Bond Length and Reactivity: the *gauche* Effect. A Combined Crystallographic and Theoretical Investigation of the Effects of β-Substituents on C–OX Bond Length

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The 'variable oxygen probe' is applied to systems with the general structure Y–C–C–OX (Y = F, H, SiR_3), using both crystal structure correlations (including 25 new structures) and *ab initio* calculations (SCF[DZP]), for 20 structures, $Y–CH_2–CH_2–OX$: Y = H, F and SiH_3 (*gauche* and *trans*); X = CH_3, CHO (*E* and *Z*) and NO_2. The calculations reproduce conformational preferences well (all our 2-fluoroethyl derivatives crystallise with F *gauche* to OX). Both crystal and calculated structures give linear bond-length/pK_{HOX} correlations. From the crystal structures: definitive correlations are derived for primary and secondary alcohol derivatives; no significant difference is observed between axial and equatorial cyclohexyl systems; β-fluorine has a small bond-shortening effect on the C–OX bond, which is greatest for the best leaving groups OX; and data for two systems with β-silicon are consistent with a bond-lengthening effect. The inductive effect of β-fluorine, observed as its effect on the C–OX bond length, shows no significant dependence on geometry.

Calculated bond lengths give similar results, but show the different sensitivities to varying OX expected from frontier orbital considerations ($\sigma_{Y-C} - \sigma^*_{C-OX}$ for Y = Si > H > F). The length of the C–OX bond in $Y–CH_2–CH_2–OX$ is a linear function of the electronegativity of Y. 1,3-Interaction energies calculated (at the MP2[DZP] level) for the isodesmic reaction $Y–CH_2–CH_2–OX + CH_3–CH_3 \longrightarrow CH_3–CH_2–OX + Y–CH_2–CH_3$ give a measure of the destablising effect of β-fluorine and the stabilising effect of β-silicon in these systems. In three different systems which react with participation of adjacent σ-bonds, the lengthening of the C–OX bond, observed in the ground state using the variable oxygen probe, is not accompanied by significant involvement of the adjacent orbitals. It is suggested that C–OX bond breaking, and the further structural reorganisation, are not closely coupled in such reactions.

Unique mechanistic insight is available from the systematic study of ground-state structures of suitable organic compounds.[1,2] We have identified a simple relationship—the longer the bond the faster it breaks—between the length of the bond to oxygen in systems R–OX and the rate at which the same bond is broken in ionic reactions in solution.[3]

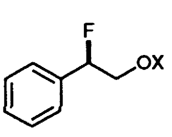
$$R–OX \longrightarrow R^+ + {}^-OX$$

The basis of this relationship is the contribution to the ground-state structure of the valence bond tautomeric form $R^+\ {}^-OX$. The contribution, and hence the length of the bond, increases with increasing stability of either R^+ or XO^-. Thus the 'variable oxygen probe' OX can be used to study the effects on the structure of a selected group R of graduated increments of positive charge, and we have observed structural changes associated with the early stages of the bond-breaking process in several systems.[4–6]

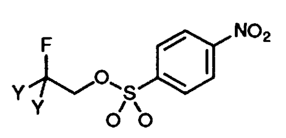
We report an investigation of the effects of substituents (Y) in the 2-position of primary and secondary alcohol derivatives, *i.e.*, in compounds with the general structure Y–C–C–OX. Substituents in this position may prefer to be *gauche* rather than antiperiplanar (the *gauche* effect[7,8a]), and can have a profound effect on reactivity. Rates of C–OX cleavage can be enormously enhanced by antiperiplanar silicon (Y = R_3Si),[9] whereas electron-withdrawing 2-substituents (Y = OX′ or halogen) reduce reactivity. This latter effect has not been studied systematically, except in some early work by Hine,[10] who found seven- to eight-fold retardations in the rates of substitution reactions of 2-alkoxy, -fluoro, -chloro and -bromo-ethyl halides by PhS^-. Such factors are already large enough to be useful in synthesis. They account, for example, for the regioselective ring opening of some epoxides, such as those derived from allylic alcohols;[11] and for the extra stability of the bistoluene-*p*-sulfonate and even the bis-perchlorate[12] esters of 1,2-diols. The cumulative effect of more than one electron-withdrawing group can be large. S_N2 reactions of 2,2,2-trifluoroethyl halides are at least 10^4 times slower than those of parent, non-fluorinated, compounds;[13] and the stabilising effect of multiple hydroxy substitution on derivatives such as sulfonate esters of sugars is well known.[14]

There is good but scattered evidence that there are parallel and substantial effects on bond lengths. Allen *et al.*,[15] in their compendium of average bond lengths derived from organic structures in the Cambridge Structural Database (CSD), quote different values for the length of the C–F bond in monofluoro-compounds (1.399 ± 0.017 Å) and in 1,2-difluorides (1.371 ± 0.007 Å). (This difference is almost the same as that between the lengths of C–F bonds in CH_3F and CH_2F_2.[8b]) We have noted previously[3b] the very short C–OP bond length in the dimethylphosphinate ester of perfluoropinacol.[16] And the C–O-ester bonds of carboxylate and sulfate esters of pyranose sugars are systematically shorter than those of the corresponding derivatives of cyclohexanol.

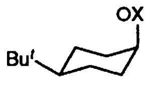
Structures in the CSD are generally too disparate for a detailed examination of specific effects and, in particular, how they depend on geometry. There is strong experimental evidence that the effect on reactivity of β-silicon depends strongly on



1pNP, X = 4-nitrophenyl
1pN3, X = 4-nitrobenzoyl
1Ts, X = 4-tolylsulfonyl
1ClS, X = 4-chlorosulfonyl
1NS, X = 4-nitrosulfonyl

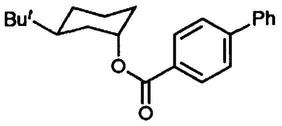


2a Y = H
2f Y = F



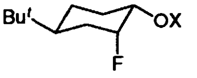
3pPB, X = 4-phenylbenzoyl
3Ms, X = methylsulfonyl

4pPB, X = 4-phenylbenzoyl
4Ms, X = methylsulfonyl

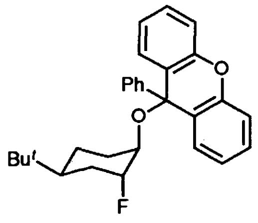


5pPB

6pPB, X = 4-phenylbenzoyl
6DPP, X = diphenylphosphoryl
6NpS, X = naphthalen-2-ylsulphonyl



7pPB, X = 4-phenylbenzoyl
7Ms, X = methanesulfonyl



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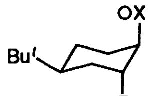
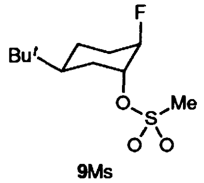
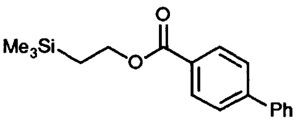


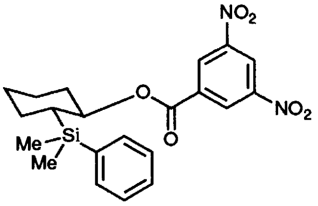
8pPB, X = 4-phenylbenzoyl
8DPP, X = diphenylphosphoryl
8Ms, X = methylsulfonyl



9Ms



10pPB



11

geometry,[9] as expected if it involves a σ–σ* interaction. But the effects of electron-withdrawing substituents are likely to be primarily inductive, and it is not clear whether there is a preferred geometry for through-bond interactions of this sort. So we set out to compare the crystal structures, and in particular the C–OX bond lengths, of series of 2-fluoro and 2-trialkylsilyl alcohol derivatives, with those of the parent, unsubstituted compounds. Full crystallographic data for 25 compounds (structures **1**–**11**) were measured specifically for this investigation.

