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HASE-TRANSFER CATALYSIS IN COBALT CATALYZED CARBONYLAION OF SECONDARY BENZYL HALIDES

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ummary

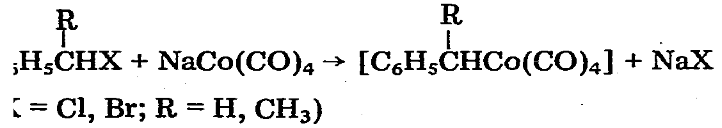
Application of the phase-transfer technique to the cobalt carbonyl-catalyzed rbonylation of secondary benzyl halides gives either monocarbonyl and ouble carbonyl insertion or coupling of organic halides as the major reaction, epending on the experimental conditions. Alcohols or ethers mainly give salts f carboxylic acids. Use of higher pressures of CO association with a hydrorbon organic phase, favours coupling rather than carbonylation. A possible action mechanism is discussed.

troduction

Some examples of transition metal-catalyzed carbonylation of organic lides under phase-transfer conditions have been reported recently [1]. The chnique combines the advantages of homogeneous and heterogeneous talysis, the acids formed being continuously extracted by aqueous alkaline ase and removed from the catalyst containing organic phase [2]. We have ow applied this technique to the cobalt-catalyzed carbonylation of secondary nzyl halides with the aim of obtaining better yields and selectivities than ose obtained from carbonylation under homogeneous conditions [3].

esults and discussion

To get more information about reactivity of secondary benzyl halides in e carbonylation we first obtained some kinetic data, for the reaction between $aCo(CO)_4$ and either α-chloro- or α-bromo-phenylethane (eq. 1). Oxidative ldition of organic halides to cobaltate is of course, a fundamental step in the talytic cycle.



$$\mathrm{{}_5H_5\overset{\overset{R}{|}}{C}HX + NaCo(CO)_4 \rightarrow [C_6H_5\overset{\overset{R}{|}}{C}HCo(CO)_4] + NaX} \qquad (1)$$

= Cl, Br; R = H, CH_3)

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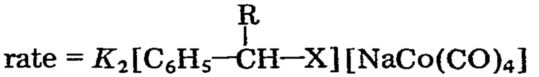
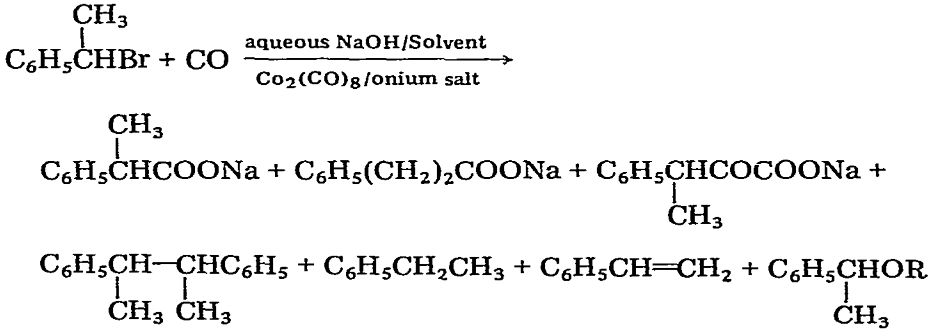
We compared the results with those previously obtained for the analogous reaction of benzyl chloride [4]. As in that earlier study, the reaction was monitored by the disappearance of the infrared band of $NaCo(CO)_4$ and was shown to be first order in each of the two reactants (eq. 2).



$$\text{rate} = K_2[C_6H_5{-}\overset{\displaystyle R}{\overset{|}{C}}H{-}X][NaCo(CO)_4] \qquad (2)$$

The K_2 values obtained in various solvents are listed in Table 1. The data in Table 1 show that α-chlorophenylethane is at least one order of magnitude less reactive than benzylchloride, as expected for an S_N2 mechanism. Alcohols of low polarity and poor cation coordinating solvents are the most effective reaction media, once more confirming the great importance of assistance to the leaving group by the protic solvents and by the cation associated with the cobaltate anion. Finally α-bromophenylethane at 21°C and benzyl chloride at 50°C in t-amyl alcohol show reactivities of the same order of magnitude.

