The acid-catalysed rearrangements of 4,5-bis(2-thienylhydroxymethyl)-1,3-dithiole-2-thione

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Under strongly acidic conditions, the title compound **1** readily participates in several possible rearrangement pathways, affording a product distribution which is relative to the choice of solvent and acid catalyst. Thus, using chloroform or acetone as the solvents and HBr or $HClO_4$ as the catalysts, compounds **2**–**4** have been isolated and fully characterised; in addition, compound **5** was identified in the reaction mixture and characterised by ^{1}H NMR spectroscopy. The reaction kinetics of the transformations have been studied by ^{1}H NMR spectroscopy, using deuterated chloroform or acetone as the NMR solvents. A key intermediate in the reaction mechanisms is the allylic carbocation **6**, which rearranges to give the fused system **3**; in the presence of bromide anions, the carbocation forms an ion-pair intermediate **7**, leading to the formation of compounds **2**, **4** and/or **5**, depending on the solvent.

Introduction

The reactions of nucleophilic substitution at a saturated carbon atom represent a classical and perhaps the most deeply explored area of investigation in reaction mechanisms. The consistent work of thousands of chemists over seven decades has led to a detailed understanding of reaction mechanisms, which has contributed immensely to the development of modern physical organic chemistry. Nevertheless, many uncertainties remain in the area which are still far from being resolved. Some of the most puzzling of these involve carbocation intermediates, which can be formed during the course of a process. Even the mere fact of their participation in different reactions has been the subject of continued controversy, and the opinions concerning the mechanism of, for example, solvolysis reactions, range from the suggested S_N1 mechanism in the case of alkyl halides[1] to the highly coordinated S_N2 mechanism for secondary alkyl sulfonates.[2] The stability of carbocations derived from benzyl chlorides in solvolytic reactions depends substantially on the substituents in the benzene ring, and provides a mechanistic spectrum ranging from S_N1 with electron donating substituents[3,4] to S_N2 with electron withdrawing substituents.[4] It is not surprising that the description of the structure and the kinetic properties of the ion pairs, as well as the mechanisms of their formation and further transformations *in situ*, remain far from complete. In parallel with an increase in the development of equipment, experimental techniques and a more detailed study of classical model systems, an investigation into novel substrates is essential for further progress in the field. Moreover, kinetic and mechanistic approaches towards the study of transformations of practically important intermediates, are undoubtedly powerful instruments for the consideration of reaction pathways in the design of new compounds.

During the course of our work on the synthesis of functionalised terthiophene derivatives,[5] we discovered that 4,5-bis(2-thienylhydroxymethyl)-1,3-dithiole-2-thione **1** in acidic media gave several rearrangement products, depending on the choice of reagent. The acid-catalysed rearrangements of **1** represent an interesting area of carbocation chemistry and can give a deeper insight into the intimate details of carbocation transformations. Subsequently, we decided to conduct a series of kinetic investigations into the behaviour of **1** under acidic conditions, using ^{1}H NMR spectroscopy; herein, we report and discuss the results of our current studies.

