6	0.220	Br	31.4	0.110	79.5:20.5
53.8	0.298	Cl	22.0	0.111	90.5:9.5

[a] The isomerization was carried out in 1.0 mL of ethylbenzene at 125 °C for 50 h.

(particle size was 5–15 μ) provided by Nakarai Chemicals, Ltd., Kyoto, was used without further purification. Nitrogen was purified by passing through a tube containing copper turnings in a furnace at 170 °C followed by drying with phosphorus pentoxide. Solvents were dried with calcium hydride and distilled before use. Other chemicals were used without further purification.

Reaction of Diiodomethane with Copper. The reaction was carried out in a two-necked flask equipped with a magnetic stirrer and a reflux condenser connected with a gas buret. Copper powder (1.14 g, 18.0 mmol) was allowed to react with a small amount (0.05 g, 0.2 mmol) of iodine in 3.0 mL of benzene at room temperature under stirring. After the brown color of iodine disappeared, diiodomethane (2.28 g, 8.51 mmol) was added to the reaction mixture and the flask was closed. The reaction flask was set in an oil bath whose temperature was kept at 70 °C, and the mixture was allowed to react under stirring. The reaction was very slow and most of the copper powder appeared to remain unchanged in the reaction mixture after 50 h. At this time, however, the bath was removed and the gaseous products were analyzed. The total amount of the evolved gas was determined by the gas buret. The gas was analyzed by VPC and mass spectrometry. The analyses indicated the formation of ethylene and cyclopropane in 6 and 3% yields, respectively, based on diiodomethane. Ethane, propylene, propane, and C_4 compounds were not detected in the gaseous products.

Reaction of Copper with Diiodomethane and Cyclohexene. Copper (0.51 g, 8.0 mmol) was allowed to react with iodine (0.05 g, 0.2 mmol) and diiodomethane (0.64 mL, 8.0 mmol) in the presence of cyclohexene (1.64 mL, 16.0 mmol) in 3.0 mL of benzene at 80 °C for 74 h under stirring. Filtration of the reaction mixture gave 1.47 g (3.86 mmol) of γ-copper(I) iodide which was identified by X-ray powder data. VPC analysis of the filtrate showed the formation of 2.05 mmol of bicyclo[4.1.0]heptane and the presence of 4.15 mmol of unchanged diiodomethane in the reaction mixture. The structure of bicyclo[4.1.0]heptane was ascertained by comparison of its ¹H NMR and IR spectra with those of an authentic sample.[6a]

Reaction of copper (1.02 g, 16.0 mmol) with diiodomethane (0.64 mL, 8.0 mmol) and iodine (0.05 g, 0.2 mmol) in the presence of cyclohexene (1.64 mL, 16.0 mmol) in 3.0 mL of benzene at 80 °C for 74 h under stirring gave 2.79 g (7.32 mmol) of γ-copper(I) iodide. VPC analysis of the filtrate showed the formation of 4.60 mmol of bicyclo[4.1.0]heptane and the presence of 0.78 mmol of unchanged diiodomethane. These experimental results indicate that 1 mol of diiodomethane consumed 2 mol of copper.

Synthesis of Cyclopropane Derivatives from Olefins, Organic *gem*-Dihalides, and Copper. General Procedure. The reaction vessel was a two-necked flask equipped with a reflux condenser and a magnetic stirrer. Copper powder was allowed to react with a small amount of iodine in a solvent at room temperature. After the brown color of iodine disappeared, olefin and organic *gem*-dihalides were added, and the mixture was heated at the prescribed temperature under stirring. After the reaction, the inorganic materials were separated by filtration. A fine glass fiber paper was suitable for this purpose. Yields were determined by VPC analysis of the reaction mixture and products were isolated by collection from the filtrate by VPC and were analyzed. Results are given in Tables I and III. Spectral and elemental analyses of some cyclopropane derivatives are given below. The other cyclopropane derivatives were identified by comparison of their ¹H NMR and IR spectra with those of authentic samples prepared using appropriate literature methods.

m-Chlorophenylcyclopropane: n^{30}_D 1.5482; ¹H NMR (CCl₄) τ 3.0 (m, 4 H), 8.2 (m, 1 H), 9.2 (m, 4 H). Anal. (C₉H₉Cl) C, H, Cl.

cis-1,2-Diphenylcyclopropane: n^{30}_D 1.5840; ¹H NMR (CCl₄) τ 3.1 (m, 10 H), 7.59 (m, 2 H), 8.7 (m, 2 H). Anal. (C₁₅H₁₄) C, H.

