PERKIN 2
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Hydrosilane reduction and 1,5-hydride transfer in the [2-(3-ethoxythienyl)]di(1-adamantyl)methyl cation†

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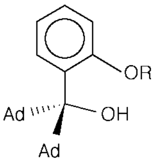
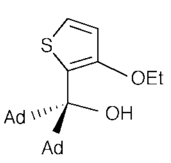
The carbocation formed by reaction of *anti*-[2-(3-ethoxythienyl)]di(1-adamantyl)methanol with trifluoroacetic acid (TFA) in dichloromethane is reduced by hydrosilanes, to give both *syn* and *anti* [2-(3-ethoxythienyl)]diadamantylmethanes, but also undergoes an intramolecular 1,5-hydride shift to give a carboxonium ion, reduction of which gives the *anti* isomer.

Reports of higher order hydride transfers in carbocations, *i.e.* other than 1,2- and 1,3-hydride transfers (which occur mainly in norbornane derivatives[1]), are comparatively rare.[2–5] By generating a carbocation in which all other options are closed it is possible, however, to observe 1,4- and 1,5-hydride transfers from a suitable group located at an appropriate distance[6] from the electron-deficient centre. In particular, that obtained by reaction of (2-methoxyphenyl)diadamantylmethanol, **1S-Me**, undergoes intramolecular 1,5-hydride shift from the methoxy group to give a carboxonium ion.[5] Intermolecular reduction of this carbocation by a hydrosilane gives exclusively the deoxygenation product with the benzylic hydrogen remote from the substituent (*anti*) while reduction of the carboxonium ion leads to the *syn* isomer. 1,5-Hydride transfer is much faster in the case of the 2-ethoxy derivative, **1S-Et**.[5]



1S-R



2A

Quantum mechanical calculations of the energies and geometries of the intermediate cations allow an explanation of these results and predict similar behaviour in heteroaryl compounds. Low-level DFT calculations on the *tert*-butyl derivatives using the Xα(3-21G)//STO-3G approach[7]‡ indicate that the hypothetical carboxonium ion derived from 2-anisyldi(*tert*-butyl)methanol is 3.6 kcal mol^{-1} more stable than the carbocation precursor, whereas the difference for the 2-ethoxyphenyl derivative is 14.3 kcal mol^{-1} in favour of the carboxonium ion.§ In contrast, the carboxonium ion derived from the corresponding 2-(3-methoxythienyl) system is 1.5 kcal mol^{-1} less stable than the carbocation.

Part of this difference in the relative energies of the two species in the benzenoid and thienyl systems is due to the fact that the geometry of the [2-(3-methoxythienyl)]di(*tert*-butyl)methyl cation allows better resonance stabilization than in the 2-anisyl cation. Whereas in the latter the carbocation plane is calculated to be about 80° to that of the aryl ring, in the former this value falls to 30°. If in the thienyl system the methoxy group is replaced by ethoxy the carboxonium ion is favoured but by only 4.6 kcal mol^{-1}, a figure comparable to that for the 2-anisyl derivative. It is interesting therefore to investigate the behaviour of the [2-(3-ethoxythienyl)]di(1-adamantyl)methyl cation generated from **2A**.

Treatment of 3-ethoxythiophene[8] with *n*-butyllithium in diethyl ether, followed by reaction with di(1-adamantyl) ketone, gives predominantly the 2-substituted derivative, **2A**.¶ The NMR and IR behaviour of this new alcohol is similar to that of the 2-alkoxyphenyl analogues, **1S**,[5] though the ^{1}H NMR shift of the OH proton is lower and the IR ν_{OH} frequency slightly higher, indicating somewhat weaker hydrogen bonding.

