Cyclopropanation of Dimethyl Fumarate and Maleate with *gem*-Dihalides Catalyzed by Co(0)- or Ni(0)-Complex and Zinc

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The reaction of bis(acetonitrile)bis(diethyl fumarate)cobalt(0) with dibromomethane gave diethyl *trans*-1,2-cyclopropanedicarboxylate in a 67% yield based on the cobalt complex. Dimethyl *cis*-1,2-cyclopropanedicarboxylate was obtained in a 52% yield from the reaction of dimethyl maleate with dibromomethane in the presence of acetonitrilebis(dimethyl maleate)nickel(0) accompanied by the formation of the *trans*-isomer in a 14% yield. The addition of zinc gave cyclopropanes in over 100% yields based on cobalt or nickel. 3-Methyl- and 3,3-dimethyl-1,2-cyclopropanedicarboxylic acid esters were produced by the reaction of dimethyl fumarate or maleate with 1,1-dibromoethane and 2,2-dibromopropane. The yield in the cobalt catalyst system decreases with an increase of substituents of *gem*-dibromides, while that in the nickel catalyst system does not vary appreciably. A small amount of dimethyl isopropenylsuccinate was formed as a by-product in the reaction of 2,2-dibromopropane. A mechanism is briefly discussed which involves metallacyclobutane as an intermediate.

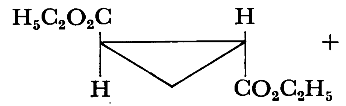
In the previous paper,[1] we reported the cyclopropane synthesis in which electron-deficient olefins were allowed to react with dibromomethane by the catalysis of Ni(0)-complexes and zinc. We have found that the best catalytic species are those coordinated by olefin and solvent molecules without additional ligands. Their candidates are bis(acetonitrile)bis(dialkyl fumarate)-cobalt(0) and acetonitrilebis(dialkyl maleate)nickel-(0). The treatment of the complexes with dibromomethane gave cyclopropane derivatives in the absence of Lewis acids or sodium iodide.[1b]

1,2-Cyclopropanedicarboxylic acid esters are produced from base-catalyzed reactions of α-substituted acrylic esters with α-halo esters,[2] or from reactions of α-halo esters with acrylic esters or of polyhalo compounds with α,β-unsaturated diesters by copper–isonitrile complexes.[3] The cyclopropanation of dialkyl fumarate and maleate with *gem*-dihalides in the presence of Co(0)- or Ni(0)-complex and zinc serves as a method of the synthesis of 3-alkyl-1,2-cyclopropanedicarboxylic acid esters. We have studied the effects of several variables on the yield and on the stereochemistry.

Results and Discussion

Cyclopropanation of Dimethyl Fumarate with Dihalomethanes Catalyzed by Bis(acetonitrile)bis(dimethyl fumarate)cobalt(0) (1) and Zinc. The stoichiometric reaction of bis-(acetonitrile)bis(diethyl fumarate)cobalt(0) with dibromomethane in acetonitrile gave diethyl *trans*-1,2-cyclopropanedicarboxylate in a 67% yield based on cobalt (Eq. 1). The cyclopropanation needs neither Lewis

$Co(E\text{-}H_5C_2O_2CCH{=}CHCO_2C_2H_5)_2(CH_3CN)_2 + CH_2Br_2$

$\longrightarrow$  $+ CoBr_2$ (1)

acids nor sodium iodide nor zinc, differing from that of monosubstituted olefins with electron-withdrawing groups.[1] As the data in Table 1 indicate, the addition of zinc increases the yield based on cobalt to over 100%. Zinc reduces cobalt bromide formed in Eq. 1 to regenerate a catalytic species in the presence of dimethyl fumarate (Eq. 2). A small amount of reduction product

$$CoBr_2 + \underset{H_3CO_2C}{\overset{H}{\ }}\!\!>C{=}C<\!\!\underset{H}{\overset{CO_2CH_3}{\ }} + Zn \xrightarrow{CH_3CN} \underset{\mathbf{1}}{Co(E\text{-}H_3CO_2CCH{=}CHCO_2CH_3)_2(CH_3CN)_2} + ZnBr_2 \quad (2)$$

was formed by the zinc bromide–zinc system.[4] The reduction is suppressed by the addition of sodium iodide which does not affect the yield of cyclopropane.

