Facile 1,3- and 1,5-Chlorine Migration

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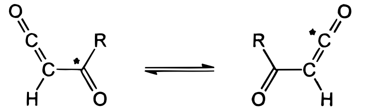
High-level ab initio molecular orbital calculations, using the G2(MP2,SVP) theory (and semiempirical methods) have been used to examine several 1,3- and 1,5-chlorine migrations. It is found that the interaction of chlorine lone pair electrons with a low-lying LUMO accelerates the Cl shift dramatically (lone pair−LUMO-mediated pericyclic reaction). The activation barriers for the 1,3-migration in chloro oxo ketene **1** (Cl(C=O)CH=C=O) and the 1,5-migration in (2-(chlorocarbonyl)-vinyl)ketene **2** (Cl(C=O)CH=CHCH=C=O) are only 53 and 61 kJ mol^{-1}, respectively, compared to the 216 and 173 kJ mol^{-1} barriers for the corresponding unassisted 1,3- and 1,5-sigmatropic shifts of Cl in 3-chloro-1-propene and 5-chloro-1,3-pentadiene. The transition structures for **1** and **2** reveal that migration of the chlorine atoms takes place in the molecular planes. The 1,5-chlorine shift in 6-chlorocyclohexa-2,4-dienone (**3**) has a significantly higher barrier due to a lack of appropriate orbital interaction. The related 1,3-shift in the (chlorocarbonyl)imine−α-chloro isocyanate system is also dramatically accelerated compared with conventional pericyclic 1,3-Cl migration.

Introduction

Interest in the study of concerted processes in organic chemistry has increased markedly since the development of the general theory of orbital symmetry by Woodward and Hoffmann.[1] Thermal and photochemical [1,*n*] sigmatropic rearrangement is one of the more fascinating of these processes, and it has been the subject of several reviews.[2] Not only carbon and hydrogen migrations, but also shifts of other functionalities including halogen atoms have been documented.[3]

Although numerous examples of experimental and some semiempirical studies on the migrations of chlorine,[4] bromine,[5] and iodine[6] appeared in the literature, to date there has been a lack of high-level ab initio investigation. In particular, the 1,5-sigmatropic rearrangement of chlorine is a well-explored reaction. Both NMR and semiempirically determined energy barriers have been reported, lying between 110 and 140 kJ mol^{-1}.[4b−d]

Further motivation for the current paper resulted from ongoing studies of the thermal oxoketene−oxoketene rearrangement, which involves a 1,3-shift (eq 1).[7] Both experimental[8] and theoretical[9] investigations have shown that the rate of the 1,3-migration is strongly dependent on the nature of the substituent R.



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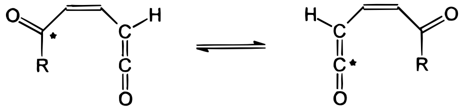
In particular, the electron-rich *n*-donating methylthio and dimethylamino groups are found to dramatically accelerate this rearrangement. The stabilizing effect of the electron-rich substituents was rationalized in terms of the favorable donor−acceptor interaction between the group R and the vacant central carbon p orbital of the ketene LUMO in the molecular plane (Figure 1). Since halogens possess unshared pairs of electrons, 1,3-halogen migrations in α-oxo ketenes are also expected to be favorable processes (eq 1, R = Cl). One may further extend this idea of donor−acceptor interaction to the vinylogous 1,5 shift depicted in eq 2.



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We have examined the 1,3- and 1,5-shifts of Cl (eqs 1 and 2; R = Cl) by high-level ab initio and semiempirical calculations. In addition, the out-of-plane 1,5-Cl migration in chlorocyclohexadienones[4b] (eq 4) and the 1,3-Cl migration in chloromethyl isocyanate[10] (eq 5) are studied.

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1996.

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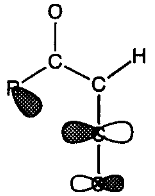


Figure 1. Lone pair−LUMO interaction involved in the 1,3-R shift of α-oxoketenes (eq 1).

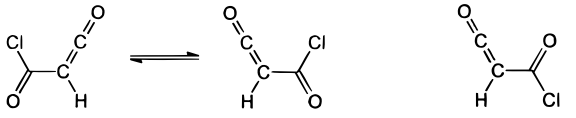
The reactions are compared with the conventional pericyclic 1,3- and 1,5-shifts of Cl in 3-chloropropene and 5-chloro-1,3-pentadiene.

