Tetrahedron Vol. 43, No. 5, pp. 881 to 889, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00

N-ARYL-ETHENESULPHENAMIDES; THERMAL TRANSFORMATION OF TWO N-(1-NAPHTHYL)-ETHENESULPHENAMIDES INTO 1H-BENZ[g]INDOLES

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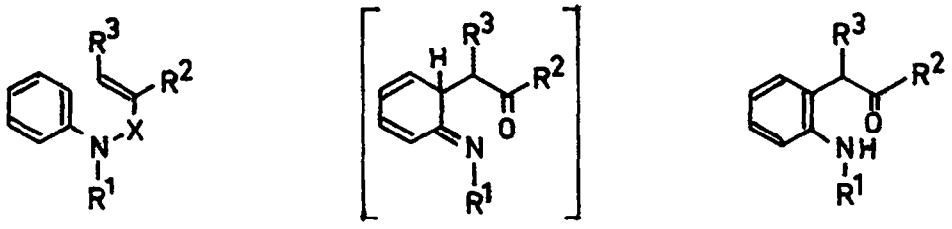
(*Received in Belgium* 10 *October* 1986)

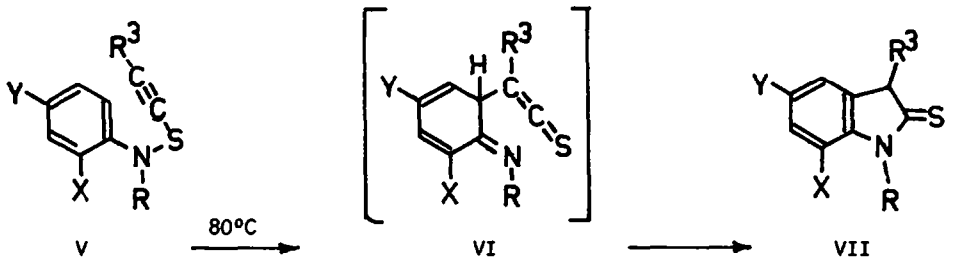
Abstract- Reaction of vinylmagnesium bromide with morpholine or piperidine-N-sulphenyl chlorides 3a,b affords the N-ethenylthio-morpholine and -piperidine 4a,b. When treated with stoichiometric amounts of an arylamine and methanesulphonic (or trifluoroacetic) acid, the sulphenamides 4 are converted into N-aryl-ethenesulphenamides 6a-e. On heating in toluene, two of these sulphenamides 6d and 6e undergo [3.3]-sigmatropic rearrangements followed by cyclisation of the intermediate amino-thioaldehydes yielding the corresponding 1H-benz[g]indoles 8a,b.

Although 1-aza-1'oxa-[3.3]-sigmatropic rearrangements of unsaturated derivatives I of N-acyl-N-aryl-hydroxylamines have been reported [1], analogous reactions of related systems IV containing a sulphenamide group have not been investigated to our knowledge.