To complement the crystallographic investigation we have also carried out *ab initio* calculations on nine representative derivatives of ethanol, YCH_2CH_2OX, where Y = H, F and SiH_3, and X = CH_3, CHO and NO_2. This gives us a data set, free of the random errors associated with experimental measurements, but covering the same ground, which should help to confirm and identify trends of interest.

Methods and Results

Crystal structures.—Details of compounds **1**–**11**, together with full crystallographic and structural data, have been published.[17] The set of structures represents the usual compromise between the desirable and the possible. Many more than the 25 compounds were prepared: some did not crystallise, some gave poor crystals, and some gave beautiful crystals which did not diffract usefully. The majority of our silicon derivatives, in particular, gave no useful results, and we could obtain structures for only two (**10** and **11**). We used derivatives of 2-fluoro-2-phenylethanol, rather than of 2-fluoroethanol itself, because of their higher melting points and better crystallinity. The same factors account for the large number of 4-phenylbenzoate esters, which we found gave particularly good crystals.

All the 2-substituted alcohols, apart from the commercially available 2-fluoro- and 2,2,2-trifluoro-ethanol, were prepared by opening the relevant epoxides, using the silyl lithium reagent,[17m] or HF-pyridine.[18] The *trans*-2-fluorocyclohexanols thus obtained were converted into the *cis* epimers, *via* the acetates, under Mitsonobu conditions.[17i]

Our original intention was to obtain accurate data for two sets each of 2-fluoro and 2-trialkylsilyl derivatives, with the C–F or C–Si bond alternatively *gauche* and antiperiplanar to the C–OX bond; and with leaving groups, OX, ranging from *O*-alkyl to *O*-sulfonyl. We also needed, for comparison, accurate standard values for the C–OX bond lengths concerned in the absence of F or Si, and for this reason measured the structures of 2-phenylethyl toluene-*p*-sulfonate and of various derivatives of axial (**3** and **5**) and equatorial (**4** and **6**) cyclohexanols. All the primary 2-fluoroalkyl derivatives crystallised with the C–F and C–OX bonds *gauche* to each other; as they are also in the (secondary) derivatives (**6** and **7**) of 2-fluorocyclohexanol. Antiperiplanar geometry was imposed on 2-fluorocyclohexanol derivatives (**8** and **9**) by the presence of a 4- or 5-*tert*-butyl group.

Selected data summarising the observed geometry of the Y–C–COX substructure are shown in Tables 1–3.

Standard Bond Lengths for Parent Compounds.—Mean values derived from the Cambridge Structural Database (CSD) are available[3b,15] for the length of the C–OX bond in primary-alkyl alkyl and aryl ethers and carboxylate esters, and Allen *et al.*[15] give a mean value of 1.465(14) Å for the corresponding sulfonates. The length of the C–OTs bond in 2-phenylethyl toluene-*p*-sulfonate [1.459 and 1.465(4) Å for the two molecules in the asymmetric unit[17a]] shows that the introduction of the 2-phenyl group has no significant effect on this bond length in the ground state, and we use a mean value of 1.462(4) Å for the length of the C–OTs bond in derivatives of primary alcohols. The four-point plot of these bond lengths *vs.* mean pK_as of the leaving groups gives a good straight line (Fig. 1), with correlation coefficient $r = 0.995$.

$$\text{Bond length } (RCH_2\text{–}OX) = 1.458 - 2.02 \times 10^{-3}\text{p}K_{HOX}\ \text{Å} \quad \text{(i)}$$

The standard bond lengths required for unsubstituted cyclohexanol derivatives are established in the same way. In this case we must distinguish axial and equatorial C–OX bonds, which will not necessarily have equal lengths. Thus the mean database secondary-C–O-ester bond length is 1.460(2) Å,[3b,15] but for esters of cyclohexanols this rises to 1.467 Å; of these the three axial derivatives give a mean value of 1.488 Å, compared with 1.465 Å for 14 equatorial derivatives. Our structures for the 4-phenylbenzoate esters (**3**pPb and **4**pPb) of *cis* and *trans*-4-*tert*-butylcyclohexanol, have C–O-ester bond lengths of 1.458(2) Å and 1.464(2) Å, respectively, for the equatorial and axial pair. For the same derivative (**5**pPB) of *trans*-3-*tert*-butylcyclo-

Table 1 Selected structural data for 2-substituted ethanol derivatives

	Bond lengths[a]			Bond angles[a]			Torsion angles[a]		
Compound	*a*	*b*	*f*	*ax*	*ab*	*bf*	*bax*	*abf*	*R*
PhCH$_2$CH$_2$OTs[17a]	1.459(4)	1.514	—	117.9(2)	108.6	—	146.6	—	5.9
b	1.465(4)	1.520	—	118.3(2)	108.3	—	145.5	—	5.9
1pNP[17b]	1.420(3)	1.468	1.341	118.6(2)	109.7	112.5	177.1	52.8	5.47
1pNB[17b]	1.456(4)	1.484	1.393	113.9(2)	107.6	109.3	177.2	68.1	5.42
1Ts[17c]	1.442(6)	1.483	1.376	116.8(3)	109.1	109.2	176.7	65.1	7.5
1C1S[17c]	1.451(4)	1.490	1.359	116.6(2)	108.9	110.2	177.3	66.0	5.29
1NS[17c]	1.459(4)	1.477	1.355	118.1(2)	108.3	112.2(3)	173.8	60.3	6.1
2aNS[17d]	1.463(4)	1.454	1.306	120.8(2)	107.3	114.4	156.8	60.6	4.6
2fNS[17d]	1.435(3)	1.455	1.302 1.292 1.314	118.7(2)	106.3	113.7 112.5 111.6	166.5	58.1 63.1 179.9	4.6

[a] Bond lengths and angles are defined in terms of the bonds in the $F\overset{f}{-}C\overset{b}{-}C\overset{a}{-}O\overset{x}{-}X$ unit. In structures with two or more equivalent F–C or C–C bonds all values are quoted. Standard errors are given in the first column. Others are to within ±1 of the error quoted. [b] Two molecules in the unit cell.

