Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

HYPERVALENT IODINE IN SYNTHESIS 55: AN EFFICIENT METHOD FOR SYNTHESIS OF ARYL SULFIDES BY PALLADIUM-CATALYZED REACTION OF HYPERVALENT IODONIUM SALTS WITH MERCAPTANS

Li Wang [a] & Zhen-Chu Chen [b]
[a] Department of Chemistry , Zhejiang University , (Xi-Xi Campus), Hangzhou, 310028, P. R. China
[b] Department of Chemistry , Zhejiang University , (Xi-Xi Campus), Hangzhou, 310028, P. R. China

To cite this article: Li Wang & Zhen-Chu Chen (2001) HYPERVALENT IODINE IN SYNTHESIS 55: AN EFFICIENT METHOD FOR SYNTHESIS OF ARYL SULFIDES BY PALLADIUM-CATALYZED REACTION OF HYPERVALENT IODONIUM SALTS WITH MERCAPTANS, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:8, 1227-1232, DOI: 10.1081/SCC-100104008

To link to this article: http://dx.doi.org/10.1081/SCC-100104008

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SYNTHETIC COMMUNICATIONS, 31(8), 1227–1232 (2001)

HYPERVALENT IODINE IN SYNTHESIS 55: AN EFFICIENT METHOD FOR SYNTHESIS OF ARYL SULFIDES BY PALLADIUM-CATALYZED REACTION OF HYPERVALENT IODONIUM SALTS WITH MERCAPTANS

Li Wang and Zhen-Chu Chen*

Department of Chemistry, Zhejiang University
(Xi-Xi Campus) Hangzhou, 310028, P. R. China

ABSTRACT

The synthesis of aryl sulfides was carried out in high yields by the palladium-catalyzed cross-coupling reaction of diaryliodonium salts with mercaptans at room temperature in THF.

Aryl sulfides have received considerable interest because of their antimicrobial activity and application in organic synthesis.[1,2] Although there are many methods for the preparation of sulfides, the one most widely used for the preparation of aryl sulfides is the arylation of mercaptans with aryl halides.[2] Due to aryl halides' low reactivity, the reaction usually needs more time, high temperatures, and generally gives poor yields. Recently, transition metal catalyzed cross-coupling reaction of sulfur nucleophiles with organic electrophiles (i.e., aryl halides and triflates) is recognized to

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* Corresponding author.

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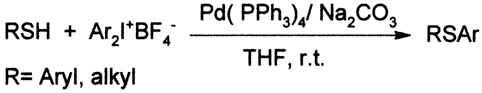
be a powerful tool for preparing aryl sulfides.[3–9] However, it still has some disadvantages, such as longer reaction time, high temperature, and use of either a strong base or specific sulfur nucleophiles.

As an alternative to organic electrophiles, we have reported the palladium-catalyzed cross-coupling reaction of hypervalent iodonium salts with organoboron compounds[10,11] and Grignard reagents.[12] It showed that diaryliodonium salts are efficient electrophilic arylation agents,[13–16] and it prompted us to extend the palladium-catalyzed arylation to mercaptans for an efficient synthesis method of aryl sulfides. Here we report the palladium-catalyzed cross-coupling of diaryliodonium salts with mercaptans (Scheme 1).[17]



$$\mathrm{RSH} + \mathrm{Ar_2I^+BF_4^-} \xrightarrow[\text{THF, r.t.}]{\mathrm{Pd(PPh_3)_4/Na_2CO_3}} \mathrm{RSAr}$$

R= Aryl, alkyl

Scheme 1.

We have found that, in the presence of sodium carbonate, palladium-catalyzed cross-coupling of diaryliodonium salts with mercaptans takes place smoothly, reaching completion within 1 h at room temperature in THF. The results are summarized in Table 1. All products gave satisfactory m.p., IR, and ^{1}H NMR spectra. The reaction was found to be general and applicable to aliphatic or aromatic mercaptans. Several diaryliodonium salts containing various substituents, such as methoxy, methyl, chloro, and nitro groups, were successfully reacted. The present method is suitable not only for the synthesis of symmetric aryl sulfides, but also for the synthesis of unsymmetric aryl sulfides.

In conclusion, we have provided a simple efficient synthesis method of aryl sulfides by palladium-catalyzed cross-coupling of diaryliodonium salts with mercaptans. It has some advantages over previous methods, such as mild reaction conditions, fast reaction rates, and good yields. Furthermore, the range of applications of diaryliodonium salts as electrophilic arylating agents in organic synthesis has been extended.

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.

Table 1. The Preparation of Aryl Sulfides[a]

