Tetrahedron Vol 36, pp 3517 to 3522
© Pergamon Press Ltd., 1980. Printed in Great Britain

0040 4020/80/1215 3517 $02.00/0

SYNTHESIS OF *gem*-DIALKOXYCARBONYLCYCLOPROPANE DERIVATIVES FROM OLEFINS BY THE REACTION WITH DIBROMOMALONIC ESTERS AND COPPER IN DIMETHYL SULPHOXIDE

NARIYOSHI KAWABATA* and MASAMI TANIMOTO

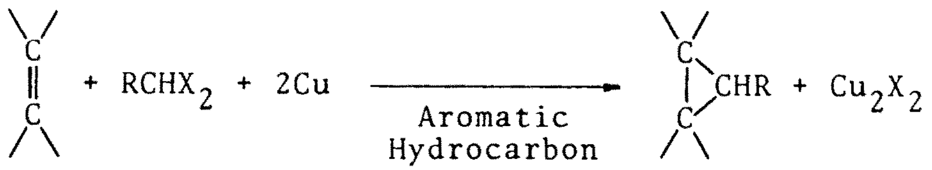
Department of Chemistry, Faculty of Polytechnic Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

(*Received in Japan 7 February 1980*)

Abstract– A novel method for the synthesis of *gem*-dialkoxycarbonylcyclopropane derivatives is reported which involves the reaction of olefins with dibromomalonic esters and Cu in dimethyl sulphoxide. The reaction was applicable to a wide range of olefins and proceeded smoothly at moderate temperature to give the cyclopropane derivatives often in good yields. Cu was converted to Cu(II) bromide during the reaction. The reaction was weakly electrophilic and proceeded non-stereospecifically, and a stepwise mechanism involving addition and elimination appeared favourable for the reaction. In contrast, in the previously reported examples of the cyclopropanation of olefins by organic *gem*-dihalides and Cu in an aromatic hydrocarbon, Cu was converted to Cu(I) halides and a concerted cycloaddition of carbenoid intermediates appeared favourable.

Several methods have been used for the synthesis of *gem*-dialkoxycarbonylcyclopropane derivatives from olefins. The reaction of olefins with diazomalonic esters gives the corresponding *gem*-dialkoxycarbonylcyclopropane derivatives.[1,2] The reaction of olefins with malonic esters in the presence of Cu(II) halide gives the corresponding *gem*-dialkoxycarbonylcyclopropane derivatives in only 8–18% yields.[3] The reaction of olefins with Cu(I) oxide-isocyanide complex[4] and that with malonic or bromomalonic esters in the presence of a base[5,6] give the corresponding *gem*-dialkoxycarbonylcyclopropane derivatives, but the olefins applicable to these procedures are limited only to α,β-unsaturated carbonyl compounds and nitriles. Other route to *gem*-dialkoxycarbonylcyclopropane derivatives are the reaction of 1,4-dibromo-2-alkene with sodiomalonic esters,[7] the reaction of *gem*-dibromocyclopropane derivatives with diethyl carbonate and butyllithium,[8] and the reaction of dimethyl vinyl sulphonium salts with sodiomalonic esters.[9]

Recently we have reported the synthesis of cyclopropane derivatives from olefins by the reaction with organic *gem*-dihalides and Cu.[10–13] This reaction proceeded stereospecifically and gave the cyclopropane derivatives often in good yields. The reaction did not give isomeric olefins difficult to separate which would be expected from the insertion of free carbene into C–H bonds.



(1)

(R=H,[10] F,[13] Cl,[13] Br,[13] I,[13] COOR',[10] CH$_3$,[11] and COC$_6$H$_5$.[12] X=Br, I.)

As an extension of this work, we have investigated the reaction of bromomalonic esters with Cu powder in the presence of olefins, and found a useful method for the synthesis of *gem*-dialkoxycarbonylcyclopropane derivatives from olefins.

Reaction of olefins with diethyl dibromomalonate with Cu in an aromatic hydrocarbon

The reaction of diethyl dibromomalonate with Cu powder in C$_6$H$_6$ at 75° gave tetraethyl ethylenetetracarboxylate in 52% yield after 24 hr.

