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INDOLE- AND PYRROLE-SULFONIUM YLIDES

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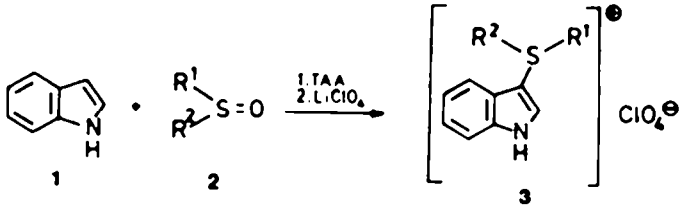
Abstract. Electrophilic substitution of indole and pyrrole with sulfoxides and acid anhydrides leads to the formation of indole-3-sulfonium salts and pyrrole-2-sulfonium salts. These are deprotonated with potassium carbonate to give indole-3-sulfonium ylides and pyrrole-2-sulfonium ylides. An indole-2-sulfonium ylide was obtained by methylation and subsequent deprotonation of 2-(methylthio)indole.

Indole ylides are a relatively unknown class of compounds. The only representatives reported so far, some 3-(dimethylsulfonio)indolides substituted and unsubstituted in the 2-position, have been prepared by Daves and coworkers[1,2,3] as well as by Hocker et al[4]. The 2-unsubstituted 3-(dimethylsulfonio)indolide (4a) was obtained by methylation of 3-(methylthio)indole with methyl iodide and subsequent deprotonation with sodium hydride in ether. The intermediate sulfonium salt for the 3-(dimethylsulfonio)-2-phenylindolide is accessible by condensing 2-phenylindole with dimethylsulfoxide, a reaction of limited scope. In this paper we report therefore a straight forward approach to indole- and pyrrole-sulfonium ylides by electrophilic substitution of the heterocyclic rings with sulfoxides in the presence of acid anhydrides[5].

Indole-3-sulfonium Ylides

The attack of electrophiles in the 3-position of indole is well documented[6]. Tomita et al.[7] have shown recently that sulfur electrophiles, e.g. succinimido-sulfonium salts, also form substitution products at C-3. Even better electrophiles are acyloxysulfonium salts, easily obtained by mixing sulfoxides and acid anhydrides at lower temperatures[8]. In our hands trifluoroacetic anhydride (TAA) or trifluoromethanesulfonic anhydride (TFMSA) have proven to be excellent activating agents for the sulfoxide bond[9].

By simply stirring equimolar amounts of indole (1), sulfoxide (2) and TAA in CH_2Cl_2 at -30°C, and adding subsequently an aqueous solution of lithium perchlorate, the cristalline 3-indolylsulfonium perchlorates 3 are precipitated with diethyl ether from the organic phase. By this method aliphatic, aromatic and cycloaliphatic sulfoxides have been transformed into the corresponding sulfonium salts 3.



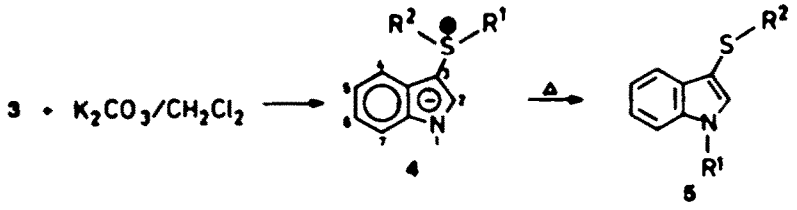
1 2 3

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

+) This paper is dedicated to Prof.E.C.Taylor with best wishes for his 65th birthday

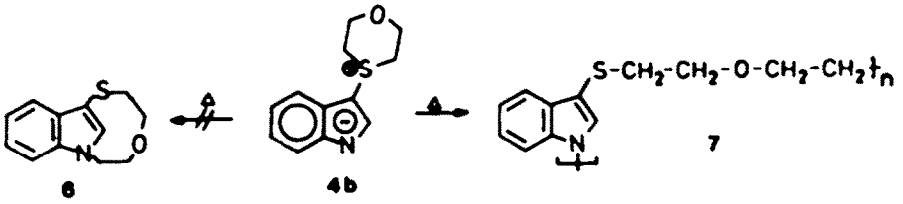
Structure 3 is supported by elemental analysis and spectroscopic data (see experimental part). As expected for a substitution at C-3 of the indole ring, the hydrogen at C-2 is shifted to rather low field in ^1H NMR spectra (δ = 7.95–8.25) and characterized by a coupling of about 3.4 Hz to the NH group. In most cases deprotonation of 3 can be achieved conveniently with potassium carbonate in CH_2Cl_2 at room temperature. The indole-3-sulfonium ylides 4 are formed in nearly quantitative yield as colourless crystals. Further purification by recrystallization is generally accompanied by heavy loss of material.

In the ^1H NMR spectra of the ylides 4 the hydrogen at C-2 is recorded as a singlet and a signal for NH is missing. In general all peaks are shifted to higher field compared with the corresponding sulfonium salt 3. This is especially true for the ylide carbon C-3 in the ^{13}C NMR spectra, showing a shift difference between 11 and 18 ppm: e.g. δ = 93.5ppm (3a) and δ = 76.7ppm (4a)[10].



4	R^1	R^2	mp [°C]
a	CH_3	CH_3	121
b	$[CH_2]_2$-O-$[CH_2]_2$		191
c	p-CH_3-C_6H_4	p-CH_3-C_6H_4	162

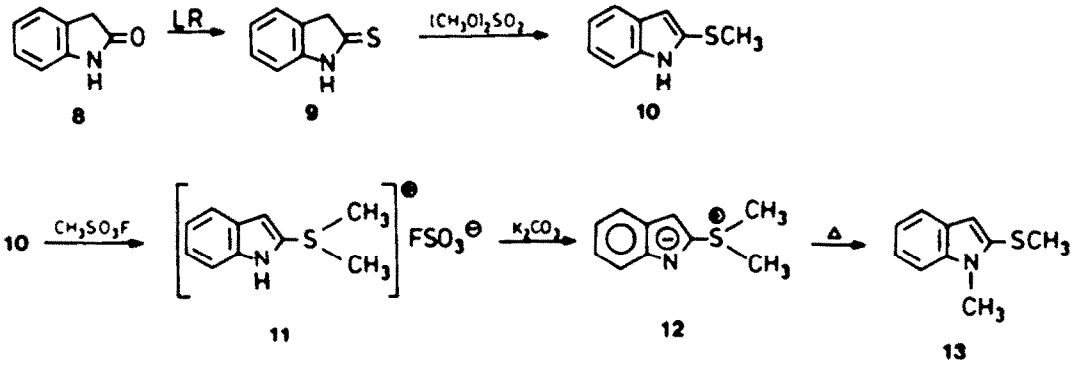
Attempts to deprotonate the (3-indolyl)tetrahydrothiophenium perchlorate (3c) with K_2CO_3 in CH_2Cl_2 always lead to an oil of high viscosity, which could not be crystallized or purified further. We suppose that the ylide formed in the first step is unstable and that a subsequent intermolecular transalkylation between the sulfonium group and the indole nitrogen leads to a polymeric material. This interpretation is supported by the behaviour of the 3-(4-oxa-thianium)indolide (4b). When 4b is heated for about 15 minutes to 150–170°C, it melts and resolidifies to a crystalline compound, which is not the expected indolophane 6, but a polymer with the repeating unit 7, according to molecular weight determination by a cryoscopic method and by mass spectroscopy. The well resolved ^1H and ^{13}C NMR data of 7 clearly indicate the migration of a carbon atom from sulfur to nitrogen (see experimental part). Thus the two ^{13}C peaks for the oxa-thianium ring in 3d are transformed into four signals in the product 7 corresponding to S-CH_2, N-CH_2 and two O-CH_2 carbon atoms.



