CHEMISTRY LETTERS, pp. 851-854, 1986.

COBALT CARBONYL-CATALYZED POLYCARBONYLATION OF ARYL HALIDES IN NaOMe/MeOH UNDER PHOTOSTIMULATION

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Cobalt carbonyl-catalyzed polycarbonylation of polychlorobenzenes could be easily achieved in NaOMe/MeOH under photostimulation. Moreover, under the present conditions, the carbonylation at ortho position(to another halogen atom or carboxyl group) proceeds in high selectivity($>$84%).

There has been considerable interest in the cobalt carbonyl-catalyzed carbonylation of aryl halides.1,2) We have reported in our previous publications,3,4) that the cobalt carbonyl-catalyzed photostimulated carbonylation of aryl halides can be very easily performed at meta or para position(to another halogen atom or carboxyl group) in aqueous sodium hydroxide under mild conditions. We have also reported concurrently that the carbonylation at ortho position did not proceed so easily because of the steric effect and that reduction and double-carbonylation were observed to occur considerablly as the side reactions. In recent work,2) carbonylation at ortho position gave also an insufficient result. Although benzene polycarboxylic acids are of great industrial value, no publication has been made that the cobalt carbonyl-catalyzed carbonylation of aryl halides at ortho position proceed in good yields under mild conditions.

In this communication we wish to report that sodium methoxide-methanol system is very much efficient for the cobalt carbonyl-catalyzed photostimulated carbonylation of aryl halides, especially at ortho positions.

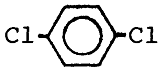
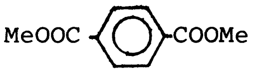
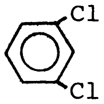
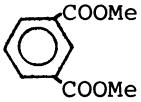
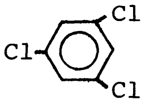
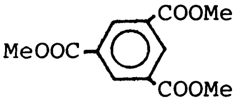
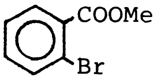
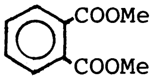
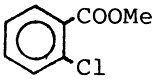
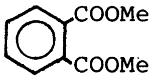
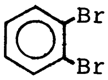
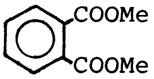
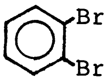
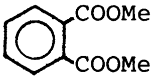
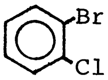
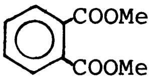
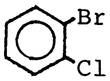
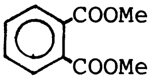
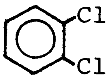
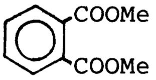
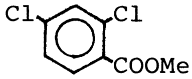
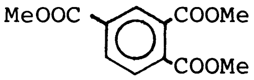
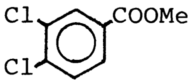
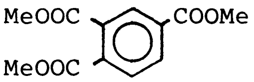
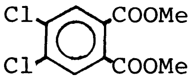
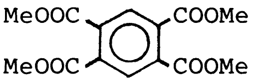
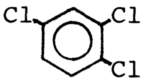
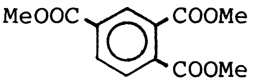
$$\underset{(X=Cl,Br)}{ArX} + CO + NaOMe \xrightarrow[h\nu(350\ nm),\ 65\ °C]{NaOMe/MeOH,\ Co_2(CO)_8,\ CO(2\ kg\ cm^{-2})} ArCOOMe + NaX$$

Experimental apparatus and procedure were the same used previously.3,4) In case where the starting halides had at least one carboxyl group, they were employed as their methyl esters because of their sparing solubility in methanol. Identification of the reaction products was performed by means of GLC, NMR spectroscopy, and GC-mass spectrometry using authentic samples as reference.

The results are listed in Table 1. From these data, the following conclusions can be made.

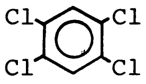
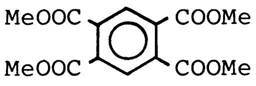
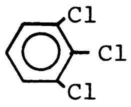
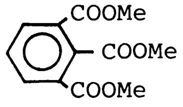
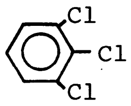
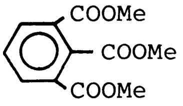
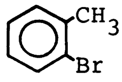
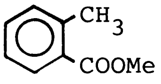
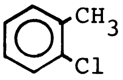
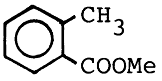
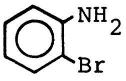
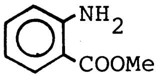
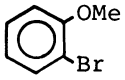
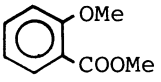
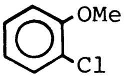
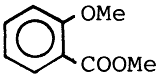
1) The carbonylation at meta or para position could be easily performed under these conditions(Runs 1-3), as well as in aqueous sodium hydroxide reported in our