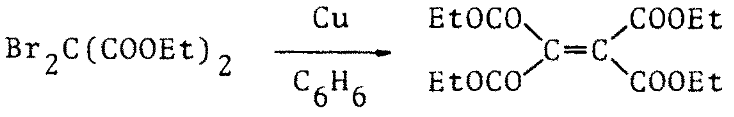


Table 1. Synthesis of *gem*-dialkoxycarbonylcyclopropane derivatives from olefins by reaction (2)[a]

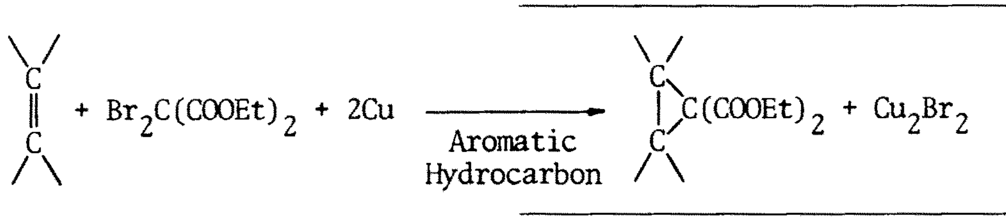
Olefin	Temp. (°C)	Time (h)	Product	Yield[b] (%)
Cyclohexene	65	40	7,7-Diethoxycarbonylbicyclo[4.1.0]heptane	12
cis-Cyclooctene	75	24	9,9-Diethoxycarbonyl-cis-bicyclo[6.1.0]nonane	56
1-Heptene	75	24	1,1-Diethoxycarbonyl-2-pentylcyclopropane	31
1-Octene	75	24	1,1-Diethoxycarbonyl-2-hexylcyclopropane	29
Acrylonitrile	60	24	1-Cyano-2,2-diethoxycarbonylcyclopropane	61
Ethyl acrylate	70	24	1,1,2-Triethoxycarbonylcyclopropane	18
Styrene	100[c]	40	1,1-Diethoxycarbonyl-2-phenylcyclopropane	trace

[a] Reactions were carried out with 4.0 mmol of olefin, 8.0 mmol of diethyl dibromomalonate, 18.0 mmol of Cu 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] Toluene was used instead of C_6H_6.

The reaction of dibromomalonic ester with Cu in the presence of olefins gave the corresponding *gem*-dialkoxycarbonylcyclopropane derivatives in 12–61% yields. Some experimental results are given in Table 1. All products were identified by comparison of their ^{1}H NMR and IR spectra with those of authentic samples, or showed satisfactory analytical data and expected spectra. Vpc analysis of the reaction mixture showed that the reaction did not give isomeric olefins.



$$\mathrm{>C{=}C<} + \mathrm{Br_2C(COOEt)_2} + 2\mathrm{Cu} \xrightarrow[\text{Hydrocarbon}]{\text{Aromatic}} \mathrm{>C(-C<)C(COOEt)_2} + \mathrm{Cu_2Br_2} \qquad (2)$$

Reaction 2 with styrene gave the phenylcyclopropane derivative in low yield, and the principal side reaction was the polymerisation. The phenylcyclopropane derivative was not unstable under the reaction condition. A large amount of tetraethyl ethylenetetracarboxylate was detected in the reaction mixture.

In the previous examples of reaction 1, acrylonitrile and acrylic esters did not give the corresponding cyclopropane derivatives.[10–13] The result was interpreted in terms of the large spread in relative reactivity.[10] On the contrary, acrylonitrile gave the corresponding cyclopropane derivative in a fair yield in reaction 2. The result will be discussed later again. Except for this point, reaction 2 appeared to show an essentially similar nature to that of previous examples of reaction 1, and the concerted cycloaddition mechanism via carbenoid intermediate would reasonably explain the experimental results.

Reaction of olefins with diethyl dibromomalonate and Cu in dimethyl sulphoxide

In previous examples of reaction 1, ethereal and other polar solvents conspicuously reduced the yields of cyclopropane derivatives.[10–13] Actually no cyclopropane derivative was obtained in ethereal solvents. However, reaction 2 with acrylonitrile gave the corresponding cyclopropane derivative in a fair yield as was given in Table 1. This finding prompted us to investigate the effect of polar solvent in the cyclopropanation of olefins by dibromomalonic esters and Cu. We found that the reaction proceeded smoothly even in polar solvents and gave cyclopropane derivatives in good yields. Some experimental results are given in Table 2. In polar solvents, especially in dimethyl sulphoxide (DMSO), the reaction of dibromomalonic esters with Cu proceeded rapidly, and the reaction in the presence of olefins gave the corresponding cyclopropane derivatives in much better yields than in an aromatic hydrocarbon.