Leaving (3-dimethylsulfonio)indolide (4a) in solution several days at room temperature or heating it shortly, transalkylation leads the formation of 1-methyl-3-(methylthio)indole (5a). By heating diaryl indole ylides only decomposition is observed. One of the decomposition products of 4c was identified as di-p-tolyl sulfide.

Indole-2-sulfonium Ylides

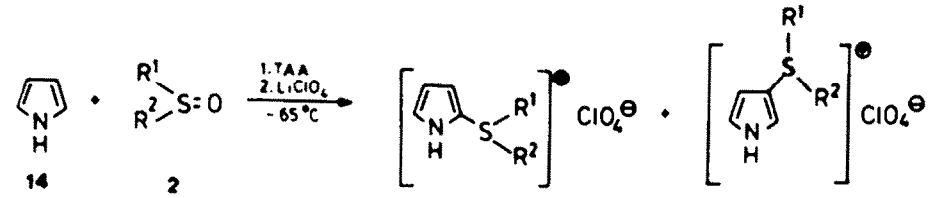
There are no methods available for a regiospecific electrophilic substitution at the 2-position of indole. Therefore indole-2-sulfonium ylides can only be obtained by a more classical approach. By treatment of the 2-indolinone (8) with Lawesson reagent (LR) the 2-indolinthione 9 was obtained and directly methylated with dimethyl sulfate to form the 2-(methylthio)indole (11)[11]. Strong alkylating agents such as methyl fluorosulfonate convert 11 into the sulfonium salt 12, which can be deprotonated in the usual way by K_2CO_3 to give the 2-(dimethylsulfonium)indolide (13) as white needles. 13 has only a limited stability. Rearrangement to the 1-methyl-2-(methylthio)indole (13) is complete within a few days at room temperature, even in the solid state.



8 9 10 11 12 13

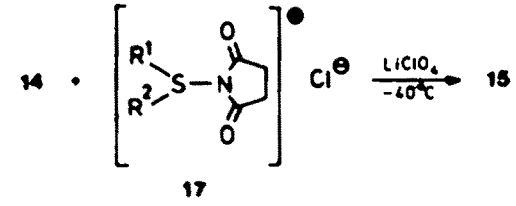
Pyrrole-2-sulfonium Ylides

Electrophilic substitution of pyrrole (14) with sulfoxides 2 and TAA leads to a mixture of the 2- and 3-sulfonium salts 15 and 16, even at -65°C. The 2-isomer prevails and may be obtained in pure form by recrystallization. With a less reactive electrophile, such as the azasulfonium salt 17, the 2-isomer 15 is the only reaction product. This has already been shown by Huchowski et al.[12], who prepared the chloride of 15a by this route. In the same way 15b and 15c are also accessible, but the reaction fails for the synthesis of diarylsulfonium salts such as 15d and 15e.



14 2 15 16

15	R^1	R^2	mp [°C]	yield [%]	ratio 15:16
a	CH_3	CH_3	129	94	9:1
b	$[CH_2]_4$		73	56	5.7:1
c	$[CH_2]_2$-O-$[CH_2]_2$		130	54	13.3:1
d	C_6H_5	C_6H_5	185	97	9:1
e	p-CH_3-C_6H_4	p-CH_3-C_6H_4	154	66	19:1

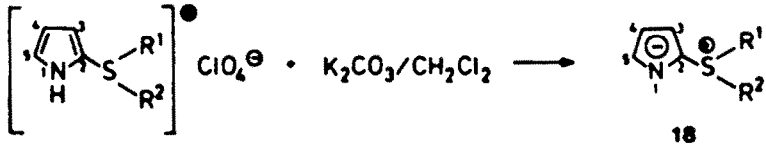


17

The formation of pyrrole-3-sulfonium salts 16 is favoured by substituents at the nitrogen atom. Starting with N-(trimethylsilyl)pyrrole, dialkyl or cycloalkyl sulfoxides and TAA, the trimethylsilyl group is split off during the reaction and a nearly 1:1 ratio of the sulfonium salts 15 and 16 was isolated. With silyl groups even more bulky, e.g. (dimethyl-tert.butyl)silyl, the 3-isomer prevails; the yields, however, drop drastically.

The structural assignment of 15 and 16 is supported by elemental analysis and spectroscopic data. Thus in the ^{1}H NMR spectra the 2-isomers 15 show a coupling constants of about 4 Hz, characteristic for 3-H and 4-H[13] (e.g. 15a: $^3J_{3,4}$ = 3.9 Hz, $^3J_{4,5}$ = 2.8 Hz and $^3J_{3,5}$ = 1.5 Hz). The ^{13}C NMR spectra allow a differentiation between 15 and 16 based on the C-H coupling constants; the carbon atoms α to nitrogen generally show ^{1}J-coupling constants about 10 Hz bigger than those of the β-carbons[14] (e.g. 15: $^1J_{C-3,H}$ = 178 Hz, $^1J_{C-4,H}$ = 176 Hz, $^1J_{C-5,H}$ = 189 Hz). A 2D ^{1}H/^{13}C correlation indicates that the hydrogen atom at lowest field (5-H) is attached to the carbon at lowest field (C-5); the same is true for the carbon and hydrogen peaks at highest field (4-H and C-4). The pyrrole-2-sulfonium salts 15 can be deprotonated most conveniently by stirring with K_2CO_3 in CH_2Cl_2. The ylides obtained are in general colourless, crystalline and hygroscopic solids, stable at room temperature. The preparation of analytically pure samples by recrystallization or reprecipitation is accompanied by heavy loss of material. In most cases, however, further purification is unnecessary. The pyrrole-2-sulfonium ylides 18 form a new class of sulfur ylides. Only the most simple representative, the 2-(dimethylsulfonio)pyrrolide (18a), has been described independently in a dissertation by Hanke, that has come to our attention after completion of this work[15].

