Double Carbonylation of Substituted Benzyl Chlorides with Cobalt Carbonyl Anion by Phase Transfer Catalysis to give Arylpyruvic Acids

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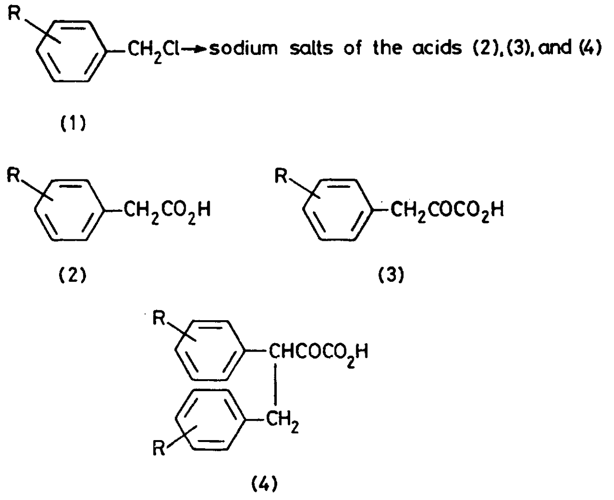
Summary When the phase transfer catalysis technique is used to carbonylate benzyl chlorides with the $Co(CO)_4^-$ anion, a double carbonylation, giving arylpyruvic acids, is observed besides the expected monocarbonylation giving arylacetic acids; this reaction strongly depends on the electronic effects of the substituents on the aromatic ring.

CARBONYLATION of organic halides is a well known process to obtain acids,[1] and recent results have shown the phase transfer technique to be very useful for generating metal carbonyl anionic species[2] and for carbonylating organic halides, with cobalt carbonyl anion as a catalyst.[3] Here we report further details of that reaction, focusing our results on double carbonylation, which, despite its theoretical and practical interest, is still unrecognized.[4]

The cobalt carbonyl anion was first generated from $Co_2(CO)_8$ at room temperature in a two-phase system consisting of dibenzyl ether, aqueous sodium hydroxide (5 M), and TEBA (triethylbenzylammonium chloride) under an inert atmosphere; the carbonylation of a substituted benzyl chloride [50:1 chloride: $Co_2(CO)_8$] was then carried out at 60 °C, under CO (1 atm) the mixture being stirred at 1100 r.p.m. Typical results, obtained according to Scheme 1, are given in the Table.



SCHEME 1.

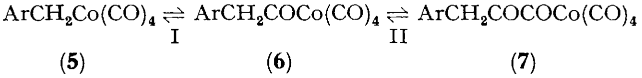
TABLE. Carbonylation of the halides (**1**)[a]

R	(**2**)	:	(**3**)	:	(**4**)	Overall[b] yield/%
H	100	:	0	:	0	60
m-CF_3	100	:	0	:	0	34
o-Me	60	:	0	:	40	78
m-Me	82	:	0	:	18	58
p-Me	70	:	0	:	30	75
o,o', *p*-Me_3	50	:	50	:	0	21

[a] The structures of the products were determined on the basis of analytical and spectral data (i.r., ^1H and ^{13}C n.m.r., and mass spectra of the methyl esters). In particular, evidence of the presence of the keto group in (**3**) and (**4**) came from the ^{13}C n.m.r. spectra ($CDCl_3$; Me_4Si ref.) of the methyl esters: in addition to the C=O ester carbon signal near 162 p.p.m. there was a signal near 192 p.p.m., characteristic of a 'keto' carbon. The alkylated structures (**4**) were proved by the presence of an ABX system for the $CHCH_aH_b$ group [^1H n.m.r.: δ ($CDCl_3$; Me_4Si ref.) *ca.* 5 (1H, q) and 2·6—3·6 (2H, m)]. [b] Experiments were run under the same conditions, and yields (relative to halide consumed) of (**2**) + (**3**) + (**4**) were not optimized.