Results and discussion

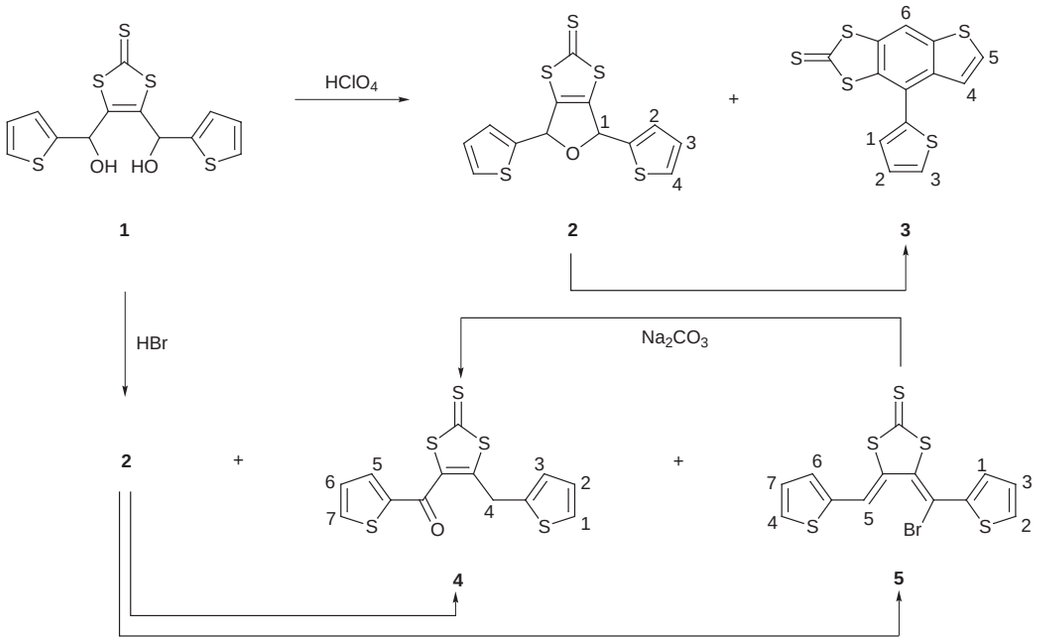
The potential for rearrangement in diol **1** in acidic media can be anticipated from the allylic nature of the carbocation, which is generated *via* protonation and subsequent loss of one molecule of water from the bisalcohol **1**. Intramolecular transformations are well-known processes in allylic systems,[6,7] and these reactions continually attract the attention of investigators in the search for new experimental data relating structure and reactivity in organic chemistry.[8] The carbocation derived from **1** represents a unique example of an allylic cation bearing two different reactive functionalities (thiophene ring and hydroxy group), linked *via* a methine bridge to its 3-position. This makes the species able to react by several different parallel pathways (which can be controlled by the reaction conditions), rendering the system a versatile substrate for the detailed investigation of carbocation behaviour. The starting material possesses a number of features which are favourable for its kinetic study. These include: easy accessibility and stability under ambient conditions, suitable rates of reactions involved for NMR-monitoring, variety of the final products and a high sensitivity of the product distribution to the experimental conditions. Our investigations of the reaction kinetics and product distribution were conducted in two solvents (deuterated acetone and chloroform), at room temperature and constant acid concentration (conc. aqueous HBr or $HClO_4$).

Identification and characterisation of the products

Kinetic results show that by the action of strong acids, diol **1** quantitatively decomposes to form four major products (**2**–**5**, Scheme 1), of which **2**–**4** were isolated and fully characterised.

The ^{1}H NMR spectrum of **2** indicates a symmetrical structure with two equivalent 2-substituted thiophene rings and two equivalent aliphatic protons; carbonyl and hydroxy groups were absent in the molecule (IR evidence).

According to its ^{1}H NMR spectrum, compound **3** contains



Scheme 1

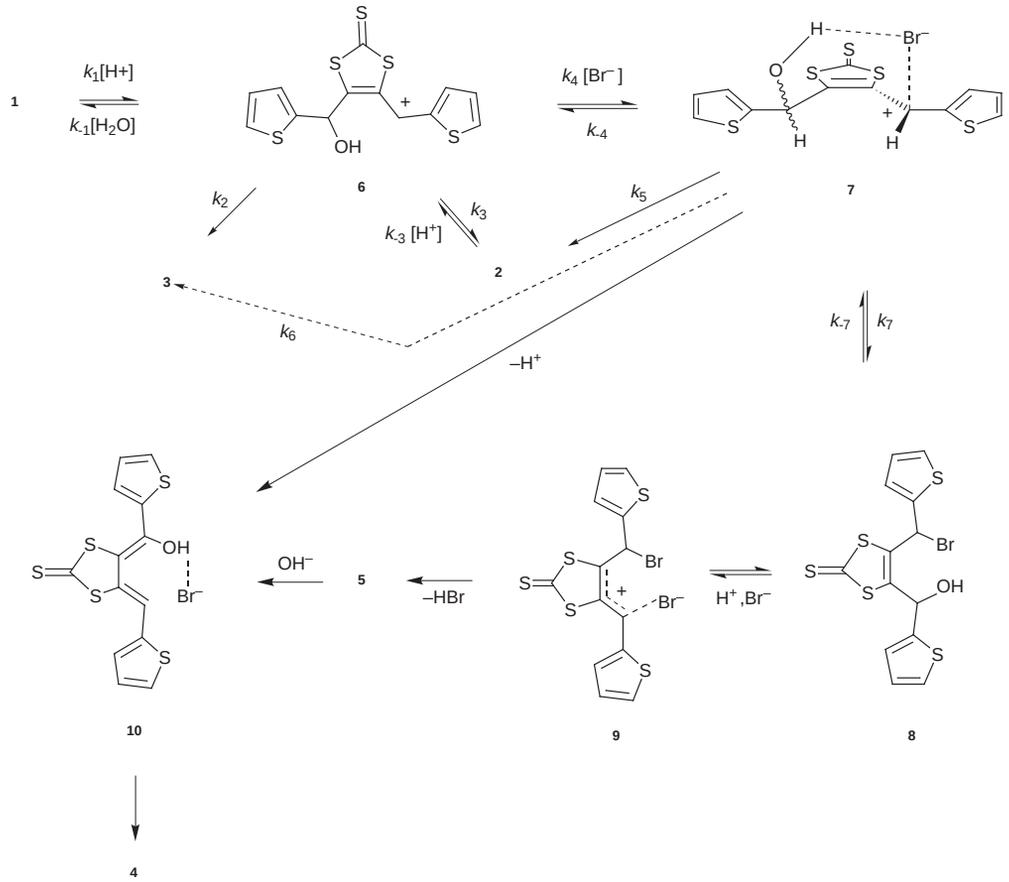
six protons, which suggests that it was formed from **1** by the elimination of two molecules of water. The IR spectrum of **3** also highlighted the absence of either carbonyl or hydroxy groups. Three of the proton signals for compound **3** are commensurate with the splitting pattern expected from a 2-substituted thiophene ring system. The chemical shifts, in $CDCl_3$, were found at: 7.54 (dd, $J = 5.1$ and 1.1 Hz), 7.30 (dd, $J = 3.7$ and 1.2 Hz) and 7.21 (dd, $J = 5.1$ and 3.7 Hz), corresponding to the protons *3*, *1* and *2*, respectively. The remaining signals arise most probably from two vicinal aromatic protons (*4* and *5*, $J_{4\text{-}5} = 5.7$ Hz), of which *4* is weakly coupled to the aromatic proton *6* ($J_{4\text{-}6} = 0.8$ Hz). The coupling between protons *5* and *6* is too weak to be observed because of an unfavourable angle between the corresponding C–H bonds.

