Trifluoroacetylation and ionic hydrogenation of [2-(3-alkoxythienyl)]di(1-adamantyl)methanols †

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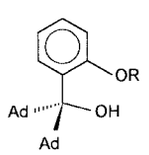
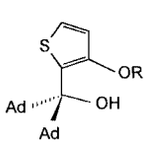
Lithiation of 3-alkoxythiophenes followed by reaction with di(1-adamantyl) ketone leads to *anti*-[2-(3-alkoxythienyl)]di(1-adamantyl)methanols where the C–OH proton is intramolecularly hydrogen-bonded to the alkoxy group. The structure of the 3-methoxy derivative was confirmed by a single crystal X-ray diffraction study. Reaction of this alcohol with trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) in dichloromethane gives a trifluoroacetate, the initially formed carbocation undergoing an intramolecular 1,5-hydride shift to give a carboxonium ion. However, in the absence of anhydride, trifluoroacetate is formed to the extent of about 15% only. Ionic hydrogenation with TFA and an organosilane in dichloromethane gives *syn*- and *anti*-[2-(3-methoxythienyl)]-diadamantylmethanes by reduction of the carbocation, with a preference for the isomer with the Ad_2CH hydrogen close to methoxy. The corresponding 3-ethoxy compound behaves quite differently: in TFA–dichloromethane a trifluoroacetate is formed which then eliminates acetaldehyde to give *anti*-[2-(3-hydroxythienyl)]diadamantylmethane. In the presence of an organosilane *syn*- and *anti*-[2-(3-ethoxythienyl)]diadamantylmethanes are formed together with the 3-hydroxy derivative. Isotope labelling experiments show that the *anti* deoxygenation product is obtained by reduction of both the carbocation and the carboxonium ion. The 3-isopropoxy derivative reacts sluggishly with TFA and, with an organosilane, tends to give preferentially the less stable, *syn* deoxygenation product. The activation energies for *syn* to *anti* rotation in the [2-(3-alkoxythienyl)]diadamantylmethanes indicate significant differences in the steric effects of the alkoxy groups.

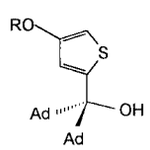
A carbocation in solution usually has several options available: do nothing (stable carbocations, usually in superacids), react with the solvent or other nucleophiles, undergo a sigmatropic shift leading to skeletal rearrangement, eliminate a proton to form an olefin, fragment to give a molecule and a smaller carbocation or undergo intramolecular hydride transfer. Most of these topics have been and continue to be studied extensively; we shall focus on hydride transfers. Hydride transfers involving 1,2 and 1,3 shifts are well documented, occurring mainly in norbornane derivatives,[1] but reports of higher-order transfers are comparatively rare.[2–5] If, however, one generates a carbocation in which all other options are closed, it is possible to observe 1,4- and 1,5-hydride transfers provided that there is a suitable substituent located at an appropriate distance[6] from the electron-deficient centre. *ortho*-Substituted aryldi(1-adamantyl)methyl cations generated in non-nucleophilic solvents meet these criteria, insofar as the adamantyl groups hinder nucleophilic attack, have no proton accessible for elimination and are highly reluctant to rearrange or to cleave. Reaction of (2-ethylphenyl)- or (2-isopropylphenyl)di(1-adamantyl)-methanols with TFA in dichloromethane is followed by a rapid intramolecular 1,4-hydride shift from the alkyl group.[4] In the same way, the carbocation obtained by reaction of (2-alkoxyphenyl)diadamantylmethanols, **1S-R**, undergoes an intramolecular 1,5-hydride shift from the alkoxy group, this being faster for ethoxy than for methoxy, to give a carboxonium ion.[5] This latter reacts with nucleophiles to give a trifluoroacetate and a phenoxymethanol, which is isolated as the corresponding phenol. In the presence of an organosilane, intermolecular reduction of the carbocation competes with the intramolecular reaction. We now present work on heteroaromatic analogues, the [2-(3-alkoxythienyl)]di(1-adamantyl)methanols, **2A-R** (R = Me, Et or iPr), which show rather different behaviour, with respect both to each other and to the previous structures.‡



1S-R



2A-R



3-R

Results and discussion

Alcohol synthesis and structure

Treatment of a 3-alkoxythiophene[8] with *n*-butyllithium in diethyl ether, followed by reaction with di(1-adamantyl) ketone, gives predominantly the 2-substituted derivatives, **2A-R** (R = Me, Et or iPr), with a small amount, *ca.* 10%, of another material identified as the 4-substituted isomer, **3-R**. A single crystal X-ray diffraction study on **2A-Me** established it as the *anti* isomer, *i.e.* the OH group being *anti* with respect to the

† Tables 5 and 6, with data for kinetic simulations of product compositions for the reaction of **2A** with TFA and dimethylphenylsilane or triethylsilane, are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b002186p/

‡ Part of this work has been presented as a Communication.[7]

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Table 1 Selected bond lengths, bond angles and torsion angles for *anti*-[2-(3-methoxythienyl)]di(1-adamantyl)methanol, **2A-Me**

Bond lengths/Å		Bond angles/°		Torsion angles/°	
S(1)–C(2)	1.722(1)	C(2)–S(1)–C(5)	93.8(1)	C(3)–C(2)–C(10)–O(11)	5
S(1)–C(5)	1.694(2)	C(2)–C(3)–O(1)	121.3(1)	C(3)–C(2)–C(10)–C(101)	117
C(2)–C(3)	1.371(2)	C(4)–C(3)–O(1)	124.1(1)	C(3)–C(2)–C(10)–C(201)	−109
C(3)–C(4)	1.426(2)	S(1)–C(2)–C(3)	108.0(1)	S(1)–C(2)–C(10)–O(11)	−172
C(4)–C(5)	1.337(2)	C(2)–C(3)–C(4)	114.6(1)	S(1)–C(2)–C(10)–C(101)	−60
C(3)–O(1)	1.370(2)	C(3)–C(4)–C(5)	111.8(1)	S(1)–C(2)–C(10)–C(201)	74
C(2)–C(10)	1.541(2)	S(1)–C(5)–C(4)	111.9(1)	C(2)–C(10)–C(101)–C(102)	−160
C(10)–C(101)	1.608(2)	S(1)–C(2)–C(10)	122.2(1)	C(2)–C(10)–C(101)–C(108)	78
C(10)–C(201)	1.599(2)	C(3)–C(2)–C(10)	129.8(1)	C(2)–C(10)–C(101)–C(109)	−43
		C(2)–C(10)–C(101)	109.5(1)	C(2)–C(10)–C(201)–C(202)	173
		C(2)–C(10)–C(201)	109.5(1)	C(2)–C(10)–C(201)–C(208)	56
		C(101)–C(10)–C(201)	120.7(1)	C(2)–C(10)–C(201)–C(209)	−63
				O(1)–C(3)–C(2)–C(10)	2
				C(6)–O(1)–C(3)–C(2)	170

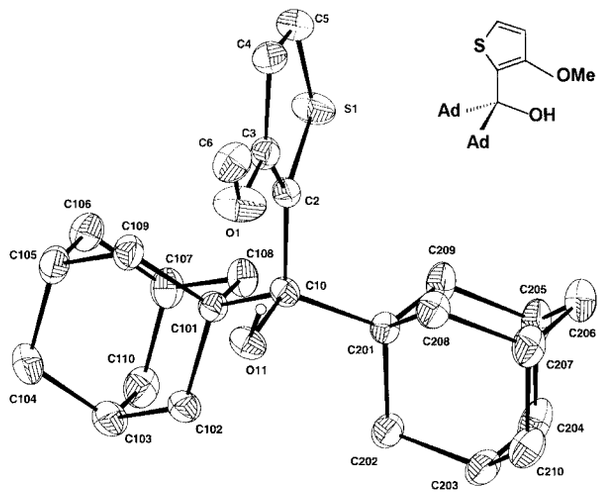


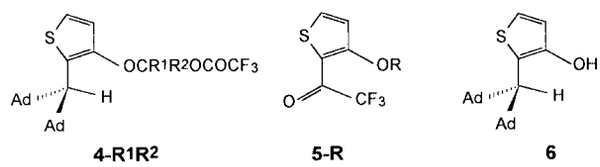
Fig. 1 CAMERON diagram for *anti*-[2-(3-methoxythienyl)]di(1-adamantyl)methanol, **2A-Me**, showing 30% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

sulfur atom, but close to the methoxy group.§ The hydroxy proton is at a distance of 1.78 Å from the methoxy oxygen atom, the O···O distance is 2.62 Å and the O–H···O angle 156°. These are fairly typical values for this type of hydrogen bond.[10] All other features (Table 1, Fig. 1) are consistent with those of aryl- and heteroaryldiadamantylmethyl derivatives previously studied.[4,11,12] The NMR and IR behaviour of these new alcohols is similar to that of the 2-alkoxyphenyl analogues, **1S**.[5] The ^{1}H NMR shifts are lower and the IR ν_{OH} frequencies slightly higher, indicating somewhat weaker hydrogen bonding.