The results of this preliminary study indicated that it should be possible to carry out the carbonylation of secondary benzylbromides under phase transfer conditions at room temperature using alcohols or ethers as organic phases (see below). Analysis of the product mixture from the cobalt-catalyzed carbonylation of α-bromophenylethane under phase-transfer conditions revealed a complex constitution, as shown by eq. 3.



$$C_6H_5\overset{\displaystyle CH_3}{\overset{|}{C}}HBr + CO \xrightarrow[Co_2(CO)_8/\text{onium salt}]{\text{aqueous NaOH/Solvent}}$$

$$C_6H_5\overset{\displaystyle CH_3}{\overset{|}{C}}HCOONa + C_6H_5(CH_2)_2COONa + C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCOCOONa + \qquad (3)$$

$$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HC_6H_5 + C_6H_5CH_2CH_3 + C_6H_5CH{=}CH_2 + C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HOR$$

(R = H, alkyl group)

TABLE 1

K_2 VALUES (eq. 2) OBTAINED IN VARIOUS SOLVENT [a]

Solvent	R	X	$K_2 \times 10^3$ [b] (M^{-1} sec^{-1})	R	X	$K_2 \times 10^3$ [4] [b] (M^{-1} sec^{-1})
t-Amyl alcohol	CH_3	Cl	1.60	H	Cl	22.4
2-Pentanol	CH_3	Cl	0.40	H	Cl	12.8
Cyclohexanol	CH_3	Cl	0.17	H	Cl	11.4
Isopropyl ether	CH_3	Cl	0.72	H	Cl	11.1
t-Butyl methyl ether	CH_3	Cl	0.47	—	—	—
Tetrahydrofuran	CH_3	Cl	~0	H	Cl	0.42
N,N-Dimethylformamide	CH_3	Cl	0	H	Cl	0.01
t-Amyl alcohol	CH_3	Br	5.1 [c]	—	—	—

[a] All the experiments were run under N_2 using $[NaCo(CO)_4]$ 0.025 — 0.03 *M* and $[C_6H_5CHRX]$ 0.3 — 0.55 *M*. The same K_2 values (±10%) were obtained under second order conditions. [b] *T* 50°C. [c] *T* 21°C.

At least three acids were obtained, α- and β-phenylpropionic acids, and α-keto-β-phenylbutyric acid, the last formed by double CO insertion. 2,3-Diphenylbutane, ethylbenzene, styrene, α-phenylethanol or α-phenylethyl ethers, (the last named when an alcohol is used as organic phase) are the components of the neutral fraction.

In addition to the CO pressure and the temperature, the nature of solvents, the type of ammonium salt and the concentration of inorganic base, strongly affect the reaction. Either acids or coupling products can be obtained as main products of the catalytic reaction depending on experimental conditions.

Monocarbonylation

Formation of acids was the main reaction when alcohols and ethers were used as organic phase. In order to obtain α-phenylpropionic acid in the highest yield and selectivity we carried out the carbonylation of α-bromophenylethane under phase-transfer conditions in several alcohols and ethers and in presence of some ammonium salts. The most important results are summarized in Table 2. With the system n-butanol/50% aqueous KOH, in the presence of ammonium salts such as phenyltrimethylammonium iodide and bromide or α-phenylethyltrimethylammonium iodide, α-phenylpropionic acid was selectively obtained in good yields (entries 1, 2). Comparable results were obtained when α-chlorophenylethane was used (entry 6). Benzyltrimethylammonium chloride also proved to be effective but it was carbonylated to phenylacetic acid under the conditions used [5]. With t-amyl alcohol the selectivity was slightly lower (entries 8,10), and became unsatisfactory at lower temperatures (entry 11). The yield and/or selectivity were lower when we used α-phenylethanol, n-amyl alcohol (entries 15, 16), and other alcohols not shown in the Table, such as isobutyl, s-butyl and isopropyl alcohol and cyclohexanol.

Less satisfactory yields were obtained when ethers, such as diphenyl and t-butyl methyl ether, were used (entries 17, 18). It is important to point out that the reaction also occurred in the absence of ammonium salts, but under these conditions, more β-phenylpropionic acid was formed (entries 4, 5, 9, 12, 21).

α-Arylpropionic acids were selectively formed also from derivatives bearing electron-withdrawing or electron-releasing groups on the aromatic ring. Results are reported in Table 3. The reaction could also be successfully applied to the synthesis of antiphlogistic compounds as shown by the last two examples shown in the Table.

