ELSEVIER

Journal of Organometallic Chemistry 486 (1995) 297–300

Journal of Organometallic Chemistry

Preliminary communication

Palladium catalyzed carbonylation of iodoarenes in aqueous solubilized systems

Andrei V. Cheprakov, Natalia V. Ponomareva, Irina P. Beletskaya *

Department of Chemistry, Moscow State University, 119899 Moscow, Russian Federation

Received 4 July 1994

Abstract

Iodobenzene and substituted iodobenzenes can be easily carbonylated into benzoic acids under mild conditions, with simple palladium salts as catalysts and normal pressure of CO, by using aqueous microemulsions of the oil-in-water kind as the reaction media. Surfactants of all three kinds, anionic, nonionic, and cationic, and simple aliphatic alcohols can be used to form the microemulsion media for carbonylation. The use of nonionic surfactants, the derivatives of polyethyleneglycol, is the most advantageous method as the surfactant is highly efficient in small amounts without a cosurfactant because of its strong solubilizing ability.

Keywords: Palladium; Carbon monoxide; Carbonylation; Water

1. Introduction

Continuous efforts are now being made to carry out transition metal catalized reactions in aqueous media in the attempt to develop new environmentally safe technologies [1,2]. However, such reactions are usually limited to water-soluble organic substrates [3] (sometimes only one of the reagents must be water-soluble while the other may be hydrophobic, e.g. as in the Heck arylation of acrylic acid [4] or cross-coupling with sodium tetraphenylborate [5]) and often require a water-soluble form of the active catalytic species be involved (e.g. through the use of sophisticated hydrophilic ligands) [6]. There might be another, much cheaper and potentially more universal approach to this problem based on the well known solubilization phenomena—i.e. the ability of aqueous solutions of surfactants to solubilize considerable amounts of hydrophobic materials. Such phenomena have been extensively investigated and exploited before in the, so-called, "micellar catalysis" [7]. The catalysis has been mainly of pure scholarly interest to organic chemists because the amounts of solubilized substrates are quite low in simple micelles, far from practical preparative loads. The dispersion systems in which much heavier amounts of hydrophobic liquid can be solubilized in aqueous solution are also well known, but received amazingly scarce attention from organic chemists. However, the use of such systems, and in the first place the simplest and most spectacular of them—microemulsions (otherwise known as "swollen micelles" or "solubilized systems") [8,9]—can afford practical loadings of organic substrate to be solubilized and processed at very low cost (sparse examples of the use of such systems, mostly for non-catalytic organic reactions, can be found in Ref. [10]).

As an introductory example here we describe the hydroxycarbonylation of iodoarenes catalyzed by simple palladium complexes in aqueous microemulsions of the oil-in-water type. The hydroxy- (or alkoxy-) carbonylation of haloarenes is one of the classical homogeneous catalytic reactions for which an extensive body of experimental data exists, allowing comparison [11]. One of the latest works by Grushin and Alper describes an ingenious indirect way to perform this reaction in aqueous solution. Iodoarene is first oxidized in situ to the corresponding iodoxy derivative, which (partly because of its greater solubility in water, and perhaps also because of its higher reactivity towards oxidative addition) undergoes a facile Pd-catalyzed car-

---

* Corresponding author.

SSDI 0022-328X(94)05102-X

bonylation [12]. In this article we describe a simpler—essentially direct—way to perform the carbonylation of water-insoluble iodoarenes in aqueous media.

