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2-Hydroxyselenophenes. I. Tautomeric Properties and Alkylation of the Selenolene-2-one and 5-Methyl-selenolene-2-one Systems

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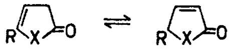
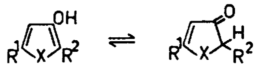
The unsubstituted 2-hydroxyselenophene system was prepared by hydrogen peroxide oxidation of 2-selenopheneboronic acid, while the 5-methyl-substituted system was prepared by acid-catalysed dealkylation of 2-*tert*-butoxyselenophene. Both systems exist mainly as 3-selenolene-2-ones, and for the 5-methyl derivative it was possible to isolate the β,γ-unsaturated form and follow the tautomeric isomerisation. The activation parameters thus obtained are compared with those previously obtained for the corresponding furan and thiophene systems.

Upon alkylation by using an ion-pair extraction method, the 5-methyl-substituted selenolene-2-one system gives mainly *C*-alkylation with the soft acid methyl iodide and mainly *O*-alkylation with the hard acid dimethyl sulfate.



A B

I X= O
II X= S
III X= Se

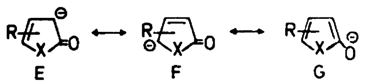


C D

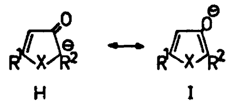
IV X= O
V X= S
VI X= Se

For the hydroxy derivatives of the five-membered heterocycles furan, thiophene and selenophene, it has been shown that the 5-alkyl substituted 2-hydroxy compounds exist in an equilibrium between the two unsaturated γ-lactones A and B [1-3] undergoing carbon-carbon tautomerism, while the 2,5-dialkyl substituted 3-hydroxy derivatives exist in a oxo-enol equilibrium (C and D),[4,5] with possibilities for carbon-oxygen tautomerism. For the 5-methyl- and 5-*tert*-butylthiolene-2-one systems (II), the mechanism of tautomerisation has been studied in more detail in methanol as solvent and by using pyridines as base catalysts. Under these conditions, the isomerisation was found to follow a two-step mechanism of the classical type, obeying both parts of the Hughes-Ingold's rule.[7] In a previous paper,[6] the rates of the tautomeric rearrangement of 5-methyl- and 5-*tert*-butyl-β,γ-butenolide (IA) were compared with those of their sulfur analogues, the thiolene-2-ones (IIA). In benzene solution with triethylamine as base, the butenolides were found to tautomerise at rates three to four powers of ten slower than those of the thiolene-2-ones.[7] In this paper, the study of the influence of the heteroatom on the rates of isomerisation will be extended to that of selenium.

During our current investigation of the hydroxy derivatives of the five-membered heterocycles, we have also studied the reactions of their trident (E – G) and ambident (H,I) anions with alkylating reagents. For these experiments, the ion-pair extraction method has been found to be the superior one, and the alkylating agents used have been methyl iodide (soft) and dimethyl sulfate (hard).[5,8,9] It has been shown that the product distribution is not very sensitive to the counterion, but to the position and size of the substituent [9] and to the alkylating reagent used. Methyl iodide favours *C*-alkylation and dimethyl sulfate *O*-



VII X = O
VIII X = S
IX X = Se



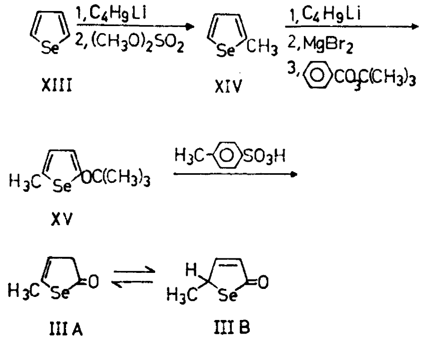
X X = O
XI X = S
XII X = Se

alkylation.[8] However, the butenolide anion (VII E-G) showed no oxygen reactivity, in contrast to the sulfur analogue.[8] In the 3-hydroxy substituted series, on the other hand, even the furan system (X H, I) showed oxygen reactivity, but still the reaction at carbon was the predominant one. In this series, the selectivity was higher for both dimethyl sulfate in *O*-alkylation and methyliodide in *C*-alkylation for the 3-hydroxyselenophene system (XII H, I) compared to the thioselenophene system XI H, I).[5] The influence of the selenium atom in the 2-hydroxy series will be discussed in this paper.