Table 2 Selected structural data for 2-fluorocyclohexanol derivatives

	Bond lengths[a]			Bond angles[a]			Torsion angles[a]		
Compound	*a*	*b*	*f*	*ax*	*ab*	*bf*	*bax*	*abf*	*R*
3pBP[17e]	1.464(2)	1.505 1.506	—	116.9(1)	106.3 110.0	—	82.1 156.3	—	4.0
3Ms[17g]	1.480(3)	1.507 1.502		120.1(1)	105.9 108.9	—	140.3 99.5		7.0
4pPB[17e]	1.458(2)	1.516 1.505	—	117.1(2)	107.3 110.4	—	86.9 151.6	—	5.0
4Ms[17g]	1.485(9)	1.476 1.478	—	119.5(4)	108.5 108.2	—	138.7 99.5		7.0
5pPB[17f]	1.461(2)	1.499 1.516	—	118.1(1)	109.7 105.5	—	83.3 154.6	—	5.0
6pPB[17h]	1.453(2)	1.491	1.394	116.8(2)	107.1	109.4	150.6	60.7	6.0
6DPP[17h]	1.463(2)	1.500	1.383	122.9(1)	109.0	108.6	122.9	63.0	2.8
6NpS[17h]	1.466(3)	1.504	1.392	119.5(2)	106.5	108.8	143.9	62.9	5.3
7pPB[17i]	1.457(2)	1.509	1.419	117.1(1)	111.5	107.2	81.1	58.0	4.5
7Ms[17i]	1.470(5)	1.499	1.397	121.2(2)	106.4	107.1	147.4	54.0	4.2
8PiX[17j]	1.430(2)	1.497	1.416	117.9(1)	105.7	105.5	137.5	169.7	4.8
8pPB[17j]	1.457(3)	1.512	1.417	116.4(2)	109.6	104.8	81.2	71.1	6.3
8DPP[17j]	1.465(5)	1.520	1.382	123.8(2)	108.4	105.1	100.5	172.5	4.8
8Ms[17j]	1.465(2)	1.517	1.406	120.5(1)	104.8	105.3	143.8	171.9	4.9
9Ms[17k]	1.475(4)	1.513	1.413	119.8(2)	102.8	105.5	145.3	172.1	5.8

[a] Bond lengths and angles are defined in terms of the bonds in the $F\overset{f}{-}C\overset{b}{-}C\overset{a}{-}O\overset{x}{-}X$ unit. In structures with two or more equivalent F–C or C–C bonds all values are quoted. Standard errors are given in the first column. Others are to within ±1 of the error quoted.

Table 3 Selected structural data for 2-silylethanol derivatives

	Bond lengths[a]			Bond angles[a]			Torsion angles[a]		
Compound	*a*	*b*	*s*	*ax*	*ab*	*bs*	*bax*	*abs*	*R*
10pBP[17l]	1.466(3)	1.503	1.876	116.7(2)	112.0	113.4	82.0	178.1	5.3
11[17m,b]	1.472(3) 1.475(2)	1.520 1.525	1.894 1.890	118.9(2) 119.8(2)	107.6 106.4	117.5 116.6	123.6 135.7	64.5 65.5	4.8

[a] Bond lengths and angles are defined in terms of the bonds in the $Si\overset{s}{-}C\overset{b}{-}C\overset{a}{-}O\overset{x}{-}X$ unit. Standard errors are given in the first column. Others are to within ±1 of the figure given. [b] Two molecules in the unit cell.

hexanol, which also has an axial ester group, the length is 1.461(2) Å. These data, and those discussed below for the methanesulfonate esters, convince us that there is no significant difference in length between axial and equatorial C–O-ester bonds; and we take a best value of 1.462(4) Å for any 4-phenylbenzoate ester of a simple cyclohexanol.

The mean value for the length of the C–O bond of an alkyl sulfonate ester, taken from a published survey of the CSD,[15] is 1.465(14) Å. For secondary alkyl sulfonates this rises to 1.475 Å, and for a data set restricted to cyclohexyl derivatives the figure is higher still. For the subset of 10 equatorial compounds the mean C–O bond length is 1.483 Å, and for 11 axial esters the mean is 1.484 Å. A set of simple axial and equatorial cyclohexyl toluene-*p*-sulfonates measured by James *et al.* in the 1970s is particularly relevant to this work. These authors found equatorial C–O bond lengths of 1.51(1), 1.473(5) and 1.474(2) Å, and values of 1.503(3), 1.479(5), 1.482(7) and 1.498(4) for axial derivatives.[19a–g] It would be surprising if this variability were real, and in several cases the data are less reliable than one would like, because of high *R*-factors and temperature factors. And it is clearly not possible to decide whether the C–O bond lengths of these simple axial and equatorial derivatives do or do not differ.

Our new data for methanesulfonates (**3**Ms and **4**Ms, Table 2) are also not as accurate as we would like, but the C–O bond lengths agree with the mean values for axial and equatorial toluene-*p*-sulfonates cited above, and are not significantly different for the two isomers. The conformations around the sulfonate group are similar in the two compounds, with C–O bond lengths of 1.485(9) and 1.480(3) Å for the equatorial and axial isomer, respectively. (The pK_a values of toluene-*p*- and methane-sulfonic acid are thought to differ by less than one unit[20] so we can safely ignore the difference of leaving group between the methanesulfonates and the toluene-*p*-sulfonates.)

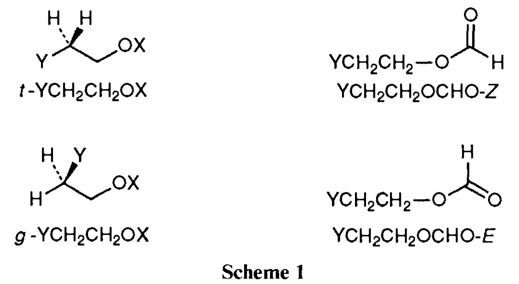
We conclude that there is no significant difference in C–O bond length between axial and equatorial cyclohexyl sulfonate esters, and that the best data are consistent with a value of 1.483(4) Å. We note that the mean C–O bond length for three 2-hydroxycyclohexyl arenesulfonates that we measured recently is marginally shorter than this, at 1.477(2) Å.[21]

These best values for cyclohexyl carboxylate and sulfonate esters, which turn out not to differ from the database means quoted above, combined with mean database values[15] for secondary alkyl and aryl ethers, allow us to define the linear relationship (correlation coefficient, $r = 0.999$) with the pK_a [eqn. (ii)].

$$\text{Bond length (cyclohexyl–OX)} = 1.475 - 2.90 \times 10^{-3}\ \mathrm{p}K_{\mathrm{HOX}}\ \text{Å} \quad \text{(ii)}$$

This equation is derived for derivatives of cyclohexanol, but may be expected to apply generally to derivatives of secondary alcohols.

Calculations.—Full *ab initio* calculations were carried out for three systems, CH_3CH_2OX, FCH_2CH_2OX and $H_3SiCH_2CH_2OX$, each with three representative leaving groups, OMe, OCHO and ONO_2, covering a wide range of basicity. (The pK_as of MeOH, formic acid and nitric acid are 15.5,[22] 3.77[22] and −1.3,[20] respectively.) In the case of the F and Si derivatives both antiperiplanar (*trans*, *t*, see Scheme 1) and *gauche* (*g*) conformations were calculated, as were both *E* and *Z* conformations of the five formate esters, making a total of 20 structures.



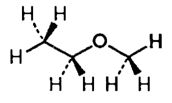
Scheme 1

Ab initio *Methodology and Results.*—The 20 systems were studied using *ab initio* quantum methods for closed-shell molecules. Stationary point geometries were determined using the restricted Hartree–Fock (RHF) scheme, referred to here as the SCF method. Double-ζ plus polarization basis sets (DZP) were used. Specifically the atomic contracted Gaussian basis sets may be designated[23–25] Si (11s7p1d/6s4p1d), C (9s5p1d/4s2p1d), N (9s5p1d/4s2p1d), F (9s5p1d/4s2p1d) and H (4s1p/2s1p). Chosen polarization orbital exponents were $\alpha_d(\mathrm{Si}) = 0.45$, $\alpha_d(\mathrm{C}) = 0.8$, $\alpha_d(\mathrm{N}) = 0.8$, $\alpha_d(\mathrm{O}) = 0.9$, $\alpha_d(\mathrm{F}) = 1.2$ and $\alpha_p(\mathrm{H}) = 1.0$. All calculations were performed using the Cambridge Analytic Derivatives Package (CADPAC)[26] on a CONVEX C210 computer.