2. Results and Discussion

For most of our experiments we used the cheapest and most widely used industrial anionic surfactant—sodium dodecyl sulfate (SDS). This surfactant alone in concentrations well above the critical micelle concentration in water forms opaque dense systems of very low solubilizing properties; iodobenzene is virtually insoluble in such a system. The addition of cosurfactant (any alcohol of moderate chain length from propyl to hexyl) gives transparent systems with very high solubilizing ability. For example, 10 ml of such microemulsion (containing 0.4–0.5 g SDS and 0.5–1 ml ROH) may contain up to 2 mmol of iodobenzene; which gives up to a 0.2 M pseudo-solution of iodobenzene in water. Loadings of hydrophobic oils in simple micellar solutions used in micellar catalysis are usually at least 4–5 orders of magnitude lower. In such solutions iodoarenes undergo ready hydroxycarbonylation under atmospheric pressure of CO, in the presence of catalytic amounts of simple palladium complexes ($PdCl_2$, $PdCl_2(MeCN)_2$, $Pd(OAc)_2$), and base at 50–80°C (see Table 1)

$$\mathrm{ArI} \xrightarrow[\text{o/w microemulsion, 50–80°C}]{\text{Pd-cat, base, 1 atm CO}} \mathrm{ArCOOH}$$

Substituted iodobenzenes can also be readily carbonylated. Solid substrates can be solubilized either above their melting points (e.g. iodotoluene or chloroiodobenzene) or by addition of a drop of any inert highly penetrating oil (small rigid molecules such as benzene, toluene, etc.) to “oilify” the substrate and form the microemulsion. Curiously enough cetyltrimethylammonium bromide, which is also known as a phase-transfer catalyst, proved less efficient for the carbonylation reactions. The reaction in cationic microemulsion proceeds sluggishly and gives a dark palladium sol.

The behaviour of nonionic surfactants such as BRIJ-35 (monolauryl ether of polyethyleneglycol with an average chain length of 23 oxyethylene units) and IGEPAL CO (nonylphenyl ethers of PEG with a variable number of oxyethylene units) is particularly interesting. While the microemulsions formed by nonionic surfactants are less stable than those of ionic surfactants, carbonylation proceeds readily in the absence of a cosurfactant. The amount of surfactant can be reduced to very low levels (0.1%) whilst maintaining efficiency (we made no effort to lower the surfactant content further). Such systems are visually either unstable milky emulsions or even completely separated two-phase systems, which means that these systems are macroheterogeneous in comparison with conventional microemulsions which are microheterogeneous thermodynamically stable systems. Iodobenzene in such systems undergoes ready carbonylation into benzoate ion, and the reaction mixture after 0.5–3 h at 50–80°C

Table 1
Carbonylation of iodobenzenes p-YC_6H_4I in aqueous microemulsions [a]

Y	ArI (mmol)	Temp. (°C)	Time (h)	Cat [b]	Surfactant	Cosurfactant	Base	Yield (%)
H	2	50	4	A	SDS	BuOH	K_2CO_3	70
H	2	80	4	C	SDS	BuOH	K_2CO_3	84
Cl	1	70	4	A	SDS	BuOH	KOH	94
OMe [c]	1	50	4	A	SDS	BuOH	KOH	96
Me	1	50	4	A	SDS	BuOH	K_2CO_3	92
H	1	50	4	B	BRIJ-35	BuOH	K_2CO_3	99
H	3.2	50	4	A	SDS	BuOH	K_2CO_3	92
H	1	50	4	A	SDS	-	K_2CO_3	22
H	3.2	85	4	B	SDS	BuOH	K_2CO_3	91
H	2	85	4	B	SDS	BuOH	K_2CO_3	94
H	2	70	4	A	CTMAB	BuOH	K_2CO_3	60
H	2	70	4	A	BRIJ-35 [d]	-	K_2CO_3	95
H	2	70	4	A	BRIJ-35 [e]	-	K_2CO_3	93
H	4	70	0.5	B	ICO-990 [f]	-	K_2CO_3	97

[a] Typical experimental procedure: 0.5 g surfactant, 1 ml butanol, 10 ml water, 2 mmol base (K_2CO_3 or KOH), 2 mmol aryl iodide are mixed together by gentle stirring to form transparent microemulsion. After warming up to the required temperature, 0.1–0.2 mol% of palladium salt were added and the air was displaced by CO. Reaction mixture was stirred in the atmosphere of CO.

