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Hypervalent Iodine in Synthesis XXXII: A Novel Way for the Synthesis of N-Sulfonylsulfilimines from Sulfides and Sulfonamides Using Iodosobenzene Diacetate

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HYPERVALENT IODINE IN SYNTHESIS XXXII: A NOVEL WAY FOR THE SYNTHESIS OF N-SULFONYLSULFILIMINES FROM SULFIDES AND SULFONAMIDES USING IODOSOBENZENE DIACETATE

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Abstract: A number of N-sulfonylsulfilimines have been prepared through a novel way for the reaction of iodosobenzene diacetate with sulfides and sulfonamides under mild conditions.

Sulfilimines have received considerable interest because of their particular applications in organic synthesis. As the important part of the sulfilimines, N-sulfonylsulfilimines were well studied in recent years.[1-6]

In early years, N-sulfonylsulfilimines were prepared either by treating the corresponding sulfides with chloramine-T,[7] or by the reaction of the sulfoxides with sulfonamide[8] or sulfinylsulfonamide[9] or sulfonylisocyanate.[10] Among these, the first method is most commonly used. To date, some methods were developed,

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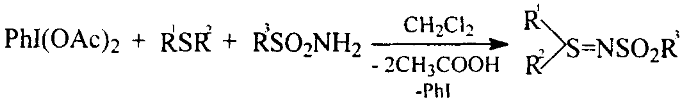
such as the reaction of p-toluensulfonyl azide with sulfides,[11] treatment of tetra-butylammonium N-chloro-p-toluenesulfonamide with sulfides,[12] the means of tin-mediated Friedal-Crafts reactions,[13] treatment of sulfides and sulfonamides with lead(IV)-acetate,[14] and recently, Takada[15] reported that [N-(p-tolysulfonyl)imino]phenyliodinane (PhI=NTs) could be used as a nitrene transfer reagent to the synthesis of N-sulfonylsulfilimines.

Following our finding that N-sulfonyltriphenylarsinimes can be synthesized by a one-pot reaction of triphenylarsine with sulfonamides and iodosobenzene diacetate,[16] we investigated the possibility of extending the one-pot reaction to synthesis N-sulfonylsulfilimines.According to the analysis, we treated $PhI(OAc)_2$ with sulfonamides and sulfides. We found this reaction took place readily to give corresponding N-sulfonylsulfilimines.(Scheme 1)



$$\mathrm{PhI(OAc)_2} + \overset{1}{R}S\overset{2}{R} + \overset{3}{R}SO_2NH_2 \xrightarrow[\substack{-2CH_3COOH \\ -PhI}]{CH_2Cl_2} (R^1)(R^2)S{=}NSO_2R^3$$

1 **2** **3** **4**

(Scheme 1)

To the stirred solution of appropriated sulfonamide and sulfide in CH_2Cl_2 was added the $PhI(OAc)_2$. The mixture was stirred for 30 min., then triethylamine was added and the reaction was continued for 1 hr.. After workup and isolation, the corresponding N-sulfonylsulfilimine was obtained as shown in Table I.

Table I. Synthesis N-sulfonylsulfilimines by reaction of iodosobenzene diacetate with sulfides and sulfonamides

Entry	R^1	R^2	R^3	Yield* (%)	M. P. (℃)	Lit. M. P. (℃)
4a	C_2H_5	C_2H_5	p-$CH_3C_6H_5$	55	143-144	144.5-145.5[17]
4b	C_2H_5	C_2H_5	C_6H_5	47	112-114	115[18]
4c	C_2H_5	C_2H_5	p-ClC_6H_5	58	139-140	—
4d	C_3H_7	C_3H_7	p-$CH_3C_6H_5$	61	108-110	110-111.5[17]
4e	C_3H_7	C_3H_7	p-ClC_6H_5	60	134-135	—
4f	$PhCH_2$	$PhCH_2$	p-$CH_3C_6H_5$	51	191-193	192-193[17]
4g	$PhCH_2$	$PhCH_2$	C_6H_5	45	152-153	153[18]
4h	$PhCH_2$	$PhCH_2$	p-ClC_6H_5	59	208-209	—
4i	$PhCH_2$	Ph	p-$CH_3C_6H_5$	53	138-140	137-138[19]
4j	$PhCH_2$	Ph	p-ClC_6H_5	64	178-180	—

* isolated yields.

As it indicated, this reaction can not only be suitable for the preparation of symmetric N-sulfonylsulfilimines but also of unsymmetric ones.