The ^{1}H NMR spectrum of **4**, isolated from the reaction solution (non-deuterated acetone or chloroform), shows eight protons, two of which are equivalent and aliphatic (*4*, 4.47 ppm). These signals are weakly coupled with an aromatic proton (*3*, 7.07 ppm, $J_{3\text{-}4} = 0.8$ Hz), suggesting the presence of a 2-thienylmethyl system, in which the remaining two protons are *1* (7.38 ppm) and *2* (6.98 ppm). The three remaining signals are typical for a 2-thenoyl system, and are found at: 8.12 (*5*-H), 7.34 (*6*-H) and 8.15 (*7*-H) ppm (Scheme 1). These assignments were confirmed by decoupling experiments, whilst the presence of a carbonyl group in **4** is evident from its IR spectrum.

The signals in the aromatic region of the ^{1}H NMR spectrum of **4** (from the reaction solution [$^2H_6$]acetone–HBr), were essentially identical to that described above. However, the signal of the methylene group in **4** consisted of an overlapped doublet at 4.47 ppm ($J = 0.8$ Hz) and a triplet at 4.45 ppm ($J = 2.4$ Hz); the latter also showed a scarcely observable doublet splitting. Since the spectrum of **4** obtained in non-deuterated acetone did not contain the triplet, this signal can be attributed to the presence of a CHD fragment in the molecule. This is in good agreement with the observed value of the coupling constant $^2J_{HD}$ and with the difference in the chemical shifts between the doublet and the triplet.[9] The decoupling of *3*-H in **4** (7.06 ppm) led to the expected disappearance of the doublet splittings, however, the triplet splitting was not removed by decoupling any of the aromatic protons in **4**. The considerable broadening of the signal due to the interaction of the methylene proton with *1*-H in the thiophene ring, and possibly due to a somewhat hindered rotation of the methylene group, led to a substantial enhancement of the central peak in the triplet, with respect to the theoretical ratio 1 : 1 : 1. The ratio of the doublet:triplet intensities was *ca.* 1 : 1.3, which corresponds to approximately 70% of the methylene groups being monodeuterated. Accordingly, the overall intensity of the methylene signals, compared to the aromatic protons, was somewhat higher than 1H, which means that very few (if any) of the methylene groups were dideuterated. This ratio remained constant for at least 20 h. However, after treatment of the reaction solution with an excess of solid sodium carbonate, the signal corresponding to the methylene protons in **4** almost completely disappeared. Therefore, unlike α-proton-bearing ketones, compound **4** does not undergo acid-catalysed proton exchange, but is sensitive to base catalysis which is a common feature of extended unsaturated ketones.[10]

