Journal of Organometallic Chemistry, 134 (1977) C11–C14

Preliminary communication

PHASE-TRANSFER CATALYZED ORGANOMETALLIC CHEMISTRY. THE COBALT CARBONYL-CATALYZED CARBONYLATION OF HALIDES

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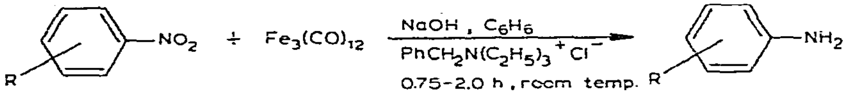
(Received March 4th, 1977)

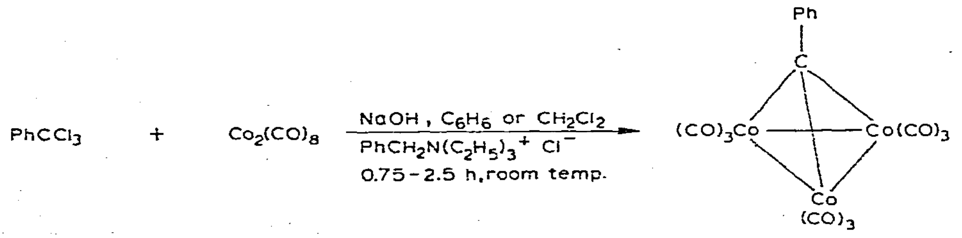
Summary

Bromides react with carbon monoxide, benzyltriethylammonium chloride, 5*N* sodium hydroxide, and a catalytic amount of dicobalt octacarbonyl in benzene, at room temperature and atmospheric pressure, to give carboxylic acids in good to excellent yields. A novel double carbon monoxide insertion occurred in one case.

Recently, we have found phase-transfer catalysis to be an exceedingly useful technique in organometallic chemistry. Metal carbonyl anions can be readily generated by this method, and used to effect stoichiometric reduction of nitroarenes to anilines (eq. 1) [1], and for synthesizing π-allyl [2], cluster (eq. 2) [2], and *ortho*-metalated complexes (eq. 3) [3].



(1)



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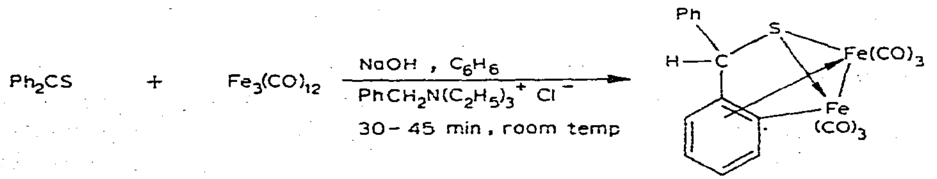
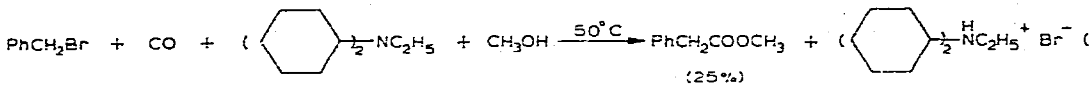


(3)

This communication reports the first example of a phase-transfer catalyzed metal carbonyl catalyzed reaction.

The cobalt carbonyl-catalyzed carbonylation of halides to carboxylic acid derivatives is a useful reaction in organic synthesis [4]. It is effected in the presence of excess base, for 1—25 hours at 0—100°C, depending on the alkylating agent (e.g. benzyl bromide, eq. 4).



(4)

The yields which have been reported have generally been based on the quantity of carbon monoxide absorbed, or by vapor-phase chromatography, rather than on the actual amount of acid derivative isolated.

The results for the phase-transfer catalyzed carbonylation of halides are listed in Table 1. These reactions were all run for 10—12 hours, at room temperature

