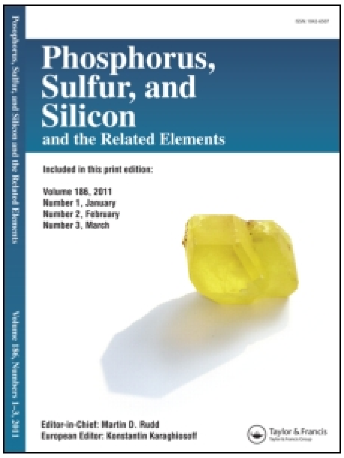


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Reaction Between Diphenyliodonium Iodide and Disulfides in the Presence of a Zn/AlCl$_3$ System: A Convenient Method for the Synthesis of Organic Sulfides

Barahman Movassagh[a]; Amir Mossadegh[a]
[a] Department of Chemistry, K. N. Toosi University of Technology, Tehran, Iran

To cite this Article Movassagh, Barahman and Mossadegh, Amir(2005) 'The Reaction Between Diphenyliodonium Iodide and Disulfides in the Presence of a Zn/AlCl$_3$ System: A Convenient Method for the Synthesis of Organic Sulfides', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 10, 2275 — 2278

To link to this Article: DOI: 10.1080/104265090920796

URL: http://dx.doi.org/10.1080/104265090920796

Phosphorus, Sulfur, and Silicon, 180:2275–2278, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090920796

The Reaction Between Diphenyliodonium Iodide and Disulfides in the Presence of a Zn/AlCl$_3$ System: A Convenient Method for the Synthesis of Organic Sulfides

Barahman Movassagh
Amir Mossadegh
Department of Chemistry, K. N. Toosi University of Technology,
Tehran, Iran

A convenient method for the synthesis of alkyl aryl- and diaryl sulfides by the reaction of diphenyliodonium iodide and disulfides in the presence of Zn/AlCl$_3$ system in acetonitrile is reported.

Keywords Diphenyliodonium iodide; disulfides; sulfides; Zn/AlCl$_3$ system; zinc thiolate

INTRODUCTION

Organic disulfides are not conventional starting materials for the preparation of sulfides. However, heterolytic or homolytic cleavage of the S—S bond by carbanions or carbon free radicals, or the abstraction of the sulfur atoms by certain reagents, may be of use for the preparation of some sulfides.[1] Cleavage of disulfide bonds by carbanions is known to give sulfides in such reactions with phenyl lithium,[2] lithium acetylides,[3] and benzyne.[4] Benzyl sulfides also have been prepared via reaction of benzyl bromide with disulfides promoted by a Sm/BiCl$_3$ system in an aqueous media.[5] Recently we reported the synthesis of sulfides through a simple reaction of disulfides with alkyl or aryl halides using a Zn/AlCl$_3$ system.[6]

Received July 20, 2004; accepted October 13, 2004.

The authors are thankful to K.N. Toosi University of Technology Research Council for partial support of this work.

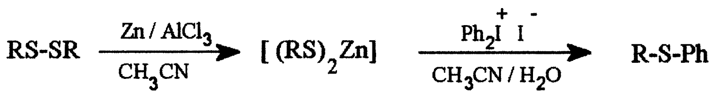
Address correspondence to Barahman Movassagh, K.N. Toosi University of Technology, Department of Chemistry, P.O. Box 15875-4416, Tehran, Iran. E-mail: bmovass1178@yahoo.com

While most alkyl aryl sulfides are generally prepared by the reaction of alkali metal salts of thiols with alkyl halides,[1] methods for the preparation of aryl sulfides suffers from limited applicability in that activated reactants, severe reaction conditions, complicated procedures, or a combination of these requirements are involved.[1,7]

RESULTS AND DISCUSSION

In the course of our study to explore an alternative route for the preparation of alkyl aryl- and diarylsulfides from disulfides, we found that diaryliodonium salts are efficient electrophilic arylating agents for this purpose. These tricoordinate iodine species are, in general, ionic substances; chlorides, bromides, and iodides possess some covalent characters in a manner similar to that in the aryliodo dichlorides.[8] These salts are more susceptible to nucleophilic displacement because their positive charges should facilitate polar fission of the bonds to the aromatic systems.[8] There are strong indications that the reactions of diphenyliodonium salts with bases proceeded by nucleophilic rather than by radical attack on the 1-carbons of the diphenyliodonium salts to give iodobenzene and the phenyl derivatives of the bases.[8b] Here we introduce a convenient route for the preparation of various alkyl aryl- and diaryl sulfides via reaction of diphenyliodonium iodide salt and disulfides promoted by a Zn/$AlCl_3$ system. Simple stirring of disulfides with metallic zinc dust in the presence of anhydrous aluminum chloride in acetonitrile at 80°C produced the zinc thiolate. This was followed by the addition of diphenyliodonium iodide which gave, after workup, the desired sulfides (Scheme 1) in 75–90% yield as shown in Table I. As indicated in Table I, relatively shorter reaction times and higher yields are obtained for aryl, compared to alkyl, disulfides.

In summary, the present work shows a new general, simple, mild, and superior procedure for the synthesis of various alkyl aryl- and diaryl sulfides, and the range of useful applications of diaryliodonium salts as highly electrophilic arylating reagents in organic synthesis has been extended.