Compound **5** (30–35% based on **1**) was detected in the ^{1}H NMR spectrum of the reaction mixture only when the reaction was carried out in acetone with HBr as a catalyst/reagent. Apart from **5**, the only identified major component in the mixture was **4** (15–20% based on **1**). The remainder of the starting material was converted into a complex mixture of products, whose signals could not be assigned. The same product distribution was observed when **2** was used as the starting material instead of **1**. Although **5** was rather stable under the reaction conditions (10–30% decomposition in the reaction mixture after 20 h), when we tried to isolate the product by flash chromatography, **5** decomposed at room temperature within several minutes to give ketone **4** and some by-products. Consequently, we could not record the spectrum of the pure compound under ambient conditions. Upon addition of an excess of solid sodium bicarbonate to the reaction solution, compound **5** was quickly and completely converted, yielding an additional amount of **4** (*ca.* 15% based on **1**), together with some by-products. This transformation occurred faster than the proton exchange process in **4**, which gave us the opportunity of monitoring each of the separate processes in the reaction mixture by NMR spectroscopy. Although some of its ^{1}H NMR signals were overlapped with those of **4**, all the peaks belonging to compound **5** were reliably identified (see Chart 1).

The major ^{1}H NMR splittings represent the presence of two non-equivalent groups of protons in adjacent positions within the aromatic rings: presumably those of the thiophene units (*1*, *2*, *3* and *4*, *6*, *7*; Chart 1). The chemical shifts and the coupling constants in the compound were determined from decoupling experiments. The large value of the chemical shift for the remaining proton *5* suggests a vinylic (or aromatic) nature,



Scheme 2

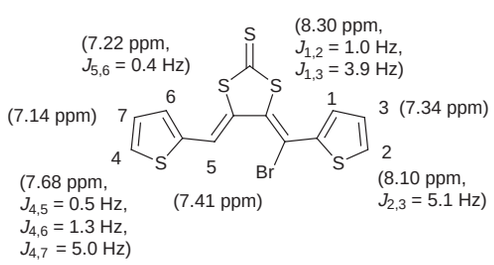


Chart 1

whilst its weak coupling to two other protons indicates its remote position. For olefinic proton *5* (α-substituent at thiophene ring; Chart 1), one can expect a weak but observable coupling to the protons *6* and *4* (*cf.* the coupling between protons *4* and *6* in **3**), whereas for the α-protons at the saturated carbon atoms in compounds **1** and **4**, the only directly observed splittings were those due to the protons in positions 3 of the thiophene rings. Assuming that no redox processes took part in the system, the odd number (seven) of observed signals suggests that **5** is formed by the elimination of one molecule of water from **1**. The compound should also contain either a bromine atom or a hydroxy group, the signal of which would be unobservable in the acidic medium. Since **5** converts to **4** under mild conditions (sodium carbonate, ambient temperature), its formation probably does not involve any changes of the carbon skeleton. Therefore, compound **5** does not contain any additional cyclic structure and must possess two aliphatic double bonds. Hence, the most probable structure of **5** is that shown in Scheme 1, since vinylic alcohols are generally unstable; all attributions of chemical shifts and coupling constants in the ^{1}H NMR spectrum satisfy this structure (Chart 1).

Mechanisms of rearrangements

Kinetic investigations show that **3** and **4** are both stable in the presence of HBr or $HClO_4$, whilst **2** is an intermediate substance, which decomposes during the kinetic experiment with rates of *ca.* 2 times (in [$^2H_6$]acetone) or 20–40 times (in $CDCl_3$) slower than that of **1**.

Reaction in the presence of $HClO_4$. When $HClO_4$ was used as a catalyst (in deuterated acetone or $CDCl_3$), the only final product was compound **3**, which was isolated in a yield of *ca.* 80%. The reaction rate in acetone at the chosen acid concentration and temperature was too fast to be measured precisely (*ca.* 85% of **1** was consumed in 6 min), and the corresponding rate constant was estimated as *ca.* 4×10^{-3} s^{-1}. At a lower temperature (which enabled the kinetics to be followed by NMR), the maximum yield of **2** at any one time was observed to be *ca.* 10% relative to **1**, and diminished to zero by the end of the experiment. The result proves that **2** is not the only (or even major) intermediate in the formation of **3**, whilst the ratio of rate constants k_2/k_3 was found to be *ca.* 5. The formation of **2** and **3** in the parallel routes (Scheme 2), can be explained by the acid-catalysed formation of carbocation **6** (by analogy, for example, with the formation of free benzhydryl carbocations in strong acids).[11] Intramolecular nucleophilic attack by the remaining hydroxy group on the carbocationic centre is expected to furnish dihydrofuran **2**, whereas intramolecular electrophilic attack of the carbocation on the 3-position of the thiophene ring bearing the carbinol functionality, followed by dehydration of the resulting unsaturated monoalcohol and the aromatisation of the 6-membered ring, is the most likely mechanism for the formation of compound **3**. In turn, the disappearance of **2**, detected at the beginning of the NMR kinetic experiment (presumably to form **3**), is most likely to proceed *via* the same intermediate carbocation **6**, which is regained by the acid-catalysed ring-opening of the dihydrofuran **2**.

