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PARTICIPATION OF BETA CARBON—SILICON BONDS IN THE DEVELOPMENT OF POSITIVE CHARGE IN FIVE-MEMBERED RINGS

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ABSTRACT

The development of positive charge β to silicon in a saturated five-membered ring has been studied in the *cis*- and *trans*-2-(trimethylsilyl)cyclopentyl trifluoroacetates. The *cis* substrate solvolyzes in 97% trifluoroethanol at 25° C about 5 times faster than the analogous six-membered ring, after correction for differences in ring strain. The *trans* substrate solvolyzes about 360 times more slowly than the analogous six-membered ring. These changes are in agreement with a hyperconjugative mechanism for interaction between the silyl group and the developing positive charge. The expected cosine-squared dependence of hyperconjugation on the Si—C—C—X dihedral angle suggests that the *cis* dihedral angle is reduced somewhat from the 60° in the six-membered ring, and the *trans* dihedral angle is reduced substantially from the 180° in the six-membered ring.

Silicon strongly stablizes the development of positive charge on an atom two bonds away, for example in the reaction $Me_3SiCH_2CH_2X \rightarrow Me_3SiCH_2CH_2^+$.[1] This effect is generally attributed to hyperconjugation between the Me$_3$Si—C bond and the developing empty *p* orbital on carbon. Consequently, there is a strong stereochemical component, whereby the effect is largest when the Si—C bond and the devloping *p* orbital are parallel. We have found that a rigid antiperiplanar (axial–axial) relationship between Me$_3$Si and a trifluoroacetate leaving group in the cyclohexane framework imparts an acceleration of some 12 orders of magnitude, in comparison with cyclohexyl trifluoroacetate.[1] The *gauche* (axial–equatorial) arrangement has a significant but much smaller acceleration, only four orders of magnitude.

The six-membered ring was chosen for our initial study[1] because of its well defined dihedral angles, about 180° and 60° in the above two cases. We adapted the mathematics for the dependence of beta hydrogen–deuterium isotope effects (which also derive from hyperconjugative interactions) on dihedral angles to the present context, as in equation (1), in which $k_{\mathrm{Si},\theta}$ is the rate for a

$$\log (k_{\mathrm{Si},\theta}/k_{\mathrm{H}}) = \cos^2\theta[\log(k^{\mathrm{V}}_{\mathrm{Si},0^\circ}/k_{\mathrm{H}}{}^{\mathrm{V}})] + \log(k^{\mathrm{I}}{}_{\mathrm{Si}}/k_{\mathrm{H}}{}^{\mathrm{I}}) \qquad (1)$$

silylated system with Si—C—C—X dihedral angle θ, k_{H} is the rate of the unsilylated model, the superscript V refers to the hyperconjugative or vertical contribution to the rate, and the superscript I refers to the inductive contribution. Thus the hyperconjugative contribution has a cosine-squared dependence on dihedral angle. According to equation (1), the maximum acceleration occurs equally at 0° or 180°, when overlap is best ($\cos^2\theta = 1$). The maximum

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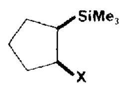
acceleration, $\log(k^{V}_{\mathrm{Si},0^{\circ}}/k_{\mathrm{H}}^{V})$, then is modulated by the term $\cos^2\theta$. The inductive term is much smaller and additive. From the study of biased six-membered rings, we found that the maximum hyperconjugative term is about 10^{10} and the inductive term is 10^2 for 97% aqueous trifluoroethanol at 25° C.

In the present work we have extended this study to a case in which the dihedral angles are not known: five-membered rings. Such systems can adopt envelope, half-chair (twist), or even planar conformations. Constraints of bond angles prevent the achievement of a 180° antiperiplanar geometry between vicinal groups. Consequently, reduced silicon participation is expected in the development of beta positive charge. In order to study this phenomenon in five-membered rings, we have prepared compounds **1** and **2**, which respectively have *cis* and *trans* geometries between the ring substituents. We report herein the preparation and solvolysis of these substrates. From the observed rate accelerations, we are able to estimate the average dihedral angles between the substituents in the transition states to development of positive charge.



