

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

By HERVÉ DES ABBAYES\* and ANNE BULOUP

(Laboratoire de Chimie des Organométalliques, E.R.A. C.N.R.S. No. 477, Université de Rennes, 35042 Rennes Cedex, France)

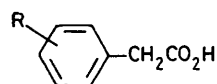
**Summary** When the phase transfer catalysis technique is used to carbonylate benzyl chlorides with the  $\text{Co}(\text{CO})_4^-$  anion, a double carbonylation, giving arylpyruvic acids, is observed besides the expected monocarbonylation giving arylacetic acids; this reaction strongly depends on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

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

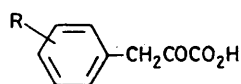
The cobalt carbonyl anion was first generated from  $\text{Co}_2(\text{CO})_8$  at room temperature in a two-phase system consisting of dibenzyl ether, aqueous sodium hydroxide (5 M), and TEBA (triethylbenzylammonium chloride) under an inert atmosphere; the carbonylation of a substituted benzyl chloride [50:1 chloride:  $\text{Co}_2(\text{CO})_8$ ] 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.



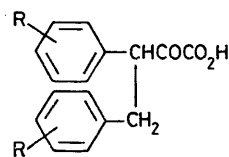
(1)



(2)



(3)



(4)

SCHEME 1.

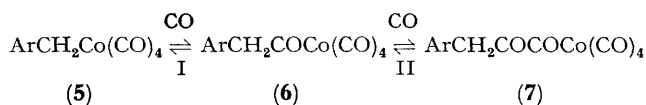
TABLE. Carbonylation of the halides (1)<sup>a</sup>

R	(2)	:	(3)	:	(4)	Overall <sup>b</sup> yield/%
H	100	:	0	:	0	60
<i>m</i> -CF <sub>3</sub>	100	:	0	:	0	34
<i>o</i> -Me	60	:	0	:	40	78
<i>m</i> -Me	82	:	0	:	18	58
<i>p</i> -Me	70	:	0	:	30	75
<i>o,o'</i> , <i>p</i> -Me <sub>3</sub>	50	:	50	:	0	21

<sup>a</sup> The structures of the products were determined on the basis of analytical and spectral data (i.r., <sup>1</sup>H and <sup>13</sup>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 <sup>13</sup>C n.m.r. spectra (CDCl<sub>3</sub>; Me<sub>4</sub>Si 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  $\text{CHCH}_2\text{H}_3$  group [<sup>1</sup>H n.m.r.:  $\delta$  (CDCl<sub>3</sub>; Me<sub>4</sub>Si ref.) *ca.* 5 (1H, q) and 2.6—3.6 (2H, m)]. <sup>b</sup> 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<sub>3</sub>, 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<sup>5</sup> (Scheme 2) between species (5) [arising from nucleophilic attack of  $\text{Co}(\text{CO})_4^-$  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



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<sup>-</sup> anion would attack (7) by phase transfer catalysis according to the interfacial mechanism,<sup>6</sup> 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.

(Received, 1st August 1978; Com. 829.)

<sup>1</sup> 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.

<sup>2</sup> 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.

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

<sup>4</sup> 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)<sub>5</sub> was prepared by action of pyruvoyl chloride on Mn(CO)<sub>5</sub><sup>-</sup> 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<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, fortuitously observed in our study on the carbonylation of benzyl bromides (ref. 3a).

<sup>5</sup> Z. Nagy-Magos, G. Bor, and L. Marko, *J. Organometallic Chem.*, 1968, **14**, 205.

<sup>6</sup> E. V. Dehmlow, *Angew. Chem. Internat. Edn.*, 1977, **16**, 493.