SELENONIUM YLIDES OF CYCLOPENTADIENE, INDOLE AND PYRROLE

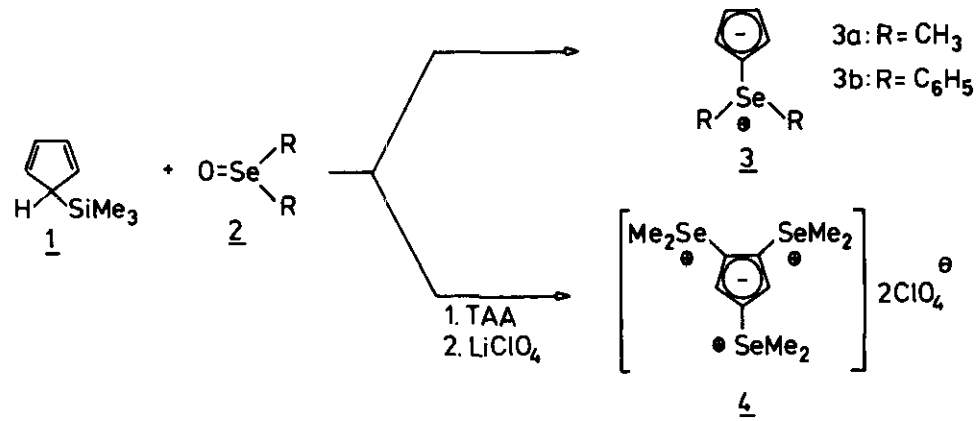
Klaus Hartke* and Hans Henning Wendebourg

Institut für Pharmazeutische Chemie der Universität Marburg,
Marbacher Weg 6, D-3550 Marburg/Lahn, Germany

Abstract - Selenonium cyclopentadienides 3 have been prepared from (trimethylsilyl)cyclopentadiene and dialkyl or diaryl selenoxides. Selenonium salts of indole and pyrrole are accessible by an electrophilic substitution with selenoxides and trifluoracetic anhydride. In some cases deprotonation leads to stable ylides.

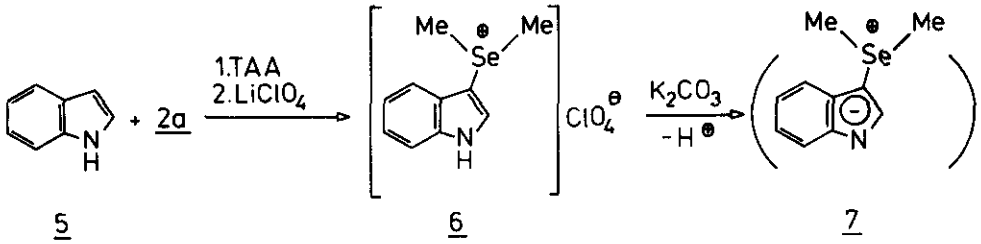
Selenonium ylides of cyclopentadiene, unsubstituted in the five-membered ring, have not been described in the literature[1]. Only a few representatives with a highly substituted cyclopentadiene ring could be prepared: e.g. diphenylselenonium tetraphenylcyclopentadienide from diphenyl selenide and diazotetraphenylcyclopentadiene[2] or diphenylselenonium 3,4-dicyano-2,5-bis(ethoxycarbonyl)cyclopentadienide from diphenyl selenide and the corresponding aryliodoniocyclopentadienide[3].

The reaction of (trimethylsilyl)cyclopentadiene (1) with dimethyl sulfoxide, first reported by McLean[4] and recently studied in more detail by our group[5] also works with dialkyl and diaryl selenoxides. By simply mixing equimolar amounts of 1 and dimethyl selenoxide (2a, R = Me) an exothermic reaction occurs and the selenonium ylide 3a separates by addition of diethyl ether in form of a brick-red powder (yield 98%). In the case of diphenyl selenoxide (2b, R = C_6H_5) the reaction must be started by gentle heating with an excess of 1. Structure 3 is supported by elemental analysis[6] and spectroscopic data[7]; for the rather unstable 3b a correct elemental analysis is still missing.