A possible reaction mechanism is indicated in Scheme 1. Oxidative addition of the secondary benzyl halides to tetracarbonylcobaltate anion gives a branched alkylcobalt complex. This complex is in equilibrium with the corresponding branched acylcobalt complex; it also can isomerize to the linear one via β-hydrogen elimination and α-addition to the resulting coordinated olefin [6]. The main role of the ammonium compound is to facilitate the nucleophilic attack on the branched acyl complex to form the α-arylpropionic acid, thus preventing or curtailing isomerization. In absence of the ammonium salt the base concentration in the organic phase is sufficient to transform $Co_2(CO)_8$ into $Co(CO)_4^-$, but it is not enough for a fast attack on the acyl complex, and so isomerization of secondary to primary alkyl group becomes competitive.

TABLE 2 [a]

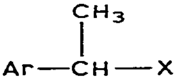
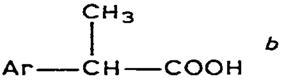
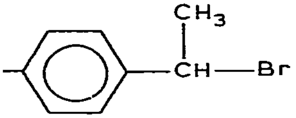
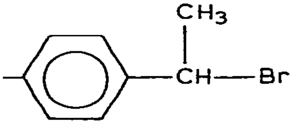
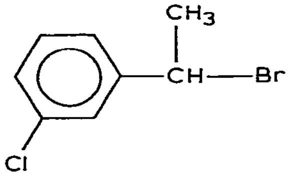
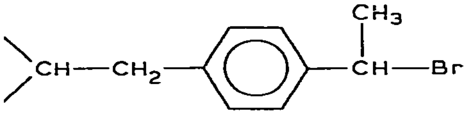
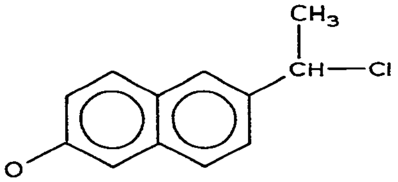
CARBONYLATION OF α-BROMOPHENYLETHANE UNDER PHASE-TRANSFER CONDITIONS

Entry	Solvent	Ammonium salt	Base	$C_6H_5CH(CH_3)COOH$ (Yield (%)) [b]	$C_6H_5(CH_2)_2COOH$ (Yield (%)) [b]
1	n-Butanol	$C_6H_5N(CH_3)_3Br$	50% KOH	55	—
2	n-Butanol	$C_6H_5CH(CH_3)N(CH_3)_3I$	50% KOH	55	—
3	n-Butanol	$C_6H_5CH(CH_3)N(CH_3)_3I$	40% NaOH	48	—
4	n-Butanol	—	40% NaOH	47	3
5	n-Butanol	—	50% KOH	49	3
6 [c]	n-Butanol	$C_6H_5N(CH_3)_3Br$	50% KOH	58	1
7	t-Amyl alcohol	$C_6H_5CH(CH_3)N(CH_3)_3I$	50% KOH	45	—
8	t-Amyl alcohol	$C_6H_5CH(CH_3)N(CH_3)_3I$	40% NaOH	56	2
9	t-Amyl alcohol	—	40% NaOH	43	12
10	t-Amyl alcohol	$C_6H_5N(CH_3)_3I$	50% KOH	61	5
11 [d]	t-Amyl alcohol	$C_6H_5N(CH_3)_3I$	50% KOH	51	15
12	t-Amyl alcohol	—	50% KOH	51	8
13	t-Amyl alcohol	$C_6H_5CH_2N(CH_3)_3Cl$	40% NaOH	55	—
14	t-Amyl alcohol	$(C_4H_9)_4NBr$	40% NaOH	39	8
15	α-Phenylethanol	$C_6H_5CH(CH_3)N(CH_3)_3I$	50% KOH	39	—
16	n-Amyl alcohol	$C_6H_5N(CH_3)_3I$	50% KOH	41	4
17	Diphenyl ether	$C_6H_5N(CH_3)_3Br$	50% KOH	40	2
18	t-Butyl methyl ether	$C_6H_5CH(CH_3)N(CH_3)_3I$	50% KOH	40	1
19	t-Butyl methyl ether	$C_6H_5CH_2N(CH_3)_3Cl$	50% KOH	42	—
20	t-Butyl methyl ether	$(C_4H_9)_4NBr$	50% KOH	3	0.5
21	t-Butyl methyl ether	—	50% KOH	50	7

[a] Unless otherwise indicated all the experiments were run at 35°C under atmospheric pressure of CO for 4 h using $C_6H_5CH(CH_3)Br$ as starting material and $Co_2(CO)_8$ as catalyst in the ratio $C_6H_5CH(CH_3)Br/Co_2(CO)_8$ 20—40. [b] The yields are based on the organic halide introduced. Most of the remaining product consisted of styrene and 2,3-diphenylbutane, α-phenylethyl butyl ether is also present (entries 1—6). [c] Starting material $C_6H_5CH(CH_3)Cl$; T 45°C; reaction time 24 h. [d] T 20°C.

