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Iron Pentacarbonyl-Mediated Stereoselective Carbonylation of *trans*- and *cis*-Monobromocyclopropanes

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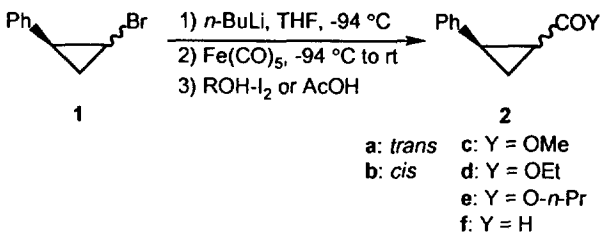
The cyclopropane moiety is present in a large number of natural products and pharmaceutically interesting compounds. *gem*-Dihalocyclopropanes which can be readily prepared from the addition reaction of dihalocarbene with olefins are one of the most versatile starting materials for the synthesis of the substituted cyclopropanes.[1] Reductive carbonylation of *gem*-dibromocyclopropanes is the most valuable method for the synthesis of cyclopropanecarboxylic acid derivatives. Although $Ni(CO)_4$,[2~4] $Fe(CO)_5$,[5] and $CoCl_2 \cdot 6H_2O/Ni(CN)_2 \cdot 4H_2O$[6] (phase transfer conditions, PTC) have been utilized for the conversion of the *gem*-dibromocyclopropanes to the cyclopropanecarboxylic acid derivatives, these did not afford desirable yield and stereoselectivity. On the other hand, we reported recently that tetracarbonylhydridoferrate, $HFe(CO)_4^-$, generated by the reaction of $Fe(CO)_5$ with alkaline medium worked as an efficient reducing agent for the mono-dehalogenation of *gem*-dihalocyclopropanes.[7] The isolation of its stereoisomers led us to look for the stereoselective synthesis of cyclopropanecarboxylic acid derivatives using the monobromocyclopropanes. Herein we report the $Fe(CO)_5$-mediated diastereoselective carbonylation of the *trans*- and *cis*-1-bromo-2-phenylcyclopropanes.



Scheme 1.

Results and Discussion

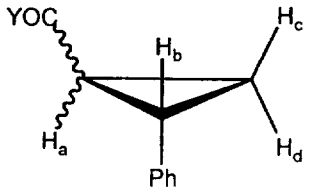
Although many transition metal salts have been utilized for the carbonylation of *gem*-dihalocyclopropanes to give the cyclopropanecarboxylic acid derivatives, the reactions using monohalocyclopropanes have been scarcely explored. Several attempts for the carbonylation reaction of the bromocyclopropane **1** were not successful under the reported systems.[2~6] However, halogen-lithium exchange was essential for the carbonylation of **1**. Treatment of *trans*-1-bromo-2-phenylcyclopropane (**1a**) (1 mmol) with *n*-BuLi (1.2 equiv) followed by successive addition of iron pentacarbonyl (1.2 equiv) in tetrahydrofuran at −94 ℃ and methanol-I_2 afforded *trans*-1-methoxycarbonyl-2-phenylcyclopropane (**2ac**) stereospecifically in 86% yield (Scheme 1). When the reaction using other alcohols such as ethyl and *n*-propyl alcohols was also applied to this carbonylation under the identical reaction conditions, the corresponding 1-alkoxycarbonyl-2-phenylcyclopropanes were obtained stereospecifically in high yields. When this lithiation-$Fe(CO)_5$-induced alkoxycarbonylation also proceeded with *cis*-1-bromo-2-phenylcyclopropane (**1b**) under the similar reaction conditions, the stereochemistry of the carbonylated cyclopropanes was always *cis*. The addition of acetic acid to the reaction mixture in place of alcohol-I_2 afforded the cyclopropanal stereospecifically, which was oxidized spontaneously to the cyclopropanecarboxylic acid under air. Typical results are summarized in Table 1. The multiplicities and coupling constants of the carbonylated cyclopropanes are shown in Experimental Section.