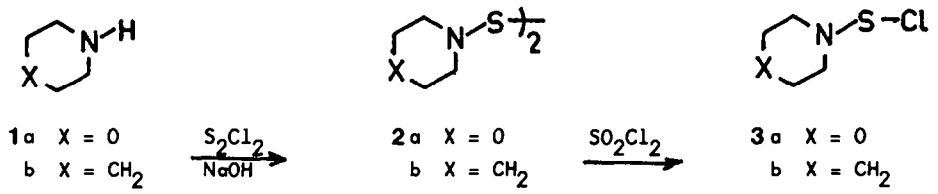


I X = O ⟶ II ⟶ III
IV X = S

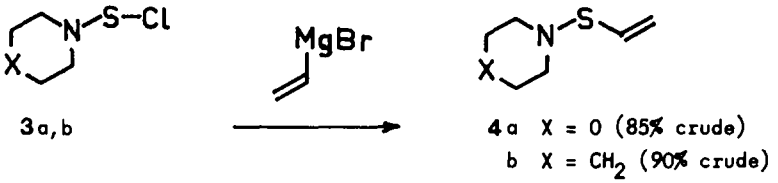
These N-aryl-1-alkenesulphenamides IV would be of interest as they might undergo an 1-aza-1'-thia-[3.3]-sigmatropic rearrangement to give o-amino-phenyl substituted thiocarbonyl compounds which could further cyclise to form indoles. This anticipation was based on the following known facts: i) the smooth rearrangements of some allyl vinyl sulphide derivatives [2]; ii) the thermal unstability of the N-S bond in sulphenamides [3] and iii) the mild thermal transformation of N-aryl-1-alkynesulphenamides V which undergo [3.3]-sigmatropic rearrangements followed by cyclisation of the intermediate amino-thioketenes VI yielding indoline-2-thiones VII [4]:



The new N-aryl-ethenesulphenamides 6a-e were obtained by a route similar to our previously reported preparation of the N-aryl-1-alkynesulphenamides V [4b]. The aminosulphenyl chlorides 3a,b are known to be easily prepared [5]:



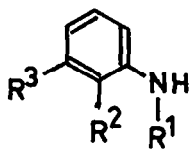
It has now been found that the Grignard derivative of vinyl bromide reacts smoothly with the aminosulphenyl chlorides 3a,b to afford the N-ethenylthio-morpholine or -piperidine 4a,b with good yields:



Like the nucleophilic displacement of the chlorine atom of 3b by alkynyl-lithium derivatives [4b], it is probable that the reaction 3 → 4 is facilitated by the participation of the lone pair of electrons on the nitrogen atom.

Following some previous reports on transaminations of sulphenamides [6,4b], the sulphenamides 4a or 4b dissolved in an anhydrous aprotic solvent, such as dichloromethane or dimethoxymethane, were treated with equimolar amounts of an arylamine 5 and a strong acid such as methanesulphonic acid ou trifluoroacetic acid between 0°C and room temperature for several hours. The ammonium salts were removed by washing with water and the N-aryl-ethenesulphenamides 6a-e were easily isolated from the organic phase.

When heated at reflux in benzene, toluene or xylene for 3 hrs, the ethenesulphenamides 6a,b,c did not give the expected indoles, but were recovered along with the benzenamines 5, the amounts of which increased with the temperature. These benzenamines 5 were probably formed by a homolytic cleavage of the N-S bond with loss of the sulphur bearing fragment. The unsaturated character of this fragment leads to polymerisation. No o- or p-ethenylthiobenzenamine corresponding to the previously reported thermal rearrangement of sulphenanilides [3] has been detected in our products.



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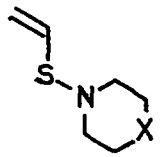
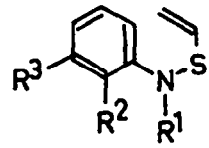


4a,b

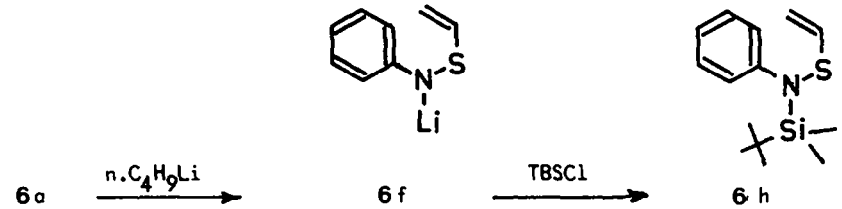
$\xrightarrow{H^+}$



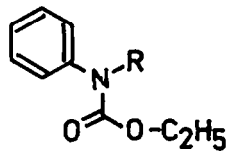
6	R^1	R^2	R^3	yields of purified products
a	H	H	H	60 %
b	CH_3	H	H	90 %
c	H	H	NO_2	75 %
d	H	-(C_4H_4)-		42 %
e	CH_3	-(C_4H_4)-		49 %

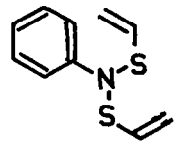
Inspection of the putative intermediate II (S instead of O) suggested to us that the [3.3]-sigmatropic rearrangement of IV should be aided by an appropriately selected substituent R^1. An electron withdrawing group R^1 would be favorable on account of some previous results in other [3.3]-sigmatropic rearrangements [1c,e,f,7]. However, our attempts to react the secondary sulphenamide 6a with some acylating and sulphonylating agents in several conditions were unsuccessful.