RESULTS AND DISCUSSION

Preparation. The two methods most frequently used for preparation of the hydroxy derivatives of the five-membered heterocycles are oxidative cleavage of boronic acids or esters with hydrogen peroxide, and acid-catalysed dealkylation of *tert*-butoxy derivatives. In our previous work, we have preferred to use the oxidative cleavage method because it is very mild. In the preparation of the 5-alkylsubstituted thiolene-2-ones, for instance, the kinetically controlled β,γ-unsaturated compounds (II A) were isolated. In the furan series, this is really an advantage as these isomers cannot be obtained by alkaline work up.[7] However, this method also has limitations, since the boronic acids, influenced by electron-donating substituents, easily undergo deboronation, and the dealkylation method can therefore be a useful complement.

The unsubstituted, as well as the 5-methylselenolene-2-one systems (III A – B) have been prepared by Morel *et al.*[3] by the acid-catalysed dealkylation of the 2-*tert*-butoxy derivatives according to a procedure developed by Lawesson and coworkers.[10] When we used the oxidative cleavage method for the preparation of these compounds, only the unsubstituted compound was obtained and the yield was rather low (31 %). In the 5-methylsubstituted case, the deboronation became the main reaction. However, by repeating the reaction route of Morel *et al.* *via* 5-methyl-2-*tert*-butoxythiophene (XV) the 5-methylselenolene-2-one system was obtained in acceptable yield (61 %), but under these conditions a side reaction also took place. Besides the described 5-methyl selenolene-2-one system a considerable amount of 3-*tert*-butyl-5-methyl-3-selenolene-2-one was obtained. This side reaction was not observed by Lawesson *et al.* in the thiophene series [10] or by Morel *et al.* in their preparation of the 5-methylselenolene-2-one system.[3] However, when we repeated these reactions we found transalkylation in both cases. Alkylation of 3-thiolene-2-one with isobutylene under the same conditions also gives 3-alkylated products. Under the preparative conditions 3- and 5-alkylated and 3,5-dialkylated products are formed in 17, 1 and 2 % yield, respectively.



Indirectly, both the unsubstituted and the 5-methylsubstituted selenolene-2-one systems show enolic properties, as they could be transformed to the acetoxy derivatives when treated with acetyl chloride. At equilibrium the 3-selenolene-2-one form (III B) dominates in both systems. Due to hyperconjugation of the methyl substituent, 7 % of the 4-selenolene-2-one form (III A) could be observed for the 5-methyl-substituted derivative in benzene solution. In the 3-*tert*-butyl-5-methyl-substituted compound, this effect was over-compensated by the stabilization of the *tert*-butyl group with the α,β-double bond, as only the 3-selenolene-2-one form (XVII B) could be observed.

Under the rather vigorous conditions used for the preparation of the selenolene-2-one system, the thermodynamic equilibrium mixture is obtained. However, the thermodynamically more stable α,β-conjugated form (III B) can be converted into the β,γ-unsaturated form (III A) by dissolving the tautomeric mixture in cold alkali and acidifying. This is in agreement with Hughes-Ingold's rule, which states that when a proton is added to the mesomeric anion (IX E – G) of a weakly dissociating tautomer, the thermodynamically less stable tautomer (III A) is first formed. It is interesting to note that in the thiophene series the anion could be generated by extraction with sodium hydroxide solution, while in the selenophene series we were only successful by using tetrabutylammonium hydroxide (*cf.* Experimental part). The more unstable enol form, obtained by protonation of IX G, could, however, not be isolated, which is also the case in the thiophene series.