Substitution on the aromatic ring plays a key role in the double carbonylation by phase transfer catalysis. With R = H or *m*-CF_3, which is strongly electron-withdrawing, no keto-acid appeared. With R = Me, double carbonylation occurred, whatever the position of the substituent (*o*, *m*, or *p*), suggesting that the electron releasing effect of the methyl group is more important than its position; moreover, further alkylation occurred, giving the substituted arylpyruvic acid (**4**). When the aromatic ring bore three methyl groups (in *o,o'*, and *p* positions) double carbonylation became an important pathway, giving only the simple arylpyruvic acid (**3**). In all these cases, the expected arylacetic acid (**2**) was produced besides the keto-acid (**3**) or (**4**).

We suggest that, in addition to the well known equilibrium I[5] (Scheme 2) between species (**5**) [arising from nucleophilic attack of $Co(CO)_4^-$ on the halide (**1**) by phase transfer catalysis] and (**6**) [giving the acid (**2**)], a further equilibrium II exists in the organic layer, and the special conditions



$$\underset{(5)}{\mathrm{ArCH_2Co(CO)_4}} \underset{\mathrm{I}}{\overset{\mathrm{CO}}{\rightleftharpoons}} \underset{(6)}{\mathrm{ArCH_2COCo(CO)_4}} \underset{\mathrm{II}}{\overset{\mathrm{CO}}{\rightleftharpoons}} \underset{(7)}{\mathrm{ArCH_2COCOCo(CO)_4}}$$

SCHEME 2

that are operative when using the phase transfer technique could 'trap' the arylpyruvoyl cobalt carbonyl species (**7**) to give either (**3**) or (**4**). The OH^- anion would attack (**7**) by phase transfer catalysis according to the interfacial mechanism,[6] acting either as a nucleophile [giving (**3**)] or as a base and a nucleophile giving (**4**). This effect of the phase boundary is supported by the importance of the stirring speed on the reaction, for example, when R = *p*-Me, and the stirring speed was lowered to 500 r.p.m., no double carbonylation occurred.

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[1] T. A. Weil, L. Cassar, and M. Foa, 'Organic Synthesis via Metal Carbonyls,' vol. II, Wiley, New York, 1977, p. 517; R. F. Heck, *Adv. Catalysis*, 1977, **26**, 323.

[2] H. des Abbayes and H. Alper, *J. Amer. Chem. Soc.*, 1977, **99**, 98; H. Alper, H. des Abbayes, and D. des Roches, *J. Organometallic Chem.*, 1976, **121**, C31.

[3] (a) H. Alper and H. des Abbayes, *J. Organometallic Chem.*, 1977, **134**, C11; (b) L. Cassar and M. Foa, *ibid.*, C15.

[4] A recent review on carbon monoxide insertion (A. Wojcicki, *Adv. Organometallic Chem.*, 1973, **11**, 87) does not report any example of double CO insertion, except in a speculative mechanism (p. 106); meanwhile, an organometallic species such as $MeCOCOMn(CO)_5$ was prepared by action of pyruvoyl chloride on $Mn(CO)_5^-$ anion, and was found to have a high kinetic stability (C. P. Casey, C. A. Bunnell, and J. C. Calabresse, *J. Amer. Chem. Soc.*, 1976, **98**, 1166). A patent (R. Perron, Rhône-Poulenc S.A., Ger. Offen., 2,600,541) on the double carbonylation of benzyl halides (but not using phase transfer technique) was indexed in *Chem. Abs.* (1977, **86**, 55171n) at the same time as we mentioned a double carbonylation of *o*-$MeC_6H_4CH_2Br$, fortuitously observed in our study on the carbonylation of benzyl bromides (ref. 3a).

[5] Z. Nagy-Magos, G. Bor, and L. Marko, *J. Organometallic Chem.*, 1968, **14**, 205.

[6] E. V. Dehmlow, *Angew. Chem. Internat. Edn.*, 1977, **16**, 493.