The cyclopropanation proceeded slowly as shown in Fig. 1. An increase in the amount of zinc results in an increase in the yield and reduction in the reaction time. Excess cobalt compound rather decreased the yield. When cobalt halides with water of crystallization were used, the yield decreased due to the production of a considerable amounts of succinate. Manganese can be substituted for zinc as a reductant although it takes a long time to prepare Co(0)-complex.

The best yield based on dibromomethane is obtained when a 1 : 1 fumarate : dibromomethane mole ratio is used. A slight excess of dibromethane is necessary for the reaction of fumarate to proceed to completion. The

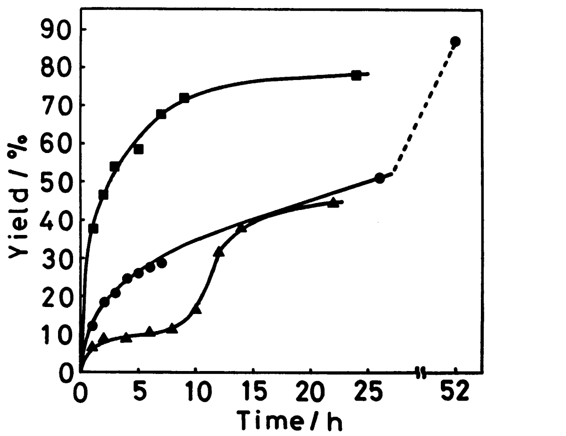


Fig. 1. Time dependence of the yields of cyclopropane derivatives in the reaction of dimethyl fumarate and maleate with dibromomethane catalyzed by the following systems. ●: (Fumarate) [Co] 1 mmol, NaI 2.5 mmol, Zn 15 mmol; ▲: (maleate) [Ni] 1 mmol, NaI 5 mmol, Zn 5 mmol; ■: (maleate) [Ni] 5 mmol, NaI 5 mmol, Zn 15 mmol.

Table 1. Cyclopropanation of dimethyl fumarate with dibromomethane catalyzed by Co(0)-complex and zinc[a)]

Catalytic system				CH_2Br_2 (mmol)	Time h	Conv.[b)] %	Yield[c)]/%	
X in CoX_2	(mmol)	NaI (mmol)	Zn (mmol)				Cyclopropane[d)]	Succinate
Cl	1	0	5	5	136	76	56	5.8
		0	8	6	63	98	64	3.4
		2.6	5	5	68	64	55	1.2
		2.5	8	5	91	100	76	1.4
		2.5	8	6	44	100	89	2.6
		5.0	8	6	44	97	85	1.6
		5.0	8	10	42	100	91	0.8
		2.5	30	6	3	91	83	7.7
		2.5	Mn 7	6	69	85	71	0.4
		LiI 3.0	5	5	117	69	48	tr
		KI 3.0	5	5	66	67	47	tr
	5	2.5	15	6	65	98	44	8.8
Br[e)]	1	2.5	8	6	47	91	58	13
I[f)]	1	2.5	8	6	65	86	55	14
Cl[g)]	1	2.5	8	6	114	77	15	0.6
Cl[h)]	1	2.5	5	5	89	94	57[i)] (8 : 92)	tr
Cl	1	0	8	CH_2Cl_2 15	280	100	8.0	80
		2.5	8	CH_2BrCl 6	70	94	91	6.4
		2.5	8	CH_2ClI 6	0.25	(100)[j)]	23	0
		2.5	8	CH_2I_2 5	52	100	32	7.6

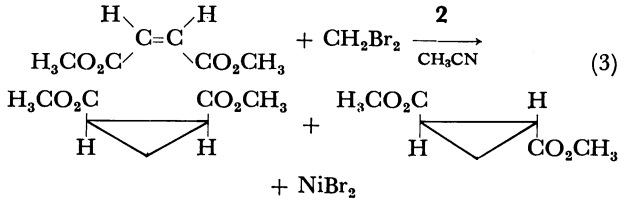
a) To the Co(0)-fumarate complex prepared *in situ* from CoX_2, dimethyl fumarate (5 mmol), NaI, and zinc in CH_3CN (10 ml) was added dibromomethane and the mixture was stirred at room temperature for a given period of time. b) Conversion of dimethyl fumarate. c) Yield based on dimethyl fumarate. d) Dimethyl *trans*-1,2-cyclopropanedicarboxylate. e) $CoBr_2 \cdot 6H_2O$. f) $CoI_2 \cdot 4H_2O$. g) THF(10 ml) was used as solvent. h) Dimethyl maleate (5 mmol) was used in the place of fumarate. i) Total yield of dimethyl *cis*- and *trans*-1,2-cyclopropanedicarboxylate. The number in parenthesis is the ratio of *cis* to *trans*. j) Conversion of chloroiodomethane.

yield in the reaction of dimethyl fumarate with dihalomethanes is in the order: $CH_2BrCl > CH_2Br_2 > CH_2I_2 > CH_2ClI \gg CH_2Cl_2$. This contrasts with the observation that some modifications are needed to use dibromomethane as a reactant in the Simmons-Smith reaction.[5)]

Lithium and potassium iodides are less effective than sodium iodide and bring about a decrease in the yield. Acetonitrile is superior to THF as a solvent because the former causes stabilization of the cobalt(0)-complex.