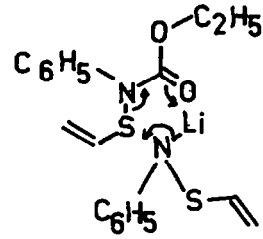
Reaction of the sulphenamide 6a with methanesulphonyl chloride and triethylamine in dichloromethane between -60°C and room temperature gave C_6H_5-NH-SO_2-CH_3. When treated with an equivalent of n.butyllithium in tetrahydrofuran at -70°C, the sulphenamide 6a afforded the lithio-derivative 6f which was found to be stable after heating the THF solution at 65°C for 2 hrs. Reaction of the lithio-derivative 6f with p.toluenesulphonyl chloride between -70°C and room temperature gave C_6H_5-NH-SO_2-C_7H_7 as the sole identified product. However, the reaction of 6f with tert.butyl-dimethylsilyl chloride afforded the silylated sulphenamide 6h which was found to be stable after heating a solution of it in 1.2-dichlorobenzene at 150°C for 2.5 hrs.



When treated with one equivalent of ethyl chloroformate, the lithio-sulphenamide 6f gave three products 7a (41%), 7b (32%) and 6g (27%) which were separated by chromatography. The formation of these products could be explained by the likely hypothesis that the expected N-ethoxycarbonyl-sulphenamide reacts rapidly as a sulphenylation agent on the lithio-derivative 6f (fig. VIII).

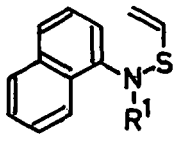


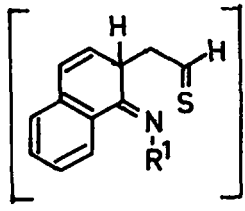


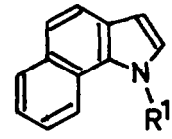


6f $\xrightarrow{ClCO_2C_2H_5}$ 7a R = H; b R = $CO_2C_2H_5$ 6g VIII

Our sought for synthesis of the indole ring system succeeded with the two N-(1-naphthyl)-ethenesulphenamides 6d and 6e; heating a 0.1 molar solution in toluene for several hours (6d: 4 hrs; 6e: 2 hrs) resulted in a smooth transformation into the corresponding 1H-benz-[g]indoles 8a,b. It is probable that the [3.3]-sigmatropic rearrangement 6 → IX is assisted by the presence of the naphthalene ring system which allows provisional dearomatisation into the amino-thioaldehyde IX [8].

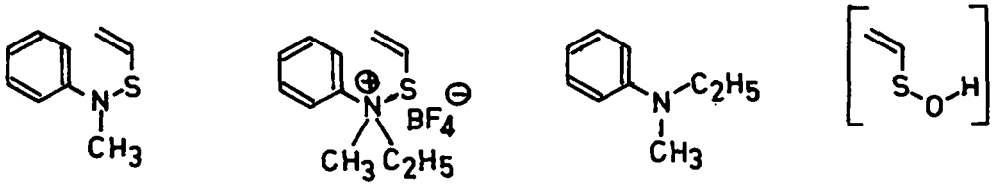






6d R^1= H; e R^1= CH_3 $\xrightarrow{\sigma\,[3.3]}$ IX $\xrightarrow{-H_2S}$ 8a R^1= H 83 %; b R^1= CH_3 72%

