Stereomutation of cyclic sulfonium and selenonium compounds[1]

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Received (in Cambridge, UK) 28th September 1999, Accepted 21st December 1999

New cyclic sulfonium and selenonium compounds have been synthesized in procedures of a few steps: the diastereoisomeric mixtures *cis*/*trans*-3-methyl-1-phenylthiolanium perchlorate **1**, *cis*/*trans*-3-methyl-1-ethylthiolanium hexafluorophosphate **2**, *cis*/*trans*-3-methyl-1-phenylselenolanium hexafluorophosphate **3**, and the diastereoisomerically pure *trans*-4-*tert*-butyl-1-phenylthianium hexafluorophosphate **4**. After enrichment of the main isomer, the rates of stereomutation at the chalcogenonium centre were determined by NMR spectroscopy, and the activation enthalpies and entropies were calculated. The selenonium compound **3** showed an increased configurational stability in water. Inversion of configuration was about 50 times slower than that of the sulfonium compound **1**. Unexpectedly, the selenonium compound **3** showed a 70-fold acceleration of the stereomutation rate in the solvent DMF and a large activation entropy.

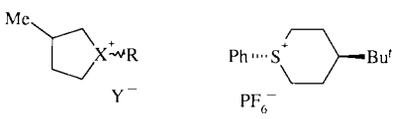
Introduction

The syntheses, stereochemistry, and preparative uses of sulfonium and selenonium salts have been widely studied.[2] The isomerization of chiral tricoordinate sulfonium compounds may occur *via* different mechanisms:[3] 1) a nucleophilic attack of the counter ion (S_N2) followed by reformation of the sulfonium compound, 2) a heterolytic scission (S_N1) into a neutral sulfide and a carbocation with successive recombination, a process which is favoured by stabilized carbocations, and 3) a non-dissociative process, pyramidal inversion *via* a trigonal-planar transition state. We have already reported the last process to be the cause of the loss of biological activity of the natural co-enzyme (*S*)-*S*-adenosyl-L-methionine (SAM) and determined the kinetic constants.[4] In contrast, the homologous (*S*)-*Se*-adenosyl-L-selenomethionine did not show any configurational change after heating for 8 h at 70 °C.[5] These findings correlate with the reported increased configurational stabilities of selenonium compounds[6] which so far have only permitted an estimation of stereomutation velocities.[7] We now wish to report the measurement of the isomerization rate of a cyclic selenonium salt.

Results and discussion

By applying a patented procedure for the synthesis of 2-aryl-substituted cyclic sulfonium compounds[8] to other substrates, we synthesized the diastereoisomeric mixtures **1** and **2** and the diastereoisomerically pure *trans*-**4** in a few steps and low yields (2–5%). The acidic condensation could also be expanded to the synthesis of the selenonium compound **3** (yield: 20%).

The NMR spectra of the literature-known *cis*- and *trans*-1,3-dimethylthiolanium tetrafluoroborate have been consistent with a predominant half-chair-conformation both in the *cis*- and in the *trans*-isomer.[9] Because of the similarity of the spectroscopic data of **1**, **2**, and **3** we assumed the same conformation for the latter and assigned the *trans*-configuration in each case to the main diastereoisomer. The configuration of *trans*-**4** was similarly determined by comparison with known spectroscopic data[10] and a chair conformation was established. Because of the second stereogenic centre, configurational changes at the chalcogenonium atom could easily be analyzed by NMR spectroscopy. After enrichment of the main compound (*trans*) by fractional crystallization up to 85–95%, we studied the kinetics of the stereomutation at different temperatures by following signal intensities in the NMR spectra.



