

# Ketene–acetylene [2 + 2] cycloadditions: cyclobutenone and/or oxete formation? †

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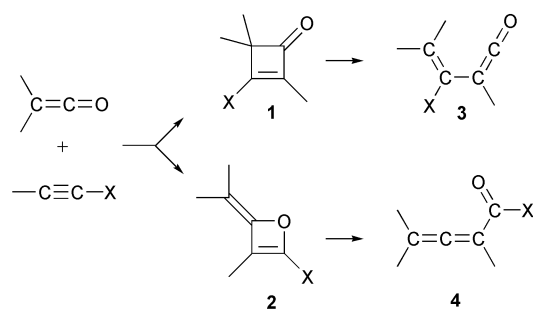
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The [2 + 2] cycloaddition of monosubstituted acetylenes to ketene has been studied by *ab initio* (G2(MP2,SVP) and DFT (B3LYP/6-31Gd)) methods. The activation barrier decreases with increasing electron-donating ability of the acetylene substituent, and it can be roughly correlated with the energy of the acetylene HOMO. The addition to the C=C bond of ketene (giving cyclobutenones) is preferred for the less electron-rich acetylenes, but for the most electron rich ones (X = NH<sub>2</sub> and NMe<sub>2</sub>) the addition to the C=O bond (giving oxetes) becomes competitive, with activation barriers as low as *ca.* 45 (30) kJ mol<sup>-1</sup> for the two computational methods used. The cyclobutenones and oxetes can undergo ring opening to vinylketenes and acylallenes, respectively. Furthermore, the latter two compounds can interconvert by a 1,3-shift of the substituent X. The acylallenes become thermodynamically more stable than the vinylketenes for  $\pi$ -(lone pair) donating substituents X, and the 1,3-shift barrier also decreases, to *ca.* 130 kJ mol<sup>-1</sup> for X = NMe<sub>2</sub>. In contrast, the 1,3-shifts of CH<sub>3</sub> and H have very high barriers.

## Introduction

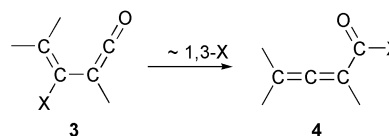
Ketenes are highly versatile synthetic intermediates,<sup>1–3</sup> and unlike most unsaturated compounds, they undergo thermal [2 + 2] as well as [2 + 4] cycloadditions readily.<sup>1–4</sup> Cycloaddition to the ketene may involve either the C=C or, less commonly, the C=O bond.<sup>1–4</sup> There are two possible outcomes of the [2 + 2] cycloaddition of a ketene to an acetylene: addition to the C=C double bond to give a cyclobutenone **1**, or addition to the C=O double bond to give an oxete **2** (Scheme 1).



Scheme 1 Cycloaddition pathways.

The cyclobutenones can undergo electrocyclic ring opening to vinylketenes **3**,<sup>5</sup> and these are useful in further synthetic transformations. The methyleneoxetes **2** are usually assumed intermediates that have not been isolated,<sup>6</sup> and the evidence for their existence is almost exclusively the formation of acylallenes **4**, *e.g.* in the reaction between ketenes and ynamines (X = NR<sub>2</sub>).<sup>7–9</sup> Compounds that were first thought to be oxetes<sup>3,10</sup> were later shown to be allenes.<sup>8</sup>

We have shown that vinylketenes rearrange readily to acylallenes by means of a 1,3-shift of electron rich substituents X such as amino and alkoxy groups (Scheme 2).<sup>11</sup> Moreover, this is



Scheme 2 1,3-X shift.

a general reaction for acyl- and imidoalkynes,<sup>12</sup> thioacylketenes,<sup>13</sup> and thioacylisocyanates,<sup>14</sup> and the 1,3-shift of amino groups are particularly fast.<sup>15</sup> These 1,3-shifts can be described as “pseudopericyclic” reactions.