Returning to the N-phenyl ethenesulphenamide case, it seemed to us that if a corresponding aza-sulphonium salt could be prepared, the [3.3]-sigmatropic rearrangement should occur through a cationic charge-accelerated process observed with other unsaturated sulphonium salts [9,10]. Among the rare examples for the preparation of aza-sulphonium salts from sulphenamides, the alkylation of dimorpholine sulphide with triethyloxonium tetrafluoroborate has been reported [11]. When treated with this alkylating agent in dichloromethane at 0°C, the sulphenamide 6b gave, after aqueous work up, N-ethyl N-methyl aniline 9. It is likely that the alkylation occurred on the nitrogen atom to yield a thio-ammonium salt [12] X which was hydrolysed to the final product 9 and the unstable ethenesulphenic acid XI.



6b → X → 9 XI

Our results show that i) N-ethenylthio-piperidine or -morpholine 4 are easily prepared by reaction of aminosulphenyl chlorides 3 with vinyl magnesium bromide; various N,N-dialkyl-1-alkenesulphenamides should be accessible with other vinylic Grignard derivatives; ii) the acid-catalysed transaminations of the compounds 4 with arylamines provide a convenient

route to the N-aryl-ethenesulphenamides 6 and iii) the 1H-benz[g] indole ring system can be prepared by mild heating of the naphthalenic substrates 6 [22].

Acknowledgements. This work was supported by the Centre National de la Recherche Scientifique, France (E.R.12; A.T.P. Hétérochimie Moléculaire) which is gratefully acknowledged. The authors thank Dr Brian P. McDonald for reading the manuscript.

EXPERIMENTAL

Boiling and melting points are uncorrected. The purity of the described products has been checked by thin layer chromatography (silica gel 60F-254 Merck).
The ^{1}H NMR spectra were recorded on a Cameca 250 Spectrometer; ^{1}H chemical shifts are given in δ (ppm) from internal TMS.
The ^{13}C NMR spectra were recorded on a Brucker WH 90 MHz and a Brucker AL 100 MHz spectrometer. ^{13}C chemical shifts are given in δ (ppm) from TMS with the solvent peaks as internal standard; CH and CH_3 resonances appear as positive (+) and quaternary and CH_2 carbons as negative (-) signals by multiplicity determination [13].
The mass spectra were recorded on a Nermag R10-10B spectrometer, with electronic impact 70 ev (E.I.) or chemical ionisation with NH_3 (C.I.).

The N,N'-dithiobis-morpholine and -piperidine 2a,b were easily prepared with good yields from the corresponding amines 1 and sulfur monochloride in hexane in presence of aqueous sodium hydroxide following the procedure of Hatch [14].

The morpholine- and piperidine-N-sulphenyl chlorides 3a,b were prepared following the procedure using sulphuryl chloride described for diethylamine-N-sulphenyl chloride [15]. The morpholine N-sulphenyl chloride ($bp_{0.2}$=45°C) has δ ^{1}H NMR ($CDCl_3$): 3.37-3.47 (m, 4H); 3.77-3.87 (m, 4H); δ ^{13}C NMR ($CDCl_3$): 58.7 (t); 66.4 (t). The ^{1}H NMR data of piperidine-N-sulphenyl chloride 3b are given in a previous paper [4b].

1-Ethenylthio-piperidine 4b. General procedure

In a dry flask, a solution 0.5 M of vinyl magnesium bromide (10.5 mmol) in tetrahydrofuran [16] was cooled and stirred at -78°C under argon. Piperidine N-sulphenyl chloride (1.52 g; 10 mmol) was rapidly added; the reaction was exothermic. The mixture was stirred at -78°C for 15 min and warmed to room temperature. After stirring for 2.5 hrs, pentane (25 ml) and water (10 ml) were added. The organic phase was decanted and the aqueous layer was washed with pentane (3 x 20 ml). The organic phases were washed with brine and dried (potassium carbonate). The solvents were evaporated under reduced pressure leaving a yellow oil (90 %) with an unpleasant odour. An attempt to distil the product under high vacuum led to a significant loss in material (30-40%). For microanalysis, a small sample was distilled (Kugelrohr, 35-45°C, 0.1 mm). The spectral data are indicated in the table. The crude product was used for the following transaminations.