Table V. Competitive Reaction of Styrene and *p*-Chlorostyrene with Varied Molar Ratio

p-chlorostyrene/styrene	k_x/k_y
0.221	0.464
0.656	0.536
1.777	0.498
4.542	0.496

endo-7-Methoxycarbonylbicyclo[4.1.0]heptane: n^{30}_D 1.4697; $\nu_{C=O}$ (liquid film) 1732 cm⁻¹; ¹H NMR (CCl₄) τ 6.38 (s, 3 H), 7.7–9.2 (m, 11 H). With aid of a shift reagent, tris(dipivaloylmethanato)europium (Eu(DPM)₃), the absorption of the ring proton geminal to COOCH₃ was shown to exhibit a triplet (J = 9.4 Hz). Anal. (C₉H₁₄O₂) C, H.

exo-7-Methoxycarbonylbicyclo[4.1.0]heptane: $nc30_D$ 1.4698; $\nu_{C=O}$ (liquid film) 1727 cm⁻¹; ¹H NMR (CCl₄) τ 6.41 (s, 3, H), 7.7–9.1 (m, 11 H). With aid of Eu(DPM)₃, the absorption of the ring proton geminal to COOCH₃ was shown to exhibit a triplet (J = 4.2 Hz). Anal. (C₉H₁₄O₂) C, H.

endo-8-Methoxycarbonylbicyclo[5.1.0]octane: n^{30}_D 1.4742; $\nu_{C=O}$ (liquid film) 1730 cm⁻¹; ¹H NMR (CCl₄) τ 6.40 (s, 3 H), 7.4–9.2 (m, 13 H). With aid of Eu(DPM)₃, the absorption of the ring proton geminal to COOCH₃ was shown to exhibit a triplet (J = 8.3 Hz). Anal. (C₁₀H₁₆O₂) C, H.

exo-8-Methoxycarbonylbicyclo[5.1.0]octane: n^{30}_D 1.4747; $\nu_{C=O}$ (liquid film) 1727 cm⁻¹; ¹H NMR (CCl₄) τ 6.41 (s, 3 H), 7.5–9.4 (m, 13 H). With aid of Eu(DPM)₃, the absorption of the ring proton geminal to COOCH₃ was shown to exhibit a triplet (J = 3.9 Hz). Anal. (C₁₀H₁₆O₂) C, H.

endo-9-Methoxycarbonyl-*cis*-bicyclo[6.1.0]nonane: n^{30}_D 1.4790; $\nu_{C=O}$ (liquid film) 1726 cm⁻¹; ¹H NMR (CCl₄) τ 6.41 (s, 3 H), 7.7–9.2 (m, 15 H). With aid of Eu(DPM)₃, the absorption of the ring proton geminal to COOCH₃ was shown to exhibit a triplet (J = 8.6 Hz). Anal. (C₁₁H₁₈O₂) C, H.

exo-9-Methoxycarbonyl-*cis*-bicyclo[6.1.0]nonane: n^{30}_D 1.4793; $\nu_{C=O}$ (liquid film) 1726 cm⁻¹; ¹H NMR (CCl₄) τ 6.42 (s, 3 H), 7.7–9.4 (m, 15 H). With aid of Eu(DPM)₃, the absorption of the ring proton geminal to COOCH₃ was shown to exhibit a triplet (J = 4.2 Hz). Anal. (C₁₁H₁₈O₂) C, H.

cis-1-Butyl-2-methoxycarbonylcyclopropane: n^{30}_D 1.4290; $\nu_{C=O}$ (liquid film) 1728 cm⁻¹; ¹H NMR (CCl₄) τ 6.37 (s, 3 H), 8.2–9.7 [m, 13 H, including 8.53 (m, 1 H, ring proton geminal to COOCH₃), 8.63 (m, 6 H, (CH₂)₃), and 9.09 (t, J = 5.0 Hz, 3 H, CH₃)]. Anal. (C₉H₁₆O₂) C, H.