Contrary to the previous examples of reaction 1, reaction 2 with acrylonitrile gave the corresponding cyclopropane derivative in a fair yield. This result can be understood when we assume that acrylonitrile acted as a polar solvent in this case.

Since the reaction of styrene with dibromomalonic esters and Cu proceeded very smoothly in DMSO and

Table 2. Reaction of styrene with diethyl dibromomalonate and Cu in polar solvents[a]

Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
Dimethyl sulphoxide	75	2	99
N,N-Dimethylformamide	75	2	47
N,N-Dimethylformamide	75	15	68
Tributylamine	85	5	69
Tetrahydrofuran	55	20	trace
Toluene	100	40	trace

[a] Reactions were carried out with 4.0 mmol of styrene, 8.0 mmol of diethyl dibromomalonate, 18.0 mmol of Cu, and 0.2 mmol of I_2 in 3.0 ml of the solvent.

[b] Yield of 1,1-diethoxycarbonyl-2-phenylcyclopropane determined by VPC analysis of the reaction mixture, and was based on styrene.

Table 3. Synthesis of *gem*-diethoxycarbonylcyclopropane derivatives from olefins by reaction (3)

Olefin	Temp. (°C)	Time (h)	Product	Yield[c] (%) A[a]	B[b]
Styrene	75	2	1,1-Diethoxycarbonyl-2-phenylcyclopropane	99	95
p-Methylstyrene	75	2	1,1-Diethoxycarbonyl-2-*p*-methylphenylcyclopropane	57	48
p-Chlorostyrene	75	2	1-*p*-Chlorophenyl-2,2-diethoxycarbonylcyclopropane	92	81
m-Chlorostyrene	75	2	1-*m*-Chlorophenyl-2,2-diethoxycarbonylcyclopropane	70	89
m-Trifluoromethylstyrene	75	2	1,1-Diethoxycarbonyl-2-*m*-trifluoromethylphenylcyclopropane	71	93
Acrylonitrile	60	2	1-Cyano-2,2-diethoxycarbonylcyclopropane		62
Acrylonitrile	75	2	1-Cyano-2,2-diethoxycarbonylcyclopropane	97	
Ethyl acrylate	75	2	1,1,2-Triethoxycarbonylcyclopropane	2	46
cis-Cyclooctene	75	2	9,9-Diethoxycarbonyl-*cis*-bicyclo[6.1.0]nonane	4	34
1-Octene	75	2	1,1-Diethoxycarbonyl-2-hexylcyclopropane	5	69
cis-β-Methylstyrene	75	2	1,1-Diethoxycarbonyl-2-methyl-3-phenylcyclopropane	6[d]	28[e]
trans-β-Methylstyrene	75	2	1,1-Diethoxycarbonyl-2-methyl-3-phenylcyclopropane	8[f]	24[g]

[a] Reactions were carried out with 4.0 mmol of olefin, 8.0 mmol of diethyl dibromomalonate, 18.0 mmol of Cu, and 0.2 mmol of I_2 in 6.0 ml of DMSO.

[b] Reactions were carried out with 4.0 mmol of olefin, 8.0 mmol of diethyl dibromomalonate, 9.0 mmol of Cu, and 0.1 mmol of I_2 in 6.0 ml of DMSO.

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

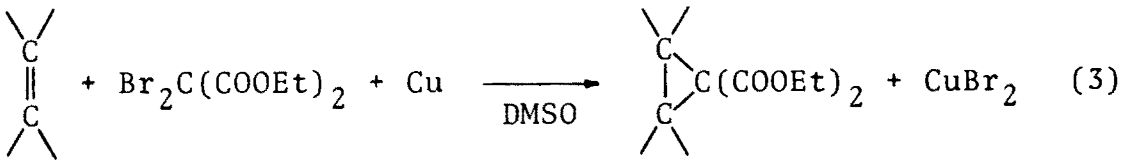
[d] A 11:89 mixture of cis and trans isomers was obtained.

[e] A 7:93 mixture of cis and trans isomers was obtained.

[f] A 12:88 mixture of cis and trans isomers was obtained.

[g] A 6:94 mixture of cis and trans isomers was obtained.

gave the cyclopropane derivatives in excellent yields, we carried out the reaction with other olefins in the solvent. Some experimental results are given in Table 3.