When dimethyl maleate was allowed to react with cobalt chloride in the presence of zinc, a red-brown solution was obtained in the same manner as for dimethyl fumarate. The treatment of the solution with dibromomethane gave a large amount of dimethyl *trans*-1,2-cyclopropanedicarboxylate and very little of the *cis*-isomer. The red-brown solution containing Co(0)-complex was decomposed in air and analysis of the residual substrate gave almost pure dimethyl fumarate. The isomerization of dimethyl maleate occurred neither in the presence of **1** nor in the zinc bromide–zinc system. It may be assumed that the active catalyst for the isomerization of maleate is a cobalt(I) species which is formed in the course of the reduction.

*Cyclopropanation of Dimethyl Maleate with Dihalomethanes Catalyzed by Acetonitrilebis(dimethyl maleate)nickel(0) (**2**) and Zinc.* Three-coordinate acetonitrilebis(olefin)-nickel(0) (olefin=dimethyl maleate and fumarate) is prepared from nickel bromide, an olefin, and zinc in acetonitrile.[6)] Maleate is not isomerized during the preparation of the Ni(0)-complex in contrast to the case of the cobalt complex. The reaction of dimethyl maleate with dibromomethane in the presence of **2** gave dimethyl *cis*-1,2-cyclopropanedicarboxylate in a 52% yield based



(3)

on nickel and the *trans*-isomer in a 14% yield (Eq. 3). Analysis of residual olefins shows a 90:10 dimethyl maleate: fumarate mole ratio. The addition of zinc increased the yield based on nickel in the same manner as in the cyclopropanation of the cobalt catalyst system (Table 2). Total yields of cyclopropane derivatives increased with an increase in the amounts of zinc and

TABLE 2. CYCLOPROPANATION OF DIMETHYL MALEATE AND FUMARATE WITH DIBROMOMETHANE CATALYZED BY Ni(0)-COMPLEX AND ZINC[a]

Catalytic system			CH_2Br_2	Time	Conv.[b]	Yield[b]/%	
Ni (mmol)	NaI (mmol)	Zn (mmol)	(mmol)	h	%	Cyclopropane[c] (*cis* : *trans*)	Succinate
Dimethyl maleate							
1	0	5	5	24	37	33 (81 : 19)	4.2
	5	5	5	24	42	31 (90 : 10)	0.4
	5	7	5	24	78	46 (83 : 17)	1.0
	5	10	5	24	94	56 (77 : 23)	2.0
	7	10	5	24	93	54 (70 : 30)	0.8
	5	13	5	24	100	63 (79 : 21)	1.8
	5	10	7	48	99	69 (75 : 25)	1.0
	5	Mn 10	5	24	100	64 (78 : 22)	2.0
1[d]	5	5	5	48	56	16 (92 : 8)	1.2
3	7	15	5	8	97	53 (88 : 12)	1.6
5	5	15	5	24	95	78 (91 : 9)	3.0
1	5	5	CH_2Cl_2 5	24	8	0	4.0
	5	5	CH_2BrCl 5	24	43	37 (94 : 6)	4.8
	5	10	CH_2BrCl 5	48	90	73 (86 : 14)	9.6
	5	5	CH_2ClI 5	24	37	17 (90 : 10)	tr
	5	5	CH_2I_2 5	24	46	22 (83 : 17)	tr
Dimethyl fumarate							
1	5	5	5	48	34	34 (0 : 100)	0
	5	10	5	25	74	50 (0 : 100)	0.2
5	5	15	5	40	89	59 (0 : 100)	1.9
5	5	15	10	41	99	78 (0 : 100)	0.8

a) To the *in situ* prepared Ni(0)-complex from $NiBr_2$, dimethyl maleate (5 mmol) or fumarate (5 mmol), NaI, and zinc in CH_3CN (10 ml) was added dibromomethane and the mixture was stirred at room temperature for a given period of time. b) Based on olefin. c) Dimethyl *cis*- and *trans*-1,2-cyclopropanedicarboxylate. d) THF (10 ml) was used as solvent.

nickel compounds. In the presence of a small amount of zinc, cyclopropanation started under the catalysis of Ni(0)-complex prepared beforehand, followed by a slow reaction step, until the fast reaction set in (Fig. 1). A large excess of zinc suppressed the slow step to make the whole reaction proceed smoothly.

