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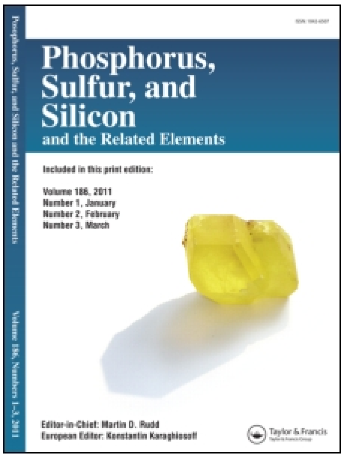

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C-S Bond Cleavage Reactions of Sulfonediimines

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C-S BOND CLEAVAGE REACTIONS OF SULFONEDIIMINES

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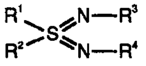
Abstract Nucleophilic C-S bond cleavage of Sulfonediimines to Sulfinamidine-type Structures is discussed

Sulfonediimines 1 are characterized by a versatile functional group. Besides CH- and NH-acidity (R^1/R^2 = alkyl; R^3/R^4 = H) they offer nucleophilic basic nitrogens and potentially asymmetric sulfur as well. Under these aspects they have been investigated in our group since many years.[1,2]

In certain cases, however, they are susceptible to C-S bond cleavage. Especially if a positve charge is built up on sulfur either by protonation or electron withdrawing groups on one or both nitrogens (R^3/R^4 = acyl; sulfonyl) loss of S-alkyl/ benzyl-groups has been observed.[1] Thus in protic-polar solvents and / or presence of other nucleophiles often quantitative conversion to sulfinamidines 2 can be achieved.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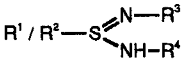
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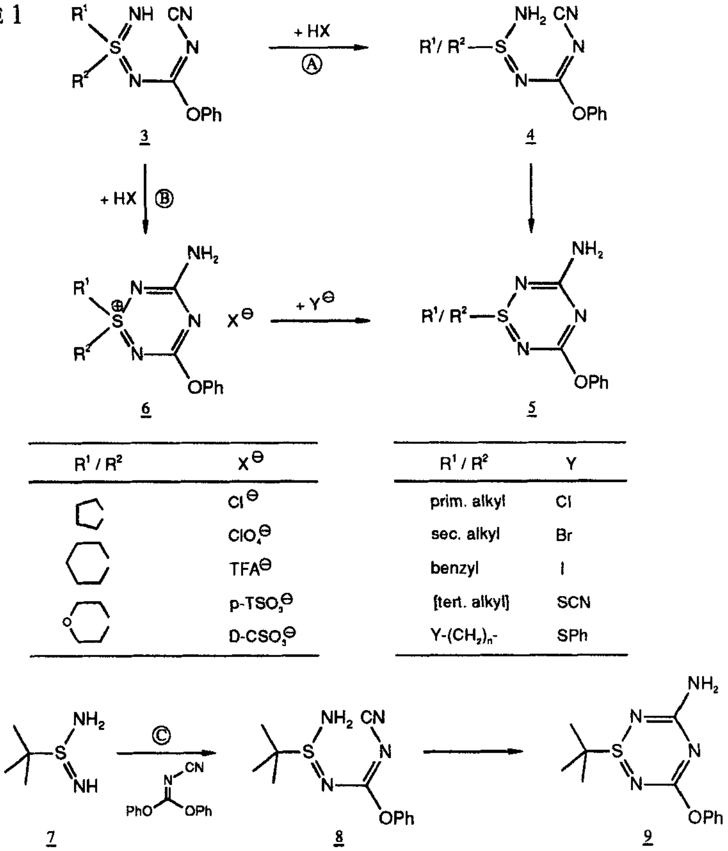
According to recent findings[3,4] this concept has been successfully applied to synthesize 1,2,4,6-thia(IV)triazines 5 from sulfonediimine precursors 3 via pathways A and B (Scheme 1). In boiling ethanol with HX = p-TsOH or CF_3COOH as catalyst, for example, 3 (R^1 = alkyl; R^2 = benzyl) are converted to sulfinamidines 4 which undergo further cyclization to 5 either in boiling DMF or dioxane/HX. The ease of C-S bond cleavage follows the order tert. alkyl > sec.alkyl ≈ benzyl > prim. alkyl. The t-butyl derivates 8 and 9, however, may be prepared via pathway C directly from the unsubstituted sulfinamidine[5] 7.

Thiophane-, thiacyclohexane-, or thioxane-derived sulfondiimines of type 3 cyclize with acids in various solvents (CH_2Cl_2; dioxane; HOAc) to give the 1,2,4,6-thia(VI)-triazinium salts 6. These may be either isolated or further transformed with appropriate nucleophiles (Y^-) into thia(IV)triazines of type 5 simply by heating in DMF, dioxane or acetone. Subsequent nucleophilic displacement in the S-alkyl chain of 5 (Y = I) allows the introduction of numerous substituents. Furthermore thia(IV)triazines 5 (and sulfinamidines 4 as well) may undergo nucleophilic displacement of the phenoxy-group, addition of heterocumulenes to NH_2, or oxidation on sulfur with $KMnO_4$ to give the corresponding S-oxides.

SCHEME 1



R¹ / R²	X⊖
	Cl⊖
	ClO_4⊖
	TFA⊖
	p-TSO_3⊖
	D-CSO_3⊖

R¹ / R²	Y
prim. alkyl	Cl
sec. alkyl	Br
benzyl	I
[tert. alkyl]	SCN
Y-$(CH_2)_n$-	SPh

According to the asymmetric sulfur they can be resolved into enantiomers via HPLC-technique on ß-cyclodextrine (ChiraDex®) column which offers the possibility to study stereochemical aspects.

(This paper is dedicated to Prof. Dr. B. Unterhalt)

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