Trifluoroacetylation of *anti*-[2-(3-alkoxythienyl)]di-(1-adamantyl)methanols

(i) *anti*-[2-(3-Methoxythienyl)]di(1-adamantyl)methanol, 2A-Me. Alcohol **2A-Me** was treated with TFA (4% v/v) in deuteriated dichloromethane at 25 °C in an NMR tube. ^{1}H NMR spectra taken over a period of 14 h show small CH_2 and CH signals at 5.90 and 2.73 ppm, respectively, but the large number of signals in the aromatic region indicates that several competing processes occur simultaneously and that 1,5-hydride transfer followed by trifluoroacetate formation is a minor process, representing only about 15% of the products. Addition of trifluoroacetic anhydride (TFAA, 4% v/v) to the alcohol before TFA considerably simplifies the situation, the ^{1}H NMR spectrum after about 2 h corresponding to trifluoroacetate, **4-HH**,

§ Since S has priority over C, the 2-(3-alkoxythienyl) isomer with OH close to alkoxy is denoted *anti*, whereas this situation for the 2-anisyl derivative corresponds to the *syn* isomer, C–OMe having priority over CH.[9]

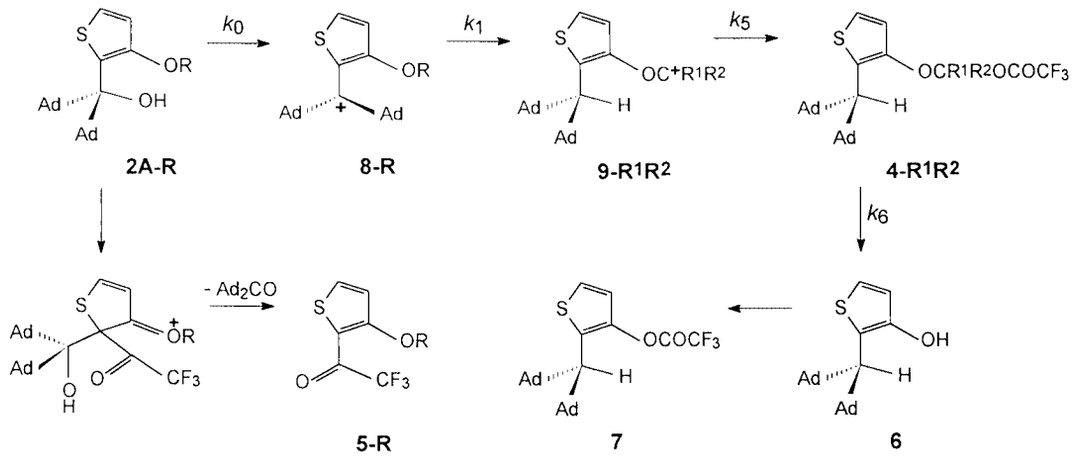


and another material, identified by its NMR and mass spectra as 2-(trifluoroacetyl)-3-methoxythiophene, **5-Me**, in a ratio of about 4.5:1. An estimate based on the ^{13}C NMR spectrum suggests that some 25% of the sample is diadamantyl ketone. Despite the slight discrepancy in the estimates, this and the trifluoroacetyl derivative no doubt result from trifluoroacetylation at the 2-position of the thiophene ring followed by dealkylation. A similar protiodealkylation occurs in the 2-(*N*-methylpyrrolyl) analogue.[12] The overall rate constant for trifluoroacetylation at the 2-position and at the methoxy group under these conditions, *ca*. 9.6×10^{-4} s^{-1}, is similar to that of the 2-anisyl derivative, 7×10^{-4} s^{-1}.[5]

Both 2- and 3-(trifluoroacetyl)thiophene have been reported;[13] the ^{1}H NMR spectrum of **5-Me** is consistent with that of the former, but the ^{13}C shifts of the two aromatic CH carbons in no way agree with additivity of the 3-OMe and 2-$COCF_3$ substituent effects. The quaternary carbons were assigned on the basis of the highly contrasted effects of the methoxy group on the position to which it is attached and upon the adjacent carbon.

Attempts to replace the diadamantylmethanol substituent by trifluoroacetyl by reaction of other (2-thienyl)diadamantylmethanols under the same conditions were fruitless.[14] This suggests that the intermediate formed by attack of trifluoroacetyl cation is necessarily stabilized by the 3-alkoxy group.

(ii) *anti*-[2-(3-Ethoxythienyl)]di(1-adamantyl)methanol, 2A-Et. ^{1}H NMR monitoring of the reaction of **2A-Et** with TFA (4% v/v) in dideuteriodichloromethane at 25 °C reveals that 1,5-hydride transfer occurs readily: a trifluoroacetate, **4-MeH**, is first formed, and this then eliminates the ethyl group in the form of acetaldehyde to give a 3-hydroxythienyl derivative, **6**, 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). From the rate of consumption of **2A-Et**, the position of the concentration maximum for **6** and kinetic simulation by KINAL,[15] the first-order rate constants for the reactions of the alcohol and the trifluoroacetate are estimated to be 4.7×10^{-3} and 2.9×10^{-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]



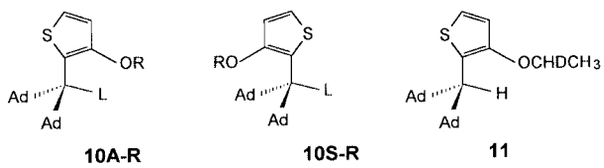
Scheme 1

(iii) ***anti*-[2-(3-Isopropoxythienyl)]di(1-adamantyl)methanol, 2A-iPr.** The reaction of **2A-iPr** with TFA under the same conditions as above is unexpectedly sluggish and leads to a considerable number of products. One which can be identified is the 3-hydroxythienyl compound, **6**; this represents about 50% of the products after 20 h, and is accompanied by acetone (singlet at 2.32 ppm). These are the products expected of 1,5-hydride transfer followed by acid-catalysed elimination of the isopropyl group. Running the same experiment in the presence of TFAA gives a more rapid (initial first-order rate constant, *ca.* 1.5×10^{-3} s^{-1}), somewhat cleaner reaction with one intermediate and two ultimate products. The intermediate is the 3-hydroxy derivative, **6**, and the minor product, representing about 8% of the aromatic signals, is recognizable as **5-Me**. The major product was identified by running the reaction on a larger scale, in non-deuteriated solvent, followed by aqueous work-up. The ^{13}C NMR spectrum shows it to contain a trifluoroacetate group, suggesting that it is the 3-(trifluoroacetoxy)thienyl derivative, **7**. This was confirmed by treating **6** with TFAA (4% v/v) in CD_2Cl_2 whereupon the same product was obtained; the reaction was accelerated by the addition of TFA (4% v/v) to give a first-order rate constant of *ca.* 2.1×10^{-3} s^{-1}, slightly greater than that for the disappearance of the alcohol under the same conditions. The analogous acetylation of various 3-hydroxythiophenes has been reported.[16]

The results for the three alcohols are compatible with the mechanism outlined in Scheme 1, where a carbocation **8-R** is first formed. This then undergoes a 1,5-hydride shift to give the carboxonium ion **9-R^{1}R^2**. This is the sole reaction of **2A-Et** in TFA whereas with **2A-Me** and **2A-iPr** there are several competing reactions. For these latter alcohols, in the presence of TFAA trifluoroacetylation at the 2-position, followed by elimination of diadamantyl ketone, to give **5-R** competes with 1,5-hydride transfer. Reaction of **9-R^{1}R^2** with trifluoroacetate anion leads to **4-R^{1}R^2** which, depending on the substituents at the carboxonium carbon, is stable (R^1 = R^2 = H), eliminates acetaldehyde at a measurable rate (R^1 = Me, R^2 = H) or is too unstable to be detected (R^1 = R^2 = Me).

Ionic hydrogenation of *anti*-[2-(3-alkoxythienyl)]di(1-adamantyl)-methanols

(i) ***anti*-[2-(3-Methoxythienyl)]di(1-adamantyl)methanol, 2A-Me.** Deoxygenation of the 3-methoxythienyl derivative in the presence of triethylsilane (TES) (TES:**2A-Me** = 4–16 : 1) gives in all cases a roughly 3 : 2 mixture of two isomeric [2-(3-methoxythienyl)]diadamantylmethanes, **10-Me** (Table 2). There is no evidence for the formation of trifluoroacetate, **4-HH**, and no reason, therefore, to believe that intramolecular hydride shift competes with intermolecular hydride transfer under these conditions. Equilibration of the **10-Me** mixture at 150 °C



results in an isomer ratio of about 17 : 1, the same material predominating; the major component is therefore more stable than the other isomer by about 2.2 kcal mol^{-1}.¶ Comparison of ^1H and ^{13}C NMR data with those for 2-thienyl and 2-(3-methylthienyl) derivatives[17] indicates that it is the *anti* isomer, **10A-Me**.‖ This structure is analogous to the *syn* isomer in the 2-anisyl system, with the Ad_2CH hydrogen in both cases close to the methoxy group.[5] In previous work it was found that the stability difference between the two [2-(3-methylthienyl)]-diadamantylmethane rotamers is greater than for the corresponding alcohols, about 4 and 2 kcal mol^{-1}, respectively. The finding that the difference is smaller for the [2-(3-methoxythienyl)]diadamantylmethanes is consistent with other evidence that the methoxy group is smaller than methyl in such situations.[18] Since it is the interaction of this substituent with the adamantyl groups which is responsible for the higher steric energy of the *syn* isomer, its size is important. When there is no substituent at the 3-position, then there is no difference in the stabilities of the *syn* and *anti* (2-thienyl)diadamantylmethanes.[17] This trend in steric effects on the difference in the energies of the rotamers is therefore monotonic.

