Alkyl(aryl)-dialkylamino-succinimidosulfonium Salts from Sulfenamides[1]

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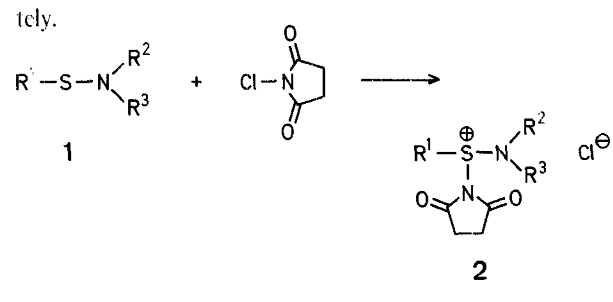
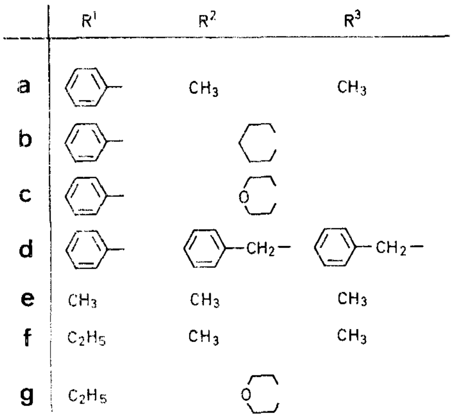
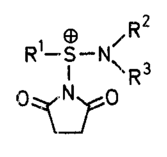
N,*N*-Dialkylsulfenamides (**1**) are converted to the alkyl(aryl)-dialkylamino-succinimidosulfonium chlorides (**2**) by treatment with *N*-chlorosuccinimide in dichloromethane solution. The adducts **2**, for which a tetracovalent type of structure may also be discussed[2], can be isolated under anhydrous conditions as crystalline solids by precipitation with dry ether. Their thermal instability allows storage only below 0°. At higher temperatures relatively fast decomposition takes place. As degradation products of crystalline **2a** or **2d** in solution, for example, benzenesulfenyl chloride, succinimide, *N*-benzenesulfenylsuccinimide, and secondary products of the dialkylamine moiety, e.g. the alkylidenealkylamine hydrochloride, have been identified.

Decrease of the nucleophilic activity of the anion in the chlorides **2** by means of anion-exchange with silver tetrafluoroborate affords salts which are considerably more stable. Thus, the tetrafluoroborates **3** can be handled without decomposition up to their melting points (Table 1). In the N.M.R.-spectra of **2** as well as of **3** for the succinimide methylene protons a singlet occurs at $\delta = 3.0-3.4$ ppm (solvent CD_3CN or $CDCl_3$). The structure analogy with the *N*-chlorosuccinimide adducts of dialkyl sulfides described by Vilsmaier and coworkers[3], is consistent with the strong I.R.-absorption at 1740–1755 cm^{-1}. In addition, solvolysis experiments have established the existence of the sulfur-imide-nitrogen bond. The nucleophilic attack of ammonia and primary or secondary amines upon **2** namely effects ring-opening to give the sulfinamidine derivatives **4** (Table 2). No displacement of succinimide was detected; this has, however, been easily achieved with primary amines in case of the *N*-chlorosuccinimide adducts of dialkyl sulfides[4, 5]. The different reaction course may be attributed to the possibility of charge delocalisation from sulfur to the attached amine nitrogen atom. In water or methanol, however, the salts **2** are easily solvolysed under elimination of succinimide and formation of sulfinamides. Nucleophilic displacement on the sulfonium sulfur of **2** by means of carbanions of methylene-active components has been utilised for the synthesis of novel sulfur ylides[1]. More details on the reactions of azasulfonium salts of type **2** and **3** will be reported separately.







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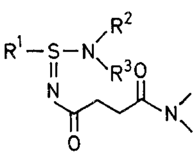

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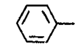
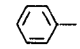
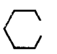
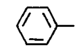
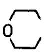
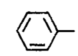
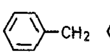
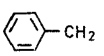
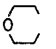
Preparation of Alkyl(aryl)-dialkylamino-succinimidosulfonium Chlorides (2); General Procedure:

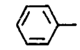
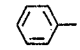
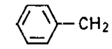
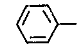
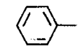
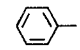
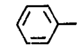
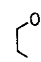
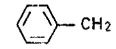
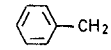
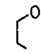
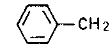
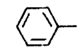
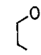
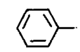
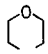
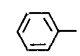
Under anhydrous conditions a solution of *N*-chlorosuccinimide (0.05 mol) in dichloromethane (125 ml) is stirred at 0° and treated

Table 1. Data for Alkyl(aryl)-dialkylamino-succinimidosulfonium Tetrafluoroborates (**3**)

