PERKIN 2 COMMUNICATION

Formation of silylketenes *via* a 1,3-silyl shift. A theoretical study

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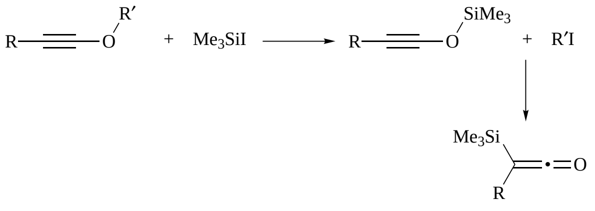
***Ab initio* and semiempirical calculations show that the formation of silylketenes from silyloxyacetylenes by a 1,3-silyl shift should occur through a concerted closed-shell mechanism involving retention (rather than inversion) of configuration at the silicon centre.**

Silylketenes are stable versatile organic reagents which are involved in numerous important reactions, *e.g.* Lewis acid-promoted [2 + 2] cycloaddition reactions with carbonyl compounds, Wittig-type reactions, diazomethane insertions and nucleophilic additions of carbon or heteroatomic nucleophiles.[1] The first member of this family, trimethylsilylketene, was prepared for the first time in 1964 by Shchukovskaya *et al.* by thermolysis of ethoxy(trimethylsilyl)acetylene at 120 °C.[2] Since this pioneering work, various kinds of silylketenes have been prepared by a number of other methods.[3] Sakurai *et al.*, in particular, showed that alkyl(trimethylsilyl)ketenes can be prepared from ethoxyalkynes in the presence of trimethylsilyliodide.[4] This procedure was then generalized[5] and we used hexyl(trimethylsilyl)ketene, prepared from ethoxyoctyne, in our syntheses of lipstatin[6] and tetrahydrolipstatin,[7] two bioactive β-lactones.

The reaction could proceed through the initial formation of a silyl ynol ether which would then undergo a 1,3-silyl shift to yield a silylketene (Scheme 1). Such a mechanism is in agreement with the well known ability of trimethylsilyliodide to cleave ethers[8] and the observed formation of ethyliodide as the reaction by-product. It must however be said that a concerted mechanism cannot be excluded.

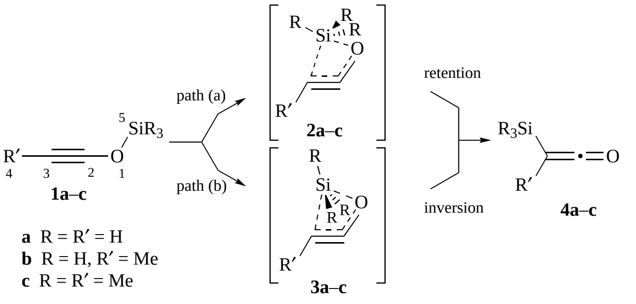


Scheme 1

As part of our theoretical interest in the chemistry of ketenes, formation of β-lactones through [2+2] cycloaddition[9] and thermolysis of alkoxyalkynes into ketenes,[10] we report here our preliminary investigation on the formation of silylketenes *via* a 1,3-silyl shift from silyl ynol ethers.

Calculations were performed both at the *ab initio* (HF and MP2 calculations with 6-31G* and 6-31++G** bases)[11] and semiempirical (AM1/RHF and AM1/CI)[12] levels. Transition states were located by minimizing the gradient norm of the energy and were characterized by one negative eigenvalue of the Hessian matrix. All reaction paths were established unambiguously by the intrinsic reaction coordinate (IRC) at the semiempirical level.

A careful search of the potential energy surface of the parent reaction enabled us to identify two distinct concerted reaction paths (Scheme 2): path (a) involving a silyl shift with retention of configuration on the silicon atom and path (b) involving a silyl shift with inversion of configuration on the same centre.



