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COBALT CARBONYL CATALYZED POLYCARBONYLATION OF POLYHALOGENATED AROMATICS UNDER PHOTOSTIMULATION

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Cobalt carbonyl catalyzed polycarbonylation of much less reactive polychlorobenzenes could be easily achieved under photostimulation in aqueous sodium hydroxide. All these reactions could be performed without any organic solvent(in some cases, ethanol was used as a co-solvent) and any phase transfer catalyst.

Carbonylation of polyhalogenated aromatics affording benzene polycarboxylic acids has been of a great industrial value. However, these reactions have been performed under high CO pressure(100-300 atm) and at high temperature(200-350 °C) in the presence of transition-metal catalysts.$^{1)}$ This kind of reactions has been applied as the main method for the carbonylation of aryl halides.

Recent investigations by Caubere and his co-workers have demonstrated that a phase transfer catalysis is an effective technique for the cobalt carbonyl catalyzed photocarbonylation of aryl halides.$^{2)}$ However, under the phase transfer catalysis conditions, monocarbonylated compound is the sole product, namely, polycarbonylated product cannot be obtained.

In this communication, we wish to report the first example of the cobalt carbonyl catalyzed polycarbonylation of polyhalogenated aromatics, especially of polychlorobenzenes, under mild conditions.

$$\underset{(X=Cl,Br)}{ArX} + CO + 2NaOH \xrightarrow[h\nu(350\text{ nm}),\ 65\ ^\circ C]{\text{aqueous NaOH, }Co_2(CO)_8} ArCOONa + NaX + H_2O$$

A typical reaction was carried out as follows. To a 75 ml Pyrex autoclave equipped with an efficient mechanical stirrer were added aqueous 2.5 mol dm^{-3} sodium hydroxide(20 ml), $Co_2(CO)_8$(0.2 mmol), and the starting halide(2.0 mmol). The reaction mixture was heated to 65 °C under pressurized CO(2 kg cm^{-2}) with stirring. Irradiation was achieved with a high pressure Hg lamp(500 W) placed about 30 cm from the autoclave.

In cases that the starting materials had at least one carboxyl group, the carbonylation could be easily achieved in aqueous sodium hydroxide. The results for these cases are listed in Table 1. On the other hand, in cases that the starting halides had no carboxyl group, the carbonylation could not proceed so fast because of their sparing solubility in aqueous sodium hydroxide(Runs 11 and 15 in Table 2). In these cases, ethanol could be used as a very efficient co-solvent. The results for the latter case are summarized in Table 2.

Table 1 Carbonylation of Halogenated Benzenecarboxylic Acids[a)]

Run	Starting halide	Time/h	Conv./%[b)]	Products(Yield/%)[c)]
1	4-Chlorobenzoic acid	6	94.8	Terephthalic acid(93.4)
2	3-Chlorobenzoic acid	6	98.7	Isophthalic acid(94.0)
3	2-Chlorobenzoic acid	18	83.2	Benzoic acid(11.3) Phthalic acid(34.2)
4	4-Chlorophthalic acid	6	95.4	Trimellitic acid(95.0)
5	3,5-Dichlorobenzoic acid	20	100	Trimesic acid(88.6)
6	4,5-Dichlorophthalic acid	24	100	Trimellitic acid(52.6) Pyromellitic acid(29.8)
7	*o*-Chlorophenylacetic acid	24	97.0	Phenylacetic acid(3.7) Homophthalic acid(87.4)
8	2,4-Dichlorobenzoic acid	6	99.3	4-Chlorobenzoic acid(23.6) Terephthalic acid(10.2) 4-Chlorophthalic acid(13.9) 2-Chloroterephthalic acid (40.2) Trimellitic acid(13.1)
9	3,4-Dichlorobenzoic acid	6	100	4-Chlorobenzoic acid(14.6) Terephthalic acid(14.4) 2-Chloroterephthalic acid (57.3) Trimellitic acid(10.8)

a)Aqueous 2.5 mol dm^{-3} sodium hydroxide(20 ml) was used as the solvent. $Co_2(CO)_8$: 0.2 mmol; Halide: 2.0 mmol; P(CO): 2 kg cm^{-2}; 65 °C. b)Determined by GLC analysis with internal standards. c)Determined by GLC as methyl esters by esterification of acids with diazomethane.