[b] A = $PdCl_2(MeCN)_2$; B = $Pd(OAc)_2$, C = $PdCl_2$.

[c] A drop of toluene added, see text.

[d] Reaction in the presence of 1 mol% BRIJ-35.

[e] Same as previous, but with 0.3 mol% BRIJ-35.

[f] Reaction in the presence of 0.1 mol% nonionic surfactant Igepal CO-990.

turns into a transparent aqueous solution of potassium benzoate from which crystalline benzoic acid can be precipitated on acidification giving an almost quantitative yield. We believe that such efficiency can be attributed to the structure of these surfactants. Indeed, the molecule of such nonionic surfactants consists of two parts: a lypophilic tail forming micelle core and hydrophilic polyoxythylene chains which form an inter-phase layer (so-called "palisade") [8]. The palisade layer, which may be viewed as a microreactor filled with hydrated polyethyleneglycol, is well known as a solubilization site for both polar hydrophobic organic molecules (e.g. aromatic compounds) and ions drawn inside owing to complexation equilibria. It is noteworthy that the phase transfer catalysis of carbonylation and other palladium catalyzed reactions by polyethyleneglycols taken as bulk solvents is well known [13]. It might seem that the most obvious explanation for the action of such surfactants is trivial facilitation of mixing owing to emulsification. However, it appears that this is not the case. Comparison of the efficiency of different nonionic surfactants, the derivatives of nonylphenol (commercial Igepal series) with varying lengths of polyoxyethylene tails, reveal that performance depends heavily on the length of the hydrophilic tail, though the stability of the emulsion phase has an inverse relationship with this factor. The most efficient surfactants are BRIJ-35, and especially Igepal CO-990 (100 ethyleneoxide units), though both are too hydrophilic and therefore very poor emulsifiers. While being good emulsifiers, the surfactants with smaller hydrophilic chains (8–15) were almost totally inefficient in carbonylation reactions. Recently, it became known [8] that dilute aqueous solutions of such nonionic surfactants without added cosurfactant readily solubilize hydrophobic compounds in considerable amounts forming isotropic phases ("Shinoda's microemulsions", as compared with canonical "Schulman's microemulsions" formed by much larger amounts of surfactant and cosurfactant). Solubilization in such systems depends very strongly on temperature with the highest load of solubilizate near the so called phase-inversion temperature. The relative behaviour of different nonionic surfactants in our system prompts us to suggest that these Shinoda's microemulsions are indeed the systems responsible. Further investigation of these phenomena is underway.

Thus, aqueous microemulsions of different kinds formed in the presence of various surfactants proved to be excellent media for carrying out palladium catalyzed hydroxycarbonylation reactions. The advantages of such systems in comparison with more conventional techniques are readily seen.

(i) No excess of organic solvent is needed to form the new phase—the substrate itself serves as such.

(ii) The systems are formed spontaneously—no vigorous mechanical or ultrasonic agitation is needed to obtain and maintain them.

(iii) All reagents are taken in stoichiometric or catalytic amounts, without the huge excess of concentrated alkali hydroxides seen in PTC methods.

(iv) Anionic and nonionic surfactants are generally much cheaper than cationic PTC agents.

(v) The surfactants used are easily recyclable, cheap, nontoxic, biodegradable and thus environmentally safe, bulk industrial chemicals.

(vi) Ultralow surface tension, one of the most characteristic features of microemulsion phenomena, allows fast end easy mixing of the reagents and very facile uptake and distribution of the gaseous reagent (here, CO) into the bulk of reaction mixture.

Acknowledgment

The research described in this article was made possible in part by Grant no. M2M00 from the International Science Foundation.

References

[1] I.P. Beletskaya, in Z. Yoshida and Y. Oshiro (eds.), *New Aspects of Organic Chemistry*, Kodansha-VCH, Tokyo, 1992.