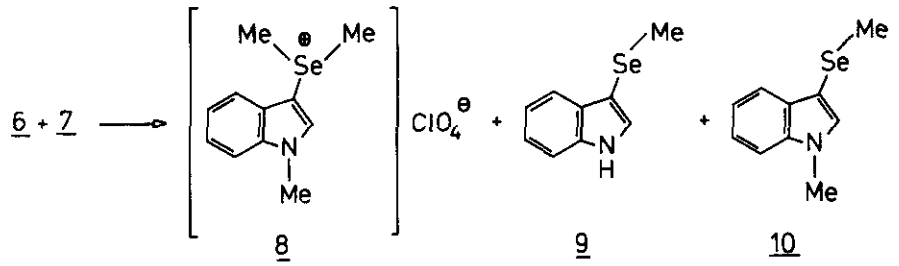


When dimethyl selenoxide is made more electrophilic by O-acylation with trifluoroacetic anhydride (TAA) at -30°C, a trissubstitution is observed with the formation of 4, isolated as perchlorate [brown powder, yield 36% (after recrystallisation from nitromethane)]. Under similar conditions the reaction with diphenyl selenoxide, TAA and 1 only leads to decomposition.

Recently we have been able to show that sulfonium ylides of indole and pyrrole can be obtained by treating these heterocycles with sulfoxides and TAA followed by deprotonation[8]. A similar reaction sequence is also applicable to the aliphatic selenoxides 2. Thus indole (5) and dimethyl selenoxide (2a) react in the presence of TAA at -30°C in CH_2Cl_2 to form the dimethyl 3-indolylselenonium cation (6). After treating the reaction mixture with a saturated solution of lithium perchlorate in water, 6 separates from the organic phase by addition of diethyl ether as perchlorate salt in form of colorless needles (yield 92%)[9]. Deprotonation of 6 with potassium carbonate at room temperature leads to a mixture of the selenonium salt 8 and the selenides 9 and 10. This is probably the result of an intermolecular methyl transfer between 6 and the postulated ylide 7. The reaction of indole (5) with diphenyl selenoxide (2b) does not form the expected selenonium salt, the only product isolated is diphenyl selenide.

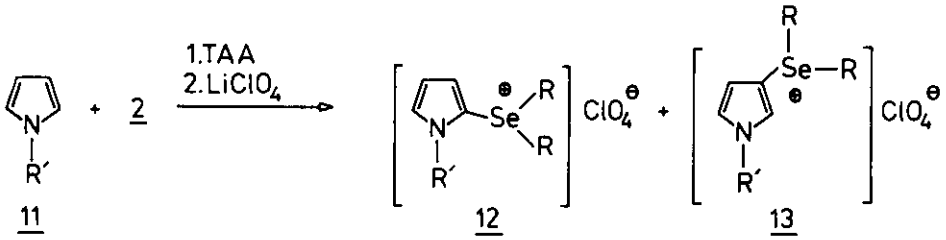


5 6 7



8 9 10

Electrophilic substitution of pyrrole or N-alkylpyrroles with dialkyl or diaryl selenoxides in the presence of TAA gives rise to the 2-pyrrolylselenonium salts 12 or to a mixture of the 2- and 3-pyrrolylselenonium salts 12 and 13[10]. Nearly pure 2-isomer 12b can be obtained by recrystallisation from ethanol. The 2-pyrrolylselenonium salts 12 are remarkably unstable in the presence of acids. They are quantitatively rearranged to the 3-pyrrolyl selenonium salts 13, probably by a [1.5] sigmatropic process[11]. Thus pure 13a is obtained from 12a in nitromethane within 15 min at room temperature after addition of trifluoroacetic acid[12].



12 $\xrightarrow{H^{\oplus}}$ 13

	R´	R	12 : 13	yield
a	H	CH_3	98 : 2	87%
b	H	C_6H_5	75 : 25	46%
c	CH_3	CH_3	50 : 50	73%

Deprotonation of 13a does not lead to a stable ylide; a decomposition similar to that described for the dimethyl 3-indolyl-selenonium perchlorate (6) takes place. The same is true for the dimethyl 2-pyrrolylselenonium perchlorate (12a). After treating 13b even with strong bases such as sodium bis(trimethylsilyl)amide or butyl lithium only starting material 13b could be recovered. The diphenyl derivative 12b, however, is deprotonated by potassium carbonate to give the perfectly stable diphenyl 2-pyrrolylselenonium ylide (16, yield 100%)[13]