1: R = Ph, X = S, Y = ClO_4
2: R = Et, X = S, Y = PF_6
3: R = Ph, X = Se, Y = PF_6

trans-**4**

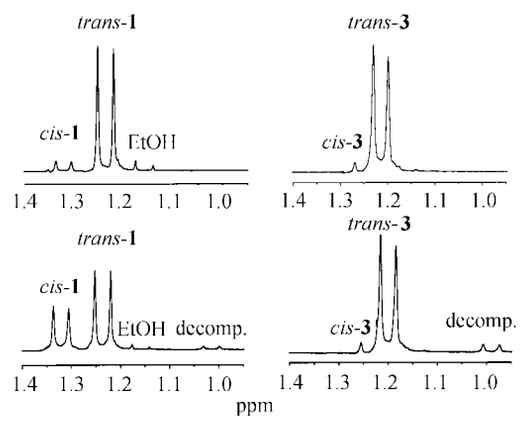


Fig. 1 ^{1}H NMR spectra of the methyl groups of **1** (left) and **3** (right): start (above) and after 4 h at θ = 94 °C (below) (200 MHz, D_2O).

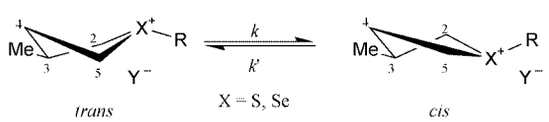


Fig. 1 shows a section of the NMR spectra of **1** and **3** before and after warming. While in the case of the sulfonium compound **1** isomerization was complete after 4 hours, no change could be observed in the spectrum of the selenonium

DOI: 10.1039/a907801k

Table 1 Kinetic and thermodynamic parameters for the stereomutation at the chalcogenonium centre for **1**–**4**

Compd. (solvent)	θ/°C	K	$k/10^{-6}$ s^{-1}	Activation parameters
1 (D_2O)	63.9	0.647 ± 0.049	5.97 ± 0.22	$\Delta G_{353}^{\ddagger}$ = 117 kJ mol^{-1}
	80.2	0.618 ± 0.047	39.1 ± 2.6	$\Delta H^{\ddagger}$ = 112 kJ mol^{-1}
	93.8	0.664 ± 0.050	169 ± 10	$\Delta S^{\ddagger}$ = −14 J mol^{-1} K^{-1}
2 (D_2O)	80.2	0.679 ± 0.025	6.24 ± 0.27	$\Delta G_{353}^{\ddagger}$ = 122 kJ mol^{-1}
	85.7	0.667 ± 0.050	12.9 ± 0.5	—[a]
	93.8	0.671 ± 0.075	29.7 ± 1.3	—[a]
3 (D_2O)	63.2	—[b]	—[c]	$\Delta G_{353}^{\ddagger}$ = 128 kJ mol^{-1}
	80.3	—[b]	0.82 ± 0.33[d]	—
	94.0	—[b]	3.7 ± 1.5[d]	—
3 ([$^2H_7$]DMF)	65.7	0.667 ± 0.100	13.2 ± 0.5	$\Delta G_{353}^{\ddagger}$ = 115 kJ mol^{-1}
	80.0	0.616 ± 0.123	59.0 ± 2.5	$\Delta H^{\ddagger}$ = 104 kJ mol^{-1}
	94.0	0.600 ± 0.120	249 ± 16	$\Delta S^{\ddagger}$ = −31 J mol^{-1} K^{-1}
4 ([$^2H_7$]DMF)	80.2	0.247 ± 0.021	15.4 ± 0.2	$\Delta G_{353}^{\ddagger}$ = 120 kJ mol^{-1}

[a] The errors Δk were too big to determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ within this small temperature range. [b] The equilibrium constants could not be determined due to decomposition reactions. [c] No change in the NMR spectra could be observed. [d] Based on the assumption of $K = 0.643$.

compound **3** at that time. In both cases signals of decomposition products had appeared.

