

THE REACTION OF ORGANIC HALIDES WITH COBALT CARBONYL

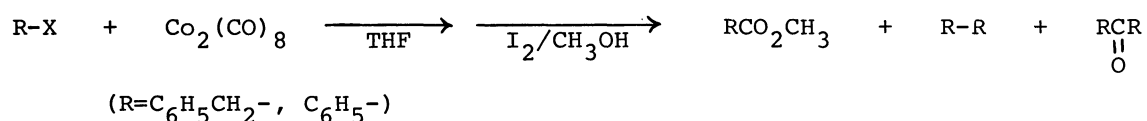
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The reaction of benzyl bromide or iodobenzene with cobalt carbonyl gave an ester and a symmetrical ketone when the reaction mixture was decomposed with iodine-methanol. The reaction between benzoyl chloride and cobalt carbonyl afforded  $C_6H_5CCO_3(CO)_9$ .

The reactions of organic halides with metal carbonyls have been extensively studied. Various useful synthetic reactions have been developed especially by the study of the reactions of organic halides with iron and nickel carbonyls.<sup>1)</sup> Little study, however, has been done on the reaction of organic halides with cobalt carbonyl,  $Co_2(CO)_8$ . Most of the known reactions are limited to those of polyhalides. For example, the reaction of  $Co_2(CO)_8$  with chloroform has been known to give  $HCCO_3(CO)_9$ <sup>2)</sup> and the reaction with iodotrifluoromethane to give  $FCCO_3(CO)_9$  (by thermal reaction) or  $F_3CCO(CO)_4$  (under UV irradiation).<sup>3)</sup> Geminal dihalides react with  $Co_2(CO)_8$  to give olefins<sup>4)</sup> and addition of carbon tetrachloride to olefins is catalyzed by  $Co_2(CO)_8$ .<sup>5)</sup>

In this paper, we wish to report the reactions of  $Co_2(CO)_8$  with simple organic halides such as benzyl bromide, iodobenzene, and benzoyl chloride.

The reactions of these organic monohalides (25 mmol) with  $Co_2(CO)_8$  (25 mmol) in tetrahydrofuran (THF) were carried out at appropriate temperatures for several hours. The reaction mixture was then decomposed with iodine-methanol to give products. The results of the reactions using iodobenzene and benzyl bromide are summarized in Table 1.



From benzyl bromide, methyl phenylacetate is obtained exclusively or predominantly at lower temperatures. These results suggest the presence of a stable acyl cobalt complex intermediate at 15°C (run 1). The acyl cobalt intermediate does not survive for a prolonged reaction period (run 2) or at higher temperatures (run 3 and 4) and decomposes to give dibenzyl ketone in a good yield (run 4). On the other hand, iodobenzene shows lower reactivity (run 5) than benzyl bromide.

It is interesting to note that iodobenzene reacts with  $Ni(CO)_4$ <sup>6)</sup> in THF to give benzil and does not react with  $Fe(CO)_5$ <sup>7)</sup> in the same solvent. In contrast, the reaction with  $Co_2(CO)_8$  is found to give benzophenone exclusively (run 6).

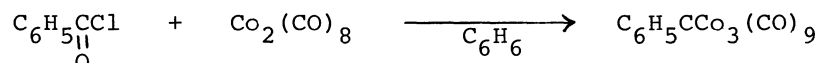
Table 1. Reaction of  $\text{Co}_2(\text{CO})_8$  with organic halides in THF\*<sup>1</sup>

Run	R-X	Temp. (°C)	Time (hr)	Product (%) * <sup>2</sup>		
				$\text{RCO}_2\text{CH}_3$	R-R	RCOR
1	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	15	8	36.9	-	-
2	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	15	24	39.6	trace	17.0
3	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	50	24	10.2	trace	45.7
4	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	70	24	-	8.7	72.0
5	$\text{C}_6\text{H}_5\text{I}$	60	20	-	-	trace
6	$\text{C}_6\text{H}_5\text{I}$	70	20	-	-	45.3

\*<sup>1</sup> At the end of the reaction, the reaction mixture was decomposed with  $\text{I}_2/\text{CH}_3\text{OH}$ .

\*<sup>2</sup> Based on organic halides used.

The reaction of benzoyl chloride (24 mmol) with  $\text{Co}_2(\text{CO})_8$  (24 mmol) was carried out at 80°C for 24 hr in benzene (80 ml). After removal of benzene, red brown crystals, isolated by column chromatography (silica gel), were recrystallized from hexane and identified to be  $\text{C}_6\text{H}_5\text{CCo}_3(\text{CO})_9$ <sup>2)</sup> (19.5%), mp 103-104°C.



It is known that the trinuclear complex is formed from the reaction of benzotrichloride with  $\text{Co}_2(\text{CO})_8$  or cobalt tetracarbonylate anion.<sup>8)</sup> Under similar conditions, the reactions of benzoyl chloride with  $\text{Fe}_3(\text{CO})_{12}$ <sup>9)</sup> and  $\text{Ni}(\text{CO})_4$ <sup>6)</sup> gave triphenyl methane and dibenzoyloxystilbene, respectively.

The unique reactivity of  $\text{Co}_2(\text{CO})_8$  shown in the present work may be useful in organic synthesis. The study of the synthetic application is now in progress.

#### References

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