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COBALT CARBONYL-CATALYZED DOUBLE-CARBONYLATION OF *o*-HALOGENATED BENZOIC ACIDS UNDER PHOTOSTIMULATION

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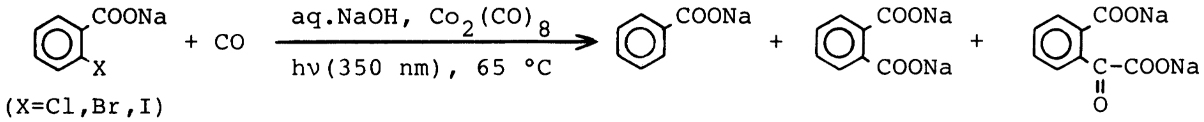
Cobalt carbonyl-catalyzed double-carbonylation of *o*-dihalobenzenes and *o*-halogenated benzoic acids, affording phthalonic acid, was observed in aqueous sodium hydroxide under photostimulation.

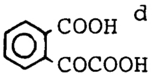
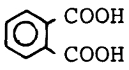
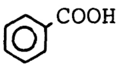
Since several years, much attention has been devoted to transition metal-catalyzed double-carbonylation of organic halides. These reactions are classified into two categories: one is the reactions catalyzed by cobalt carbonyl,1) and the other is those catalyzed by palladium species.2) However, cobalt carbonyl-catalyzed double-carbonylation of aryl halides has never been reported. In our previous publication,3) we reported that the cobalt carbonyl-catalyzed photostimulated carbonylation of aryl halides was easily achieved in aqueous sodium hydroxide at meta or para position to another halogen or carboxyl group and the reaction at ortho position did not proceed easily because of the steric hindrance and the ease of reductive dehalogenation,4) and gave a complex mixture of the products.

On detailed investigation of the by-products generated in the carbonylation at ortho position, it has been found that phthalonic acid, the double-carbonylation product, was formed in considerable amounts (Table 1).



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} NaOH (20 ml) or the mixture of aqueous 4 mol dm^{-3} NaOH (12 ml) and ethanol (7.2 ml), $Co_2(CO)_8$ (0.2 mmol), and the starting halide (2.0 mmol). The reaction mixture was heated at 65 °C under pressurized CO (2 kg cm^{-2}) with stirring. Photoirradiation was performed with a high pressure Hg lamp (500 W) placed at a distance of about 30 cm from the autoclave.

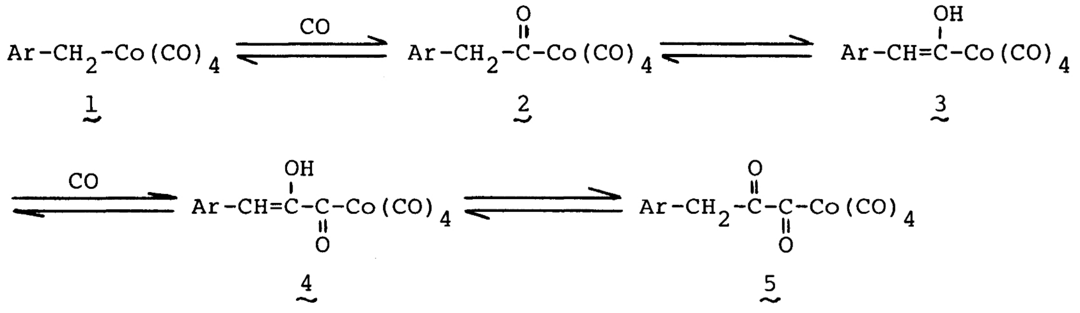
Table 1. Double-carbonylation of *o*-dihalobenzenes and *o*-halogenated benzoic acids[a]

Run	Starting halide	Time/h	Conv./%[b]	Products (Yield/%)[c]		
				 [d]		
1	*o*-Dichlorobenzene	24	100[e]	12.6	23.0	24.9
2	*o*-Bromochlorobenzene	20	98.8[e]	9.7	24.8	13.2
3	*o*-Dibromobenzene	4	98.8	12.6	31.8	54.9
4	*o*-Chlorobenzoic acid	18	83.2	29.1	34.2	11.3
5	*o*-Bromobenzoic acid	4	100	38.6	28.2	13.1
6[f]	*o*-Bromobenzoic acid	4	93.6	36.2	38.1	16.4
7[g]	*o*-Bromobenzoic acid	4	100	33.7	31.8	15.2
8	*o*-Iodobenzoic acid	4	100	28.6	32.6	32.6

a) The mixture of aqueous 4 mol dm^{-3} NaOH (20 ml) and ethanol (7.2 ml)(Runs 1-3) or aqueous 2.5 mol dm^{-3} NaOH (20 ml)(Runs 4,5, and 8) was used as the solvent. b) Determined by GLC with internal standard. c) Determined by GLC as methyl esters obtained by reaction of acids with diazomethane. d) Identified by GLC(with two different columns), IR and NMR spectroscopy, and GC-mass spectrometry with the authentic sample prepared by literature method.[5] e) *o*-Chlorobenzoic acid was obtained in 40.3%(Run 1) and 42.8%(Run 2) yields, respectively. f),g) Aqueous 2.5 mol dm^{-3} KOH (20 ml) and aqueous 2.5 mol dm^{-3} LiOH (20 ml) were used as the solvents, respectively.