Reaction in the presence of HBr. The major products in the case of HBr were compounds **2**, **4** and **5**, whilst only trace

Table 1 Kinetics of the rearrangements of **1** (0.13 M) in the presence of HBr (0.16 M) and ethylenetrithiocarbonate (0.052 M) in [$^2H_6$]acetone at 20 °C

	S (normalised)				Relative yield (%)			$k \times 10^4/s^{-1}$		
Time/s	**1**	**4**	**5**	Soln[a]	**1**[b]	**4**	**5**	**1**	**4**	**5**
0	1.23	0	0	0.68	0	0	0			
180	1.16	0	0	6.9	5.8	0	0			
600	0.81	0.023	trace	11	34	16	trace	7.09	2.87	
900	0.55	0.052	0.055		55	36	28	9.01	4.94	3.69
1200	0.55	0.052	0.073	10	56	36	38	6.8	3.71	3.92
1500	0.41	0.074	0.105		67	51	54	7.43	4.77	5.21
2280	0.25	0.097	0.135	9.4	80	67	69	7.0	4.84	5.2
4260	0.082	0.136	0.19		93	94	97	6.37	6.51	
9000	0	0.145	0.19		100	100[c]	100[d]			

[a] This is the signal of protonated methyl groups of acetone. [b] Consumed substrate. [c] Yield 31% based on **1**. [d] Yield 18% based on **1**.

amounts of **3** (<3%) were detected in both of the solvents studied (acetone or chloroform). A typical reaction kinetic in the HBr–acetone medium is presented in Table 1 which demonstrates a slight delay in the appearance of **4** and **5**, compared to the decrease of starting diol **1**, confirming the formation of the relatively long-lived intermediate in the reaction (compared to **6**). The rate constant for the consumption of the starting diol **1**, $k_1 = (7.27 \pm 0.95)\ 10^{-4}\ s^{-1}$, is *ca.* 6 times lower than that in the presence of perchloric acid, which illustrates the higher protonating ability of $HClO_4$.

The remarkable change in product distribution in the presence of $HClO_4$ and HBr can be attributed to the effect of the bromide ion, due to a higher degree of nucleophilicity of Br^- (as compared to ClO_4^-) and its ability to form rather strong hydrogen bonds with hydroxy protons. In low and medium polarity solvents, the bromide ion is known to form contact ion pairs with carbocations,[12] whilst the perchlorate anion is only capable of the formation of labile solvent-separated ion pairs.[13] Therefore, in the presence of bromide ions, carbocation **6** can exist as the hydrogen-bonded ion-pair intermediate **7**. The formation of allylic carbocation–molecule contact pairs, as intermediates in highly aqueous media, has been reported previously in acid-catalysed intramolecular allylic rearrangements,[7] whilst nucleophilic solvent participation was quite recently demonstrated in the solvolysis of 4-methoxybenzyl chloride and bromide.[14] The formation of **7** from **6** is expected to be a diffusion-limited process with a second-order rate constant of $k_4 \approx 10^{10}$–$10^{11}\ M^{-1}\ s^{-1}$,[15] which pre-determines extremely short lifetimes of free carbocations in the presence of bromide anions. Similarly, hydrogen bonding has been found to be the major stabilisation factor in tight carbanion ion pairs involved in proton-transfer reactions in highly aqueous media, whereas electrostatic stabilisation is of relatively small importance.[16]