Scheme 2

It appears from Tables 1 and 2 that, regardless of the calculation level, reaction path (a) involving retention of configuration of the silicon centre is favoured over reaction path (b) involving inversion of configuration of the same centre. However, note that the difference is much more pronounced in *ab initio* calculations than in semiempirical ones. This preference for retention path (a) is in full agreement with recent results reported by Yamabe[13] and Kira[14] and their co-workers on the 1,3-sigmatropic silyl shift in allylsilane. Yamabe *et al.* propose that this stems from the fact that the silyl radical adopts a pyramidal form in contrast to the methyl radical and that in path (a) the silicon atom remains sp^3-hybridized along the entire reaction path which is not the case in path (b) (Fig. 1).

The small impact of the basis extension (from 6-31G* to 6-31++G**) in *ab initio* calculations should be noted. This result is in contrast to our calculations on the 1,5-hydrogen shift in silylketene formation.[10] Such a difference could result from the lower importance of diffuse orbitals (which are introduced at that extended level) in the 1,3-silyl shift when compared with the 1,5-hydrogen shift. Indeed, since the reactive heart is smaller in the present case, the electron displacement is sufficiently well accounted for by the 6-31G* basis. The relatively small difference between the treatment of the silicon atom in the two bases can also be invoked.

It should be noted that AM1/CI calculations (CI = 8) did not lead to significant diminution of the activation energy (Tables 1 and 2). In either case the contribution of the lowest closed-shell configuration remains 99%, indicating clearly the closed-shell character of the mechanism. Furthermore, when calculated with CI = 20, but without optimisation of the CI = 8 geometry,

Table 1 Main parameters of transition state **2a**

Method	E_a/kcal mol^{-1}	Δ_rH/kcal mol^{-1}	r_{O1-C2}/Å	r_{O1-Si}/Å	r_{C3-Si}/Å	∠C_2C_3Si/°	∠$O_1C_2C_3$/°	∠C_2O_1Si/°	∠O_1SiC_3/°	∠$C_2O_1SiC_3$/°
HF/6-31G*	51.4	2.02	1.263	2.057	2.432	59.4	161.4	74.0	65.1	0
HF/6-31++G**	50.3	−1.1	1.253	2.061	2.467	58.5	162.7	74.5	64.2	0.6
MP2/6-31G*	37.8	1.25	1.283	1.990	2.434	57.6	160.9	74.0	67.3	−0.4
MP2/6-31++G**	37.6	−8.3	1.278	2.036	2.457	58.0	161.8	74.0	66.2	0.3
AM1/RHF	54.4	−28.3	1.266	2.379	2.438	70.7	155.4	72.8	61.0	0
AM1/CI = 8	54.9	−24.4	1.250	2.332	2.485	71.3	150.7	77.7	60.3	0

Table 2 Main parameters of transition state **3a**

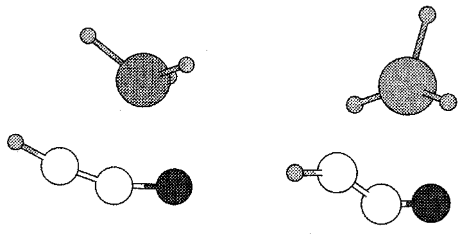
Method	E_a/kcal mol^{-1}	Δ_rH/kcal mol^{-1}	r_{O1-C2}/Å	r_{O1-Si}/Å	r_{C3-Si}/Å	∠C_2C_3Si/°	∠$O_1C_2C_3$/°	∠C_2O_1Si/°	∠O_1SiC_3/°	∠$C_2O_1SiC_3$/°
HF/6-31G*	72.9	2.02	1.236	2.035	2.431	62.9	153.9	79.0	64.1	0
HF/6-31++G**	73.4	−1.1	1.233	2.066	2.465	63	155	79.0	63.2	0
MP2/6-31G*	57.1	1.25	1.263	2.048	2.321	67.4	147.0	78.4	67.1	0
MP2/6-31++G**	59.7	−8.3	1.255	2.321	2.455	71.5	150.4	77.0	61.1	0
AM1/RHF	58.8	−28.3	1.254	2.324	2.454	71.7	150.4	77.0	60.9	0
AM1/CI = 8	54.5	−24.4	1.267	2.362	2.436	70.2	155.5	72.9	61.3	0

Table 3 Main parameters of transition states **2b,c** and **3b,c** (AM1/RHF)