N-Aryl-ethenesulphenamides 6a,b,c

A solution of benzenamine 5 (10 mmol) in anhydrous dichloromethane (10 ml) was stirred at 0°C and treated with methanesulphonic acid (0.960 g; 10 mmol); the benzenaminium methanesulphonate precipitated. Then a solution of 1-ethenylthio-piperidine 4b (11 mmol) in dichloromethane (5ml) was added and the mixture was stirred at 0°C for 2 hrs.
When 4-ethenylthio-morpholine 4a was used, the mixture was stirred at 0°C for 30 min, then at room temperature for 3 hrs.
Water (5 ml) was added and the mixture extracted with dichloromethane (3 x 5 ml). The organic phases were washed with saturated brine and dried (potassium carbonate). Removal of the solvent under reduced pressure at room temperature afforded the crude products which were purified by flash-chromatography (kieselgel Merck 70-230 mesh) using pentane-dichloromethane 60/40 as eluent. The yields are indicated in the main text and the spectral date are given in the table. The compound 6c was crystalline, mp. 87°C.

Table. Spectral data of ethenesulphenamides 4a,b and 6a-f

	^{1}H NMR ($CDCl_3$/TMS_{int}) δ (ppm)	^{13}C NMR ($CDCl_3$) δ (ppm)	M.S. m/e (rel. int. %)
*4a	3.00-3.07 (m,4H); 3.70-3.77 (m,4H); 5.32 (d, J=10 Hz, 1H); 5.40 (d, J=17 Hz, 1H); 6.70 (dd, J=10 and 17 Hz, 1H).	55.3 (-); 67.0 (-); 110.4 (-); 132.0 (+)	145 (M^+, 100); 86 (12).
*4b	1.36-1.50 (m,2H); 1.58-1.70 (m,4H); 2.96-3.05 (m, 4H); 5.25 (d, J=10 Hz, 1H); 5.34 (d, J=17 Hz, 1H); 6.70 (dd, J=10 and 17 Hz, 1H).	23.2 (t); 27.2 (t); 57.0 (t); 109.4 (t); 132.8 (d).	143 (M^+,62); 84 (55); 83 (33); 60 (45); 59 (6); 58 (2); 56 (42); 55 (100).
6a	4.90 (br s,1H); 5.14 (d,J=16.5 Hz,1H); 5.18 (d, J=10 Hz, 1H); 6.38 (dd, J=10 and 16.5 Hz, 1H); 6.90-6.98 (m,1H); 7.00-7.08 (m,2H); 7.24-7.34 (m, 2H).	107.6 (t); 114.4 (d); 120.1 (d); 128.8 (d); 134.9 (d); 146.0 (s).	151 (M^+,100); 136 (10); 118 (25); 106 (18); 93 (15); 92 (60); 65 (23); 59 (11); 58 (13).
*6b	3.39 (s,3H); 4.97 (d,J=16.5 Hz,1H); 5.14 (d, J=10 Hz, 1H); 6.31 (dd,J=10 and 16.5 Hz, 1H); 6.86-6.94 (m,1H); 7.02-7.10 (m,2H); 7.24-7.34 (m, 2H).	44.0 (q); 107.9 (t); 115.1 (d); 119.5 (d); 129.0 (d); 133.3 (d); 149.4 (s).	165 (M^+,100); 150 (5); 132 (36); 108 (86); 79 (45); 77 (96); 52 (46).