12b $\xrightarrow{K_2CO_3}$ 16

ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

1. For a review see: Studies in Organic Chemistry 16, D.Lloyd, Non-benzenoid Conjugated Carbocyclic Compounds, p. 19, Elsevier, Amsterdam-Oxford-New York-Tokyo 1984.
2. D.Lloyd and M.I.C.Singer, Chem.Commun., 1967, 390.
3. K.Friedrich, W.Amann, and H.Fritz, Chem.Ber., 112, 1267 (1979).
4. S.McLean and G.W.B.Reed, Can.J.Chem., 48, 3110 (1970).
5. K.Hartke and W.Morick, Tetrahedron Lett., 1984, 5985 and Chem.Ber., 118, 4821 (1985).
6. For all new compounds mentioned correct elemental analysis have been obtained.
7. (Dimethylselenonio)cyclopentadienide (3a): ^{1}H Nmr($CDCl_3$): δ = 2.76ppm [s, $Se(CH_3)_2$], 6.28 (broad s, ring H). ^{13}C Nmr($CDCl_3$): δ = 27.6ppm [$Se(CH_3)_2$],

85.7 (C-1), 108.1 and 111.5 (C-2, -3). (Diphenylselenonio)cyclopentadienide (3b): ^{1}H Nmr($CDCl_3$): δ = 6.3ppm (m, 5-ring H), 7.5 (broad s, phenyl H). ^{13}C Nmr($CDCl_3$): δ = 84.1ppm (C-1), 111.4, 113.1 (C-2, -3), 129.6, 130.2, 131.3, 132.9 (phenyl C).

8. K.Hartke and D.Strangemann, Heterocycles, 24, 2399 (1986).
9. (1H-Indol-3-yl)dimethylselenonium perchlorate (6): ^{1}H Nmr(CD_3NO_2): δ = 3.15ppm [s, $Se(CH_3)_2$], 7.1-7.9 (m, 2-H, 4-H to 7-H), 10.0 (broad s, NH). ^{13}C Nmr(CD_3NO_2): δ = 24.9ppm [$Se(CH_3)_2$], 93.9 (C-3), 114.8, 119.3, 123.4 and 125.4 (C-4 to C-7), 126.4 and 138.2 (C-3a, -7a), 132.5 (C-2).
10. (1H-Pyrrol-2-yl)dimethylselenonium perchlorate (12a): ^{1}H Nmr(CD_3CN, D_2O): δ = 2.92 [s, $Se(CH_3)_2$], 6.34 (dd, 4-H), 6.80 (dd, 3-H), 7.17 (dd, 5-H). ^{13}C Nmr(CD_3NO_2): δ = 26.5 [$Se(CH_3)_2$], 107.1 (C-2), 112.1 (C-4), 117.8 (C-3), 127.6 (C-5).
11. A similar rearrangement was observed for the related 2-pyrrolyl-sulfonium salts (H.H.Wendebourg, PH.D. thesis in preparation). In these cases, however, the activation energy is normally higher and heating for several hours is required to effect the transposition: e.g. (1H-pyrrol-2-yl)dimethylsulfonium perchlorate rearranges to the 3-isomer by heating under reflux for 4.5 hours in trifluoroacetic acid as solvent. A methyl group in the 5-position facilitates the rearrangement significantly. Thus (5-methyl-1H-pyrrol-2-yl)dimethylsulfonium perchlorate gives the 3-isomer within 30 min at room temperature.
12. (1H-Pyrrol-3-yl)dimethylselenonium perchlorate (13a): ^{1}H Nmr(CD_3NO_2, D_2O): δ = 3.03ppm [s, $Se(CH_3)_2$], 6.66 (dd, 4-H), 7.15 (dd, 5-H), 7.49 (dd, 2-H). ^{13}C Nmr(CD_3NO_2): δ = 26.1ppm [$Se(CH_3)_2$], 102.3 (C-3), 108.8 (C-4), 123.5, 124.8 (C-2, -5).
13. (1H-Pyrrol-2-yl)diphenylselenonium perchlorate (12b): ^{1}H Nmr(CD_3CN, D_2O): δ = 6.44ppm (dd, 4-H), 6.58 (dd, 3-H), 7.30 (dd, 5-H), 7.55-7.75 (m, phenyl H). ^{13}C Nmr(CD_3NO_2): δ = 106.6ppm (C-2). 113.0 (C-4). 121.2 (C-3), 129.5 (C-5), 129.4, 131.7, 132.7 and 134.8 (phenyl C). 2-(Diphenylselenonio)pyrrolide (16): ^{1}H Nmr(acetone-d_6): δ = 6.25ppm (dd, 4-H), 6.60 (dd, 3-H), 7.25 (dd, 5-H), 7.4-8.1 (m, phenyl H). ^{13}C Nmr(acetone-d_6): δ = 110.5ppm (C-4), 111.4 (C-2), 116.6 (C-3), 138.5 (C-5), 131.2, 132.4 and 135.0 (phenyl C).

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