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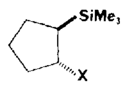

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RESULTS

cis-2-(Trimethylsilyl)cyclopentanol, **1**-OH, was prepared in the same way that the analogous six-membered ring had been prepared.[1] 1-Chlorocyclopentene was converted to 1-(trimethylsilyl)cyclopentene, which was epoxidized with *meta*-chloroperbenzoic acid. Reduction of the epoxide with lithium aluminum hydride provided the *cis* alcohol, **1**-OH. The *trans* six-membered ring had been obtained by ring opening of cyclohexene oxide with trimethylsilylpotassium.[1] The same procedure with cyclopentene oxide failed, presumably because of unfavorable dihedral angles for approach of the anion. (Exploration of this reaction as a function of ring size in fact showed that the reaction occurs with good yield only with the six-membered ring. Reaction with the five-, seven-, and eight-membered rings and even some acyclic compounds gave little or no yield.) Hydroboration of 1-(trimethylsilyl)-cyclopentene followed by oxidation successfully produced *trans*-2-(trimethylsilyl)cyclopentanol, **2**-OH.

The trifluoroacetates of both isomers were prepared and found to be stable compounds. The rate of the *cis* isomer, **1**-O(CO)CF_3, was measured directly at 25·0° C in three water–trifluoroethanol mixtures. Measurements for the more reactive *trans* isomer, **2**-O(CO)CF_3, were carried out at low temperatures in two water-trifluoroethanol mixtures and extrapolated to 25·0° C. Freezing of the solvent prevented measurements below 80% trifluoroethanol. The unsubstituted substrate, cyclopentyl trifluoroacetate, was selected as the unsilylated model (k_{H} in equation (1)). These rates are given in Table 1. Rate ratios for the five- and six-membered rings are collected in Table 2.

Molecularity of the reaction was determined by means of Raber–Harris plots.[1,2] Additional data were needed in aqueous ethanol mixtures (Table 3). Some of these measurements had to be made at low temperatures and extrapolated to 25·0° C. The Raber–Harris plots for cyclopentyl trifluoroacetate, **1**-O(CO)CF_3, and **2**-O(CO)CF_3 are given in Figures 1–3.

Table 1. Rate measurements in aqueous trifluoroethanol solvents

System	%TFE[a]	temp, °C	r	k, s^{-1}
cyclopentyl trifluoroacetate	60	80·0	0.9994	9·45 × 10^{-5}
		90·0	0·9994	1·07 × 10^{-4}
		25·0[b]		4·11 × 10^{-5}
	70	95·0	0·999	1·04 × 10^{-4}
		90·0	0·9997	8·06 × 10^{-5}
		25·0[b]		1·35 × 10^{-6}
	80	90·0	0·9992	2·02 × 10^{-5}
		95·0	0·998	2·67 × 10^{-5}
		25·0[b]		2·29 × 10^{-7}
	97	25·0[c]		4·47 × 10^{-9}
1-O(CO)CF_3	60	25·0	[d]	1·06 × 10^{-3}
	80	25·0	[d]	9·57 × 10^{-4}
	97	25·0	[d]	8·19 × 10^{-4}
2-O(CO)CF_3	80	−16.0	0·998	1·94 × 10^{-3}
		−11·0	0·999	3·23 × 10^{-3}
		25·0[b]		7·66 × 10^{-2}
	97	−20·0	0·9995	2·03 × 10^{-3}
		−9·0	0·995	5·20 × 10^{-3}
		25·0[b]		6·15 × 10^{-2}

[a] Percentage by weight.
[b] Extrapolated from other temperatures.
[c] Extrapolated from the other solvents.
[d] Average of several runs.

Table 2. Rate ratios of trifluoroacetates in 97% trifluoroethanol at 25°C

Substrate	k, s^{-1}	k_{rel}	k_{rel}
cyclopentyl	4·47 × 10^{-9}	1	
1 (*cis*)	8·1 × 10^{-4}	1·83 × 10^{5}	1
2 (*trans*)	6·15 × 10^{-2}	1·38 × 10^{7}	75·9
cyclohexyl[a]	7·05 × 10^{-10}	1	
cis[a]	2·36 × 10^{-5}	3·3 × 10^{4}	1
trans[a]	4·0 × 10^{0}	5·7 × 10^{9}	1·7 × 10^{5}

[a] Six-membered analogues; data from Reference 2.