Computational Methods

Standard ab initio molecular orbital calculations[11] were carried out with the GAUSSIAN 94 system of programs.[12] The structures and energies of compounds **1**−**3** and related structures were examined at the G2(MP2,SVP) level of theory.[13] This corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* energies together with zero-point vibrational and isogyric corrections. In the G2(MP2,SVP) theory, the basis-set extension energy contribution is calculated at the MP2 level and the QCISD(T) energy is evaluated using the 6-31G* basis set. It has been shown that the accuracy of the G2(MP2, SVP) method is comparable to that of the G2(MP2)[14] theory but computationally more efficient.[13] The frozen-core approximation was employed for all correlated calculations. Semiempirical calculations at the AM1[15] and PM3[16] levels were performed using MOPAC 6/PC.[17] Calculated geometries and absolute and relative energies are summarized in Tables 1 and 2.

Discussion

1,3-Shift. In general, α-oxo ketenes can exist as a mixture of two conformers: *s-trans* (**1a**) and *s-cis* (**1b**). Our calculations reveal a slight preference for the *s-trans* isomer **1a** by 4.2 kJ mol^{-1}.[18]



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1a **1a'** **1b**

Table 1. Calculated (MP2/6-31G*) Structural Parameters for Equilibrium and Transition Structures[a]

parameter	**TS1**	**1a** (*s-trans*)	**1b** (*s-cis*)
C1−Cl	2.207	2.904	3.937
C3−Cl	2.207	1.813	1.791
C1=O	1.177	1.169	1.169
C3=O	1.177	1.205	1.210
C1−C2	1.383	1.339	1.339
C2−C3	1.383	1.445	1.449
O=C1−C2	149.4	178.2	180.0
O=C3−C2	149.4	126.3	127.3
C2−C3−Cl	92.6	113.1	111.5
Cl−C3−C2−C1	0	0	180
O=C3−C2−C1	180	180	0

parameter	**TS3**	**2a**	**2b**
C1−Cl	2.123	2.825	4.713
C5−Cl	2.123	1.810	1.779
C1=O	1.185	1.173	1.172
C1−C2	1.393	1.342	1.358
C2−C3	1.390	1.437	1.420
C3−C4	1.390	1.363	1.369
C4−C5	1.393	1.451	1.428
O=C1−C2	142.0	169.3	162.3
O=C5−C4	142.0	125.4	125.4
Cl−C5−C4	106.5	115.7	115.3
Cl−C5=O	111.5	118.9	119.4
Cl−C5−C4−C3	0	0	180
O=C1−C2−C3	180	180	180
O=C5−C4−C3	180	180	0

parameter	**TS6**	**3a**
C1−Cl	2.483	2.685
C2−Cl	2.467	1.812
C1=O	1.230	1.231
C1−C2	1.482	1.531
C2−C3	1.390	1.467
C3−C4	1.400	1.355
C4−C5	1.400	1.459
C5−C6	1.390	1.349
C6−C1	1.482	1.491
C2−C1−C6	111.0	117.1
C1−C2−C3	118.2	115.1
O=C1−C2−C3	−140.6	−157.8
Cl−C1−C2−C3	100.3	120.6

[a] Bond lengths in Å and bond angles in deg.

The transition state for the 1,3-Cl migration **1a** ⇄ **1a′** (**TS1**, Figure 2) is predicted to lie 53 kJ mol^{-1} above the *s-trans* oxoketene. This calculated barrier is significantly less than that for the 1,3-H shift in formylketene (144 kJ mol^{-1}) but comparable to those for the amino (71 kJ mol^{-1}) and thio (47 kJ mol^{-1}) substituents.[9b] Therefore, chlorine is also an excellent migrating group. This is readily explained in terms of the lone pair−LUMO interaction shown in Figure 1. Thus, we predict 1,3-Cl migration in α-oxo ketenes to be an observable process. We are currently investigating the scope of such rearrangements experimentally.

In contrast to the very facile Cl migration in α-oxo ketenes, the calculation of the activation energy for the corresponding 1,3-Cl shift in 3-chloro-1-propene reveals a barrier of 216 kJ mol^{-1} and an out-of-plane transition state (**TS2**, Figure 2), thereby demonstrating the importance of the above-mentioned ketene orbitals.

1,5-Shift. In order to compare the 1,3-Cl shift in α-oxo ketene with a possible 1,5-shift, we have chosen the vinylogous (2-(chlorocarbonyl)vinyl)ketene (**2**), which should give a planar six-membered transition state for the 1,5-Cl migration. However, the additional ethenyl group leads to an increased number of conformers. We have considered all possible conformers of **2** with respect to single and double bond isomerizations, resulting in a total of eight conformers.