Tautomeric rearrangement. Since the ^{1}H absorption bands of the ring and the side-chain protons have different δ-values (*cf.* Tables 6, 8) for the two tautomeric forms of 5-methylselenolene-2-one, NMR could be used as an analytical tool for the kinetic experiments. When benzene was used as solvent and pyridine as base, first-order kinetics with half-lives suitable for this type of NMR determination were obtained for both 5-methyl-4-selenolene-2-one and 5-methyl-4-thiolene-2-one. Another solvent-base system, methanol-pyridine, which was suitable for the study of thiolene-2-ones, caused ring-opening leading to methyl levulinate and loss of selenium in the case of 5-methyl-4-selenolene-2-one.

Table 1. Values for $k_A + k_B$ in benzene solution.

Temp. °C	Pyridine conc. M	$(k_A + k_B) \times 10^4$ (min^{-1})	r
5-Methylthiolene-2-one			
20	0.60	2.28 ± 0.04	0.998
30	0.60	5.2 ± 0.1	0.996
40	0.60	9.9 ± 0.2	0.998
40	0.48	7.1 ± 0.1	0.998
40	0.24	3.18 ± 0.06	0.998
50	0.60	19.8 ± 0.3	0.999
5-Methylselenolene-2-one			
20	0.60	4.7 ± 0.1	0.997
30	0.60	10.3 ± 0.2	0.998
40	0.60	22.7 ± 0.4	0.998
40	0.48	16.1 ± 0.3	0.998
40	0.24	7.0 ± 0.1	0.999
50	0.60	38.6 ± 0.8	0.998

Table 2. Equilibrium constants and specific rate constants at different base concentrations in benzene solution at 40 °C.

K	Pyridine conc. M	$k_A \times 10^4$ (min^{-1})	$k_A \times 10^4$ (min^{-1})
5-Methylthiolene-2-one			
4.1 ± 0.2	0.60	7.9 ± 0.1	2.0 ± 0.1
4.1 ± 0.2	0.48	5.7 ± 0.1	1.39 ± 0.09
4.1 ± 0.2	0.24	2.56 ± 0.05	0.62 ± 0.04
5-Methylselenolene-2-one			
14.5 ± 0.7	0.60	21.2 ± 0.4	1.5 ± 0.1
14.7 ± 0.7	0.48	15.1 ± 0.3	1.03 ± 0.07
14.4 ± 0.7	0.24	6.5 ± 0.1	0.45 ± 0.03

The rearrangement was performed at three different base concentrations, 0.60, 0.48 and 0.24 M, and four temperatures, 20, 30, 40 and 50 °C. The experimental results are collected in Table 1. The specific rates of isomerisations were found to be proportional to the base concentration (Table 2), showing that the rearrangement is first-order with respect to the base. The results in all the isomerisation experiments satisfied eqn. (1), corresponding to

$$\ln \frac{AK - B}{A_0K - B_0} = -(k_A + k_B)t \qquad (1)$$

a reversible process (eqn. 2).

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B \qquad (2)$$

The least-squares method was used for obtaining the best fit of the experimental results to eqn. (1). The algebraically calculated values for $(k_A + k_B)$ and their standard deviations are given in Table 1. Since the quotient k_A/k_B can

Table 3. Equilibrium constants and specific rate constants at different temperatures in benzene solution. (Base conc. 0.60 M.)

Temp. °C	K	$k_A \times 10^4$ (min^{-1})	$k_B \times 10^4$ (min^{-1})
5-Methylthiolene-2-one			
20	4.4 ± 0.2	1.86 ± 0.03	0.42 ± 0.03
30	4.3 ± 0.2	4.2 ± 0.1	0.98 ± 0.07
40	4.1 ± 0.2	7.9 ± 0.1	2.0 ± 0.1
50	3.9 ± 0.2	15.8 ± 0.2	4.0 ± 0.3
5-Methylselenolene-2-one			
20	15.7 ± 0.8	4.4 ± 0.1	0.28 ± 0.02
30	15.6 ± 0.8	9.7 ± 0.2	0.62 ± 0.05
40	14.5 ± 0.7	21.2 ± 0.4	1.5 ± 0.1
50	14.1 ± 0.7	36.0 ± 0.8	2.6 ± 0.2

Table 4. Enthalpies, free energies and entropies of activation in benzene solution at 25 °C.