Activation parameters provide additional information about molecularity and are presented in Table 4.

The *cis* substrate gave over 97% cyclopentene and less than 3% alcohol as the product. The *trans* substrate gave exclusively cyclopentene in 80% aqueous ethanol but some alcohol in 97% trifluoroethanol. Cyclopentyl trifluoroacetate gave mostly cyclopentene.

Table 3. Rate measurements in aqueous ethanol solvents

System	%EtOH[a]	temp, °C	*r*	*k*, s^{-1}
cyclopentyl trifluoroacetate	50	60·0[b]		2·01 × 10^{-4}
		50·0[b]		1·37 × 10^{-4}
		25·0[c]		4·70 × 10^{-5}
	60	60·0[b]		1·33 × 10^{-4}
		50·0[b]		8·38 × 10^{-5}
		25·0[c]		2·68 × 10^{-5}
	70	60·0[b]		6·85 × 10^{-5}
		70·0[b]		1·09 × 10^{-4}
		25·0[c]		1·05 × 10^{-5}
	80	70·0	0·99997	6·18 × 10^{-5}
		75·0	0·99992	7·72 × 10^{-5}
		80·0	0·99993	1·04 × 10^{-4}
		85·0	0·9995	1·14 × 10^{-4}
		25·0[c]		5·82 × 10^{-6}
1-O(CO)CF_3	50	25·0[b]		1·45 × 10^{-4}
	60	25·0[b]		1·67 × 10^{-4}
	70	25·0[b]		5·95 × 10^{-5}
	80	25·0[b]		4·20 × 10^{-5}
		35.0[b]		2·38 × 10^{-4}
		40·0[b]		4·14 × 10^{-4}
		45·0[b]		7·79 × 10^{-4}
2-O(CO)CF_3	60	0·0	0·9995	2·75 × 10^{-4}
		10·0	0·998	4·56 × 10^{-4}
		25·0[c]		9·56 × 10^{-4}
	70	0·0	0·9998	5·62 × 10^{-4}
		10·0	0·996	1·52 × 10^{-3}
		25·0[c]		5·97 × 10^{-3}
	80	0·0[b]		1·57 × 10^{-4}
		10·0	0·998	7·66 × 10^{-4}
		15·0	0·997	1·69 × 10^{-3}
		25·0[b]		4·07 × 10^{-3}

[a] Percentage by volume.
[b] Average of two runs.
[c] Extrapolated from other temperatures.

DISCUSSION

The tests for molecularity indicate that there is a change in mechanism on introduction of the trimethylsilyl group. The Raber–Harris plot for cyclopentyl trifluororoacetate (Figure 1) gives two separate lines, characteristic of a bimolecular reaction between substrate and solvent (k_s). Similar results were obtained with cyclohexyl trifluoacetate,[1] so that these two substrates may be compared on a common mechanistic basis. Single line plots, however, are obtained for both *cis*- and *trans*-2-(trimethylsilyl) cyclopentyl trifluoroacetate, indicative of a unimolecular (k_C) reaction (Figures 2 and 3), as was similarly observed with silylated six-membered rings.[1] At high levels of water (50% ethanol for the *cis* substrate, 60% ethanol for the *trans* substrate)

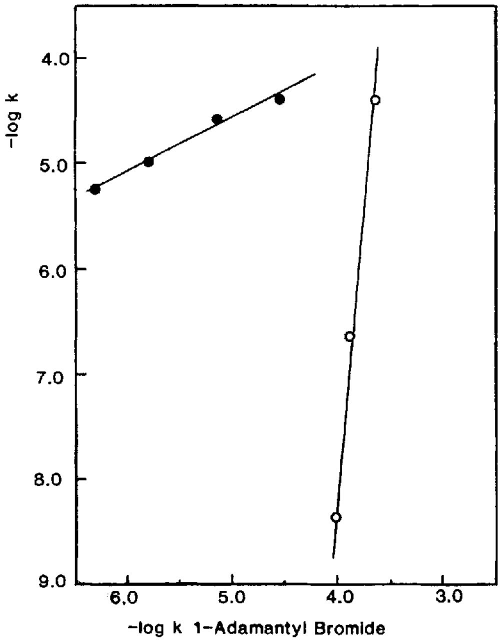

Figure 1. The Raber–Harris plot for cyclopentyl trifluoroacetate. Closed circles are for aqueous ethanol, open circles for aqueous trifluoroethanol