3[a]

ATION OF α-ARYLPROPIONIC ACIDS

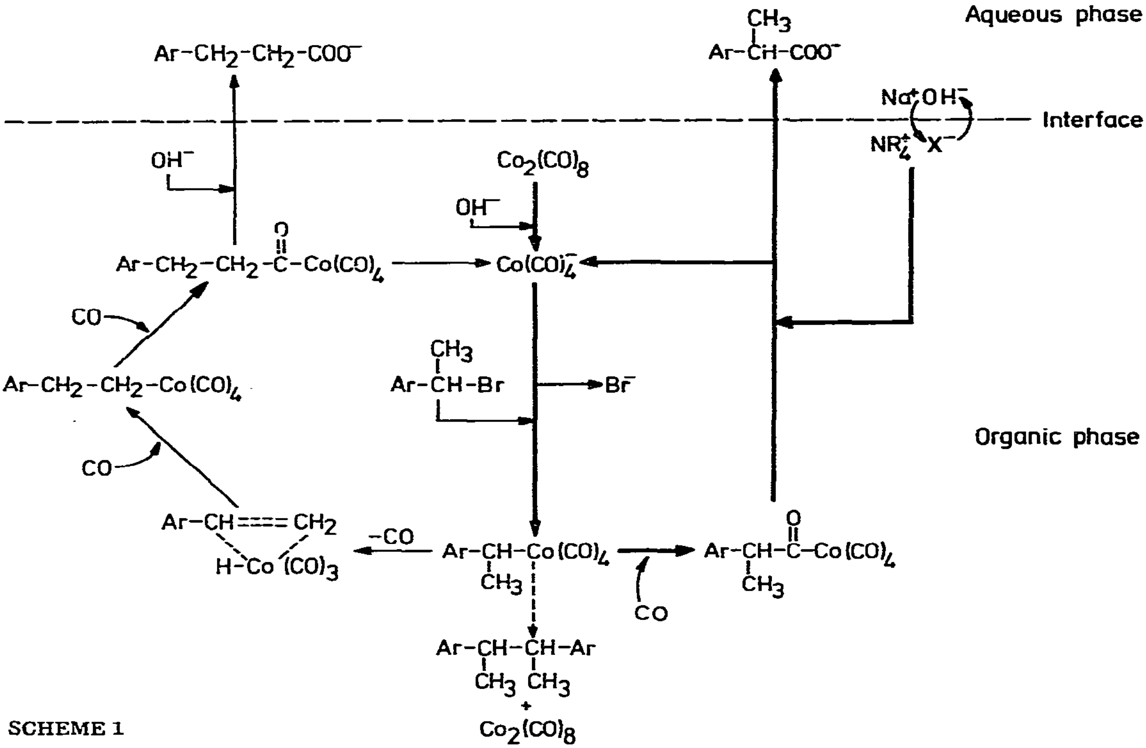
 $Ar-CH(CH_3)-X$	 $Ar-CH(CH_3)-COOH$ [b] (Yield (%))
	47
	49[c]
	40
	54
	35

s otherwise indicated, all the experiments were run in n-butanol/50% KOH in the presence of
$(CH_3)_3Br$ at 35°C; P(CO) 1 atm; $ArCH(CH_3)X/Co_2(CO)_8$ 20—40. [b] The yields based on the intro-
organic halide were not optimized. Most of the remaining product consists of $ArCH{=}CH_2$,
$CH_3)CH(CH_3)Ar$ and $ArCH(CH_3)OC_4H_9$. [c] $C_6H_5CH(CH_3)N(CH_3)_3I$ was used as ammonium salt.

upling and dehydrohalogenation products are formed in secondary reac-
. The coupling reaction is discussed in detail below. To simplify the Scheme
rmation of dehydrohalogenated product (styrene) is not included. This
duct can be formed by two routes: base-induced HX elimination from the
ic halide and β-hydrogen abstraction from the alkylcobalt complex.