Salt	R^1	R^2	R^3	Yield (%)	m.p.	Empirical formula[a]
3a		H_3C	H_3C	89	169–170° (dec.)	$C_{12}H_{15}N_2O_2SBF_4$ (338.1)
3b				85	150–151°	$C_{15}H_{19}N_2O_2SBF_4$ (378.2)
3c				81	176–177° (dec.)	$C_{14}H_{17}N_2O_3SBF_4$ (380.1)
3d				85	156–158°	$C_{24}H_{23}N_2O_2SBF_4$ (490.3)
3g	C_2H_5			90	182–183° (dec.)	$C_{10}H_{17}N_2O_3SBF_4$ (332.1)

[a] All compounds gave satisfactory elemental analyses (C ±0.25%, H ±0.32%, N ±0.41%, S ±0.45%).

Table 2. Data for Sulfinamidines (**4**)

Sulfinamidine 4	R^1	R^2	R^3	R^4	R^5	Yield (%)	m.p.	I.R.[a] ν_{NH}	cm − 1 ν_{CO}	Empirical formula[b]
a		CH_3	CH_3	H	H	70	100°	3370 3185	1675 1555	$C_{12}H_{17}N_3O_2S$ (267.4)
b		CH_3	CH_3	H		77	83–84°	3270	1660 1560	$C_{19}H_{23}N_3O_2S$ (357.5)
c		CH_3	CH_3	H		67	139–140°	3255 3190	1680 1595	$C_{18}H_{21}N_3O_2S$ (343.5)
d		CH_3	CH_3	H	C_2H_5	76	85°	3300	1665 1565	$C_{14}H_{21}N_3O_2S$ (295.4)
e				H		82	115–117°	3258	1660 1570	$C_{21}H_{25}N_3O_3S$ (399.52)
f	C_2H_5	CH_3	CH_3	H		78	66–68°	3285	1670 1555	$C_{15}H_{23}N_3O_2S$ (309.4)
g	C_2H_5			H		89	92–94°	3210	1645 1575	$C_{17}H_{25}N_3O_3S$ (351.5)
h				C_2H_5	C_2H_5	77	91–92°	—	1630 1585	$C_{18}H_{27}N_3O_3S$ (365.5)
i		CH_3	CH_3			80°	oil		1648 1593	$C_{16}H_{23}N_3O_3S$ (337.4)
j		CH_3	CH_3	C_2H_5	C_2H_5	78°	oil	—	1643 1597	$C_{16}H_{25}N_3O_2S$ (323.5)

[a] Oils as film, solids in KBr.

[b] All compounds gave satisfactory elemental analyses (C ±0.46%, H ±0.23%, N ±0.33%, S ±0.40%) and ^{1}H-N.M.R. spectra (which will be reported separately).

slowly with the sulfenamide (0.05 mol) in dichloromethane (25 ml) from a dropping funnel. The chlorides **2** may be precipitated by addition of ether and isolated by filtering, washing with ether, and drying in a nitrogen stream (yields approx. 90%). Because of the ease of hydrolysis and thermal decomposition only **2a–2c** were analysed by chloride titration (found 93–95% of the calculated Cl). Adducts **2d–2g** were identified in solution by N.M.R. or by further reactions.

Preparation of Alkyl(aryl)-dialkylamino-succinimidosulfonium Tetrafluoroborates (3); General Procedure:

Under anhydrous conditions *N*-chlorosuccinimide in acetonitrile solution is treated at −40° with one equivalent of sulfenamide and subsequently with silver tetrafluoroborate. The suspension is stirred overnight and filtered. Addition of ether to the reduced filtrate until cloudiness, and subsequent cooling in a freezer affords the crystalline and stable tetrafluoroborates **3** (yields 80–90%).

Preparation of Sulfinamidine Derivatives (4); General Procedure:

4a–4d: Under anhydrous conditions a suspension of the alkyl(aryl)-dialkylamino-succinimidosulfonium chloride (**2**; 0.02 mol) in ether (120 ml) was treated between −40 and 0° with two equivalents of the amine component (manifold excess in case of ammonia and ethylamine). After stirring for 30–60 min, the sulfinamidines **4** were separated from the precipitate by extraction with chloroform. Removal of the solvent yields oily products which crystallize after standing in a freezer. They were recrystallised ether from chloroform/ether (**4a**), toluene (**4b**), isopropanol (**4c**), or ligroin (**4d**).

4e–4j: The reactions were carried out between −40 and 0° in acetonitrile or dichloromethane solution by generation of salts **2** *in situ* from the sulfenamides and *N*-chlorosuccinimide, followed by addition of the amine component and isolation of **4** from the solvent phase. Recrystallisation was from benzene (**4e**, **4g**), ether (**4f**), or ligroin (**4h**).

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