Relative energies of *gauche*/*trans* structures were calculated at the SCF (DZP) level. They were also calculated at the MP2 (DZP) level, using the SCF (DZP) optimised geometries (all variables were optimised). [It would have been too expensive to optimise all structures at the MP2 level. However, when a representative pair, (*Z*)- and (*E*)-ethyl formate, were optimised at the higher level (see below) the difference in energies scarcely changed.] Selected calculated geometrical parameters, and relative energies Δ*E*, are shown in Tables 4–6, for the four, eight and eight structures with Y = H, F and SiH_3.[25] All the reported structures are minima, as verified by a second-derivative frequency analysis. Total energies, needed for calculation of 1,3-interaction energies (see below) were also calculated for ethane, $EtSiH_3$ and EtF.

It is seen from the Tables that the values for Δ*E* at the correlated level (MP2) show trends very similar to the values of Δ*E* at the SCF level. [A detailed comparison of total energies shows that the higher-level calculation gives values lower by an almost constant 0.169(4) Hartrees per non-hydrogen atom, less than 0.3%]. This is a good justification for the use of the SCF model to determine the structures. Probably the most serious deficiency in the calculations is the use of the DZP basis set, but this will not be of sufficient importance to change the important trends. Further, many of the bond lengths will be too short, by as much as 0.01–0.02 Å for single bonds (and more for double bonds): this is the usual error associated with SCF neglect of electron correlation. (The comparison with data from crystal structure determinations is analysed below.) Again, we do not expect this deficiency to be important in comparisons of similar species.

Details of SCF Studies.—CH_3CH_2OMe: only one minimum (structure **12**) was found. Structure **13** was identified as a rotational transition state.



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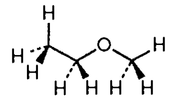
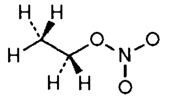
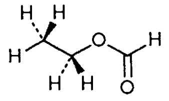


13

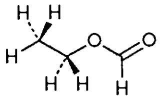
When OMe was replaced by ONO_2 a single minimum was located (structure **14**), whereas the formate ester structure (OMe replaced by OCHO) gave two minima, corresponding to the *E* and *Z* conformations (**15E** and **15Z**) of the ester group.



14



15*Z*



15*E*

Similar results were obtained with 2-substituted derivatives of **12**, **14** and **15**. Here the substituent can replace either an antiperiplanar or a *gauche* hydrogen, and the two corresponding minima were found in each case for the methyl ethers: Y = F (**16***g* and **16***t*) and Y = SiH_3 (**19***g* and **19***t*), and for the nitrate esters: Y = F (**17***g* and **17***t*) and Y = SiH_3 (**20***g* and **20***t*). For the formate esters four minima (structures **18***gZ*, **18***tZ*, **18***gE* and **18***tE*) were located for Y = F, and four more for Y = SiH_3: **21***gZ*, **21***tZ*, **21***gE* and **21***tE*.

Discussion

Crystal Structure Correlations: the Effect of β-Fluorine.—In our earlier work[2,3] we found a simple, linear, relationship

Table 4 Calculated data for ethanol derivatives[a]

Compound	Bond lengths[b]		Bond angles[b]		Torsion angle[c]	
	a	b	ax	ab	bax	ΔE^d
CH_3CH_2OMe	1.3982	1.5171	114.05	108.93	180	
CH_3CH_2OCHO (*E*)	1.4208	1.5148	117.68	108.01	180	5.32 (4.57)
CH_3CH_2OCHO (*Z*)	1.4289	1.5146	117.41	107.72	180	0
$CH_3CH_2ONO_2$	1.4397	1.5146	116.24	105.68	180	

[a] From SCF calculations with DZP basis set. Full structural data are available from the authors. [b] Bond lengths and angles are defined as for Table 1. [c] Torsion angle of 180° fixed by symmetry. [d] Relative energy (kcal mol^{-1}), from MP2 (DZP) calculations, based on the SCF (DZP) geometries. SCF values in parentheses.

Table 5 Calculated structural data for 2-fluoroethanol derivatives[a]

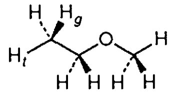
Compound	Bond lengths[b]			Bond angles[b]			Torsion angles[c]		
	a	b	f	ax	ab	bf	bax	abf	ΔE^d
g-FCH_2CH_2OMe	1.3914	1.5094	1.3664	114.35	109.54	110.64	179.95	72.23	0.052 (0.633)
t-FCH_2CH_2OMe	1.3933	1.5149	1.3692	114.21	107.11	108.79	180.00	180.00	0
g-FCH_2CH_2OCHO (*E*)	1.4095	1.5115	1.3681	118.89	111.57	109.45	176.74	53.89	3.96 (4.75)
g-FCH_2CH_2OCHO (*Z*)	1.4202	1.5070	1.3640	117.11	108.23	110.97	179.19	50.30	0
t-FCH_2CH_2OCHO (*E*)	1.4132	1.5150	1.3650	117.81	106.26	108.00	180.00	180.00	5.87 (5.62)
t-FCH_2CH_2OCHO (*Z*)	1.4213	1.5144	1.3651	117.25	105.86	111.05	180.00	180.00	0.660 (0.267)
g-$FCH_2CH_2ONO_2$	1.4310	1.5085	1.3601	115.91	106.32	110.37	179.58	61.551	0
t-$FCH_2CH_2ONO_2$	1.4307	1.5174	1.3622	114.26	104.23	107.29	180.00	180.00	0.734 (0.353)

[a] From SCF calculations with DZP basis set. Full structural data area available from the authors. [b] Bond lengths and angles are defined as for Table 1. [c] Angles of 180° defined by symmetry. [d] Relative energy (kcal mol^{-1}), from MP2 (DZP calculations, based on the SCF (DZP) geometries. SCF values in parentheses.

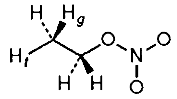
Table 6 Calculated structural data for 2-silylethanol derivatives[a]

Compound	Bond lengths[b]			Bond angles[b]			Torsion angles[c]		
	a	b	s	ax	ab	bs	bax	abs	ΔE^d
g-$H_3SiCH_2CH_2OMe$	1.3994	1.5243	1.8923	114.26	108.91	111.14	179.75	54.73	0 (0)
t-$H_3SiCH_2CH_2OMe$	1.3979	1.5225	1.8874	113.94	109.15	114.73	180.00	180.00	0.461 (0.355)
g-$H_3SiCH_2CH_2OCHO$ (*E*)	1.4222	1.5211	1.8980	117.78	108.18	115.11	179.86	55.91	5.50 (5.65)
g-$H_3SiCH_2CH_2OCHO$ (*Z*)	1.4305	1.5213	1.8971	117.53	107.82	115.02	179.83	53.90	0.371 (0.350)
t-$H_3SiCH_2CH_2OCHO$ (*E*)	1.4217	1.5187	1.8913	117.63	108.33	114.58	180.00	180.00	5.38 (5.24)
t-$H_3SiCH_2CH_2OCHO$ (*Z*)	1.4294	1.5187	1.8914	117.27	108.06	114.30	180.00	180.00	0 (0)
g-$H_3SiCH_2CH_2ONO_2$	1.4416	1.5211	1.8994	116.35	106.06	116.20	179.97	57.13	0.467 (0.606)
t-$H_3SiCH_2CH_2ONO_2$	1.4420	1.5170	1.8944	116.17	106.02	113.85	180.00	180.00	0 (0)

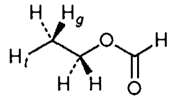
[a] From SCF calculations with DZP basis set. Full structural data are available from the authors. [b] Bond lengths and angles are defined as for Table 3. [c] Angles of 180° are defined by symmetry. [d] Relative energy (kcal mol^{-1}), from MP2 (DZP) calculations, based on the SCF (DZP) geometries. SCF values in parentheses.



