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# Hypervalent Iodine in Synthesis. Part XXIX: Palladium-catalyzed Carbonylation of Diaryliodonium Salts by Chloroform and Alkali†

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Diaryliodonium salts are catalytically carbonylated by CO generated *in situ* from chloroform and aqueous alkali in the presence of $(Ph_3P)_2PdCl_2$ in good yields under $N_2$ at 50 °C.

The transition metal-catalyzed carbonylation of various organic substrates is of significant importance in organic synthesis. A great variety of inexpensive, simple, and highly efficient carbonylations have been observed,[1] and particular interest would be the carbonylation of organic halides. Recently, Grushin and Alper reported a novel method for the preparation of aromatic carboxylic acids from iodoarenes by palladium-catalyzed carbonylation with chloroform and alkali.[2] Although the reaction is very simple, clear and convenient, without requiring toxic and dangerous carbon monoxide as participant, its overall timescale limits its application.

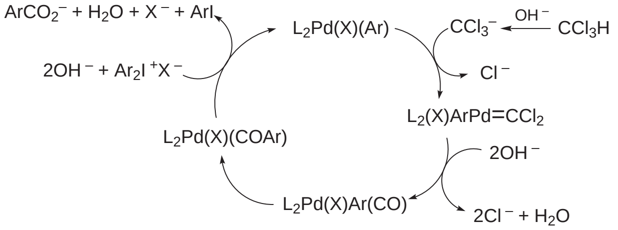
Recent developments in hypervalent iodine chemistry have shown that organoiodine(III) compounds are good substitutes for organic halides in most cases due to their high reactivity which leads to improvements in many reactions.[3] In connection with our programs to utilize hypervalent iodine compounds in organic synthesis,[4] we have investigated the carbonylation of diaryliodonium salts with chloroform and alkali. Here we report the results which are summarized in Scheme 1 and Table 1.

$$ArI^+ArX^- + CHCl_3 \xrightarrow[\text{ii, } H_3^+O]{\text{i, 5\%}(Ph_3P)_2PdCl_2\text{, aq. KOH, 50 °C}} ArCO_2H$$

**Scheme 1**

We have found that palladium-catalyzed carbonylation of diaryliodonium salts with chloroform and alkali takes place smoothly, reaching completion within 1 h at 50 °C. Chloroform can be used in a large excess acting as both the reagent and the organic phase. Several diaryliodonium salts containing various substituents such as methyl, methoxyl, chloro, bromo and nitro groups, were successfully carbonylated with chloroform and alkali. Additionally, the reaction can be carried out readily not only for symmetric iodonium salts but also for unsymmetric iodonium salts which produce single products with elimination of iodobenzene as expected. Under similar conditions, phenylethynylphenyliadonium salt also reacts with chloroform and alkali in the presence of catalytic amounts of $(Ph_3P)_2PdCl_2$ to give 3-phenylpropynoic acid (Table 1, entry 9).

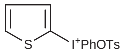
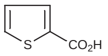
A plausible mechanism for the palladium-catalyzed carbonylation of diaryliodonium salts by chloroform and alkali is analogous to that of iodoarenes and is shown in Scheme 2.



**Scheme 2** L = $PPh_3$.

In conclusion, we describe a simple, efficient method for the palladium-catalyzed carbonylation of diaryliodonium salts by chloroform and alkali, which may be a valuable alternative to that of iodoarenes.