2b is calculated to be the most stable conformer. **2e**−**2h** lie within 4 kJ mol^{-1} of **2b**, while **2c** and **2d** are about

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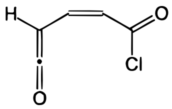
Table 2. Calculated Total and Relative Energies

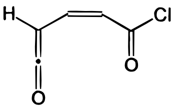
	absolute energies			relative energies		
species	G2 (MP2, SVP) (hartrees)	AM1 (kJ mol^{-1})	PM3 (kJ mol^{-1})	G2 (MP2, SVP) (kJ mol^{-1})	AM1 (kJ mol^{-1})	PM3 (kJ mol^{-1})
1a	−724.702 34	−200.4	−226.6	0.0	0.0	1.0
1b	−724.700 74	−201.8	−233.6	4.2	−1.3	−7.0
TS1	−724.682 28	−112.1	−175.6	52.7	88.3	51.0
2a	−801.937 22	−118.4	−131.9	28.9	23.9	21.3
2b	−801.948 22	−142.3	−153.2	0.0	0.0	0.0
2c	−801.944 65	−140.0	−162.5	9.4	2.3	−9.3
2d	−801.944 54	−143.8	−164.8	9.6	−1.5	−11.6
2e	−801.946 72	−127.2	−132.0	3.9	15.1	21.2
2f	−801.947 67	−141.8	−158.6	1.4	0.5	−5.4
2g	−801.947 05	−139.8	−162.9	3.1	2.5	−9.7
2h	−801.946 87	−143.6	−165.3	3.5	−1.3	−12.1
TS3	−801.924 90	−69.4	−109.9	61.2	72.9	43.3
3a	−766.032 65	−44.7	−47.3	0.0	0.0	0.0
TS5	−765.986 73	145.4	108.1	120.6	190.1	155.4
4a	−666.790 77	−57.3	−86.2	0.0	0.0	0.0
4b	−666.807 25	−80.8	−89.1	−43.3	−23.5	−2.9
TS6	−666.740 15	104.4	51.5	132.9	161.7	137.7

10 kJ mol^{-1} higher in energy (Table 2). Structure **2a**, preorientated for the 1,5-chlorine shift, is found to be 29 kJ mol^{-1} higher in energy.

The 1,5-Cl migration in **2a**, which is orientated favorably for the 1,5-shift, is predicted to have an activation barrier of 32 kJ mol^{-1}, via the planar six-membered ring transition structure **TS3** (Figure 3). The overall activation barrier for conformer **2b**, the most stable conformer, is therefore 61 kJ mol^{-1}. Hence, 1,5-Cl migration in **2** is predicted to be even more facile but comparable with the 1,3-shift. The small computed barrier confirms our hypothesis that the donor−acceptor interaction between the lone pair electrons of chlorine and the vacant carbon p orbital of the ketene LUMO is the key factor in stabilizing the transition state for 1,5-migration in **2**.



2a



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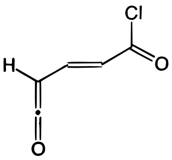

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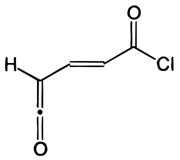

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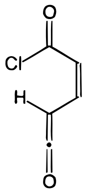
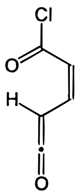


2e



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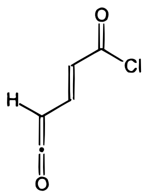

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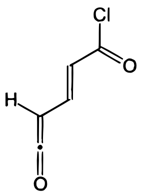


2h

As for the 1,3-shift, we also calculated the barrier for the conventional pericyclic 1,5-Cl migration in 5-chloro-1,3-pentadiene (**TS4**, Figure 3). This kind of reaction requires the movement of the chlorine atom above the molecular plane as there is no additional stabilizing effect from the orthogonal orbitals of a ketene function. The transition state (Figure 3) lies 173 kJ mol^{-1} above the equilibrium structure.

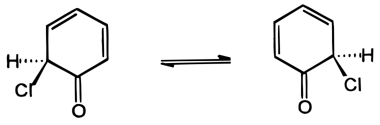
To explain the facile 1,3- and 1,5-shifts, let us consider the orbital interactions involved. For concerted 1,3-H migration in allylic systems there exists only the antarafacial pathway, which results in high steric strain and poor orbital overlap and is hence almost unknown.[19] Chart 1 depicts the orbitals involved in the normal 1,3- and 1,5-pericyclic rearrangements.