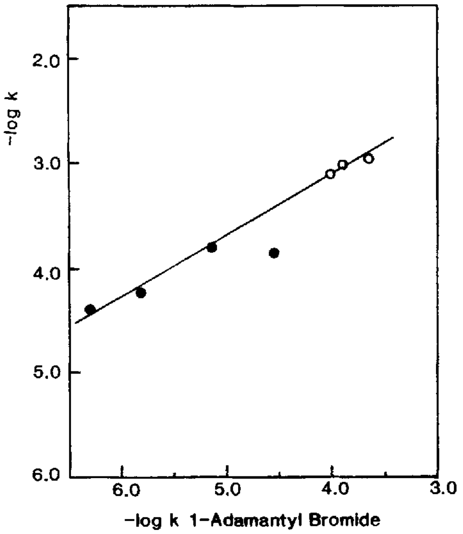

Figure 2. The Raber–Harris plot for *cis*-2-(trimethylsilyl)-cyclopentyl trifluoroacetate (1-O(CO)CF_3)

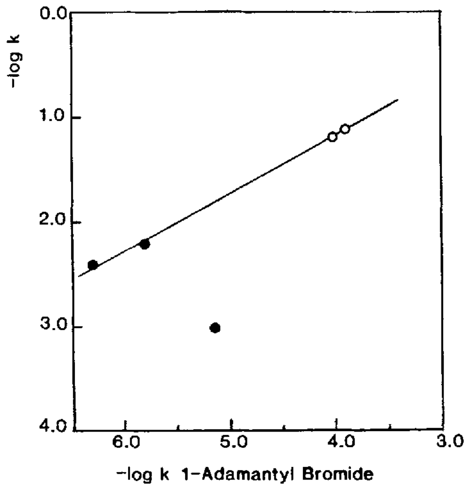

Figure 3. The Raber–Harris plot for *trans*-2-(trimethysilyl)-cyclopentyl trifluoroacetate (2-O(CO)CF_3)

Table 4. Activation parameters in 80% ethanol

Systems	no. of temp	$\Delta G^\ddagger$, kcal/mol	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	r
cyclopentyl	4	24·5	9·9	−49·1	0·98
1 (*cis*)	4	23·4	27·0	12·1	0·997
2 (*trans*)	4	20·9	20·7	0·5	0·991

there is some deviation from the linear plot, consistent with a possible bimolecular contribution or with possible heterogeneity of medium when the water concentration reaches a certain level.

These results with the silylated substrates are not consistent with a concerted fragmentation, which should not show the mechanistic parallel with the k_C model, 1-adamantyl bromide, in Figures 2 and 3. Direct (nonvertical) participation by Me_3Si in the departure of the leaving group remains a viable possibility, but we continue to adhere to the current position that a vertical interaction between Me_3Si—C and the developing positive charge is the major mechanism.[1]

The activation parameters (Table 4) provide an alternative test for molecularity. The activation entropy for cyclopentyl trifluoroacetate is large and negative, as expected for a reaction that requires some organization of solvent. For the two silylated substrates, $\Delta S\ddagger$ is negligible or slightly positive, as expected for a reaction in which the number of particles is increasing. An identical pattern for the activation entropy was observed for the analogous six-membered rings.[1] Thus introduction of a trimethylsilyl group adjacent to a solvolytic leaving group in these rings causes a fundamental mechanistic change irrespective of the dihedral arrangements.