*6c	5.13 (d,J=16.5 Hz,1H); 5.15 (br s , 1H); 5.26 (d, J=10 Hz, 1H); 6.39 (dd, J=10 and 16.5 Hz,1H); 7.34 (ddd,J=8,2.25 and 1.2 Hz,1H); 7.44 (dd, J=8 and 8 Hz, 1H); 7.78 (ddd,J=8,2.25 and 1,2 Hz,1H); 7.90 (dd, J=2.25 and 2.25 Hz, 1H).	108.9 (-); 109.3 (+); 115.0 (+); 120.5 (+); 129.8 (+); 133.9 (+); 147.9 (-); 149.3 (-).	196 (M^+,57); 195 (44); 149 (17); 138 (12); 117 (29); 91 (40); 65 (29); 64 (63); 63(74); 59 (100); 58 (80); 52 (36).
*6d	5.12 (d, J=16.5 Hz, 1H); 5.19 (d, J=10 Hz, 1H); 5.52 (br s, 1H); 6.41 (dd, J=10 and 16.5 Hz,1H); 7.30-7.62 (m, 5H); 7.78-7.95 (m, 2H).	108.1 (-); 109.0 (+); 119.5 (+); 120.5 (+); 124.1 (-); 125.3 (+); 125.7 (+); 126.3 (+); 128.8 (+); 134.3 (-); 134.8 (+); 141.1 (-).	201 (M^+,24); 168 (8); 143 (12); 142 (47); 116 (10); 115 (100); 89 (10); 63 (10); 59 (24); 58 (20).
6e	3.35 (s,3H); 5.33 (d,J=10 Hz,1H); 5.45 (d, J=16.5 Hz, 1H); 6.60 (dd, J=10 and 16.5 Hz, 1H); 7.30-7.44 (m,2H); 7.45-7.60 (m,2H); 7.60-7.66 (m,1H); 7.82-7.90 (m,1H); 8.26-8.34 (m, 1H).	46.0 (+); 110.7 (-); 118.1 (+); 124.0 (+); 124.9 (+); 125.0 (+); 125.5 (+); 126.0 (+); 128.3 (+); 128.7 (-); 133.6 (+); 134.9 (-); 148.2 (-).	215 (M^+,53); 156 (86); 154 (50); 129 (99); 128 (100); 127 (21); 115 (40); 59 (54); 58 (39).
6h	0.25 (s,6H); 0.94 (s,9H); 5.14 (d, J=10 Hz,1H); 5.20 (d, J=16 Hz,1H); 6.32 (dd,J=10 and 16 Hz,1H); 6.99-7.08 (m,1H); 7.20-7.32 (m,4H).	2.8 (q); 20.4 (s); 27.3 (q); 106.9 (t); 123.3 (d); 125.7 (d); 128.2 (d); 137.1 (d); 150.0 (s).	265 (M^+,17); 208 (26); 174 (27); 150 (36); 149 (40); 118 (38); 91 (31); 84 (35); 73(100); 59(45); 58(26); 57 (40).

* Satisfactory microanalyses were obtained for these compounds (C,H and N).

N-(1-Naphthyl)-ethenesulphenamides 6d,e

- A solution of 1-amino-naphthalene (2.15 g, 15 mmol) and N-ethenylthio-morpholine 4a (2.29 g; 15.8 mmol) in dichloromethane (45 ml) was stirred at 0°C under argon. Then trifluoroacetic acid (1.15 ml; 15 mmol) was added and the mixture was stirred at 0°C for 2.5 hrs. The same work up as above furnished a crude product which was purified by flash-chromatography on silicagel using pentane/dichloromethane, 70/30 as eluent; mp. 29-30°C.
- A solution of 1-methylamino-naphthalene (1.5 g; 10 mmol) and N-ethenylthio-morpholine 4a (1.52 g; 10.5 mmol) in dimethoxymethane (30 ml) was stirred at 0°C. Then trifluoroacetic acid (0.76 ml; 10 mmol) was added and the mixture was stirred at 0°C for 4 hrs. The work up gave a crude product which was purified by flash-chromatography on silicagel using pentane as eluent.

The yiels of which are indicated in the main text and the spectral data are given in the table.