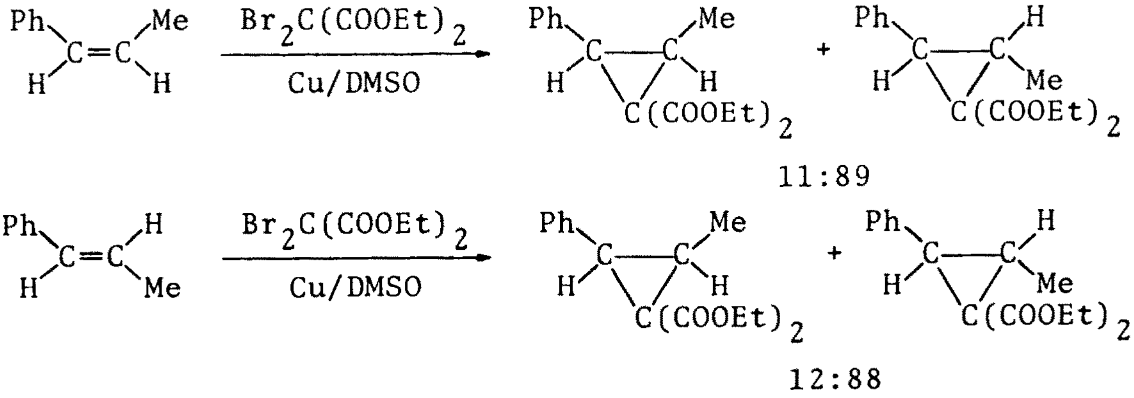
$$\gt C{=}C\lt \; + \; \mathrm{Br_2C(COOEt)_2} \; + \; \mathrm{Cu} \xrightarrow[\mathrm{DMSO}]{} \gt\underset{\mathrm{C(COOEt)_2}}{C{-}C}\lt \; + \; \mathrm{CuBr_2} \qquad (3)$$

In the previous examples of reaction 1, 1 mol of the organic *gem*-dihalide consumed 2 mol of Cu, and gave the corresponding Cu(I) halide in a quantitative yield.[10] In the reaction 3, however, 1 mol of dibromomalonic ester consumed 1 mol of Cu and gave Cu(II) bromide in a quantitative yield, which was isolated as a coordinated complex with two molecules of DMSO, and was identified by comparison of its spectral data with those of an authentic sample.[14]

Table 3 shows that reaction 3 is useful for the synthesis of *gem*-dialkoxycarbonylcyclopropane derivatives from olefins. The *gem*-dialkoxycarbonylcyclopropanation by Cu(I) oxide-isocyanide complex[4] and that by malonic or bromomalonic esters in the presence of a base[5,6] are limited only to α,β-unsaturated carbonyl compounds and nitriles. On the contrary, reaction 3 is applicable to conjugated and unconjugated olefins as well as to α,β-unsaturated carbonyl compounds and nitriles as can be seen in Table 3.

Reaction 3 was found to give higher yields of cyclopropane derivatives from several olefins when smaller amount of Cu was used as can be seen in Table 3. In such cases, the principal side reaction was the formation of tetraethyl ethylenetetracarboxylate, the formation of which decreased when the amount of Cu was reduced.

Reaction (3) did not give isomeric olefins difficult to separate, which would be expected from the insertion of free carbene into C–H bonds. Reaction 3 gave *gem*-dialkoxycarbonylcyclopropane derivatives in a non-stereospecific way. From both *cis*- and *trans*-β-methylstyrene was obtained about 1:9 mixture of *cis*- and *trans*-isomers of the corresponding cyclopropane derivatives. Isomerization of *cis*- and *trans*-β-methylstyrene and that of *cis*- and *trans*-1,1-diethoxycarbonyl-2-methyl-3-phenylcyclopropane were not observed under the experimental condition.



The relative reactivity of substituted styrenes in reaction 3 was investigated. Logarithm of the relative reactivity was plotted against Hammett σ-value in Fig. 1. Thus the reaction was concluded to be weakly electrophilic.