The deprotonation of the sulfonium salts 15 is accompanied by a high field shift of the 3-H and 4-H signals in the ^{1}H NMR spectrum; in 18d this effect is also observed for 5-H. The ylides 18 are further characterized by a general decrease in the coupling constants for the pyrrole protons, especially for $^3J_{4,5}$ (e.g. 18a: $^3J_{3,4}$ = 3.4 Hz, $^3J_{4,5}$ = 1.5 Hz, $^4J_{3,5}$ = 1.2 Hz). In the ^{13}C NMR spectra of 18 the signal for C-2 is found between 105 and 109 ppm; a position also observed for the corresponding salts 15. C-5, however, shows a strong downfield shift of about 10 Hz and C-3 as well as C-4 show a moderate to strong upfield shift.



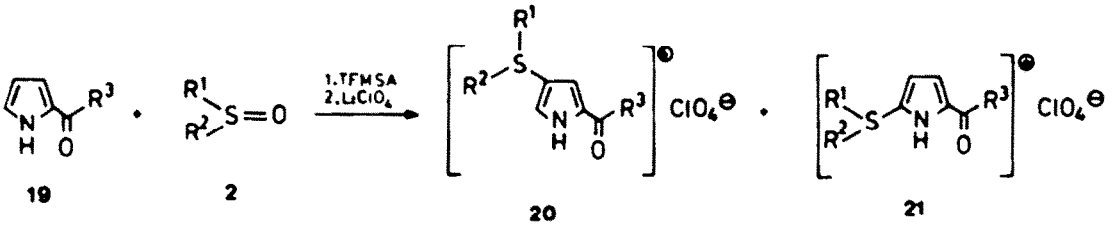
15

18

18	R^1	R^2	mp [°C]
a	CH_3	CH_3	62
b	$[CH_2]_4$		99
c	$[CH_2]_2$-O-$[CH_2]_2$		175
d	p-CH_3-C_6H_4	p-CH_3-C_6H_4	184

Pyrrole-3-sulfonium Ylides

Pyrroles with an electron withdrawing group in the 2-position direct an incoming electrophile to the 4- or 5-position[16]. The 4-position is favoured when the -M effect of the 2-substituent or the hardness of the attacking electrophile is increased[17]. (2-Acetyl)pyrrole and methyl pyrrole-2-carboxylate are only substituted by the most reactive sulfoxides such as dimethyl sulfoxide and tetrahydrothiophene sulfoxide. Even in these cases the yields do not exceed 50% if trifluoroacetic anhydride (TAA) is used as an activator. With trifluoromethanesulfonic anhydride (TFMSA), however, and temperatures about -10°C the reaction proceeds well giving a mixture of the pyrrole-3-sulfonium perchlorate 20 and the pyrrole-2-sulfonium perchlorate 21. With the exception of 20c the predominating isomer 20 could be isolated by fractional recrystallization. The substitution pattern is clearly indicated by the coupling constants. $^4J_{1,4}$ about 4.2 Hz for the 3-isomer 20 and $^3J_{3,4}$ about 1.8 Hz for 2-isomer 21.



19 2 20 21

20	R^1	R^2	R^3	mp [°C]	yield [%]	ratio 20: 21
a	CH_3	CH_3	CH_3	204 (dec.)	80	5.7:1
b	$[CH_2]_4$		CH_3	205 (dec.)	94	33:1
c	CH_3	CH_3	OCH_3	-	70	0.5:1
d	$[CH_2]_4$		OCH_3	225	72	7.3:1

Deprotonation of 20 can be achieved again with K_2CO_3/CH_2Cl_2. Nevertheless the expected pyrrole-3-sulfonium ylides possessing an electron-withdrawing group in the pyrrole ring are less stable than the unsubstituted pyrrole-2-sulfonium ylides 18 and could not be isolated in pure form. 20a gave a mixture of decomposition products whereas 20b and 20d lead to a polymeric material, probably similar in structure to 7.

Meanwhile we have succeeded in preparing pyrrole-3-sulfonium salts unsubstituted in the 5-membered ring by an acid catalysed rearrangement of the pyrrole-2-sulfonium salts 15[18]. Their syntheses and deprotonation will be discussed in a following paper.

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E X P E R I M E N T A L

Melting points were determined with a Leitz-Heiztischmikroskop HM-Lux and are uncorrected. IR spectra were recorded with a Perkin-Elmer 257 or 298 spectrophotometer, mass spectra with the Vacuum Generators 70-70 instrument. ^1H NMR spectra were obtained on a T 60 (60 MHz) or a XL 100 (100 MHz) of Varian Associates as well as on a GX 400 (400 MHz) of Jeol. ^{13}C NMR spectra were recorded with a Varian XL 100 or a Jeol FX 100 spectrometer. Multiplicities are indicated as s (singlet), bs (broad singlet), d (doublet), dd (double doublet), t (triplet), bt (broad triplet), q (quartet) and m (multiplet).

(1H-Indol-3-yl)dimethylsulfonium perchlorate (3a). To a stirred solution of indole (1) (0.59g, 5 mmol) and dimethyl sulfoxide (2a) (0.39g, 5 mmol) in dry CH_2Cl_2 (20ml) trifluoroacetic anhydride (TAA) (1.05g, 5 mmol) in CH_2Cl_2 (5ml) is added dropwise during 15 min. After warming up to room temperature the reaction mixture is shaken with a saturated solution of lithium perchlorate in water (20ml) and the aqueous phase extracted 3 times with nitromethane (10ml). The combined organic layers are dried over $CaCl_2$ and diethyl ether is added up to a beginning cloudiness. The crystalls separating in an ice bath are filtered off and recrystallized from methanol with addition of charcoal: 0.80g (58%) colourless crystalls, mp. 141°C. $C_{10}H_{12}ClNO_4S$ (277.7), calc.

C 43.25 H 4.36 N 5.04 S 11.55; found C 43.16 H 4.27 N 4.85 S 11.59. IR(KBr): 3160, 3090, 2970, 1415, 1250, 1090, 1025, 755, 635, 435cm^{-1}. ^{1}H NMR(CD_3NO_2, 400 MHz): 10.34 (bs, NH), 8.18 (d, 2-H, $^3J_{1,2}$ = 3.4 Hz), 7.95 (d, 4-H, J = 7.9 Hz), 7.74 (d, 7-H, J = 7.9 Hz), 7.45 (t, 6-H, J = 7.2 Hz), 7.40 (t, 5-H, J = 7.2 Hz), 3.40 [s, $S(CH_3)_2$]. ^{13}C NMR(CD_3NO_2): 138.4, 125.0 (C-3a, -7a), 134.8 (C-2), 125.6, 123.8, 119.2, 115.2 (C-4, -5, -6, -7), 93.5 (C-3), 29.9 [$S(CH_3)_2$].