le carbonylation

ien carbonylation of α-bromophenylethane was carried out in the two



SCHEME 1

phase system t-amyl alcohol/20% aqueous NaOH, double CO insertion was observed, and under particular conditions the α-ketoacid $C_6H_5CH(CH_3)COCOOH$ became the main component of the acid fraction (Table 4). No example of double CO insertion [10,7] in carbonylation of secondary benzyl halides has been previously reported. The ketoacid was obtained in the highest yield at 35°C under 2 atm of CO in presence of α-phenylethyltrimethylammonium iodide (entry 1). It is noteworthy that this acid was also present, although to a smaller extent, when the reaction was carried out at atmospheric pressure and in absence of ammonium salts (entries 4, 6, 7). According to the mechanism proposed by Cassar [2] the possibility of double CO insertion is related to enolization of the intermediate acyl complex. Scheme 2 summarizes the equilibria which could be involved.

Mobility of the benzylic hydrogen is a necessary requisite for enolization and consequently for formation of ketoacid; in fact no CO insertion into the linear acyl complex was observed. Since better yields of ketoacid are obtained when the ammonium salt is present, it is possible that the latter facilitates enolization by stabilizing the enolate anion. In absence of the ammonium salt the enolization occurs to a smaller extent and the double CO insertion is so slow that isomerization to the linear acyl complex becomes competitive before monocarbonylation takes place. Upon increasing the reaction temperature or replacing t-amyl alcohol by n-butanol, the attack of OH^- on the acyl complex is too fast, and the double CO insertion is reduced or prevented (entries 2, 5). It should also be noted that a more efficient OH^- transfer in the organic phase can also result in increase of by-products such as styrene (entries 1, 4 and 6, 7).

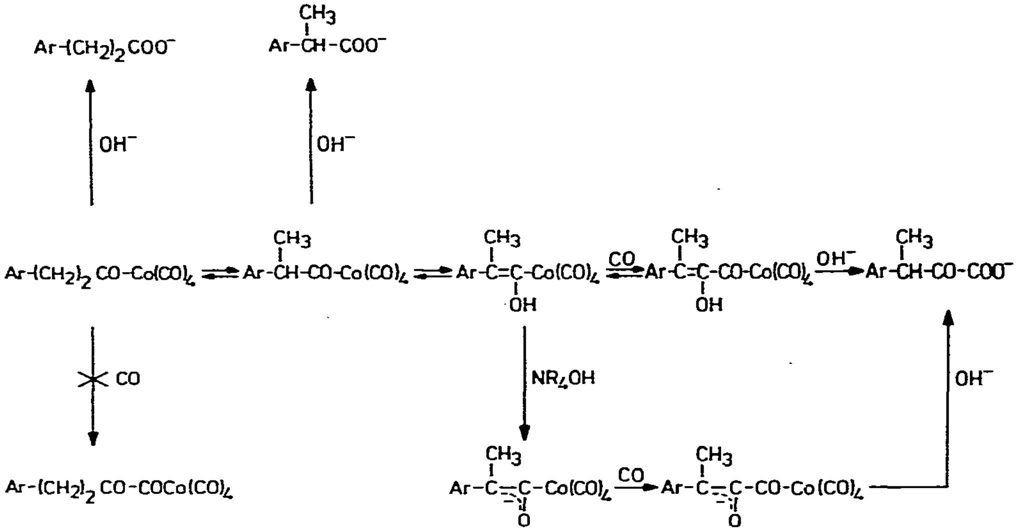
TABLE 4

DOUBLE CARBONYLATION IN TWO PHASE SYSTEMS [a,b]

Entry	Temperature (°C)	P (atm)	$C_6H_5\overset{CH_3}{\overset{\vert}{C}}HCOOH$ (Yield (%))	$C_6H_5(CH_2)_2COOH$ (Yield (%))	$C_6H_5\overset{CH_3}{\overset{\vert}{C}}HCOCOOH$ (Yield (%))	$C_6H_5CH{=}CH_2$ (Yield (%))	$(C_6H_5{-}\overset{CH_3}{\overset{\vert}{C}}H)_2$ (Yield (%))	$C_6H_5\overset{CH_3}{\overset{\vert}{C}}HOH$ (Yield (%))
1	35	2	10.0	1.3	55.0	20	6	4.2
2	45	2	35.6	1.8	7.7	30	8	12
3	25	2	13.5	2.2	41.4	15	20	5
4 [c]	35	2	19.0	15.0	45.2	5.5	8	6
5 [d]	35	2	57.0	8.0	traces	12.5	4.5	4.1
6	35	1	28.4	2.5	27.5	25	7	6.5
7 [c]	35	1	31.4	23.4	10.7	13	11	7.5

