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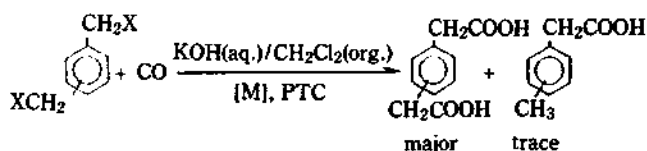
Iron Carbonyl Complex Catalyzed Carbonylation of Xylylene Dihalides under Phase Transfer Catalyst (I)

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Recent investigations have demonstrated that the phase transfer catalysis is an exceedingly useful technique in organometallic chemistry¹. One of the most useful phase transfer reactions is the carbonylation of organic halides to carboxylic acids by metal carbonyls such as cobalt carbonyl^{2,5} and iron carbonyl⁶, and also by palladium complexes⁷ at room temperature under an atmospheric pressure of carbon monoxide. The metal carbonyl complexes are the key intermediates generated, in these reactions, under the phase transfer conditions.

Various xylylene dihalides were reacted with carbon monoxide in the presence of phase transfer catalysts and metal carbonyls to give the corresponding carboxylic acids, phenylenediacetic acid in moderate yields with a trace amount of tolylacetic acid in a two-phase system, 2M-KOH (aq.)-CH₂Cl₂(org.) at -3°C to 7°C for 20 hrs. The reaction was depicted in Scheme and the results were listed in Table 1.



X; Br, Cl

M; Fe(CO)₅, Co₂(CO)₈, Re₂(CO)₁₀

PTC; Crown ether or quaternary ammonium salt

Scheme

Table 1 showed that iron pentacarbonyl in the presence of dibenzo-18-crown-6-ether as a phase transfer catalyst was the most efficient catalyst for the carbonylation of xylylene dibromide. Accordingly, in these conditions was the product obtained in moderate yield at 7°C (entry No. 2), but no carbonylation occurred at an elevated temperature, 80°C (entry No. 6). When a small amount of acetonitrile was added, the yield was slightly increased (entry No. 3).

On the other hand, the carbonylated products obtained from the *ortho*- and *meta*-xylylene dibromides were obtained

Table 1. Products Obtained from the Carbonylation of Xylylene Dihalides by using Organometallic Phase Transfer Catalysis

Entry No.	Substrate	Catalyst	PTC ^a	Reaction Temp.(°C)	Condition Time(hr)	Yield(%) ^b
1	<i>para</i> -	Fe(CO) ₅	DBCE	-3	20	38
2	<i>para</i> -	Fe(CO) ₅	DBCE	7	17	41
3 ^c	<i>para</i> -	Fe(CO) ₅	DBCE	7	17	46
4	<i>para</i> -	Fe(CO) ₅	DBCE	17	20	33
5	<i>para</i> -	Fe(CO) ₅	DBCE	30	30	27
6	<i>para</i> -	Fe(CO) ₅	DBCE	80	20	-
7	<i>para</i> -	Fe(CO) ₅	Aliq	7	20	-
8	<i>para</i> -	Fe(CO) ₅	BTMH	7	20	28
9	<i>meta</i> -	Fe(CO) ₅	DBCE	7	20	tr
10	<i>ortho</i> -	Fe(CO) ₅	DBCE	7	20	tr
11	<i>para</i> -	Co ₂ (CO) ₈	DBCE	7	20	20
12	<i>para</i> -	Re ₂ (CO) ₁₀	DBCE	7	20	20
13 ^d	<i>para</i> -	Fe(CO) ₅	DBCE	7	20	4

^a PTC: DBCE; dibenzo-18-crown-6-ether, Aliq; tricaprylylmethylammonium chloride, BTMH; benzyltrimethylammonium hydroxide. ^b Isolated yields: Based on the amount of xylylene dihalide used. ^c Added small amount of acetonitrile. ^d When *p*-xylylene dichloride was used as a reactant, *p*-phenylenediacetic acid(4%) and *p*-tolylacetic acid(17%) were obtained.

in trace amounts under the similar conditions and intractable unknown materials were mainly formed. Dibenzo-18-crown-6-ether was more effective than the quaternary ammonium salts such as tricaprylylmethylammonium chloride (Aliquat 336) and benzyltrimethylammonium hydroxide (BTMH) (entry No. 7 and No. 8). Iron pentacarbonyl was more active than other metal carbonyl complexes such as rhenium carbonyl and cobalt carbonyl complexes (entries No. 11 and No. 12). Surprisingly, when *para*-xylylene dichloride was reacted with carbon monoxide under the same condition, *para*-tolylacetic acid was the major product (17%) and *para*-phenylene-

diacetic acid was a minor product(4%)(entry No. 13).