Selectivity for the *cis*-isomer formation decreases slightly with an increase in the amount of zinc. Appreciable retention of stereochemistry in the maleate can be explained if isomerization of maleate rarely occurs and no isomerization of dimethyl *cis*-1,2-cyclopropanedicarboxylate takes place, unlike cyclopropanation by the copper–isonitrile system.[3b] No isomerization of dimethyl maleate occurred in the presence of **2**. It may be assumed, as in the reaction with cobalt catalyst system, that the isomerization catalyst is a nickel(I) species. Bromo(dimethyl maleate)nickel(I) is inert to the isomerization.[7] Nickel(I) species responsible for the isomerization of maleate are presumed to be bromobis(dimethyl maleate)nickel(I) and bis(dimethylmaleate)-nickel(I) tribromozincate on the assumption that dimerization of terminal olefins is catalyzed by (π-C_3H_5)-NiBr and (π-C_3H_5)$Ni(AlCl_4)$.[8]

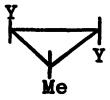
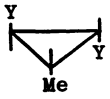
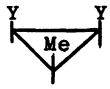
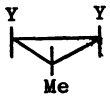
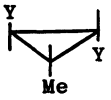
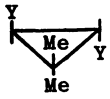
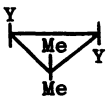
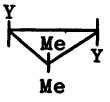
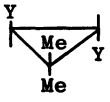
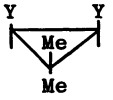
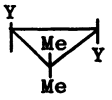
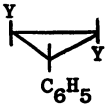
A concomitant formation of the *trans*-isomer is originated from the cyclopropanation of fumarate. The initial rate for the formation of dimethyl *cis*-1,2-cyclopropanedicarboxylate from **2** and dibromomethane was 2.8×10^{-3} mol^{-1} min^{-1}, while that for the formation of the *trans*-isomer from acetonitrilebis(dimethyl fumarate)-nickel(0) (**3**) and dibromomethane was 1.4×10^{-4} mol l^{-1} min^{-1}. However, the cyclopropanation of the mixture of equal moles of maleate and fumarate gave the *trans*-isomer in a six-fold ratio to the *cis*-isomer, indicating that the coordinating strength of fumarate is greater than that of maleate. Dimethyl fumarate which is once formed inhibits the cyclopropanation of dimethyl maleate.

Manganese can be substituted for zinc as a reductant. The order of effectiveness of dihalomethanes is the same as that in the cyclopropanation of dimethyl fumarate by the cobalt catalyst system.

The cyclopropanation of dimethyl fumarate gave the corresponding cyclopropane derivative in yields similar to those in the reaction of dimethyl maleate. The cobalt catalyst system for the cyclopropanation of dimethyl fumarate is superior to the nickel one although it takes a longer reaction time.

Cyclopropanation of Dimethyl Fumarate and Maleate with gem-Dihalides. The cyclopropanation of dimethyl fumarate and maleate with *gem*-dihaloalkanes gave

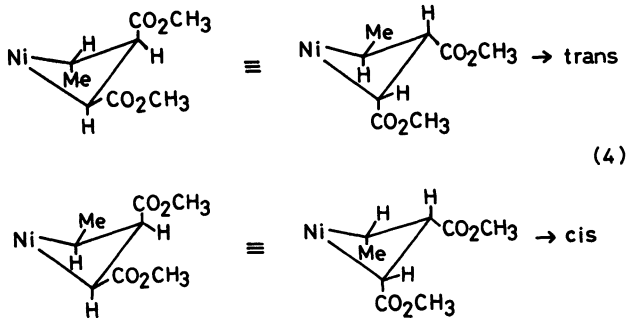
TABLE 3. CYCLOPROPANATION OF DIMETHYL FUMARATE AND MALEATE WITH *gem*-DIHALIDES CATALYZED BY Co(0)- OR Ni(0)-COMPLEX AND ZINC[a)]