The concept of pseudopericyclic reactions has enjoyed increasing interest in recent years through the work of Birney and others.<sup>16</sup> A pericyclic reaction<sup>17</sup> becomes pseudopericyclic when one of the normal orbitals (usually a p orbital) in the continuous array is replaced by another, orthogonal, orbital. The orthogonal orbital may be another p orbital, a lone pair, or a d orbital. The orthogonality introduces an orbital switching or disconnection, which has the consequence that all reactions become allowed in terms of orbital symmetry. In Lemal and coworkers' original study,<sup>18</sup> a lone pair was doing the switching. Disconnections due to incorporation of d orbitals were described by Craig, albeit in a different context.<sup>19</sup> Wentrup and Netsch pointed out that orthogonal p orbitals make the 1,3-shifts in  $\alpha$ -oxoketenes allowed.<sup>12e</sup> An important driving force for this latter reaction is a favourable interaction between a high-lying orbital on the migrating group and the ketene LUMO, which has a p orbital in the plane of the substituent.<sup>12a,12d,15b</sup> In the series of compounds studied here, the energy of the lone pair of the migrating group is the decisive factor in lowering the barrier for the 1,3-shift. When no such high energy lone pair is available (X = H and CH<sub>3</sub>), the barrier becomes very high.

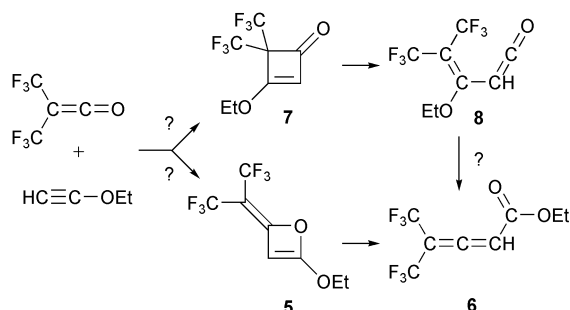
There have been previous theoretical treatments of the 1,3-shifts in the oxoketene–oxoketene,<sup>12a,d,16b,20</sup> imidoalkyne–oxoketenimine,<sup>21</sup> vinylketene–acylallene,<sup>11</sup> acylisocyanate–acylisocyanate,<sup>12a</sup> acylthioalkyne–thioacylketene,<sup>13</sup> and acylisothiocyanate–thioacylisocyanate<sup>14</sup> rearrangements.

Since most of the work on [2 + 2] cycloadditions of ketenes has involved ynamines (X = NR<sub>2</sub>), one has to question the

† Electronic supplementary information (ESI) available: tables of absolute energies of all calculated species. See <http://www.rsc.org/suppdata/ob/b3/b309549e/>

evidence for the formation of oxetes **2**. Could it be that it is simply the 1,3-shift of X in **3** that is being observed?

In the reaction between bis(trifluoromethyl)ketene and ethoxyacetylene an intermediate was observed by  $^{19}\text{F}$ -NMR spectroscopy at  $-80\text{ }^\circ\text{C}$ , which rearranged rapidly to allene **6** on warming to  $30\text{ }^\circ\text{C}$ .<sup>22</sup> The intermediate was assigned as oxete **5**, but it could also have been the vinylketene **8**, formed *via* cyclobutenone **7** (Scheme 3). Fluorinated ketenes are known for their extraordinary stability.<sup>2,22</sup>



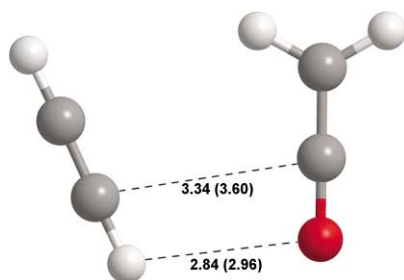
**Scheme 3** Reaction between bis(trifluoromethyl)ketene and ethoxyacetylene.

Because of the uncertainties delineated above, we set out to investigate the course of ketene–acetylene [2 + 2] cycloadditions theoretically. The results are reported herein.

## Results and discussion

In order to gain insight into the potential mechanism of these cycloadditions, we calculated the two pathways leading, in the case of a C=C addition to cyclobutenones **1** and vinylketenes **3**, and in the case of the alternative C=O addition to oxetes **2** and acylallenes **4**, including all transition states connecting the minimum structures **1–4** and the 1,3-shift transition state interconverting **3** and **4** (Schemes 1 and 2). Additionally, both isomeric forms, *s-cis* and *s-trans* of the latter two molecules were included. The most reliable energy data obtained are based on the G2(MP2,SVP) method. However, the increasingly popular hybrid functional method B3LYP/6-31G(d) which has proven to give satisfactory results in this type of application<sup>23</sup> is used for comparison. The study was carried out using a large variety of substituents, X = H, CH<sub>3</sub>, OH, OCH<sub>3</sub>, F, Cl, SH, NH<sub>2</sub>, N(CH<sub>3</sub>)<sub>2</sub>.