Reaction of ethenesulphenamide 6a with ethyl chloroformate

A solution of ethenesulphenamide 6a (0.9 g; 6 mmol) in tetrahydrofuran (12 ml) was stirred at -65°C and treated with a solution of n.butyllithium in hexane (6 mmol). After warming to -20°C then cooling at -65°C, ethyl chloroformate (0.650 g; 6 mmol) was added. The mixture was stirred at -65°C for 75 min then at room temperature for 70 min. The usual work up with water and pentane afforded a crude product containing the three compounds 7a, 7b and 6g in the approximate ratios 41:32:27 (^{1}H NMR). Chromatography on silicagel using pentane, pentane/dichloromethane, 50/50 then dichloromethane afforded the pure compounds:

7a: ^{1}H NMR ($CDCl_3$) δ: 1.28 (t, J=7.25 Hz, 3H); 4.22 (q, J=7.25 Hz, 2H); 7.00 (br s, 1H); 7.06 (dd, J=7.5 and 7.5 Hz, 1H); 7.30 (dd, J=7.5 and 8 Hz, 2H); 7.42 (d, J=8 Hz, 2H).

^{13}C NMR ($CDCl_3$) δ: 14.5 (q); 60.9 (t); 118.5 (d); 122.9 (d); 128.5 (d); 137.7 (s); 153.5 (s).

M.S. m/e (E.I.): 165 (M^+, 45); 120 (11); 106 (68); 93 (100); 77 (29); 66 (37).

7b: ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, J=7.25 Hz, 6H); 4.24 (q, J = 7.25 Hz, 4H); 7.17-7.26 (m, 2H); 7.36-7.50 (m, 3H).

^{13}C NMR ($CDCl_3$) δ: 13.8 (q); 62.8 (t); 127.7 (d); 127.8 (d); 128.6 (d); 138.2 (s); 152.7 (s).

M.S. m/e (C.I.): 255 (M^++18); 238 (M^++1).

6g: ^{1}H NMR ($CDCl_3$) δ: 5.16 (d, J = 16 Hz, 2H); 5.33 (d, J=10 Hz, 2H); 6.52 (dd, J=16 and 10 Hz, 2H); 6.98 (dd, J = 7.5 and 7.5 Hz, 1H); 7.30 (dd, J=7.5 and 7.5 Hz, 2H); 7.46 (d, J = 7.5 Hz, 2H).

^{13}C NMR ($CDCl_3$) δ: 108.7 (-); 117.0 (+); 121.9 (+); 128.9 (+); 132.5 (+); 149.5 (-).

M.S. m/e (E.I.): 209 (M^+,8); 150 (34); 117 (46); 104 (37); 93 (28); 85 (30); 77 (100); 65 (33); 59 (38); 58 (37); 51 (36).

1H-Benz[g]indoles 8a,b

- A solution of N-(1-naphthyl)-ethenesulphenamide 6d (1 g) in toluene (50 ml) was heated at reflux. The progress of the reaction was followed by T.L.C. (silicagel; eluent: pentane/dichloromethane, 70/30). After 4 hrs refluxing, the reaction was terminated and the solvent was removed under reduced pressure. The crude product was purified by flash-chromatography on silica gel using pentane/dichloromethane 8/2 as eluent. A white yellowish powder (0.69 g; 83 %) was obtained and crystallised from dichloromethane:pentane, mp = 168°C (literature: mp. 174°C [17]; 179-180°C [18]; 170-180°C [19]; 172°C [20]; 179°C [21]).

^{1}H NMR ($CDCl_3$) δ: 6.74 (dd, J=3 and 2 Hz, 1H); 7.32 (dd, J=3 and 3 Hz, 1H); 7.47 (ddd, J= 8, 7.5 and 1.1 Hz, 1H); 7.56 (d, J=9 Hz, 1H); 7.57 (ddd, J=8, 7.5 and 1.1 Hz, 1H); 7.77 (d, J=9 Hz, 1H); 7.98 (dd, J=8 and 1.1 Hz, 1H); 8.04 (dd, J=8 and 1.1 Hz, 1H); 8.90-9.02 (m, N-H).