Variation of the hydride donor leads to somewhat unexpected results: *n*-hexylsilane (NHS) gives only the more stable, *anti* isomer, while diphenylsilane (DPS) gives very predominantly this isomer, and dimethylphenylsilane (DMPS) slightly less so (Table 2). In the case of triphenylsilane (TPS) the reaction is slower but the isomer ratio is very similar to that for DPS. Only for the very bulky organosilane, tris(trimethylsilyl)-silane (TTMSS), is the less stable, *syn* isomer the major product. In this last case the reaction is slow and the ^1H NMR spectrum indicates that about 29% of the product mixture after 20 h is trifluoroacetate, **4-HH**. A similar inversion in the stereoselectivity of hydride transfer to a carbocation has been observed for *meta*-substituted aryldiadamantylmethyl cations,[19] where approach from the face remote from the substituent is much preferred for TTMSS as compared to smaller organosilanes.

The only effect of replacing normal TES by deuteriated TES (TES-*d*) is to eliminate the Ad_2CH signals of the product [2-(3-

¶ 1 cal = 4.184 J.

‖ 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.[9] This practice, though incorrect, has the advantage that analogous structures bear the same descriptor.

methoxythienyl)]diadamantylmethanes. The methyl groups are not affected and the isomer ratio is unchanged within experimental error. It is clear therefore that both isomers are formed by direct hydride transfer from the hydro- or deuterioorganosilane to the initially formed carbocation.

(ii) *anti*-[2-(3-Ethoxythienyl)]di(1-adamantyl)methanol, 2A-Et. In the presence of an organosilane, such as TES or DMPS, the reaction of **2A-Et** with TFA in dichloromethane gives both *anti* and *syn* [2-(3-ethoxythienyl)]diadamantylmethanes, **10A-Et** and **10S-Et**, but also the 3-hydroxy compound, **6**, the yield of **10S-Et** increasing mainly at the expense of **6** as the organosilane concentration is increased (Table 3).

Replacing DMPS by deuteriated material (DMPS-*d*) reveals that the *anti* deoxygenation product is formed by reduction of both the carbocation, **8-Et**, and the carboxonium ion, **9-MeH**, in contrast to what is observed for **1A-Me**.[5] There are two isotopically distinct isomers, one with the label on the diadamantylmethyl group, **10A-Et**, and the other where the methylene of the ethoxy group is half-labelled, **11** (Scheme 2). 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 expressed in terms of rate constant ratios and the organosilane concentration. An obvious result is that the ratio of **10S-Et** to **10A-Et** should be a constant equal to k_2/k_3: experimentally the value is 2.21 ± 0.11. Other expressions suggest linear relationships between k_2/k_1, k_3/k_1 and k_4/k_5 and the organosilane concentration, but the plots, though approximately linear, give unreliable values. A better approach is to solve the kinetic differential equations by means of KINAL,[15] using the yields of the four products as targets for the optimization of three rate constants. In fact, since the sum of the four yields is assumed to be 100%, there are only three independent values and a perfect fit is always obtained. This treatment 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 (Table 5, Supplementary Material).

For normal DMPS the *anti* deoxygenation product, **10A-Et**, 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] but remain within the range (between

Table 2 *syn*/*anti* Ratios (**10S-R : 10A-R**) for reduction of [2-(3-alkoxythienyl)]di(1-adamantyl)methanols, **2A-R**, by TFA–organosilane in dichloromethane at 20 ± 2 °C; $[\mathbf{2A\text{-}R}]_o = 0.0192$; $[TFA]_o = 0.5$; $[XYZSiH]_o = 0.076$

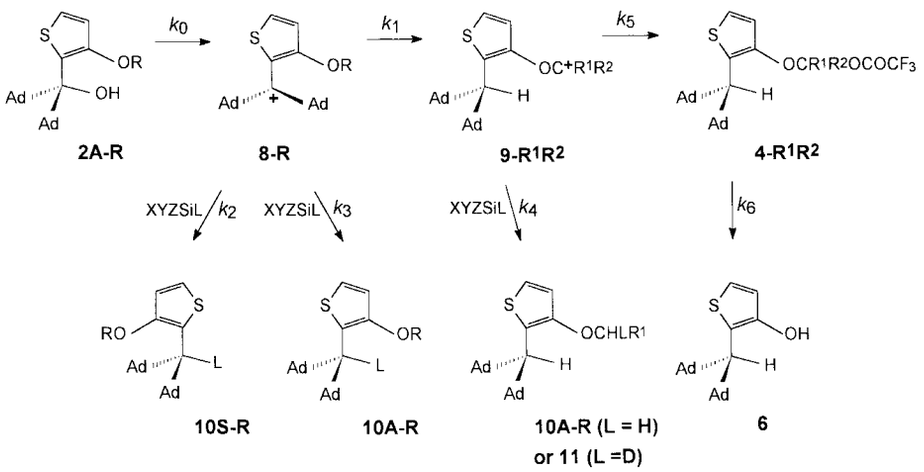
XYZSiH	R = Me	R = Et	R = i-Pr
NHS	≈0.02	>0.09 [a,b]	0.33
DPS	0.10	>0.37 [a,c]	2.5
TPS	0.11	— [a,d]	>50
TIPS	— [d]	0.0 [a,e]	— [d]
TES	0.36 [f]	3.2 [a,g]	≈50
DMPS	0.31	2.2 [a,g]	≈40 [h]
TTMSS	2.58 [i]	0.22 [a,j]	>50

[a] *anti* formed wholly or partly by reduction of carboxonium ion. [b] 6% *syn*, 67% *anti*. [c] 6% *syn*, 16% *anti*. [d] No reduction. [e] 30% *anti*. [f] Unchanged when TES-*h* is replaced by TES-*d*. [g] Several deuteriosilane concentrations (see text). [h] Unchanged when DMPS-*h* is replaced by DMPS-*d*. [i] After 20 h; 29 ± 3% of the product mixture is trifluoroacetate, **4-HH**. [j] 5% *syn*, 23% *anti*.

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

XYZSiL	$[XYZSiL]_o$	%**10A-Et**	%**10S-Et**	%**6**	%**11**
NHS-*h*	0.0755	68	6	26	
NHS-*h*	0.1495	81	8	11	
NHS-*h*	0.2260	85	8	7	
NHS-*h*	0.2905	86	8	6	
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	
TES-*d*	0.0750	2	8	42	48
TES-*d*	0.1459	4	16	25	56
TES-*d*	0.2173	8	21	18	53
TES-*d*	0.2849	9	24	13	54
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	

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



Scheme 2

1.4 and 1.9) reported for other systems at 25 °C. The lowest values were considered to support a single electron transfer (SET) mechanism,[20] but Mayr, working at −70 °C, subsequently showed that relatively small kinetic isotope effects were compatible with a synchronous hydride shift (SHT) mechanism.[21] Moreover, this mechanism is supported by *ab initio* calculations.[22]

It is difficult to perform the same experiments with any other organosilane, since the 3-hydroxy compound **6** tends to predominate. With TES-*d* the yield of **10A-Et** is so small that it is difficult to estimate accurately, which means that the **10S-Et**:**10A-Et** ratio is not well defined, particularly at low deuteriosilane concentration. However, a reasonable estimate by KINAL simulation would be 3.2, and this taken with the data for TES-*h* gives kinetic isotope effects similar to but slightly smaller than those for DMPS. Values of the rate constant ratios for TES-*d* are $k_2/k_1 = 1.32 \pm 0.06$ M^{-1}, $k_3/k_1 = 0.41 \pm 0.11$ M^{-1}, and $k_4/k_5 = 15.7 \pm 1.1$ M^{-1} for the four organosilane concentrations examined, and the corresponding isotope effects are 1.45, 1.45 and 1.32 (Table 6, Supplementary Material). Comparison of the rate constant ratios for the reactions of normal or labelled DMPS and TES with the [2-(3-ethoxythienyl)]-diadamantylmethyl cation shows that the latter is less reactive by a factor of 6.0 ± 1.5, whereas reactivities with the carboxonium ions are very similar. These results are consistent with what is observed for the 2-anisyldiadamantylmethyl cation.[5] However, the outstanding feature of these results is that the *syn*/*anti* ratio is for both DMPS and TES about 10 times higher than for the methoxy derivative. For NHS and DPS, in the absence of studies with labelled organosilanes, we can only set a lower limit to the *syn*/*anti* ratio, assuming (very improbably) that all **10A-Et** is formed by reduction of the carbocation. The values, 0.09 and 0.37, respectively, are already substantially higher than that for **2A-Me** (Table 2).