It is known that ketenes form van der Waals complexes with ethylenes and, of particular interest in the present study, with acetylenes in the gas phase.<sup>24</sup> Microwave spectroscopy shows complexation in the plane of the ketene with the acetylene triple bond closer to the central (C<sub>α</sub>) than the CH<sub>2</sub> carbon atom of the ketene. The structural features are well reproduced by our MP2/6-31G(d) calculations (see Fig. 1), taking into account the flexible nature of such a complex. The two molecular axes are tilted by 26° from parallel (exp. ~25°) and the dihedral angle of the four carbon atoms is zero. The orientation of the two



**Fig. 1** MP2/6-31G(d)-optimised van der Waals complex between ketene and acetylene. Bond lengths are in Å (experimental data in parentheses).

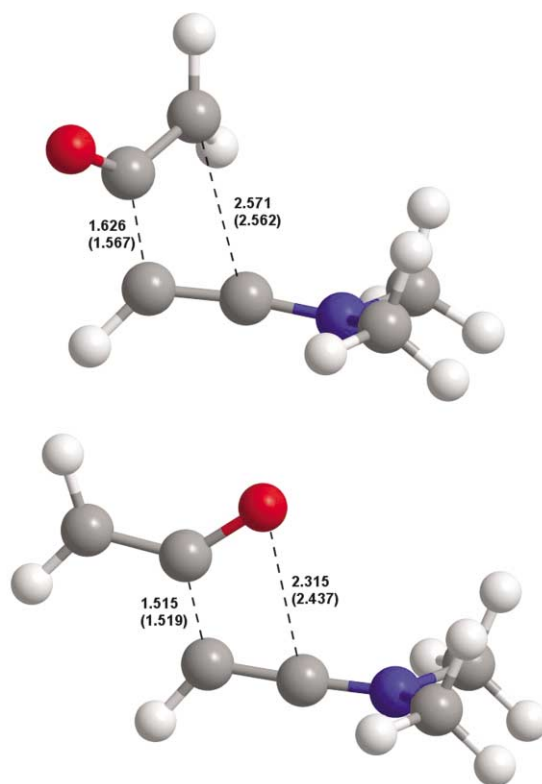
**Table 1** G2(MP2,SVP)-calculated activation barriers (kJ mol<sup>-1</sup>) relative to ketene and substituted acetylenes HCCX for the initial cycloaddition reactions (B3LYP/6-31G(d) values in parentheses)

Activation barriers	Cycloaddition to:	
	C=C bond	C=O bond
H	133 (113)	246 (203)
F	125 (108)	202 (204)
Cl	125 (109)	209 (175)
CH <sub>3</sub>	119 (101)	207 (174)
SH	110 (83)	154 (125)
OH	107 (80)	144 (126)
OCH <sub>3</sub>	92 (70)	110 (100)
NH <sub>2</sub>	81 (50)	87 (66)
N(CH <sub>3</sub> ) <sub>2</sub>	45 (29)	43 (35)

molecules is in contradiction to the classical [ $\pi_2_s + \pi_2_a$ ] cycloaddition orientation where the reactants are almost orthogonally arranged.<sup>17</sup>

The first part of the investigation compared the barriers for the initial cycloadditions. Table 1 gives the required activation energies for the C=C and the C=O pathways. It can be seen that the former reaction is more or less clearly favoured. With the exception of the dimethylamino group (45 kJ mol<sup>-1</sup>), all barriers are calculated to be between 81 and 133 kJ mol<sup>-1</sup>. The required activation energies for the addition to the carbonyl function of a ketene are significantly higher (144–246 kJ mol<sup>-1</sup>) than the corresponding C=C addition barriers. Exceptions are found for electron-rich groups X where the differences are much smaller or close to zero (X = methoxy, amino and dimethylamino). The latter finding of a slightly preferred C=O addition pathway leading to a dimethylamino-substituted oxete is the first indication for the formation of oxetes. There is theoretical evidence in the literature for a related reaction: In case of the addition of selenoketene to ethylene both C=Se and C=C addition barriers are calculated to have the same energy.<sup>25</sup>

Fig. 2 gives a representation of the calculated dimethylamino-substituted transition states for both additions. Both structures



