Sulfur Ylides from Alkyl(aryl)-dialkylamino-succinimidosulfonium Chlorides[1]

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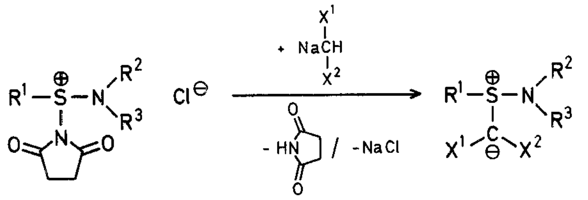
From the alkyl(aryl)-dialkylamino-succinimidosulfonium chlorides (**1**), which are accessible from reactions of sulfenamides with *N*-chlorosuccinimide[1], a series of novel stabilized sulfur ylides **2–6** has been synthesised. These compounds are formed under displacement of succinimide upon nucleophilic attack with sodium salts of active methylene compounds (e.g. malonic or acetoacetic esters, 1,3-diketones, and bis-sulfonylmethanes, respectively). The reactions can be easily performed by *in situ* generation of the adducts **1** in acetonitrile solution followed by addition of solutions of the sodium salts. The yields vary in the range 30–70% (Table). Deprotonation reactions by the carbanions often afford the active methylene components as predominant side-products beside succinimide.

Nucleophilic displacement reactions on the sulfonium sulfur atom by means of carbanions have been reported also for *S*—*O*- and *S*—*N*-sulfonium salts of dialkyl sulfides[2–6]. As a general route for the synthesis of carbosulfuranes, however, this is believed to be restricted to highly stabilised ylides carrying electronegative groups on the carbanion[2,3]. According to the stabilising effect of X^1 and X^2 in ylides **2–6** by delocalisation of the negative charge, the typical I.R.-absorption bands of the carbonyl and sulfonyl groups are more or less shifted to lower wave-numbers (Table). In water the ylides are hydrolytically inert. From thermal decomposition reactions of **6a** in boiling dioxan and of **4b** in boiling toluene, the sulfides **7** were isolated indicating intramolecular proton transfer under fragmentation to an imine and **7**.



1a-d **2-6 a,b,c,d**

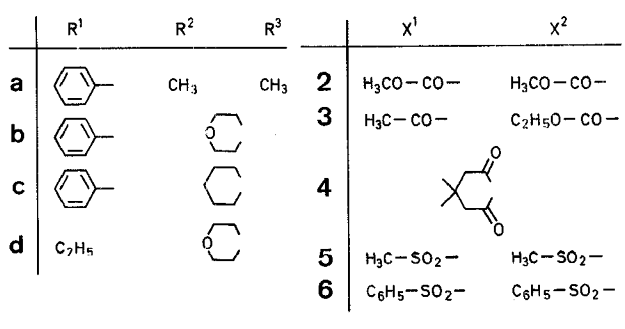


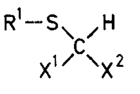
Table. Physical Data for Sulfur Ylides (**2–6**)

Ylide	Yield (%)	m.p.	I.R.[a] ν_{max} cm^{-1}	Empirical formula[b]
2a	>50	oil	1650 (C=O)	$C_{13}H_{17}NO_4S$[c] (283.3)
2b	58	115–116°	1628 (C=O)	$C_{15}H_{19}NO_5S$ (325.4)
2c	>50	oil	1650 (C=O)	$C_{16}H_{21}NO_4S$[c] (323.3)
2d	>30	oil	1645 (C=O)	$C_{11}H_{19}NO_5S$[c] (277.3)
3a	27	59–61°	1674 (C=O) 1602 (C=O)	$C_{14}H_{19}NO_3S$ (281.3)
3b	32	93–94°	1680 (C=O) 1600 (C=O)	$C_{16}H_{21}NO_4S$ (323.4)
4a	57	109–110°	1580 (C=O)	$C_{16}H_{21}NO_2S$ (291.3)
4b	60	154–155°	1590 (C=O)	$C_{18}H_{23}NO_3S$ (333.4)
4c	>50	oil	1580 (C=O)	$C_{19}H_{25}NO_2S$ (331.4)
4d	46	99–100°	1575 (C=O)	$C_{14}H_{23}NO_3S$ (285.4)
5a	43	137–138°	1283 (SO_2) 1116 (SO_2)	$C_{11}H_{17}NO_4S_3$ (323.5)
5b	47	162–163° (dec.)	1300 (SO_2) 1110 (SO_2)	$C_{13}H_{19}NO_5S_3$ (365.5)
5c	42	167° (dec.)	1296 (SO_2) 1111 (SO_2)	$C_{14}H_{21}NO_4S_3$ (363.5)
5d	41	172–173°	1290 (SO_2) 1115 (SO_2)	$C_9H_{19}NO_5S_3$ (317.4)
6a	64	156° (dec.)	1300 (SO_2) 1133 (SO_2)	$C_{21}H_{21}NO_4S_3$ (447.5)
6b	33	170–171° (dec.)	1305 (SO_2) 1140 (SO_2)	$C_{23}H_{23}NO_5S_3$ (489.6)
6c	35	163–164° (dec.)	1320 (SO_2) 1136 (SO_2)	$C_{24}H_{25}NO_4S_3$ (487.7)
6d	59	159–160° (dec.)	1302 (SO_2) 1132 (SO_2)	$C_{19}H_{23}NO_5S_3$ (441.6)

[a] Oils as film, solids in KBr.

[b] All compounds gave satisfactory elemental analyses (C ±0.4%, H ±0.38%, N ±0.34%, S ±0.53%) except where otherwise indicated.

[c] On the basis of ¹H-N.M.R. spectra identified compounds.



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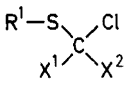

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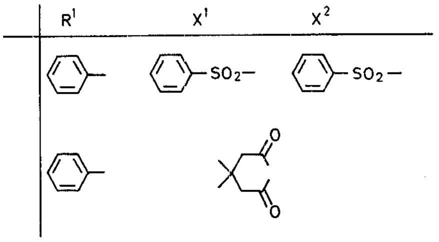

Furthermore, the ylides **2–6** are characterised by a sulfur nitrogen bond which can be easily cleaved by reagents such as benzoyl or hydrogen chloride. From ylides **4a**, **4b**, and **6b** for example, with benzoyl chloride the cleavage products are α-chlorosulfides **8** and *N*,*N*-dialkylbenzamides, whereas reaction with hydrogen chloride affords both **7** and **8** the ratio of which is mainly depending on the type of solvent. Further details on reactions of ylides **2–6** as well as N.M.R.-studies will be reported separately.

Preparation of Sulfur Ylides (2–6); General Procedure:
Under anhydrous conditions at −40° in acetonitrile (100 ml) the alkyl(aryl)-dialkylamino-succinimidosulfonium chlorides **1** are formed from equimolar amounts (0.02 mol) of the corresponding sulfenamide and *N*-chlorosuccinimide. The mixture is treated with one equivalent of the sodium salt of the active methylene component, stirred overnight and filtered. After removal of the solvent, the oily residue is dissolved in chloroform and washed several times with water. The dried solution is completely removed from the chloroform and the oily crude products are crystallised by treating with solvents or standing in a freezer (recrystallisation of **2** in ligroin, tetrahydrofuran/cyclohexane, of **3** in ligroin/ether, of **4** in ligroin, of **5–6** in ethanol, benzene).

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