Bulky organosilanes such as TTMSS and triisopropylsilane (TIPS) tend to give rather large amounts of **6** and smaller amounts of **10-Et**, mainly or exclusively **10A-Et**. This suggests that there is little direct reaction with the carbocation, none in the case of TIPS, and that products are formed by reduction of or nucleophilic attack on the carboxonium ion.

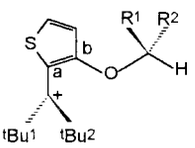
(iii) ***anti*-[2-(3-Isopropoxythienyl)]di(1-adamantyl)methanol, 2A-iPr.** Treatment of **2A-iPr** in dichloromethane with excess TES followed by TFA gives a single product, readily identified as *syn*-[2-(3-isopropoxythienyl)]diadamantylmethane, **10S-iPr**. Neither the *anti* isomer nor the 3-hydroxythienyl derivative could be detected. This means that 1,5-hydride transfer is much slower than intermolecular hydride transfer with this reagent, and that the organosilane approaches the carbocation exclusively from the face remote from the isopropoxy group. A similar result is obtained with DMPS, while NHS and DPS give *syn*/*anti* ratios substantially greater than for the methoxy and ethoxy derivatives (Table 2). Reaction with TPS and TTMSS gives essentially the 3-hydroxy derivative, **6**, and other unidentified products; the non-polar fraction isolated by alumina chromatography contained only **10S-iPr**. With TIPS there is no deoxygenation product. Reaction with deuteriated DMPS gives again **10S-iPr** but with the Ad_2CH hydrogen replaced by deuterium.

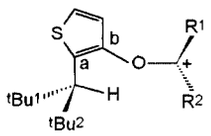
Rotation barriers for *anti*-[2-(3-alkoxythienyl)]di(1-adamantyl)-methanes

Activation energies for rotation about the sp^2–sp^3 C–C bond in aryl- and heteroaryldiadamantylmethyl derivatives are an indication of the steric requirements of the ring systems and of any substituent close to the relevant bond.[17] Though interaction between an *ortho* substituent in a benzenoid system (or a 3-substituent in five-membered heterocyclics) and the adamantyl groups destabilizes the ground state, the effect is significantly greater in the rotation transition state. Consequently, the more bulky the substituent, the greater the rotation barrier. It was interesting therefore to measure the barriers for the *anti*-[2-(3-alkoxythienyl)]di(1-adamantyl)methanes prepared in this work. In the case of the 3-methoxy derivative the product obtained by deoxygenation consists largely of the *syn* isomer, **10S-Me**, but a mixture enriched with the *anti* isomer can be obtained by crystallizing out the *syn* from *n*-hexane. The rotation barrier for **10A-Me**, measured in chloroform at 130 °C, is 28.5 kcal mol^{-1}. This value fits in neatly between those previously determined for the systems where there is methyl (34.6 kcal mol^{-1} at 178 °C) or hydrogen (20.2 kcal mol^{-1} at 87–137 °C) at the 3-position.[17] This order of substituent effect on rotation barriers has been observed elsewhere.[18] Activation energies for **10A-Et** and **10A-iPr** under the same conditions are 29.6 and 30.8 kcal mol^{-1}, respectively.

Intuitively, one would expect that the steric energy of the rotation transition state would be governed by interactions between the common oxygen atom and the closest adamantyl group, with the variable alkyl group too remote to have any effect. Yet these results seem to show that both ethyl and isopropyl are significantly more space-demanding than the methyl group in this situation. The only structural feature that rotation and hydride transfer from an organosilane to the carbocation have in common is that the adamantyl group bonds to the Ad_2C carbon are at about 30° to the plane of the thiophene ring, but the adamantyls are both on one side of the plane in rotation, on opposite sides in hydride transfer. Moreover, in hydride transfer there is the organosilane to take into consideration. Nevertheless, the fact remains that in both reactions the more extended

Table 4 Calculated heats of formation (kcal mol^{-1}) and selected torsion angles (°) for [2-(3-alkoxythienyl)]di(*tert*-butyl)methyl cations and the corresponding carboxonium ions





R	Me[a]	Et[b]	iPr[c]	iPr[c]	Me[a]	Et[b]	iPr[c]
ΔH_f°	77.7	62.6	49.4	46.1	79.2	58.0	48.3
Cb–Ca–C–tBu[1]	32	31	31	38	114	115	115
Cb–Ca–C–tBu[2]	−150	−150	−150	−146	−107	−107	−107
Ca–Cb–O–C	180	173	171	178	178	175	130
Cb–O–C–R^1	—	178	−153[d]	69	—	180	178
Cb–O–C–R^2	—	—	85[d]	−62	—	—	2

[a] $R^1 = R^2 = H$. [b] R^1 = Me, R^2 = H. [c] $R^1 = R^2$ = Me. [d] This conformation has a lower STO-3G energy than the other.

alkoxy groups appear to be more space-demanding. Moreover, the differences in activation energy involved are of a similar order of magnitude. For example, for DPS, going from a *syn*/*anti* ratio of 0.1 to 2.5 represents an overall swing in the activation energy of 1.9 kcal mol^{-1} as 3-OMe is replaced by 3-OiPr.

DFT quantum mechanical calculations

It was of interest to determine theoretically the energies of the carbocation and carboxonium ion intermediates implicated in this work and that on the *ortho*-anisyl analogues. Semiempirical methods have been found to be unreliable for comparing rotamer energies; *ab initio* methods are excessively time-consuming for large species. We therefore compromised by replacing the 1-adamantyl groups by *tert*-butyls and applying low-level DFT calculations using the X*a*(3-21G)//STO-3G method. This method has been shown to be at least as good as and more economical on computer time than the more sophisticated self-consistent hybrid B3LYP model using the 6-311G(*d*,*p*) basis. It is, moreover, adequately parametrized for second-row elements, which B3LYP is not.[23]

The calculations 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. 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 81° to that of the aryl ring, in the former this value falls to 31° (Table 4).

The calculations (though by no means quantitative, insofar as solvation has been neglected) are in agreement with the experimental observation that formation of the carboxonium ion is easy from **1S-Me**[5] and comparatively difficult from **2A-Me**. Another interesting point is that the calculated difference in the geometries of the carbocations means that the two faces are less differentiated in the 3-methoxythienyl system and that the substituent is more remote from the charged carbon and does not lie in the approach trajectory of the organosilane. This clearly is consistent with the fact that deoxygenation products are formed by reduction of the same ion, though it does not explain why small organosilanes appear to approach predominantly from the side closest to the methoxy group.

Replacement of the methoxy group by ethoxy in either structure has, of course, a marked effect upon the stability of the 1,5-hydride shifted cation, because the ion is now formally secondary rather than primary. This difference is most pronounced in the 2-alkoxyphenyl series where the difference between carbocation and carboxonium ion is now 14.3 kcal mol^{-1} in favour of the latter. The difference is much smaller, only 4.7 kcal mol^{-1}, for the 3-ethoxythienyl system. Calculations on the 3-isopropoxythienyl derivatives indicate, rather surprisingly, that further methylation of the formally positively charged carbon of the carboxonium ion does not increase its relative stability. The carboxonium ion from the 3-isopropoxythienyl derivative is calculated to be only 1.1 kcal mol^{-1} more stable or 2.2 kcal mol^{-1} less stable (depending on the conformation considered) than the corresponding carbocation. The O–CHR^1R^2 bond, which for the Me and Et derivatives is in the plane of the ring, is swung about 50° out of the plane, presumably to reduce steric interactions, but at the same time this reduces charge delocalization by the ring. The carboxonium ion from the 2-isopropoxyphenyl analogue is only slightly more stable relative to the carbocation than for the 2-ethoxyphenyl derivative, by 15.6 and 14.3 kcal mol^{-1}, respectively.

These results are qualitatively consistent with the experimental observation that, of the three 3-alkoxythienyl derivatives studied, only the 3-ethoxy undergoes 1,5-hydride transfer readily. The energy calculations 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 those from **2A-Me** and **2A-Et** are reduced at both faces. On going from 3-methoxy to 3-ethoxy, however, there is a marked shift towards attack at the *syn* face of the carbocation, despite the fact that this latter group is in a fully staggered conformation with the terminal methyl as far away from the cationic centre and the ring as is possible.

The 3-isopropoxy group causes little or no change in the interplanar angle (31° or 38°, depending on the conformation, as compared to 31–32° for OMe and OEt). One of the methyl groups must project out of the plane, but it is hard to appreciate intuitively why this should have such a dramatic effect upon the *syn*/*anti* ratio.

Conclusion

A heteroaromatic with an alkoxy group adjacent to the position where lithiation takes place gives an intramolecularly hydrogen-bonded alcohol when the organolithium compound is added to a highly congested ketone.