gem-Dihalide (mmol)	Catalyst	(mmol)	Olefin	Time h	Yield of product[b)] %	
CH_3CHBr_2 6	Co[c,d)]	1	Fumarate	47		68 (3.1, —)
5	Ni	5	Fumarate	27		58 (2.4, —)
5	Ni	5	Maleate	27		7
						40 (5.2, —)
						23
$(CH_3)_2CCl_2$ 6	Co[c)]	5	Fumarate	64		22 (36, 3.4)
$(CH_3)_2CBr_2$ 5	Co[c,d)]	5	Fumarate	48		20 (28, 1.3)
$(CH_3)_2CBr_2$ 5	Co[c,d,e)]	5	Fumarate	70		10 (35, 36)
5	Ni[d)]	5	Fumarate	27		44 (3.4,3.0)
5	Ni[d)]	5	Maleate	27		34 (10, 2.6)
						5
CH_5CHCl_2 5	Co	1	Fumarate	144		19

a) To the Co(0)- or Ni(0)-complex prepared *in situ* from $CoCl_2$ or $NiBr_2$, an olefin (5 mmol), NaI (5 mmol), and zinc (8 mmol) in CH_3CN (10 ml) was added *gem*-dihalide and the mixture was stirred at room temperature for a given period of time. b) Yield based on olefin. $Y=CO_2CH_3$. The numbers in parentheses are yields of dimethyl succinate and isopropenyl succinate. c) NaI (2.5 mmol). d) Zn (15 mmol). e) H_2O (0.1 ml) was added.

dimethyl 3-substituted *trans*- and *cis*-1,2-cyclopropanedicarboxylates under the catalysis of Co(0)- or Ni(0)-complex–zinc system (Table 3). The yield decreases with an increase of substituents of *gem*-dihaloalkanes in the cobalt system. A 1:1 cobalt:dimethyl fumarate mole ratio gave the best yield in the cyclopropanation with 2,2-dibromopropane. There is little difference in yields between the reactions of 2,2-dichloro- and 2,2-dibromopropane.

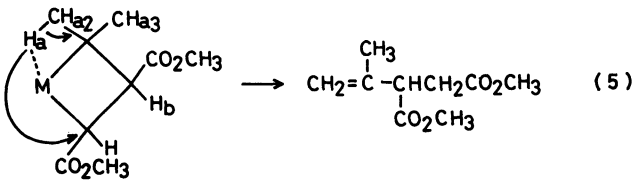
The reaction of dimethyl maleate with 1,1-dibromoethane catalyzed by the nickel catalyst system gave cyclopropane derivatives in a 70% yield: the ratio of *cis*-dicarboxylate to the *trans*-isomer is 67:33 which is somewhat less than that produced in the reaction with dibromomethane. The ratio of the *cis*-methyl isomer to the *trans*-isomer in *cis*-dicarboxylates is 15:85. It has been proposed that cyclopropanation proceeds *via* metallacyclobutane as an intermediate.[1] If the reductive elimination of a nickelacyclobutane intermediate takes place with retention of configuration, the configuration of the nickelacyclobutane would be that in which the methyl group is predominantly *trans* to both methoxy carbonyl groups by 1,2- and 1,3-steric repulsion. This leads to the *trans*-isomer (Eq. 4). In the reaction of



(4)

dimethyl maleate with 2,2-dibromopropane, dimethyl 3,3-dimethyl-1,2-cyclopropanedicarboxylate (*cis*:*trans*=87:13) was obtained in a 39% yield.

Dimethyl isopropenylsuccinate was concomitantly produced in the reaction of dimethyl fumarate and maleate with 2,2-dibromopropane in both cobalt and nickel systems. Two mechanisms have been proposed for the olefin formation from platinacyclobutanes which involves splitting of α-C–H bond[9] and that of β-C–H bond.[10] The postulated intermediate has seven hydrogen atoms bonded to β-carbons and one hydrogen atom bonded to α-carbons (Eq. 5). If dimethyl isopropenylsuccinate is produced from metallacyclobutane,[11] its formation must be originated from splitting of β-C–H_a bond in methyl groups not of β-C–H_b bond in the methine group. The hydrogen of a methyl group is more easily split off than that of the methine group in platinacyclobutane.[9a,b] The addition of water promotes