Plausible reaction pathway for the carbonylation of *trans*-

Table 1. $Fe(CO)_5$-Mediated Carbonylation of *trans*- and *cis*-1-Bromo-2-phenylcyclopropanes

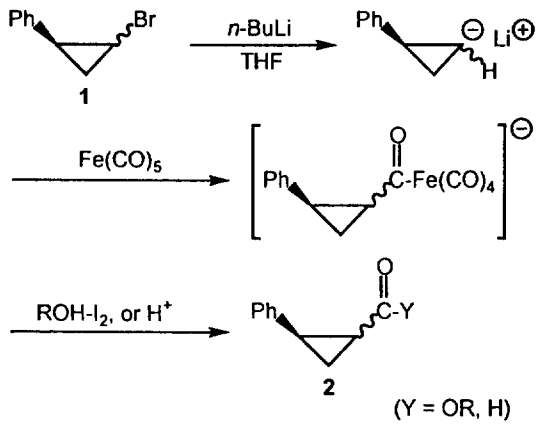
Run	Bromocyclo propane **1**	ROH or AcOH	Product	Yield (%)[a]
1	**1a**	MeOH	**2ac**	86
2	**1a**	EtOH	**2ad**	70
3	**1a**	*n*-PrOH	**2ae**	84
4	**1b**	MeOH	**2bc**	70
5	**1b**	EtOH	**2bd**	70
6	**1b**	*n*-PrOH	**2be**	86
7	**1b**	AcOH	**2bf**	61

[a]Isolated yield.



2

Figure 1.



Scheme 2.

and *cis*-1-bromo-2-phenylcyclopropane (**1a** and **1b**) is shown in Scheme 2. The bromide-lithium exchange reaction of the bromocyclopropanes with *n*-butyl lithium gives a cyclopropyl lithium which reacts with iron pentacarbonyl to produce lithium acyltetracarbonylferrate. This is followed by oxidative cleavage of the ferrate with iodine or acetic acid to give the cyclopropanecarboxylic acid derivatives **2**. Considering the stereochemistry of the products, all steps described above proceed with retention.

Experimental Section

General Procedure. Commercially available organic and inorganic compounds were used without further purification except for THF, which was distilled by known method. ^1H NMR (300 MHz) spectra were recorded on a Varian Unity Plus 300 spectrometer using Me_4Si as an internal standard in $CDCl_3$. Chemical shifts are reported in δ units downfield from Me4Si. IR spectra were recorded on a Mattson Galaxy 6030 (FT) infrared spectrophotometer. Mass spectra were obtained on a Shimadzu QP-1000 spectrometer. The isolation of pure product was carried out with thin-layer chromatography (silica gel 60 GF_{254}, Merck).

Procedure for the $Fe(CO)_5$-Mediated Carbonylation of *trans(cis)*-1-Bromo-2-phenylcyclopropane. To a dried THF solution (10 mL) of *trans(cis)*-1-bromo-2-phenylcyclopropane (0.20 g, 1 mmol) was added *n*-BuLi (1.2 mmol, 1.6 M in hexane) under argon. After the reaction mixture was stirred for 15 min at −94 ℃, $Fe(CO)_5$ (0.22 g, 1.2 mmol) was added by syringe. The mixture was stirred for 1 h at −94 ℃ and elevated to rt. Alcohol-I_2 (5 mL) was added to the mixture and then stirred for 24 h under air. The reaction mixture was diluted with diethyl ether (50 mL), washed with aqueous sodium thiosulfate solution (3×20 mL) to remove excess iodine, and washed with water (2×20 mL). The organic phase was dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure left a liquid which was separated by TLC using ethyl acetate/hexane (1/5) mixture as an eluent to give the corresponding diastereoselective cyclopropanecarboxylic acid esters.

Similar treatment of the lithium acylferrate with acetic acid (5 mL) in place of alcohol-I_2 also afforded the cyclopropanal, which was oxidized spontaneously to the cyclopropanecarboxylic acid under air. Cyclopropanecarboxylic acid derivatives prepared by the above procedure were fully characterized spectroscopically as shown below.

***trans*-1-Methoxycarbonyl-2-phenylcyclopropane (2ac).** 86% yield; a yellow oil; IR (neat) 1726 (C=O) cm^{-1}; ^1H NMR δ 1.37 (ddd, J_{da}=6.6, J_{db}=9.3, J_{dc}=4.6 Hz, $1H_d$), 1.65 (ddd, J_{ca}=9.0, J_{cb}=4.4, J_{cd}=4.6 Hz, $1H_c$), 1.96 (ddd, J_{ba}=4.2, J_{bc}=4.4, J_{bd}=9.3 Hz, $1H_b$), 2.57 (ddd, J_{ab}=4.2, J_{ac}=9.0, J_{ad}=6.6 Hz, $1H_a$), 3.76 (s, 3H), 7.11-7.14 (m, 2H, Ar), 7.24-7.39 (m, 3H); MS m/z (relative intensity) 176 (M^+, 39), 145 (19), 144 (35), 121 (36), 117 (100), 91 (32).