trans-1-Butyl-2-methoxycarbonylcyclopropane: n^{30}_D 1.4291; $\nu_{C=O}$ (liquid film) 1731 cm⁻¹; ¹H NMR (CCl₄) τ 6.40 (s, 3 H), 8.5–9.8 [m, 13 H, including 8.65 (m, 6 H, (CH₂)₃) and 9.09 (t, J = 5.1 Hz, 3 H, CH₃)]. The absorption due to the ring proton geminal to COOCH₃ overlapped with that of butyl protons. Anal. (C₉H₁₆O₂) C, H.

cis-1-Hexyl-2-methoxycarbonylcyclopropane: n^{30}_D 1.4357; $\nu_{C=O}$ (liquid film) 1729 cm⁻¹; ¹H NMR (CCl₄) τ 6.38 (s, 3 H), 8.2–9.5 [m, 17 H, including 8.56 (m, 1 H, ring proton geminal to COOCH₃), 8.68 (m, 10H, (CH₂)₅), and 9.10 (t, J = 5.0 Hz, 3 H, CH₃)]. Anal. (C₁₁H₂₀O₂) C, H.

trans-1-Hexyl-2-methoxycarbonylcyclopropane: n^{30}_D 1.4359; $\nu_{C=O}$ (liquid film) 1732 cm⁻¹; ¹H NMR (CCl₄) τ 6.39 (s, 3 H), 8.5–9.7 [m, 17 H, including 8.66 (m, 10 H, (CH₂)₅) and 9.11 (t, J = 5.0 Hz, 3 H, CH₃)]. The absorption due to the ring proton geminal to COOCH₃ overlapped with that of hexyl protons. Anal. (C₁₁H₂₀O₂) C, H.

cis-1-Methoxycarbonyl-2-phenylcyclopropane: n^{30}_D 1.5194; $\nu_{C=O}$ (liquid film) 1730 cm⁻¹; ¹H NMR (CCl₄) τ 2.82 (m, 5 H), 6.62 (lit.[37] 6.61) (s, 3 H), 7.0–9.5 (m, 4 H). Anal. (C₁₁H₁₂O₂) C, H.

trans-1-Methoxycarbonyl-2-phenylcyclopropane: n^{30}_D 1.5232; $\nu_{C=O}$ (liquid film) 1726 cm⁻¹; ¹H NMR (CCl₄) τ 2.85 (m, 5 H), 6.32 (lit.[37] 6.32) (s, 3 H), 7.6 (m, 1 H), 7.9–9.0 (m, 3 H). Anal. (C₁₁H₁₂O₂) C, H.

cis,trans-1-Methoxycarbonyl-2,3-diphenylcyclopropane: $\nu_{C=O}$ (liquid film) 1727 cm⁻¹; ¹H NMR (CCl₄) τ 2.82 (narrow m, 10 H), 6.55 (lit.[37] 6.53) (s, 3 H), 6.2–7.9 (m, 3 H). Anal. (C₁₇H₁₆O₂) C, H.

Isomerization of *cis*-1,2-Diphenylcyclopropane. Pure *cis*-1,2-diphenylcyclopropane was isolated by a collection from the reaction mixture of *cis*-stilbene with diiodomethane and copper by VPC. The isolated *cis*-1,2-diphenylcyclopropane (42.1 mg, 0.216 mmol) was

heated in 1.0 mL of ethylbenzene in the presence of copper(I) iodide (41.0 mg, 0.108 mmol) at 125 °C for 50 h under stirring. VPC analysis of the reaction mixture showed that 1,2-diphenylcyclopropane was a 97.0:3.0 mixture of cis and trans isomers.

Isomerization of *cis*-Stilbene. Pure *cis*-stilbene was heated at 125 °C for 50 h in ethylbenzene in the presence of copper(I) halide under stirring. VPC analysis of the mixture showed that *cis*-stilbene was partly isomerized to the trans isomer. Results are summarized in Table IV. *trans*-Stilbene did not isomerize under the condition.