Although dihedral angles are reasonably well known in six-membered rings, such is not the case for these five-membered rings. Comparison of the rates of the two ring sizes is instructive (Table 2). Cyclopentyl trifluoroacetate is 6·3 times more reactive than cyclohexyl trifluoroacetate, probably because of the higher ground state energy of the five-membered ring due to higher angle and eclipsing strain. The *cis* five-membered ring is 34·7 times as fast as the unbiased six-membered ring. (The comparison is made between **1**-O(CO)CF_3 and the unbiased *cis*-2-(trimethylsilyl)cyclohexyl trifluoroacetate.[1] Placement of a *tert*-butyl group at the 4 position of the six-membered ring freezes the other substituents into specific axial or equatorial locations but has almost no effect on the rate.) In addition to ground state differences, the five-membered ring has an acceleration from silicon by a factor of about 5·5 (34·7/6·3). Since the major mechanism for stabilization of positive charge by a beta silicon is thought to be hyperconjugation,[1] the magnitude of the effect would depend on the square of the cosine of the Si—C—C—X dihedral angle (equation (1)). The dihedral angle is about 60° in the *cis* six-membered ring, so that from the shape of the cosine-squared dependence the increased rate indicates the average dihedral angle must be smaller than 60°.

On the other hand, the *trans* five-membered ring reacts 65 times more slowly than the unbiased six-membered, or 360 (65 × 5·5) when corrected for ground state differences.* (The

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*The comparison is made between **2**-O(CO)CF_3 and the unbiased *trans*-2-(trimethylsilyl)cyclohexyl trifluoroacetate.[1] If the comparison were made with the biased trans diaxial form with a 4-*tert*-butyl group, the five-membered ring would appear some 400 times slower still. No qualitative conclusions would be changed had we compared flexible five-membered rings with the rigid (biased) six-membered rings.

rate of *trans*-2-(trimethylsilyl)cyclohexyl trifluoroacetate was measured by two quite different methods.[1] The result was the same within a factor of 6. These comparisons with the *trans* six-membered ring are only approximate. This spread of the numbers has no influence on our final conclusions.) The *trans* six-membered ring reacts from the optimal 180° conformation, so that the slower *trans* five-membered ring must have reduced hyperconjugation on the average because of its smaller and less favorable dihedral angle (less than 180°). The cosine-squared dependence has a maximum at 0° as well as 180°. The fact that the *cis* five-membered ring is several orders of magnitude slower than even the unbiased* *trans* (180°) six-membered ring requires that the five-membered ring not be planar. A planar ring would have resulted in the favorable 0° dihedral angle for the *cis* form.

Saturated five-membered rings are usually described in terms of envelope and half-chair (twist) conformations.[3] It is quite likely that **1**- and **2**-O(CO)CF_3 exist as mixtures of conformations, but the rates require that the average dihedral angle between the C—Si and the C—X (X = O(CO)CF_3) bonds be smaller than 180° in the *trans* form and smaller than 60° in the *cis* form. Quantitative application of the cosine-squared dependence of the rate acceleration (equation (1)) provides an approach to a more accurate definition of the dihedral angles in the five-membered systems. The quantity $k^{\mathrm{V}}_{\mathrm{Si},0^\circ}/k_{\mathrm{H}}^{\mathrm{V}}$ is known to be 10^{10} (the hyperconjugative contribution) and $k^{\mathrm{I}}_{\mathrm{Si}}/k_{\mathrm{H}}^{\mathrm{I}}$ to be 10^2 (the inductive contribution).[1] Since $k_{\mathrm{Si},\theta}/k_{\mathrm{H}}$ is measured for the *cis* and *trans* five-membered rings ($1{\cdot}83 \times 10^5$ and $1{\cdot}38 \times 10^7$ respectively in Table 2), equation (1) may be solved for $\cos^2\theta$ in each case. In this way, the average *cis* dihedral angle was calculated to be about 50° and the average *trans* dihedral angle to be about 147°. These angles should be considered to be very approximate, but at least they provide a rough indication of the angular relationships in the five-membered rings.

CONCLUSIONS

Introduction of a trimethysilyl group that is beta to a position at which positive charge develops in a five-membered ring causes large rate enhancements (10^5–10^7 for trifluoroacetates in 97% trifluoroethanol). The *trans* arrangement is less effective than in the six-membered ring, and the *cis* arrangement is slightly more effective than in the six-membered ring, in agreement with the expectations of a hyperconjugative cosine-squared dependence of the rate acceleration on the Si—C—C—X (X = trifluoroacetate) dihedral angle. Thus the *trans*/*cis* ratio is only 75 in the five-membered ring, compared with 10^5 in the six-membered ring.[1]