(1H-Indol-3-yl)bis(phenylmethyl)sulfonium perchlorate (3b). Indole (1) (0.59g, 5mmol), bis(phenylmethyl)sulfoxide (1.15g, 5mmol) and TAA (1.05g, 5mmol) gave after recrystallization from ethanol colourless crystals (1.14g, 53%), mp. 166° C (dec.). $C_{22}H_{20}ClNO_4S$ (429.9), calc. C 61.46 H 4.69 N 3.26 S 7.46; found C 61.39 H 4.61 N 3.14 S 7.17. IR(KBr): 3300, 3120, 2910, 1500, 1425, 1250, 1090, 1020, 770, 715, 635cm^{-1}. ^{1}H NMR([D_6]Aceton): 11.65 (bs, NH), 7.05–8.05 (m, aromat. H, 2-H), 5.40 (s, CH_2). ^{13}C NMR(CD_3NO_2): 138.5, 126.2 (C-3a, -7a), 137.6 (C-2), 131.8, 131.1, 130.5, 129.5 (Benzyl), 125.9, 124.3, 119.5, 115.3 (C-4, -5, -6, -7), 87.7 (C-3), 49.6 (CH_2).

(1H-Indol-3-yl)tetrahydrothiophenium perchlorate (3c). Indole (1) (0.59g, 5mmol), tetrahydrothiophene sulfoxide (2c) (0.52g, 5mmol) and TAA (1.05g, 5mmol) gave after recrystallization from ethanol colourless, hygroscopic crystalls (1.30g, 86%), mp. 106°C. $C_{12}H_{14}ClNO_4S$ (303.8), calc. C 47.45, H 4.65 N 4.61 S 10.56; found C 47.25 H 4.54 N 4.39 S 10.61. IR(KBr): 3100, 2980, 2910, 1420, 1245, 1090, 770, 755, 645, 635cm^{-1}. ^{1}H NMR(CD_3CN): 10.70 (bs, NH), 7.95 (d, 2-H), 7.05–7.85 (m, aromat.H), 3.25–4.15 (m, SCH_2), 2.10–2.90 (m, $SCH_2\underline{CH}_2$). ^{13}C NMR(CD_3NO_2): 138.2, 125.6 (C-3a, -7a), 134.3 (C-2), 125.7, 123.9, 118.9, 115.0 (C-4, -5, -6, -7), 95.0 (C-3), 48.8 (SCH_2); 30.2 ($SCH_2\underline{C}H_2$).

(1H-Indol-3-yl)4-oxa-thianium perchlorate (3d). Indole (1) (0.59g, 5mmol), thioxane sulfoxide (2d) (0.60g, 5mmol) and TAA (1.05g, 5mmol) gave after recrystallization from methanol with charcoal colourless crystalls (1.60g, 100%) that turn yellow exposed to light, mp. 180°C. $C_{12}H_{14}ClNO_5S$ (319.8), calc. C 45.07 H 4.41 N 4.38 S 10.03; found C 44.92 H 4.45 N 4.29 S 9.95. IR(KBr): 3360, 3130, 2950, 1475, 1420, 1290. 1090, 755, 630, 475cm^{-1}. ^{1}H NMR(CD_3NO_2): 10.30 (bs, NH), 8.20 (d, 2-H), 7.20–8.00 (m, aromat.H), 3.40–4.70 (m, thioxane H). ^{13}C NMR(CD_3NO_2): 138.3, 125.5 (C-3a, -7a), 135.7 (C-2), 125.9, 124.1, 119.2, 115.3 (C-4, -5, -6, -7), 91.2 (C-3), 66.1 (OCH_2), 40.6 (SCH_2).

(1H-Indol-3-yl)diphenylsulfonium perchlorate (3e). Indole (1) (0.59g, 5mmol), diphenyl sulfoxide (2e) (1.01g, 5mmol) and TAA (1.05g, 5mmol) gave after recrystallization from methanol with charcoal colourless crystalls (1.00g, 50%), mp. 136°C. $C_{20}H_{16}ClNO_4S$ (401.9), calc. C 59.78 H 4.01 N 3.49 S 7.98; found C 59.63 H 4.00 N 3.38 S 7.92. IR(KBr): 3300, 3050, 2970, 1420, 1150, 1120, 1095, 755, 635, 505cm^{-1}. ^{1}H NMR(CD_3NO_2): 10.80 (bs, NH), 8.25 (d, 2-H), 7.15–8.00 (m, aromat. H). ^{13}C NMR(CD_3NO_2): 139.0, 125.4 (C-3a, -7a), 137.9 (C-2), 135.1, 132.4, 130.9, 127.6 (phenyl), 126.2, 124.5, 119.5, 115.5 (C-4, -5, -6, -7), 91.8 (C-3).

(1H-Indol-3-yl)bis(4-methylphenyl)sulfonium perchlorate (3f). Indole (1) (0.59g, 5mmol), di-p-tolyl sulfoxide (1.15g, 5mmol) and TAA (1.05g, 5mmol) gave after recrystallization from methanol with charcoal colourless crystalls (1.50g, 71%) that turn yellow exposed to light, mp. 215°C. $C_{22}H_{20}ClNO_4S$ (429.9), calc. C 61.46 H 4.69 N 3.26 S 7.46; found C 61.47 H 4.66 N 3.31 S 7.67. IR(KBr): 3290, 3090, 2990, 1490, 1415, 1250, 1105, 810, 765, 630, 520cm^{-1}. ^{1}H NMR(CD_3NO_2): 10.55 (bs, NH), 8.19 (d, 2-H), 7.15–7.81 (m, aromat. H), 2.48 (s, CH_3). ^{13}C NMR(CD_3NO_2): 146.9, 133.0, 130.8, 124.2 (tolyl), 139.0, 125.4 (C-3a, -7a), 137.3 (C-2), 126.1, 124.3, 119.5, 115.4 (C-4, -5, -6, -7), 92.9 (C-3), 21.6 (CH_3).

3-(Dimethylsulfonio)indolide (4a). A suspension of 3a (1.39g, 5mmol) in CH_2Cl_2 (50ml) is stirred for 12 h with K_2CO_3 (10g) at room temperature. After filtration the solvent is removed in vacuo and the remaining solid recrystallized from THF/diethyl ether: colourless crystalls, mp. 121°C (lit.[3] mp. 125°C). $C_{12}H_{13}NOS$ (219.3), calc. C 67.76 H 6.25 N 7.90 S 18.09; found C 67.52 H 6.13 N 7.59 S 18.03. MS(70 eV): m/e = 177 (64.5%, M^+), 162 (100%). IR(KBr): 3040, 2920, 1600, 1415, 1255, 1220, 1170, 815, 745, 510cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.90 (s, 2-H), 7.80 (d, 4-H, J = 7.9 Hz), 7.54 (d, 7-H, J = 7.6 Hz), 7.16 (t, 6-H, J = 7.5 Hz), 7.09 (t, 5-H, J = 7.4 Hz), 3.00 [s, $S(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): 151.0, 127.7 (C-3a, -7a), 146.1 (C-2), 120.2, 120.0, 119.4, 115.7 (C-4, -5, -6, -7), 76.7 (C-3), 31.0 [$S(CH_3)_2$].

