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SULFONIOINDOLIDES AND SULFONIOPYRROLIDES

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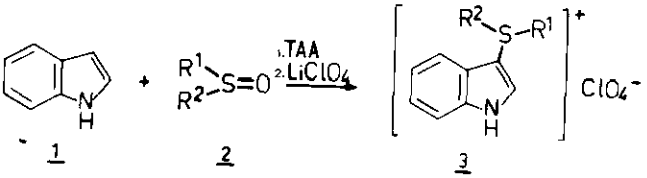
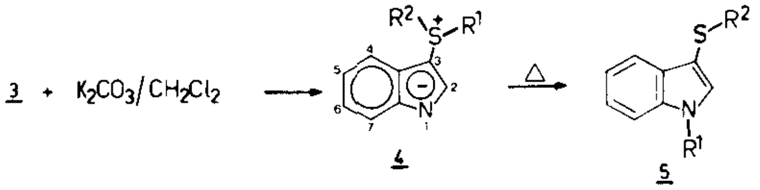
Abstract- Sulfoxides react with indoles and pyrroles in the presence of trifluoroacetic anhydride to form 3-indolylsulfonium- and 2- or 3-pyrrolylsulfoniom salts. Deprotonation gives rise to sulfonioindolides and sulfoniopyrrolides.

Recently we described the reaction of cyclopentadiene, trimethylsilylcyclopentadiene and fulvenes with dialkyl, cycloalkyl or diaryl sulfoxides in the presence of trifluoroacetic anhydride (TAA) to form mono-, bis- or trissulfonio substituted derivatives[1]. Under similar conditions these sulfoxides are also able to substitute the indole ring in the 3-position to give the 3-indolylsulfonium salts 3, which are best isolated as perchlorates[2,3].



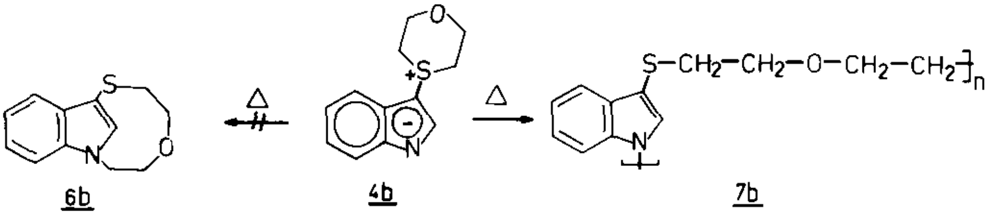
3	R^1	R^2	mp [°C]	yield [%]
a	CH_3	CH_3	141	58
b	$C_6H_5-CH_2$	$C_6H_5-CH_2$	166	53
c	$[CH_2]_4$		106	86
d	$[CH_2]_2O[CH_2]_2$		180	100
e	C_6H_5	C_6H_5	136	50
f	$p-CH_3-C_6H_4$	$p-CH_3-C_6H_4$	215	71

Deprotonation of 3 with potassium carbonate in dichloromethane leads to the formation of the 3-sulfonioindolides 4, a practically unknown class of sulfonium ylides, the first member of which, 4a, has been prepared a few years ago[3]. Some of the 3-sulfonioindolides 4 are obtained in analytically pure form without major difficulties by recrystallisation or reprecipitation; others are rather unstable and tend to include solvent as well as other minor impurities[4]. In general chromatographic procedures are unsuitable for purification, as the active surface of the sorption materials tends to decompose the ylides.



4	R^1	R^2	mp [°C]
a	CH_3	CH_3	121
b	$[CH_2]_2O[CH_2]_2$		191
c	$p\text{-}CH_3\text{-}C_6H_4$	$p\text{-}CH_3\text{-}C_6H_4$	162

By heating the 3-sulfonioindolides 4 the N-substituted indoles 5 are formed[5]. This is mainly an intermolecular process; the 3-sulfonioindolides with a cycloaliphatic ring (e.g. 4b) do not lead to the expected indolophanes such as 6b but rather to oligomeric or polymeric material such as 7b. The ^1H and ^{13}C NMR data of 7b in Table 1 and 2 clearly indicate an N-alkylation by the sulfonio group. The molecular weight determinations by cryoscopy, however, do not support a monomeric structure. 3-Sulfonioindolides 4 with aromatic S-substituents (e.g. 4c) simply decompose on heating; one of the decomposition products has been identified as the diaryl sulfide.



The following procedure is representative for the preparation of 3, 4 and 5 (or 7): To a solution of thioxane sulfoxide (5mmol) and indole (5mmol) in 20ml of anhydrous CH_2Cl_2 at -30°C are added dropwise 5mmol of TAA in 5ml of CH_2Cl_2. After 15 min the reaction mixture is treated with 20ml of a saturated aqueous solution of $LiClO_4$. The organic layer is separated, 3d precipitated by the addition of ether and recrystallised from methanol. A solution of 3d in CH_2Cl_2 is stirred with solid K_2CO_3 for 10 h at room temperature and 4b isolated after filtration and evaporation. A recrystallisation is possible from CH_2Cl_2/ethanol. When solid 4b is heated to 150-170°C for 15 min, 7b is formed and may be recrystallised from $CHCl_3$ or THF. Compounds 3d, 4b and 7b as representative examples are characterised by the NMR data given in Table 1 and 2.