Competitive Reactions. In a two-necked flask equipped with a reflux condenser and a magnetic stirrer, 1.33 mmol in all of two olefins, 0.38 g (6.00 mmol) of copper, 15 mg (0.06 mmol) of iodine, and 0.72 g (2.66 mmol) of diiodomethane were allowed to react in 2.0 mL of benzene at 75 ± 1 °C under stirring. After the reaction, the organic layer was analyzed by VPC. The relative reactivity was calculated by the equation[38] $k_x/k_y = (P_x/P_y)(O_y/O_x)$, where P is the moles of product and O is that of reactant. The quasi-first-order kinetics with respect to reactants was ascertained in each reaction as illustrated in Table V.

Reaction of Copper with Methyl Dibromoacetate. Reaction of copper powder (1.14 g, 18.0 mmol) with iodine (0.10 g, 0.4 mmol) and methyl dibromoacetate (1.85 g, 8.0 mmol) was carried out in 3.0 mL of benzene at 75 °C. After 88 h the mixture was separated by filtration. X-ray powder data of the solid (2.55 g) revealed that it was principally γ-copper(I) bromide with small amounts of copper metal and γ-copper(I) iodide. The powder data also indicated that the solid contained none of α- and β-copper(I) bromide and copper(II) bromide. VPC analysis of the filtrate showed the formation of methyl monobromoacetate in 5–7% yield. The analysis also showed the presence of 21–25% of unchanged methyl dibromoacetate and a trace of dimethyl maleate and dimethyl fumarate. In addition, a large amount of unidentified product was detected.

References and Notes

(1) Preliminary communication: Kawabata, N.; Naka, M.; Yamashita, S. *J. Am. Chem. Soc.* **1976**, *98*, 2676–2677.
(2) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Holness, C. M. *Org. React.* **1973**, *20*, 1–131.
(3) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.*, **1959**, *81*, 4256–4264.
(4) Richardson, D. B.; Durrett, L. R.; Martin, J. M.; Putnam, W. E.; Slaymaker, S. C.; Dvoretzky, I. *J. Am. Chem. Soc.* **1965**, *87*, 2763–2765.
(5) Wittig, G.; Schwarzenbach, K. *Angew. Chem.* **1959**, *71*, 652.
(6) (a) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron* **1968**, *24*, 53–58. (b) Nishimura, J.; Kawabata, N.; Furukawa, J. *ibid.* **1969**, *25*, 2647–2659. (c) Nishimura, J.; Furukawa, J.; Kawabata, N.; Koyama, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1127–1130. (d) Nishimura, J.; Furukawa, J. *Chem. Commun.* **1971**, 1375–1376.
(7) Butlerow, A. *Justus Liebigs Ann. Chem.* **1861**, *120*, 356.
(8) Posner and Brunelle[9] reported reaction of *gem*-dihalides with lithium di-