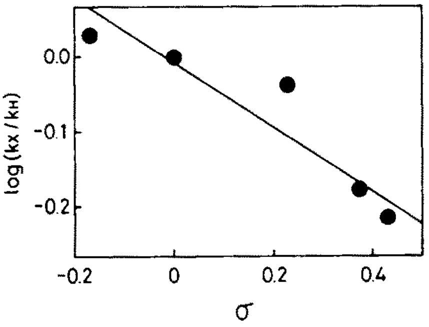
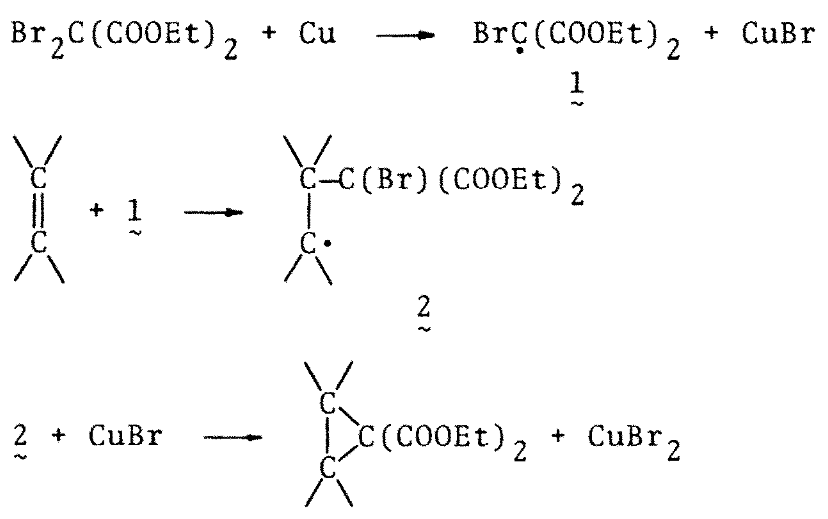


Fig. 1. The Hammett correlation of relative reactivity of substituted styrenes in reaction (3) at 75 .

Although no detailed investigation of the mechanism of the reaction has been made, several experimental observations have suggested a reasonable interpretation. We propose the following mechanism for reaction (3).



Since reaction (3) proceeded non-stereospecifically contrary to the previous examples of reaction (1), the concerted cycloaddition mechanism via carbene or carbenoid intermediate may be unlikely. The stepwise mechanism involving addition and elimination may reasonably explain the non-stereospecific nature of the reaction. The addition of a radical **1** to olefinic double bond seems to be consistent with the findings that the reaction showed a ρ-value of -0.4 in the relative reactivity of substituted styrenes. Mechanism involving carbanion may be unlikely, because the reaction showed the electrophilic nature.

EXPERIMENTAL

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

Materials. Diethyl dibromomalonate was prepared according to the lit.[15] *cis-β*-Methylstyrene[16] and *trans-β*-methylstyrene[17] were prepared by lit methods and purified by collection using vpc. Other olefins were commercially available and were purified by distillation. The ordinary commercial grade of Cu powder was used without further purification. Solvents were dried with CaH_2 and distilled before use. Other chemicals were used without further purification.

Synthesis of gem-*dialkoxycarbonylcyclopropane derivatives from olefins by the reaction with diethyl dibromomalonate and Cu*

General procedure. The reaction vessel was a 2-necked flask equipped with a reflux condenser and magnetic stirrer. Cu was allowed to react with a small amount of I_2 in a solvent at room temp. After the brown colour of I_2 disappeared, olefin and diethyl dibromomalonate were added and the mixture was heated at the prescribed temp under stirring. After the reaction, the mixture was submitted for the analysis of products. In the cases where an aromatic hydrocarbon was used as the solvent (the reaction 2), the inorganic materials were separated from the mixture by filtration. In the cases of the reactions carried out in a polar solvent (reaction 3), the organic materials were extracted by hexane from the mixture. Yields were determined by vpc analysis of the organic layer, and the products were isolated by collection from the organic layer by vpc and were analyzed. Results are given in Tables 1, 2 and 3. ^{1}H NMR and IR spectra of 7,7-diethoxycarbonylbicyclo[4.1.0]heptane,[1] 1,1-diethoxycarbonyl-2-phenylcyclopropane,[9] 1-cyano-2,2-diethoxycarbonylcyclopropane,[4] tetraethyl ethylenetetracarboxylate[18] were respectively identical with those of authentic materials. Spectral and elementary analyses of the other *gem*-dialkoxycarbonylcyclopropane derivatives are given below. All products showed characteristic absorption of ester CO group in their IR spectra.