EXPERIMENTAL SECTION

1-(Trimethylsilyl)cyclopentene. In a three-necked flask with a gas inlet and a rubber septum was mixed Na chips and 300 ml of dry diethyl ether. Under a N_2 atmosphere, 1-chloropentene (6·35 g, 60 mmol) and chlorotrimethylsilane were added in turn via a syringe. After 10 days of stirring at room temperature, the reaction was quenched by careful addition of 50 ml of H_2O. The phases were separated, and the aqueous portion was extracted with ether (3 × 50 ml). The combined organics were dried ($MgSO_4$). Distillation of the residue after evaporation of solvent gave the desired product: 4·46 g, 53%; bp 148–150°C (760 mmHg); ^{1}H-NMR ($CDCl_3$) δ 0·1 (s, 9, $SiMe_3$), 1·9 (br m, 2, β CH_2), 2·5 (br m, 4, α CH_2), 6·1 (br s, 1, vinyl proton).

1-(Trimethylsilyl)cyclopentene oxide. *m*-Chloroperbenzoic acid (10·8 g, 80% purity, the rest of the material being *m*-chlorobenzoic acid, 50 mmol) was dissolved in 200 ml of cooled (0° C) CH_2Cl_2. A solution of 1-(trimethylsilyl)cyclopentene (4·46 g, 31·8 mmol) in 10 ml of CH_2Cl_2 was then added dropwise with stirring. After having been stirred at room temperature overnight, the mixture was cooled again and the solid (*m*-chlorobenzoic acid) was removed by means of filtration. The filtrate was washed with 10% aqueous NaOH solution and water and dried. After evaporation of solvent, vacuum distillation gave the product: 2·94 g, 59·3%; bp 65–67° C (17 mmHg); ^{1}H-NMR ($CDCl_3$) δ 0·1 (s, 9, $SiMe_3$), 1·0–2·1 (br m, 6, CH_2), 3·2 (s, 1, CH).

cis-2-(Trimethylsilyl)cyclopentanol (1-OH). A solution of 1-(trimethylsilyl)cyclopentene oxide (2·92 g, 18·8 mmol) was added dropwise to a suspension of $LiAlH_4$ (1·6 g, 42 mmol) in 50 ml of dry diethyl ether, which had been cooled with an ice bath. The mixture was stirred overnight at room temperature, and water (30 ml) was added cautiously. The solid was filtered off, and the filtrate was washed with ether. The combined ethereal solution was dried ($MgSO_4$). Distillation of the residue after solvent evaporation afforded the product: 1·53 g, 52%; bp 79–80° C (16 mmHg); ^{1}H-NMR ($CDCl_3$) δ 0·1 (s, 9, $SiMe_3$), 0·6–2.1 (br m, 8, CH_2, CHSi, OH), 4·5 (br s, 1, CHO); ^{13}C-NMR ($CDCl_3$) δ −1·28 ($SiMe_3$), 24·3, 25·7, 35.3, 37.9 ($CH_2CH_2CH_2CHSi$), 76·7 (CHO). Anal. calcd. for $C_8H_{18}SiO$: C, 60·72; H, 11·39; Si, 17·76. Found: C, 60·61; H, 11·42; Si, 17·53.

trans-2-(Trimethylsilyl)cyclopentanol (2-OH). According to the method of Larson *et al.*,[4] a mixture of BF_3 etherate (5·98 g, 52 mmol) in 5 ml of dry diglyme was added under N_2 dropwise to a solution of $NaBH_4$ (1·55 g, 40·9 mmol) in 15 ml of diglyme. The borane so generated was passed first through a saturated solution of $NaBH_4$ in diglyme (to remove trace amounts of BF_3) and then through a dry ice–acetone trap. The gas was then bubbled into a solution of 1-(trimethylsilyl)cyclopentene (3·68 g, 26·3 mmol) in 50 ml of dry tetrahydrofuran (THF) at room temperature. After addition of the BF_3 etherate solution was complete, the diglyme solution was heated to 80° C for 2 h. The THF solution was then stirred for 48 h at room temperature. Then, 7 ml of 3 N aqueous NaOH solution was added, followed by dropwise addition of 7 ml of 30% H_2O_2 solution. After an additional 2 h of stirring, the reaction was quenched by addition of 10 ml of H_2O. The phases were separated, and the organic portion was dried ($MgSO_4$). After removal of solvent, distillation at reduced pressure gave the product: 2·18 g, 53%; bp 69–73° C (5 mmHg) (lit.[4] 75–80° C (10 mmHg)); ^{1}H-NMR ($CDCl_3$) δ 0·1 (s, 9. $SiMe_3$), 0·8–2·1 (br m, 8, CH_2, CHSi, OH), 4.2 (br s, 1, CHO); ^{13}C-NMR ($CDCl_3$) δ −2·72 ($SiMe_3$), 24·35, 26·57, 36·01, 37·48 ($CH_2CH_2CH_2CHSi$), 76·14 (CHO). Anal. calcd. for $C_8H_{18}SiO$: C, 60·72; H, 11·39; Si, 17·76. Found: C, 59·54; H, 11·46; Si, 18·54.