Table 1: ^1H NMR Data of 3d, 4b and 7b

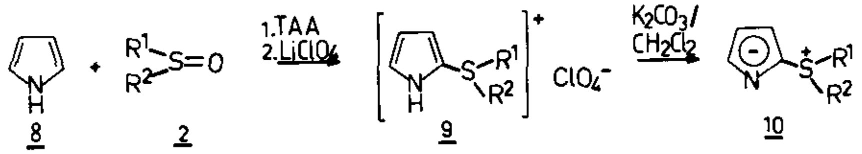
	NH	2-H	phenyl	N-CH_2	O-CH_2	S-CH_2
3d[a)]	10.3	8.20(d)	7.2-8.0(m)		3.4-4.7(m)	
4b[b)]	-	7.80(s)	6.7-7.7(2m)		3.3-4.4(m)	
7b[c)]	-	7.4-7.7(m)	6.7-7.1(m)	3.7-4.0(t)	3.1-3.6(m)	2.4-2.8(t)

Table 2: ^{13}C NMR Data of 3d, 4b and 7b

	C-7a-3a	C-2	C-4, -5, -6, -7	C-3	O-CH_2	N-CH_2	S-CH_2
3d[a)]	138.3; 125.5	135.7	125.9; 124.1; 119.2; 115.3	91.2	66.1	-	40.6
4b[d)]	150.5; 129.2	146.5	121.5; 120.9; 119.7; 117.4	80.0	66.7	-	41.7
7b[c)]	136.5; 130.1	134.1	122.1; 120.1; 119.3; 109.7	103.0	70.0; 69.3	46.2	35.7

a) in CD_3NO_2 b) in $[D_6]$DMSO c) in $CDCl_3$ d) in CD_3OD

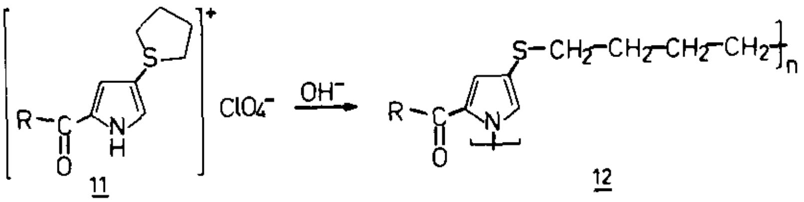
The reaction of pyrrole 8 with the sulfoxides 2 in the presence of TAA leads to a mixture of the 2-pyrrolyl- and 3-pyrrolylsulfonium salts, from which the major isomer 9 can be isolated in pure form by recrystallisation. The formation of the 3-isomeres may be avoided by using azasulfonium salts (obtained from the corresponding sulfides and N-chlorosuccinimide) as less reactive electrophilic agents[6]. Deprotonation of 9 with potassium carbonate in dichloromethane gives rise to the crystalline 2-sulfoniopyrrolides 10. Compounds 10a-d are the first representatives of this new class of sulfur ylides in the pyrrole series[7]. The structure 10 is supported by elemental analysis and spectroscopic data; for 10a ^1H NMR ($CDCl_3$): δ (ppm) 7.41 (t, 5-H), 6.77 (dd, 3-H), 6.29 (dd, 4-H), 2.93 (s, CH_3); ^{13}C NMR ($CDCl_3$): δ (ppm) 138.4 (C-5), 116.1 (C-3), 109.8 (C-4), 106.4 (C-2), 31.4 (SCH_3).



9, 10	R^1	R^2	mp 9	mp 10
a	CH_3	CH_3	129°C	62°C
b	$[CH_2]_4$		192°C*	99°C
c	$[CH_2]_2O[CH_2]_2$		130°C	175°C
d	p-CH_3-C_6H_4	p-CH_3-C_6H_4	154°C	184°C

*) as tetraphenyl borate salt

Pyrroles with an electron withdrawing group at C-2 undergo electrophilic substitution more difficult. With sulfoxides as electrophiles a more potent activator than TAA is needed. With trifluoromethanesulfonic anhydride and tetrahydrothiophene sulfoxide the sulfonium salts 11a-b have been obtained. The position of the sulfonium group at C-4 is clearly demonstrated by the coupling constant between 3-H and 5-H ($^4J_{3,5}$ = 1.8 Hz) in the ^{1}H NMR spectrum of 11, the coupling constant $^3J_{3,4}$ (about 4 Hz) is missing. Deprotonation of 11 with K_2CO_3/CH_2Cl_2 at room temperature does not lead to the expected sulfoniopyrrolide but directly to the rearranged N-alkylated oligomer respective polymer 12.



11	R	mp
a	CH_3	252°C
b	OCH_3	225°C

ACKNOWLEDGEMENT

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4. For all new compounds mentioned correct elemental analysis have been obtained.

5. The rearrangement of 4a has already been reported in l.c.3.

6. This observation goes back to F.Franco, R.Greenhouse and J.M.Muchowski, J.Org.Chem., 47, 1682 (1982). These authors prepared in this way dimethyl-(2-pyrrolyl)sulfonium chloride and decomposed the salt directly by heating to 2-(methylthio)pyrrole.

7. Compound 10a has been obtained independently by M.Hanke, dissertation TU Munich 1980. These unpublished results have come to our attention only a few weeks ago by a new volume of Houben-Weyl: H.Heydt and E.Vilsmaier in Organische Schwefel-Verbindungen, Vol. E11, p.466, editor D.Klamann, Georg Thieme Verlag, Stuttgart 1985.

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