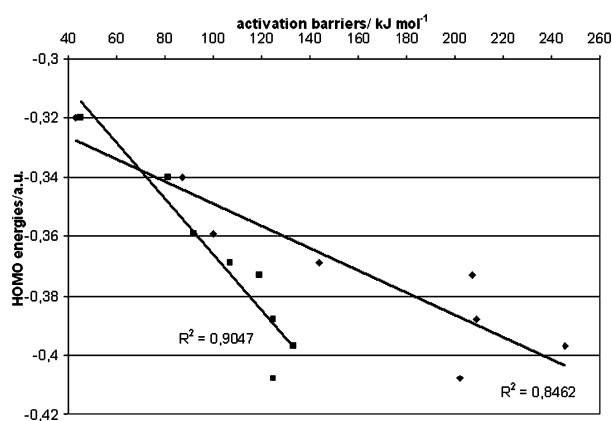
**Fig. 2** Calculated transition state structures for the C=C (above) and the C=O addition of ketene to dimethylethyamine. Distances given are MP2/6-31G(d) values (B3LYP/6-31G(d) data in parentheses) in Å.

are highly asynchronous and exhibit initial C–C bond formation between the central ketene and the acetylene carbon atom at the unsubstituted end. The geometries of the transition states resemble those found for similar reactions, *e.g.* addition of  $\text{H}_2\text{C}=\text{C}=\text{X}$  to ethenes, where  $\text{X}=\text{O}, \text{S}, \text{Se}$ .<sup>25</sup> The dihedral angle of C–C–C–X ( $\text{X}=\text{CH}_2, \text{O}$ ; the four bond-forming centres) is zero for the TS for addition to the C=O group (as expected for a planar pseudopericyclic reaction<sup>16</sup>), but about  $45^\circ$  for the transition state of the C=C addition, so the latter requires some rotation before forming the second bond.

Since the mechanism of [2 + 2] cycloaddition of ketenes is discussed controversially in the literature,<sup>1,26</sup> we tried to locate zwitterionic intermediate structures in order to find evidence for a stepwise mechanism. All attempts failed; the species either dissociated to ketene and the substituted acetylene or formed the cyclic product of the addition. We therefore conclude that the reactions proceed *via* an asynchronous concerted pathway, described by Wang and Houk as a [2 + 2 + 2] reaction.<sup>26a</sup>

The B3LYP/6-31G(d) results are qualitatively in very good agreement, giving an identical activation energy ordering for the formation of cyclobutenones **1** and a very similar one for carbonyl addition. Also, the decreasing difference in activation barriers between the two pathways is reproduced; however, even for  $\text{X}=\text{N}(\text{CH}_3)_2$  the C=C addition is preferred. The overall values are a little smaller than the G2(MP2,SVP) data, which is not surprising since DFT methods tend to underestimate activation barriers.<sup>27</sup> In general, the relatively fast DFT approach used herein has proved to give at least qualitatively reliable results for the reaction studied, although it seems to favour the C=C addition for low barriers.

In order to identify the origin of the different barriers for different substituents X, we have examined the orbital interactions which control the additions. It is found that the reactions take place *via* an initial HOMO (acetylene)–LUMO (ketene) interaction. The energetic ordering (in a.u.) of the HOMOs in the acetylenes is computed as follows: F (–0.408) < H (–0.397) < Cl (–0.388) <  $\text{CH}_3$  (–0.373) < OH (–0.369) <  $\text{OCH}_3$  (–0.359) < SH (–0.345) <  $\text{NH}_2$  (–0.340) <  $\text{N}(\text{CH}_3)_2$  (–0.320). With the exception of the SH group, this ranking correlates well with the determined activation energies (Fig. 3). The agreement is slightly better for the addition to the carbon–carbon double bond.



**Fig. 3** Correlation of cycloaddition activation energies with energies of substituted acetylene HOMOs (squares represent C=C, diamonds C=O addition).

As mentioned in the introduction, the intermediate products **1** and **2** can both undergo ring openings and form vinylketenes **3** and acylallenes **4**, respectively. We have also investigated these processes and the 1,3-shift interconverting **3** and **4**. The results are given in Table 2, and a set of graphs comparing all the energies of all the species and transition states is shown in Fig. 4.

