

Preliminary communication

PHASE TRANSFER CATALYSIS USING COBALT TRICARBONYL NITROSYL

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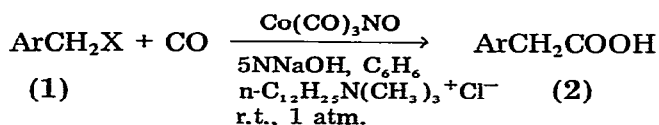
Summary

The first example of the use of a mononuclear cobalt complex in a phase-transfer catalyzed process is described. The carbonylation of halides catalyzed by cobalt tricarbonyl nitrosyl gives, depending on the organic substrate, appreciably different results as compared with dicobalt octacarbonyl.

The past five years have witnessed the development of phase-transfer catalysis as a method of considerable importance in organometallic chemistry [1]. One of the most useful phase-transfer reactions is the carbonylation of halides to carboxylic acids catalyzed by dicobalt octacarbonyl [2–4]. In several instances [2,4] an alkylated (or unalkylated) phenylpyruvic acid derivative is formed as a by-product in the carbonylation of benzylic halides. These by-products result from a novel double carbonylation reaction, the latter possibly proceeding by a mechanism involving an enol intermediate [5].

The cobalt tetracarbonyl anion is the key anionic species generated, in these reactions, from dicobalt octacarbonyl. We were interested in examining the utility of a mononuclear cobalt catalyst for the carbonylation reaction. Since nitrosyl ligands are better π -acceptors than carbonyl ligands [6,7], it seemed worthwhile to investigate the influence of a nitrosyl ligand on the phase transfer process. Consequently, cobalt tricarbonyl nitrosyl was chosen as the mononuclear cobalt catalyst.

A series of benzylic halides (1) were subjected to carbonylation at room



*E.W.R. Steacie Fellow, 1980–82.

TABLE 1

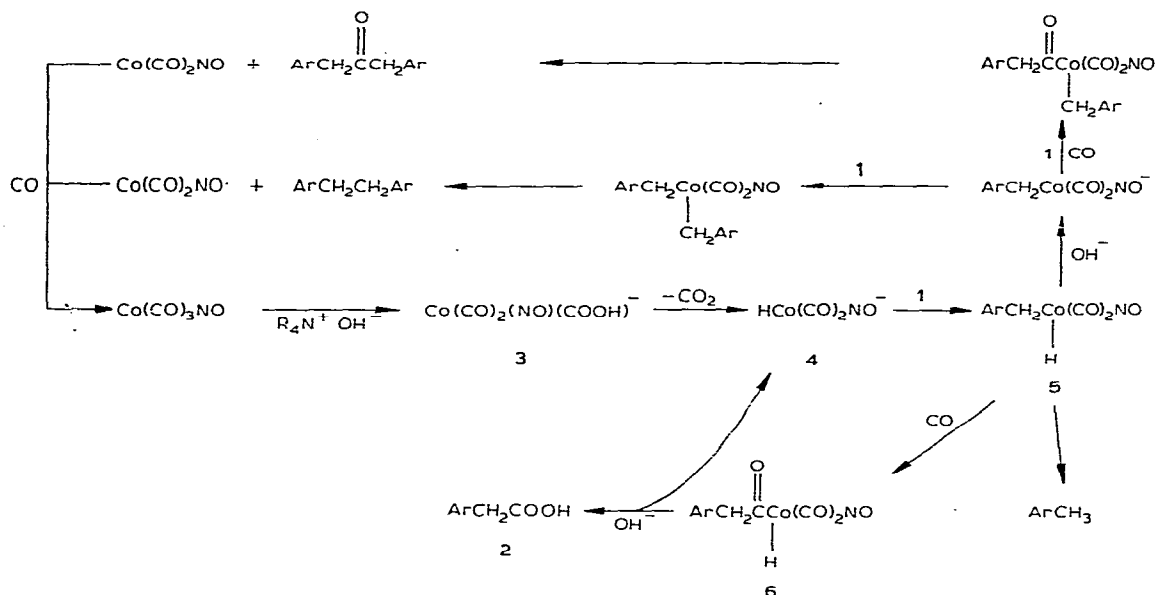
PRODUCTS OBTAINED FROM PTC CARBONYLATION OF HALIDES WITH $\text{Co}(\text{CO})_3\text{NO}$