^{1}H NMR monitoring of the reaction of **2A** with TFA (4% v/v) in dichloromethane at 25 °C reveals that a trifluoroacetate, **3**, is first formed, and that this then breaks down to acetaldehyde and a 3-hydroxythienyl derivative, **4**, which slowly decays to unidentified products. The integrated intensity of the identifiable signals falls by about 15% in the time during which the reaction can be usefully monitored (4–5 half-lives of the alcohol). The first two reactions occur at similar rates. From the rate of consumption of **2A**, the position of the maximum in the concentration of **3** and kinetic simulation by KINAL,[9] the first-order rate constants for the reactions of the alcohol and the trifluoroacetate are estimated to be $4.7 \pm 1.0 \times 10^{-3}$ and $2.9 \pm 0.3 \times 10^{-3}$ s^{-1}, respectively. The first rate constant probably corresponds to k_0 and the second clearly to k_6 (Scheme 1). The former is somewhat higher than for **1S-Me** (7×10^{-4} s^{-1});[5] no value corresponding to k_6 has been previously reported, the trifluoroacetate being either stable once formed or too unstable to be detected at all.[4,5]

In the presence of a hydrosilane, such as triethylsilane (TES) or dimethylphenylsilane (DMPS), the reaction of **2A** with TFA in dichloromethane gives both *anti* and *syn* [2-(3-ethoxythienyl)]diadamantylmethanes, **5A** and **5S**, but also the 3-hydroxy compound, **4**, the yield of **5S** increasing mainly at the expense of **4** as the hydrosilane concentration is increased (Table 1).||

Experiments with deuteriated dimethylphenylsilane (DMPS) show clearly that the *anti* deoxygenation product is formed by reduction of both the carbocation, **6**, and the carboxonium ion, **7**, in contrast to what is observed for **1A-Me**. There are two isotopically distinct isomers, one with the label on the diadamantylmethyl group, **5A**, and the other where the methylene of the ethoxy group is half-labelled, **8** (Scheme 1). The relative yields of all four components of the product mixture can be determined from the ^{1}H NMR spectrum.

If the steady state assumption is applied to the intermediate carbocation and carboxonium ion the relative yields can be evaluated in terms of the rate constants and the organosilane concentration. One obvious result is that the ratio of **5S** to **5A** should be a constant equal to k_2/k_3. The data confirm this expectation, the value being 2.21 ± 0.11. Other relationships, expressing product ratios in terms of rate constant ratios and the organosilane concentration, result from this treatment but, although the various plots are approximately linear, the resulting values of k_2/k_1, k_3/k_1 and k_4/k_5 vary widely. A more rigorous approach is to solve the kinetic differential equations by means of the kinetic analysis programme, KINAL,[9] using the yields of

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† Details of general methods, alcohol synthesis, trifluoroacetylation, ionic hydrogenation, DFT calculations and kinetic modelling are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/a9/a909571c/ otherwise available from BLDSC (SUPPL. NO. 57691, pp. 8) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

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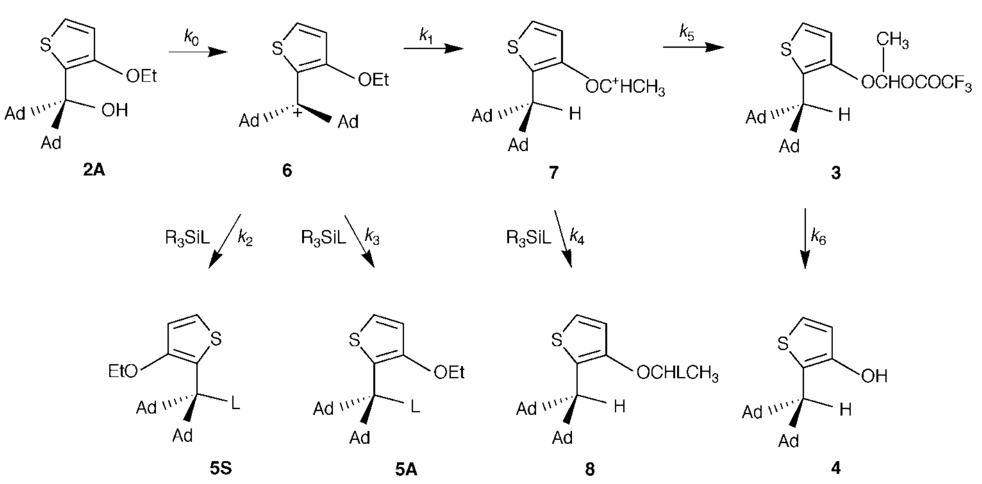

Scheme 1

Table 1 Relative yields (±1–2%) for reaction of 2-(3-ethoxythienyl)-di(1-adamantyl)methanol, **2A**, with TFA–hydrosilane in dichloromethane; $[\mathbf{2A}]_o = 0.018$–0.019; $[\mathrm{TFA}]_o = 0.48$–0.50