The kinetic behaviour of **7** is dramatically different from that of carbocation **6**. Firstly, the possibility of intramolecular electrophilic attack of the carbocation on the thiophene ring in **7** is hindered conformationally, as well as by the bulky nature of the bromide ion. Secondly, the intermediate **7** can facilitate ring-closure to form **2** *via* front-sided nucleophilic attack (involving a four-membered cyclic transition state which has been suggested for related systems),[17] although only trace amounts of **2** (<5%) were detected during the kinetic experiment, indicating that routes to **4** or **5** are faster. Thirdly, the bromide anion may facilitate deprotonation of the hydroxy group, which should accelerate the formation of **4**. A collapse of **7** into **8** seems to be very likely since the rate constant k_7 should be very large ($\approx 10^8$–$10^{10}\ s^{-1}$), which is characteristic for $Ph_2CH^+Br^-$ ion pairs in medium polarity solvents.[12] For these reasons, we believe that the reaction pathways in the presence of HBr, to give **2**, **4** and **5**, predominate *via* intermediate **7**. Assuming that, in the presence of $HClO_4$, the only intermediate is **6** and that in the presence of HBr a conversion of **7** into **3** does not take place, the change in product distribution (from 80% of **3** in the case of $HClO_4$ to less than 3% of **3** in the case of HBr) testifies that more than 95% of the reaction flow involving HBr proceeds through **7**.

The extreme difference in the kinetic behaviour of **6** and **7** is illustrated by the following consideration. The rate of the transformation of **6**→**3** is at least 50 times higher than that of **6**→**4**, since no observable amounts of **4** were detected in the presence of $HClO_4$. In the presence of HBr, the ratio of [**3**]:[**4**] is less than 0.2; this corresponds to a 250-fold change in the selectivity, even if we assume as a limit that no amount of **4** is formed from **6**.

In the case of HBr, the relative rates of the reactions leading to compounds **2**, **4** and **5** depend upon the solvent. In $CDCl_3$, compound **5** was not detected, whilst at $t = 15$ min the peak yield of **2** was *ca.* 30%. After 20 h the amount of **2** had decreased to 17%, whilst **4** was found to constitute 63% of the reaction mixture (all values are based on the amount of starting diol **1**). In acetone, compounds **4** and **5** were formed simultaneously in a ratio of *ca.* 2:1 (Table 1), with only trace amounts of **2** observed during the run. The data show that in chloroform the fraction of **2** increases when HBr is used as the catalyst as compared to $HClO_4$, whereas the opposite is true in acetone, although the difference between the solvent effects could be partly due to the heterogeneity of the reaction medium [$CDCl_3$ + HBr(aq)].

The classical question concerning a short-lived intermediate is the reversibility of its formation. In the case of a rapid equilibrium between **1** and **6** (k_1/k_{-1}), the appearance of an additional pathway *via* **7** in the presence of HBr, which becomes the dominant pathway (*ca.* 95% of the overall transformation of **1**, as estimated above), should have led to a large increase (>20 times) in the observed rate of the consumption of **1**, assuming that the rate constant of the direct ionisation step k_1 in the presence of HBr is equal to that in the presence of $HClO_4$. Since such an increase in the rate was not observed in the experiment (moreover, the rate dropped by *ca.* 6 times) step k_1/k_{-1} is most probably irreversible and, consequently, almost all the cations formed undergo further transformations into the corresponding products, whilst the ionising power of HBr is *ca.* 6 times less than that of $HClO_4$. This does not contradict the formation of **8** from **7** since, due to the greater nucleophilicity of the bromide ion with respect to a water molecule, the rate constant of its interaction with the relatively stable carbocation is expected to be several orders of magnitude higher than that for water.[18]

The formation of monodeuterated **4** in [$^2H_6$]acetone can only take place if the incoming proton in the methylene group originates from either a deuterated water molecule or the remaining hydroxy group, but not from the methine group which converts into the carbonyl functionality. Since non-deuterated **4** in our experiments did not undergo deuterium exchange under the reaction conditions, a likely pathway for the formation of **4**

involves unsaturated alcohol **10** as an intermediate, the conversion of which represents an example of a base-catalysed enol–ketone rearrangement by bromide ions.[19] However, the ratio of $[CH_2]:[CHD] \approx 3:7$ does not correspond to the ratio of $[OH]:[OD] \approx 1:40$ in the system after completing the deuterium exchange between water, HBr and acetone.† The solvent deuterium exchange is at least half-completed at the time when *ca.* 6% of the starting diol **1** is consumed (Table 1), and consequently it cannot affect the ratio of $[CH_2]:[CHD]$ in the product to the observed extent. Moreover, the same ratio of $[CH_2]:[CHD]$ was obtained in a separate experiment when HBr was added to acetone in order to allow the exchange to proceed completely before the addition of **1**. Formally, this phenomenon can be described as the deuterium isotope effect, k_H/k_D *ca.* 17, and leads to the predominant formation of the protonated methylene groups with respect to deuterated ones. Even taking into account the possible experimental errors, the magnitude of this effect is much higher than the maximum theoretical value for the primary deuterium isotope effect ($k_H/k_D = 6.9$); similar large isotope effects have been observed in different systems and they are usually attributed to some contribution of a tunnelling effect.[20] Another reason for the extremely high observed value of k_H/k_D could be the preferential transfer of the proton from the disappearing methine group to the developing methylene one.