However, if the migrating atom is capable of undergoing inversion[1,20] or if interaction with additional (orthogonal) orbitals is possible, as in the case of ketenes and other cumulenes, then the migration can also proceed via a suprafacial pathway.[7a] Thus, for migrating groups other than hydrogen, 1,3-rearrangements become feasible, as demonstrated in Chart 2: interaction of the filled lone pair orbital of the migrating atom with the vacant central carbon p orbital of the ketene LUMO (which is perpendicular to the normal π system).

In contrast to the clearly pericyclic chlorine rearrangements in 3-chloro-1-propene and 5-chloro-1,3-pentadiene, where the chlorine migrates above the molecular planes, one can describe the in-plane 1,*n*-shifts involving ketene functions as pseudopericyclic, as there is "a disconnection (or orthogonality[7a]) in the cyclic array of overlapping orbitals".[21] However, the chlorine migration in ketenes may be conveniently described as a "lone pair−LUMO-mediated pericyclic reaction". Note that these reactions are not subject to the normal rules[1] of orbital symmetry.

The donor−acceptor interaction in **TS3** is facilitated by the fact that both the donor and acceptor orbitals lie in the molecular plane. Thus, one would anticipate a higher barrier for systems that prohibit such a favorable orbital overlap. This is readily illustrated by the 1,5- Cl shift in 6-chlorocyclohexa-2,4-dienone (**3**, eq 4).

Hartshorn et al. have examined an analogous system



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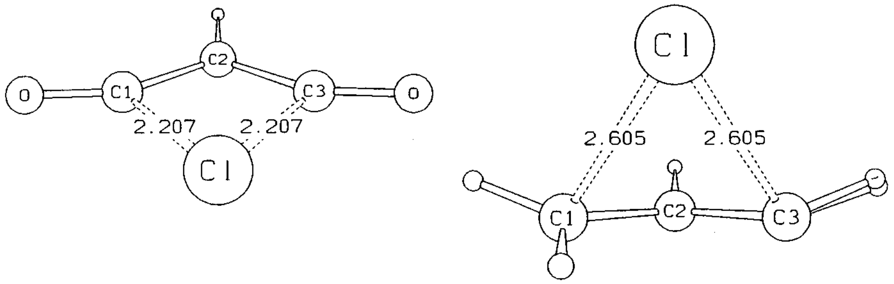
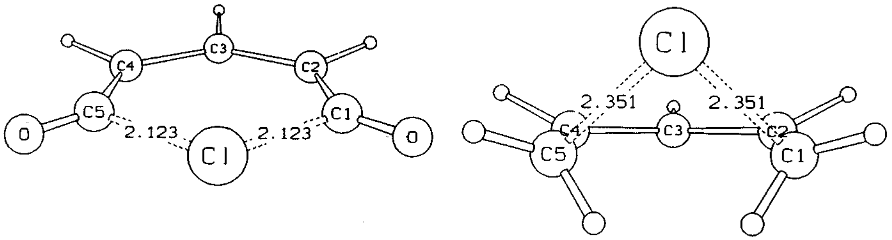
3a **3a'**



TS1 **TS2**

Figure 2. **TS1** for **1a** ⇄ **1a′** (eq 3) and **TS2** for the 1,3-Cl migration in 3-chloro-1-propene.



TS3 **TS4**

Figure 3. **TS3** for 1,5-Cl shift in (2-(chlorocarbonyl)vinyl)ketene and **TS4** for 1,5-Cl shift in 5-chloro-1,3-pentadiene.

Chart 1. Orbital Interactions for Pericyclic 1,3- and 1,5-Shifts.

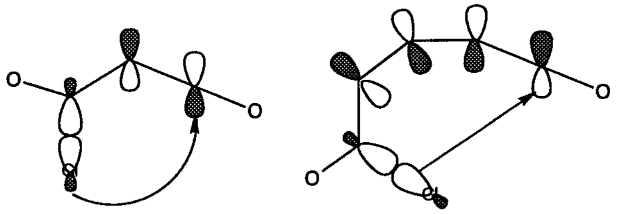
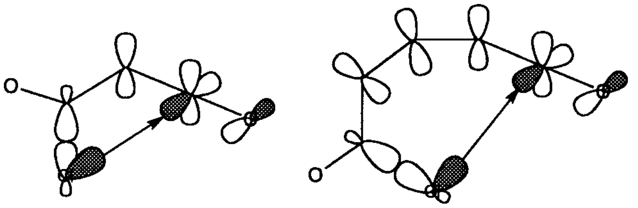
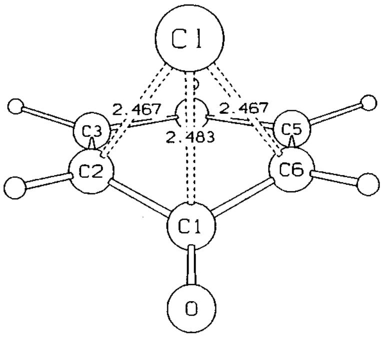


Chart 2. Orbital Interactions for Lone Pair–LUMO-Mediated Pericyclic 1,3- and 1,5-Shifts.