	5-Methyl-selenolene-2-one	5-Methyl-thiolene 2-one
Assoc. with k_A		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	54 ± 2	53 ± 1
$\Delta G^{\ddagger}$ (kJ mol^{-1})	102 ± 5	103 ± 2
$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	-161 ± 7	-169 ± 3
Assoc. with k_B		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	57 ± 3	56 ± 1
$\Delta G^{\ddagger}$ (kJ mol^{-1})	108 ± 5	107 ± 2
$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	-172 ± 8	-171 ± 3

be derived from the composition of the equilibrium mixture, it is possible thereby also to determine the individual rate constants at different base concentrations and temperatures. These data are given in Tables 2 and 3.

The activation parameters are determined in accordance to Frost and Pearson [11] and are collected in Table 4.

The equilibrium constants at different temperatures were found to satisfy function (3).

$$\ln K = -(\Delta H/RT) + C \qquad (3)$$

The heat of reaction, ΔH, was determined by the method of least-squares and the thermodynamic constants were found to be $\Delta H = -3.6 \pm 0.5$ kJ mol^{-1}, $\Delta G = -7 \pm 1$ kJ mol^{-1} and $\Delta S = 11 \pm 2$ J K^{-1} mol^{-1} for 5-methylselenolene-2-one at 25 °C and $\Delta H = -3.2 \pm 0.2$ kJ mol^{-1}, $\Delta G = -3.6 \pm 0.5$ kJ mol^{-1} and $\Delta S = 1.5 \pm 0.3$ J K^{-1} mol^{-1} for 5-methylthiolene-2-one at 25 °C. These values are in good agreement with those obtained as differences of the activation parameters in Table 4.

In order to obtain information about the nature of the mechanism of this rearrangement, a benzene solution, 5 M in CD_3OD, 0.62 M in lactone and 0.6 M in pyridine was examined. As in the cases of 5-methyl-4-thiolene-2-one [12] and of 5-methyl-β,γ-butenolide,[7] it was found that the unconjugated isomer of 5-methylselenolene-2-one undergoes hydrogen-deuterium exchange more rapidly than the conjugated form. Furthermore, exchange of the methylenic protons for deuterium was complete before any tautomerisation of the unconjugated form or ring-opening of the lactone was observed. Since the hydrogen exchange in the 3-position is more rapid than isomerisation, nothing can be said about the degree of the intramolecular mechanism for the rearrangement except that the 5-proton is involved in the rate-determining step. During the last decade it has been shown that besides the intermolecular mechanism, there exists a competing mechanism which under certain conditions becomes predominant. In this mechanism the proton-transfer is intramolecular and involves ion pairs as intermediates. Bergson and Weidler [13] and Cram *et al.*,[14] the pioneers in this field, elegantly established this mechanism for tautomerisation in a series of investigations.[15]

From Table 3 it is seen that the rate for replacement of the proton in the 5-position of

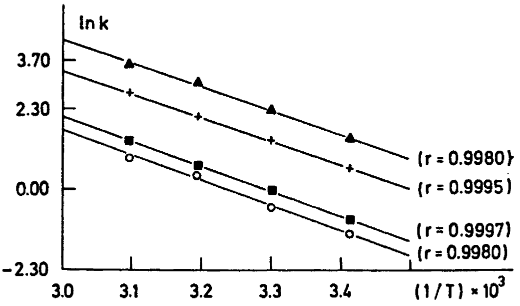


Fig. 1 Arrhenius plots for 5-methyl-thiolene-2-one and 5-methyl-selenolene-2-one in benzene solution ▲ $= k_A^{Se}$; $+ = k_A^{S}$; ■ $= k_B^{S}$; and ○ $= k_B^{Se}$ (*cf.* Table 3).

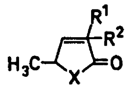
the selenophene system is more rapid than that of the thiophene system and that the rate for deprotonation is somewhat slower in the selenophene system than in the thiophene system.

The activation enthalpies for the replacement of the proton in the 5-position are the same in both systems, as shown by the fact that ln k_A^S parallels ln k_A^{Se} in Fig. 1, and thus the difference in the free energy is due to a contribution from the activation entropy term, which is somewhat lower in the selenophene system (*cf.* Table 4). The similarity between the activation parameters for the proton abstraction step is reflected in Fig. 1, where the lines for ln k_B^S and ln k_B^{Se} are parallel and very close to each other.