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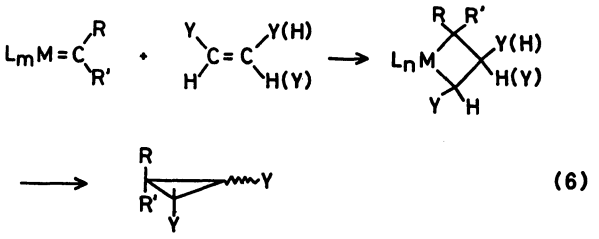
the olefin production in the reaction of dimethyl fumarate with 2,2-dibromopropane catalyzed by the cobalt catalyst system. Photolysis of platinacyclobutane gives mainly propylene in solvents of low dielectric constant (*e.g.* CH_2Cl_2), but mainly cyclopropane in solvents of high dielectric constant (*e.g.* CH_3CN, Me_2SO):[12] ionization of the platinacyclobutane precedes the formation of cyclopropane. Water, which has a high dielectric constant, should favor the formation of the ionized species. However, the effect of the solvent on the reaction of fumarate with 2,2-dibromopropane is opposite to that on the reaction of platinacyclobutane.

Mechanism. We have proposed a mechanism which involves metallacyclobutane as an intermediate. The cyclopropanation of electron-deficient monosubstituted olefins needs Lewis acids or sodium iodide and zinc as promotors in most cases.[1] Both components are not necessary for the cyclopropanation of dimethyl fumarate and maleate with *gem*-dihalides catalyzed by cobalt(0)- or Ni(0)-complex. Only the cyclopropane derivative of dimethyl fumarate was obtained in the competitive reaction between dimethyl fumarate and methyl acrylate, indicating that the coordinating strength of the former is greater than that of the latter. It may be concluded that the cyclopropanation of olefins coordinated strongly to the metal center does not need promotors such as Lewis acids nor sodium iodide. We added sodium iodide to prevent reduction of olefins by the zinc bromide–zinc system.[4]

Acetonitrile is the most suitable solvent among several examined. It is required for stabilization of Co(0)- and Ni(0)-olefin complexes. Tetrahydrofuran is preferable to acetonitrile for the cyclopropanation of monosubstituted olefins[1] in which Lewis acids or sodium iodide in combination with tetrahydrofuran may promote the catalysis of the nickel complex catalyst.

Metal–carbene complexes are generated by the reaction of Co(0)- or Ni(0)-complex with *gem*-dihalides.[13] Cobalta- and nickelacyclobutanes are produced from the reaction of metal–carbene complexes with olefins in a similar manner as titana- and tungstenacyclobutanes.[14] Reductive elimination of metallacyclobutanes gives exclusively cyclopropane derivatives unless R=R′=CH_3. It is not known at present whether too many hydrogens bonded to β-carbons facilitate their splitting, or whether the metallacyclobutane is distorted due to the bulkiness of two alkyl groups to accelerate access of hydrogens of β-carbons to the active center.



(6)

M = Co, Ni ; R, R' = H, CH_3, C_6H_5 ; Y = CO_2CH_3 .

Experimental

All operations were done under an atmosphere of nitrogen. Chloroiodomethane was prepared by treating dichloromethane with sodium iodide in *N,N*-dimethylformamide.[15] Other chemicals were analytical grade commercial materials and used without further purification. Bis(acetonitrile)bis(diethyl fumarate)cobalt(0) was prepared from the reaction of cobalt chloride with diethyl fumarate in the presence of zinc in acetonitrile according to the method of Agnes *et al.*[16] Acetonitrilebis(dimethyl maleate)nickel(0) (**2**) was prepared according to the literature method.[6] ^{1}H NMR spectra were measured on a JEOL PM-60 spectrometer and ^{13}C NMR spectra on a JEOL FX-100 spectrometer. GLC analysis and preparative purification were performed on a Shimadzu GC-6A gas chromatograph equipped with FID and 3 mm×4 m (PEG 20M 20% on Celite 545) and 5 mm×3 m (silicon SE-30 20% on Celite 545) columns were used.

Reaction of Bis(acetonitrile)bis(diethyl fumarate)cobalt(0) with Dibromomethane. To a solution of bis(acetonitrile)bis(diethyl fumarate)cobalt(0) (1 mmol) in acetonitrile (5 ml) was added dibromomethane (2 mmol) and the reaction mixture was stirred for 7 h. Diethyl *trans*-1,2-cyclopropanedicarboxylate was obtained in a 67% yield based on cobalt.

*Reaction of **2** with Dibromomethane.* To a solution of **2** (1 mmol) in acetonitrile (10 ml) were added dimethyl maleate (3 mmol) and dibromomethane (5 mmol) and the reaction mixture was stirred for 24 h. Dimethyl *cis*-1,2-cyclopropanedicarboxylate and the *trans*-isomer were obtained in 52 and 14% yields based on nickel, respectively.

