Stereoselective Halolactonization of α-Phenylsulfonyl-γ,δ-Unsaturated Amides

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Iodine-induced lactonization of α-Phenylsulfonyl-γ,δ-Unsaturated Amides provided 2,4-trans-substitued γ-butyrolactones in high selectivity. NBS-or NCS-induced lactonization of N,N-dimethyl-2-(phenylsulfonyl)-4-pentenamide in DME-H_2O(2 : 1 vol) gave 2-halo-4-(halomethyl)-2-(phenylsulfonyl)-γ-butyrolactone.

Introduction

Lactonic functionality is fairly common among natural products and in a variety of biologically active molecules[2,3]. For this reason, the asymmetric induction of lactonic system is still a challenging problem in a very active area of organic synthesis[4]. Lactonizations of γ,δ-unsaturated acids and amides comprise the largest subject of this area[5]. Bartlett[5] has shown a moderate 1,3-cis selectivity in the iodolactonization of γ,δ-unsaturated acids and Yoshida[6] has reported a 1,3-trans asymmetric induction in the halolactonization of α-substituted γ,δ-unsaturated amides.

Recently we have developed a method for the iodine induced enoletherification of α-allyl substituted β-keto sulfones [7]. During our studies for this reaction, it has been found that the I_2-induced cyclization of N,N-dimethyl-2-(phenylsulfonyl)-pentenamide under 1.2 eq. $NaHCO_3$ and 2.2 eq. I_2 in CH_3CN gave γ-butyrolactone. Therefore, we have investigated the halolactonization of α-phenylsulfonyl-γ,δ-unsaturated amides because of the bulkiness of sulfonyl group and the ease of reductive desulfonylation[8-12].

Experimental

NMR data were obtained from a Bruker AM-200 spectrometer or Varian T-60 spectrometer using TMS as an internal standard. Infrared spectra were measured on a Bomem MB-100 FT-IR spectrophotometer. Mass Spectra were obtained on a Hewlett Packard 5985A GC/MS system using the electron impact method (70 eV). Melting points were determined on a Büchi 535 melting point apparatus and were uncorrected. Analytical TLC was perfomed on a precoated glass plates (0.25 mm) coated with silical gel $60F_{254}$ (E. Merck). Merck silica gel 60 (230-400 mesh) was used for column chromatography.

General Procedure for the Preparation of α-Phenylsulfonyl-γ,δ-Unsaturated Amides (3)

3 mmol of methyl phenyl sulfone (1) was dissolved in 10 m*l* THF and cooled to −30 ℃. 4.2 m*l* of 1.6 M n-BuLi (6 mmol) was dropped slowly to the above solution. After 30 min, the suspended reagent was treated dropwise with N,N-dimethylcarbamoyl chloride (3.15 mmol) and the solution was stirred for 5 min. Then allylic bromide (4 mmol) was added. The resulting solution was warmed to room temperature and stirred for an additional 5 to 20 hr. Normal work-up gave a solid product which was recrystallized from CCl_4.

N,N-Dimethyl-2-phenylsulfonylpent-4-enamide (3a). mp. 136-137 ℃; ^{1}H NMR ($CDCl_3$) δ 2.67 (dd, J=7 Hz, 2H), 2.97 (s, 3), 4.38 (t, J=7 Hz, 1H), 4.85-5.97 (m, 3H), 7.45-7.97 (m, 5H); IR (KBr) 1647 (C=O), 1313 and 1147 (SO_2).

***t*-N,N-Dimethyl-5-phenyl-2-phenylsulfonylpent-4-enamide (3b).** mp. 159.5-161℃; ^{1}H NMR ($CDCl_3$) δ 2.80 (dd, J=7 Hz, 2H), 2.97 (s, 3H), 3.10 (s, 3H), 4.43 (dd, J=8 Hz, 1H), 5.65-6.57 (m, 2H), 7.27 (m, 5H), 7.50-7.97 (m, 5H); IR (KBr) 1646 (C=O), 1304 and 1144 (SO_2).

***t*-N,N-Dimethyl-2-phenylsulfonylhex-4-enamine (3c).** mp. 119.5-121.5 ℃; ^{1}H NMR ($CDCl_3$) δ 1.58 (d, J=6 Hz, 1H), 2.42 (m, 2H), 2.97 (s, 3H), 3.10 (s, 3H), 4.33 (dd, J=8 Hz, 1H), 4.89-5.73 (m, 2H), 7.47-7.90 (m, 5H), IR (KBr) 1650 (C=O), 1304 and 1146 (SO_2).