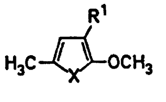
Alkylation reactions. The results of the alkylation experiments of the 5-methyl-2-hydroxyselenophene system with the ion pair extraction method using methyl iodide and dimethyl sulfate as alkylating reagents are collected in Table 5. For convenience, the results obtained under the same conditions for the 5-methyl-2-hydroxythiophene system [8] are also presented. Again it is demonstrated that the soft methyl iodide favours *C*-alkylation and the hard dimethyl sulfate *O*-alkylation. However, the selectivity of the mono alkylated selenophene system is lower than that of the thiophene system, which can be seen from the amount of dialkylated products formed. This increase in reactivity may be due to a higher lipophilicity of the selenophene system or to the lower stability of the anion in the selenophene system compared to the thiophene system. So far only the dissociation constants of the latter system are known, and the CH acidity was found to be of the same magnitude as the OH acidity of the corresponding phenols.[16] From the data in Table 5 it is interesting to note that the tendency for *O*-alkylation is somewhat more pronounced in the thiophene system than in the selenophene system, indicating that the former system is the more aromatic.

The ^{1}H NMR data for the starting materials characterized as acetoxy derivatives and the

Table 5. Alkylation of the 5-methyl-2-hydroxyselenophene and 5-methyl-2-hydroxythiophene system with methyl iodide and dimethyl sulfate.



1, $R^1=R^2=H$
2, $R^1=H$: $R^2=CH_3$
4, $R^1=R^2=CH_3$



3, $R^1=H$
5, $R^1=CH_3$

Substrate system	5-Methyl-2-hydroxyselenophene		5-Methyl-2-hydroxythiophene	
Reagent	CH_3I	$(CH_3O)_2SO_2$	CH_3I[a]	$(CH_3O)_2SO_2$[a]
Yield (%)	37	44	53	89
Products (relative yields, %)				
X	Se	Se	S	S
1	5	–	–	–
2	38	6	86	4
3	4	76	12	90
4	50	3	2	2
5	3	15	–	4

[a] After addition of [Eu(FOD)$_3$].

Table 6. IR and ^{1}H NMR data for 3-R^1-5-R^2-3-selenolene-2-ones. The NMR parameters were obtained in deuteriochloroform solutions at 60 MHz.

		δ				J				C=O
R^1	R^2	R^1	R^2	4-H	5-H	4-R^1 (Hz)	5-R^1 (Hz)	5-R^2 (Hz)	45 (Hz)	cm^{-1} film
H	H	6.31	—	7.66	4.40	6.4	2.0	—	2.9	1700
H	CH_3	6.20	1.75	7.31	4.81	6.4	2.0	7.8	2.7	1690
CH_3	CH_3	1.91	1.72	7.03	4.65	1.4	2.0	7.4	2.8	1680
$C(CH_3)_3$	CH_3	1.27	1.75	7.07	4.58	—	—	7.4	2.7	1685

Table 7. ^{1}H NMR data for 2-R^1-3R^2-5-R^3-2-oxyselenophenes. The NMR parameters were obtained in deuteriochloroform solutions at 60 MHz.

			δ				J			
R^1	R^2	R^3	R^1	R^2	R^3	4-H	4-CH_3 (Hz)	34 (Hz)	45 (Hz)	35 (Hz)
OCH_3	H	CH_3	3.86	5.98	2.41	6.43	1.3	4.0	—	—
OCH_3	CH_3	CH_3	3.84	1.98	2.44	6.42	1.3	—	—	—
$OC(CH_3)_3$	H	CH_3	1.36	6.21	2.44	6.47	1.3	3.9	—	—
O_2CCH_3	H	H	2.18	6.74	7.48	6.96	—	4.1	6.2	1.5
O_2CCH_3	H	CH_3	2.14	6.54	2.39	6.54	1.3*[a]	4.1*[a]	—	—

Taken from Ref. 8.