We assumed the pyramidal inversion to be the most probable mechanism for inversion of configuration at the chalcogenonium centre since, on the one hand, an S_N1 mechanism would lead to unstable carbocations and, on the other hand, the respective counter ions are poor nucleophiles for an S_N2 mechanism. On the basis of a first order kinetics we determined the rate constants k by linear regression with eqn. (1) (where t

$$kt = \frac{K}{K+1} \ln \frac{(K+1)x_{t=0} - 1}{(K+1)x_t - 1} \qquad (1)$$

time, $x_{t=0}$ and x_t partial quantity of the *trans*-isomer at the time $t = 0$ and t, K equilibrium constant) and the activation parameters by applying the Eyring equation.

Table 1 summarizes the kinetic and thermodynamic parameters for the stereomutation at the chalcogenonium centre for **1**–**4**. The values of the equilibrium constants K show little temperature and solvent dependence with a *trans*:*cis* ratio of about 60:40 for the 5-membered rings and 80:20 for the 6-membered ring. A comparison of the rate constants of **1** and **2** shows the accelerating effect of the substitution of a primary alkyl by an aromatic group which we interpreted as mainly a result of steric effects.[11] Both k values are much smaller than that of the noncyclic (*S*)-*S*-adenosyl-L-methionine (SAM)[4] at comparable temperatures, a result that is plausible for a pyramidal inversion mechanism where the C–S–C angle has to be opened accompanied by increased ring strain in the transition state. Apart from isomerization, secondary reactions *i.e.* decomposition reactions were taking place in the case of **1**. This was indicated by the appearance of new signals in the NMR spectra (see Fig. 1) and by the turbidity of the samples. Since the isomerization of **1** also occurred in the crystalline state but without the appearance of new NMR signals, we assumed S_N2 reactions of the solvent molecules with **1** to be the cause of decomposition. These side reactions were irrelevant for the determination of k because at the end of the kinetic run only 4% of **1** had decomposed. In contrast, **2** did not show any signs of decomposition during warming. The faster reaction of **1** with solvent molecules could be explained by an accelerating I-effect of the phenyl group for an S_N2 substitution.

As was shown in Fig. 1, the stereomutation of the selenonium compound **3** is much slower than that of the sulfonium compound **1**. In contrast, the decomposition reactions are much faster. Because of this, we were not able to determine equilibrium constants. For an estimation of the rate constants k we took the mean value of K for **1** instead (0.643, *trans*:*cis* = 60.8:39.2). This assumption led to k values that were about 50 times smaller than that of **1** in water.

The different counter ions should have a very small influence on the process due to dissociation in solution. The nature of the chalcogen atom seems to be much more important. In calculations of simple model compounds a distinctly higher barrier of inversion for selenonium as compared to sulfonium compounds was found.[12] The results can even be interpreted rather simply with the VSEPR model. Since the C–Se bonds are longer than the C–S bonds, the repulsion of the valence shell electrons is smaller and so is the tendency for stereomutation.

To exclude the effects of decomposition reactions, we performed a model calculation of a worst case scenario in which the stereomutation of **3** is simulated by the decomposition of only one of the two diastereoisomers. With the measurable decomposition of **3** and an assumed S_N2 mechanism we calculated pseudo stereomutation rates k_ψ. Even under the very improbable assumption that only one isomer decomposes, the resulting k_ψ values were within the error range. This meant that the decomposition reactions disturbed the accuracy of the determination of k but they did not prevent it.

In order to determine stereomutation rates for the selenonium compound **3**, we changed the solvent to [$^2H_7$]DMF which has a higher boiling point and good solubilizing properties. Unexpectedly, **3** stereomutated much faster than in D_2O. The decomposition reactions also were accelerated, but not as much, therefore allowing the determination of equilibrium constants and stereomutation rates in this case. The latter were about 70 times larger than in D_2O and remained the same at a 20-fold concentration. Such a strong accelerating solvent effect has up to now not been reported for the stereomutation of sulfonium compounds.[13] The reason for this behaviour cannot yet be given on the basis of the present data. The polar aprotic solvent DMF possibly causes a change in the mechanism of stereomutation.

