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COBALT CARBONYL CATALYZED $S_{RN}1$ CARBONYLATION OF ARYL AND VINYL HALIDES BY PHASE TRANSFER CATALYSIS

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Summary : The phase transfer catalyzed, cobalt carbonyl catalyzed carbonylation (1 atm. P.) of aryl and vinyl bromides under photostimulation (350 nm) affords the corresponding unsaturated acids in high yield.

Recent investigations have demonstrated that phase transfer catalysis is a useful technique in organometallic chemistry[1]. Thus, an efficient cobalt carbonyl catalyzed carbonylation of benzyl halides has been reported[2].

However, although it has been claimed[2a] that $CoCO_4^-$ anions generated from Co_2CO_8 by the phase transfer process were considerably more nucleophilic than $CoCO_4^-$ produced by conventional methods, cobalt catalyzed carbonylation of aryl halides has never been reported[3]. In such reactions, the problem arises, as usual, from the low reactivity of unactivated aryl halides toward nucleophilic substitutions. It is well established since the works of Bunnett and coll.[4] that this difficulty may be circumvented, for numerous aryl halides, under $S_{RN}1$ conditions.

On the other hand, we have recently investigated[5] the mechanism of the carbonylation of aryl halides by CoCRACO[6] (NaH-Am^{t}ONa-Co(OAc)$_2$-CO) at atmospheric pressure in aprotic media. During this study, we demonstrated, for the first time, that in the presence of sodium alkoxides, $NaCoCO_4$ is a very efficient catalyst for the photostimulated $S_{RN}1$ carbonylation of aryl halides under atmospheric pressure[5].

Thus, it could be conjectured that under UV irradiation, $S_{RN}1$ carbonylation of aryl halides could be performed under phase transfer catalysis conditions.

This communication reports the first examples of phase transfer catalyzed, cobalt carbonyl catalyzed carbonylation of aryl and vinyl bromides under photostimulation.

Preliminary experiments indicated that benzyltriethylammonium chloride, the phase transfer agent often used for the carbonylation of benzyl halides[2], was not convenient in performing photostimulated reactions. Indeed, in our experimental conditions (vide infra) the only reaction we observed was the carbonylation of the ammonium salt to phenylacetic acid. This observation must be related to the very recent discovery[7] of the carbonylation of benzyltriethylammonium chloride with acetylcobalt carbonyl (from CH_3I, Co_2CO_8 and CO under phase transfer conditions).

On the contrary, tetrabutylammonium bromide was found to be efficient in performing the carbonylation of aryl halides according to the scheme :

$$\text{ArX} + \text{CO} + 2\ \text{NaOH} \xrightarrow[h\nu\ (350\ \text{nm})]{\text{NaOH aqueous benzene, } Co_2CO_8,\ Bu_4\overset{+}{N}\ Br^-} \text{ArCOONa} + \text{NaX} + H_2O$$

Reactions were carried out by simple stirring of the reaction mixture (aryl halide : 20 mmoles, C_6H_6 : 25 ml, 5N NaOH : 50 ml, $Bu_4N^+\ Br^-$: 2 mmoles, Co_2CO_8 : 1 mmole, under a slow stream of carbon monoxide) in a Pyrex flask irradiated by 350 nm ultraviolet lamps in a Rayonet photochemical reactor. Heating was achieved by means of a 100 W tungsten lamp placed under the reaction flask[8].

The results for the phase transfer catalyzed carbonylation of aryl halides are listed in Table I.

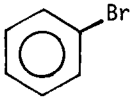
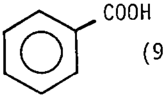
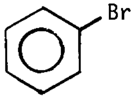
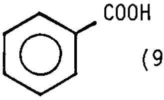
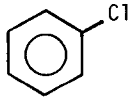
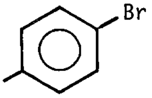
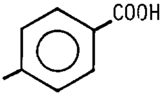
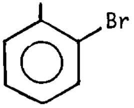
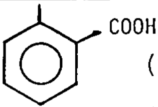
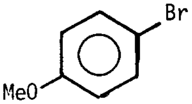
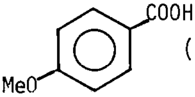
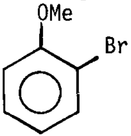
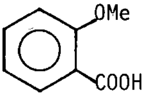
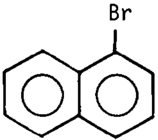
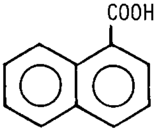
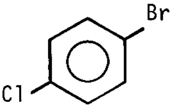
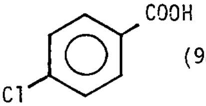
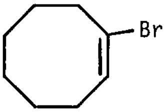
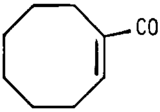
From these data, it may be concluded that aryl bromides are very easily carbonylated under the conditions used. The yields are generally quantitative and the reactions are highly catalytic toward cobalt. The only observed side reaction (reduction of the aryl halide) was never significant except for ortho bromoanisole. We have no clear explanation of this observation.

Curiously, in the conditions used, carbonylation did not occur with chlorobenzene. This lack of reactivity has been used for the selective carbonylation of parachlorobromobenzene to parachlorobenzoïc acid. It must be emphasized that during classical $S_{RN}1$ reactions performed with dihalobenzenes, selective mono substitutions are not possible[4].

Finally, we succeeded in extending our reaction conditions to the carbonylation of vinyl bromides as may be seen from the results obtained with 1-bromo cyclooctene and β bromostyrene.

In conclusion, photostimulated catalytic carbonylation of aryl and vinyl bromides by phase transfer catalysis at atmospheric pressure constitutes a new and very interesting

TABLE I - Cobalt carbonyl catalyzed carbonylation of aryl and vinyl halides (a)(b)

Halide	Reaction temperature	Reaction time (b)	Unreacted halide (c)	Acid (yield %) (d)
	65°C	1.5 h	3 %	 (95)
	32°C	12 h	-	 (97)
	65°C	13 h	100 %	-
	65°C	1.5 h	2 %	 (97)
	65°C	2.25 h	3 %	 (96)
	65°C	2 h	3 %	 (94)
	65°C	2 h	3 %	 (47) (e)
	65°C	5 h	3 %	 (96)
	65°C	1 h	-	 (98)
	65°C	5 h	-	 (98)
C_6H_5-CH=CHBr	65°C	8 h	35 %	C_6H_5-CH=CH-COOH (62)

(a) The relative proportions of the reactants are given in the text ; (b) Reaction times were not optimized. Indeed, it may be thought from lit. data[9] that more efficient stirring would result in shorter reaction times ; (c) Determined by GLC analysis with internal standards ; (d) Isolated yields based on aryl halide. Products were identified by comparison of their physical and spectroscopic properties with those of reference samples ; (e) Anisole was produced in 45 % yield, as indicated by GLC analysis with internal standards.

synthesis of unsaturated acids. Extension to other halides as well as to other metal carbonyls are presently under intensive exploration in our laboratory and will be published later.

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8) In the absence of the 350 nm ultraviolet lamps, heating with the 100 W tungsten lamp slowly promoted carbonylations. On the contrary when heating was achieved with an oil bath, no carbonylation occurred. Thus, it must be concluded that these reactions could also be stimulated by visible radiation, an observation which is under an investigation in our laboratory.

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