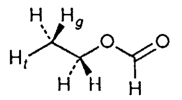
16*g*, H_g = F
16*t*, H_t = F



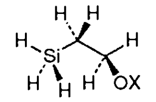
17*g*, H_g = F
17*t*, H_t = F



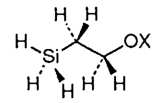
18*gZ*, H_g = F
18*tZ*, H_t = F



18*gE*, H_g = F
21*gE*, H_t = F



19*g*, X = CH_3
20*g*, X = NO_2
21*g*, X = *E*-, *Z*-CHO



19*t*, X = CH_3
20*t*, X = NO_2
21*t*, X = *E*-, *Z*-CHO

between the length of the C–OX bond in systems R–OX and the leaving group capability of the XO^- anion, as measured by the pK_a of its conjugate acid HOX. This relationship holds for a wide range of systems involving C–OX, N–OX and P–OX bonds, as long as the conformation of the group R is constant. It also allows us to define two parameters—the length of the bond and its sensitivity to changing leaving group—each of which is of interest as an index of reactivity. These are defined above [eqns. (i) and (ii)] for unsubstituted derivatives of primary alcohols and of cyclohexanol.

We measured structures for five derivatives of 2-fluoro-2-phenylethanol, three of them arenesulfonates. The fluorine atom is *gauche* to the C–OX bond in each case (dihedral angle F–C–C–OX 60 ± 8°), but the C–OX bond lengths do not fall into any simple pattern. This is illustrated by Fig. 1, where the bond-length data for all five 2-fluoro-2-phenylethanol derivatives are shown on the plot for unsubstituted primary alkyl compounds. The average C–OX bond length is clearly shorter in the 2-fluoro system, but the correlation with pK_a is irregular, and it is not possible to quantify the result. We have found similar behaviour before in systems where the conformation can vary, and this is a possible part explanation here also. Although

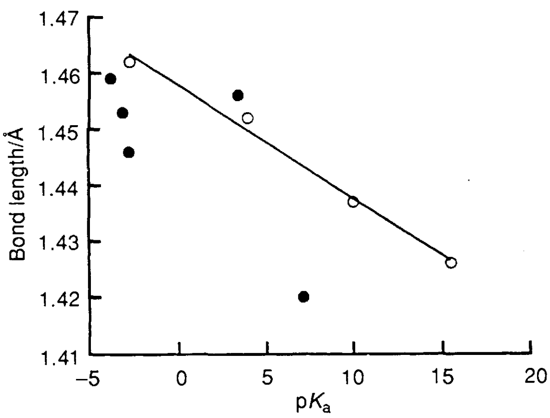


Fig. 1 Plot of C–OX bond length for (○) aliphatic derivatives RCH_2OX *vs.* the pK_a of the conjugate acid (HOX) of the leaving group. ●, The same parameters for derivatives of 2-fluoro-2-phenylethanol, taken from Table 1.

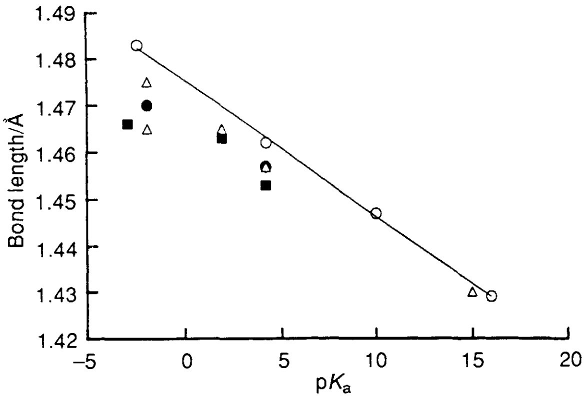


Fig. 2 Plot of C–OX bond length for unsubstituted derivatives R_2CHOX of cyclohexanol *vs.* the pK_a of the conjugate acid (HOX) of the leaving group [○ and least-squares line defined by eqn. (ii)]. Other symbols represent the same parameters for derivatives of 2-fluorocyclohexanol; △ axial OX (compounds **8** and **9**), filled symbols for equatorial (**6** and **7**). Data from Table 2.

all five compounds crystallise with the C–F bond *gauche* to C–OX, the phenyl group is antiperiplanar in three cases (the ether, the ester and the 4-nitrobenzenesulfonate) but *gauche* to C–OX in the other two arenesulfonates; as it is also in 2-phenylethyl toluene-*p*-sulfonate. We can draw no firm conclusions from these data about the effect of the introduction of β-fluorine on C–OX bond length in derivatives of primary alcohols.

A firm indication that β-fluorine can have a significant effect in these systems comes from the comparison of the structures of the 4-nitrobenzenesulfonates of 2-fluoroethanol and 2,2,2-trifluoroethanol (**2a** and **2f**). The C–OS bond length in the monofluoro-derivative (**2a**) is 1.463(3) Å, not significantly different from that in 2-phenylethyl toluene-*p*-sulfonate [1.459(4) Å]; but in the trifluoroethyl ester the bond is clearly shorter, at 1.435(3) Å. Similarly Touilloux *et al.*[27] find a C–O-ester bond length of 1.441(5) Å in 2,2,3,3,3-pentafluoropropyl 4-chlorobenzoate, also significantly shorter than expected for a primary ester. Although the effect of a single β-fluorine atom on the length of the CH_2–OX bond is evidently insignificant, at least when it is *gauche* to the C–OX bond, the cumulative effect of three or more fluorines is readily apparent. Whether the effect of a single antiperiplanar fluorine would be larger is one of the fundamental questions we hope to answer, so we went on to prepare a series of derivatives of 2-fluorocyclohexanol, for which the conformation can be specified with some confidence.

Bond-length data for ten compounds appear in Fig. 2, where they are compared with the best values for the parent, unsubstituted cyclohexanol derivatives discussed above. In this system the conclusions are clear. First, the C–OX bond is shorter for the 2-fluoro compound in every case. The effect is never large, but is largest for the best, sulfonate, leaving groups. That is to say, the sensitivity to the pK_a of the leaving group is reduced by the introduction of β-fluorine. Second, there is once more no significant difference between axial and equatorial cyclohexanol derivatives. And third, since the axial and equatorial derivatives have fluorine antiperiplanar and *gauche*, respectively, to the OX bond, there is no evidence to suggest that the effect depends on the dihedral angle F–C–C–OX. The sensitivity to the leaving group is measured by the slope of the best (least squares) line correlating the data for fluoro-derivatives in Fig. 2. The most extensive set of data, for compounds (**8** and **9**) with axial OX, is correlated by a line $l = 1.467 - 2.39 \times 10^{-3}$ pK_{HOX}, with $r = 0.973$. Including the equatorial derivatives reduces the correlation coefficient to $r = 0.957$, but has only a small effect on the slope and intercept [eqn. (iii)].