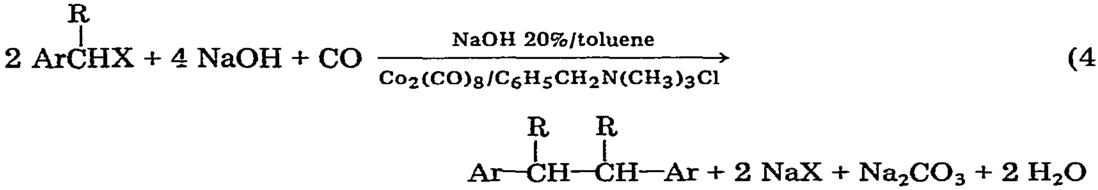
[a] $C_6H_5CH(CH_3)Br$ was used as starting material and $Co_2(CO)_8$ as catalyst in the ratio $C_6H_5CH(CH_3)Br/Co_2(CO)_8$ 20—40; the reaction time was 8 h; unless otherwise indicated, the reactions were carried out in the system t-amyl alcohol/20% aqueous NaOH in the presence of $C_6H_5CH(CH_3)N(CH_3)_3I$. [b] The yields are based on the organic halide introduced. [c] No ammonium salt was used. [d] n-Butanol was used as organic phase, $C_6H_5CH(CH_3)OC_4H_9$ was also present (9.3%).

SCHEME 2



Coupling reactions

The coupling reaction predominated when carbonylation was carried out in the two phase system, aromatic hydrocarbon/aqueous NaOH (eq. 4).



$$2\,\mathrm{Ar}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{HX} + 4\,\mathrm{NaOH} + \mathrm{CO} \xrightarrow[\mathrm{Co_2(CO)_8/C_6H_5CH_2N(CH_3)_3Cl}]{\mathrm{NaOH\ 20\%/toluene}} \mathrm{Ar{-}}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}Ar} + 2\,\mathrm{NaX} + \mathrm{Na_2CO_3} + 2\,\mathrm{H_2O} \qquad (4)$$

($R = CH_3, C_2H_5, C_6H_5$)

Dehalogenation products $ArCH_2R$ were also present in the product mixture.

TABLE 5

COUPLING REACTIONS OF SOME SECONDARY BENZYL HALIDES

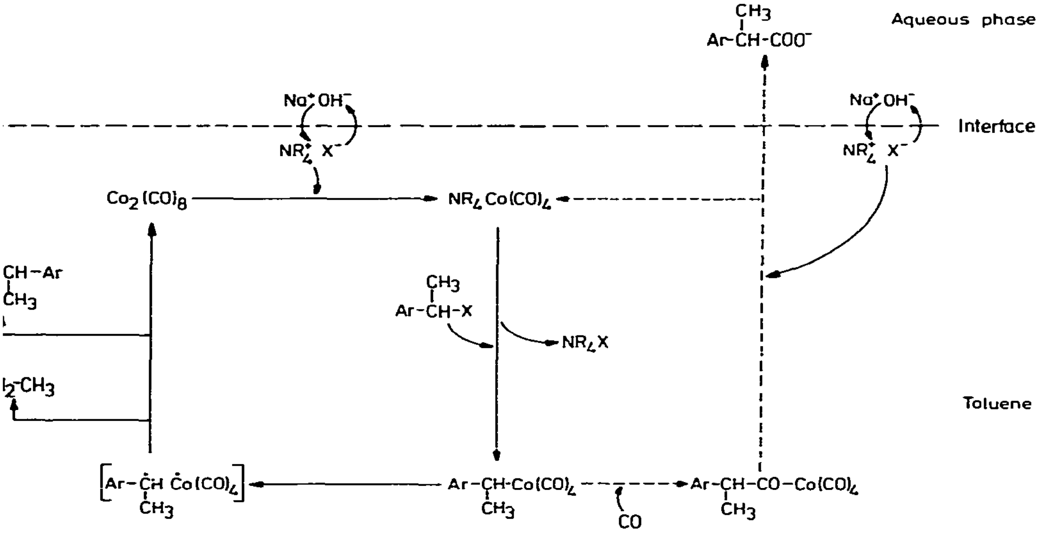
ArCHRX	P(CO) (atm)	T (°C)	$\mathrm{Ar}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{HAr}$ (Yield %) [a]
$C_6H_5CH(CH_3)Br$	5	30	81
$C_6H_5CH(CH_3)Br$	1	30	30 [b]
$C_6H_5CH(CH_3)Br$	5	30	3 [c]
p-$CH_3C_6H_4CH(CH_3)Br$	5	35	60
m-$ClC_6H_4CH(CH_3)Br$	5	35	30 [d]
$C_6H_5CH(C_2H_5)Br$	5	35	20 [e]
$C_6H_5CH(C_6H_5)Br$	1	10	76
$C_6H_5CH(C_6H_5)Cl$	1	45	94