General Procedures for the Reaction of Dimethyl Fumarate or Maleate with gem*-Dihalides Catalyzed by* in Situ *Prepared Co(0)- or Ni(0)-complex and Zinc.* A 100-ml two-necked flask was charged with anhydrous cobalt chloride (1 mmol) or nickel bromide (1 mmol), sodium iodide, and zinc powder (8 mmol). Acetonitrile (10 ml) was introduced and the mixture was stirred magnetically for 20—30 min at room temperature to form the red-brown catalyst solution. *gem*-Dihalide (5 mmol) was then added and reacted at room temperature for the specified time.

The reactions between dimethyl fumarate or maleate and *gem*-dihalides are summarized in Tables 1, 2, and 3. Spectral and elemental analyses of some cyclopropane derivatives are given below.

Dimethyl c-*3-Methyl*-r-*1*, t-*2-Cyclopropanedicarboxylate*: ^{1}H NMR ($CDCl_3$) δ=1.24 (d, 3H), 1.6—2.5 (m, 3H), 3.68 (s, 6H). ^{13}C NMR ($CDCl_3$) δ=11.2 (HC–$\underline{C}H_3$), 23.8 (H$\underline{C}$–CH_3), 27.9 (*r*-1-$\underline{C}HCO_2CH_3$), 28.3 (*t*-2-$\underline{C}HCO_2CH_3$), 51.8 (*r*-1-$CO_2\underline{C}H_3$), 52.0 (*t*-2-$CO_2\underline{C}H_3$), 170.4 (*r*-1-$\underline{C}O_2CH_3$), 172.3 (*t*-2-$\underline{C}O_2CH_3$). Found: C, 55.94; H, 7.27%. Calcd for $C_8H_{12}O_4$: C, 55.80, H, 7.02%.

Dimethyl c-*3-Methyl*-r-*1*, c-*2-Cyclopropanedicarboxylate*: ^{13}C NMR ($CDCl_3$) δ=8.5 (CH$\underline{C}H_3$), 19.0 ($\underline{C}HCH_3$), 24.1 ($\underline{C}HCO_2CH_3$), 51.7 ($CO_2\underline{C}H_3$), 169.5 ($\underline{C}O_2CH_3$). Found (mixture of dimethyl *c*-3- and *t*-3-methyl-*r*-1,-*c*-2-cyclopropanedicarboxylate): C, 55.50; H, 7.10%. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.02%.

Dimethyl t-*3-Methyl*-r-*1*, c-*2-Cyclopropanedicarboxylate*: ^{13}C NMR ($CDCl_3$) δ=16.8 (CH$\underline{C}H_3$), 20.6 ($\underline{C}HCH_3$), 29.2 ($\underline{C}HCO_2CH_3$), 52.0 ($CO_2\underline{C}H_3$), 170.2 ($\underline{C}O_2CH_3$).

Dimethyl trans-*3,3-Dimethyl-1,2-Cyclopropanedicarboxylate*: ^{1}H NMR ($CDCl_3$) δ=1.29 (s, 6H), 2.21 (s, 2H), 3.65 (s, 6H). ^{13}C NMR ($CDCl_3$) δ=20.4 (($\underline{C}H_3)_2C$), 30.4 ($(CH_3)_2\underline{C}$), 33.6 ($\underline{C}HCO_2CH_3$), 51.8 ($CO_2\underline{C}H_3$), 170.8 ($\underline{C}O_2CH_3$).

Dimethyl cis-*3,3-Dimethyl-1,2-Cyclopropanedicarboxylate*: ^{1}H NMR ($CDCl_3$) δ=1.21 (s, 3H), 1.39 (s, 3H), 1.87 (s, 2H), 3.64 (s, 6H). ^{13}C NMR ($CDCl_3$) δ=15.5 (*cis*-$\underline{C}H_3$), 26.0 (($CH_3)_2$-$\underline{C}$), 27.9 (*trans*-$\underline{C}H_3$), 31.8 ($\underline{C}HCO_2CH_3$), 51.6 ($CO_2\underline{C}H_3$), 169.4 ($\underline{C}O_2CH_3$).