***trans*-1-Ethoxycarbonyl-2-phenylcyclopropane (2ad).** 70% yield; a yellow oil; IR (neat) 1725 (C=O) cm^{-1}; ^1H NMR δ 1.32 (t, J=7.1 Hz, 3H), 1.33 (ddd, J_{da}=6.5, J_{db}=8.5, J_{dc}=4.7 Hz, $1H_d$), 1.64 (ddd, J_{ca}=9.2, J_{cb}=5.4, J_{cd}=4.7 Hz, $1H_c$), 1.94 (ddd, J_{ba}=4.2, J_{bc}=5.4, J_{bd}=8.5 Hz, $1H_b$), 2.56 (ddd, J_{ab}=4.2, J_{ac}=9.2, J_{ad}=6.5 Hz, $1H_a$), 4.21 (q, J=7.2 Hz, 2H), 7.11-7.13 (m, 2H, Ar), 7.14-7.34 (m, 3H); MS m/z (relative intensity) 190 (M^+, 31), 145 (19), 144 (21), 135 (19), 117 (100), 91 (33).

***trans*-1-*n*-Propoxycarbonyl-2-phenylcyclopropane (2ae).** 84% yield; a yellow oil; IR (neat) 1725 (C=O) cm^{-1}; ^1H NMR δ 0.98 (t, J=7.4, 3H), 1.35 (ddd, J_{da}=6.4, J_{db}=8.4, J_{dc}=4.5 Hz, $1H_d$), 1.64 (ddd, J_{ca}=9.3, J_{cb}= 5.1, J_{cd}=4.5 Hz, $1H_c$), 1.73 (m, 2H), 1.95 (ddd, J_{ba}=4.2, J_{bc}=5.1, J_{bd}=8.4 Hz, $1H_b$), 2.59 (ddd, J_{ab}=4.2, J_{ac}=9.3, J_{ad}=6.4 Hz, $1H_a$), 4.08 (t, J=6.7 Hz, 2H), 7.10-7.14 (m, 2H, Ar), 7.15-7.35 (m, 3H); MS m/z (relative intensity) 204 (M^+, 10), 145 (18), 144 (17), 118 (11), 117 (100), 91 (23).

***cis*-1-Methoxycarbonyl-2-phenylcyclopropane (2bc).** 70% yield; a yellow oil; IR (neat) 1732 (C=O) cm^{-1}; ^1H NMR δ 1.39 (ddd, J_{ca}=5.6, J_{cb}=8.4, J_{cd}=6.5 Hz, $1H_c$), 1.76 (ddd, J_{da}=8.8, J_{db}=8.4, J_{dc}=6.5 Hz, $1H_d$), 2.16 (ddd, J_{ba}=8.4, J_{bc}=8.4, J_{bd}=8.4 Hz, $1H_b$), 2.63 (ddd, J_{ab}=8.4, J_{ac}=5.6, J_{ad}=8.8 Hz, $1H_a$), 3.47 (s, 3H), 7.26-7.31 (m, 5H); MS m/z (relative intensity) 176 (M^+, 33), 145 (20), 144 (37), 121 (36), 117 (100),

91 (30).

cis-1-Ethoxycarbonyl-2-phenylcyclopropane (2bd). 70% yield; a yellow oil; IR (neat) 1728 (C=O) cm^{-1}; ^1H NMR δ 1.00-1.20 (m, 3H), 1.36 (ddd, J_{ca}=5.2, J_{cb}=8.3, J_{cd}=6.3 Hz, $1H_c$), 1.76 (ddd, J_{da}=8.2, J_{db}=8.0, J_{dc}=6.3 Hz, $1H_d$), 2.16 (ddd, J_{ba}=8.0, J_{bc}=8.3, J_{bd}=8.0 Hz, $1H_b$), 2.62 (ddd, J_{ab}=8.0, J_{ac}=5.2, J_{ad}=8.2 Hz, $1H_a$), 3.90-3.92 (m, 2H), 7.29-7.31 (m, 5H); MS m/z (relative intensity) 190 (M^+, 27), 145 (24), 144 (23), 135 (21), 117 (100), 91 (24).

cis-1-n-Propoxycarbonyl-2-phenylcyclopropane (2be). 86% yield; a yellow oil; IR (neat) 1729 (C=O) cm^{-1}; ^1H NMR δ 0.78-0.83 (m, 3H), 1.30-1.33 (m, 2H), 1.37 (ddd, J_{ca}=8.4, J_{cb}=8.6, J_{cd}=6.2 Hz, $1H_c$), 1.76 (ddd, J_{da}=8.4, J_{db}=8.2, J_{dc}=6.2 Hz, $1H_d$), 2.16 (ddd, J_{ba}=8.4, J_{bc}=8.6, J_{bd}=8.2 Hz, 1 H_b), 2.62 (ddd, J_{ab}=8.4, J_{ac}=8.4, J_{ad}=8.4 Hz, $1H_a$), 3.80-3.82 (m, 2H), 7.23-7.32 (m, 5H); MS m/z (relative intensity) 204 (M^+, 3), 145 (15), 144 (12), 118 (11), 117 (100), 91 (28).