In contrast to the 2-anisyl analogue, where intermolecular hydride transfer takes place exclusively *anti* to the methoxy group, with the carbocation derived from the 2-(3-methoxythienyl) compound, **2A-Me**, this reaction occurs preferentially at the face closest to the methoxy group. A partial explanation of this finding is provided by DFT calculations which indi-

cate that the carbocation is more nearly coplanar with the (hetero)aryl ring in the thienyl than in the benzenoid system. The [2-(3-methoxythienyl)]diadamantylmethyl cation is thermodynamically favoured with respect to the 1,5-hydride-shifted carboxonium ion and, in the absence of a water scavenger, its formation can be followed by a variety of reactions, of which trifluoroacetylation at methoxy is of minor importance. The corresponding 3-ethoxythienyl derivative, **2A-Et**, reacts rather differently: because the carboxonium ion formed by 1,5 transfer of a methylene proton can be stabilized by the methyl group this reaction occurs much more readily. The resulting species reacts either with trifluoroacetate anion to form an unstable trifluoroacetate, which then loses acetaldehyde to give a 3-hydroxy derivative, or is reduced by an organosilane to give the *anti* deoxygenation product. This same product is, however, also formed by reduction of the original carbocation, at the same time as the *syn* isomer, but *syn* isomer formation is much favoured as compared to **2A-Me**. For **2A-iPr** trifluoroacetylation is again slow, because of steric hindrance to stabilization of the carboxonium ion by conjugation with the ring, and the carbocation is reduced by the more reactive organosilanes with a marked preference for hydride transfer to the face of the carbocation remote from the 3-substituent. The rotation barriers for the [2-(3-alkoxythienyl)]diadamantylmethanes show a monotonic increase with the effective size of the alkoxy group on going from OMe to OEt to OiPr. One would have predicted that the steric energy of the rotation transition state was governed by interactions between the common oxygen atom and the closest adamantyl group, with the alkyl group too remote to have any effect. This is clearly not the case, and the alkyl group is seen to have a parallel effect upon the stereoselectivity of carbocation reduction.

Experimental

General methods

NMR measurements were performed on a Bruker AS 200 FT instrument operating at 200 MHz (proton) or 50 MHz (carbon). Chemical shifts are given in ppm and J values in Hz; coupling constants below 0.5 Hz were not determined systematically. Measurements were made in hexadeuteriobenzene, deuteriochloroform, pentadeuteriopyridine, hexadeuteriodimethyl sulfoxide or dichlorodideuteriomethane (reference values: $\delta_H = 7.16$, 7.26, 8.71, 2.50 and 5.32 ppm for ^{1}H; $\delta_C = 128.0$, 77.0, 149.9, 39.5 and 53.8 ppm for ^{13}C). Carbon and hydrogen shifts of the heterocyclic system are numbered: C2, C3, *etc*. Generally, the proton signals were assigned on the basis of shifts, coupling constants[24] and spectrum simulation by the gNMR programme (Cherwell Scientific).[25] The corresponding ^{13}C signals were identified by heteronuclear correlation experiments. IR spectra were measured in carbon tetrachloride on a Nicolet Magna 860 FTIR spectrometer with 1 cm^{-1} resolution. GC/MS measurements were performed on a CP-Sil 5 capillary column coupled to a Finnigan MAT ITD 800B Ion Trap Detector with chemical ionization (isobutane) or electron impact. Gas chromatography was performed on a 30 cm 10% SE30 on Chrompack column. Column chromatography was performed on silica gel 60 (Merck) in light petroleum (boiling range 35–60 °C)–dichloromethane mixtures or on alumina (Merck, Brockmann III) in light petroleum–diethyl ether mixtures. Melting points were determined in capillary glass tubes on a Mettler FP5 instrument with a heating rate of 3 °C min^{-1}.

Synthesis of [2-(3-alkoxythienyl)]di(1-adamantyl)methanols

To a solution of 3-alkoxythiophene[8] (5 mmol) and TMEDA (0.75 cm^3, 5 mmol) in sodium–dry diethyl ether (15 cm^3) stirred at room temperature under argon was added a solution of *n*-butyllithium in hexane (1.6 M, 3 cm^3, 4.8 mmol). After 30 min di(1-adamantyl) ketone (0.30 g, 1.0 mmol, no solvent) was added. After 0.5–1 h the reaction mixture was quenched with water and the organic material extracted with hexane, washed with water and dried. Evaporation of the solvents gave a brown residue which was purified by column chromatography on alumina to give the required alcohol and mixed fractions containing also the isomeric [2-(4-alkoxythienyl)]di(1-adamantyl)-methanol, **3-R**, identified by its ^{1}H and ^{13}C NMR spectra; no attempt was made to purify this material or to characterize it further.

***anti*-[2-(3-Methoxythienyl)]di(1-adamantyl)methanol, 2A-Me.** Yield 77%; mp 167 °C (hexane); ν_{OH}/cm^{-1} (CCl_4) 3511; δ_C (chloroform) 29.3 (6 CH), 37.1 (6 CH_2), 38.6 (6 CH_2), 46.0 (2 C_q), 60.1 (CH_3), 87.3 (OH), 116.0 (C4), 120.9 (C5), 123.8 (C2) and 155.1 (C3); δ_H (chloroform) 1.60–2.2 (br m, Ad), 3.84 (CH_3), 5.80 (OH, constant for 0.00032–0.16 M), 6.82 (H4, J 5.6) and 7.08 (H5, J 5.6); δ_H(OH) 6.01, 5.78 and 6.05 ppm in C_6D_6, DMSO-d_6 and C_5D_5N, respectively; $\Delta\delta/\Delta T = -1.77 \pm 0.07$ ppb/°C in the last solvent. (Found: C, 75.4; H, 8.9; S, 7.8. $C_{26}H_{36}O_2S$ requires C, 75.68; H, 8.79; S, 7.77%). **3-Me** (9%, impure): δ_C (chloroform) 29.1 (6 CH), 36.9 (6 CH_2), 38.7 (6 CH_2), 44.9 (2 C_q), 56.8 (CH_3), 84.4 (OH), 93.2 (C5), 115.8 (C3), 150.3 (C2) and 157.0 (C4); δ_H (chloroform) 1.60–2.2 (br m, Ad), 2.31 (OH), 3.81 (CH_3), 6.10 (H5, J 1.5) and 6.62 (H3, J 1.5).

***anti*-[2-(3-Ethoxythienyl)]di(1-adamantyl)methanol, 2A-Et.** Yield 79%; mp 150 °C (hexane); ν_{OH}/cm^{-1} (CCl_4) 3495; δ_C (chloroform) 15.3 (CH_3), 29.3 (6 CH), 37.2 (6 CH_2), 38.7 (6 CH_2), 46.0 (2 C_q), 68.8 (CH_2), 87.3 (OH), 116.5 (C4), 120.8 (C5), 124.0 (C2) and 154.2 (C3); δ_H (chloroform) 1.39 (CH_3, J 7.0), 1.6–2.2 (br m, Ad), 4.08 (CH_2, J 7.0), 6.02 (OH), 6.79 (H4, J 5.6) and 7.07 (H5, J 5.6); δ_H(OH) 6.25, 5.96 and 6.29 ppm in C_6D_6, DMSO-d_6 and C_5D_5N, respectively; $\Delta\delta/\Delta T = -1.91 \pm 0.03$ ppb/°C in the last solvent. (Found: C, 76.1; H, 8.9; S, 7.3. $C_{27}H_{38}O_2S$ requires C, 76.01; H, 8.98; S, 7.50%). **3-Et** (7%, impure): δ_C (chloroform) 14.8 (CH_3), 29.0 (6 CH), 36.9 (6 CH_2), 38.7 (6 CH_2), 44.9 (2 C_q), 65.0 (CH_2), 84.4 (OH), 93.6 (C5), 115.8 (C3), 150.0 (C2) and 156.1 (C4); δ_H (chloroform) 1.43 (CH_3, J 7.0), 1.60–2.2 (br m, Ad), 2.30 (OH), 4.01 (CH_2, J 7.0), 6.08 (H5, J 1.6) and 6.63 (H3, J 1.6).

***anti*-[2-(3-Isopropoxythienyl)]di(1-adamantyl)methanol, 2A-iPr.** Yield 73%; mp 146 °C (methanol); ν_{OH}/cm^{-1} (CCl_4) 3486; δ_C (chloroform) 22.4 (2 CH_3), 29.3 (6 CH), 37.2 (6 CH_2), 38.7 (6 CH_2), 46.1 (2 C_q), 75.0 (CH), 87.3 (OH), 116.5 (C4), 120.7 (C5), 124.3 (C2) and 152.9 (C3); δ_H (chloroform) 1.34 (CH_3, J 6.1), 1.61 and 1.8–2.1 (br m, Ad), 4.46 (CH, J 6.1), 6.09 (OH), 6.78 (H4, J 5.6) and 7.07 (H5, J 5.6); δ_H(OH) 6.29, 6.01 and 6.34 ppm in C_6D_6, DMSO-d_6 and C_5D_5N, respectively; $\Delta\delta/\Delta T = -1.93 \pm 0.04$ ppb/°C in the last solvent. (Found: C, 76.3; H, 9.3; S, 7.2. $C_{28}H_{40}O_2S$ requires C, 76.32; H, 9.16; S, 7.26%). **3-iPr** (10%, impure): δ_C (chloroform) 22.0 (2 CH_3), 29.0 (6 CH), 36.9 (6 CH_2), 38.7 (6 CH_2), 44.9 (2 C_q), 71.9 (CH), 84.4 (OH), 95.4 (C5), 116.6 (C3), 149.6 (C2) and 154.7 (C4); δ_H (chloroform) 1.36 (CH_3, J 6.1), 1.60–2.2 (br m, Ad), 2.29 (OH), 4.40 (CH, J 6.1), 6.09 (H5, J 1.4) and 6.60 (H3, J 1.4).