N,N-Dimethyl-5-methyl-2-phenylsulfonylhex-4-enamide (3d). mp. 83-84 ℃; ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 3H), 1.63 (s, 3H), 2.58 (dd, J=7 Hz, 2H), 2.93 (s, 3H), 3.03 (s, 3H), 4.23 (dd, J=8 Hz, 1H), 4.84 (m, 1H), 7.36-7.86 (m, 5H); IR (KBr) 1649 (C=O), 1303 and 1144 (SO_2).

General Procedure for Iodolactonization of α-Phenylsulfonyl-γ,δ-Unsaturated Amides

To a solution of γ,δ-unsaturated amide (1 mmol) in 8 m*l* of DME-H_2O(2 : 1 vol) was added I_2 (1.2-3 eq., see Table 2) at an ambient temperature. The homogeneous reaction mixture was stirred for the period of time indicated in Table 2. The resultant solution was diluted with ethyl acetate, treated with saturated sodium thiosulfate, and then extracted twice with ethyl acetate. The combined extracts were washed with saturated sodium thiosulfate. Removal of the solvent afforded crude product which was purified by column chromatography or preparative TLC on silica gel using EtOAc/n-Hex (1 : 2) as an eluent.

***cis* and *trans*-4-Iodomethyl-2-phenylsulfonyl-γ-butyrolactone.** mp. 74.5-76 ℃ and 90-92 ℃; ^{1}H NMR ($CDCl_3$) δ 2.3-2.5 and 2.6-2.74 (m, 1H), 2.75-2.95 and 3.05-3.25 (m, 1H), 3.38 and 3.33 (two d, J=5 Hz, 2H), 4.13-4.30 (m 1H), 4.5-4.8 (m, 1H), 7.50-7.76 (m, 3H), 7.8-8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 4.9766 and 7.23 (CH_2I), 29.05 and 30.40 (C-3), 64.28 and 65.17 (C-2), 76.875 and 77.17 (C-2), 129.33, 129.57, 134.89, 136.32 ($PhSO_2$), 166.98 (C-1); IR (film) 1779 (C=O), 1319 and 1170 (SO_2), 1082 (C-O); Mass, m/z (%) 366 (M^+, 0.2), 77 (100).

***trans*-4-(1-Iodoethyl)-2-phenylsulfonyl-γ-butyrolactone.** mp. 88-90 ℃; ^{1}H NMR ($CDCl_3$) δ 1.93 (d, J=6.9) Hz,

3H), 2.33-2.52 (m, 1H), 3.13-3.26 (m, 1H), 4.09-4.25 (m, 1H), 4.29-4.45 (m, 1H), 7.54-7.76 (m, 3H), 7.88-7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 23.89 (Me), 28.43 (CHI), 30.14 (C-3), 65.30 (C-2), 82.23 (C-4), 129.33, 129.62, 134.88, 136.34 ($PhSO_2$), 166.93 (C-1); IR (KBr) 1768 (C=O), 1320 and 1152 (SO_2), 1193 and 1084 (C-O); Mass, m/z (%) 253 (M^+-127(I), 11.7), 77 (100), 111 (50.3).

For *cis*-isomer. mp. 108.5-109.5 ℃; ^1H NMR ($CDCl_3$) δ 1.936 (d, J=7.0 Hz, 3H), 2.39-2.56 (m, 1H), 3.08-3.22 (m, 1H), 4.14-4.41 (m, 3H), 7.55-7.77 (m, 3H), 7.90-8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 23.81 (Me), 28.36 (CHI), 29.40 (C-3), 64.92 (C-2), 81.75 (C-4), 129.35, 129.82, 134.90, 136.34 ($PhSO_2$), 166.94 (C-1); IR (KBr) 1782 (C=O), 1311 and 1151 (SO_2), 1182 and 1085 (C-O); Mass, m/z (%) 253 (M^+-127(I), 10), 77 (100), 111 (52.5).