In contrast to **4**, the intensity of the methine proton signal in **5** shows that this group is not essentially deuterated. However, the base-catalysed (Na_2CO_3) hydrolysis of **5** in the reaction solution leads to the deuterated derivative **4**, which supports the mechanism suggested above.

Conclusions

We have demonstrated that, by the action of strong acids, **1** undergoes rearrangements which proceed *via* carbocation intermediates to give compounds **2**–**5**, as well as some minor by-products. In the presence of perchloric acid, the reaction proceeds through the free carbocation **6** or a solvent-separated ion pair, which predominate in the formation of the fused structure **3**. The ion pair **7** is formed in the presence of HBr, leading to the formation (as major products) of **2**, **4** and **5**, in ratios which are substantially dependent upon the solvent used. This marked change in the product distribution characterises **1** as a useful substrate for the detailed investigation of the structure and properties of carbocation intermediates. Diol **1** represents a new class of model substrate, the properties of which comprise a wide range of possible transformations as compared to other well-known systems, such as benzhydryl, 1- and 2-phenylethyl, benzyl and allyl species.[21]

Experimental

General

Melting points were taken using Electrothermal Melting Point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC 250 instrument; chemical shifts, given in ppm, are relative to tetramethylsilane as internal standard; all *J* values are in Hz. IR spectra were recorded on a Mattson Genesis Series FTIR spectrometer. Mass spectra (EI) and high resolution mass spectra were recorded on a 7070E VG Analytical Mass Spectrometer.

The starting compound **1**[5] and ethylenetrithiocarbonate[22] were prepared as described elsewhere.

† The latter value corresponds to the ratio of exchangeable proton/deuterium concentrations in the system: 6.2 mg = 0.076 mmol HBr, 6.8 mg = 0.76 mequiv. H_2O, 23 mg = 0.13 mequiv. OH in **1**, 0.09 mequiv. of protium (including water) present in the solvent calculated from its NMR spectrum in the presence of the standard, *vs.* 0.5 cm^3 of [$^2H_6$]-acetone containing 44 mequiv. of deuterium.

4,6-Di(2-thienyl)-4,6-dihydro[1,3]dithiolo[4,5-*c*]furan-2-thione (2). Two drops of conc. HBr were added to a suspension of **1** (400 mg, 1.13 mmol) in dichloromethane (10 cm^3). After the mixture was stirred at room temperature for 20 min, the product was isolated by column chromatography (silica, CH_2Cl_2–petroleum ether = 1:1 v/v). The major fraction was treated with cold acetone–water (10:1 v/v, 15 cm^3), and the insoluble yellow precipitate was filtered and washed with a small amount of cold acetone to give **2** (55 mg, 14%), mp 134 °C (decomp.); HRMS found 339.91634, $C_{13}H_8S_5O$ requires 339.91788; $\delta_H(CDCl_3)$ 7.40 (2H, dd, *J* 5.1 and 1.0), 7.17 (2H, dd, *J* 3.6 and 1.0), 7.02 (2H, dd, *J* 5.1 and 3.6) and 6.38 (2H, s); ν_{max}/cm^{-1} (KBr) 3070, 1294, 1108, 1061, 994, 922, 710 and 486.

8-(2-Thienyl)thieno[2,3-*f*][1,3]benzodithiole-2-thione (3). A mixture containing **1** (200 mg, 0.56 mmol), 3 drops of 60% aqueous $HClO_4$ and CH_2Cl_2 (10 cm^3), was stirred at room temperature for 5 h. After the addition of $NaHCO_3$ (0.5 g), the solvent was removed *in vacuo* and the residue treated with hot ethyl acetate (20 cm^3). The solution was filtered through a layer of silica, before reducing the volume of the solvent to 2–3 cm^3. Finally, the product was precipitated by the addition of CH_2Cl_2 (5 cm^3) and petroleum ether (5 cm^3) to give **3** (140 mg, 78%) as yellow crystals, mp 199–201 °C; HRMS (M^+) 321.90635, calculated for $C_{13}H_6S_5$ 321.90732; $\delta_H(CDCl_3$, 50 °C) 7.93 (1H, d, *J* 0.8), 7.54 (1H, dd, *J* 5.1 and 1.1), 7.49 (1H, d, *J* 5.7), 7.39 (1H, dd, *J* 5.7 and 0.8), 7.30 (1H, dd, *J* 3.7 and 1.2) and 7.21 (1H, dd, *J* 5.1 and 3.7); ν_{max}/cm^{-1} (KBr) 3075, 1369, 1065, 890, 853, 828 and 698.

