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A CONVENIENT PREPARATION OF NITRILES BY REACTION OF FREE SULFIMIDE WITH ALDEHYDES

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Diphenyl free sulfimide was found to react readily with aldehydes affording the corresponding nitriles in high yields.

Diaryl N-unsubstituted (free) sulfimides are relatively strong bases (e.g., pKa value of diphenyl free sulfimide ; 8.5) and good nucleophiles.[1] Indeed, diaryl free sulfimides have been found to react with a variety of acylating agents affording the corresponding diaryl N-acyl-sulfimides,[2] and to undergo the Michael-type addition to electrophilic olefins affording the corresponding aziridines in good yields.[3,4] As a further extention of the synthetic utilizations of free sulfimides, we have carried out the reaction of diphenyl free sulfimide with aldehydes, and found that several aldehydes were readily transformed to the corresponding nitriles in high yields. This paper describes a convenient one-pot preparation of nitriles by the reaction of diphenyl free sulfimide with several aldehydes.

A typical reaction is the following : Diphenyl free sulfimide (900mg, 4.1mmol) and benzaldehyde (424mg, 4mmol) were dissolved in 10 ml of benzene in a sealed tube. The mixture was kept standing at 80°C for 5 h. After removing benzene in vacuo, benzonitrile and diphenyl sulfide were isolated by column chromatography in 65.8%(271mg) and 91.0%(693mg) yields, respectively. The products obtained were identified by comparing their ir, nmr, mass spectra and mp or bp with those of the authentic samples. Similar reactions of diphenyl free sulfimide with other aldehydes were also carried out, and the results obtained are summarized in Table.

Inspection of the Table reveals that the reaction can be applied to both aryl and alkyl aldehydes such as p-substituted benzaldehydes and caprylic aldehyde which afforded the corresponding nitriles in high yields. Even with dialdehyde, such as p-phthalaldehyde, the corresponding dinitrile was obtained.

In the reaction with trans-cinnamaldehyde, trans-cinnamonitrile was obtained in a decent yield in which no aziridine formation was observed even though the reaction of diphenyl free sulfimide with such electrophilic olefins as dibenzoylethylene, benzalacetophenone and benzalacetone afforded the corresponding aziridines, via the Michael-type addition.[3] Meanwhile, the reaction with phenylacetaldehyde was somewhat different. The main product was not phenylacetonitrile but a complex mixture of the products. Although the mechanism for the reaction is still to be studied, this reaction would offer a convenient one-pot procedure to prepare various nitriles from the corresponding aldehydes and free sulfimide.

Table. The Reaction of Aldehydes with Diphenyl Free Sulfimide in Benzene at 80°C for 5 h.

Aldehyde	Yield(%)*		Nitrile	
	Sulfide	Nitrile	bp(mp)(°C)	ir(ν_{CN},cm^{-1})
C_6H_5CHO	91.0 (quant)	65.8 (quant)	191	2220
p-$CH_3C_6H_4CHO$	92.7 (91.0)	80.0 (90.0)	103-106/20mmHg	2220
p-ClC_6H_4CHO	88.9 (92.0)	88.0 (82.0)	(91-92)	2220
p-$CH_3OC_6H_4CHO$	83.6 (81.7)	75.2 (86.1)	(58)	2210
p-HOC_6H_4CHO	90.0 (95.0)	83.6 (94.0)	(109-110)	2225
$CH_3(CH_2)_6CHO$	90.5 (98.0)	94.0 (82.3)	198-200	2230
$CH_3(CH_2)_7CHO$	88.0 (quant)	89.9 (78.0)	224	2230
trans-PhCH=CHCHO	88.0 (96.0)	82.9 (91.5)	254-255	2210
p-$OHCC_6H_4CHO$	78.2	69.5	(140-141)	2220

*) The yields determined by GLC analysis are shown in parentheses.

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