	E_a/kcal mol^{-1}	Δ_rH/kcal mol^{-1}	r_{O1-C2}/Å	r_{O1-Si}/Å	r_{C3-Si}/Å	∠C_2C_3Si/°	∠$O_1C_2C_3$/°	∠C_2O_1Si/°	∠O_1SiC_3/°	∠$C_2O_1SiC_3$/°
2b	54.2	−20.5	1.262	2.320	2.482	68.9	155.0	75.1	61.0	0
3b	59.2	−20.5	1.251	2.324	2.463	71.8	150.0	77.5	60.7	0
2c	46.2	−13.9	1.264	2.392	2.589	67.9	157.7	75.7	58.7	0
3c	69.0	−13.9	1.254	2.421	2.535	71.6	153.4	76.2	58.8	0

Table 4 Main parameters of transition states **2d,e** and **3d,e** (AM1/RHF)

	E_a/kcal mol^{-1}	Δ_rH/kcal mol^{-1}	r_{O1-Si}/Å	r_{C2-Si}/Å	r_{C3-Si}/Å	∠C_2C_3Si/°	∠$O_1C_2C_3$/°	∠O_1SiC_3/°	∠$C_2O_1SiC_3$/°	∠$C_8SiC_2O_1$/°
2d in-plane	54.0	−26.0	2.360	2.362	2.516	68.5	156.8	60.2	−0.4	−155.5
2d out-of-plane	50.3	−26.0	2.357	2.358	2.520	68.2	157.2	60.2	0	53.5
3d in-plane	55.1	−26.0	2.358	2.405	2.485	71.6	151.5	60.0	0	8.3
3d out-of-plane	61.2	−26.0	2.360	2.401	2.493	71.2	152.2	60.0	−0.6	−92.8
2e in-plane	50.5	−25.1	2.329	2.362	2.555	67.0	157.3	60.0	0	174.9
2e out-of-plane	49.8	−25.1	2.363	2.363	2.534	67.8	157.8	60.0	0	68.4
3e in-plane	54.1	−25.1	2.361	2.408	2.489	71.6	151.6	60.0	0	0
3e out-of-plane	62.0	−25.1	2.358	2.402	2.495	71.2	152.1	60.0	−0.8	−93.5



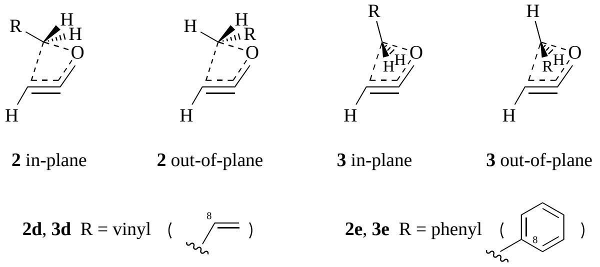
2a **3a**

Fig. 1 Structure of transition states **2a** (left) and **3a** (right) (HF/6-31G*)

contribution of the same configuration only dropped to 94–95% and the activation energy remained quasi-stable (ΔE_a < 4–5 kcal mol^{-1}).

We then studied at a semiempirical level the effect of methyl substituents. Not surprisingly, the introduction of a methyl group on C3 has little effect on the activation energy of either reaction path. In contrast, the substitution of SiH_3 for $SiMe_3$ has a much greater impact on the activation energy of path (b) than of path (a); substitution on the silicon atom is clearly in favour of the retention path because of steric reasons presumably (Table 3).

We also examined the influence of unsaturated substituents, *e.g.* vinyl and benzyl, on the competition between the retention *vs.* inversion of the silicon atom. It appears that regardless of the substituents or its position (in-plane or out-of-plane), the retention path remains the more favoured reaction path (Scheme 3, Table 4).



Scheme 3

In conclusion, we have shown that the 1,3-silyl shift that might be involved in the formation of silylketenes from alkoxyalkynes in the presence of trimethylsilyliodide, occurs with retention of configuration at the silicon centre. This finding is in agreement with recent calculations dealing with a 1,3-silyl sigmatropic shift in allylsilanes.[13,14]

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