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 XXII: A Novel Way for the Preparation of Unsymmetric S-Aryl Thiosulfonates by the Reaction of Potassium Thiosulfonates with Diaryliodonium Salts

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Published online: 22 Aug 2006.

To cite this article: Min Xia & Zhen-Chu Chen (1997) Hypervalent Iodine in Synthesis XXII: A Novel Way for the Preparation of Unsymmetric S-Aryl Thiosulfonates by the Reaction of Potassium Thiosulfonates with Diaryliodonium Salts, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:8, 1309-1313, DOI: 10.1080/00397919708006058

To link to this article: http://dx.doi.org/10.1080/00397919708006058

SYNTHETIC COMMUNICATIONS, 27(8), 1309-1313 (1997)

HYPERVALENT IODINE IN SYNTHESIS XXII: A NOVEL WAY FOR THE PREPARATION OF UNSYMMETRIC S-ARYL THIOSULFONATES BY THE REACTION OF POTASSIUM THIOSULFONATES WITH DIARYLIODONIUM SALTS

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Abstract: Unsymmetric S-aryl thiosulfonates can be generated through a novel way for the reaction of potassium thiosulfonates with diaryliodonium salts in good yields under mild conditions.

Thiosulfonates have been reported[1] to be powerful sulfenylating agents which react faster and more completely than disulfides; in addition, they are more stable and easier to handle than sulfinyl chlorides. In our course of studies on the applications of hypervalent iodine reagents in organic synthesis, we have offered a method for the preparation of S-aryl thiosulfonates through the

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oxidation of disulfides or thiophenols by phenyliodine (Ⅲ) bis-(trifluoroacetate)[2],but it can not be suitable for the preparation of unsymmetric S-aryl thiosulfonates.

According to the retrosynthetic analysis, we assumed that unsymmetric S-aryl thiosulfonates could be generated by the reaction of a salt of thiosulfonic acid with an equivalent reagent of aryl cation. (Scheme 1)

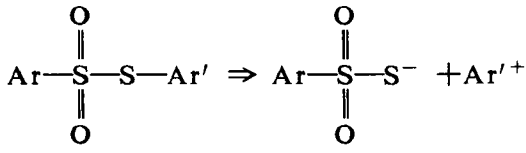
As indicated in our previous papers[3], diaryliodonium salts are one of the best transfer reagents of aryl cations, we examined the reaction of potassium thiosulfonates with diaryliodonium salts as a general, efficent and new method for the preparation of unsymmetric S-aryl thiosulfonates[4].

We found this reaction took place readily to give corresponding S-aryl thiosulfonates(Scheme 2)

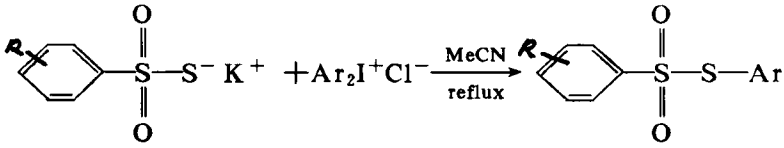
To the stirred solution of appropriate potassium thiosulfonates in MeCN was added the diaryliodonium salts. Then refluxing for required time until the diaryliodonium salts almost completely disappeared. After workup and isolation, the corresponding S-aryl thiosulfonates were obtained in good yields, as shown in Table 1.

As it indicates, this reaction can not only be suitable for the preparation of unsymmetric S-aryl thiosulfonates but also of symmetric ones.

In general, unsymmetric S-aryl thiosulfonates are generated by the formation of S—S bond, i.e. sulfenyl chlorides with sulfinic acids[6], sulfonyl halides with silver thiolates[7], sulfenyl halides with sodium sulfinates [8]etc, and some other methods, such as thiosulfonates exchange reaction[9], oxidation of thiosulfinates with sodium metaperiodate[10], sulfenic sulfonic thioanhydrides with nucleophilic reagents by desulfurizition,[11], and so on. However, the present reaction represents a new method for the preparation of S-aryl thiosulfonates via the formation of C—S bond.



(Scheme 1)



(1) (2) (3)

(3)	R	Ar	(3)	R	Ar
a	H	p—ClC_6H_4	f	H	p—$O_2NC_6H_4$
b	p—CH_3	p—ClC_6H_4	g	p—Cl	C_6H_5
c	p—CH_3	C_6H_5	h	o—CH_3	C_6H_5
d	p—CH_3	p—$O_2NC_6H_4$	i	p—CH_3	p—$CH_3C_6H_4$
e	H	p—$CH_3C_6H_4$			

(Scheme 2)

In the summary, we have presented a new, simple and general method for the preparation of S-aryl thiosulfonates, especially unsymmetric S-aryl thiosulfonates by the reaction of potassium thiosulfonates with diaryliodonium salts. It has some advantages over others such as mild reaction conditions, accessible starting materials, simple procedure and avoiding the use of toxic and unstable agents.

Experimental:

General procedure for the preparation of unsymmetric S-aryl thiosulfonates:

Under stirring, 2 mmol of appropriate diaryliodonium salt was added to the solution of 2.5 mmol potassium thiosulfonate in

Table 1. Unsymmetric S-aryl thiosulfonates from potassium thiosulfonates with diaryliodonium salts.

Entry	reaction time(h)	yields (%)	m. p. (℃)	lit. m. p[5] (℃)	I. R. (KBr, cm^{-1})	^1H—NMR (ppm, $CDCl_3$)
3a	8	51	70—72	72—73	1330, 1155	7. 23—7. 96(m, 9H)
3b	7. 5	57	86—88	90—91	1330, 1155	2. 38(s, 3H) 7. 03—7. 66(m, 8H)
3c	12	61	76—77	78—79	1330, 1140	2. 38(s, 3H) 7. 13—7. 69(m, 9H)
3d	5	59	127—129	130—131	1340, 1130	2. 32(s, 3H) 7. 03—7. 66(m, 8H)
3e	14	61	51—54	53—54	1330, 1145	2. 32(s, 3H) 7. 13—7. 72(m, 9H)
3f	5	68	102—104	103—104	1340, 1130	7. 06—7. 69(m, 9H)
3g	6. 5	65	87—88	83—84	1330, 1150	7. 00—7. 67(m, 9H)
3h	15	48	liquor	—	1330, 1150	2. 61(s, 3H) 6. 54—7. 50(m, 9H)
3i	15	50	76—78	76—78	1330, 1145	2. 33(s, 3H) 2. 26(s, 3H) 7. 17—7. 83(m, 8H)

30 ml MeCN. After refluxing for required time until the solid almost completely disappeared, the mixture was filtered and the filtrate was evaporated in a rotary evaporator under vacuum. The residue was isolated by TLC with petroleum ether (b. p. 30—60℃) and CH_2Cl_2 in the ratio of 2 to 1 as the developer to give the product which could be recrystalized with MeOH. All products were identified by comparison of melting points with literature values and by I. R. and ^1H-NMR spectral data.

Acknowledgement: Financial support of this work by NSF of Zhejiang and NSF of P. R. China.

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(Received in the UK 18th June 1996)