Table 8. IR and ^{1}H NMR data for 3,3-R^1-5-methyl-selenolene-2-ones. The NMR parameters were obtained in deuteriochloroform solutions at 60 MHz.

	δ			J			
R^1	R^1	CH_3	4-H	4-CH_3 (Hz)	3-CH_3 (Hz)	34 (Hz)	C=O (cm^{-1}) film
H	3.52	2.27	5.55	1.70	2.50	2.70	1725
CH_3	1.21	2.22	5.48	1.70	—	—	1715

products isolated from the alkylation experiments are collected in Tables 6–8.

EXPERIMENTAL

The 3-selenolene-2-one system. Butyllithium in hexane (33 ml; 1.66 M) was added dropwise to 6.55 g (0.050 mol) of selenophene [17,18] in 150 ml of dry ether with stirring under nitrogen. The addition was made at such a rate that gentle reflux was maintained. When the addition was complete, refluxing and stirring were continued for another 15 min, whereupon the temperature was decreased to −70 °C and the selenienyllithium was treated with 7.3 g (0.050 mol) of triethylborate in 100 ml of dry ether. After stirring at −70 °C for 4 h, the reaction mixture was allowed to warm to room temperature and then treated dropwise with 10.1 ml of 30 % hydrogen peroxide solution. After complete addition, the reaction mixture was refluxed for 1 h with vigorous stirring. The reaction mixture was cooled, the layers separated and the aqueous phase extracted with ether. The combined ethereal phases were washed with cold water until the separating water did not oxidize ferrous ammonium sulfate, dried over magnesium sulfate and distilled. 2.3 g (31 %) of the product, b.p. 96 °C/9 mmHg, $n_D^{20} = 1.5955$ (lit. value [3] b.p. 121 °C/20 mmHg), was obtained. For IR and NMR data see Table 6.

2-Acetoxyselenophene (procedure A). 11.4 g (0.0776 mol) of the 3-selenolene-2-one system was treated with an excess of acetyl chloride.

The reaction mixture was refluxed and the reaction followed by gas chromatography (Reoplex 400, 5 %, 3 m × 3 mm). After 45 h all of the starting material had disappeared. The excess of acetyl chloride was evaporated and the residue dissolved in ether. The ether solution was washed with 2 M sodium hydroxide and then with water until neutral reaction, whereupon it was dried over magnesium sulfate. The ether was removed and the residue distilled, giving 8.3 g (57 %) of the product, b.p. 62 – 64 °C/0.8 mmHg, $n_D^{20} = 1.5575$. IR spectrum (film): C = O = 1755 cm^{-1}. For NMR data see Table 7. [Found: C 38.19; H 3.24; Se 41.10; M.wt. 190. Calc. for $C_6H_6O_2Se$: C 38.11; H 3.19; Se 41.76; M.wt. 189.07.]

*5-Methyl-2-*tert*-butoxyselenophene* was prepared according to Ref. 10 from 34.2 g (0.236 mol) of 2-methylselenophene,[5] 162 ml of 1.48 N butyllithium in hexane, 7.5 g (0.31 mol) of magnesium, 13 ml (0.24 mol) of bromine and 39 ml (0.19 mol) of *tert*-butyl perbenzoate. Distillation gave 33.1 g (80 %) of the product, b.p. 61 – 62 °C/1.5 mmHg, $n_D^{20} = 1.5195$. (Lit. value[3] b.p. 58 °C/1.3 mmHg.) For NMR data see Table 7.