The stereomutation rate of **4** in [$^2H_7$]DMF is in the order of magnitude of a literature-known thianium compound[14] and is smaller than that of **1** in D_2O. The latter can be interpreted by the increased strain of the 6-membered ring compared to the 5-membered during the planar transition state necessary for the pyramidal inversion mechanism. An extraordinarily fast stereomutation in DMF as for **3** is not observed.

Fig. 2 shows the Eyring plots of the rate constants given in Table 1. While the small differences in the free enthalpies of activation $\Delta G_{353}^{\ddagger}$ for **1** in D_2O (117 kJ mol^{-1}) and **3** in [$^2H_7$]-DMF (115 kJ mol^{-1}) reflect the slightly different stereomutation velocities, a fairly large difference was found in the enthalpies $\Delta H^{\ddagger}$ (**1**: 112 kJ mol^{-1}, **3**: 104 kJ mol^{-1}) as well as in the entropies $\Delta S^{\ddagger}$ of activation (**1**: −14 J mol^{-1} K^{-1}, **3**: −31 J mol^{-1} K^{-1}). Thus the stereomutation of the sulfonium compound in D_2O is mainly controlled by the enthalpy while this process for the selenonium compound **3** in DMF is much more affected by the entropy.

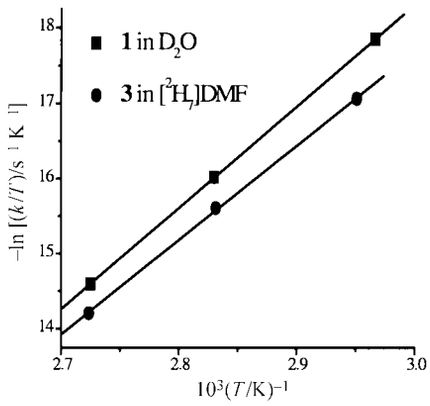


Fig. 2 Eyring plots for the stereomutation of **1** in D_2O and **3** in $[^2H_7]$DMF.

Experimental

General

Melting points were recorded on a Büchi 510 apparatus and are uncorrected. Elemental analyses were carried out by the Beller microanalytical laboratory in Göttingen. IR spectra were measured as KBr disks under normal conditions on a Perkin-Elmer FTIR 1750 Fourier transform infrared spectrophotometer. ^1H and ^{13}C NMR spectra were obtained under normal conditions on a Bruker AC 200 spectrophotometer at 200.14 and 50.323 MHz respectively, and *J* values are given in Hz. Tentative assignments are marked with an asterisk.

Materials

2-Methylbutane-1,4-diol was prepared by reduction of methylsuccinic acid with $LiAlH_4$ in ether;[15] yield 54%; bp 124–125 °C (11 Torr). Benzenethiol and ethanethiol were purchased from Merck KGaA and used without further purification. Benzeneselenol was prepared by addition of black selenium to an ethereal solution of phenylmagnesium bromide;[16] yield 41%; bp 64–66 °C (12 Torr). 3-*tert*-Butylpentane-1,5-diol was prepared in 4 steps from 4-*tert*-butylcyclohexanone;[17] overall yield 52%; bp 88–92 °C (0.018 Torr). Hexafluorophosphoric acid was purchased from Fluka Feinchemikalien GmbH and used without further purification.