Hydrosilane	$[R_3SiL]_o$	%**5A**	%**5S**	%**4**	%**8**
TES-h	0.0726	53	11	37	
TES-h	0.1500	63	19	18	
TES-h	0.2245	61	28	11	
TES-h	0.2893	60	32	9	
DMPS-h	0.0760	45	36	19	
DMPS-h	0.1124	46	42	12	
DMPS-h	0.1502	46	45	9	
DMPS-h	0.1906	43	51	6	
DMPS-h	0.2228	44	52	4	
DMPS-h	0.2613	43	55	3	
DMPS-d	0.0750	12	24	33	31
DMPS-d	0.1115	15	33	21	32
DMPS-d	0.1526	17	38	14	31
DMPS-d	0.1875	18	43	11	27
DMPS-d	0.2207	20	44	9	27
DMPS-d	0.2600	22	47	6	25
DMPS-d	0.2958	22	49	6	24
TIPS-h	0.0753	30	0	70	
TTMSS-h	0.0760	23	5	73	

Data rounded to nearest integer: total = 100 ± 1%. Calculations performed on data before rounding.

the four products as targets for the optimization of three rate constants. This leads to average values of $k_2/k_1 = 5.81 \pm 0.32$ M^{-1}, $k_3/k_1 = 2.63 \pm 0.08$ M^{-1} and $k_4/k_5 = 14.7 \pm 0.9$ M^{-1} for the seven organosilane concentrations examined.

For normal DMPS the *anti* deoxygenation product, **5A**, is generated by two different routes which can be evaluated empirically by assuming that k_2/k_3 remains 2.21, *i.e.* that isotope effects are the same for these two reactions of the organosilane. The optimized rate constants now have substantially higher values: $k_2/k_1 = 10.3 \pm 0.6$ M^{-1}, $k_3/k_1 = 4.65 \pm 0.28$ M^{-1} and $k_4/k_5 = 22.2 \pm 2.3$ M^{-1}, making the corresponding kinetic deuterium isotope effects 1.77, 1.77 and 1.51, respectively, all with a margin of error of 10–20%. These values are slightly higher than those for cations derived from 2-alkoxyphenyl-diadamantylmethanols.[5] Values between 1.4 and 1.9 have been reported for other systems at 25 °C, the lowest values being considered as evidence for a SET mechanism,[10] though Mayr subsequently showed that they were compatible with a SHT mechanism,[11] which is, moreover, supported by *ab initio* calculations.[12]

Bulky hydrosilanes such as tris(trimethylsilyl)silane (TTMSS) and triisopropylsilane (TIPS) tend to give rather large amounts of **4** and smaller amounts of **5**, mainly or exclusively **5A**. This suggests that there is little direct reaction with the carbocation, especially for TIPS, and that products are formed by reduction of or nucleophilic attack on the carboxonium ion.

The ease with which 1,5-hydride transfer occurs in the carbocation from **2A** is consistent with the energy calculations which put it on a par with the 2-anisyl system, **1S-Me**. The major difference is that the carbocation from **1S-Me** is reduced only at the *anti* face, whereas that from **2A** is reduced at both faces. The calculated difference in the geometries of the carbocations means that the two faces are less differentiated in the 3-ethoxythienyl system and that the substituent does not lie in the approach trajectory of the hydrosilane to the charged carbon. This explains why both deoxygenation products can be formed by reduction of the same ion.

Notes and references

‡ This model is comparable in accuracy to B3LYP/6-311(d,p)//B3LYP/6-311(d,p), but is more economical on computer time and, most importantly, is parametrized for second-row elements.

§ 1 cal = 4.184 J.

¶ Since S has priority over C, the 2-(3-ethoxythienyl) isomer with OH close to ethoxy is denoted *anti*, whereas this situation for the 2-alkoxyphenyl derivatives corresponds to the *syn* isomer, C–OR having priority over CH.

|| We use the same conformational descriptor, *anti* or *syn*, for an alcohol and the alkane obtained by removal of the oxygen atom, despite the fact that OH and H do not have the same priority with respect to carbon.

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