Entry	$Ar_2I^+BF_4^-$	RSH	Product	Yield (%)[b]
1	$(p\text{-}CH_3C_6H_4)_2I^+BF_4^-$	PhSH	$p\text{-}CH_3C_6H_4SPh$	95
2	$(p\text{-}CH_3OC_6H_4)_2I^+BF_4^-$	PhSH	$p\text{-}CH_3OC_6H_4SPh$	91
3	$(p\text{-}ClC_6H_4)_2I^+BF_4^-$	PhSH	$p\text{-}ClC_6H_4SPh$	89
4	$(m\text{-}NO_2C_6H_4)_2I^+BF_4^-$	PhSH	$m\text{-}NO_2C_6H_4SPh$	86
5	$Ph_2I^+BF_4^-$	PhSH	PhSPh	97
6	$Ph_2I^+BF_4^-$	$p\text{-}CH_3C_6H_5SH$	$PhSC_6H_4CH_3\text{-}p$	93
7	$(p\text{-}CH_3C_6H_4)_2I^+BF_4^-$	$p\text{-}CH_3C_6H_5SH$	$p\text{-}CH_3C_6H_4SC_6H_4CH_3\text{-}p$	94
8	$(m\text{-}NO_2C_6H_4)_2I^+BF_4^-$	$p\text{-}CH_3C_6H_5SH$	$m\text{-}NO_2C_6H_4SC_6H_4CH_3\text{-}p$	83
9	$Ph_2I^+BF_4^-$	$C_6H_5CH_2SH$	$PhSCH_2C_6H_5$	91
10	$Ph_2I^+BF_4^-$	C_2H_5SH	$C_6H_5SC_2H_5$	88
11	$(p\text{-}CH_3C_6H_4)_2I^+BF_4^-$	C_2H_5SH	$p\text{-}CH_3C_6H_4SC_2H_5$	90

[a] Reagent and conditions: 1 mmol iodonium salt, 1 mmol Na_2CO_3, 5 mol% $Pd(PPh_3)_4$ and 1 mmol mercaptans, in 5 mL THF at room temperature under nitrogen atmosphere; [b] Isolated yields.

General Procedure for Synthesis of Aryl Sulfides

To a stirred solution of diaryliodonium tetrafluoroborate (1 mmol), Pd $(PPh_3)_4$ (58 mg, 5 mol%), Na_2CO_3 (106 mg, 2 mmol), and anhydrous THF (5 mL) under nitrogen atmosphere was added mercaptan at room temperature. The mixture was stirred at room temperature for an hour. The solvent was evaporated off. To the residue, a saturated NH_4Cl solution (5 mL) was added and then 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 hexane as a developer to afford the desired product, aryl sulfide.

4-Methylphenyl Phenyl Sulfide (entry 1,6)

M.p. 15°C (Lit.[18] 15.7°C) ^1H NMR 2.32 (s,3H), 7.45–6.90 (m,9H) I.R. 3045, 2920, 1587, 1490, 1442, 1400, 1210, 1090, 1020, 800, 740, 690 cm^{-1}.

4-Methyoxyphenyl Phenyl Sulfide (entry 2)

Oil ^{1}H NMR 3.80 (s,3H) 6.90–7.45 (m,9H) I.R. 3050, 1580, 1470, 1440, 1250, 1080, 1045, 830, 780, 690 cm^{-1}.

4-Chlorophenyl Phenyl Sulfide (entry 3)

Oil ^{1}H NMR 7.10–7.60 (m, 9H) I.R. 3050, 1585, 1485, 1385, 1075, 1000, 800, 750, 690 cm^{-1}.

3-Nitrophenyl Phenyl Sulfide (entry 4)

M.p. 41°–42°C (Lit.[19] 42.5°C) ^{1}H NMR 7.20–8.15 (m,9H) I.R. (KBr) 3040, 1585, 1560, 1500, 1350, 1300, 730, 700, 670 cm^{-1}.

Diphenyl Sulfide (entry 5)

Oil ^{1}H NMR 7.00–7.35 (m, 10H) I.R. 3050, 1580, 1470, 1440, 1080, 1030, 740, 690 cm^{-1}.

4.4′ -Dimethyldiphenyl Sulfide (entry 7)

M.p. 55°–56°C (Lit.[20] m.p. 57.3°C) ^{1}H NMR 2.34 (s,6H) 6.90–7.30 (m,8H) I.R. 3060, 2950, 1595, 1480, 1070, 1005, 790 cm^{-1}.

3-Nitrophenyl 4′-methylphenyl Sulfide (entry 8)

M.p. 60°–61°C (Lit.[21] m.p. 61°C) ^{1}H NMR 7.10–8.10 (m,8H) 2.30 (s,3H) I.R. 3045, 2870, 1630, 1570, 1480, 1450, 1390, 1300, 1175, 1110, 1070, 1005, 900, 830, 790 cm^{-1}.

Benzyl Phenyl Sulfide (entry 9)

M.p. 38°–40°C (Lit.[22] m.p. 39°–40°C) ^{1}H NMR 4.00 (s, 2H) 6.95–7.40 (m,10H) I.R. 3050, 2910, 1578, 1480, 1408, 1240, 1090, 1070, 1030, 920, 740 cm^{-1}.

Ethyl Phenyl Sulfide (entry 10)

Oil ^{1}H NMR 1.3 (t, 3H, J 7.1 Hz) 2.90 (q,2H, J7.1 Hz), and 7.2–7.4 (5H,m) I.R. 3050, 2900, 1580, 1470, 1440, 1080, 1030, 740, 690 cm^{-1}.

Ethyl 4-Methylphenyl Sulfide (entry 11)

Oil ^{1}H NMR 1.3 (3H, t, J 7.1 Hz), 2.30 (s,3H) 2.90 (q, 2H, J 7.1 Hz), 7.2–7.4 (m,4H) I.R. 3050, 2895, 1580, 1470, 1440, 1080, 1030, 740, 690 cm^{-1}.

ACKNOWLEDGMENTS

We appreciate the financial support of the National Science Foundation of China (Project 29472036).

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Accepted June 18, 2000