ArCH_2X		Products ^a	Yield ^b (%)	Yield $[\text{Co}_2(\text{CO})_8]$ ^c (%)
Ar	X			
Ph	Br	PhCH ₂ COOH	58	85
		PhCH ₂ CH ₂ Ph	9	5
		(PhCH ₂) ₂ CO	7	10
		PhCHO	4	—
<i>p</i> -CNC ₆ H ₄	Br	<i>p</i> -COOHC ₆ H ₄ CH ₂ COOH	80	50
		(<i>p</i> -CNC ₆ H ₄ CH ₂) ₂ CO	2	—
		<i>p</i> -CNC ₆ H ₄ CH ₃	—	36
		(<i>p</i> -CNC ₆ H ₄ CH ₂) ₂	—	5
β -naphthyl	Br	β -C ₁₀ H ₇ CH ₂ COOH	44	64
		β -methylnaphthalene	6	9
		β -naphthaldehyde	5	—
		(β -C ₁₀ H ₇ CH ₂) ₂	—	5
		(β -C ₁₀ H ₇ CH ₂) ₂ CO	—	6
<i>o</i> -CH ₃ C ₆ H ₄	Br	<i>o</i> -CH ₃ C ₆ H ₄ CH ₂ COOH	68	30
		(<i>o</i> -CH ₃ C ₆ H ₄ CH ₂) ₂	12	7
		(<i>o</i> -CH ₃ C ₆ H ₄ CH ₂) ₂ CO	10	13
		<i>o</i> -xylene	4	5
		<i>o</i> -CH ₃ C ₆ H ₄ CHCOCOOH	—	34
		<i>o</i> -CH ₃ C ₆ H ₄ CH ₂		
<i>p</i> -CH ₃ C ₆ H ₄	Cl	<i>p</i> -CH ₃ C ₆ H ₄ CH ₂ COOH	48	52.5
		<i>p</i> -CH ₃ C ₆ H ₄ CH ₂ COCOOH	6	—
		<i>p</i> -CH ₃ C ₆ H ₄ CHCOCOOH	6	22.5
		<i>p</i> -CH ₃ C ₆ H ₄ CH ₂		

^a Products were identified on the basis of analytical and spectral data (IR, NMR, mass spectral). ^b Yields are of pure materials (not GC yields). ^c Yields of products derived from bromides are taken from ref. 2, and that of the chloride is reported in ref. 4.

temperature and atmospheric pressure of carbon monoxide, using sodium hydroxide (5 *N*), benzene, dodecyltrimethylammonium chloride as the phase transfer catalyst, and cobalt tricarbonyl nitrosyl as the metal catalyst. These reaction conditions are even applicable to *p*-methylbenzyl chloride, the latter requiring a reaction temperature of 60°C in the case of $\text{Co}_2(\text{CO})_8$ [4]. The yields of carboxylic acids (2) and reaction by-products are listed in Table 1, together with literature data obtained in the case of $\text{Co}_2(\text{CO})_8$.

Indeed, there are significant differences in the use of $\text{Co}(\text{CO})_3\text{NO}$ as a catalyst for the carbonylation reaction, compared to $\text{Co}_2(\text{CO})_8$. First, and most striking, is the failure to observe any double carbonylation with *o*-methylbenzyl bromide as reactant, and *p*-methylbenzyl chloride gave the alkylated α -keto acid in much lower yield than that observed with $\text{Co}_2(\text{CO})_8$, with an equal amount of unalkylated α -keto acid being produced as well (not observed with $\text{Co}_2(\text{CO})_8$). Second, while the yields of phenylacetic and β -naphthylacetic acids are lower for $\text{Co}(\text{CO})_3\text{NO}$ than for $\text{Co}_2(\text{CO})_8$, the carboxylic acids are produced in approximately the same [*p*-CH₃C₆H₄CH₂COOH] or significantly higher [*o*-CH₃C₆H₄CH₂COOH, *p*-COOHC₆H₄CH₂COOH] yields when methyl or cyano substituents are present on the benzene ring. Third, aldehydes were formed as low yield by-products in several instances, along with ketones and hydrocarbons (the latter by-products were previously observed with $\text{Co}_2(\text{CO})_8$).



SCHEME 1

Most of the reaction products can be accounted for by the pathway outlined in Scheme 1. Addition of hydroxide ion to a carbonyl carbon of the catalyst would give the anion 3, which on loss of carbon dioxide would afford the hydride 4. Reaction of the latter with 1 would then lead to the alkyl-metal hydride 5 (reaction of 1 with 3 is an alternate possibility). Reductive elimination would give the hydrocarbon, while reaction of 5 with CO, followed by base cleavage, would generate the acid 2 and regenerate 4. The dibenzyl and ketone by-products may also arise from 5 as depicted in the Scheme (radical intermediates are also conceivable) and the double carbonylation products obtained with *p*-methylbenzyl chloride may be formed from 6 via an enol analog of that previously proposed for the $\text{Co}_2(\text{CO})_8$ catalyzed reaction [5].

The nitrosyl ligand may be responsible for the formation of aldehydes as low yield by-products. Good analogy exists in organic chemistry for the conversion of benzyl halides or alcohols, and quaternary ammonium salts to aldehydes by nitrosobenzenes under basic conditions [8].

In conclusion, cobalt tricarbonyl nitrosyl is an effective mononuclear metal catalyst for the phase transfer catalyzed carbonylation of halides to carboxylic acids. In addition, since little or no double carbonylation is observed in these reactions, separation of the acid products from the aqueous phase is either simple or completely unnecessary.

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