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Carbonylation of Benzal Chlorides to Alkyl Phenylacetates using $Fe(CO)_5$

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Received May 18, 1990

Various substituted benzal chlorides are converted into alkyl phenylacetates ($ArCH_2COOR$) under CO atmosphere on reaction with a catalytic amount of $Fe(CO)_5$, a base, and an alcohol. The optimum conditions are found as atmospheric pressure of CO, 40 °C, potassium hydroxide as base, and medium of alcohol.

Introduction

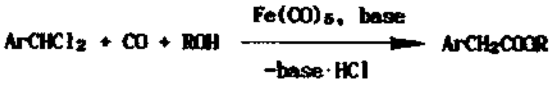
The technology of transition metal complexes catalyzed carbonylation reaction is being currently used for large volume chemicals.[1] Many applications are reported on the carbonylation of benzyl halides with CO using cobalt,[2] Iron,[3] ruthenium,[4] rhodium,[5] and palladium[6] complexes. However, there are a few reports on the carbonylation of benzal halides as the geminal dihalide compound to give alkyl phenylacetates[7] and phenylacetic acids.[8] As the similar report, cobalt catalyzed carbonylation of methylene dihalides leads to the corresponding carboxylates in the presence of Zn powder.[9]

We herein wish to report a simple method for $Fe(CO)_5$ catalyzed carbonylation of benzal chlorides which leads to alkyl phenylacetates in moderate yields in the presence of base under CO atmosphere.

Results and Discussion

Benzal chlorides react with a variety of alcohols in a catalytic amount of $Fe(CO)_5$ at 40 °C under an atmospheric pressure of CO for 20 hours to give alkyl phenylacetates in moderate yields.

particularly, in these reactions, the effects of reaction parameters on the alkoxycarbonylation of benzal chlorides in the presence of alcohols are discussed in details below. In Table 1, a series of bases are screened for carbonylation of benzal chloride with ethanol at atmospheric pressure of CO. Base in this reaction is used for the purpose of both acid scavenger and catalyst activator. Of the several different bases examined (KOH, K_2CO_3, NaOEt, $Ca(OH)_2$), KOH is by far the best for selective carbonylation (No. 1), although side products such as toluene and benzaldehyde are generated in some extents. When NaOEt is used, the reaction proceeds in small quantities and remained part is recovered as reactant (Nos. 10–11). When $Ca(OH)_2$ is used, the reaction does not proceed (Nos. 12–13).



$$ArCHCl_2 + CO + ROH \xrightarrow[-base\cdot HCl]{Fe(CO)_5,\ base} ArCH_2COOR$$

Equation 1

In the use of KOH, the reaction temperature gives a small contribution in the reaction course. At room temperature, product obtained in lower yield (28%, No. 3) than temperature range of 40 °C to 70 °C (40%, Nos. 1, 4). And CO pressure inversely effects on the formation of carbonylated product (No. 14). But in the case of K_2CO_3, CO pressure does not change very significantly the amounts of carbonylated product (Nos. 9, 15–16).

Table 2 summarizes the carbonylation of various benzal chlorides in the presence of KOH. In the case of benzal chloride, the highest yield of carbonylated product is obtained using ethanol. Other alcohols, such as methanol, n-, iso-propanol, or n-butanol give low yields compared with ethanol.

The carbonylation of substituted benzal chlorides is studied using ethanol. Chlorobenzal- and methylbenzal chlorides give similar yields for carbonylation compared with

Table 1. $Fe(CO)_5$-Catalyzed Carbonylation of Benzal Chloride at Various Condition[a]

No.	Base (mmol)		Temp. (°C)	P_{co} (atm)[b]	$C_6H_5CH_2COOC_2H_5$ Yield(%)[c]
1	KOH	(5)	40	1	40(38)
2	—	—	40	1	8
3	KOH	(5)	20	1	28
4	KOH	(5)	70	1	40
5	KOH	(45)	40	1	4
6	KOH	(10)	40	1	5
7	KOH	(2.5)	40	1	14
8	K_2CO_3	(2.5)	40	1	14
9	K_2CO_3	(2.5)	70	1	25
10	NaOEt	(5)	40	1	trace
11	NaOEt	(5)	70	1	12
12	$Ca(OH)_2$	(2.5)	40	1	0
13	$Ca(OH)_2$	(2.5)	70	1	0
14	KOH	(5)	40	60	13
15	K_2CO_3	(2.5)	70	30	21
16	K_2CO_3	(2.5)	70	5	24
17[d]	KOH	(5)	40	1	35

[a] Benzal chloride (0.325 g. 2 mmol). base, ethanol (10 m*l*). and $Fe(CO)_5$ (0.04 g. 0.2 mmol). for 20 h. under CO. [b] At room temperature. [c] GLC yield by phenyl ether as internal standard and parenthesis is isolated yield. [d] Using preactivated catalyst.