The 5-methyl-2-hydroxyselenophene system. 5-Methyl-2-*tert*-butoxyselenophene (16.0 g; 0.073 mol) and 0.1 g of *p*-toluenesulfonic acid were placed in a distillation flask while a vigorous stream of nitrogen was passed through the reaction mixture, the flask was heated with an oil bath at 155 °C, whereupon the reaction started with isobutylene evolution. After 5 min, the gas evolution had ceased and the oil bath was removed. The residue was distilled under nitrogen at reduced pressure, giving 11.00 g of a fraction with b.p. 85 – 89 °C/5.0 mmHg containing 82 % of the 5-methyl-2-hydroxyselenophene system and 18 % of the 5-methyl-3-*tert*-butyl-2-hydroxyselenophene system. Redistillation gave, after a forerun containing both 5-methyl-3- and 4-selenolene-2-one, a fraction containing 7.2 g (61 %) of 5-methyl-3-selenolene-2-one, b.p. 93 °C/10 mmHg, $n_D^{20} = 1.5789$. For IR and NMR data, see Table 6. The second fraction (2.9 g) contained comparable amounts of the 5-methyl-2-hydroxyselenophene and 5-methyl-3-*tert*-butyl-2-hydroxyselenophene systems, b.p. 95 – – 103 °C/10 mmHg.

*5-Methyl-3-*tert*-butyl-3-selenolene-2-one* was obtained pure by preparative gas chromatography (OV 17, 15 %, 2.7 m × 9 mm) of the second fraction described above, $n_D^{20} = 1.5358$. For IR and NMR data, see Table 6. [Found: C 49.76; H 6.68; Se 35.40; M.wt. 218. Calc. for $C_9H_{14}OSe$: C 49.77; H 6.50; Se 36.46; M.wt. 217.17.]

Alkylation of 3-thiolene-2-one with isobutene. 3-Thiolene-2-one (2.0 g; 0.020 mol) and 0.05 g of *p*-toluenesulfonic acid were mixed in a distillation flask. The mixture was heated to 150 – 155 °C and isobutene was bubbled in. The reaction was followed on GLC (OV 17, 3 %, 3 m × 3 mm). No starting material remained after 90 min.

The alkylated products were distilled, giving 0.61 g, b.p. 65 – 80 °C/0.8 mmHg, of a mixture of 3-*tert*-butyl-3-thiolene-2-one (17 %), 5-*tert*-butyl-3-thiolene-2-one (1 %) and 3,5-di-*tert*-butyl-3-thiolene-2-one (2 %). [NMR, GLC.]

The mixture was eluted on silica gel 60 with chloroform and hexane (1:1) as solvent. The elution was followed on GLC.

*3-*tert*-Butyl-3-thiolene-2-one* and *5-*tert*-butyl-3-thiolene-2-one* had the same spectroscopic data as given in the literature.[2,9]

*3,5-Di-*tert*-butyl-3-thiolene-2-one:* IR (film) C = O = 1685 cm^{-1}. NMR ($CDCl_3$): δ 1.24 (3*t*-Bu), 1.03 (5*t*-Bu), 7.04 (4-H), 4.04 (5-H, J_{45} 2.4 Hz. MS: $M^+ - 56$.

5-Methyl-2-acetoxyselenophene was prepared according to procedure A from 1.62 g (0.010 mol) of the 5-methyl-2-hydroxyselenophene system. After 8 h, the reaction was over and distillation gave 1.3 g (63 %) of the product, b.p. 56 – 57 °C/0.6 mmHg. Recrystallization from ethanol gave white crystals, m.p. 34.0 – – 34.5 °C. IR (KBr): C = O = 1755 cm^{-1}. For NMR data, see Table 7. [Found: C 41.43; H 3.93; Se 38.81; M.wt. 204 Calc. for $C_7H_8O_2Se$: C 41.40; H 3.97; Se 38.87; M.wt. 203.10.]

5-Methyl-4-selenolene-2-one. After isomerisation, the pure 4-selenolene form was obtained by dissolving 5.88 g (0.037 mol) of the tautomeric mixture in cold ether and extracting the ethereal phase three times with a cold solution of 12.5 g (0.037 mol) of tetrabutylammonium hydrogen sulfate, 3.0 g (0.075 mol) of sodium hydroxide and 25 ml of water. Immediately after separation, the alkaline phase was poured into an ice-cooled 1 M sulfuric acid solution covered with ether. The ether phase was separated and the water phase extracted twice with ether. The combined ether phases were washed with water until neutral reaction of the separating water was obtained, dried over magnesium sulfate and distilled; b.p. 75 – 76 °C/9 mmHg, $n_D^{20} = 1.5706$. The yield of this procedure was 1.84 g (31.3 %). For IR and NMR data, see Table 8.