3-(4-Oxa-thianium)indolide (4b). 3d (1.60g, 5 mmol) and K_2CO_3 gave after recrystallization from acetone/diethyl ether colourless crystals, mp. 191°C. $C_{12}H_{13}NOS$ (219.3), calc. C 65.72 H 5.97 N 6.39 S 14.62; found C 65.71 H 5.90 N 6.33 S 14.46. MS(70 eV): m/e = 219 (100%, M^+). IR(KBr): 3050, 2910, 1590, 1415, 1375, 1250, 1095, 765, 755, 480cm^{-1}. ^{1}H NMR([D_6]DMSO): 7.95 (s, 2-H), 7.43-7.62 (m, aromat. H), 6.88-6.97 (m, aromat. H), 3.20-4.32 (m, thioxane H). ^{13}C NMR(CD_3OD): 150.5, 129.2 (C-3a, -7a), 146.5 (C-2), 121.5, 120.9, 119.7, 117.4 (C-4, -5, -6, -7), 80.0 (C-3), 66.7 (OCH_2), 41.7 (SCH_2).

3-Bis(4-methylphenyl)sulfonio indolide (4c). 3f (2.15g, 5 mmol) and K_2CO_3 gave after recrystallization from THF/petrolether colourless crystals, mp. 162°C. $C_{22}H_{19}NS$ (329.5), calc. C 80.20 H 5.81 N 4.25 S 9.73; found C 80.00 H 5.80 N 4.04 S 9.82. MS(70 eV): m/e = 329 (4.0%, M^+), 214 (100%). IR(KBr): 3040, 2920, 1595, 1415, 1255, 1220, 1160, 825, 750, 505cm^{-1}. ^{1}H NMR($CDCl_3$): 8.00 (s, 2-H), 6.70-7.85 (m, aromat. H), 2.35 (s, CH_3). ^{13}C NMR($CDCl_3$): 151.7, 128.2 (C-3a, -7a), 148.8 (C-2), 142.4,130.5, 128.3, 127.5 (tolyl), 119.8, 119.3, 116.0 (C-4, -5, -6, -7), 74.9 (C-3), 21.0 (CH_3).

Poly[1H-indol-1,3-diyl-3-(1-thia-4-oxa-1,6-hexanediyl)] (7). 4b (1.10g, 5 mmol) was heated to 150-170°C for 15 min. After cooling, the remaining oil crystallized by addition of diethyl ether: white-grey powder, mp. 113°C. $(C_{12}H_{13}NOS)_n$ (219.3)$_n$, calc. C 65.72 H 5.97 N 6.39 S 14.62; found C 65.14 H 5.89 N 6.21 S 14.40. IR(KBr): 3040, 2910, 2850, 1495, 1455, 1350, 1125, 1105, 1010, 745cm^{-1}. ^{1}H NMR($CDCl_3$): 7.40-7.70 (m, 2-H), 6.70-7.10 (m, aromat. H), 3.70-4.00 (bt, NCH_2), 3.10-3.60 (m, OCH_2), 2.40-2.80 (bt, SCH_2). ^{13}C NMR ($CDCl_3$): 136.5, 130.1 (C-3a, -7a), 134.1 (C-2), 122.1, 120.1, 119.3, 109.7 (C-4, -5, -6, -7), 103.0 (C-3), 70.0, 69.3 (OCH_2), 46.2 (NCH_2), 35.7 (SCH_2).

2-(Methylthio)indole(10). A suspension of 2-indolinone (8) (3.99g, 30 mmol) and Lawesson reagent (6.07g, 30 mmol) in toluene (15.0ml) is stirred at room temperature for 48 h. The reaction mixture is filtered, the solvent removed in vacuo, the residue dissolved in 5% aqueous NaOH (50ml) and treated dropwise with dimethyl sulfate (4.16g, 33 mmol) in methanol (15ml). After 12 h ether is added, the organic layer dried over $CaCl_2$, the solvent evaporated and the remaining oil distilled (Kugelrohr): 2.0g, 41%. Recrystallization from n-hexane gave colourless crystals (mp. 51°C), see lit.[11].

(1H-Indol-2-yl)dimethylsulfonium fluorosulfonate (11). To a solution of 10 (1.63g, 10 mmol) in dry CH_2Cl_2 (6ml) is added dropwise with stirring methyl fluorosulfonate (1.20g, 10.5 mmol) in CH_2Cl_2 (4ml). After 12 h the white precipitate (2.35g, 85%) is filtered off and washed with ether, mp. 122°C. $C_{10}H_{12}NO_3S_2F$ (277.3), calc. C 43.31 H 4.36 N 5.05 S 23.12; found C 43.14 H 4.29 N 4.91 S 23.40. IR(KBr): 3420, 1305, 1285, 1080, 1005, 755, 590, 580cm^{-1}. ^{1}H NMR([D_6]DMSO): 12.6 (bs, NH), 7.73 (d, 7-H, J = 8.1 Hz), 7.61 (d, 4-H, J = 8.4 Hz), 7.45 (d, 3-H, J = 1.9 Hz), 7.38, 7.19 (t, 4-, 5-H, J = 7.7 Hz), 3.39[$S(CH_3)_2$]. ^{13}C NMR([D_6]DMSO): 138.8, 126.1 (C-7a, -3a), 116.9 (C-2), 125.4, 121.7, 121.1, 112.6 (C-4, -5, -6, -7), 111.9 (C-3), 29.2 (CH_3).

2-(Dimethylsulfonio)indolide (12). With 11 (1.48g, 5 mmol) following the procedure for 4a. Colourless needles (0.53g, 60%) from $CHCl_3$/ether, mp. 88-89° C. $C_{10}H_{11}NS \cdot 0.5\ H_2O$ (186.3), calc. C 64.48 H 6.49 N 7.52; found C 64.65 H 5.93 N 7.19. ^{1}H NMR($CDCl_3$, 400 MHz): 7.67 (d, J = 8.6 Hz) and 7.62 (d, J = 8.0 Hz) [7-, 4-H], 7.14 (t, J = 8.3 Hz) and 6.97 (t, J = 7.5 Hz) [5-, 6-H], 7.00 (s, 3-H), 3.07 [s, $S(CH_3)_2$]. ^{13}C NMR($CDCl_3$): 149.3, 129.4 (C-7a, -3a), 119.0 (C-2), 122.0, 120.6, 118.4, 117.9 (C-4, -5, -6, -7), 107.5 (C-3), 30.4 [$S(CH_3)_2$].