Trifluoroacetylation of [2-(3-alkoxythienyl)]di(1-adamantyl)-methanols

***anti*-[2-(3-Methoxythienyl)]di(1-adamantyl)methanol, 2A-Me.** *NMR study.* (i) Alcohol **2A-Me** (*ca*. 10 mg, 0.024 mmol) was treated with TFA (0.02 cm^3) in deuteriated dichloromethane (0.5 cm^3) at 25 °C. The ^{1}H NMR spectrum showed over 14 h slow changes in the aromatic region, with the appearance of several new 5.5 Hz doublets, and of signals attributable to trifluoroacetate **4-HH** at 7.13, 5.90 and 2.75 ppm, corresponding to about 15% conversion.

(ii) To the alcohol (12 mg, 0.03 mmol) in deuteriated

dichloromethane (0.5 cm^3) were added successively trifluoroacetic anhydride (0.02 cm^3) and TFA (0.02 cm^3). The ^1H NMR spectrum showed progressive appearance of CH_2 and benzylic CH peaks at 5.90 and 2.74 ppm, respectively, at the expense of the methyl signal at 3.90 ppm, as well as doublets centred at 7.14 and 6.91 ppm. After 2 h these new signals, attributed to a trifluoroacetate, **4-HH**, represented 82% of the aromatics, coupled proton signals at 7.92 and 6.98 ppm, associated with a methyl group signal at 4.05 ppm, accounting for the rest. First-order rate constant, based on the rate of disappearance of the alcohol, $9.6 \pm 0.6 \times 10^{-4}$ s^{-1} (4 runs).

Aqueous work-up. Alcohol **2A-Me** (103 mg, 0.25 mmol) was stirred with TFA (0.2 cm^3) and TFAA (0.2 cm^3) in dichloromethane (5 cm^3) at room temperature for 3 h and then quenched. GC-MS indicated that the residue after washing, drying and evaporation of solvent consisted of: diadamantyl ketone: *m/z* (ITD-CI) 300, 299 (M+1, 80%), 298, 297, 269, 136, 135 (100%), 107, 93, 79; trifluoroacetate, **4-HH**: *m/z* (ITD-CI) 509, 508 (M, 23%), 507, 506, 396, 395, 373, 259, 136, 135 (100%), 107, 93, 79; δ_C (chloroform) 29.1 (6 CH), 36.9 (6 CH_2), 39.2 (2 C_q), 42.4 (6 CH_2), 57.8 (CH), 90.7 (CH_2), 114.3 (CF_3, *J* 286), 115.9 (C4), 121.2 (C5), 126.5 (C2), 151.0 (C3) and 156.6 (CO, *J* 43); δ_H (chloroform) 1.60–2.1 (br m, Ad), 2.72 (br, Ad_2CH), 5.87 (CH_2), 6.88 (H4, *J* 5.5) and 7.09 (H5, *J* 0.7 and 5.5); 2-(trifluoroacetyl)-3-methoxythiophene, **5-Me**: *m/z* (ITD-CI) 212, 211 (M+1, 100%), 210, 141; *m/z* (ITD-EI) 210, 141 (100%), 126, 98, 70, 69, 46, 45; δ_C (chloroform) 59.2 (CH_3), 113.9 (C2), 116.0 (C4), 116.3 (CF_3, *J* 289), 137.4 (C5), 164.9 (C3) and 172.1 (CO, *J* 38); δ_H (chloroform) 4.03 (CH_3), 6.91 (H4, *J* 5.5) and 7.75 (H5, *J* 5.5). Two minor products (<5%) detected by GC-MS were not identified. The ^{13}C NMR spectrum indicated that about 25% of the CH_2 and CH signals associated with the adamantane group were attributable to diadamantyl ketone. On a larger scale, the residue was taken up in boiling hexane, treated with animal charcoal, filtered and allowed to crystallize at 0 °C to give **4-HH** as a white solid, mp 142 °C (Found: C, 66.0; H, 7.1. $C_{28}H_{35}F_3O_3S$ requires C, 66.12; H, 6.94%).

***anti*-[2-(3-Ethoxythienyl)]di(1-adamantyl)methanol, 2A-Et.** *NMR study.* Alcohol **2A-Et** (*ca.* 10 mg, 0.023 mmol) was treated with TFA (0.02 cm^3) in deuteriated dichloromethane (0.5 cm^3) at 25 °C. The ^1H NMR spectrum showed over 30 min changes in the aromatic region, with the appearance of 5.5 Hz doublets, indicating the formation of a new material which then disappeared in favour of a second compound; this latter was completely degraded overnight. Associated changes in the aliphatic part of the spectrum indicated that the first compound was a trifluoroacetate, **4-MeH**, and the second a hydroxy derivative, **6**, accompanied by acetaldehyde. **2A-Et**: δ_H (dichloromethane–TFA) 1.38 (CH_3, *J* 7.0), 1.5–2.1 (br m, Ad), 4.16 (CH_2, *J* 7.0), 6.79 (H4, *J* 5.5) and 7.18 (H5, *J* 5.5); **4-MeH**: δ_H (dichloromethane–TFA) 1.5–2.1 (br m, Ad), 1.75 (CH_3, *J* 5.1), 2.74 (br, Ad_2CH), 6.51 (CH_3CH, *J* 5.1), 6.85 (H4, *J* 5.5) and 7.10 (H5, *J* 0.8 and 5.5); **6**: δ_H (dichloromethane–TFA) 1.5–2.1 (br m, Ad), 2.42 (br, Ad_2CH), 6.71 (H4, *J* 5.5) and 7.04 (H5, *J* 0.8 and 5.5); acetaldehyde: δ_H (dichloromethane–TFA) 2.34 (CH_3, *J* 3.1) and 9.75 (CH). Integration of the various signals gave the relative concentrations of **2A-Et**, **4-MeH** and **6**, from which rough first-order rate constants for the two successive reactions ($4.7 \pm 1.0 \times 10^{-3}$ and $2.9 \pm 0.3 \times 10^{-3}$ s^{-1}) were evaluated from the rate of disappearance of **2A-Et**, the position of the maximum in the concentration of **4-MeH** and by simulation.[15] Due to degradation of **6** the total integrated intensity of the identifiable products fell by about 15% during the course of a run. This was simulated by postulating a first-order rate constant for this reaction.

Aqueous work-up. A solution of alcohol **2A-Et** (0.34 g; 0.8 mmol) in dichloromethane (20 cm^3) under argon at room temperature was stirred for 45 min with TFA (0.8 cm^3). After quenching with water and pentane, washing with water, drying and evaporation of solvent, the yellow residue was chromatographed on silica gel to give **6** (0.185 g, 61%): mp 206 °C (hexane); ν_{OH}/cm^{-1} (CCl_4) 3600, 3616; δ_C (chloroform) 29.1 (6 CH), 36.9 (6 CH_2), 39.2 (2 C_q), 42.5 (6 CH_2), 58.9 (CH), 118.1 (C4), 119.3 (C2), 120.1 (C5) and 151.3 (C3); δ_H (chloroform) 1.5–2.1 (br m, Ad), 2.41 (Ad_2CH), 4.33 (OH), 6.67 (H4, *J* 5.4) and 6.98 (H5, *J* 5.5). (Found: C, 78.2; H, 8.8; S, 8.1. $C_{25}H_{34}OS$ requires C, 78.49; H, 8.96; S, 8.36%).

***anti*-[2-(3-Isopropoxythienyl)]di(1-adamantyl)methanol, 2A-iPr.** *NMR study.* (i) Alcohol **2A-iPr** (*ca.* 11 mg, 0.023 mmol) was treated with TFA (0.02 cm^3) in deuteriated dichloromethane (0.5 cm^3) at 25 °C. Over about 2 h the ^1H NMR spectrum showed changes in the aromatic region, with the appearance of 5.5 Hz doublets, at 7.21 and 6.77 ppm and at 7.04 and 6.71 ppm. The latter were associated with a peak at 2.42 ppm, indicating that these signals correspond to the 3-hydroxy derivative, **6**; they make up about 50% of the aromatic proton signals after 20 h. Compound **6** was accompanied by a 6 times stronger signal at 2.32 ppm, characteristic of acetone. The other major product is clearly neither a trifluoroacetate nor a 2-trifluoroacetyl derivative, but could not be identified. The appearance of a multitude of small peaks in the 2–5 ppm range indicated considerable degradation of the thiophene system.

