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NOVEL METHODS FOR THE SYNTHESIS OF N-TRICHLOROACETYL- AND N-FORMYL-S,S-DIARYLSULFILIMINES

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Abstract: N-Trichloroacetyl-S,S-diarylsulfilimines are prepared in quantitative yields from sulfilimines and trichloroacetamide; whereas N-formyl-S,S-diarylsulfilimines are obtained quantitatively by alkaline cleavage of N(1-hydroxy-2,2,2-trichloroethyl)-S,S-diarylsulfilimines.

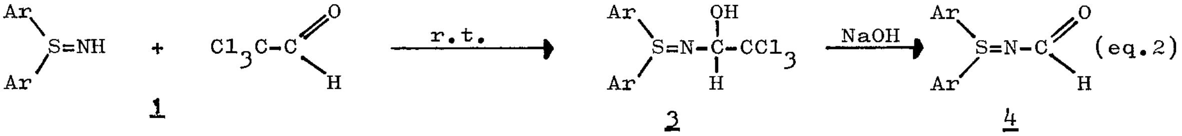
Sulfilimines[1] are a relatively new class of sulfur nitrogen ylides, which have been recognized as valuable intermediates in organic synthesis. Their nucleophilic, basic nitrogen provides a site for electrophilic attack, and the thioether function represents a good leaving group. Only recently Ketcha and co-workers[2] showed, that 2-oxazolin-4-ones can be easily prepared by reacting N-acylsulfilimines with diphenyl ketene. We want now to report two alternative methods for N-acylation of sulfilimines[3]. When equimolar amounts of diarylsulfilimines 1a-1c and trichloroacetamide were dissolved in acetonitrile at r.t., ammonia developed immediately. After evaporation of the solvent, the colorless oil was set aside (2 days vacuum) until the gas development had ended and the resulting N-trichloroacetyl-S,S-diarylsulfilimines 2a-2c had crystallized (eq. 1). In all cases quantitative yields were observed.

$$Ar_2S{=}NH + Cl_3C{-}CONH_2 \xrightarrow{-NH_3} Ar_2S{=}N{-}\overset{O}{\overset{\|}{C}}{-}CCl_3$$

(eq. 1)

2	Ar	Fp(°C)	IR (cm^{-1} in KBr) $\nu_{C=O}$	^{13}C-NMR δ_{CCl_3}	(ppm in CDCl$_3$) δ_{CO}
a	p-Tolyl	109	1615	95.40 (S)	170.92 (S)
b	Phenyl	104	1620	95.28 (S)	171.69 (S)
c	p-Bromophenyl	124	1620	94.85 (S)	171.50 (S)

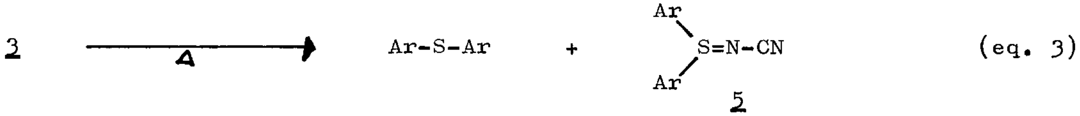
Equimolar amounts of diarylsulfilimines 1b and 1c with either chloral or chloral hydrate form N(1-hydroxy-2,2,2-trichloroethyl)-S,S-diarylsulfilimines 3b, 3c in good yields, when reacted overnight in acetonitrile (eq. 2).



(eq.2)

	Ar	Yields(%)	Fp(°C)	IR (cm^{-1} in KBr) ν_{OH}	IR (cm^{-1} in KBr) $\nu_{C=O}$	^1H-NMR (ppm in DMSO-d_6) δ_{CH}	^1H-NMR (ppm in DMSO-d_6) δ_{OH}
3b	Phenyl	53	113	3300-2800	-	5.14(s)	6.68(s)
3c	p-Bromophenyl	85	152	3300-2800	-	5.00(s)	6.60(s)
4b	Phenyl	100	93	-	1590,1570	8.20(s)	-
4c	p-Bromophenyl	100	135	-	1580,1560	8.28(s)	-

Addition of sodium hydroxide solution (30%) to 3b, 3c gave the N-formyl-diarylsulfilimines 4b, 4c in quantitative yields. Diarylsulfilimines are known to transform several aldehydes to the corresponding nitriles in high yields[4]. Adducts between aldehyde and diphenylsulfilimine of type 3 have been postulated to be the first step in this synthesis[5]. Our attempts to isolate the corresponding condensation products with other aldehydes than chloral failed. However, we observed, that the conversion of aromatic aldehydes to nitriles also occurred, when stirring the reaction mixture in acetonitrile at r.t. overnight, instead of refluxing in benzene for 5 h. Thermal decomposition of 3 in refluxing benzene did not yield trichloroacetonitrile but a 1:1 mixture of thioether and N-cyano-S,S-diarylsulfilimines 5 (eq. 3).



(eq. 3)

5	Ar	Yields(%)	Fp(°C)	IR (cm^{-1} in KBr) $\nu_{C\equiv N}$	^{13}C-NMR (ppm in $CDCl_3$) δ_{CN}
b	Phenyl	50	(62-63)[7]	2150	119.89 (s)
c	p-Bromophenyl	50	138	2150	119.64 (s)

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