$$\text{Bond length (2-F-cyclohexyl–OX)} = 1.465 - 2.24 \times 10^{-3}\,\text{p}K_{HOX} \quad \text{(iii)}$$

Crystal Structure Correlations: the Effect of β-Silicon.—With only two structures so far available, one derived from a primary alcohol, with a trimethylsilyl group antiperiplanar to the C–OX bond, the other from cyclohexanol with a phenyldimethylsilyl group *gauche*, we cannot define the effect of a β-silyl group in terms of a correlation like eqn. (iii). And conclusions based on data for individual structures must be treated with due caution. Nevertheless we have good structures for esters **10pPB** and **11**, with the bonus of a second molecule in the asymmetric unit for **11**. Both show C–O-ester bond lengths significantly longer than expected for the parent compounds. For trimethylsilylethyl 4-phenylbenzoate, which crystallises, as expected on both steric and stereoelectronic grounds, in the extended conformation (dihedral angle Si–C–C–O 178.1°) the observed value is 1.466(3) Å. This compares with an expected value [eqn. (i)] of 1.450 Å. For the 3,5-dinitrobenzoate of *trans*-2-phenyldimethylsilylcyclohexanol (**11**) the silyl group is *gauche* (dihedral angle Si–C–C–O = 65 ± 0.5° for the two molecules), and the C–O-ester bond lengths 1.472(3) and 1.475(2) Å. These values are clearly high compared with our preferred standard of 1.462(4) Å for an equatorial cyclohexyl 4-phenylbenzoate, and even with the appropriate correction, using eqn. (ii), for the low pK_a of 3,5-dinitrobenzoic acid, the expected value is no more than 1.466 Å. Thus the little evidence we have is consistent with the introduction of β-silicon having a significant positive effect on the length of the C–O-ester bond,* but we can say nothing about the geometrical dependence of the effect.

Limitations of Crystal Structure Correlations.—Successful crystal structure correlations require high quality data, preferably many of them, and even with good data individual data points may on occasion deviate markedly from otherwise good correlations for no apparent reason. The plots shown in Figs. 1 and 2 illustrate the point nicely. The points for unsubstituted compounds (open circles, on the least squares line) are derived from large numbers of structures from the CSD, purged of outliers and of structures with high *R*-factors. The excellent correlation of bond length with pK_a indicates that random factors such as crystal packing have been screened or averaged out. In sharp contrast are the filled circles of Fig. 1, representing

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* Only one simple 2-silyloxy derivative is currently to be found in the CSD. This is the trimethylsilylethyl ether of a synthetic alcohol precursor of cytochalasin C.[28] It does in fact have a notably long C–OX bond (1.463 Å) antiperiplanar to trimethylsilyl, but we choose not to use this datum because of the high *R*-factor (7.8%).

five individual structures. This series was designed to reveal trends, but appears to be subject to more than one effect, of which varying conformation, as discussed above, may be one. The contrast in Fig. 2 is less marked. An excellent correlation is observed for the unsubstituted series, as before. And in this case, largely because we have more than twice as many individual data points, it is now possible to discern a convincing correlation for them also.

The more subtle the effect of interest, the smaller will be the absolute magnitude of any effect on structural parameters, and the larger the number of structures likely to be needed to reveal it. And as these absolute magnitudes approach experimental error, differences in crystal-structure correlations will no longer be observable, except with large and perfect data sets.

Comparison with Calculated Structures.—A perfect data set is not a realistic expectation for a series of X-ray crystal structures (although data collection at very low temperatures can reduce experimental error to ±0.001 Å). But a perfect, in the sense of internally self-consistent, set of data is an entirely reasonable expectation for a series of calculated structures. The systems we have studied previously by crystal-structure correlation techniques have been too complex for high-level calculations of series of structures to be practical. But advances in computational chemistry have reached a point where it is now a reasonable proposition to calculate *ab initio* structures complex enough, and in sufficient numbers, to be interesting to the organic chemist. We have calculated structures for several series of compounds related to the crystal structures discussed above. We selected three derivatives each of ethanol and of its 2-F and 2-SiH_3-substituted derivatives. The hetero-atom was fixed alternatively antiperiplanar and *gauche* to the C–OX bond before the structure was optimised, making five systems in all. The three derivatives, chosen to give a range of leaving group OX to match the series of crystal structures, were the methyl ether, and the formate and nitrate esters (X = CH_3 CHO and NO_2, respectively). As discussed in the Results section above, two important minima were located for each formate ester, corresponding to the *E* and *Z* conformations about the ester O–C=O bond.* Selected calculated data for the twenty structures appear in Tables 4–6.

The calculated bond lengths differ in detail from those observed for the crystalline primary alkyl derivatives. The observed shortening of the C–C bond in Y–C–C–OX with increasing electron-withdrawal by both Y and X is not reproduced. For polar bonds like C–OX and C–F, the calculated lengths are generally shorter by 0.02–0.03 Å;† whereas the calculated lengths of C–Si and especially C–C bonds, though closer to, are mostly longer than those observed in the crystal, in the small number of cases where close comparisons are possible.

For example, the mean observed C–C and C–O bond lengths in 2-phenylethyl toluene-*p*-sulfonate are 1.517 and 1.462 Å, respectively, while the calculated values for ethyl nitrate are 1.515 and 1.440 Å (Tables 1 and 4). Similarly, for 2-trimethylsilylethyl 4-phenylbenzoate (**10**pPB) the three bond lengths of the Si–C–C–O substructures are 1.876, 1.503 and 1.466, respectively, compared with calculated values for the same bonds in the corresponding conformer (**21***tZ*) of 2-silylethyl formate of 1.894, 1.517 and 1.442 Å.

Differences, and thus trends in bond lengths, are expected to be reproduced in the calculated structures most accurately, and where direct comparisons are possible we find good correlations between calculated and experimental bond lengths. We can construct three-point plots of observed C–OX bond lengths *vs.* the calculated values for primary alkyl derivatives taken from Tables 4–6, using eqns. (i)–(iii) to correct the experimental data to match the pK_as of methanol and formic and nitric acids. In all three cases where this is possible we find excellent linear relationships, with correlation coefficients, $r \approx 0.998$ (Table 7). For the primary alkyl series the observed bond lengths are 20% less sensitive than the calculated values to changing leaving group. The (secondary) cyclohexyl systems, as expected, show a higher sensitivity than calculated (45% higher than observed) for primary. And the data for 2-fluorocyclohexyl derivatives parallel those calculated for the 2-fluoroethyl series almost exactly, with a slope close to unity, the intercept thus reflecting the difference in absolute magnitude of the C–OX bond length of 0.041 Å between the two series.

From a comparison of C–OX bond lengths (Tables 5 and 6) for the *trans* and *gauche* conformers of 2-fluoro and 2-silylethyl derivatives it is apparent that the calculated differences are smaller than the experimental errors of the crystallographic measurements. This is the likely explanation for our failure to observe such differences between diastereoisomers in the 2-substituted cyclohexyl system; though differences are expected to be more significant at secondary centres, in so far as an increase in the C–OX bond length corresponds to the early stages of an S_N1 process. On the other hand, the introduction of fluorine or silicon at C(2) is predicted to induce small but measurable differences, as observed. The quantitative effects are best assessed in terms of structure–reactivity correlations.