Table 2. $Fe(CO)_5$-Catalyzed Carbonylation of Benzal Chlorides[a]

No.	$XC_6H_4CHCl_2$ X	ROH	$C_6H_5CH_2COOR$ R	Yield (%)[b]
1	H	CH_3OH	CH_3	32
2	H	C_2H_5OH	C_2H_5	40(38)
3	H	$n-C_3H_7OH$	$n-C_3H_7$	10
4		iso-C_3H_7OH	iso-C_3H_7	10
5	H	$n-C_4H_9OH$	$n-C_4H_9$	11
6	*o*-Cl	C_2H_5OH	C_2H_5	34 (28)
7	*p*-Cl	C_2H_5OH	C_2H_5	40 (35)
8	*o*-CH_3	C_2H_5OH	C_2H_5	40 (32)
9	*p*-CH_3	C_2H_5OH	C_2H_5	17 (44)

[a] Benzal chloride (2 mmol). KOH(0.33g. 5 mmol). alcohol (10 m*l*). and $Fe(CO)_5$ (0.04 g. 0.2 mmol) at 40 °C for 20 h under CO (1 atm). [b] GLC yield by phenyl ether as internal standard.

benzal chloride. ortho-Substituted benzal chlorides give some lower yields of carbonylated products than para substituents. In para-substituted benzal chlorides. an electron donating group attached to the aromatic ring facilitates carbonylation reaction is some extents (Nos. 6-9).

Preactivated catalyst system shows slower generation of ethyl phenylacetate than in situ generated catalyst system (Figure 1). And, we do not observe alkyl-α-chlorophenylacetate as a plausible intermediate and further carbonylation product, dialkyl phenylmalonate. Unluckly. conversion of benzal chloride can not be checked owing to its unstability.

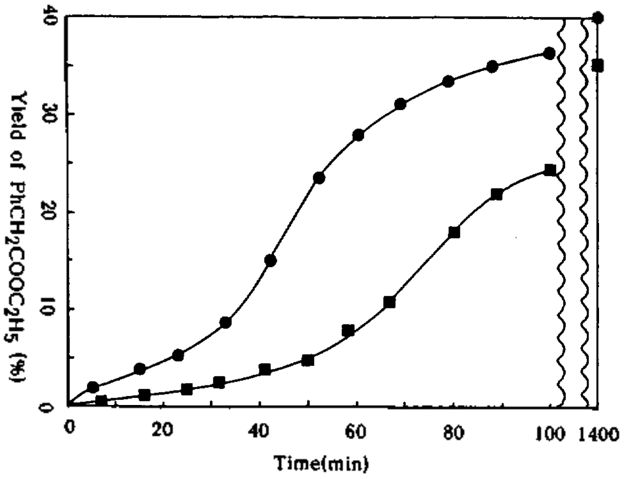


Figure 1. Plot of the percent generation of ethyl phenylacetate with time with preactivated catalyst (■, $PhCHCl_2$ is added after 1 h) or in situ activated catalyst (●, $PhCHCl_2$ and $Fe(CO)_5$ are added at same time) ($PhCHCl_2$, 2.0 mmol; $Fe(CO)_5$, 0.20 mmol; KOH, 5.0 mmol; EtOH, 10 m*l*; CO, 1 atm, 40 °C).

Experimental

^1H-NMR spectra were recorded on a Varian EM-360 A spectrometer using CCl_4 and a Bruker AM-300 spctrometer using $CDCl_3$ with $Si(CH_3)_4$ as internal standard. Infrared spectra were obtained in a Perkin-Elmer IR-843 spectrophotometer. Mass spectra were recorded on a Shimadzu QP-1000 GC-MS spectrometer at 70 eV. Quantitative analysis of the products was performed on a Shimadzu GC-3BT gas chromatography using a 3 mm i.d. × 3 m column packed with Apiezon-L using diphenyl ether as internal standard. Solvents were purified by standard methods. Bases were used without further purification. Benzal chloride derivatives were prepared by the literature methods.[10] $Fe(CO)_5$ was purchased from Strem Chemicals and used without further purification.

General procedures are as follows; in a 100 m*l* 3 neck flask, benzal chloride (0.325 g, 2 mmol), ethanol (10 m*l*), KOH (0.33 g, mmol), diphenyl ether (0.200 g) as internal standard, and $Fe(CO)_5$ (0.04 g, 0.2 mmol) were placed under N_2 atmosphere. Carbon monoxide was charged and then the mixture was stirred in an oil bath at 40 °C for 20 hours. After cooling, the gas was purged and the mixture was monitored by gas chromatography. Reaction mixture was filtered, concentrated, and separated to give ethyl phenylacetate (0.125 g, 38%) by preparative TLC (SiO_2, ethyl acetate: hexane = 1:9).