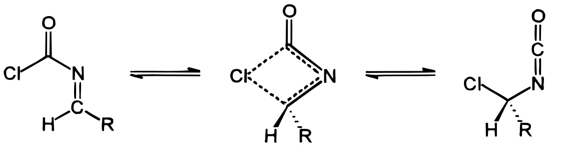
with semiempirical methods.[4b] They reported a PM3-calculated barrier of 139 kJ mol^{-1} for the rearrangement of 4,6-dichloro-2,5,6-trimethylcyclohexa-2,4-dienone to 4,6-dichloro-2,3,6-trimethylcyclohexa-2,4-dienone. We calculate 1,5-Cl migration in **3** to have a moderate barrier of 121 kJ mol^{-1}, via transition structure **TS5** (Figure 4), which is analogous to **TS4**.

Chlorocarbonylimine–α-Chloroisocyanate Interconversion. It is known that the 1,3-Cl migration in carbamoyl chlorides of type **4a** to give α-chloro isocyanates (eq 5) is a facile process.[22] In agreement with these experimental findings, our calculations of the chlorotropic equilibrium (eq 5, R = H) favor the α-chloro isocyanate form **4b** by 48 kJ mol^{-1}.



TS5

Figure 4. **TS5** for 1,5-Cl shift in 6-chlorocyclohexa-2,4-dienone.



(5)

4a **TS6** **4b**

The barrier for the tranformation of **4a** to **4b** via **TS6** is predicted to be 133 kJ mol^{-1} at the G2(MP2,SVP) level of theory. Again, **TS6** turns out to be almost planar (28°, Figure 5), thus indicating another example of a lone pair–LUMO-mediated pericyclic reaction.

Semiempirical Calculations. Both semiempirical methods predict the *s-cis* isomer of α-oxo ketene **1** to be more stable, in contrast to the ab initio results. PM3 favors **1b** by 7 kJ mol^{-1}, AM1 only by little more than 1 kJ mol^{-1}. AM1 clearly overestimates the activation barrier associated with the 1,3-rearrangement (88 kJ mol^{-1}). PM3, however, predicts the transition state **TS1**

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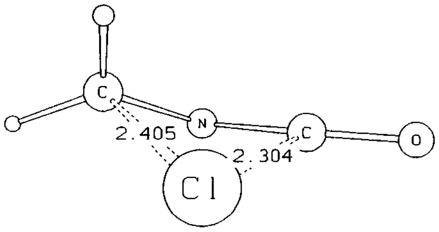

TS6

Figure 5. **TS6** for the chlorotropic equilibrium **4a** ⇄ **4b**.

to be 51 kJ mol^{-1} above the *s-trans* oxo ketene in very good agreement with the G2(MP2,SVP) result.

Conformer **2a** is calculated to be the least stable isomer using both semiempirical models. However, AM1 gives a better description of the energetic distribution of the remaining seven isomers than does PM3. Again, the AM1-predicted activation barrier is too high, whereas PM3 tends to slightly underestimate the energy of the transition state.

The activation energy for isomerization of **3a** is determined to be 155 (PM3) or 190 kJ mol^{-1} (AM1), again showing a better agreement with the ab initio results for PM3.

The same is true for the chlorotropic equilibrium **4a** ⇄ **4b**. PM3 reproduces the ab initio calculated barrier very well (138 kJ mol^{-1}), while AM1 is again too high (162 kJ mol^{-1}).

In general, PM3 seems to be the more reliable semiempirical method for the prediction of activation barriers in the examples presented here.

Conclusions

The 1,3-Cl shifts in α-oxo ketenes (eqs 1 and 3), the vinylogous 1,5-Cl shifts in (2-(chlorocarbonyl)vinyl)ketene (eq 2) and the 1,3-Cl shift interconverting (chlorocarbonyl)imine and chloromethyl isocyanates (eq 5) are dramatically accelerated in comparison with conventional pericyclic 1,3- and 1,5-shifts of Cl. These facile chlorine shifts are mediated by a favorable in-plane interaction between a filled chlorine lone pair orbital and a vacant carbon p orbital on the ketene or isocyanate moiety. It may be expected that this principle of lone pair−LUMO-mediated pericyclic reaction applies also to the migration of other halogens (particularly Br) and other cumulenes.

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