^{13}C NMR ($CDCl_3$) δ: 104.3 (+); 119.3 (+); 120.8 (+); 120.8 (+); 121.8 (-); 122.2 (+); 123.9 (+); 123.9 (-); 125.4 (+); 128.9 (+); 130.5 (-); 130.5 (-).

M.S. m/e (E.I.): 168 (M^++1, 17); 167 (M^+, 100); 166 (M^+ -1, 24); 140 (18); 139 (31).

- In a similar way, a 0.1 M solution of N-methyl-N-(1-naphthyl)-ethenesulphenamide 6e in toluene was refluxed for 2 hrs. After flash-chromatography on silica gel using pentane/dichloromethane 9/1 as eluent, the pure N-methyl 1H-benz[g]indole 8b was obtained as a crystalline product (72%) which was crystallised from ether and pentane, mp 64-65.5°C. The overall yield starting from 1-methylamino-naphthalene is 35 %; it increased to 44 % if the intermediate sulphenamide 6e was not chromatographed and used crude for the thermal transformation.

^{1}H NMR ($CDCl_3$) δ: 4.26 (s, 3H); 6.64 (d, J=3 Hz, 1H); 7.07 (d, J=3 Hz, 1H); 7.46 (ddd, J=8, 7.5 and 1.3 Hz, 1H); 7.55 (d, J=8.5 Hz, 1H); 7.56 (ddd, J=8, 7.5 and 1.5 Hz, 1H); 7.76 (d, J=8.5 Hz, 1H); 8.00 (dd, J=8 and 1.5 Hz, 1H); 8.51 (dd, J=8 and 1.3 Hz).

^{13}C NMR ($CDCl_3$) δ: 37.9 (+); 102.0 (+); 120.4 (+); 120.8 (+); 121.0 (+); 123.1 (+); 123.3 (-); 125.0 (+); 125.8 (-); 128.9 (+); 129.0 (+); 129.9 (-); 131.3 (-).

M.S. m/e (E.I.): 182 (M^+ +1, 15); 181 (M^+, 100); 180 (M^+ -1, 53); 166 (M^+ -15, 13); 152 (15); 140 (15); 139 (24); 63 (15).

Found: C, 85.68; H 6.17; N, 7.92. $C_{13}H_{11}N$ requires: C, 86.16; H, 6.12; N, 7.73 %.

Reaction of ethenesulphenamide 6b with triethyloxonium tetrafluoroborate

A solution of ethenesulphenamide 6b (0.520 g, 3.15 mmol) in anhydrous dichloromethane (3 ml) was stirred under argon at 0°C and treated with freshly prepared crystalline triethyloxonium tetrafluoroborate (0.6 g,3.15 mmol). After stirring at 0°C for 3 hrs, the work up with aqueous sodium bicarbonate afforded a crude product, the ^{1}H NMR spectrum of which indicated the presence of starting sulphenamide 6b (38 %) and N-ethyl-N-methyl-aniline (62 %) which were separated by flash-chromatography. The N-ethyl-N-methyl-aniline has ^{1}H NMR ($CDCl_3$) δ: 1.12 (t, J=7.5 Hz, 3H); 2.92 (s, 3H); 3.42 (q, J=7.5 Hz, 2H); 6.70-6.82 (m, 3H); 7.20-7.40 (m, 2H); M.S. m/e: 135 (M^+, 30); 120 (100); 104 (28); 77 (76); 51 (65) and 50 (36).

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22. Note added in proof: Following the suggestion of a referee on the known catalysis of the Fischer indole synthesis by some Lewis or Bronsted acids, we treated the sulphenamide 6b with 1,5 equiv. of freshly fused zinc chloride in anhydrous ether-dichloromethane at room temperature for 4 hrs; the sulphenamide 6b was recovered unchanged. We had not tried the action of Bronsted acids because the sulphenamides are known to be easily cleaved by these acids.