Table 2 Carbonylation of Polyhalogenated Benzenes[a)]

Run	Starting halide	Time/h	Conv./%[b)]	Products(Yield/%)[c)]
10	*p*-Dichlorobenzene	20	100	Terephthalic acid(88.4)
11[d)]	*p*-Dichlorobenzene	20	3.8	Terephthalic acid(1.7)
12	*p*-Bromochlorobenzene	20	100	Terephthalic acid(78.9)[e)]
13	*p*-Dibromobenzene	4	100	Terephthalic acid(82.5)
14	*m*-Dichlorobenzene	20	100	Isophthalic acid(91.6)
15[d)]	*m*-Dichlorobenzene	20	50.1	Isophthalic acid(47.0)
16	*m*-Bromochlorobenzene	20	100	Isophthalic acid(91.3)
17	*m*-Dibromobenzene	2	100	Isophthalic acid(93.7)
18	*o*-Dichlorobenzene	24	100	Benzoic acid(23.5) *o*-Chlorobenzoic acid(40.4) Phthalic acid(21.7) (Chlorobenzene(7.0))[b)]
19	*o*-Bromochlorobenzene	20	98.8	Benzoic acid(13.2) *o*-Chlorobenzoic acid(40.3) Phthalic acid(24.8) (Chlorobenzene(7.0))[b)]
20	*o*-Dibromobenzene	4	98.8	Benzoic acid(57.9) Phthalic acid(31.8)
21	1,3,5-Trichlorobenzene	20	100	Trimesic acid(85.5)
22	1,3,5-Tribromobenzene	4	98.9	Trimesic acid(93.4)

a)The mixture of aqueous 4 mol dm^{-3} sodium hydroxide(12 ml) and ethanol(7.2 ml) was used as the solvent except Runs 11 and 15. See footnotes of Table 1. b) and c) See footnotes of Table 1. d)Aqueous 2.5 mol dm^{-3} sodium hydroxide(20 ml) was used as the solvent. e)*p*-Chlorobenzoic acid(11.4%) was obtained.

The conclusions to be drawn from the data in Table 1 and Table 2 are as follows.

1)Under the conditions employed, the carbonylation of much less reactive aryl chlorides can be easily achieved in high yields at meta or para position to another halogen atom or carboxyl group(Runs 1,2,4,5,10,12,14,16, and 21). In these cases, although the reduction of aryl halides was observed as the only side reaction, it was not so significant(3-8%).

2)On the contrary, the carbonylation at ortho position gives complex mixture of the products and the reduction was considerably observed(Runs 3,6,8,9,18,19, and 20). In addition, lower yields of the polycarbonylation products indicated that the carbonylation at ortho position cannot proceed easily. This fact may be attributed to the steric hindrance and the ease of dehalogenation at ortho position.[3)] This assumption can be proved by the result of Run 7 in Table 1, namely, less hindered *o*-chlorophenylacetic acid can be easily carbonylated affording homophthalic acid in high yield.

In all cases, no reaction proceeded without irradiation under these conditions. Although its initial step is not certain, the formation of charge-transfer complex, [ArX, $Co(CO)_4^-$], followed by photostimulation forming anion radical, [$ArX^{\overset{\cdot}{-}}$, $\cdot Co(CO)_4$], is most probable, as proposed by Caubere.[2)]

Finally, on detailed investigation of by-products of the carbonylation at ortho position(Runs 3 and 18-20), it was found that phthalonic acid was formed in considerable amount(10-30%). The same by-product was also formed by the carbonylation of *o*-bromobenzoic acid and *o*-iodobenzoic acid.

We have no definite information on this observation and no clear explanation of the reduction of aryl halides. These two questions are presently under intensive exploration in our laboratory and the results will be published later.

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