TABLE 1

PRODUCTS OBTAINED FROM THE CARBONYLATION OF HALIDES

$ArCH_2Br$	Acid[a]	Yield[b] (%)	Neutral products[a]	Yield[b] (%)
Ar = Ph	$PhCH_2COOH$	85	$PhCH_2CH_2Ph$	5
			$(PhCH_2)_2CO$	10
Ar = *p*-CNC_6H_4	*p*-$COOHC_6H_4CH_2COOH$	50	*p*-$CNC_6H_4CH_3$	36
			p-$CNC_6H_4CH_2C_6H_4CN$-*p*	5
Ar = *o*-$CH_3C_6H_4$	*o*-$CH_3C_6H_4CH_2COOH$	30	*o*-Xylene	5
	o-$CH_3C_6H_4CHCOCOOH$	34	*o*-$CH_3C_6H_4CH_2CH_2C_6H_4CH_3$-*o*	7
	o-$CH_3C_6H_4CH_2$		$[o\text{-}CH_3C_6H_4CH_2]_2CO$	13
Ar = β-Naphthyl	β-$C_{10}H_7CH_2COOH$	64	β-Methylnaphthalene	9 (35)
			β-$C_{10}H_7CH_2CH_2C_{10}H_7$-β	5 (14)
			$(\beta\text{-}C_{10}H_7CH_2)_2CO$	6 (14)

[a] Products were identified by comparison of properties [e.g. IR, NMR (^1H, ^{13}C), mass spectrum] with those for authentic materials. All of the products are known except for the keto acid. The methyl ester (m.p. 64—65°C), 2,4-dinitrophenylhydrazone derivatives (m.p. 184°C) were also prepared and gave satisfactory analytical and spectral data. [b] Benzene used as organic phase: bracketed yields are for CH_2Cl_2 as organic phase. Yields are based on reactant halide.

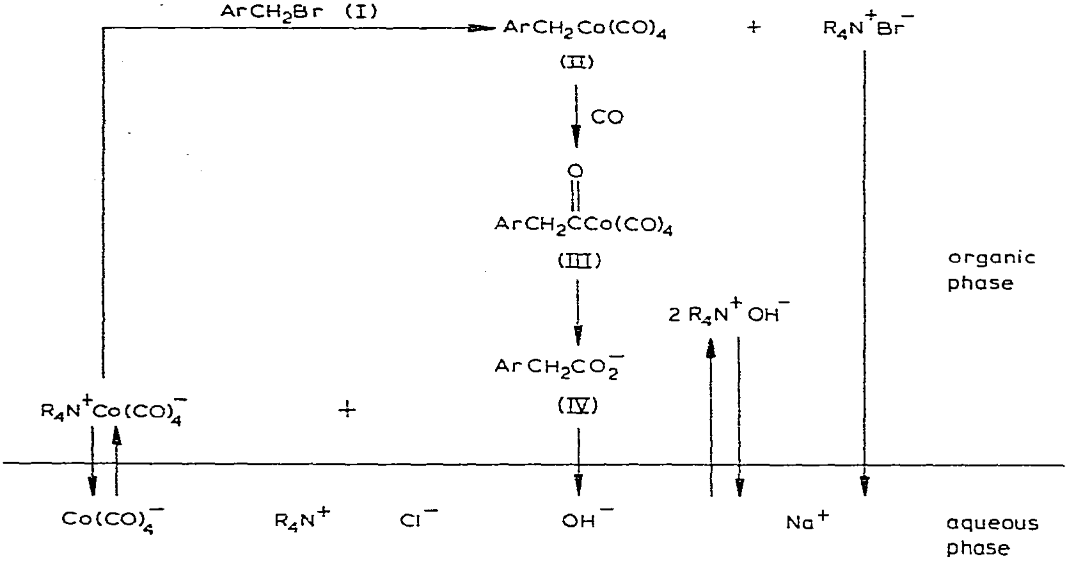
and atmospheric pressure of carbon monoxide, using a 50/1 mole ratio of halide/dicobalt octacarbonyl, 5 *N* sodium hydroxide, and benzyltriethylammonium chloride as the phase-transfer catalyst.

Phenylacetic and β-naphthylacetic acids were obtained in good yields from benzyl bromide and β-(bromomethyl)naphthalene, respectively. Hydrocarbons (resulting from debromination) and ketones were neutral by-products of these reactions. It is noteworthy that use of methylene chloride instead of benzene as the organic phase results in the formation of neutral products as the major components, with little acid being produced.

This carbonylation reaction is apparently sensitive to both inductive and steric effects. A *para*-cyano group significantly reduces the yield of acid (the nitrile function is also hydrolyzed), inhibits ketone formation, but produces a considerable amount of *p*-tolunitrile. An *ortho*-methyl group has a spectacular influence on the reaction course, since formed in good combined yields from α-bromo-*o*-xylene are the anticipated acid and the α-keto acid, the latter resulting from a formal double insertion of carbon monoxide.