(1H-Pyrrol-2-yl)dimethylsulfonium perchlorate (15a)

Procedure A: To a stirred solution of freshly distilled pyrrole (0.67g, (10 mmol) and dimethyl sulfoxide (0.78g, 10 mmol) in dry CH_2Cl_2 (40ml) TAA (2.10g, 10 mmol) in dry CH_2Cl_2 (10ml) is added dropwise during 15 min at -65°C. After warming up to room temperature the reaction mixture is shaken with a saturated solution of $LiClO_4$ in water (40ml) and the aqueous layer extracted 3 times with nitromethane. The combined organic layers are dried over $CaCl_2$ and diethyl ether is added up to a beginning cloudiness. The crystals separating in an ice bath are filtered off and recrystallized from methanol/ether with charcoal: colourless crystals (2.20g, 94%) of 15a (about 90%) and 16a (about 10%). Pure 15a is obtained by repeated recrystallization from methanol/ether: mp. 129°C (dec.) (lit.[14] mp. 128-129°C). $C_6H_{10}ClNO_4S$ (277.7), calc. C 31.65

H 4.43 N 6.15 S 14.08; found C 31.67, H 4.40 N 6.26 S 14.15. IR(KBr): 3010, 3040, 2950, 1440, 1150, 1085, 1025, 1005, 785, 635cm^{-1}. ^{1}H NMR(CD_3NO_2, D_2O): 10.53 (bs, NH), 7.39 (dd, 5-H), 7.07 (dd, 3-H) 6.43 (dd, 4-H), 3.36 [s, $S(CH_3)_2$]; $^3J_{3,4}$ = 3.9 Hz, $^3J_{4,5}$ = 2.8 Hz, $^4J_{3,5}$ = 1.5 Hz. ^{13}C NMR(CD_3CN): 128.9 (C-5, d, ^1J = 189 Hz), 120.2 (C-3, d, ^1J = 178 Hz), 112.2 (C-4, d, ^1J = 176 Hz), 107.1 (C-2), 31.1 [$S(CH_3)_2$].

Procedure B: To a stirred solution of N-chlorosuccinimide (4.00g, 30 m mol) in dry CH_2Cl_2 (300ml) under an atmosphere of nitrogen dimethyl sulfide (2.05g, 33 m mol) in CH_2Cl_2 (10ml) is added slowly at -10°C. After 1 h the reaction mixture is cooled to -40°C, pyrrole (2.00g, 29.5 m mol) in CH_2Cl_2 (10ml) is added dropwise and the temperature kept for 2 h. At room temperature the reaction mixture is shaken with a saturated solution of $LiClO_4$ in water (120ml) and worked up following procedure A. 5.37g (80%) colourless crystalls of pure 15a.

Procedure C: 1-(Trimethylallyl)pyrrole (1.39g, 10 m mol) is used instead of pyrrole following procedure A: colourless crystalls (1.00g, 44%) consisting of 15a (30%) and 16a (70%).

(1H-Pyrrol-2-yl)tetrahydrothiophenium perchlorate (15b).

Procedure A: With tetrahydrothiophene sulfoxide (1.04g, 10 m mol) following procedure A for 15a: colourless, hygroscopic crystalls (1.40g, 56%) from acetone/ether turning brown exposed to light and consisting of 15b (85%) and 16b (15%). Repeated recrystallization gives pure 15a, mp. 73°C. $C_8H_{12}ClO_4S$ (253.7), calc. C 37.87 H 4.77 N 5.52 S 12.64; found C 37.97 H 4.64 N 5.59 S 12.99. IR(KBr): 3100, 3020, 2930, 1520, 1415, 1205, 1070, 875, 755, 625cm^{-1}. ^{1}H NMR(CD_3NO_2, D_2O): 10.49 (bs, NH), 7.34 (dd, 5-H), 7.00 (dd, 3-H), 6.48 (dd, 4-H), 3.50–4.20 (m, SCH_2), 2.20–2.90 (m, $SCH_2C\underline{H}_2$); $^3J_{3,4}$ = 3.9 Hz, $^3J_{4,5}$ = 2.8 Hz, $^4J_{3,5}$ = 1.5 Hz. ^{13}C NMR(CD_3NO_2): 129.1 (C-5, d, ^1J = 191 Hz), 124.5 (C-3, d, ^1J = 177 Hz), 120.0 (C-4, d, ^1J = 175 Hz), 108.9 (C-2), 50.9 (SCH_2), 29.8 ($SCH_2\underline{C}H_2$).

Procedure B: With tetrahydrothiophene (2.91g, 33 m mol) following procedure B for 15a: colourless crystalls (5.24g, 70%) of pure 15b.

Procedure C: With tetrahydrothiophene sulfoxide (1.04g, 10 m mol) following procedure C for 15a: colourless crystalls (0.84g, 33%) consisting of 15b (70%) and 16b (30%).

(1H-Pyrrol-2-yl)4-oxa-thianium perchlorate (15c).

Procedure A: With thioxane sulfoxide (1.20g, 10 m mol) following procedure A for 15a: colourless crystalls (1.20g, 44%) from acetone/ether consisting of 15c (93%) and 16c (7%). Repeated recrystallization gives pure 15c, mp. 130°C. $C_8H_{12}ClNO_5S$ (269.7), calc. C 35.63 H 4.48 N 5.19 S 11.89; found C 35.58 H 4.57 N 5.07 S 12.07. IR(KBr): 3050, 2990, 2920, 1145, 1090, 975, 785, 635, 625, 495cm^{-1}. ^{1}H NMR(CD_3NO_2, D_2O): 10.73 (bs, NH), 7.42 (dd, 5-H), 7.21 (dd, 3-H), 6.52 (dd, 4-H), 3.50–4.70 (m, thioxane H); $^3J_{3,4}$ = 3.9 Hz, $^3J_{4,5}$ = 2.7 Hz, $^4J_{3,5}$ = 1.4 Hz. ^{13}C NMR(CD_3NO_2): 130.1 (C-5, d, ^1J = 191 Hz), 121.7 (C-3, d, ^1J = 178 Hz), 113.2 (C-4, d, ^1J = 177 Hz), 105.1 (C-2), 65.7 (OCH_2), 42.5 (SCH_2).

Procedure B: With thioxane (3.44g, 33 m mol) following procedure B for 15a: colourless crystalls (5.17g, 65%) of pure 15c.

Procedure C: With thioxane sulfoxide (1.39g, 10 m mol) following procedure C for 15a: colourless crystalls (1.08g, 40%) consisting of 15c (40%) and 16c (60%).