[a] The yields are based on the organic halide introduced. [b] Most of the remaining product consisted of styrene and α-phenylpropionic acid. [c] No ammonium salt was added. The starting material was recovered. α-Phenylethanol was the main product. [d] About 50% of the starting material was converted into m-$ClC_6H_4CH_2CH_3$ and m-$ClC_6H_4CH{=}CH_2$. [e] Phenylpropenes were the main products.

results obtained in the coupling reactions of some secondary benzyl les are summarized in Table 5. The reaction was promoted by raising the ressure; the best yield of 2,3-diphenylbutane was obtained under 5 spheres of CO.

is important to note that virtually no coupling reaction occurred in the nce of ammonium salts. As shown in Table 5, yields are also affected by resence of substituents on the aromatic ring and on the benzylic carbon. lectron-withdrawing group on the aromatic ring strongly reduced the formation of the coupling product and increased that of the dehalogenation uct.

e unfavourable effect of the ethyl group on the benzylic carbon is related eric hindrance by this group, and is in accord with the S_N2 mechanism osed for the interaction between $Co(CO)_4^-$ and the secondary benzyl le. The opposite effect of the phenyl group can be explained by a change echanism from S_N2 to S_N1. The reactions probably involved in the ytic cycle are shown in Scheme 3. The main role of the ammonium salt



ME 3

ists of inducing the conversion of $Co_2(CO)_8$ to $Co(CO)_4^-$ and keeping the yst in the organic phase. The oxidative addition of the secondary benzyl e to $NR_4Co(CO)_4$ forms the intermediate alkylcobaltcarbonyl. Under the itions used the homolytic cleavage of this complex is the main reaction robably proceeds through a geminate radical pair [8]. The benzyl radical limerize or abstract hydrogen from the medium; coupling and dehalogenaproducts, respectively, are formed and $Co_2(CO)_8$ is regenerated. In this phase system formation of acids generally occurs only to a small extent, ing that the homolytic cleavage of the alkylcobalt complex is much faster its transformation into the acylcobalt complex.

nversion of $Co_2(CO)_8$ to $Co(CO)_4^-$ under phase transfer conditions in CO sphere was reported to occur as indicated in eq. 5 [9].

$$O)_8 + CO + 4\,OH^- \rightarrow 2\,Co(CO)_4^- + CO_3^{2-} + 2\,H_2O \qquad (5)$$

It is likely that the favorable influence of CO pressure on the coupling reaction is due to a faster formation of $Co(CO)_4^-$, which leads to higher rates in the catalytic cycle.

Conclusion

The cobalt carbonyl-catalyzed carbonylation of secondary benzyl halides is quite complex, because alkyl- and acyl-cobalt carbonyls, which are essential intermediates in the catalytic cycle, can react in many different ways.

The use of the phase transfer technique allows selectivity towards monocarbonylation, double carbonylation or coupling. Ammonium salts exert a very important role in each of these three reactions, although only some of such salts are effective, and the relationship between their structure and activity is not yet clear. They provide auxiliary assistance in the mono and double carbonylation but are essential for the coupling.