***trans*-4-Iodobenzyl-2-phenylsulfonyl-γ-butyrolactone.** mp. 147.5-149.5 ℃ (decomp.); ^1H NMR ($CDCl_3$) δ 2.40-3.43 (m, 2H), 4.01 (dd, J=4 Hz, 1H), 4.68-5.03 (m, 2H), 7.23-7.40 (m, 5H), 7.50-7.77 (m, 3H), 7.80-7.99 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 30.09 (C-3), 33.56 (CHI), 65.07 (C-2), 81.60 (C-4), 127.98, 128.19, 128.89, 128.99, 129.32, 129.64, 134.90, 138.24 (Ph and $PhSO_2$), 166.77 (C-1); IR (KBr) 1779 (C=O), 1312 and 1150 (SO_2), 1181 and 1085 (C-O); Mass, m/z (%) 315 (M^+-127(I), 0.4), 77 (100), 173 (95.1).

***trans*-4-(2-Iodoisopropyl)-2-phenylsulfonyl-γ-butyrolactone.** mp. 108-110 ℃ (decomp.); ^1H NMR ($CDCl_3$), δ 1.04 (s, 3H), 1.96 (s, 3H), 2.50-2.68 (m, 1H), 3.09-3.23 (m, 1H), 3.82 (t, J=7.53 Hz, 1H), 4.18 (dd, J=10.7 Hz, 3.3), 7.55-7.76 (m, 3H), 7.89-7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 29.74, 32.93, 33.386, 48.92, 65.15 (C-2), 86.32 (C-4), 129.34, 129.38, 134.87 and 136.34 ($PhSO_2$), 166.83 (C-1); IR (KBr) 1779 (C=O), 1317 and 1149 (SO_2), 1190 and 1085 (C-O); m/z (%) 267 (M^+-127, 5.7), 77 (100), 125 (95.2).

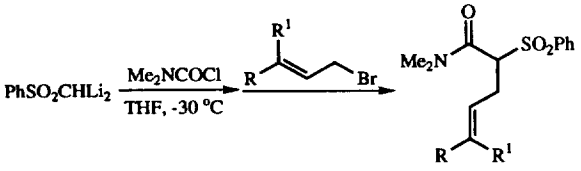
General Procedure for the NBS-or NCS-Induced Lactonization of N,N-Dimethyl-2-Phenylsulfonyl-4-Pentenamide

To a solution of 2-phenylsulfonyl-4-pentenamide(1 mmol) in 6 ml of DME-H_2O (2 : 1 vol) was added slowly various amount of NBS or NCS (See Table 3) at an ambient temperature. The reaction mixture was stirred for the period of time indicated in Table 3. The mixture was diluted with water and extracted twice with methylene chloride. The combined extracts were washed with saturated sodium bicarbonate, brine, and dried over anhydrous magnesium sulfate. Removal of the solvent gave crude product which was purified by preparative TLC on silica gel using EtOAc/*n*-Hex (1 : 3) as an eluent.

2-Chloro-4-chloromethyl-2-phenylsulfonyl-γ-butyrolactone. For less polar isomer, R_f=0.41; mp. 115.5-117.5 ℃ ^1H NMR ($CDCl_3$) δ 2.88 (dd, J=15 Hz, 1H), 3.72 (dd, J=15 Hz, 1H), 3.82 (d, J=5 Hz, 2H), 5.0-5.2 (m, 1H), 7.55-7.64 (m, 2H), 7.72-7.81 (m, 1H), 7.91-7.96 (m, 2H); mass, m/z (%), 308 (M^+4, 0.7). For more polar isomer, R_f=0.34; mp. 136-137℃; ^1H NMR ($CDCl_3$) δ 2.87 (dd, J=15 Hz, 1H), 3.42 (dd, J=3.42, 1H), 3.82 (d, J=5 Hz, 2H), 4.63-5.07 (m, 1H), 7.53-8.03 (m, 5H); IR (KBr) 1780 (C=O), 1335 and 1157 (SO_2), 1181 and 1085 (C-O).