(1H-Pyrrol-2-yl)diphenylsulfonium perchlorate (15d). With diphenyl sulfoxide (2.02g, 10 m mol) following procedure A for 15a: colourless crystalls (3.20g, 97%) from acetonitrile/ether consisting of 15d (90%) and 16d (10%). Repeated recrystallization gives pure 15d, mp. 185°C. $C_{18}H_{14}ClNO_4S$ (351.8), calc. C 54.63 H 4.01 N 3.98 S 9.11; found C 54.63 H 4.06 N 3.89 S 9.13. IR(KBr): 3240, 3130, 3070, 1445,1090, 1005, 790, 750, 630, 535cm^{-1}. ^{1}H NMR(CD_3NO_2, D_2O): 10.51 (bs, NH), 7.76 (m, aromat. H), 7.52 (dd, 5-H), 7.12 (dd, 3-H), 6.61 (dd, 4-H); $^3J_{3,4}$ = 4.0 Hz, $^3J_{4,5}$ = 2.9 Hz, $^4J_{3,5}$ = 1.6 Hz. ^{13}C NMR(CD_3NO_2): 135.4, 132.6, 131.1, 128.3 (phenyl C), 131.5 (C-5), 124.0 (C-3), 113.8 (C-4), 105.0 (C-2).

(1H-Pyrrol-2-yl)bis(4-methylphenyl)sulfonium perchlorate (15e). With di-p-tolyl sulfoxide (2.30g, 10 mmol) following procedure A for 15a: colourless crystals (2.50g, 66%) from methanol/ether consisting of 15e (95%) and 16e (5%). Repeated recrystallization gives pure 15e, mp. 154°C. $C_{18}H_{18}ClNO_4$ (379.9), calc. C 56.92 H 4.78 N 3.69 S 8.44; found C 56.70 H 4.78 N 3.59 S 8.48. IR(KBr): 3190, 3030, 2910, 1585, 1470, 1085, 805, 775, 620, 520cm^{-1}. ^{1}H NMR(CD_3NO_2, D_2O): 10.37 (ba, NH), 7.59 (m, aromat. H), 7.49 (dd, 5-H), 7.05 (dd, 3-H), 6.58 (dd, 4-H), 2.49 (s, CH_3); $^3J_{3,4}$ = 4.0 Hz, $^3J_{4,5}$ = 2.7 Hz, $^4J_{3,5}$ = 1.5 Hz. ^{13}C NMR(CD_3NO_2): 147.3, 133.2, 130.9, 125.0 (tolyl C), 131.1 (C-5), 123.4 (C-3), 113.6 (C-4), 106.0 (C-2), 21.6 (CH_3).

2-(Dimethylsulfonio)pyrrolide (18a). A suspension of 15a (2.28g, 10 mmol) in CH_2Cl_2 (100ml) is stirred for 12 h with K_2CO_3 (20g) at room temperature. After filtration the solvent is removed in vacuo and the remaining solid recrystallized from THF/ether: strongly hygroscopic, colourless crystals turning pink exposed to air and light, mp. 62°C (lit.[14] 61-62°C). C_6H_9NS (127.2), calc. C 56.65 H 7.13 N 11.01 S 25.21; found C 56.66 H 7.13 N 10.43 S 25.20. MS(70 eV): m/e = 127 (66.5%, M^+), 68 (100%). IR(KBr): 3010, 2930, 1415, 1360, 1205, 1025, 995, 745, 735, 475cm^{-1}. ^{1}H NMR($CDCl_3$): 7.41 (dd, 5-H), 6.77 (dd, 3-H), 6.30 (dd, 4-H), 2.93 [s, $S(CH_3)_2$]; $^3J_{3,4}$ = 3.4 Hz, $^3J_{4,5}$ = 1.5 Hz, $^4J_{3,5}$ = 1.2 Hz. ^{13}C NMR($CDCl_3$): 138.4 (C-5, d, ^1J = 177 Hz), 116.1 (C-3, d, ^1J = 170 Hz), 109.8 (C-4, d, ^1J = 166 Hz), 106.4 (C-2), 31.4 [$S(CH_3)_2$].

2-(Tetrahydrothiophenio)pyrrolide (18b). With 15b (2.54g, 10 mmol) following the procedure for 18a: strongly hygroscopic, colourless crystals, mp. 99°C. $C_8H_{11}NS$ (153.2), calc. C 62.70 H 7.24 N 9.14 S 20.92; found C 62.64 H 7.33 N 8.96 S 20.99. MS(70 eV): m/e = 153 (100%, M^+). IR(KBr): 3070, 2990, 2930, 1435, 1350, 1205, 1020, 885, 730, 515cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.40 (dd, 5-H), 6.80 (dd, 3-H), 6.31 (dd, 4-H), 3.40-3.70 (m, SCH_2), 2.00-2.80 (m, SCH_2CH_2); $^3J_{3,4}$ = 3.3 Hz, $^3J_{4,5}$ = 1.4 Hz, $^4J_{3,5}$ = 1.2 Hz. ^{13}C NMR($CDCl_3$): 138.7 (C-5, d, ^1J = 177 Hz), 117.2 (C-3, d, ^1J = 169 Hz), 109.8 (C-4, d, ^1J = 167 Hz), 108.9 (C-2), 48.0 (SCH_2), 28.1 (SCH_2CH_2).

2-(4-Oxa-thanio)pyrrolide (18c). With 15c (2.70g, 10 mmol) following the procedure for 18a: colourless crystals from methanol, mp. 175°C. $C_8H_{11}NOS$ (169.2), calc. C 56.77 H 6.55 N 8.28 S 18.95; found C 56.66 H 6.52 N 8.15 S 18.52. MS(70 eV): m/e = 169 (100%). IR(KBr): 3070, 2970, 2850, 1455, 1350, 1275, 1100, 985, 755, 495cm^{-1}. ^{1}H NMR($CDCl_3$): 7.34 (dd, 5-H), 6.79 (dd, 3-H), 6.28 (dd, 4-H), 2.30-4.50 (m, thioxane H); $^3J_{3,4}$ = 3.4 Hz, $^3J_{4,5}$ = 1.5 Hz, $^4J_{3,5}$ = 1.3 Hz. ^{13}C NMR($CDCl_3$): 138.9 (C-5, d, ^1J = 178 Hz), 117.8 (C-3, d, ^1J = 170 Hz), 110.4 (C-4, d, ^1J = 167 Hz), 105.9 (C-2), 64.8 (OCH_2), 41.6 (SCH_2).

2-Bis(4-methylphenyl)sulfonio pyrrolide (18d). With 15e (3.80g, 10 mmol) following the procedure for 18a: colourless crystals from THF/petrol ether, mp. 184°C. $C_{18}H_{17}NS$ (279.4), calc. C 77.38 H 6.13 N 5.01 S 11.48; found C 77.38 H 6.11 N 4.74 S 11.59. MS(70 eV): m/e = 279 (11%, M^+), 156 (100%). IR(KBr): 3040, 2900, 1485, 1345, 1010, 815, 805, 735, 525, 500cm^{-1}. ^{1}H NMR(CD_3NO_2): 7.34-7.76 (m, aromat. H), 7.25 (dd, 5-H), 6.88 (dd, 3-H), 6.21 (dd, 4-H), 2.40 (s, CH_3); $^3J_{3,4}$ = 3.4 Hz, $^3J_{4,5}$ = 1.4 Hz, $^4J_{3,5}$ = 1.2 Hz. ^{13}C NMR($CDCl_3$): 134.6, 125.0, 124.3, 124.0 (tolyl C), 133.5 (C-5, d, ^1J = 178 Hz), 116.0 (C-3, d, ^1J = 170 Hz), 108.8 (C-4, d, ^1J = 167 Hz), 105.0 (C-2), 35.9 (CH_3).