4-(2-Thenoyl)-5-(2-thienyl)-1,3-dithiole-2-thione (4). Compound **1** (50 mg, 0.14 mmol) was suspended in dichloromethane (10 cm^3) and HBr was passed through the reaction mixture for 30 min. The product was purified directly from the reaction mixture by column chromatography (silica, DCM–petroleum ether 1:1), affording **5** (30 mg, 62%) as a yellow oil; HRMS (M^+) 339.91851, calculated for $C_{13}H_8S_5O$ 339.91788; δ_H ([$^2H_6$]-acetone) 8.15 (1H, dd, *J* 5.1 and 1.0), 8.12 (1H, dd, *J* 3.6 and 1.0), 7.38 (1H, dd, *J* 5.1 and 1.3), 7.34 (1H, dd, *J* 5.1 and 3.6), 7.07 (1H, dt, *J* 3.4 and 0.9), 6.98 (1H, dd, *J* 5.1 and 3.4) and 4.47 (2H, d, *J* 0.8); ν_{max}/cm^{-1} (neat on KBr) 3098, 2921, 1625, 1407, 1258, 1060, 846, 725, 700 and 666.

4-(2-Thienylmethylene)-5-(2-thienylbromomethylene)-1,3-dithiolane-2-thione (5). ^{1}H NMR spectrum from the reaction mixture with **4** (signals of **4** are omitted), δ_H([$^2H_6$]acetone) 8.30 (1H, dd, *J* 3.9 and 1.0 Hz), 8.10 (1H, dd, *J* 5.1 and 1.1 Hz), 7.68 (1H, m),‡ 7.41 (1H, s),§ 7.34 (1H, dd, *J* 3.9 and 5.1 Hz), 7.22 (1H, m)¶ and 7.14 (1H, d, *J* 5.1 and 3.6 Hz).

NMR kinetic experiments

For a typical run, 48% HBr or 60% $HClO_4$ (13 mg) were added at room temperature to either $CDCl_3$ or [$^2H_6$]acetone (0.5 cm^3), containing compound **1** (1–2 mg in $CDCl_3$ or 20–25 mg in acetone) and ethylenetrithiocarbonate[22] (0.5–15 mg); the latter was used as the internal intensity standard (4.11 ppm, singlet in acetone). The progress of the reactions was followed by measuring the intensities of the characteristic NMR signals: **1**, 6.37 ppm; **2**, 6.77 ppm; **3**, 8.42 ppm; **4**, 4.41–4.46 ppm; **5**, 8.31 ppm (in acetone). Each experimental run was completed in 2 to 4 h which was followed by a control point after 20 h. With chloroform as the solvent, the reaction mixture was heterogeneous which, however, was not an obstacle for monitoring the course of the process. The results obtained can only be considered as

‡ This signal consists of a predominant doublet (*J* = 5.0 Hz) in which each peak is split into a doublet of doublets.
§ This is a non-resolved doublet of doublets, see Table 1.
¶ See footnote ‡; major splitting 3.6 Hz.

semi-quantitative because of integration accuracy limitations, which were caused by the low solubility of compounds **1** and **4** in chloroform, limited acquisition time and the curvature of the baseline due to the formation of by-products. The reasons above rendered the strictly statistical estimation of errors impossible, but we believe that, in general, the errors of integration did not exceed 20%, and in a few cases 50%.

The rate of each reaction was characterised by the first-order rate constant $k = 1/t \ln (S_o)/S_t)$ for the starting materials or $k = 1/t \ln (S_\infty)/(S_\infty - S_t)$ for the products where t is the time from the start of the run(s), S_o, S_t and S_∞ integral intensities of the signals, which were normalised such that $S_{standard} = 1$. All values calculated remained constant throughout the runs (3–5 points), within experimental error. The heterogeneity of the chloroform reaction mixtures did not allow the determination of the rate constants to a reliable level and also for an accurate comparison of the catalytic activity of the different acids; however, these runs provided the information on the relative reactivity of **1** and **2** and on the product distributions during the runtime.

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