methylcopper, but they did not refer to the reaction of *gem*-dihalides with copper metal.
(9) Posner, G. H.; Brunelle, D. J. *Tetrahedron Lett.* **1972**, 293–296.
(10) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1897.
(11) See ref 2, p 23.
(12) Dauben, W. G.; Berezin, G. H. *J. Am. Chem. Soc.* **1963**, *85*, 468–472.
(13) Nishimura, J.; Furukawa, J.; Kawabata, N.; Kitayama, M. *Tetrahedron* **1971**, *27*, 1799–1806.
(14) Seyferth, D.; Mui, J. Y.; Damrauer, R. *J. Am. Chem. Soc.* **1968**, *90*, 6182–6186.
(15) Leznoff, C. C. *Chem. Soc. Rev.* **1974**, *3*, 65–85, and references cited therein.
(16) Hurd, D. T.; Rochow, E. G. *J. Am. Chem. Soc.*, **1945**, *67*, 1057–1059.
(17) Simmons, H. E.; Blanchard, E. P.; Smith, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1347–1356.
(18) Büchel, K. -H.; Korte, F. *Z. Naturforsch. B* **1962**, *17*, 349–350.
(19) Kawabata, N.; Kino, H.; Miyoshi, T.; Yamashita, S. Unpublished result.
(20) Marchand, A. P.: Brookway, N. M. *Chem. Rev.* **1974**, *74*, 431–469.
(21) Dave, V.; Warnhoff, E. W. *Org. React.* **1970**, *18*, 217–401.
(22) (a) Vul'fson, N. S.; Zhurina, F. G.; Senyavina, L. B. *Dokl. Akad. Nauk SSSR* **1964**, *157*, 603–606. (b) Zhurina, F. G.; Vul'fson, N. S. *Zh. Org. Khim.* **1967**, *3*, 504–506. (c) Tsuruta, T.; Kawakami, Y. *Tetrahedron* **1973**, *29*, 1173–1178. (d) Gaudemar-Bardone, F.; Gaudemar, M. *C. R. Acad. Sci., Ser. C* **1972**, *274*, 991–992.
(23) Saegusa, T.; Ito, Y.; Yonezawa, K.; Inubushi, Y.; Tomita, S. *J. Am. Chem. Soc.* **1971**, *93*, 4049–4051.
(24) VPC analysis of the reaction mixture of cyclohexene and methyl dibromoacetate showed the formation of an unknown material in the neighborhood of 7-methoxycarbonylbicyclo[4.1.0]heptane in an estimated yield of 5%. The ¹H NMR spectrum of this material (CCl_4) [τ 4.47 (m, 1 H), 6.37 (s, 3 H), 7.15 (s, 2 H), 8.00 (m, 4 H), 8.40 (m, 4 H)] appeared consistent with methyl 1-cyclohexen-1-ylacetate. A similar result was also observed in the reaction of cyclohexene and ethyl dibromoacetate.
(25) Moser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 1135–1140.
(26) Kawabata, N.; Yamagishi, N.; Yamashita, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 466–468.
(27) Kawabata, N.; Fujii, T.; Naka, M.; Yamashita, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1005–1006.
(28) Katz, T. J.; Garratt, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 4876–4879.
(29) Kawabata, N.; Shimomura, A. Unpublished result.
(30) Miyano, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2864–2865.
(31) Auger, V. *C. R. Acad. Sci.* **1908**, *146*, 1037–1039.
(32) (a) Parrot, J.; Hervieu, J.; Ursy, Y.; Paty, M. *Bull. Soc. Chim. Fr.* **1964**, 1063–1069. (b) Sen, A. B.; Joshi, K. C. *J. Indian Chem. Soc.* **1948**, *25*, 483–484. (c) Conrad, M.; Reinbach, H. *Chem. Ber.* **1902**, *35*, 1813–1821.
(33) (a) Overberger, C. G.; Saunders, J. H. "Organic Syntheses", Collect. Vol. III; Wiley: New York, 1955; pp 204–206. (b) Gannon, W. F.; House, H. O. *ibid.*, Collect. Vol. V; 1973; pp 294–296. (c) Overberger, C. G.; Saunders, J. H.; Allen, R. E.; Gander, R. *ibid.*, Collect. Vol. III; 1955; pp 200–202. (d) Hartwell, J. L. *Ibid.*, pp 185–187.
(34) Fleming, I.; Thomas, E. J. *Tetrahedron* **1972**, *28*, 4989–5001.
(35) (a) Adams, R.; Thal, A. F. "Organic Syntheses", Collect. Vol. I; Wiley: New York, 1941; pp 436–438. (b) Lazier, W. A.; Arnold, H. R. *Ibid.*, Collect. Vol. II; 1943; pp 142–145. (c) Buckles, R. E.; Bremer, K. *ibid.*, Collect. Vol. IV; 1963; pp 777–779. (d) Buckles, R. E.; Wheeler, N. G. *ibid.*, pp 857–859.
(36) (a) Johnson, J. R. *Org. React.* **1942**, *1*, 251. (b) Wiley, R. H.; Smith, N. R. "Organic Syntheses", Collect. Vol. IV; Wiley: New York, 1963; pp 731–734.
(37) Krueger, G. L.; Kaplan, K.; Orchin, M.; Faul, W. H. *Tetrahedron Lett.* **1965**, 3979–3984.
(38) Doering, W. von E.; Henderson, W. A. *J. Am. Chem. Soc.* **1958**, *80*, 5274–5277.