9,9-*Diethoxycarbonyl*-cis-*bicyclo*[6.1.0]*nonane*. n_D^{30} = 1.4729; ^{1}H NMR (CCl_4) δ 0.7–2.3 (m, 14 H), 1.24 (t, J = 7.1 Hz, 6 H), 4.10 (q, J = 7.1 Hz, 4 H); MS *m/e* (rel %) 268 (1.05 M^+), 160 (40), 29 (100), 27 (49). (Found: C, 67.09; H, 8.86. $C_{15}H_{24}O_4$ requires: C, 67.14; H, 9.01 %.)

1,1-*Diethoxycarbonyl-2-pentylcyclopropane*. n_D^{30} = 1.4377; ^{1}H NMR (CCl_4) δ 0.5–1.9 (m, 14 H), 1.24 (t, J = 7.1 Hz, 6 H), 4.14 (q, J = 7.1 Hz, 4 H); MS *m/e* (rel %) 256 (0.53 M^+), 127 (67), 44 (44), 41 (49), 29 (100), 27 (61). (Found: C, 65.36; H, 9.38. $C_{14}H_{24}O_4$ requires: C, 65.60; H, 9.44 %.)

1,1-*Diethoxycarbonyl-2-hexylcyclopropane*. n_D^{30} = 1.4390; ^{1}H NMR (CCl_4) δ 0.5–2.2 (m, 16 H), 1.24 (t, J = 7.0 Hz, 6 H), 4.14 (q, J = 7.0 Hz, 4 H). (Found: C, 66.35; H, 9.90. $C_{15}H_{26}O_4$ requires: C, 66.64; H, 9.69 %.)

1,1,2-*Triethoxycarbonylcyclopropane*. n_D^{30} = 1.4409; ^{1}H NMR (CCl_4) δ 1.23 (t, J = 7.2 Hz, 3 H), 1.24 (t, J = 7.2 Hz, 3 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.51 (d of d, J_{cis} = 8.8 Hz and J_{gem} = 4.2 Hz, 1 H), 1.82 (d of d, J_{trans} = 6.8 Hz and J_{gem} = 4.2 Hz, 1 H), 2.43 (d of d, J_{cis} = 8.8 Hz and J_{trans} = 6.8 Hz, 1 H), 4.11 (q, J = 7.2 Hz, 4 H), 4.17 (q, J = 7.2 Hz, 2 H). (Found: C, 55.76; H, 7.09. $C_{12}H_{18}O_6$ requires: C, 55.81; H, 7.02 %.)

1,1-*Diethoxycarbonyl-2-p-methylphenylcyclopropane*. n_D^{30} = 1.4989; ^{1}H NMR (CCl_4) δ 0.86 (t, J = 7.2 Hz, 3 H), 1.28 (t, J = 7.2 Hz, 3 H), 1.53 (d of d, J_{cis} = 9.2 Hz and J_{gem} = 4.8 Hz, 1 H), 2.01 (d of d, J_{trans} = 8.0 Hz and J_{gem} = 4.8 Hz, 1 H), 2.26 (s, 3 H), 3.06 (d of d, J_{cis} = 9.2 Hz and J_{trans} = 8.0 Hz, 1 H), 3.78 (q, J = 7.2 Hz, 2 H), 4.17 (q, J = 7.2 Hz, 2 H), 6.98 (m, 4 H). (Found: C, 69.37; H, 7.48. $C_{16}H_{20}O_4$ requires: C, 69.55; H, 7.29 %.)

1-*p-Chlorophenyl-2,2-diethoxycarbonylcyclopropane*. n_D^{30} = 1.5071; ^{1}H NMR (CCl_4) δ 0.90 (t, J = 7.2 Hz, 3 H), 1.28 (t, J = 7.2 Hz, 3 H), 1.58 (d of d, J_{cis} = 9.2 Hz and J_{gem} = 5.0 Hz, 1 H), 2.03 (d of d, J_{trans} = 7.8 Hz and J_{gem} = 5.0 Hz, 1 H), 3.10 (d of d, J_{cis} = 9.2 Hz and J_{trans} = 7.8 Hz, 1 H), 3.82 (q, J = 7.2 Hz, 2 H), 4.19 (q, J = 7.2 Hz, 2 H), 7.14 (m, 4 H). (Found: C, 60.71; H, 5.90; Cl, 11.67. $C_{15}H_{17}ClO_4$ requires: C, 60.71; H, 5.77; Cl, 11.95%.)

