

PREPARATION OF CYCLIC SULFIMIDES AS
A NEW TYPE OF HETEROCYCLIC COMPOUNDS

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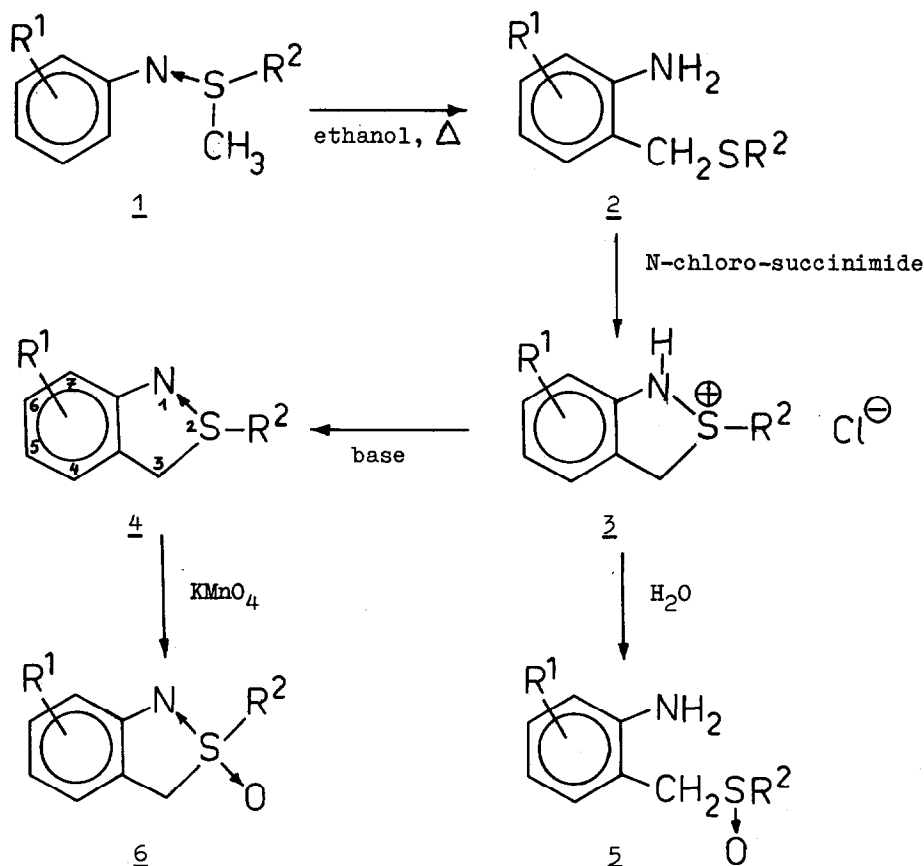
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N-Aryl-S,S-dimethyl sulfimides (1, $R^2 = CH_3$) had been prepared earlier by reaction of anilines with sulfoxides and P_4O_{10} in presence of triethylamine ¹. Rearrangement of sulfimides 1 by heating in toluene - triethylamine or in ethanol (without base) yielded o-methylthiomethyl-anilines 2 ($R^2 = CH_3$) in generally high yields ². Recently we found that sulfimides 1 are formed in high yields on reactions of anilines with sulfides and N-chloro-succinimide, tert. butyl hypochlorite or sulfuryl chloride, followed by treatment with base ³. The mild conditions and clean reactions allowed the preparation of a number of sulfimides 1 with various substituents R^1 at the aromatic ring and R^2 at the sulfur atom. Rearranged products 2 have now been found to react with N-chloro-succinimide yielding cyclic azasulfonium chlorides 3, respectively, after treatment with base, cyclic sulfimides 4, a new type of heterocyclic compounds.

The reactions were performed at low temperatures (-20°) adding equivalent amounts of N-chloro-succinimide (dissolved in dry CH_2Cl_2) to stirred solutions of rearranged products 2 in CH_2Cl_2 . Reactions were monitored by tlc (solvent : $CHCl_3$ / triethylamine = 50 : 1) and usually complete within two

hours. Azasulfonium chlorides 3 may be precipitated by partial evaporation and addition of THF - ether. Sulfimides 4 have been isolated by extracting the reaction mixture with calculated amounts of aqueous NaOH (slight excess) and evaporating carefully at low temperatures.