Table 1. Cobalt carbonyl-catalyzed carbonylation of aryl halides in NaOMe/MeOH[a]

Run	Starting halide	Time/h[a]	Conversion/%[b]	Product (Yield/%)[c],[d]	
1		36	100		(95.4)
2		36	100		(87.8)
3		40	100		(91.1)
4		1	100		(93.2)
5		20	92.1		(84.4)
6		4	98.2		(91.1)
7[e]		4	100		(97.4)
8		45	100		(94.7)
9[e]		40	100		(97.5)
10		65	100		(93.8)
11		45	100		(85.5)
12		65	100		(87.6)
13		70	100		(85.4)
14		70	100		(85.7)

(continued)

Table 1(continued)

15		96	100		(86.5)
16		95	100		(86.7)
17$^{e)}$		92	100		(83.7)
18$^{e)}$		2	100		(99.7)
19$^{e)}$		92	61.1		(59.3)
20$^{e)}$		42	100		(75.9)
21$^{e)}$		2	100		(96.5)
22$^{e)}$		45	86.5		(80.4)

a)Reaction time is not optimized, but in complete reactions, it corresponds roughly the time for complete conversion. 1.2 mol dm^{-3} NaOMe/MeOH(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 with internal standards. c)Determined by GLC by comparison with authentic samples as methyl esters obtained by reaction of acids with diazomethane. d)The figures underlined are isolated yields. e)Reactions were carried out at room temperature(25-30 °C).

previous publication.$^{3)}$

2) The carbonylation at ortho position(to another halogen atom or carboxyl group) affording methyl esters of the corresponding benzene polycarboxylic acids could be easily achieved in high yields and in high selectivity under these conditions(Runs 4-6, 8, and 10-16).

3) The reactions were usually carried out at 65 °C, but they also proceeded quite well at room temperature(25-30 °C)(Runs 7,9, and 17).

4) As far as the leaving group is concerned, bromides were much more active than the corresponding chlorides, as well known(Runs 4, 6, 7, 18, and 21). And a relatively long reaction time was necessary for the carbonylation of much clouded chlorides(Runs 12-17).

5) The carbonylation at ortho position to some other substituents could be

also easily performed affording the corresponding ortho substituted methyl benzoates in high yields(Runs 18-22), although the carbonylation of *o*-bromonitrobenzene did not occur at all, giving nitrobenzene(21%) and *o*-nitroanisole(64%) instead of methyl *o*-nitrobenzoate.

6) The yields were generally quantitative and reduction of aryl halides, as the only side reaction, was fairly suppressed(Runs 1-10: 1-7%; Runs 11-17: 7-13%; Runs 18-22: 0-2%) compared with the results of the reactions in aqueous sodium hydroxide.[3,4]

Finally, these reactions did not proceed at all without irradiation. When the light was turned off the reaction ceased completely. Thus the reaction is photocatalytic. The reaction mechanism and even active species are still obscure, but we believe that a true S_{RN} mechanism is not likely, since the presence of free aryl radicals in methanolic solvent should result in the formation of considerable amount of reduction products. In fact, methyl *o*-iodobenzoate and methyl *o*-bromobenzoate were reduced into methyl benzoate after 4h under these conditions without cobalt carbonyl in yields of 100% and 29%, respectively. Even if radicals can be formed by irradiation, these radicals are considered to exist within a solvent cage as radical pairs, as proposed by Caubere.[1] Another possibility is the formation of cobalt complexes having methoxycarbonyl group as a ligand similar to that proposed by Foa.[2]

In conclusion, the cobalt carbonyl-catalyzed photo-carbonylation of aryl halides in methanolic solvent is considered to be a new and very effective synthetic method for methyl esters of benzene polycarboxylic acids. Further investigation and application of this catalytic system are still in progress and will be described in future publications.

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3) T. Kashimura, K. Kudo, S. Mori, and N. Sugita, Chem. Lett., 1986, 299.
4) T. Kashimura, K. Kudo, S. Mori, and N. Sugita, Chem. Lett., 1986, 483.

(Received February 17, 1986)