1-m-*Chlorophenyl-2,2-diethoxycarbonylcyclopropane.* n_D^{30} = 1.5077; ^{1}H NMR (CCl_4) δ 0.90 (t, J = 7.2 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.57 (d of d, J_{cis} = 9.2 Hz and J_{gem} = 5.0 Hz, 1 H), 2.04 (d of d, J_{trans} = 8.0 Hz and J_{gem} = 5.0 Hz, 1 H), 3.09 (d of d, J_{cis} = 9.2 Hz and J_{trans} = 8.0 Hz, 1 H), 3.83 (q, J = 7.2 Hz, 2 H), 4.19 (q, J = 7.2 Hz, 2 H), 7.1 (m, 4 H). (Found: C, 60.98; H, 6.00; Cl, 11.96. $C_{15}H_{17}ClO_4$ requires: C, 60.71; H, 5.77; Cl, 11.95%.)

1,1-*Diethoxycarbonyl-2-*m-*trifluoromethylphenylcyclopropane.* n_D^{30} = 1.4620; ^{1}H NMR (CCl_4) δ 0.85 (t, J = 7.2 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.62 (d of d, J_{cis} = 9.5 Hz and J_{gem} = 5.2 Hz, 1 H), 2.09 (d of d, J_{trans} = 8.0 Hz and J_{gem} = 5.2 Hz, 1 H), 3.18 (d of d, J_{cis} = 9.5 Hz and J_{trans} = 8.0 Hz, 1 H), 3.80 (q, J = 7.2 Hz, 2 H), 4.21 (q, J = 7.2 Hz, 2 H), 7.4 (m, 4 H). (Found: C, 58.02, H, 5.36; F, 17.31. $C_{16}H_{17}F_3O_4$ requires: C, 58.18; H, 5.19; F, 17.26%.

1,1-*Diethoxycarbonyl*-cis-2-*methyl-3-phenylcyclopropane.* n_D^{30} = 1.5078; ^{1}H NMR (CCl_4) δ 1.13 (t, J = 7.2 Hz, 3 H), 1.30 (d, J = 6.2 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.6 2.2 (m, 1 H), 2.98 (d, J = 9.2 Hz, 1 H), 4.02 (q, J = 7.2 Hz, 2 H), 4.15 (q, J = 7.2 Hz, 2 H), 7.17 (m, 5 H); MS *m/e* (rel %) 276 (3.85 M^+), 184 (84), 135 (100), 129 (84), 107 (96), 105 (66), 44 (52), 29 (76).

1,1-*Diethoxycarbonyl*-trans-2-*methyl-3-phenylcyclopropane.* n_D^{30} = 1.4940; ^{1}H NMR (CCl_4) δ 0.84 (t, J = 7.2 Hz, 3 H), 1.24 (d, J = 6.2 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 2.46 (m, 1 H), 2.93 (d, J = 8.0 Hz, 1 H), 3.77 (q, J = 7.2 Hz, 2 H), 4.20 (q, J = 7.2 Hz, 2 H), 7.11 (s, 5 H). (Found: C, 69.42; H, 7.34. $C_{16}H_{20}O_4$ requires: C, 69.55; H, 7.29%.)

Reaction of styrene with diethyl dibromomalonate and Cu *in DMSO.* This reaction was carried out in order to clarify the structure of the inorganic products. Reaction of Cu powder (0.21 g, 3.3 mmol) with I_2 (0.005 g, 0.02 mmol) and diethyl dibromomalonate (1.03 g, 3.3 mmol) in the presence of styrene (0.17 g, 1.6 mmol) was carried out in 2.0 ml of DMSO at 75° for 2 hr. After the reaction, DMSO was eliminated by distillation *in vacuo*. Ether was added to the residue and the organic layer was separated by decantation. Distillation of the residue under a reduced pressure gave 1.24 g (3.3 mmol) of $CuBr_2 \cdot 2DMSO$, which was identified by comparison of its IR spectrum with that of an authentic sample.[14]

Competitive reactions. In a 2-necked flask equipped with a reflux condenser and a magnetic stirrer, 12.0 mmol of Cu powder was reacted with 0.2 mmol of I_2 in 4.0 ml of DMSO at room temp. After the brown colour of I_2 disappeared, 1.0 mmol of diethyl dibromomalonate and 4.0 mmol in all of two olefins were added and the mixture was allowed to react at 75° for 0.5 hr under stirring. After the reaction, the mixture was submitted for the analysis of the products. Yields of cyclopropane derivatives based on the olefins were less than 10% under the experimental conditions. The relative reactivity was calculated by the equation[19] $k_X/k_H = (P_X/P_H)(O_H/O_X)$, where P is the mole of product and O is that of reactant. The quasi-first order kinetics with respect reactants was ascertained in each reactions as are illustrated in Table 4.