Analytical Data of Alkyl Phenylacetates

Methyl phenylacetate: Colorless liquids. ^1H-NMR (CCl_4); δ 3.62(s, CH_2), 3.70(s, CH_3), 7.33(m, Ph). ^{13}C-NMR($CDCl_3$), δ 41(CH_3), 52(CH_2), 127(CH), 128(2CH), 129(2CH), 134(C), 172(COO). IR(neat); 1731 cm^{-1} ($\nu_{C=O}$). mass(*m/e*); 150(M^+), 91(M^+-59).

Ethyl phenylacetate: Colorless liquids. ^1H-NMR (CCl_4); δ1.25(t, CH_3), 3.60(s, CH_2), 4.15(q, CH_2), 7.30(m, pH). ^{13}C-NMR($CDCl_3$); δ 14(CH_3), 41(CH_2), 61(CH_2), 127(CH), 129(4CH), 134(C), 171(COO). IR(neat); 1727 cm^{-1}($\nu_{C=O}$).

mass(*m/e*); 164(M^+), 91($M^+ + 73$), 29($M^+ - 135$).

n–propyl phenylacetate: Colorless liquid. ^{1}H–NMR (CCl_4); δ 0.78(t, CH_3), 1.50(h, CH_2), 3.50(s, CH_2), 3.93(t, CH_2), 7.16(m, Ph). ^{13}C–NMR($CDCl_3$); δ 10(CH_3), 22(2CH_2), 42(CH_2), 62(CH_2), 127(CH), 129(2CH), 134(C), 172(COO). IR(neat); 1726cm^{-1}($\nu_{C=O}$). mass(*m/e*); 178(M^+), 91($M^+ - 87$).

Iso–propyl phenylacetate: Colorless liquid. ^{1}H–NMR(CCl_4); δ 1.22(d, 2CH_3), 3.50(s, CH_2), 5.00(h, CH), 7.33(m, Ph). mass(*m/e*); 178(M^+), 91($M^+ - 87$).

n–butyl phenylacetate: Colorless liquid. ^{1}H–NMR (CCl_4); δ 0.90(t, CH_3), 1.34(h, CH_2), 1.60(q, CH_2), 3.60(s, CH_2), 4.10(t, CH_2), 7.30(m, Ph). ^{13}C–NMR($CDCl_3$); δ 10(CH_3), 19(CH_2), 31(CH_2), 42(CH_2), 65(CH_2), 127(CH), 129(2CH), 129(2CH), 134(C), 172(COO). IR(neat); 1726 cm^{-1}($\nu_{C=O}$). mass (*m/e*); 192(M^+), 91($M^+ - 101$).

Ethyl–*o*–chlorophenylacetate: Colorless liquid. ^{1}H–NMR(CCl_4); δ 1.26(t, CH_3), 3.65(s, CH_2), 4.11(q, CH_2), 7.20(m, Ph). mass(*m/e*); 200($M^+ + 2$), 198(M^+), 127($M^+ - 71$), 125($M^+ - 73$).

Ethyl–*p*–chlorophenylacetate: Colorless liquid. ^{1}H–NMR(CCl_4; δ1.23(t, CH_3), 3.50(s, CH_2), 4.13(q, CH_2), 7.33(q, Ph). mass(*m/e*); 200($M^+ + 2$), 198(M^+), 127(M^+71), 125($M^+ - 73$).

Ethyl–*o*–Tolyacetate: Colorless liquid. ^{1}H–NMR (CCl_4); δ1.23(t, CH_3), 2.33(s, CH_3), 3.52(s, CH_2), 4.41(q, CH_2), 7.18(m, Ph). mass(*m/e*); 178(M^+), 105($M^+ - 73$).

Ethyl–*p*–tolylacetate: Colorless liquid. ^{1}H–NMR(CCl_4) δ1.20(t, CH_3), 2.33(s, CH_3), 3.48(s, CH_2), 4.13(q, CH_2), 7.13(q, Ph). mass(*m/e*); 178(M^+), 105($M^+ - 73$).

Acknowledgement. This work was supported by the Organic Chemistry Research Center–the Korea Science and Engineering Foundation (893–0306–006–2).

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Semiempirical MO Calculation of Hetero Atom Three–Membered Ring Compounds (I): N–Nitroso–aziridine, –oxaziridine, and –dioxaziridine

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Fully optimized MNDO molecular orbital calculations are described for N–nitroso–aziridine (I), –oxaziridine (II), and –dioxaziridine (III). The ground state geometries show the nonplanar configuration around the imino nitrogen. The nitroso group rotational energy barriers are 3.25, 0.43 and 1.18 kcal/mol for I, II and III, respectively. Also the calculated aziridine ring inversion barriers are 3.98, 15.61 and 27.46 kcal/mol for I, II and III, respectively.

Introduction

N–Nitrosamines are an important class of compounds as environmental carcinogens and they are widely present in many consumer products.[1] Although they have been studied for several decades in their biochemical behaviors, like carcinogenic properties, their structural infomrations are little known. Experimental[2–5] and theoretical[6] studies of N,N–dimethyl nitrosamine show a planar heavy atom structure. The heavy atom planarity can be explained by partial double bond