cis-2-Phenyl-1-cyclopropanal (2bf). 61% yield; a yellow oil; IR (neat) 1702 (C=O) cm^{-1}; ^1H NMR δ 1.60 (ddd, J_{ac}=8.4, J_{bc}=8.4, J_{cd}=5.7 Hz, $1H_c$), 1.90 (ddd, J_{da}=8.4, J_{db}=8.5, J_{dc}=5.7 Hz, $1H_d$), 2.16 (ddd, J_{ba}=8.4, J_{bc}=8.4, J_{bd}=8.5 Hz, 1 H_b), 2.85 (ddd, J_{ab}=8.4, J_{ac}=8.4, J_{ad}=8.4 Hz, $1H_a$), 7.24-7.39 (m, 5H), 8,69 (d, J=6.6 Hz, 1H); MS m/z (relative intensity) 146 (M^+, 12), 118 (10), 117 (100), 91 (21).

trans-2-Phenyl-1-cyclopropanecarboxylic acid. 50 % yield; a white solid; mp 87-88 ℃; IR (KBr) 1682 (C=O), 3758 (OH) cm^{-1}; ^1H NMR δ 1.45 (ddd, J_{da}=6.5, J_{db}=8.2, J_{dc}= 4.5 Hz, $1H_d$), 1.71 (ddd, J_{ca}=9.2, J_{cb}=5.0, J_{cd}=4.5 Hz, $1H_c$), 1.94 (ddd, J_{ba}=4.0, J_{bc}=5.0, J_{bd}=8.2 Hz, $1H_b$), 2.05 (ddd, J_{ab}= 4.0, J_{ac}=9.2, J_{ad}=6.5 Hz, $1H_a$), 7.12-7.16 (m, 2H, Ar), 7.24-7.36 (m, 3H); MS m/z (relative intensity) 162 (M^+, 2), 144 (9), 118 (11), 117 (100), 91 (34).

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Cyclic Voltammetric Study of Ferricyanide Layer Adsorbed on Gold Electrode in Sulfuric Acid Medium

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Adsorption of monolayer and subsequent formation of multilayer or thin film on the surface of various substrates in self-assembled or controlled manner have been of great concern in many fields of chemistry.[1] Electrochemical behaviors of adsorbed species by strong spontaneous bounding to the electrode surfaces had been studied theoretically[2] and experimentally.[3,4] Also electrochemical behaviors of thin films of mixed-valence transition metal hexacyanides on various substrates are under extensive study[5,6] as prospective chemically modified electrodes. In this paper, we report a cyclic voltammetric study of ferricyanide layer irreversibly adsorbed on the gold electrode surface in sulfuric acid medium, which is a well-behaving multilayer thin film formed by self-assembly methods. The proton-mediated hydrogen bonding between monolayers will be offered as the origin of binding interactions inside ferricyanide layer from our experimental results.

Experimental section

Gold wire (diameter 1 mm and 99.99% purity from Aldrich) was sealed in a glass tube using a torr seal. Its end was polished with alumina powders (1, 0.3 μ successively) and soaked in 1 : 4 mixture solution of hydrogen peroxide (30%) and concentrated sulfuric acid and then rinsed thoroughly in an ultrasonic bath with distilled water. Bare gold disk electrode prepared was dipped three hours in 1 mM $K_3Fe(CN)_6$ solution in 0.05 M sulfuric acid to attach a ferricyanide layer in self-assembled manner on its surface. Cyclic voltammetric experiments were carried out with a home-built pc-based potentiostat[7] adapting a conventional three electrode system. Bare gold disk electrode and ferricyanide-attached gold disk electrode prepared as above were employed as working electrodes. Saturated calomel electrode (SCE) and a platinum wire were chosen as a reference electrode and an auxiliary electrode, respectively. Chemicals were used as received without further purification.

Results and Discussion

Cyclic voltammograms for a ferricyanide-attached gold disk electrode at different bulk concentrations of $Fe(CN)_6^{3-}$ in aqueous 1.0 M KNO_3 are presented in Figure 1. Potential scan rate was fixed at 100 mV/s in the potential range of +0.6 V to −0.2 V *vs.* SCE. Voltammograms were obtained at 0, 1, 2, 4, 6, 8, and 10 mM of the bulk concentration of ferricyanide ion to get a concentration dependence. There are several characteristics worth to refer in the cathodic