Table 4. Competitive reaction of styrene and *p*-chlorostyrene with varied molar ratio

p-Chlorostyrene (mole fraction)	k_X/k_H
0.227	0.903
0.363	0.900
0.499	0.908
0.631	0.930
0.781	0.965

REFERENCES

[1a] B. W. Peace and D. S. Wulfman, *Synthesis* 137 (1973); [b] B. W. Peace, F. Carman and D. S. Wulfman, *Ibid.* 658 (1971).

[2a] D. S. Wulfman, *Tetrahedron* **32**, 1231 (1976); [b] D. S. Wulfman, R. S. McDaniel and B. W. Peace, *Ibid.* **32**, 1241 (1976); [c] D. S. Wulfman, B. W. Peace and R. S. McDaniel, *Ibid.* **32**, 1251 (1976); [d] D. S. Wulfman, B. G. McGibboney, E. K. Steffen, N. V. Thinh, R. S. McDaniel and B. W. Peace, *Ibid.* **32**, 1257 (1976).

[3] M. Barreau, M. Bost, M. Julia and J. Lallemand, *Tetrahedron Letters* 3465 (1975).

[4a] T. Saegusa, K. Yonezawa, I. Murase, T. Konoike, S. Tomita and Y. Ito, *J. Org. Chem.* **38**, 2319 (1973); [b] T. Saegusa, Y. Ito, K. Yonezawa, Y. Inubushi and S. Tomita, *J. Am. Chem. Soc.* **93**, 4049 (1971).

[5] P. Madsen, F. J. Preston and S. O. Lawesson, *Ark. Kemi* **28**, 395 (1967); *Chem. Abstr.* **69**, 10112b (1968).

[6] D. T. Warner and O. A. Moe, *J. Am. Chem. Soc.* **70**, 3470 (1948).

[7] R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.* 3610, 3616 (1952); 1799, 1803 (1953).

[8] T. Hiyama, S. Takehara, K. Kitatani and H. Nozaki, *Tetrahedron Letters* 3295 (1974).

[9] J. Gosselck, H. Ahlbrecht, F. Dost, H. Schenk and G. Schmidt, *Ibid.* 995 (1968).

[10a] N. Kawabata, M. Naka and S. Yamashita, *J. Am. Chem. Soc.* **98**, 2676 (1976); [b] N. Kawabata, I. Kamemura and M. Naka, *Ibid.* **101**, 2139 (1979).

[11] N. Kawabata, N. Yamagishi and S. Yamashita, *Bull. Chem. Soc. Japan* **50**, 466 (1977).

[12] N. Kawabata, T. Fujii, M. Naka, and S. Yamashita, *Ibid.* **50**, 1005 (1977).

[13] N. Kawabata, M. Tanimoto and S. Fujiwara, *Tetrahedron* **35**, 1919 (1979).

[14] D. W. Meek, D. K. Straub and R. S. Drago, *J. Am. Chem. Soc.* **82**, 6013 (1960).

[15] T. Wakui, Y. Otsuji and E. Imoto, *Nippon Kagaku Kaishi* 1686 (1974).

[16a] J. R. Johnson, *Organic Reactions* **1**, 210 (1042); [b] R. H. Wiley, N. R. Smith, R. T. Arnold, W. E. Parham and D. D. Davis, *Organic Syntheses*, Coll. Vol. IV. p. 731. Wiley, New York (1963).

[17a] C. G. Overberger and J. H. Saunders, *Organic Syntheses* Coll. Vol. III. p. 204. Wiley, New York (1955); [b] W. F. Gannon and H. O. House, *Ibid.* Coll. Vol. V. p. 294 (1973); [c] C. G. Overberger, J. H. Saunders, R. E. Allen and R. Gander, *Ibid.* Coll. Vol. III. p. 200 (1955); [d] J. L. Hartwell, *Ibid.* Coll. Vol. III. p. 185 (1955).

[18] B. B. Corson and W. L. Benson, *Ibid.* Coll. Vol. II. p. 273. Wiley, New York (1943).

[19] W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.* **80**, 5274 (1958).