The carbonylation of halides to acids can be accounted for by the pathway outlined in Scheme 1. The generation of the cobalt tetracarbonyl anion in the organic phase was previously described [2]. The $Co(CO)_4^-$ anion generated in this manner is considerably more nucleophilic than $Co(CO)_4^-$ produced by conventional methods. Reaction of the anion with the halide, I, gives II, which on ligand migration to the acyl complex (III) and subsequent clearage of the cobalt—carbon bond, would afford the carboxylate anion (IV).

SCHEME 1

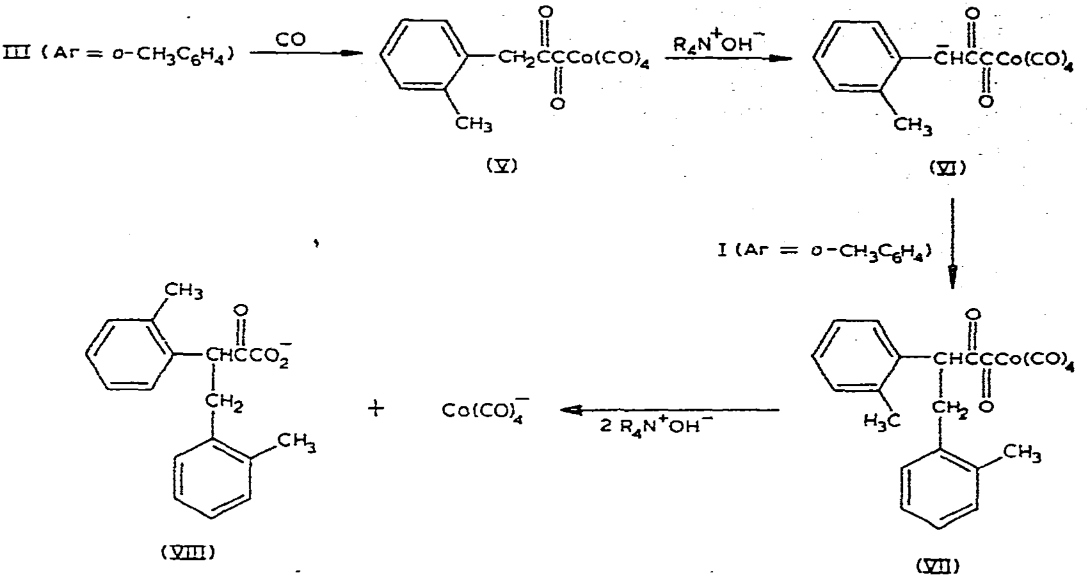


A second insertion of carbon monoxide occurs for III (Ar = o-$CH_3C_6H_4$) to give V (Scheme 2), perhaps because the electronic and steric effects of an *ortho*-methyl group renders complex III less susceptible to attack by hydroxide ion. The benzylic protons of V are more acidic than those of III, and thus hydrogen abstraction by base would afford VI. Alkylation of the latter by I would give VII, which can then undergo cleavage of the cobalt—carbon bond to form VIII, and regenerate the cobalt tetracarbonyl anion.

A manganese analog of V, $PhCH_2COCOMn(CO)_5$, has recently been prepared from $NaMn(CO)_5$ and benzylidene-1,3-dioxolan-2,4-dione in tetrahydrofuran [5].

The following general procedure was used: in a 125-ml Erlenmeyer flask were placed aqueous 5 *N* NaOH (25 ml), benzyltriethylammonium chloride (1.0 mmol), benzene (25 ml), halide (25 mmol), and dicobalt octacarbonyl (0.5 mmol). The mixture was vigorously stirred under 1 atm of CO pressure for 10—12 hours at room temperature. The solution was centrifuged, and the layers were separated. Acidification of the aqueous phase gave the carboxylic acid. The neutral products were isolated from the benzene layer.

SCHEME 2



In summary, this work has demonstrated the application of phase-transfer catalysis to the catalysis of organic reactions by metal carbonyls in good to excellent yields. In addition, the reactions occur under very mild conditions and are readily worked-up. Furthermore, phase transfer catalysis enables different kinds of reactions to occur when compared to classical methods, as witnessed by the interesting double carbon monoxide insertion reaction described above.

Acknowledgments

We are indebted to the National Research Council of Canada for support of this work.

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