2-Bromo-4-bromomethyl-1-phenylsulfonyl-γ-butyrolactone. For less polar isomer. R_f=0.41; mp. 107-109 ℃; ^1H NMR ($CDCl_3$) δ 2.92 (dd, J=15.7 and 8.2 Hz, 1H) 3.61 (d, J=4.7 Hz, 2H), 3.80 (dd, J=15.6 and 6.7 Hz, 1H), 4.9-5.2 (m, 1H), 7.5-7.63 (m, 2H), 7.70-7.79 (m, 1H), 7.92-8.10 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 32.39, 39.50, 68.11, 76.60, 128.73, 131.91, 132.40, 135.65, 166.66 (C-1); IR (film) 1785 (C=O), 1333 and 1156 (SO_2), 1178 and 1080 (C-O); Mass, m/z (%) 396 (M^+, 2.8), 398 (M^++2, 41), 400 (M^++4, 2.1), 77 (100), 141 (94.6). For more polar isomer, R_f=0.32; mp. 116.2-117.2 ℃ ^1H NMR ($CDCl_3$) δ 2.90 (dd, J=15 Hz, 1H), 3.26 (dd, J=15 Hz 1H), 3.65 (d, J=5 Hz, 2H), 4.60-5.03 (m, 1H), 7.57-8.17 (m, 5H), IR (film) 1787 (C=O), 1330 and 1155 (SO_2), 1177 and 1078 (C-O).

Table 1. Preparation of α-Phenylsulfonyl-γ,δ-Unsaturated Amides from methyl Phenyl Sulfone

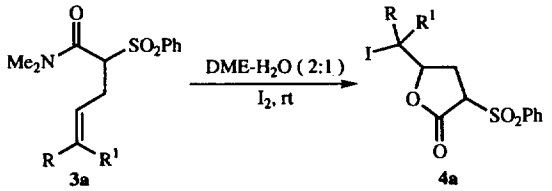


2 3

No	R	R^1	Condition	Yield (%)[a]	mp (℃)
a	H	H	rt, 20h	88	136-137
b	Ph	H	rt, 5h	94	159.5-161
c	Me	H	rt, 6h	90	119.5-121.5
d	Me	Me	rt, 6h	89	83-84

[a] Isolated yield by recrystallization of crud product from CCl_4

Table 2. Iodolactonization of α-Phenylsulfonyl-γ,δ-Unsaturated Amides



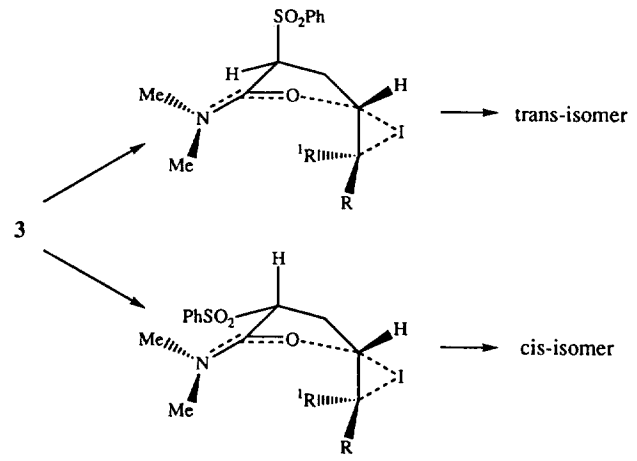
3a 4a

No	R^1	R	Condition[a]	Yield (%)[b]	*trans/cis*[c]
a	H	H	1.2 eq., 3d	70	
b	H	H	2.0 eq., 3h	95	—[d]
c	H	Me	2.0 eq., 3h	89	90 : 10
d	H	Ph	2.0 eq., 1d	65	
e	H	Ph	3.0 eq., 5h	82	>99 : 1
f	Me	Me	2.0 eq., 3h	80	>99 : 1

[a] Equivalents of I_2. [b] Isolated yield. [c] Determined by chromatographic separation. [d] Undetermined because isomers were not separated by TLC.

Results and Discussion

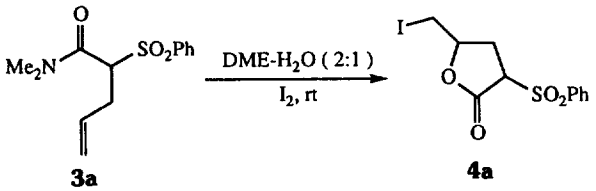
Preparations of α-phenylsulfonyl-γ,δ-unsaturated amides. The required α-phenylsulfonyl-γ,δ-unsaturated amides (**3**) were easily prepared by the allylation of enolate *in situ* generated from N,N-dimethylcarbamoyl chloride and 1.1-dilithiomethyl phenyl sulfone (**2**)[13] which is easily generated by treatment of 2 eq. of n-BuLi to a solution of methyl



Scheme 1

phenyl sulfone (**1**) in THF at −30 ℃. The results are summarized in Table 1.