SCHEME 1

TABLE I Synthesis of Alkyl Aryl- and Diaryl Sulfides From Disulfides and Diphenyliodonium Iodide in the Presence of Zn/AlCl$_3$

Run	R	Reaction time (h)	Yield (%)[a]	m.p. (°C)/b.p. (°C)/Torr	
				Found	Reported[b]
1	Ph	3	80	Oil	145/8[9]
2	4-ClC$_6$H$_4$	3.5	84	Oil	141/2[10]
3	4-MeC$_6$H$_4$	4	82	Oil	170–175/18[11]
4	2-ClC$_6$H$_4$	4.5	83	Oil	132/1[10]
5	2-NO$_2$C$_6$H$_4$	3	90	75–77	76[12]
6	4-BrC$_6$H$_4$	4	82	Semi solid	25[9]
7	4-FC$_6$H$_4$	4	80	Oil	147–148/15[13]
8	2-Naphthyl	3	88	49–51	51[14]
9	PhCH$_2$	5	78	41–42	41–42[15]
10	n-C$_4$H$_9$	7	77	Oil	117/15[16]
11	n-C$_8$H$_{17}$	8.5	75	Oil	147/18[17]

[a] Yields of pure isolated products.
[b] References for physical data of products.

EXPERIMENTAL

General

Diphenyliodonium iodide was prepared by standard procedure.[8b] All products were characterized by comparison of their spectral and physical data with those of known samples. ^{1}H NMR were recorded using a Jeol JNM-EX90A NMR spectrometer. IR spectra were obtained using a Shimadzu IR-408 spectrophotometer. Melting points were obtained by an Electrothermal 9100 apparatus and are uncorrected.

General Procedure for the Preparation of Alkyl Aryl- and Diaryl Sulfides

A mixture of the disulfide (0.5 mmol), anhydrous aluminum chloride (1 mmol), zinc dust (2 mmol), and acetonitrile (10 mL) was stirred at 80°C for 2 h until the zinc powder had almost disappeared; diphenyliodonium iodide (1 mmol) and water (2 mL) were then added at once to the solution and stirring was continued at that temperature for 3–7 h in an air atmosphere. After completion of the reaction, the solution was filtered and washed with diethyl ether. The combined Et$_2$O/CH$_3$CN solution was then washed with 5% sodium hydroxide solution (30 mL) and water (2 × 20 mL). After drying with anhydrous magnesium sulfate, the solvent was evaporated in vacuo. The crude sulfide was either recrystallized from ethanol or purified by preparative thin layer chromatography (silica gel, eluent EtOAc: Pet. ether = 1:2) to afford the desired product.

REFERENCES

[1] S. Oae, *Organic Chemistry of Sulfur*, p. 57. New York: Plenum press (1977).

[2] A. Schönberg, A. Stephenson, H. Kaltschmidt, E. Petersen, and H. Schutten, *Ber. Dt. Chem. Ges.* B, **66,** 237 (1933).

[3] J. R. Nooi and J. F. Arens, *Rec. Trav. Chem. Pays-Bas*, **80,** 245 (1961).

[4] I. Tabushi, K. Okazaki, and R. Oda, *Tetrahedron Lett.*, 3591 and 3821 (1967).

[5] G. Lu and Y. Zhang, *Synth. Commun.*, **28,** 4479 (1988).

[6] (a) B. Movassagh, M. M. Lakouraj, and Z. Fadaei, *J. Chem. Res. (S)*, 350 (2000); (b) M. M. Lakouraj, B. Movassagh, and Z. Fadaei, *Synth. Commun.*, **32,** 1237 (2002).

[7] (a) J. F. Bunnett and W. D. Merritt, *J. Am. Chem. Soc.*, **79,** 5967 (1957); (b) R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, **81,** 4927 (1959); (c) C. Palomo, M. Oiarbide, R. Lopez, and E. Gomez-Bengoa, *Tetrahedron Lett.*, **41,** 1283 (2000).

[8] (a) D. F. Banks, *Chem. Rev.*, **66**, 243 (1966); (b) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75,** 2705 and 2708 (1953).

[9] S. Suwa, T. Sakamoto, and Y. Kikugawa, *Chem. Pharm. Bull.*, **47,** 980 (1999).

[10] S. Oae and Y. H. Khim, *Bull. Chem. Soc. Jap.*, **40,** 1716 (1967).

[11] H. Burton and W. A. Davy, *J. Chem. Soc.*, 528 (1948).

[12] E. D. Amstutz, I. M. Hunsberger, and J. J. Chessick, *J. Am. Chem. Soc.*, **73,** 1220 (1951).

[13] N. J. Leonard and L. E. Sutton, *J. Am. Chem. Soc.*, **70,** 1564 (1948).

[14] F. M. Furman, J. H. Thelin, D. W. Hein, and W. B. Hardy, *J. Am. Chem. Soc.*, **82,** 1450 (1960).

[15] R. D. Rieke, S. J. Uhm, and P. M. Hudnall, *J. Chem. Soc., Chem. Commun.*, 269 (1973).

[16] (a) T. Mukaiyama and M. Ueki, *Tetrahedron Lett.*, 3429 (1967); (b) V. Horak, J. Pecka, and J. Jurjev, *Collect. Czech. Chem. Commun.*, **32,** 3386 (1967); *CA*, **67,** 85460f (1967).

[17] V. Franzen, H. I. Joschek, and C. Mertz, *Ann.*, **654,** 82 (1962).