(ii) To the alcohol (12 mg, 0.03 mmol) in deuteriated dichloromethane (0.5 cm^3) were added successively TFAA (0.02 cm^3) and TFA (0.02 cm^3). Inspection of the ^1H NMR spectrum showed that the initial product was the 3-hydroxy derivative, **6**, accompanied by acetone, but that this was progressively replaced by a species with aromatic doublets at 7.23 and 7.02 ppm and a Ad_2CH peak at 2.58 ppm; a minor product, *ca.* 8%, identified as **5-iPr**, gave 5.5 Hz doublets at 7.90 and 6.92 ppm, a 5.9 Hz multiplet at 4.71 ppm and an associated doublet at 1.41 ppm. Initial (*ca.* one half-life) first-order rate constant, based on the disappearance of the alcohol signals at 7.18 and 6.85 ppm, $1.53 \pm 0.09 \times 10^{-3}$ s^{-1} (3 runs).

Aqueous work-up. As for **2A-Me**, alcohol **2A-iPr** (110 mg, 0.25 mmol) was stirred with TFA (0.2 cm^3) and TFAA (0.2 cm^3) in dichloromethane (5 cm^3) at room temperature for 2 h and then quenched. The residue after work-up consisted essentially of: diadamantyl ketone; [2-(3-trifluoroacetoxythienyl)]diadamantylmethane, **7**: *m/z* (ITD-CI) 479, 478 (M, 21%), 384, 380, 341, 340, 231, 135 (100%), 107, 93, 79; δ_C (chloroform) 29.0 (6 CH), 36.8 (6 CH_2), 39.2 (2 C_q), 42.4 (6 CH_2), 58.9 (CH), 114.6 (CF_3, *J* 286), 118.7 (C4), 121.5 (C5), 131.0 (C2), 142.9 (C3) and 155.1 (CO, *J* 43); δ_H (chloroform) 1.60–2.1 (br m, Ad), 2.58 (Ad_2CH), 5.87 (CH_2), 7.02 (H4, *J* 5.6) and 7.18 (H5, *J* 5.6); 2-(trifluoroacetyl)-3-isopropoxythiophene, **5-iPr**: *m/z* (ITD-CI) 240, 239 (M+1, 100%), 237, 197, 196, 127, 79; δ_C (chloroform) 21.8 (2 CH_3), 75.3 (CH), 115.7 (C2), 116.4 (CF_3, *J* 289), 117.0 (C4), 137.7 (C5), 162.7 (C3) and 172.4 (CO, *J* 38); δ_H (chloroform) 1.41 (CH_3, *J* 5.9), 4.64 (CH, *J* 5.9), 6.85 (H4, *J* 5.5) and 7.72 (H5, *J* 5.5).

Trifluoroacetylation of [2-(3-hydroxythienyl)]di(1-adamantyl)-methane

To **6** (12 mg, 0.03 mmol) in deuteriated dichloromethane (0.5 cm^3) at 25 °C was added TFAA (0.02 cm^3) and TFA (0.02 cm^3). The aromatic proton signals at 7.04 and 6.71 ppm were progressively replaced by those of **7** at 7.23 and 7.02 ppm. First-order rate constant, based on the rate of disappearance of the Ad_2CH signal, $2.1 \pm 0.3 \times 10^{-3}$ s^{-1} (3 runs). On a larger scale, **6** (100 mg, 0.25 mmol) was treated with TFAA (0.5 cm^3) and TFA (0.5 cm^3) in dichloromethane (10 cm^3) at room temperature for 1 h under argon. The residue after quenching, extraction with pentane, washing with water, drying and evaporation of the solvent, was triturated with pentane to give **7** as an off-white

solid, mp 135 °C (Found: C, 67.7; H, 7.2. $C_{27}H_{33}F_3O_2S$ requires C, 67.76; H, 6.95%).

Ionic hydrogenation of [2-(3-alkoxythienyl)]di(1-adamantyl)-methanols

***anti*-[2-(3-Methoxythienyl)]di(1-adamantyl)methanol, 2A-Me.** Treatment of alcohol **2A-Me** (150 mg, 0.36 mmol) in dichloromethane (15 cm^3) with TES (0.2 cm^3, 1.25 mmol) and TFA (0.75 cm^3) at room temperature for 1 h gave [2-(3-methoxythienyl)]di(1-adamantyl)methanes, **10A-Me** and **10S-Me**, in a ratio of about 3:2 (133 mg, 91%). **10A-Me**: δ_C (chloroform) 29.2 (6 CH), 37.0 (6 CH_2), 39.2 (2 C_q), 42.4 (6 CH_2), 57.4 (CH), 58.9 (CH_3), 115.2 (C4), 119.8 (C5), 122.3 (C2) and 155.3 (C3); δ_H (chloroform) 1.5–2.1 (br m, Ad), 2.76 (br, Ad_2CH), 3.80 (CH_3), 6.86 (H4, *J* 5.5) and 7.03 (H5, *J* 0.8 and 5.5). **10S-Me**: δ_C (chloroform) 29.4 (6 CH), 37.1 (6 CH_2), 39.8 (2 C_q), 43.1 (6 CH_2), 57.7 (CH_3), 63.3 (CH), 116.9 (C4), 119.5 (C5), 121.5 (C2) and 152.4 (C3); δ_H (chloroform) 1.5–2.1 (br m, Ad), 1.96 (br, Ad_2CH), 3.80 (CH_3), 6.84 (H4, *J* 0.4 and 5.6) and 6.94 (H5, *J* 0.4 and 5.5). One recrystallization of the mixture from *n*-hexane gave crystals of almost pure **10A-Me** and mother liquors containing 60–65% of **10S-Me**. On heating in chloroform at 85–130 °C, **10S-Me** is incompletely converted to **10A-Me**, with an equilibrium ratio (**10A-Me**:**10S-Me**) of approximately 17:1 (see below—Rotation kinetics).

Treatment of the alcohol with *n*-hexylsilane in the same way gave only **10A-Me** (130 mg, 90%, mp 236 °C) (Found: C, 78.4; H, 9.3; S, 7.9. $C_{26}H_{36}OS$ requires C, 78.74; H, 9.16; S, 8.07%).

On a smaller scale, to a stirred solution of alcohol **2A-Me** (41 mg, 0.1 mmol) and an organosilane (0.4–1.6 mmol) in dichloromethane (5 cm^3) at room temperature (20 ± 2 °C) was added TFA (0.2 cm^3). After 3 h water and pentane were added, the pentane extract washed with water, then dried and the solvent evaporated under reduced pressure. Relative product yields were determined from the ^{1}H NMR spectrum in $CDCl_3$. The slower reaction in TTMSS was allowed to run for 20 h; comparison of the signal at 5.88 ppm with the aromatic proton signals indicated 29 ± 3% of trifluoroacetate, **4-HH**.

***anti*-[2-(3-Ethoxythienyl)]di(1-adamantyl)methanol, 2A-Et.** Treatment of alcohol **2A-Et** (150 mg, 0.35 mmol) in dichloromethane (15 cm^3) with TES (0.2 cm^3, 1.25 mmol) and TFA (0.75 cm^3) at room temperature for 1 h gave [2-(3-ethoxythienyl)]di(1-adamantyl)methanes, **10A-Et**, **10S-Et** and **6**, in a ratio of about 3:1:2. Column chromatography on silica gel gave a mixture of **10A-Et** and **10S-Et** (91 mg, 63%) and impure **6** (63 mg). **10A-Et**: δ_C (chloroform) 15.6 (CH_3), 29.2 (6 CH), 37.0 (6 CH_2), 39.2 (2 C_q), 42.4 (6 CH_2), 57.3 (CH), 66.9 (CH_2) (triplet at 66.6 ppm, *J* 21.1, in **11**), 115.9 (C4), 119.7 (C5), 122.5 (C2) and 154.5 (C3); δ_H (chloroform) 1.36 (CH_3, *J* 7.0), 1.5–2.1 (br m, Ad), 2.79 (br, Ad_2CH), 4.01 (CH_2, *J* 7.0), 6.83 (H4, *J* 5.5) and 7.02 (H5, *J* 0.5 and 5.5). **10S-Et**: δ_C (chloroform) 15.3 (CH_3), 29.4 (6 CH), 37.1 (6 CH_2), 39.8 (2 C_q), 43.1 (6 CH_2), 63.3 (CH) (triplet at 62.7 ppm, *J* 18, in deuteriated material), 65.9 (CH_2), 116.9 (C4), 119.3 (C5), 120.9 (C2) and 151.6 (C3); δ_H (chloroform) 1.40 (CH_3, *J* 7.0), 1.5–2.1 (br m, Ad), 1.99 (Ad_2CH), 4.04 (CH_2, *J* 7.0), 6.82 (H4, *J* 5.5) and 6.93 (H5, *J* 5.5). Recrystallization of the mixture of **10A-Et** and **10S-Et** (from several experiments) from *n*-hexane gave pure **10A-Et**: mp 189 °C (Found: C, 79.0; H, 9.3; S, 7.9. $C_{27}H_{38}OS$ requires C, 78.97; H, 9.33; S, 7.79%).