Discussion of Calculated Data.—We first subjected the calculated data to the same analysis that we used to obtain crystal structure correlations.[2–6] For each of the five sets of three alcohol derivatives we find an excellent linear correlation ($r = 0.9985$ or better, Table 8) between the length of the C–OX bond and the pK_a of the conjugate acid, HOX, of the leaving group, just as we generally find for similar series of crystal structures. This result is consistent with the observed general applicability of this structure–reactivity correlation to experimental data,[2,3] and some confirmation of the fundamental nature of these plots. The results of the analysis (Table 8) are broadly in line with expectation. Both the slope and the intercept are greatest for the *trans*-silylethyl system, and smallest for 2-fluoroethyl derivatives. [Note that the intercept of one of these plots corresponds to the C–OX bond length for an ester of an acid HOX of $pK_a = 0$, thus a derivative with a very good leaving group. For derivatives of weak acids, such as the methyl ethers, the calculated bond lengths are all closely similar, between 1.3914 and 1.3994 Å (Tables 4–6)]. But the differences between *trans* and *gauche* 2-F or 2-Si conformers remain very small for all leaving groups.

The largest differences arise in the slopes or sensitivity parameters (Table 8), though none amounts to more than 10%. Relative to the unsubstituted series these are 1.055 and 1.014 times greater for *trans* and *gauche* SiH_3, respectively, and smaller, by factors of 0.904 and 0.951 for *trans* and *gauche*-F. These results are simply explained in frontier orbital terms. A major influence on the length and the ease of cleavage of the C–OX bond in Y–C–C–OX is the strength of the σ_{C-Y}–σ^*_{C-OX} interactions; which may involve *gauche* or the more efficient[29] antiperiplanar geometry. These are stronger for σ donor

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* Note that the C–O-ester bond length is systematically longer in the *Z*-esters. This is the opposite of a prediction based on the higher gas-phase basicity of the *Z* lone pairs of the carboxylate anion (R. D. Gandour, *Biorg. Chem.*, 1981, **10**, 169), a point recently discussed elsewhere (F. H. Allen and A. J. Kirby, *J. Am. Chem. Soc.*, 1991, **113**, 8829).

† A calculation for (*E*)- and (*Z*)-ethyl formate, with full geometry optimisation at the MP2 (DZP) level, gives both C–C and C–O-ester bond lengths identical, to within experimental error, to those expected [eqn. (i)] in the crystal. However, the relative energies are almost almost unchanged. Since we are interested primarily in trends, geometries were not optimised at the MP2 level for the other structures.

Table 7 Correlations between calculated and experimental data

	(C–OX) $BL_{obs} = \alpha BL_{calc} + b$		
System	Intercept	Slope	r
RCH_2OX [eqn. (i)][a]	0.301	0.803	0.9976
Cyclohexyl–OX [eqn. (ii)][a]	−0.199	1.165	0.9988
2-F-cyclohexyl–OX (*trans*)[b]	0.041	0.998	0.9978

[a] Plotting observed C–OX bond lengths *vs.* calculated values for unsubstituted primary alkyl derivatives. [b] The same for primary *trans*-2-fluoroalkyl alkyl derivatives.

Table 8 Correlations for calculated data: C–OX bond length *vs.* pK_{HOX}

System	Intercept	10^3 Slope	r
t-$H_3SiCH_2CH_2OX$	1.4389	2.6356	0.9998
g-$H_3SiCH_2CH_2OX$	1.4389	2.5319	0.9994
CH_3CH_2OX	1.4372	2.4960	0.9990
g-FCH_2CH_2OX	1.4284	2.3743	0.9995
t-FCH_2CH_2OX	1.4286	2.2543	0.9985

Table 9 Correlations for calculated data: bond length *vs.* electronegativity[a]

System	Intercept	10^3 Slope	r
t-YCH_2CH_2OMe	1.4029	−2.40	0.9774
t-YCH_2CH_2OCHO-*Z*	1.4369	−4.00	0.9969
t-$YCH_2CH_2ONO_2$	1.4517	−5.30	0.9982

[a] Pauling electronegativities, as updated by Allred.[32]

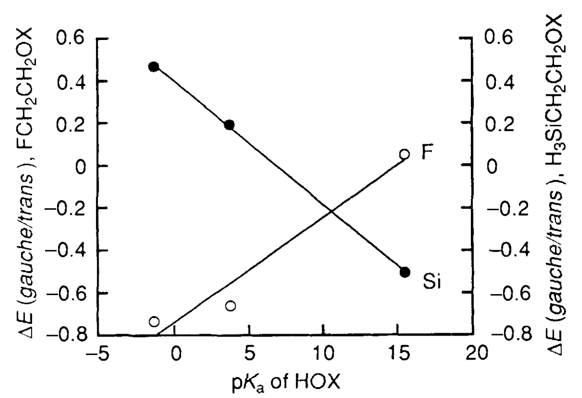

Fig. 3 Plot of calculated differences in total energy between *gauche* and antiperiplanar forms of 2-fluoro (○) and 2-silylethanol derivatives (●) against the pK_a of HOX, the conjugate acid of the leaving group. Data from Table 10.

orbitals of higher energy, thus for $\sigma_{C-Si} > \sigma_{C-H} > \sigma_{C-F}$; and strongest for *trans*-Si derivatives, which have one antiperiplanar σ_{C-Si}–σ^*_{C-OX} and two *gauche* σ_{C-H}–σ^*_{C-OX} interactions.

The largest is for antiperiplanar F. This is not unexpected, since the substitution of F for H involves a substantially greater change in electronegativity than that of Si for H. (We use the Pauling scale as updated by Allred,[30] who gives values of 1.90, 2.20 and 3.98 for Si, C and F, respectively: though the choice of scale does not affect our correlations significantly.) In fact for a given leaving group OX there is a good linear relationship between the calculated length of the C–OX bond in Y–CH_2–CH_2–OX and the electronegativity of Y. These correlations are summarised in Table 9 for the *trans* conformers. For the *gauche* isomers the correlations are almost perfect (r = 0.9994 or better).

This is a second simple correlation relating the length of the C–O bond and an independent reactivity parameter, which should also hold for experimental data. Two data sets are available from the crystallographic work where the effects of both Si and F are observed in the same system, in both cases on C–O-ester bond length. For primary alkyl derivatives no correlation with electronegativity is observable. This is not unexpected, given the limitations of the data. Although we have an accurate value for the parent primary alkyl system from eqn. (i), we have only individual data points for the 2-$SiMe_3$ (**10**pPB) and 2-F (**1**pNB) esters, and we know that the C–O-ester bond in (**1**pNB) is anomalously long (actually longer than expected for the unsubstituted *p*-nitrobenzoate, Fig. 1). For the cyclohexyl system, on the other hand, we have good correlations for both the 2-fluoro and the unsubstituted series [eqns. (ii) and (iii)], which allow reliable estimates of the C–O-ester bond lengths in the 3,5-dinitrobenzoates, to compare with the observed value for the 2-Me_2PhSi derivative (**11**). As predicted, the three bond lengths give a reasonable linear correlation (r = 0.947), when plotted against the electronegativity of the 2-substituent; but the actual values involved (1.4735, 1.467 and 1.459 Å for the 2-Si, unsubstituted and 2-F-esters, respectively) differ by no more than 2–3 typical standard deviations for crystal-structure measurements, so the correlation will not easily be observed experimentally, without very good low-temperature data.