cis/*trans*-3-Methyl-1-phenylthiolanium perchlorate 1

Following a patented procedure[8] aqueous perchloric acid (60%, 29.5 g, 0.176 mol) was added to a mixture of 2-methylbutane-1,4-diol (4.0 g, 0.038 mol) and benzenethiol (3.8 g, 0.034 mol), stirred for 14 h at 50 °C, and for 6 d at 20 °C. Water was added carefully and the mixture was extracted with dichloromethane. The combined extracts were diluted with dichloromethane and washed with water and aqueous sodium hydrogen carbonate. Removal of the solvent gave a solid which was washed several times with hot pentane and recrystallized from ethanol to give colourless needles of **1** (0.50 g, 5.2%); mp 93–98 °C [*trans*:*cis* = 79.4 : 20.6 (^1H NMR)] (Found: C, 47.5; H, 5.5. Calc. for $C_{11}H_{15}ClO_4S$: C, 47.4; H, 5.4%); ν_{max}/cm^{-1} 2969w (CH), 1475w (Ph), 1460w (CH), 1444m (Ph), 1421w (CH), 1108br s (ClO_4^-), 752m (Ph), 684m (Ph), 624s (ClO_4^-), 484w (Ph); δ_H(*trans*-**1**, D_2O, $Me_3Si[CH_2]_3SO_3Na$) 1.24 (3 H, d, ^3J 6.4, CH_3), 1.99 (1 H, dtd, ^2J 13.4, ^3J(3-H) = ^3J(5-H_b) 10.2 and ^3J(5-H_a) 8.0, 4-H_a), 2.63–2.82 (1 H, m, 4-H_b), 2.83–3.10 (1 H, m, 3-H), 3.50 (1 H, dd, ^2J 13.6 and ^3J 10.5, 2-H_a), 3.76 (1 H, ddd, ^2J 13.3, ^3J(4-H_a) 10.2 and ^3J(4-H_b) 7.1, 5-H_b), 3.84 (1 H, ddd, ^2J 13.6, ^3J 6.6 and ^4J(4-H_b) 1.3, 2-H_b), 4.22 (1 H, ddd, ^2J 13.3, ^3J(4-H_a) 8.0 and ^3J(4-H_b) 3.5, 5-H_a), 7.63–7.88 (5 H, m, Ar-H); δ_C(*trans*-**1**, D_2O, $Me_3Si[CH_2]_3SO_3Na$) 19.0 (CH_3), 38.7 (C-4), 40.6 (C-3), 50.5 (C-5), 55.3 (C-2), 129.1 (C-1′), 132.4 (C-2′/6′)*, 133.6 (C-3′/5′)*, 136.6 (C-4′); δ_H(*cis*-**1**, D_2O, $Me_3Si[CH_2]_3SO_3Na$) 1.32 (3 H, d, ^3J 6.4, CH_3), 2.10–2.32 (1 H, m, 4-H_a), 2.54–3.10 (2 H, m, 4-H_b/3-H), 3.33 (1 H, dd, ^2J 12.7 and ^3J 11.2, 2-H_a), 3.82–4.03 (2 H, m, 5-H_b/2-H_b), 4.27 (1 H, ddd, ^2J 12.0, ^3J(4-H_a) 7.8 and ^3J(4-H_b) 1.1, 5-H_a), 7.63–7.88 (5 H, m, Ar-H); δ_C(*cis*-**1**, D_2O, $Me_3Si[CH_2]_3SO_3Na$) 18.8 (CH_3), 38.9 (C-4), 41.4 (C-3), 50.5 (C-5), 56.1 (C-2), 129.5 (C-1′), 132.5 (C-2′/6′)*, 133.6 (C-3′/5′)*, 136.6 (C-4′). Fractional crystallization led to a further enrichment of *trans*-**1**; mp 100–103 °C [*trans*:*cis* = 91.2 : 8.8 (^1H NMR)].