On a smaller scale, to a stirred solution of alcohol **2A-Et** (42 mg, 0.1 mmol) and an organosilane (0.4–1.6 mmol) in dichloromethane (5 cm^3) at room temperature (20 ± 2 °C) was added TFA (0.2 cm^3). After 1.5 h water and pentane were added, the organic phase washed with water, then dried and the solvents evaporated under reduced pressure. The relative yields (±1–2%) were estimated by integration of the aromatic and Ad_2CH signals of the ^{1}H NMR spectrum.

***anti*-[2-(3-Isopropoxythienyl)]di(1-adamantyl)methanol, 2A-iPr.** Treatment of alcohol **2A-iPr** (100 mg, 0.23 mmol) in dichloromethane (10 cm^3) with TES (0.13 cm^3, 0.8 mmol) and TFA (0.5 cm^3) at room temperature for 1 h gave *syn*-[2-(3-isopropoxythienyl)]di(1-adamantyl)methane, **10S-iPr** (82 mg, 85%, mp 162 °C); δ_C (chloroform) 22.5 (2 CH_3), 29.5 (6 CH), 37.1 (6 CH_2), 40.0 (2 C_q), 43.1 (6 CH_2), 63.4 (CH), 71.2 (CH), 116.3 (C4), 119.1 (C5), 120.0 (C2) and 150.2 (C3); δ_H (chloroform) 1.36 (CH_3, *J* 6.0), 1.5–2.1 (br m, Ad), 2.02 (Ad_2CH), 4.47 (CH, *J* 6.0), 6.77 (H4, *J* 5.6) and 6.93 (H5, *J* 5.6). (Found: C, 79.2; H, 9.5; S, 8.0. $C_{28}H_{40}OS$ requires C, 79.19; H, 9.50; S, 7.54%). By heating for 5 h in $CDCl_3$ at 150 °C was obtained **10A-iPr**: δ_C (chloroform) 22.9 (2 CH_3), 29.2 (6 CH), 37.0 (6 CH_2), 39.3 (2 C_q), 42.5 (6 CH_2), 57.2 (CH), 72.6 (CH), 116.2 (C4), 119.5 (C5), 122.6 (C2) and 153.6 (C3); δ_H (chloroform) 1.31 (CH_3, *J* 6.1), 1.5–2.1 (br m, Ad), 2.79 (Ad_2CH), 4.35 (CH, *J* 6.1), 6.80 (H4, *J* 5.5) and 7.06 (H5, *J* 5.5).

Small scale experiments were performed as for **2S-Et**. In some cases, where large amounts of the 3-hydroxythienyl were formed or there remained involatile organosilane residues, the crude product was partially purified by chromatography on alumina in light petroleum in order to determine the yield of deoxygenation products and the *syn*/*anti* ratio (Table 2).

Isotope effects

Triethylsilane-*d* and dimethylphenylsilane-*d* were prepared by the reduction of the corresponding silyl chlorides by lithium aluminium deuteride in ether at reflux.[26] Small-scale experiments were carried out as described above. The Ad_2CH proton signals in the *anti* and *syn* [2-(3-methoxythienyl)]di(1-adamantyl)methanes disappear and Ad_2CD signals appear as triplets at 56.9 (*J* 19.1) and 62.8 ppm (*J* 18) in **10A-Me** and **10S-Me**, respectively. For **2A-Et**, a new product, **11**, was obtained in which the ethoxy methylene group was half-labelled, but its ^{1}H NMR signal was buried amongst the methylene signals of the other two deoxygenation products. The corresponding ^{13}C signal showed up as a triplet at 66.6 ppm (*J* 21.1). The Ad_2CD of **10S-Et** appeared at 62.7 ppm (*J* 18) but that of **10A-Et** could not be located; that of **10S-iPr** was at 62.8 ppm (*J* 18.3).

Rotation kinetics

Aliquots (0.1–0.2 cm^3) containing about 2 mg of a mixture of *anti* and *syn* [2-(3-alkoxythienyl)]diadamantylmethanes, **10A** and **10S** (or pure **10S** in the case of isopropoxy), in deuteriochloroform were sealed under vacuum in 5-mm o.d. glass tubes. Batches of tubes (8–10 samples per run) were thermostatted in an oil bath and samples withdrawn at convenient intervals. Each sample was made up to 0.45 cm^3 with chloroform for ^{1}H NMR analysis, the downfield aromatic H5 peaks being used to estimate the progress of the reaction. A further two samples taken after 10 half-lives were used to determine the equilibrium constant; an error of 0.5% in this infinity value leads to one of about 2% on the rate constant. First-order rate constants were determined from plots of log [%*syn*(*t*) − %*syn*(∞)] *vs.* time (*t*). Rate constants were as follows [**R**(*T*/°C, *k*/s^{-1}, %*syn* at equilibrium)], the error limits being the standard deviations on single runs**: Me,** 85.4, $5.55 \pm 0.05 \times 10^{-5}$, 5.5; 100.5, $2.32 \pm 0.02 \times 10^{-4}$, 5.4; 115.2, $9.08 \pm 0.14 \times 10^{-4}$, 5.5; 130.1, $3.23 \pm 0.13 \times 10^{-3}$, 5.5; **Et**, 100.5, $4.97 \pm 0.06 \times 10^{-5}$, 5.6; 115.2, $1.98 \pm 0.02 \times 10^{-4}$, 5.2; 130.1, $7.80 \pm 0.33 \times 10^{-4}$, 6.2; 145.0, $2.49 \pm 0.05 \times 10^{-3}$, 6.4; **iPr,** 115.2, $4.30 \pm 0.04 \times 10^{-5}$, 5.8**;** 130.1, $1.68 \pm 0.02 \times 10^{-4}$, 5.7; 145.0, $6.27 \pm 0.06 \times 10^{-4}$, 5.7; 160.3, $1.95 \pm 0.02 \times 10^{-3}$, 5.8. Thermodynamic parameters for the forward reaction (*syn*→*anti*) are (**R**, $\Delta H^{\ddagger}$/kcal mol^{-1}, $\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}$(115 °C)/kcal mol^{-1}): **Me**, 25.44 ± 0.24, −7.6 ± 0.6, 28.39; **Et**, 26.58 ± 0.32, −7.6 ± 0.8, 29.55; **iPr**, 27.60 ± 0.41, −8.1 ± 1.0, 30.74.

Kinetic modelling

The use of the KINAL kinetic simulation programme[15] with a Simplex routine has been described elsewhere.[5] Rate constants k_2, k_3 and k_4 in Scheme 2 were optimized for arbitrarily defined values of k_0, k_1 and k_5 (Tables 5 and 6, Supplementary material). Values of k_0 and k_1 only determine the time-scale of the reaction and must be compatible with the "infinity" time value for complete reaction; k_5 must be compatible with k_1 since, if it is too small, the programme converges badly and gives spurious results.

DFT calculations

Heats of formation of carbocations and carboxonium ions in the gas phase at 25 °C were calculated by the Xα(3-21G)//STO-3G approach.[23] The parameter α is treated as a variable and adapted "*a priori*" to each molecule, depending on the number and type of atoms involved. This model is comparable in accuracy to B3LYP/6-311(d,p)//B3LYP/6-311(d,p), but is much more economical on computer time and, most importantly, is better parametrized for species containing second-row elements. For simplicity, 1-adamantyl groups were replaced by *tert*-butyls which have similar steric requirements but are less rigid. Calculated heats of formation and selected torsion angles for the [3-(2-alkoxythienyl)]di(*tert*-butyl)methyl cations and the corresponding carboxonium ions are listed in Table 4. For the 2-alkoxyphenyldi(*tert*-butyl)methyl cations and the carboxonium ions the results are as follows [parent alcohol, carbocation ($\Delta H_f°$/kcal mol^{-1}), interplanar angle ($/°$), carboxonium ion ($\Delta H_f°$/kcal mol^{-1})]: **1S-Me**, 77.6, 81, 74.0; **1S-Et**, 66.2, 80, 51.9; **1S-iPr**, 49.9, 81, 34.3.

X-Ray crystallography

***anti*-[2-(3-Methoxythienyl)]di(1-adamantyl)methanol, 2A-Me: $C_{26}H_{36}O_2S$.** *Crystal data.* $M = 412.6$. Triclinic, $a = 6.804(3)$, $b = 11.122(2)$, $c = 15.139(2)$ Å, $\alpha = 70.85(2)$, $\beta = 86.12(3)$, $\gamma = 79.57(3)°$, $V = 4397(3)$ Å^3 (by least squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group P-1, $Z = 2$, $D_x = 1.29$ g cm^{-3}. Colourless prismatic crystals, ν(Mo-Kα) = 1.64 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.8 + 0.345 tan θ, graphite-monochromated Mo-Kα radiation. 6690 reflections measured ($1 \leq \theta \leq 30°$), 6203 unique, giving 4203 with $I > 3\sigma(i)$.

Structure analysis and refinement. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic; hydrogens located from Fourier difference map with one, overall, refined isotropic thermal parameter (263 refinable parameters). No absorption correction. Final R and R_w (Chebyshev series) values are 0.043 and 0.053. Programmes used were the PC version of CRYSTALS[27] for refinements and CAMERON[28] for views.**

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