The preferred two phase system for monocarbonylation consists of a mixture of concentrated aqueous solutions of inorganic bases (40—50%) with n-butanol or t-amyl alcohol. Under these conditions the use of some ammonium salts improves the selectivity towards formation of α-arylpropionic acids. According to Scheme 1, the role of those ammonium salts which are effective consists in making the nucleophilic attack of OH^- on the branched acyl complex so fast that isomerization is practically prevented. Lower base concentrations (20%) and particular alcohols (t-amyl alcohol) are required for double carbonylation. In the presence of ammonium salts this reaction is further facilitated and becomes the major reaction under 2 atm of CO. According to our hypothesis (Scheme 2), under phase-transfer conditions enolate anions can be formed from branched acyl complexes. Thus possible equilibria are more easily shifted towards enolization, which is an essential requisite for double CO insertion.

When the two phase system consists of non-polar and non-coordinating solvents (aromatic hydrocarbons) and 20% aqueous base, the coupling reaction becomes the main reaction under 5 atm of CO. Ammonium salts are necessary for quantitative transformation of $Co_2(CO)_8$ into $Co(CO)_4^-$ and for transferring this anion from the aqueous phase into the organic phase (Scheme 3). If the ammonium salt is omitted no tetracarbonyl cobaltate is present in the organic phase and no reaction takes place.

Experimental

Materials

The secondary benzyl halides were commercially available or were prepared from the corresponding alcohols by standard procedures. α-Chloro-6-methoxy-2-naphthylethane was made by a recently reported method [10]. The ammonium salts were commercially available, except for α-phenylethyltrimethylammonium iodide which was made by a standard method [11]. $NaCo(CO)_4$ was prepared by reduction of $Co_2(CO)_8$ with sodium amalgam in THF [12].

General procedure for the kinetic determinations

All the kinetic runs were carried out under nitrogen. Samples were analysed y use of a UNICAM SP 1100 infrared spectrophotometer using 0.1 mm CaF_2 ells. $NaCo(CO)_4$ (~0.190 g) and the solvent (40 ml) were placed under N_2 in flask (50 ml) equipped with a condenser, a magnetic stirrer bar and a serum up. The temperature was maintained to ±0.1°C by use of a thermostat. When he solution had reached the bath temperature a sample was removed and nalysed to give the initial concentration, and the secondary benzyl halide was hen added. At appropriate times samples were withdrawn and analysed by IR pectroscopy. Good linear first order plots were obtained under pseudo first rder conditions.

eneral procedure for preparation of acids

The organic solvent (25 ml), aqueous alkali hydroxide (25 ml), $Co_2(CO)_8$ 1 mmol) and ammonium salt (3 mmol) were placed under CO in a flask (100 l) equipped with magnetic stirrer, thermometer, dropping funnel and a con- enser. The experimental parameters were fixed, and the mixture was stirred s the secondary benzyl halide (20—40 mmol) was added during 3 h. Stirring as continued until the CO absorption stopped and the reaction mixture was hen acidified and worked up to give the acids, which were identified by IR, MR and mass spectrometry of their derivatives.

α-Keto-β-phenylbutyric acid was identified as its methyl ester. (*m/e* 192, 133, 32, 105, 79, 77, 59; NMR in $CDCl_3$: δ 1.46 doublet (3 H), 3.71 singlet (3 H), .51 quartet (1 H), 7.26 ppm multiplet (5 H)). This product was obtained by reating the mixture of the acids with methyl chloroformate by the general rocedure for the esterification of α-ketoacids [13] and isolated by chromato- raphy on silica gel. The product distribution was determined analysing the sters by GLC. For this the trimethylsilyl esters were prepared by treating mix- ures of acids with trimethyl chlorosilane and *N,O*-bis(trimethylsilyl acetamide) n pyridine in the standard procedure. The keto acid $C_6H_5CH(CH_3)COCOOH$ hen treated in this way gave $C_6H_5C(CH_3)=C(OSi(CH_3)_3)COOSi(CH_3)_3$ (*m/e* = 22, 307, 251, 147, 105, 73). The composition of the neutral fraction was also etermined by GLC analysis.

eneral procedure for coupling reactions

Toluene (100 ml), 20% aqueous NaOH (150 ml) benzyltrimethylammonium hloride (19 mmol), $Co_2(CO)_8$ (9 mmol), and the secondary benzyl halide 350 mmol), were introduced under CO into a stainless steel autoclave (500 ml). he mixture was stirred for 20 h under the chosen experimental conditions. hen the aqueous alkaline phase was separated, and the coupling products were solated from the organic phase by conventional techniques and identified by heir NMR and mass spectra. The quantitative determinations of these products ere made by GLC analysis using an internal standard.

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