cis/*trans*-1-Ethyl-3-methylthiolanium hexafluorophosphate 2

Aqueous hexafluorophosphoric acid (75%, 15.3 g, 0.0786 mol) was added to a mixture of 2-methylbutane-1,4-diol (4.0 g, 0.038 mol) and ethanethiol (2.3 g, 0.037 mol) in a polyethylene bottle and stirred for 1 d at 20 °C. The work-up procedure as described above for **1** gave colourless crystals of **2** (0.25 g, 2.4%); mp 53–55 °C [*trans*:*cis* = 80.2 : 19.8 (^1H, NMR)] (Found: C, 30.6; H, 5.4. Calc. for $C_7H_{15}F_6PS$: C, 30.4, H, 5.5%); ν_{max}/cm^{-1} 2978w (CH), 1459w (CH), 1422w (CH), 840br s (PF_6^-), 559s (PF_6^-); δ_H(*trans*-**2**, D_2O, $Me_3Si[CH_2]_3SO_3Na$) 1.18 (3 H, d, ^3J 6.5, $CHCH_3$), 1.42 (3 H, t, ^3J 7.3, CH_2CH_3), 1.84 (1 H, dtd, ^2J 13.2, ^3J(3-H) = ^3J(5-H_b) 10.0 and ^3J(5-H_a) 7.9, 4-H_a), 2.43–2.59 (1 H, m, 4-H_b), 2.63-2.83 (1 H, m, 3-H), 3.07 (1 H, dd, ^2J 13.5 and ^3J 10.3, 2-H_a), 3.25 (2 H, q, ^3J 7.3, CH_2CH_3), 3.31 (1 H, ddd, ^2J 13.1, ^3J(4-H_a) 10.0 and ^3J(4-H_b) 7.3, 5-H_b), 3.52 (1 H, ddd, ^2J 13.5, ^3J 6.5 and ^4J(4-H_b) 1.2, 2-H_b), 3.76 (1 H, ddd, ^2J 13.1, ^3J(4-H_a) 7.9 and ^3J(4-H_b) 3.4, 5-H_a); δ_C(*trans*-**2**, D_2O, $Me_3Si[CH_2]_3SO_3Na$) 11.9 (CH_2CH_3), 18.8 ($CHCH_3$), 38.2 (C-4), 39.5 (C-3), 39.9 (CH_2CH_3), 44.9 (C-5), 49.5 (C-2); δ_H(*cis*-**2**, D_2O, $Me_3Si[CH_2]_3SO_3Na$) 1.24 (3 H, d, ^3J 6.2, $CHCH_3$), 1.42 (3 H, t, ^3J 7.3, CH_2CH_3), 1.80–2.05 (1 H, m, 4-H_a), 2.43–2.83 (2 H, m, 4-H_b/3-H), 2.86 (1 H, dd, ^2J 12.2 and ^3J 11.0, 2-H_a), 3.27 (2 H, q, ^3J 7.3, CH_2CH_3), 3.41–3.60 (2 H, m, 5-H_b/2-H_b), 3.82 (1 H, ddd, ^2J 12.5, ^3J(4-H_a) 7.8 and ^3J(4-H_b) 1.2, 5-H_a); δ_C(*cis*-**2**, D_2O, $Me_3Si[CH_2]_3SO_3Na$) 11.9 (CH_2CH_3), 19.0 ($CHCH_3$), 37.6 (C-4), 40.3 (CH_2CH_3), 41.2 (C-3), 44.3 (C-5), 50.5 (C-2). Fractional crystallization led to a further enrichment of *trans*-**2**; mp 55–57 °C [*trans*:*cis* = 86.6 : 13.4 (^1H NMR)].

