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HYPERVALENT IODINE IN SYNTHESIS XXIV: A FACILE METHOD FOR THE PREPARATION OF ARYLSULFINIC ESTERS: OXIDATION OF DISULFIDES OR THIOPHENOLS BY PHENYLIODINE(III) BIS(TRIFLUOROACETATE) IN THE PRESENCE OF ALCOHOLS

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Abstract: Arylsulfinic esters were prepared by the oxidation of diaryl disulfides or thiophenols with phenyliodine(III) bis(trifluoroacetate) in the presence of alcohols.

Following our finding that thiosulfonic esters could be generated from disulfides by the oxidation with phenyliodine(III) bis (trifluoroacetate), PIB, in the presence of methylene chloride[1], we assumed that thiosulfinic esters might be the intermediates of this reaction. Based on the fact that thiosulfinic S-esters can be

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alcoholysis to sulfinic esters[2], we considered it was possible to prepare sulfinic esters directly from disulfides by the oxidation with phenyliodine(Ⅲ) bis(trifluoroacetate) in the presence of alcohols. (Method A)

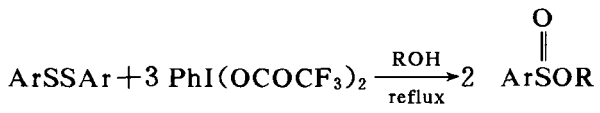
We examined the reaction of PIB with diaryl disulfides in alcohols. We found that the oxidative reaction occurred readily in a single step to give the desired sulfinic esters, which have the characteristic I. R. spectral data of $-\overset{\overset{O}{\|}}{S}-O-$ group [4]. (Scheme 1)

To the stirred solution of the appropriate diaryl disulfides in alcohols was added slowly the solution of PIB in alcohols at room temperature. Then, simple refluxing for required time gave, after workup and isolation, the corresponding sulfinic esters (3a～3g), in good yields, as shown in Table 1.

The results show that this method is suitable for the preparation of sulfinic esters of various kinds of alcohols, and it is easy for methanol or ethanol to carry out the reaction whereas as for secondary and tertiary alcohols, the reaction turned difficult with long reaction time. This may relate to the stereo hindrance effect of alcohols in the reaction.

Based on the fact that disulfides are generally formed from the oxidation of thiophenols, we investigated a one-pot procedure for the preparation of sulfinic esters from the reaction of thiophenols with PIB in the presence of alcohols (Method B) (Scheme 2). This results, 3h-3k, are shown in Table 1.

A number of methods have been reported for the preparation of sulfinic esters, i.e. (a) the alcoholysis of thiosulfinic S-esters with alcohols[2], (b) the oxidative alcoholysis of disulfides with N-bromosuccinimide [3] or lead tetracetate[4], (c) the esterification of sulfinic acids with alcohols[5], (d) the alkylalion of sulfinic acids with o-alkylisoureas[6], (e) the reaction of sulfinyl



(1) (2) (3)

(3)	Ar	R
3a	p-$CH_3C_6H_4$	Me
3b	p-$CH_3C_6H_4$	i-Pr
3c	p-$CH_3C_6H_4$	t-Bu
3d	p-ClC_6H_4	Me
3e	p-ClC_6H_4	Et
3f	p-ClC_6H_4	i-Pr
3g	p-ClC_6H_4	t-Bu

(Scheme 1)

chlorides with chlorosulfites[7], (f) the treatment of N-(alkylsulfinyl) phthalimides with alcohols[8], etc. but these methods have certain disadvantages such as the necessity of using toxic agents[4], or unstable substances[5,6], and difficultly accessible starting materials[2,7,8]. The present method has the advantages of simple procedure, non-toxic agents , easily accessible starting materials,better yields and mild conditions.

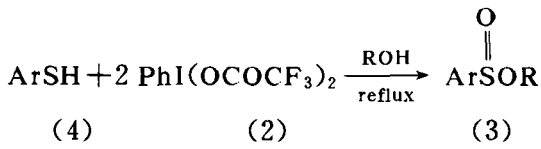
Experimental Section:

1. **General procedure for the preparation of sulfinic esters (3) with method A:**

Under stirring, the solution of 3 mmol phenyliodine(Ⅲ) bis (trifluoroacetate) in 10 ml appropriate alcohols was added to the

Table 1: Sulfinic esters 3 prepared

Entry	Ar	R	reaction time(h)	yield (%)	I.R. (KBr, cm^{-1})	^{1}H-NMR (ppm, $CDCl_3$)
3a	p-$CH_3C_6H_4$	Me	2	90	2960,1140,960	2.33(s,3H) 3.40(s,3H) 7.00−7.66(m,4H)
3b	p-$CH_3C_6H_4$	i-Pr	24	65	2960,1145,920	1.20(d,6H) 2.27(s,3H) 4.58(m,1H) 6.77−7.50(m,4H)
3c	p-$CH_3C_6H_4$	t-Bu	48	51	2960,1140,940	1.23(s,9H) 2.30(s,3H) 6.94−7.66(m,4H)
3d	p-ClC_6H_4	Me	3	87	2960,1140,960	3.43(s,3H) 7.20−7.73(m,4H)
3e	p-ClC_6H_4	Et	7	82	2950,1140,1015	1.27(t,3H) 3.94(q,2H) 7.00−8.00(m,4H)
3f	p-ClC_6H_4	i-Pr	24	63	2950,1145,920	1.23(d,6H) 4.56(m,1H) 7.23−7.72(m,4H)
3g	p-ClC_6H_4	t-Bu	48	54	2950,1150,1010	1.20(s,9H) 6.74−7.53(m,4H)
3h	C_6H_5	Me	3	91	2960,1130,960	3.46(s,3H) 7.33−7.82(m,5H)
3i	C_6H_5	Et	5	83	3000,1140,1010	1.23(t,3H) 3.90(q,2H) 7.33−7.90(m,5H)
3j	$C_6H_5CH_2$	Me	7	74	2960,1120,990	3.66(s,3H) 3.93(s,2H) 7.20−7.40(m,5H)
3k	$C_6H_5CH_2$	Et	10	70	3000,1130,1020	1.20(t,3H) 3.90(q,2H) 3.96(s,2H) 7.10−7.33(m,5H)



3	Ar	R
3h	C_6H_5	Me
3i	C_6H_5	Et
3j	$C_6H_5CH_2$	Me
3k	$C_6H_5CH_2$	Et

(Scheme 2)

solution of 1mmol disulfides in 15 ml corresponding alcohols. After refluxing for required time and removed most of the alcohol under reduced pressure, the mixture was isolated by TLC with petroleum ether (b. p. 30—60℃) and methylene chloride in the ratio of 2 to 1 as the developer to give the product. All of the products were identified with I. R. and ^{1}H-NMR spectral date.

2. Preparation of sulfinic ester (3) with method B:

Under stirring ,the solution of 2mmol phenyliodine(Ⅲ) bis (trifluoroacetate) in 10ml alcohols was added to the solution of 1mmol thiophenols in 15 ml alcohols. Then refluxed for required time and gave the products as procedure 1.

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