5-Methyl-4-thiolene-2-one was prepared as described in Ref. 2.

Alkylation of the 5-methyl-2-hydroxyselenophene system with methyl iodide. A freshly prepared solution of 7.5 g (0.022 mol) of tetrabutylammonium hydrogen sulfate, 1.80 g (0.044 mol) of sodium hydroxide and 25 ml of water was added dropwise to 3.6 g (0.022 mol) of the 5-methyl-2-hydroxyselenophene system and 6.4 g (0.045 mol) to methyl iodide in 25 ml of chloroform. During the addition, the temperature was kept at 30 °C and after the addition was complete the stirring was continued for another 10 min. The reaction mixture was acidified with 2 M hydrochloric acid, the phases were separated and the water phase was extracted with chloroform. The combined chloroform phases were evaporated, and when the residue was treated with ether, tetrabutylammonium iodide precipitated. The solid phase was filtered off and washed with ether, whereupon the filtrate was washed with water, dried over magnesium sulfate and evaporated. The residue was distilled and the fraction with b.p. 75 – 102 °C/10 mmHg was collected. The crude product and the distilled fraction were analysed by gas chromatography (OV 17, 3 %, 3 m × 3 mm) and shown to have the same proportions of the different products, which are given in Table 5. After separation by preparative gas chromatography (OV 17, 15 % and BDS, 20 %, 2.7 m × 9 mm), the structures of the products were determined by IR, NMR and mass spectroscopy. The IR and NMR data are given in Tables 6 – 8.

3,5-Dimethyl-3-selenolene-2-one. $n_D^{20} = 1.5630$.

5-Methyl-2-methoxyselenophene. $n_D^{20} = 1.5543$. [Found: C 41.06; H 4.54; Se 44.81; M.wt. 176. Calc. for C_6H_8OSe: C 41.15; H 4.60; Se 45.09; M.wt. 175.09.]

3,3-Dimethyl-5-methyl-4-selenolene-2-one. $n_D^{20} = 1.5285$.

3,5-Dimethyl-2-methoxyselenophene. $n_D^{20} = 1.5517$. [Found: C 44.16; H 5.40; Se 41.63; M.wt. 189. Calc. for $C_7H_{10}OSe$: C 44.45; H 5.33; Se 41.75; M.wt. 189.12.] The IR and NMR data are given in Tables 6 – 8.

Alkylation of the 5-methyl-2-hydroxyselenophene system with dimethyl sulfate was performed as decribed above by using 2.7 g (0.021 mol) of dimethyl sulfate instead of methyl iodide. Distillation gave 1.6 g (44 %) of a fraction with b.p. 70 – 85 °C/10 mmHg. The proportions of the four components formed are given in Table 5. After separation of the products by preparative gas chromatography, the retention times and spectroscopic data were found to be in accordance with those described above.

The NMR spectra for the kinetic experiments were obtained with a Jeol MH 100 high resolution spectrometer equipped with a vt-3c variable temperature accessory and integration unit. During the rearrangement experiments, the samples were kept in thermostats at different temperatures, and the time required for the integrations was neglected.

The tautomerisation was followed by observing the increase in intensity of the absorption band of the component formed, and the decrease in intensity of the band due to the component consumed. The intensities were determined through integration of the side-chain methyl absorptions. In the runs performed, the sums of the integrals of the increasing and decreasing bands were constant within the limit of accuracy of the instrument, which shows that no side reactions had taken place during the time reaction kinetics were studied.

The numerical treatment of the rate data was carried out on a Hewlett-Packard 9820A desk calculator equipped with a 9832A calculator plotter.

The other NMR spectra were obtained with a Varian A-60 spectrometer. The IR spectra were recorded on a Perkin-Elmer Model 257 instrument. The mass spectra were recorded on an LKB 9000 mass spectrometer, using an ion-source voltage of 70 eV. The gas chromatographs used were a Perkin-Elmer 900 analytical instrument and a Perkin-Elmer F21 preparative instrument. The quantitative analyses were corrected for the differences in the sensitivity of the detector for the different compounds.

The elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr.

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