SHORT PAPER

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Hypervalent iodine in synthesis 56: a convenient route for the synthesis of thiol esters via palladium-catalysed alkylthiocarbonylation or arylthiocarbonylation of diaryliodonium salts†

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Palladium-catalysed alkylthiocarbonylation or arylthiocarbonylation of diaryliodonium salts gives thiol esters in good yields.

Transition metal catalysed alkoxycarbonylation of organic halides is an important method for the synthesis of esters. However, to the best of our knowledge the analogous alkylthiocarbonylation or arylthiocarbonylation of organic halides for the synthesis of thiol esters is unknown.[1] In the course of our program on the palladium-catalysed reactions of hypervalent iodonium salts,[2] we found that the palladium-catalysed alkylthiocarbonylation or arylthiocarbonylation of diaryliodonium salts can occur easily to provide a novel, convenient route for the synthesis of thiol esters.

In fact, simply stirring a mixture of diaryliodonium salt, thiol, potassium carbonate and $Pd(PPh_3)_4$ in THF under one atmosphere pressure of carbon monoxide at room temperature gave, after work up and isolation, the thiol ester in good yield. (Scheme 1) The results are summarized in Table 1. All products gave satisfactory m.p., IR and ^{1}H-NMR spectra.

$$Ar_2I^+BF_4^- + RSH \xrightarrow[K_2CO_3/THF\ /R.T.]{Pd(PPh_3)_4/CO} ArCOSR$$

Scheme 1

To determine the optimum reaction conditions, we examined the carbonylation of di(*p*-methoxylphenyl)iodonium tetrafluoroborate with *p*-thiocresol. After a series of experiments, we found that among the palladium catalysts tested, including $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $PdCl_2$, and $Pd(OAc)_2$, $Pd(PPh_3)_4$ was the best choice. The reaction was found to be general and applicable to aliphatic or aromatic thiols. Several diaryliodonium salts containing various substituents, such as methoxy, methyl, chloro and nitro groups, were successfully reacted. The present method is not only suitable for the synthesis of S-aryl esters of aromatic thiocarboxylic acids but also for the synthesis of some S-alkyl esters of aromatic thiocarboxylic acids.

Thiol esters have recently received considerable interest because of their importance as acylating agents in biochemical processes[3] and organic synthesis[4]. Many methods for their synthesis have been reported,[5] such as the acylating reaction of thiols or their derivatives,[6] the Friedel-Crafts acylation of arenes with S-aryl or S-alkyl chlorothioformates,[7] the alkylation or arylation of the salts of thiocarboxylic acids,[8] the coupling reaction of Grignard reagents with S-phenyl chlorothioformate in the presence of transition metal catalysts,[9] or the hydrolysis of imidothioates, thioorthoesters[10] or ketene S,S-acetals.[11] However, these methods use either toxic and hazardous reagents or harsh conditions or uncommon starting materials, thus limiting their general effective access to thiol esters. Here we have provided a convenient route for the synthesis of thiol esters via the palladium-catalysed alkylthiocarbonylation or arylthiocarbonylation of diaryliodonium salts. The present method offers some advantages, such as accessible starting materials, mild reaction conditions, simple procedure and high yields.

In conclusion, we report the first example of metal catalysed alkylthiocarbonylation or arylthiocarbonylation of organic halides which provides a novel convenient method for the synthesis of thiol esters. Furthermore, the range of useful applications of palladium-catalysed reaction of diaryliodonium salts in organic synthesis has been extended.

Table 1 S-Aryl and S-alkyl thiocarboxylates[a]

Entry	$Ar_2I^+BF_4^-$	RSH	Product	Yield(%)[b]
1	$Ph_2I^+BF_4^-$	PhSH	PhCOSPh	76
2	$(p\text{-}CH_3C_6H_4)_2I^+BF_4^-$	PhSH	$p\text{-}CH_3C_6H_4COSPh$	72
3	$(p\text{-}CH_3OC_6H_4)_2I^+BF_4^-$	PhSH	$p\text{-}CH_3OC_6H_4COSPh$	70
4	$(p\text{-}ClC_6H_4)_2I^+BF_4^-$	PhSH	$p\text{-}ClC_6H_4COSPh$	79
5	$(m\text{-}NO_2C_6H_4)_2I^+BF_4^-$	PhSH	$m\text{-}NO_2C_6H_4COSPh$	81
6	$Ph_2I^+BF_4^-$	$p\text{-}CH_3C_6H_4SH$	$PhCOSC_6H_4CH_3\text{-}p$	77
7	$(p\text{-}CH_3OC_6H_4)_2I^+BF_4^-$	$p\text{-}CH_3C_6H_4SH$	$p\text{-}CH_3OC_6H_4COSC_6H_4CH_3\text{-}p$	72
8	$(p\text{-}ClC_6H_4)_2I^+BF_4^-$	$p\text{-}CH_3C_6H_4SH$	$p\text{-}ClC_6H_4COSC_6H_4CH_3\text{-}p$	80
9	$Ph_2I^+BF_4^-$	$C_6H_5CH_2SH$	$PhCOSCH_2C_6H_5$	65
10	$(p\text{-}CH_3C_6H_4)_2I^+BF_4^-$	C_2H_5SH	$p\text{-}CH_3C_6H_4COSC_2H_5$	70

[a] Reagent and conditions: 1 mmol iodonium salt, 1 mmol thiol, 2 mmol K_2CO_3 and 5mol% $Pd(PPh_3)_4$ in 5 ml THF at room temperature under one atmosphere of carbon monoxide.