cis-2-(Trimethylsilyl)cyclopentyl Trifluoroacetate (1-O(CO)CF_3) was prepared by reaction of the corresponding alcohol with trifluoroacetic anhydride: ^{1}H-NMR ($CDCl_3$) δ 0·1 (s, 9, $SiMe_3$), 1·0–2·1 (br m, 7, CH_2 and CHSi), 5·6 (br s, 1, CHO); IR (mull) 1773 cm^{-1} (C=O).

trans-2-(Trimethylsilyl)cyclopentyl Trifluoroacetate (2-O(CO)CF_3 was prepared from the corresponding alcohol in the same fashion as the *cis* isomer: ^{1}H-NMR ($CDCl_3$) δ 0·0 (s, 9,

$SiMe_3$), 1·0–2·1 (br m, 7, CH_2 and CHSi), 5.3 (br s, 1, CHO); ^{13}C-NMR ($CDCl_3$) δ −3·5 ($SiMe_3$), 23·9, 25·6, 33·6, 34·7 ($SiCHCH_2CH_2CH_2$), 84·0 (CHO), 101·8, 113·4, 116·0, 118·6 (q (J = 260 Hz), CF_3), 156.6, 157·0 157·4, 157·8 (q (J = 40 Hz), C═O).

Solvents

Ethanol was distilled from magnesium ethoxide as described by Lund and Bjerrum.[5] Commercial 2,2,2-trifluoroethanol was distilled from aqueous K_2CO_3, dried with P_2O_5, and fractionally distilled through a 10-in. vacuum-jacketed column packed with glass helices, bp 73·5–74·5° C. Ethanol mixtures are quoted in volume percentage and trifluorethanol in weight percentage.

Kinetic methods

Rates in aqueous solvents were determined conductometrically with an Industrial Instruments Model RC 16B2 conductivity bridge. The conductivity cell (Industrial Instruments) had black Pt electrodes, cell constant $0.42\,cm^{-1}$, and a volume of approximately 35 ml. In a typical experiment, enough substrate to make a solution approximately 10^{-3} M was added to the cell, which contained almost 20 ml of solvent. The cell was then stoppered and equilibrated in a constant temperature bath (Precision Model H8) for at least 5 min with stirring. Solvolyses were followed by taking at least 10 readings approximately equally spaced in conductance over 1–3 half-lives. The raw conductance data were then fitted to a first-order rate equation by means of a least-squares computer program. The precision of the fit to first-order kinetics was satisfactory over up to 3 half-lives in the aqueous ethanol and aqueous trifluoroethanol solvents.

Product studies

A 0·2–0·5 M solution of the substrate in the desired solvent (1 ml) was prepared in a Pyrex tube (0·8 mm in diameter). The tubes were sealed and placed in a constant temperature bath at 90° C. After 5 days, the tubes were cooled in an ice bath and opened. A filtration was then performed to remove any solid product formed. The mixtures were then analyzed with GC-MS: 20 m column with 3% Carbowax on Chromosorb W, FID detector, gas flow 10 ml/min. Under these conditions, all the components were well separated and the product alkene and alcohol had differences in retention times as much as 6 min. Cyclopentanol was identified by mass spectral peaks at *m/e* 86, 67, 57, and 44, whereas cyclopentene was identified by peaks at 68, 67, 53, and 39.

ACKNOWLEDGMENTS

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