cis/*trans*-3-Methyl-1-phenylselenolanium hexafluorophosphate 3

Aqueous hexafluorophosphoric acid (75%, 26.9 g, 0.138 mol) was added under argon to a mixture of 2-methylbutane-1,4-diol (3.6 g, 0.035 mol) and benzeneselenol (5.2 g, 0.033 mol) in a polyethylene bottle and stirred for 2 d at 20 °C. The work-up procedure as described above for **1** gave colourless crystals of **3** (2.5 g, 20%); mp 76–79 °C [*trans*:*cis* = 75.0 : 25.0 (^1H NMR)] (Found: C, 36.0; H, 4.2. Calc. for $C_{11}H_{15}F_6PSe$: C, 35.6; H, 4.1%); ν_{max}/cm^{-1} 2974w (CH), 1482w (Ph), 1463w (CH), 1445m (Ph), 1431w (CH), 839br s (PF_6^-), 742m (Ph), 684m (Ph), 559s (PF_6^-), 464w (Ph); δ_H(*trans*-**3**, $[^2H_7]$DMF, $Me_3Si[CH_2]_3SO_3Na$) 1.25 (3 H, d, ^3J 6.1, CH_3), 2.07 (1 H, dddd, ^2J 14.0, ^3J(3-H) 12.4, ^3J(5-H_b) 11.3 and ^3J(5-H_a) 7.9, 4-H_a), 2.58–2.83 (2 H, m, 4-H_b/3-H), 3.47 (1 H, dd, ^2J 12.3 and ^3J 11.2, 2-H_a), 3.76 (1 H, ddd, ^2J 11.9, ^3J(4-H_a) 11.3 and ^3J(4-H_b) 6.6, 5-H_b), 4.07 (1 H, ddd, ^2J 12.3, ^3J 5.7 and ^4J(4-H_b) 1.5, 2-H_b), 4.27 (1 H, ddd, ^2J 11.9, ^3J(4-H_a) 7.9 and ^3J(4-H_b) 2.1, 5-H_a), 7.63–8.10 (5 H, m, Ar-H); δ_C(*trans*-**3**, $[^2H_7]$DMF, $Me_3Si[CH_2]_3SO_3Na$) 19.2 (CH_3), 40.0 (C-4), 41.8 (C-3), 48.9 (C-5; ^{77}Se-satellites: ^1J 50), 52.8 (C-2; ^{77}Se-satellites: ^1J 52), 130.8 (C-1′), 132.2 (C-2′/6′; ^{77}Se-satellites: ^2J 13), 132.7 (C-3′/5′), 134.1 (C-4′); δ_H(*cis*-**3**, $[^2H_7]$DMF, $Me_3Si[CH_2]_3SO_3Na$) 1.28 (3 H, d, ^3J 6.0, CH_3), 1.72–2.08 (1 H, m, 4-H_a), 2.55–3.20 (2 H, m, 4-H_b/3-H), 3.32 (1 H, t, ^2J = ^3J 11.3, 2-H_a), 3.87 (1 H, td, ^2J = ^3J(4-H_a) 12.5 and ^3J(4-H_b) 5.5, 5-H_b), 3.97–4.07 (1 H, m, 2-H_b), 4.23–4.37 (1 H, m, 5-H_a), 7.63–8.10 (5 H, m, Ar-H); δ_C(*cis*-**3**, $[^2H_7]$DMF, $Me_3Si[CH_2]_3SO_3Na$) 18.9 (CH_3), 40.3 (C-4), 41.8 (C-3), 47.8 (C-5; ^{77}Se-satellites: ^1J 48), 54.5 (C-2; ^{77}Se-satellites: ^1J 54), 131.1 (C-1′), 132.2 (C-2′/6′), 132.7 (C-3′/5′), 134.1 (C-4′). Fractional

crystallization led to a further enrichment of *trans*-**3**; mp 89–90 °C [*trans* : *cis* = 95.0 : 5.0 (^{1}H NMR)].