Dimethyl c-*3-Phenyl*-r-*1*, t-*2-Cyclopropanedicarboxylate*: ^{1}H NMR ($CDCl_3$) δ=2.38—3.11 (m, 3H), 3.43 (s, 3H), 3.71 (s, 3H), 7.16 (s, br, 5H). ^{13}C NMR ($CDCl_3$) δ=25.8 (*cis*-$\underline{C}HCO_2CH_3$), 29.8 (*trans*-$\underline{C}HCO_2CH_3$), 32.8 ($\underline{C}HC_6H_5$), 51.8 (*cis*-$CO_2\underline{C}H_3$), 52.3 (*trans*-$CO_2\underline{C}H_3$), 168.7 (*cis*-$\underline{C}O_2CH_3$), 171.9 (*trans*-$\underline{C}O_2CH_3$). Found: C, 66.76; H, 6.15%. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02%.

Dimethyl Isopropenylsuccinate: ^{1}H NMR ($CDCl_3$) δ=1.76 (s, 3H), 2.36—2.88 (m, 3H), 3.64 (s, 3H), 3.68 (s, 3H), 4.86 (s, 2H). ^{13}C NMR ($CDCl_3$) δ=20.7 (CH_3), 35.1 (CH_2), 48.5 (CH), 51.8 ($CH_2CO_2\underline{C}H_3$), 52.2 ($CHCO_2\underline{C}H_3$), 114.3 (H_2C=), 141.3 (=$\underline{C}CH_3$), 172.1 ($CH_2\underline{C}O_2CH_3$), 172.9 ($CH\underline{C}O_2CH_3$).

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References

1) a) H. Kanai and N. Hiraki, *Chem. Lett.*, **1979**, 761; b) H. Kanai, N. Hiraki, and S. Iida, *Bull. Chem. Soc. Jpn.*, **56**, 1025 (1983).

2) a) L. L. McCoy, *J. Am. Chem. Soc.*, **82**, 6416 (1960); b) *J. Org. Chem.*, **25**, 2078 (1960); c) *J. Am. Chem. Soc.*, **84**, 2246 (1962).

3) a) T. Saegusa, K. Yonezawa, and Y. Ito, *Synth. Commun.*, **2**, 431 (1972); b) T. Saegusa, K. Yonezawa, I. Murase, T. Konoike, S. Tomita, and Y. Ito, *J. Org. Chem.*, **38**, 2319 (1973); c) Y. Ito, K. Yonezawa, and T. Saegusa, *ibid.*, **39**, 1763 (1974); d) Y. Ito, K. Yonezawa, and T. Saegusa, *ibid.*, **39**, 2769 (1974).

4) F. Toda and K. Iida, *Chem. Lett.*, **1976**, 695.

5) a) E. Legoff, *J. Org. Chem.*, **29**, 2048 (1964); b) R. D. Rieke, P. Tsu-Jung Li, T. P. Burns, and S. T. Uhm, *ibid.*, **46**, 4323 (1981).

6) F. Guerrieri and G. Salerno, *J. Organomet. Chem.*, **114**, 339 (1976).

7) M. Dubini and F. Montino, *Chim. Ind. (Milan)*, **49**, 1283 (1967).

8) a) B. Bogdanovic, B. Henc, H.-G. Karmann, H.-G. Nussel, D. Walter, and G. Wilke, *Ind. Eng. Chem.*, **62**, 34 (1970); b) B. Bogdanovic and G. Wilke, *Brennstoff-Chem.*, **49**, 323 (1968).

9) S. S. M. Ling and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, **1982**, 412.

10) a) T. H. Johnson and E. C. Hefty, *J. Org. Chem.*, **44**, 4896 (1979); b) T. H. Johnson and S.-S. Cheng, *J. Am. Chem. Soc.*, **101**, 5277 (1979); c) T. H. Johnson and E. C. Hefty, *J. Organomet. Chem.*, **212**, 23 (1981).

11) It can not be considered that isopropenylsuccinate is produced from free carbene insertion into fumarate and maleate because there is no other olefinic product than isopropenylsuccinate.

12) D. C. L. Perkins, R. J. Puddephatt, and C. F. H. Tipper, *J. Organomet. Chem.*, **186**, 419 (1980).

13) S. Takahashi, Y. Suzuki, K. Sonogashira, and H. Hagihara, *Chem. Lett.*, **1976**, 515.

14) a) P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, **98**, 6057 (1976); b) F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *ibid.*, **100**, 3611 (1978).

15) S. Miyano and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **44**, 2864 (1971).

16) G. Agnes, I. W. Bassi, C. Benedicento, R. Intrito, M. Caleaterra, and C. Santini, *J. Organomet. Chem.*, **129**, 401 (1977).