In the summary, we have found a new, simple method for the preparation of N-sulfonylsulfilimines. It has some advantages over others such as simple one-step procedure,mild reaction conditions, accessible starting materials and avoiding the use of toxic and unstable agents.

Experimental:

^{1}HNMR spectra were recorded on PMX-60 spectrometer. Infrared spectra were determined on PE-683 Infrared Spectrophotometer. Elemental analyses were performed on a Carlo Erbal 1107 instrument. Dichloromethane was distilled from CaH_2.

Typical procedure for the preparation of N-sulfonylsulfilimines: Iodosobenzene diacetate (1.61 g, 10 mmol) was added in small portions to a solution of sulfonamide (10 mmol) and sulfide (50 mmol) in 30 ml anhydrous dichloromethane with stirring. The mixtrue was stirred for 30 min., triethylamine (1.01 g, 10 mmol) was added and the reaction was continued for 1 hr. After that, the mixtrue was poured into water (150 mL) and extracted with dichloromethane (3 × 50 mL). The extract was washed with water, and dried over anhydrous $MgSO_4$. After removal of the solvent, and the residue was recrystallized from ethanol to give pure sulfilimine, representative spectroscopic and analytical data being shown below.

4a IR (KBr, cm^{-1}) 1284, 1145, 1095, 978. ^{1}HNMR (δ,ppm) 1.10 (t, 6H), 2.33 (s. 3H), 2.82 (q, 4H), 7.17 (d, 2H), 7.72 (d, 2H).

4b IR (KBr, cm^{-1}) 1286, 1145, 1095, 978. ^{1}HNMR (δ,ppm) 1.10 (t, 6H), 2.81(q. 4H), 7.3-7.7 (m, 5H).

4c IR (KBr, cm^{-1}) 1280, 1151, 1096, 983. ^{1}HNMR (δ,ppm) 1.12 (t, 6H), 2.83 (q, 4H), 7.23 (d, 2H), 7.76 (d, 2H). Anal. Calcd for $C_{10}H_{14}ClNO_2S_2$: C, 42.93; H, 5.04; N, 5.01. Found: C, 42.96; H, 5.24; N, 4.82.

4d IR (KBr, cm^{-1}) 1285, 1152, 1097, 975. ^{1}HNMR (δ,ppm) 0.90 (t, 6H), 1.4-1.8 (m, 4H), 2.32 (s, 3H), 2.80 (t, 4H), 7.20 (d, 2H), 7.75 (d, 2H).

4e IR (KBr, cm^{-1}) 1277, 1153, 1097, 980. ^{1}HNMR (δ,ppm) 0.90 (t, 6H), 1.4-1.8 (m, 4H), 2.82 (t, 4H), 7.25 (d, 2H), 7.81 (d, 2H). Anal. Calcd for $C_{12}H_{18}ClNO_2S_2$: C, 46.82; H, 5.89; N, 4.55. Found: C, 47.02; H, 6.01; N, 4.37.

4f IR (KBr, cm^{-1}) 1285, 1140, 1093, 988. ^{1}HNMR (δ,ppm) 2.28 (s, 3H), 4.02 (s, 4H), 6.9-7.7 (m, 14H).

4g IR (KBr, cm^{-1}) 1285, 1143, 1088, 982. ^{1}HNMR (δ,ppm) 4.02 (s, 4H), 7.1-7.7 (m, 15H).

4h IR (KBr, cm^{-1}) 1283, 1148, 1090, 990. ^{1}HNMR (δ,ppm) 4.06 (s, 4H), 7.0-7.6 (m, 14H). Anal. Calcd for $C_{20}H_{18}ClNO_2S_2$: C. 59.47; H, 4.49; N, 3.46. Found: C, 59.43; H, 4.48; N, 3.17.

4i IR (KBr, cm^{-1}) 1284, 1152, 1091, 965. ^{1}HNMR (δ,ppm) 2.30 (s, 3H), 4.08 (s, 2H), 6.9-7.8 (m, 14H).

4j IR (KBr, cm^{-1}) 1285, 1141, 1091, 970. ^{1}HNMR (δ,ppm) 4.12 (s, 2H), 7.0-7.8 (m, 14H). Anal. Calcd for $C_{19}H_{16}ClNO_2S_2$: C, 58.53; H, 4.14; N, 3.59. Found: C, 58.53; H, 4.06; N, 3.33.

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