The spectral data of *para*-phenylenediacetic acid are as follows; $^1\text{H-nmr}$ (DMSO- d_6): δ (ppm) 3.50(s, 4H, 2CH_2), 7.15(s, 4H, Ar). $^{13}\text{C-nmr}$ (DMSO- d_6): δ (ppm) 20.78($-\text{CH}_2-$), 122.41($>\text{C}-\text{H}$), 147.88($>\text{C}-$), 168.79($>\text{C}=\text{O}$). MS(m/e): 194. Ir(KBr) ν_{CO} : 1700cm^{-1} . m.p.; 248-250°C. On the other hand, the spectral data of *para*-tolylacetic acid are as follows; $^1\text{H-nmr}$ (CDCl_3): δ (ppm) 2.30(s, 3H, CH_3), 3.50(s, 2H, CH_2), 7.10(s, 4H, Ar). Ir(KBr): ν_{CO} : 1700cm^{-1} . m.p.; 89-90°C. These results match those from literature⁸. According to the mechanism proposed by Alper and Abbayes⁹, the iron pentacarbonyl is reacted with a hydroxide ion transferred from aqueous layer to organic layer by the phase transfer catalyst to give the tetracarbonylferrate anion, and xylylene dihalide is oxidatively added to the anion. Successively, carbon monoxide may be inserted into alkyl-metal bond to give acyl-metal complex. Finally, alkylacylmetal complex by attack of hydroxide ion gave the carboxylic acid and acylmetal complex, true catalyst, was regenerated.

Carbon monoxide was slowly bubbled for 30 minutes through the stirred solution of 2M-KOH(10 ml)-dichloromethane(10 ml) and dibenzo-18-crown-6-ether(0.3 mmol) or quaternary ammonium salt(0.6 mmol). A solution of metal complex(0.25 mmol) in 3-5 ml of dichloromethane was added and then the reaction mixture was vigorously stirred at room temperature for 1 hr. Xylylene dihalide(2.5 mmol) in 3-5 ml of dichloromethane was added and stirring was continued with carbon monoxide bubbled for 20 hrs. The phases were

carefully separated; the aqueous layer was washed with two 10 ml of ether, acidified(conc. HCl), and then extracted with four 15 ml of ether. The combined ether extracts were washed with a 20 ml of water, dried with magnesium sulfate and evaporated to give the crude products, that were purified by using vacuum sublimation apparatus.

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Enantioselective Reduction of Racemic Three-Membered Heterocyclic Compounds. 2. Reaction of Epoxides and Episulfides with (-)-Diisopinocampheylborane in the Presence of Lithium Chloride¹

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In the previous paper², we reported that the optically-active (-)-diisopinocampheylborane[(-)-IPC₂BH]-lithium chloride (1:0.1) system reduced enantioselectively racemic 1,2-epoxybutane to give optically-active R(-)-2-butanol in around 22% ee at 0°C or -20°C. We interpreted this result as the chiral IPC₂BH coordinates preferentially on R-1,2-epoxybutane rather than on S-1,2-epoxybutane in an approximate ratio of 3:2 and then the *in situ* formed lithium diisopinocampheylchloroborohydride attacks the epoxy ring of the adduct to give the alcohol product^{2,3}.

This new methodology seems to be promising for resolution of racemic three-membered heterocyclic compounds. Consequently, it appeared desirable to explore the applicability of this system to other structurally-different epoxides and another class of this series, episulfides.

Results and Discussion

The reaction mixture involves 2 equiv of racemate and 1 equiv of IPC₂BH-LiCl (1:0.1). Therefore, only 1 equiv of racemate is coordinated enantioselectively with 1 equiv of IPC₂BH, and only the coordinated compound is then reduced by the *in situ* formed IPC₂B[⊖]ClH species.

We applied this system for the resolution of three racemic aliphatic epoxides such as 1,2-epoxybutane, 1,2-epoxyoctane, and 3,3-dimethyl-1,2-epoxybutane and a racemic aromatic one such as styrene oxide at 0°C, the result of which are summarized in Table 1.

As shown in Table 1, all the epoxides examined were readily reduced to the corresponding alcohols within 3 h at 0°C to provide yields of 79-86%. Racemic 1,2-epoxybutane is