[2] C.-J. Li, *Chem. Rev.*, *93* (1993) 2023, and refs. cited therein.

[3] (a) N.A. Bumagin, V.V. Bykov and I.P. Beletskaya, *Izv. AN SSSR, ser. khim.*, (1989) 2394; (b) N.A. Bumagin, V.V. Bykov and I.P. Beletskaya, *Metallorg. Khim.*, *2* (1989) 1200; (c) N.A. Bumagin, P.G. More and I.P. Beletskaya, *J. Organomet. Chem.*, *371* (1989) 397; (d) N.A. Bumagin, L.I. Sukhomlinova and I.P. Beletskaya, *Izv. AN SSSR, ser. khim.*, (1992) 2685; (e) N.A. Bumagin, K.V. Nikitin and I.P. Beletskaya, *DAN SSSR*, *312* (1990) 1129.

[4] N.A. Bumagin, V.V. Bykov and I.P. Beletskaya, *Izv. AN SSSR, ser. khim.*, (1990) 2672.

[5] N.A. Bumagin, V.V. Bykov and I.P. Beletskaya, *DAN SSSR*, *315* (1990) 1133.

[6] (a) N.A. Bumagin, V.V. Bykov and I.P. Beletskaya, *Izv. AN SSSR, ser. khim.*, (1990) 2665; (b) J.P. Genet, E. Blart and M. Savignac, *SYNLETT*, (1992) 715; (c) C. Larpent, R. Dafard and H. Patin, *Tetrahedron Lett.*, *28* (1987) 2507; (d) M. Safi and D. Sinou, *Tetrahedron Lett.*, *32* (1991) 2025; (e) E. Blart, J.P. Genet, M. Safi, M. Savignac and D. Sinou, *Tetrahedron*, *50* (1994) 505.

[7] J.H. Fendler and E.J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975.

[8] K. Shinoda, S. Friberg, *Emulsions and Solubilization*, Wiley, New York, 1986.

[9] M. Bourrel and R.S. Schechter, *Microemulsions and Related Systems. Formulation, Solvency and Physical Properties*, Marcel Dekker, New York, 1988.

[10] (a) N. Alandis, I. Rico and A. Lattes, *Bull. Soc. Chim. France*, (1989) 252; (b) K.L.N. Phani, S. Ditchumani, S. Ravichandran, S.S. Tamil and S. Bharathey, *J. Chem. Soc., Chem. Commun.*, (1993) 179; (c) R. Schomaecker, *J. Chem. Res. (S)*, (1991) 92; (d) F.M. Menger and A.R. Erlington, *J. Am. Chem. Soc.*, *113* (1991) 9621; (e) M. Nascimento, M.C. Rezende, R. Dalla-Vecchia, P.

Cesar-de-Jesus and L.M. Aguiar, *Tetrahedron Lett.*, *33* (1992) 5891; (f) C. Larpent and H. Patin, *J. Mol. Cat.*, *72* (1992) 315.

[11] (a) A. Schoenberg, I. Bartoletti and R.F. Heck, *J. Org. Chem.*, *39* (1974) 3318; (b) J.K. Stille and P.K. Wong, *J. Org. Chem.*, *40* (1975) 532; (c) H.M. Colquhoun, D.J. Thompson and M.V. Twigg, *Carbonylation*, Plenum, New York, 1991, p. 97, and refs. cited therein.

[12] V.V. Grushin and H. Alper, *J. Org. Chem.*, *58* (1993) 4794.

[13] (a) H. Alper, K. Januszkiewicz and D.J.H. Smith, *Tetrahedron Lett.*, *26* (1985) 2263; (b) K. Osowskapacewicka and H. Alper, *J. Org. Chem.*, *53* (1988) 808; (c) X. Huang and J. Wu, *Chem. Ind. (L)*, (1990) 548; (d) J.-T. Lee and H. Alper, *Tetrahedron Lett.*, *32* (1991) 1769.