Iododine-induced lactonization α-phenylsulfonyl-γ, δ-unsaturated amides. A solution of N,N-dimethyl-2-(phenylsulfonyl)-4-pentenamide (**3a**) in DME-H_2O (2 : 1 vol) reacted during 3 days at room temperature with 1.2 eq. of I_2 to give a mixture of trans-and *cis*-4-iodomethyl-2-(phenylsulfonyl)-γ-butyrolactone (**4a**) in 70% yield (entry a, Table 2).



3a **4a**

It was found that this reaction rate was quite dependent on the amount of I_2. This reaction could be effectively accelerated and gave high yield by using excess I_2. Reaction of **3a** with 2.0 eq. of I_2 gave **4a** in 95% isolated yield after 3h (entry b, Table 2). From above result, it may be shown that molecular complex between aromatic ring and iodine was formed by noncovalent interactions.[14] Thus, all reactions for other substrates were generally carried out with excess iodine. The results are summarized in Table 2.

As shown in Table 2, cyclization led, as expected,[4] predominantly to the thermodynamically more stable trans disubstituted γ-butyrolactone. The isomeric rations of γ-butyrolactones were determined by chromatographic separation and the stereochemistry was assigned by their chemical shift in the ^1H NMR spectrum. No six-membered lactones were detectable. The IR spectra exhibit the characteristic C=O stretching vibration of γ-lactone at 1765-1782 cm^{-1}.

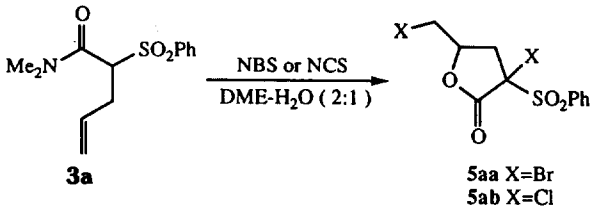
The present unique stereoselectivity may be explained in terms of interaction between the sulfonyl group and the N,N-dimethylamino group (Scheme).[6]

NCS or NBS-Induced lactonization of α-phenylsulfonyl-γ,δ-unsaturated amides. In the case of employing 1.2 eq. of N-bromosuccinimide(NBS) or N-chlorosuccinimide (NCS) as electrophilic halogen species, we have obtained 2-halo-4-(halomethyl)-2-(phenylsulfonyl)-γ-butyrolactone (**5**) in low yield. It may be shown that this product could be generated from α-halogenation and *in situ* subsequent halolactonization.

Table 3. NBS or NCS-Induced Lactonization of N,N-Dimethyl-2-Phenylsulfonyl-4-Pentenamide[a]

No	Reaction Condition	Product	Yield (%)[b]
a	1.2 eq. NBS, 4d	**5aa**	25
b	2.0 eq. NBS, 3d	**5aa**	49
c	3.0 eq. NBS, 2h	**5aa**	85
d	1.2 eq. NCS, 2d	**5ab**	29
e	4.0 eq. NCS, 40h	**5ab**	50

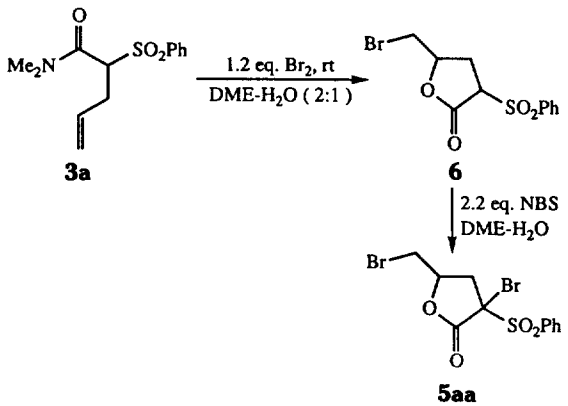
[a]All reactions were carried out in DME-H_2O (2 : 1 vol) at room temperature. [b]Isolated yield.