The structure of compounds 3 and 4 was derived from nmr data mainly. The nmr spectra (60 MHz) of azasulfonium chlorides 3 with $R^2 = CH_3$ show (besides signals in the region of aromatic protons) a singlet at ~ 2.9 ppm (corresponding sulfides 2 which might arise by oxidation of 2 show a singlet at ~ 2.5 ppm) and an AB quartet at $\sim 4.9 - 5.6$ ppm ($J = \sim 16$ Hz; sulfides 2 : $3.8 - 4.1$ ppm, $J = \sim 14$ Hz). The nmr spectra of sulfimides 4 with $R^2 = CH_3$ show a singlet at $2.3 - 2.5$ ppm (for comparison : S-methyl signals of

sulfimides 1 at 2.5 - 2.8 ppm ¹) and an AB quartet at 4.3 - 4.7 ppm (J = 15 - 16 Hz). The cyclic sulfimides 4 form stable picrates (nmr : singlet at 3.2 - 3.3 ppm, AB quartet at 5.2 - 5.9 ppm). A summary of results is given in the following Table.

Table : Cyclic Azasulfonium Chlorides 3 (Cyclic Sulfimides 4)

Products <u>3</u> or <u>4</u>	Yield ^a	M.p. ^b	Picrate	Nmr ^c (δ , ppm)
R ¹ R ²	(%)		M.p.	
7-Cl CH ₃	95	89-92	170-173	<u>4</u> : 2.34(s), 4.24(d), 4.68(d), 6.45-7.3(m)
5-Cl CH ₃	95	101-109	172-173	<u>4</u> : 2.30(s), 4.10(d), 4.56(d), 6.85-7.3(m)
5-CH ₃ CH ₃	80 ^d	oil ^e	150-152	picrate: 2.25(s), 3.32(s), 5.24(d), 5.53(d), 7.1- 7.3(m), 8.97(s), 9.77 (s)
5-COOCH ₃ CH ₃	76	113-117	188-191	<u>4</u> : 2.35(s), 3.87(s), 4.24(d), 4.60(d), 6.85(d), 7.8-8.1(m)
5-CN CH ₃	73	136-138	180-183	<u>4</u> : 2.38(s), 4.58(s, broa- dened), 6.65-7.6(m)
5-NO ₂ CH ₃	76	142-145	180-183	<u>4</u> ^f : 2.52(s), 4.69(s, broa- dened), 6.87(d), 7.9-8.3(m)
G CH ₃	74 ^h	i	-	<u>3</u> : 2.87(s), 5.58(s), 6.73 (t), 7.73(m), 7.96(m)
H CH ₃	70 ^h	oil ^e	160-162	<u>3</u> : 2.92(s), 4.91(d), 5.41(d), 7.1-7.7(m) <u>4</u> : 2.30(s), 4.10(d), 4.58(d), 6.7-7.4(m)
5-Cl 4-CH ₃ C ₆ H ₄	37 ^h	oil ^e	132-134	<u>4</u> : 2.43(s), 4.37(d), 4.98(d), 7.3-7.5(m)

^a Yields of crude materials, at least 90% pure ^b Melting with decomposition

^c CDCl₃ as solvent for 4, CD₃OD for 3, d₅-pyridine for picrates

^d Yield of picrate

^e Fast decomposition at room temperature

^f Solvent : d₆-DMSO

^h Yield of azasulfonium chloride 3

^g Starting material : 2-amino-3-methylthiomethyl-pyridine, m.p. 51-54°

ⁱ Fast hydrolysis during work-up yielding 2-amino-3-methylsulfinylmethyl-pyridine, m.p. 151.5 - 153°

The azasulfonium chlorides 3 are remarkably stable in aqueous solutions and hydrolyze slowly yielding o-alkyl- or -arylsulfinylmethyl-anilines 5, but decompose more or less readily in organic solvents. Attempts to prepare cyclic azasulfonium compounds 3 or sulfimides 4 by reaction of 5 with P_4O_{10} in presence of triethylamine failed. The stability of sulfimides 4 is strongly dependent on the nature of substituents R^1 and R^2 . Electron-donating substituents R^1 and aryl groups R^2 destabilize the ring system. Cyclic sulfimides 4 with $R^1 = CH_3$ decomposed rapidly even at 0° . A characterisation of sulfimide 4 with $R^1 = 5-Cl$ and $R^2 = 4-CH_3C_6H_4$ was possible only by careful isolation and conducting nmr spectra at temperatures below -20° . Derivatives 4 with electron-withdrawing substituents R^1 are fairly stable and could be oxidized with $KMnO_4$ in aqueous dioxane yielding cyclic sulfoximides 6 which are even more stable than corresponding sulfimides 4 [nmr data : 6, $R^1 = 5-Cl$, $R^2 = CH_3$, 3.36(s), 4.48 (s, broadened), 6.8 - 7.8 (m); 6, $R^1 = 5-CN$, $R^2 = CH_3$, 3.60(s), 4.62 (d), 5.02 (d), 6.85 - 7.7 (m)].

Several cyclic sulfoximides have been prepared recently ⁴. To our knowledge the sulfimides 4 are the first examples of sulfimides without N-sulfonyl group and with S and N in one ring.

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