trans-4-*tert*-Butyl-1-phenylthianium hexafluorophosphate *trans*-4

Aqueous hexafluorophosphoric acid (75%, 24.4 g, 0.125 mol) was added under argon to a mixture of 3-*tert*-butylpentane-1,5-diol (5.0 g, 0.031 mol) and benzenethiol (3.3 g, 0.030 mol) in a polyethylene bottle and stirred for 8 d at 50–60 °C. The work-up procedure as described above for **1** gave colourless crystals of *trans*-**4** (0.40 g, 3.5%); mp 195–199 °C [*trans* : *cis* > 99.5 : 0.5 (^{1}H NMR)] (Found: C, 47.75; H, 6.1. Calc. for $C_{15}H_{23}F_6PS$: C, 47.4; H, 6.1%); ν_{max}/cm^{-1} 2963w (CH), 1479w (Ph), 1447w (Ph), 1429w (CH), 1400w (CH), 1369w (CH), 836br s (PF_6^-), 754w (Ph), 685w (Ph), 559m (PF_6^-); δ_H([$^2H_7$]DMF, $Me_3Si[CH_2]_3SO_3Na$) 0.96 (9 H, s, $C(CH_3)_3$), 1.71 (1 H, m$_s$, 4-H), 1.88 (2 H, m$_s$, 3/5-H$_{ax}$), 2.56 (2 H, m$_s$, 3/5-H$_{eq}$), 3.98 (2 H, m$_s$, 2/6-H$_{ax}$), 4.19 (2 H, dt, ^2J 11.4 and $^3J = {}^3J$ 2.3 Hz, 2/6-H$_{eq}$), 7.77–8.28 (5 H, m, Ar-H); δ_C([$^2H_7$]DMF, $Me_3Si[CH_2]_3SO_3Na$) 27.4 (C-3/5), 28.9 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 43.9 (C-2/6), 46.6 (C-4), 127.6 (C-1′), 132.6 (C-2′/6′)*, 133.0 (C-3′/5′)*, 136.4 (C-4′).

Kinetics

For the measurement of the rates of stereomutation, solutions of the chalcogenonium salts containing the non-volatile $Me_3Si[CH_2]_3SO_3Na$ as internal standard were prepared and filled in NMR tubes, which were sealed and put in thermostated baths. After suitable time intervals, the sample was cooled down and the NMR spectrum recorded in the pulse-Fourier-transform-mode (SW sweep width in ppm, TD number of points of FID, AQ acquisition time in s, SI number of points of spectrum, and NS number of scans). The kinetic run comprised 8–12 measurements except in one case and was finished on reaching thermal equilibrium. After transformation, the relative amounts of the isomers were determined by integration of the signals of the alkyl groups attached to the ring. The rate constants were calculated by linear regression applying the equation cited. The correlation coefficients were always better than 0.995 except for **3** in D_2O. The activation parameters were calculated by the Eyring absolute kinetic equation.

1 (50.0 mg) and standard (6.1 mg) in D_2O (5.0 ml); θ 63.9 ± 0.5, 80.2 ± 0.8, and 93.8 ± 0.7 °C; SW 8.99, TD 16384, AQ 4.5, SI 8192, NS 32; integration of doublets δ_H (*trans*-**1**) 1.24 and δ_H (*cis*-**1**) 1.32.

2 (50.2 mg) and standard (5.3 mg) in D_2O (5.0 ml); θ 80.2 ± 0.8, 85.7 ± 1.2, and 93.8 ± 0.7 °C; SW 6.01, TD 8192, AQ 3.4, SI 4096, NS 32; integration of doublets δ_H (*trans*-**2**) 1.18 and δ_H (*cis*-**2**) 1.24.

3 (39.8 mg) and standard (2.2 mg) in D_2O (5.0 ml); θ 63.2 ± 0.4, 80.3 ± 0.2, and 94.0 ± 0.2 °C; SW 8.99, TD 16384, AQ 4.5, SI 8192, NS 80; integration of doublets δ_H (*trans*-**3**) 1.21 and δ_H (*cis*-**3**) 1.25.

3 (32.1 mg) and standard (2.0 mg) in [$^2H_7$]DMF (4.0 ml); θ 65.7 ± 0.8, 80.0 ± 0.2, and 94.0 ± 0.4 °C; SW 9.50, TD 16384, AQ 4.3, SI 8192, NS 64; integration of doublets δ_H (*trans*-**3**) 1.25 and δ_H (*cis*-**3**) 1.28.

trans-**4** (*ca*. 7 mg) and standard (*ca*. 1.5 mg) in [$^2H_7$]DMF (*ca*. 0.75 ml); θ 80.2 ± 0.2 °C; SW 9.50, TD 16384, AQ 4.3, SI 8192, NS 64; integration of singlets δ_H (*trans*-**4**) 0.96 and δ_H (*cis*-**4**) 0.80.

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Paper a907801k