

Preliminary communication

THE CARBONYLATION OF PHASE-TRANSFER AGENTS

SANDRO GAMBAROTTA and HOWARD ALPER*

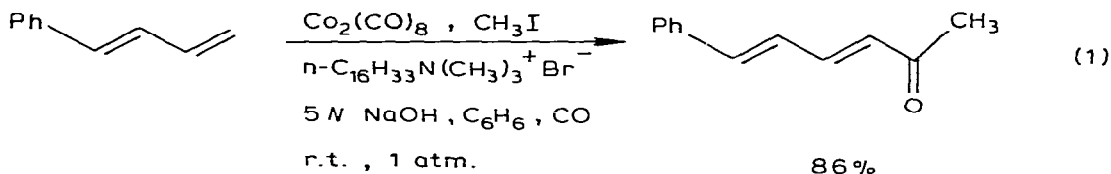
Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 9B4 (Canada)

(Received February 27th, 1980)

Summary

Quaternary ammonium halides, which are capable of forming relatively stable free radicals, can be carbonylated to carboxylic acids by reaction with carbon monoxide, cobalt carbonyl, methyl iodide, sodium hydroxide (5 N) and benzene.

Publications during the last four years have demonstrated the potential of phase transfer catalysis in organometallic chemistry [1]. A particularly useful series of reactions are those involving the cobalt carbonyl catalyzed carbonylation of halides with quaternary ammonium halides functioning as phase transfer catalysts. These reactions can be effected either as described [2,3], or in the presence of alkynes [4], dienes [5], or trienes [5]. For example, treatment of 1-phenyl-1,3-butadiene with methyl iodide, carbon monoxide, cobalt carbonyl,

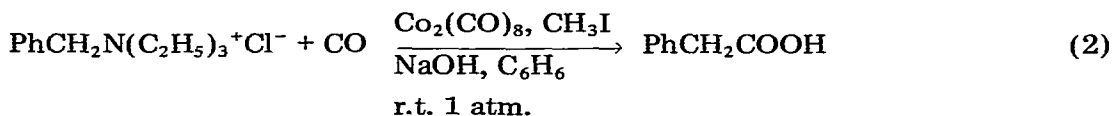


benzene, aqueous sodium hydroxide, and a quaternary ammonium halide (e.g. cetyltrimethylammonium bromide, benzyltriethylammonium chloride) as the phase transfer catalyst afforded the conjugated dienone in 86% yield (eq. 1) [5]. Acetylcobalt tetracarbonyl is the key intermediate in this reaction. We now wish to communicate the important observation that even certain phase transfer agents can be carbonylated to carboxylic acids.

Reaction of benzyltriethylammonium chloride with carbon monoxide, cobalt carbonyl, methyl iodide, sodium hydroxide, and benzene for five days at room temperature, affords phenylacetic acid in 95% yield (eq. 2). This slow, high

*E.W.R. Steacie Fellow 1980—82.

yield carbonylation reaction does not occur with the in situ generated cobalt

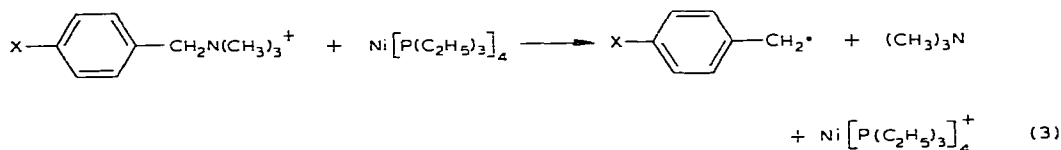


tetracarbonyl anion, but with acetylcobalt tetracarbonyl (from methyl iodide, $\text{Co}_2(\text{CO})_8$, and CO).

The carbonylation reaction is not limited to benzyltriethylammonium chloride, but is observed for other quaternary ammonium salts which are capable of forming reasonably stable free radicals or carbonium ions. Examples include benzyltrimethylammonium chloride and *N*-benzyl-*N*-methylephedrinium bromide which gave phenylacetic acid in 41 and 90% yields, respectively. Phenylacetone was not detected in any of these reactions. β -Naphthylacetic acid was similarly formed in 50% yield from β -naphthylmethyltriethylammonium bromide, and *m*-tolyltriethylammonium bromide afforded *m*-tolylacetic acid in 92% yield.

Carbonylation did not occur when cetyltrimethylammonium bromide or tetrabutylammonium bromide was treated with cobalt carbonyl, methyl iodide, and carbon monoxide in an identical manner to that described for benzyltriethylammonium chloride. Either of these salts would generate only simple, unstable, primary radicals or carbonium ions.

The carbonylation reaction may proceed via an ionic mechanism involving benzylic alcohols as intermediates. However such alcohols (e.g. 2-naphthalene-methanol) are not carbonylated to carboxylic acids under the reaction conditions. These results are also consistent with a radical mechanism analogous to that proposed by Tsou and Kochi [6] for the tetrakis(triethylphosphine)nickel induced conversion of the benzyltrimethylammonium cation to the benzyl radical (eq. 3). The involvement of radical intermediates in reactions catalyzed



by cobalt carbonyls has also been suggested recently by Wegman and Brown [7].

The following general procedure was used: to the phase transfer agent (2.0 mmol), 5 *N* sodium hydroxide (20 ml), and benzene (20 ml), was added a stoichiometric quantity of cobalt carbonyl and methyl iodide (CO atmosphere). The reaction mixture was vigorously stirred for five days at room temperature. The phases were separated, and the acidified (HCl) aqueous phase was extracted with ether. The ether extract was dried and concentrated to give the carboxylic acid.

In conclusion, the carbonylation of certain phase transfer agents is firmly established. Furthermore, one clearly should not use such quaternary ammonium salts in slow phase transfer processes. Although the results are admittedly inconclusive from a mechanistic viewpoint, they do suggest serious consideration of the possible participation of free radicals in certain organometallic phase transfer processes.

Acknowledgments

We are indebted to Imperial Oil Limited, and to the Natural Sciences and Engineering Research Council, for support of this research. We thank Dr M. Tanaka for initial experiments.

References

- 1 H. Alper, *Advan. Organometal. Chem.*, in press.
- 2 H. Alper and H. des Abbayes, *J. Organometal. Chem.*, 134 (1977) C11.
- 3 L. Cassar and M. Foa, *J. Organometal. Chem.*, 134 (1977) C15.
- 4 H. Alper, J.K. Currie and H. des Abbayes, *J. Chem. Soc., Chem. Commun.*, (1978) 311.
- 5 H. Alper and J.K. Currie, *Tetrahedron Lett.*, (1979) 2665.
- 6 T.T. Tsou and J.K. Kochi, *J. Amer. Chem. Soc.*, 101 (1979) 6319.
- 7 R.W. Wegman and T.L. Brown, *J. Amer. Chem. Soc.*, 102 (1980) 2494.