**Table 1** Palladium-catalyzed carbonylation of diaryliodonium salts by chloroform and alkali

| Entry | Substrate | Product[a] | Yield(%)[b] | Mp/°C | Mp Lit./°C |
|---|---|---|---|---|---|
| 1 | $Ph_2I^+Cl^-$ | $PhCO_2H$ | 70 | 110–112 | 112[5] |
| 2 | $(p\text{-}MeC_6H_4)_2I^+I^-$ | $p\text{-}MeC_6H_4CO_2H$ | 64 | 179–181 | 181[6] |
| 3 | $(p\text{-}MeOC_6H_4)_2I^+I^-$ | $p\text{-}MeOC_6H_4CO_2H$ | 78 | 182–184 | 184[7] |
| 4 | $(p\text{-}ClC_6H_4)_2I^+Cl^-$ | $p\text{-}ClC_6H_4CO_2H$ | 74 | 235–237 | 237–239[8] |
| 5 | $(p\text{-}BrC_6H_4)_2I^+Cl^-$ | $p\text{-}BrC_6H_4CO_2H$ | 72 | 250–252 | 251–253[9] |
| 6 | $(m\text{-}O_2NC_6H_4)_2I^+Cl^-$ | $m\text{-}O_2NC_6H_4CO_2H$ | 41 | 137–139 | 139–142[10] |
| 7 | $(p\text{-}MeC_6H_4I^+PhBr^-$ | $p\text{-}MeC_6H_4CO_2H$ | 67 | 178–180 | 181[6] |
| 8 | $(p\text{-}MeOC_6H_4I^+PhBr^-$ | $p\text{-}MeOC_6H_4CO_2H$ | 77 | 182–184 | 184[7] |
| 9 | $PhC{\equiv}CI^+PhOTs^-$ | $PhC{\equiv}CCO_2H$ | 61 | 132–134 | 135–137[11] |
| 10 |  |  | 54 | 126–128 | 129–130[12] |

[a] All of the products were identified by comparison of their melting point with authentic samples. [b] After purification by recrystallization.

## Experimental

*General Procedure for the Carbonylation of Iodonium Salts with $CHCl_3$ and Alkali.*—To a degassed mixture of 60% aqueous KOH (5 g), $CHCl_3$ (1 ml) and iodonium salt (1 ml) in a 5 ml Schlenk flask was added

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*. Part XXVIII: ref. 4.

$(Ph_3P)_2PdCl_2$ (0.05 mmol) and the biphasic mixture was vigorously stirred at 50 °C under $N_2$ until the solid iodonium salt disappeared (usually within 1 h). Water (10 ml) and ether (10 ml) were added, the aqueous layer was separated, acidified with 20% HCl and extracted with ether (2 × 10 ml). The combined ether layers were dried with anhydrous $MgSO_4$, filtered and evaporated to give the product, which was purified by recrystallization. The acids were found to be pure and identical (melting point) with authentic samples.

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## References

1 H. M. Colquhoun, O. J. Thompson and M. V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*, Plenum Press, New York, 1991.
2 V. V. Grushin and H. Alper, *Organometallics*, 1993, **12**, 3846.
3 R. M. Moriarty, W. R. Epa and A. K. Awasthi, *J. Am. Chem. Soc.*, 1991, **113**, 6315; R. M. Moriarty and W. R. Epa, *Tetrahedron Lett.*, 1992, **33**, 4095; R. J. Hinkle, G. T. Poulter and P. J. Stang, *J. Am. Chem. Soc.*, 1993, **115**, 11626; S. K. Kang, K. Y. Jung, C. H. Park and S. B. Jang, *Tetrahedron Lett.*, 1995, **36**, 8047; S. K. Kang, H. W. Lee, S. B. Jang, T. H. Kim and S. J. Pyun, *J. Org. Chem.*, 1996, **61**, 2604; S. K. Kang, T. Yamahuchi, T. H. Kim and P. S. Ho, *J. Org. Chem.*, 1996, **61**, 9082; S. K. Kang, H. W. Lee, W. K. Choi, R. K. Hong and J. S. Kim, *Synth. Commun.*, 1996, **26**, 4219.
4 *Hypervalent Iodine in Synthesis XXVIII: The Preparation and Utilization of Polymer-Supported Phenyliodine(III) Diacetate*, G. P. Wang and Z. C. Chen, *Synth. Commun.*, 1999, in press.
5 The Merck Index, 10th edn., no. 1093.
6 The Merck Index, 10th edn., no. 9363.
7 H. Gilman, W. Langham and H. B. Willis, *J. Am. Chem. Soc.*, 1940, **62**, 346.
8 F. Effenberger and P. Gleiter, *Chem. Ber.*, 1964, **97**, 480.
9 The Merck Index, 10th. edn., no. 1378.
10 O. Kamm and J. B. Segur, *Org. Synth.*, 1951, **Coll. Vol. 1**, 391.
11 A. R. Mahajan, D. K. Dutta, R. C. Boruah and J. S. Sandhu, *Tetrahedron Lett.*, 1990, **31**, 3943.
12 H. Gilman and D. A. Shirley, *J. Am. Chem. Soc.*, 1940, **71**, 1870.