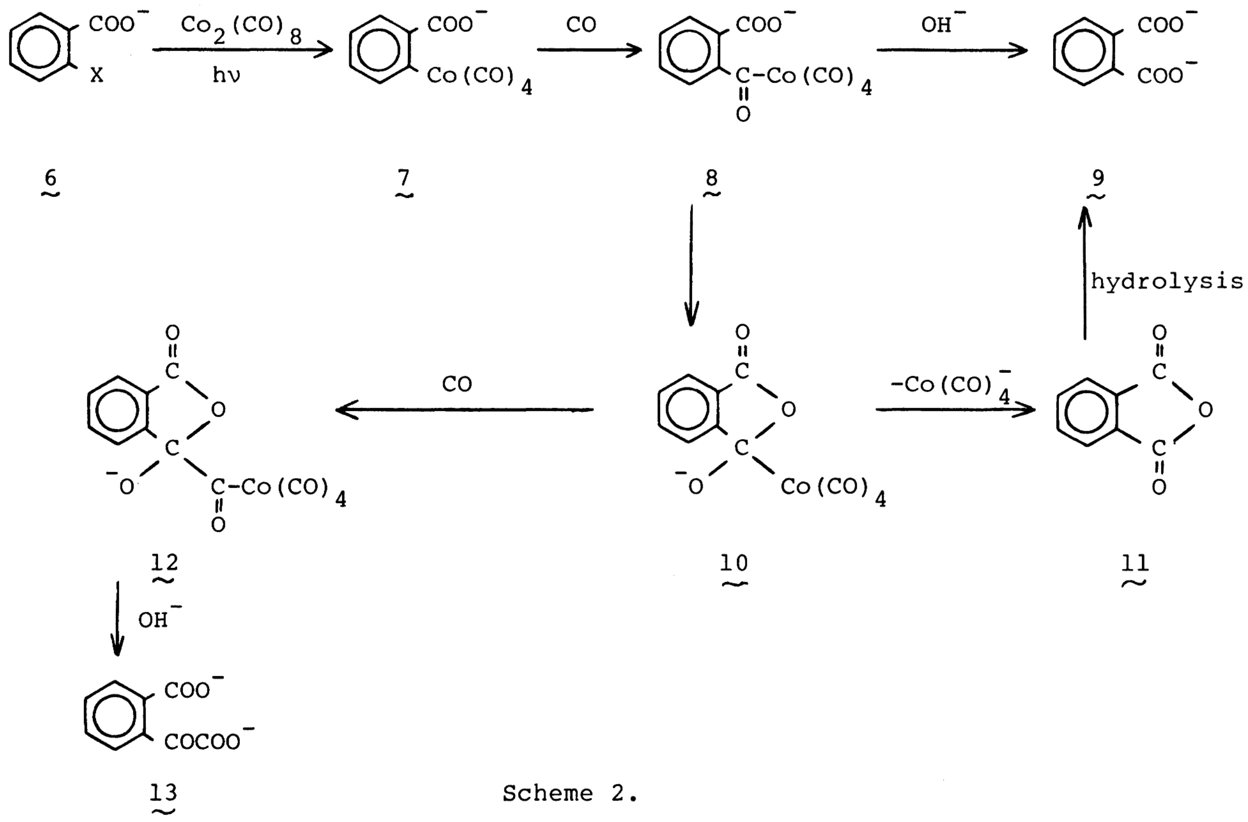
The results shown in Table 1 were obtained only in aqueous alkaline solutions (NaOH, KOH, or LiOH) and the second carboxyl group or carbonylcarboxyl group was introduced only at ortho position to the first carboxyl group. Thus it is probable that the adjacent carboxylate anion plays a key role in introduction of the second carbonyl group in aqueous alkaline solution. These reactions did not proceed under phase transfer catalysis conditions or in NaOMe/MeOH solution.[6)]

On the other hand, it has been proposed for the cobalt carbonyl-catalyzed double-carbonylation of benzyl halides that the transfromation of the acylcobalt carbonyl complex (2) into enolic form 3 is required to undergo the second CO insertion to give 4, which is in a tautomeric equilibrium with the diketo type complex 5 (Scheme 1).[7)] Mechanistic studies, recently made by Foà and his co-workers, suggested the existence of the enolic species as the intermediate 3 in the double-carbonylation.[8)]



Scheme 1.

On the basis of the information, we propose the following reaction mechanism (Scheme 2).



Scheme 2.

The aroylcobalt carbonyl complex (**8**), formed by the first CO insertion into the arylcobalt carbonyl complex (**7**), is considered to be an important intermediate. On the aroyl carbon bonded to the cobalt carbonyl moiety, the neighboring carboxylate anion makes intra-molecular nucleophilic attack forming five-membered intermediate **10** . There are two alternative routes from the complex **10** . One is the elimination of tetracarbonyl cobaltate anion to give phthalic acid (**9**) via hydrolysis of phthalic anhydride (**11**). The other is the second CO insertion (forming of **12**) followed by the nucleophilic attack of hydroxide anion to afford phthalonic acid (**13**) as the double-carbonylation product. Thus the cyclization of **8** to **10** may be the key step in driving the double-carbonylation process. Perhaps, the nucleophilic attack of the hydroxide anion on **8** may be rendered less susceptible because of the steric effect of the neighboring carboxylate anion.

Further investigations are in progress to elucidate the reaction mechanism.

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