(5-Acetyl-1H-pyrrol-3-yl)dimethylsulfonium perchlorate (20a). To a stirred solution of 2-acetyl pyrrole (19a) (3.27g, 30 mmol) and dimethyl sulfoxide (2.34g, 30 mmol) in dry CH_2Cl_2 (120ml) trifluoromethanesulfonic anhydride (TFMSA) (8.46g, 30 mmol) in CH_2Cl_2 (30ml) is added dropwise during 15 min at -10°C. At room temperature the reaction mixture is shaken with a saturated solution of $LiClO_4$ in water (120ml) and the aqueous layer is extracted 3 times with nitromethane (20ml). After drying the combined organic layers with $CaCl_2$ diethyl ether is added up to a beginning cloudiness. The crystals separating in an ice bath are filtered off and recrystallized from methanol with charcoal: colourless crystals (6.50g, 80%) consisting of 20a (85%) and 21a (15%). Repeated recrystallization from methanol leads to pure 20a, mp. 204°C (dec.). $C_8H_{12}ClNO_5S$ (269.7), calc. C 35.63 H 4.48 N 5.19 S 11.89; found C 35.56 H 4.52 N 5.13 S 11.73. IR(KBr): 3290, 3030, 2930, 1670, 1425, 1380, 1179, 1085, 630, 615cm^{-1}. ^{1}H NMR(CD_3NO_2): 10.72 (ba, NH), 7.84 (dd, 2-H), 7.62 (dd, 4-H), 3.27 (s, SCH_3), 2.49 (s, CH_3); $^3J_{1,2}$ = 3.4 Hz, $^4J_{1,4}$ = 1.9 Hz, $^4J_{2,4}$ = 1.7 Hz. ^{13}C NMR(CD_3NO_2): 189.6 (C=O), 136.3 (C-5), 131.0 (C-2, d, ^1J = 196 Hz), 115.8 (C-4, d, ^1J = 180 Hz), 105.9 (C-3), 31.6 (SCH_3), 25.9 (CH_3).

(5-Acetyl-1H-pyrrol-3-yl)tetrahydrothiophenium perchlorate (20b). With tetrahydrothiophene sulfoxide (6.30g, 30 mmol) following the procedure for 20a: colourless crystals (8.46g, 94%) consisting of 20b (97%) and 21b (3%). Repeated recrystallization from methanol leads to pure 20b, mp. 252°C (dec.). $C_{10}H_{14}ClNO_5S$ (295.7), calc. C 40.61 H 4.77 N 4.74 S 10.84; found C 40.56 H 4.70 N 4.67 S 10.99. IR(KBr): 3310, 3110, 2960, 1655, 1425, 1375, 1165, 1085, 635, 610cm^{-1}. ^{1}H NMR(CD_3CN): 10.79 (bs, NH), 7.65 (dd, 2-H), 7.31 (dd, 4-H), 3.30-4.00 (m, SCH_2), 2.43 (s, CH_3), 2.20, 2.70 (m, SCH_2CH_2); $^3J_{1,2}$ = 3.3 Hz, $^4J_{1,4}$ = 1.9 Hz, $^4J_{2,4}$ = 1.7 Hz. ^{13}C NMR(CD_3CN): 188.6 (C=O), 135.7 (C-5), 130.6 (C-2), 116.4 (C-4), 106.4 (C-3), 50.6 (SCH_2), 29.6 (SCH_2CH_2), 26.1 (CH_3).

[5-(Methoxycarbonyl)1H-pyrrol-3-yl]dimethylsulfonium perchlorate (20c) and [5-(methoxycarbonyl)1H-pyrrol-2-yl]dimethylsulfonium perchlorate (21c). With methyl pyrrol-2-carboxylate (3.75g, 30 mmol) following the procedure for 20a: colourless crystals (6.00g, 70%) consisting of 20c (34%) and 21c (66%). A separation of the isomers by recrystallization was not successfull. $C_8H_{12}ClNO_6S$ (285.7), calc. C 33.63 H 4.23 N 4.90 S 11.22; found C 33.64 H 4.12 N 4.78 S 11.17. IR(KBr): 3090, 2980, 1730, 1710, 1385, 1315, 1145, 1085, 765, 625cm^{-1}. ^{1}H NMR(CD_3NO_2, D_2O): 20c: 11.02 (bs, NH), 7.81 (d, 2-H), 7.45 (d, 4-H), 3.91 (s, OCH_3), 3.25 [s, $S(CH_3)_2$]; $^4J_{2,4}$ = 1.8 Hz; 21c: 10.93 (bs, NH), 7.17, 7.05 (d, 3-H, 4-H), 3.92 (s, OCH_3), 3.38 [s, $S(CH_3)_2$]: $^3J_{3,4}$ = 4.2 Hz.

[5-(Methoxycarbonyl)1H-pyrrol-3-yl]tetrahydrothiophenium perchlorate (20d). With methyl pyrrol-2-carboxylate (3.75g, 30 mmol) and tetrahydrothiophene sulfoxide (3.75g, 30 mmol) following the procedure for 20a: colourless crystals (6.75g, 72% consisting of 20d (88%) and 21d (12%). Repeated recrystallization from methanol leads to pure 20d, mp. 225°C. $C_{10}H_{14}ClNO_6S$ (311.7), calc. C 38.53 H 4.53 N 4.49 S 10.29; found C 38.75 H 4.50 N 4.41 S 10.29. IR(KBr): 3240, 3120, 3010, 2930, 1730, 1450, 1400, 1085, 755, 620cm^{-1}. ^{1}H NMR (CD_3NO_2): 10.56 (bs, NH), 7.74 (dd, 2-H), 7.25 (dd, 4-H), 3.40-4.20 (m, SCH_2), 3.89 (s, OCH_3), 2.30-2.90 (m, SCH_2CH_2); $^3J_{1,2}$ = 3.5 Hz, $^4J_{1,4}$ = 2.5 Hz, $^4J_{2,4}$ = 1.8 Hz.^{13}C NMR(CD_3NO_2): 161.2 (C=O), 130.4 (C-2, d, ^1J = 195 Hz), 128.1 (C-5), 115.1 (C-4, d, ^1J = 181 Hz), 107.1 (C-3), 53.0 (OCH_3), 51.1 (SCH_2), 30.1 (SCH_2CH_2).

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