1,3-*Interaction Energies: the* gauche *Effect*.—A useful generalisation,[8c] relevant to both the anomeric and the *gauche* effect, identifies 'a stereoelectronic preference for conformations in which the best donor lone pair or bond is antiperiplanar to the best acceptor bond.' This is a convincing explanation for the observed preference for the *gauche* conformation of 1,2-difluoroethane, because both steric and electrostatic forces favour the antiperiplanar geometry. In practice only a minority of compounds with the X–C–C–Y structure actually adopt the *gauche* conformation, which is favoured for the most electronegative X and Y;[31] thus 1,2-dichloroethane prefers to be antiperiplanar, and while both 2-fluoro and 2-chloroethanol favour the *gauche* conformation, X–HO hydrogen bonding is a complicating factor.[32] The 'variable oxygen probe' OX in the 2-fluoro alcohol derivatives we have studied is intermediate in electronegativity between OH and F, and permits a detailed examination of the *gauche* effect in the borderline region.

We observe *gauche* conformations for all the crystalline 2-fluoro alcohol derivatives studied in this work (**1a**–**e**, **2a**, **6**), except in those cases where the conformation is locked by the equatorial *tert*-butyl group of a cyclohexanol. In contrast, both 2-silyl alcohol derivatives adopt the antiperiplanar conformation. These preferences, and the trends expected as the effective electronegativity of the OX probe is changed, are well reproduced by the calculations. Fig. 3 shows a plot of the calculated differences in total energy between the *trans* and *gauche* conformations of FCH_2CH_2OX and $H_3SiCH_2CH_2OX$, as a function of the pK_a of HOX. Increasing the effective electronegativity of the leaving group OX (lower pK_a) strongly favours the *gauche* conformation of the fluoro alcohol derivatives, but has the opposite effect on the silyl alcohols.

Apart from reproducing the observed trends, the calculations also reproduce observed *gauche*/*trans* preferences fairly well. The two isomers are comparable in energy for 2-fluoroethyl methyl ether, and favour the *gauche* form for other fluoroethyl derivatives, and the *trans* form for the silylethyl derivatives, with better leaving groups. The exception is the silylethyl methyl ether, where the calculation predicts a preference for the *gauche* conformation of 0.5 kcal mol^{-1}. It is likely that the single molecule calculations exaggerate the stability of the *gauche* form for the silyl series, and for this compound in particular, for electrostatic reasons, as discussed below.

Table 10 Calculated energies for *trans* $\rightleftarrows$ *gauche* and isodesmic reactions

	ΔE_{calc}/kcal mol^{-1} [a]		
		Isodesmic reaction (iv)	
Compound	*trans* $\rightleftarrows$ *gauche*	*trans*	*gauche*
FCH_2CH_2OMe	0.052	−2.23	−2.28
FCH_2CH_2OCHO (*Z*)	−0.660	−3.62	−2.96
$FCH_2CH_2ONO_2$	−0.734	−4.83	−4.09
$H_3SiCH_2CH_2OMe$	−0.505	0.624	1.13
$H_3SiCH_2CH_2OCHO$ (*Z*)	0.195	0.285	0.09
$H_3SiCH_2CH_2ONO_2$	0.469	0.379	−0.09

[a] Data from MP2 (DZP) calculations based on SCF (DZP) geometries.

The interaction of the Y and the OX groups in the YCH_2CH_2OX system is assessed most simply in terms of the 1,3-interaction energies,[33] given by the net change in energy for the isodesmic reaction (iv). The calculated values of ΔE appear in Table 10. These results extend those of Radom *et al.*, who used standard bond lengths and angles to calculate energies for the *trans* and *gauche* forms of FCH_2CH_2X at the 4-31G level.[33]

$$Y\text{-}CH_2\text{-}CH_2OX + CH_3\text{-}CH_3 \longrightarrow CH_3\text{-}CH_2\text{-}OX + Y\text{-}CH_2\text{-}CH_3 \quad \text{(iv)}$$

The results are generally consistent with expectations from simple frontier orbital considerations, as discussed above in the context of effects on bond length. Stabilising σ–σ^* interactions are stronger for σ donor orbitals of higher energy, thus for $\sigma_{C-Si} > \sigma_{C-H} > \sigma_{C-F}$; and for lower energy σ^* acceptor orbitals: thus strongest for antiperiplanar σ_{C-F}–σ^*_{C-OX} and weakest for antiperiplanar σ_{C-Si}–σ^*_{C-OX}. So the F/OX interaction is destabilising because the reference H/F and H/OX interactions [eqn (iv)] are both stronger, whereas the reverse is true for Si/OX. *trans* Interactions are stronger than *gauche*, with the single exception of the methyl silylethyl ether. A likely explanation is a stabilising electrostatic interaction between Si and the oxygen atom of the OMe group which specifically favours the *gauche* conformation. The calculated atom charge on Si, of +1.43, does not differ significantly (1.42 ± 0.01) for other derivatives, whereas the charge on O, −0.58 in the ether, is reduced to 0.50 or less in the formate and nitrate esters. This *difference* of 0.08 electrons corresponds to an extra stabilisation of over 12 kcal mol^{-1} [for point charges at the distance (3.05 Å) separating Si and O in the calculated structure of **19g**].

This exception is a clear warning against over-interpretation of the 1,3-interaction energies (Table 10) calculated for the Si compounds, particularly since the absolute magnitudes are small, and become positive only with the addition of electron correlation.

Conclusions

The effects of the introduction of β-fluorine and silicon on the length of the C–OX bond in the systems we have studied are in the expected direction, but small. The crystallographic data show that the bond-shortening effects of antiperiplanar and *gauche* F are the same, to within experimental error, and calculated structures support this conclusion. The effect corresponds to a strengthening of the C–OX bond—consistent with the reduced rates of C–OX cleavage observed when an electron-withdrawing substituent is introduced at C(2)—which is not significantly dependent on the F–C–C–OX dihedral angle. It is thus not primarily the result of the difference in σ–σ^*_{C-OX} interactions between the antiperiplanar and *gauche* conformations, and is most simply rationalised in terms of through-bond electrostatic effects: the C(2)→F dipole inducing increased positive charge and thus s-character at C(1)–OX.

The calculated bond-lengthening effect of β-Si is of the same order of magnitude, and no greater than expected from electronegativity differences in the series F,H,Si. The lengthening of the C–OX bond as XO^- becomes a progressively better leaving group evidently models only the early stages of C–OX cleavage reactions; perhaps not surprisingly, since the reactions concerned are formally S_N1 processes at primary and secondary centres. In particular there is no sign from the calculations, and no evidence from crystal structures, of the enhanced σ_{C-Si}–σ^*_{C-OX} interaction which leads to the very large effects on reactivity discussed in the introduction.

This is consistent with other crystallographic correlations, involving systems ROX in which the heterolytic cleavage of the C–OX bond gives rise to 1,2-alkyl shifts[34] and non-classical cations.[35] These too show no evidence for the involvement of the adjacent centre as the C–OX bond stretches. It appears that the two processes—C–OX bond cleavage and the further structural reorganisation—are not closely coupled, at least in the early stages of such reactions. This is in contrast with such processes as the spontaneous cleavage of unsymmetrical acetals,[4] where substantial progress towards the transition state can be observed over a series of crystal structures (and where higher-energy donor orbitals are involved, and extensive further heavy-atom reorganisation is not required). This pattern of behaviour shows similarities to the apparent uncoupling of resonance and inductive contributions to transition-state stabilisation ('transition-state imbalance') recently observed in a number of reactions.[36]

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