3a

5aa X=Br
5ab X=Cl

Form this result, we think that the rate of α-halogenation is faster than the rate of halolactionization. As shown in Table 3, it was found that this process could be effectively accelerated and gave high yield by using excess electrophilic halogen species. Reaction of **3a** with 3 eq. of NBS gave **5aa** in 85% yield, while reaction of **3a** with 4 eq. of NCS gave **5ab** in 50% yield and unidentified products. It was found that **5aa** and **5ab** were divided into two isomers by TLC. **5aa** was separated to more ploar isomer (55%), mp. 116.2-117.2 ℃ and less polar isomer (45%), mp. 107-109 ℃ Also **5ab** gave more polar isomer (67%), mp. 136-137 ℃ and less polar isomer (33%), mp. 115.5-117.5℃. The relative stereochemistry of diastereomers of **5aa** and **5ab** were not established. The structures of **5aa** and **5ab** were not established. The structures of **5aa** and **5ab** were confirmed by ^1H NMR, IR, and mass spectra. On the other hand, we could not isolate 4-(halomethyl)-2-(phenylsulfonyl)-γ-butyrolactone in this reaction.



3a **6** **5aa**

Therefore we isolated 4-(bromomethyl)-2-(phenylsulfonyl)-γ-butyrolactone (**6**) from reaction of **1** with 1.2 eq. of Br_2. And 2-bromo-4-(bromomethyl)-2-(phenylsulfonyl)-γ-butyrolactone (**5aa**) were readily obtained from α-bromination of **6**

by 2.2 eq. of NBS. From this investigation, it may be shown that the appearance of 2-halo-4-(halomethyl)-2-(phenylsulfonyl)-γ-butyrolactone (**5**) in NBS or NCS-induced lactonization of **3** could be generated from α-halogenation and *in situ* subsequent halolactonization.

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Mono-dehalogenation of *gem*-Dihalocyclopropanes Using Tetracarbonylhydridoferrate

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Tetracarbonylhydridoferrate, $HFe(CO)_4^-$, generated by the reaction of $Fe(CO)_5$ with alkaline solution, is a good reducing agent for mono-dehalogenation of *gem*-dihalocyclopropanes. It also acts as a good reducing catalyst under phase transfer reaction conditions. 1,1-Dibromo-2-phenylcyclopropane and 1,1-dichloro-2-phenylcyclopropane were reduced to the corresponding mono-dehalogenated products in excellent yields. Thermodynamically stable *trans*-1-bromo-2-phenyl cyclopropane was formed as the major product over the *cis*-isomer, *trans/cis* = 3/2. The 1-bromo-2-phenyl cyclopropane radical intermediate was formed by single electron transfer from $HFe(CO)_4^-$. Dissociation of bromide anion, followed abstraction of hydrogen radical from alcoholic solvent would lead to the formation of the stable *trans*-isomer. The further mechanistic aspects were discussed.

Introduction

The tetracarbonylhydridoferrate anion, $HFe(CO)_4^-$, derived from the reaction of pentacarbonyliron and alkaline base in aqueous or alcoholic solution appears very versatile compound as the reducing reagent.[1] It has been reported that $HFe(CO)_4^-$ was able to reduce alkyl halides[2] and vinylic halides.[3] Extensive study with this reagent has also been carried out on the reductive dehalogenation of aryl iodides.[4]

gem-Dihalocyclopropanes have been shown to be extremely valuable starting materials for the preparation of cyclopropane and cyclopropene derivatives.[5] The reduction of *gem*-dihalocyclopropanes to mono-halocyclo propanes has been effected by various reducing agents such as organotin hydride,[6] Grignard reagent,[7] chromium sulfate,[8] lithium aluminum hydride,[9] potassium diphenyl phosphide,[10] and sodium hydrogen telluride,[11] or by metals such as silver.[12] Pentacarbonyliron in DMF has been also utilized for both the reduction of and the carbonylation of *gem*-dihalocyclopropanes.[13] However, these two reactions are in competition and the selective dehalogenation over the carbonylation of *gem*-dihalocyclopropanes or *vice versa* have not been achieved, especially for mono-dehalogenation.

In this paper, we wish to report that tetracarbonylhydridoferrate is a good reducing agent for mono-dehalogenation of *gem*-dihalocyclopropanes and it also acts as a good reducing catalyst under phase transfer reaction conditions.

Results and Discussion

Mono-debromination of 1,1-dibromo-2-phenylcyclopropane using $HFe(CO)_4^-$ as reducing agent. This complex was utilized to the dehalogenation of organic halides.[2-4] In the present work, it was found that the reaction