[b] Isolated yields.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Experimental

^{1}H-NMR spectra were recorded on a PMX-60 spectrometer, using CCl_4 as the solvent with TMS as an internal standard. IR spectra were determined on a PE-683 Spectrophotometer. Melting points are uncorrected.

General procedure for synthesis of thiol esters: The thiol (1 mmol) was added to a stirred solution of diaryliodonium tetrafluoroborate (1 mmol), $Pd(PPh_3)_4$ (58 mg, 5 mol%) K_2CO_3(276 mg, 2 mmol) and anhydrous THF (5 ml) under one atmosphere of carbon monoxide at room temperature. The mixture was stirred at room temperature for 7 hours, evaporated *in vacuo* and then quenched in a saturated NH_4Cl solution (5 ml), extracted with ether (2×10 ml). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by preparative thin layer chromatography on silica gel with 1:10 ethyl acetate–hexane as eluent to afford the product, thiol ester.

S-phenyl thiobenzoate (entry 1): m.p. 53-55°C (Lit.[12] 56°C), ^{1}H-NMR 7.53–7.58(m, 8H) 7.98–8.14(m, 2H); I.R.(KBr) 3020, 1675, 1490, 1450, 1200, 1030, 1000, 890, 750, 710, 680 cm^{-1}.

S-phenyl thio(4-methylbenzoate) (entry 2): m.p. 74–76°C (Lit.[13] 76–77°C) H^1-NMR 2.40(s,3H), 7.20–7.71(m, 7H) 8.00–8.20(m, 2H); I.R.(KBr) 2900, 1668, 1597,1486, 1441,1210, 1022, 895, 835, 746, 708,682 cm^{-1}.

S-phenyl thio(4-methoxybenzoate) (entry 3): m.p. 93–94°C (Lit.[14] 95°C) H^1-NMR 3.86(s,3H), 7.00–7.60(m,7H) 7.90-8.10(m, 2H); I.R.(KBr)2900, 1660,1595, 1430, 1250, 1160, 1020, 900, 830, 745, 675 cm^{-1}.

S-phenyl thio(4-chlorobenzoate) (entry 4): m.p. 81–82°C (Lit.[15] 81–82°C) H^1-NMR 7.10–7.63(m,7H) 7.86–8.15(m, 2H); I.R.(KBr)3040, 1665, 1605, 1482, 1451, 1389, 1086, 1000, 830, 802, 755, 690 cm^{-1}.

S-phenyl thio(3-nitrobenzoate) (entry 5): m.p. 130–132°C (Lit.[14] 132°C) H^1-NMR 6.91–7.65(m,6H) 8.35-8.61(m,2H) 8.92(m,1H); I.R.(KBr) 3050, 1663, 1605, 1525, 1340, 1200, 1075, 850, 800, 750, 670 cm^{-1}.

S-(4-methylphenyl) thiobenzoate (entry 6): m.p. 73–75ºC (Lit.[15] 75ºC) H^1-NMR 2.40(s,3H), 7.20–7.71 (m,7H) 8.00–8.20(m, 2H); I.R.(KBr) 2900, 1670, 1570, 1440, 1300, 1200, 1190, 890, 800, 770, 670 cm^{-1}.

S-(4-methylphenyl) thio(4-methoxybenzoate) (entry 7): m.p. 62–64 ºC (Lit.[16] 65.5ºC) H^1-NMR 2.40(s,3H), 3.83(s,3H) 7.00–7.70 (m,6H) 8.00–8.20(m, 2H); I.R.(KBr) 2950, 2889, 1660, 1590, 1560, 1495, 1450, 1415, 1300, 1260, 1160, 1020, 890, 840, 800, 720 cm^{-1}.

S-(4-methylphenyl) thio(4-chlorobenzoate) (entry 8): m.p. 108–110ºC (Lit.[14] 110ºC) H^1-NMR 2.40 (s,3H), 7.00–7.70 (m,6H) 8.00–8.20 (m, 2H); I.R.(KBr) 2900, 1680, 1585, 1480, 1440, 1390, 1200, 1165, 1075, 1008, 890, 800, 710 cm^{-1}.

S-benzyl thiobenzoate (entry 9): m.p.36–38ºC (Lit.[17] 37–39ºC) H^1-NMR 4.25(s,2H), 7.00–7.50 (m,8H) 7.80–8.10 (m, 2H); I.R.(KBr) 3030, 2900, 1660, 1595, 1575, 1490, 1450, 1400, 1310, 1205, 1175, 1070, 1030, 1000, 910, 850, 770, 690, 650 cm^{-1}.

S-ethyl thio(4-methylbenzoate) (entry 10): oil (Lit.[18] B.p$_{16}$ 140–142ºC), H^1-NMR 1.15–1.40(t,3H), 2.30(s,3H), 2.76–3.15(q,2H), 7.15–7.20 (d,2H) 7.65–7.76(d, 2H); I.R.(KBr) 3070, 3000, 2950, 1670, 1620, 1560, 1450, 1420, 1210, 1180, 920, 820, 790, 740, 720, 700, 645 cm^{-1}.

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