The transition state for C=C addition, TS C=C, is usually lower than that for C=O addition, TS C=O, but for  $\text{X}=\text{NH}_2$  and  $\text{N}(\text{CH}_3)_2$  the two barriers are very similar, and for  $\text{X}=\text{OCH}_3$  the difference in favour of C=C addition is not large. The substituents also greatly influence the stabilities of the product. For small, hard and electronegative groups X (F, O, N) the acylallenes **4** are the most stable, while the other substituents the vinylketenes **3** are more stable. For the thio and the dimethylamino groups the primary products of a C=C cycloaddition, the cyclobutenones **1**, are calculated to be the most stable structures, although only by a few  $\text{kJ mol}^{-1}$ . Barriers for the ring opening reactions of both **1** and **2** are relatively low and similar, readily taking place at or near room temperature, except for the cyclobutenone **1** with  $\text{X}=\text{H}$ . The barrier for ring opening of methoxy-substituted **2** is consistent with the proposed rearrangement of oxete **5** to allene **6** on warming to  $30^\circ\text{C}$  (Scheme 3).<sup>22</sup>

The 1,3-shift barrier is very high for  $\text{X}=\text{H}$  and  $\text{CH}_3$ , and it has never been observed experimentally for  $\text{X}=\text{CH}_3$  in any of the systems we have investigated. The 1,3-H shift typically requires FVT temperatures of  $700\text{--}800^\circ\text{C}$ . Although the barriers for the 1,3-shifts are always higher than those for ring opening of **1** or **2**, or of those for the initial cycloaddition reactions (TS C=C and TS C=O), they diminish for electron-donating substituents, particularly  $\text{NH}_2$  and  $\text{NMe}_2$ , falling to values of 188 ( $\text{NH}_2$  in **4**), 142 ( $\text{NMe}_2$  in **4**), 166 ( $\text{NH}_2$  in **3**) and 129 ( $\text{NMe}_2$  in **3**)  $\text{kJ mol}^{-1}$ . Thus the latter 1,3-shift shift will occur at slightly elevated temperature.

The experimentally studied reaction between bis(trifluoromethyl)ketene and ethoxyacetylene (Scheme 3)<sup>22</sup> is computationally too large to be evaluated at the G2(MP2,SVP) level. Therefore, we employed the B3LYP/6-31G\* level of theory for examination of this system. The barriers for the two cycloaddition pathways are 39 and 44  $\text{kJ mol}^{-1}$  for the C=C and C=O addition. These values are only slightly higher than those for the “best” system so far ( $\text{X}=\text{N}(\text{CH}_3)_2$ ) with 29 and 35  $\text{kJ mol}^{-1}$ . Taking into account the bias of the DFT approach (8  $\text{kJ mol}^{-1}$  in favour of the C=C pathway) compared to the G2(MP2,SVP) values, it would seem that both cycloaddition pathways are feasible.

## Conclusion

The activation barriers for the formation of cyclobutenones and oxetes decrease and become competitive for  $\pi$ -(lone pair) electron donating substituents (especially for  $\text{X}=\text{NH}_2$  and  $\text{NMe}_2$ ) falling to as little as 45 (30)  $\text{kJ mol}^{-1}$  for the G2(MP2,SVP) and B3LYP methods, respectively. The barriers for ring opening of both cyclobutenones and oxetes, to vinylketenes and acylallenes, respectively, also decrease, to as little as  $70\text{--}80\text{ kJ mol}^{-1}$ . Furthermore, the vinylketenes and the acylallenes can interconvert by a 1,3-shift of the substituent X. The acylallenes become thermodynamically more stable than the vinylketenes for electron-donating substituents X, and the 1,3-shift barrier also decreases, to *ca.* 130  $\text{kJ mol}^{-1}$  for  $\text{X}=\text{NMe}_2$ . Therefore, the cycloadditions and the ring opening reactions will all be fast at or near room temperature, and the thermodynamically most stable product can be expected to be formed in each reaction. The 1,3-shifts of  $\pi$ -(lone pair) donating substituents, particularly  $\text{X}=\text{NMe}_2$ , isomerising vinylketenes to acylallenes, will take place at elevated temperatures, whereas 1,3-shifts of  $\text{CH}_3$  (and other alkyl groups) is hardly ever to be expected. Also the 1,3-H shift has such a high barrier that it may only be expected under conditions of flash vacuum thermolysis.

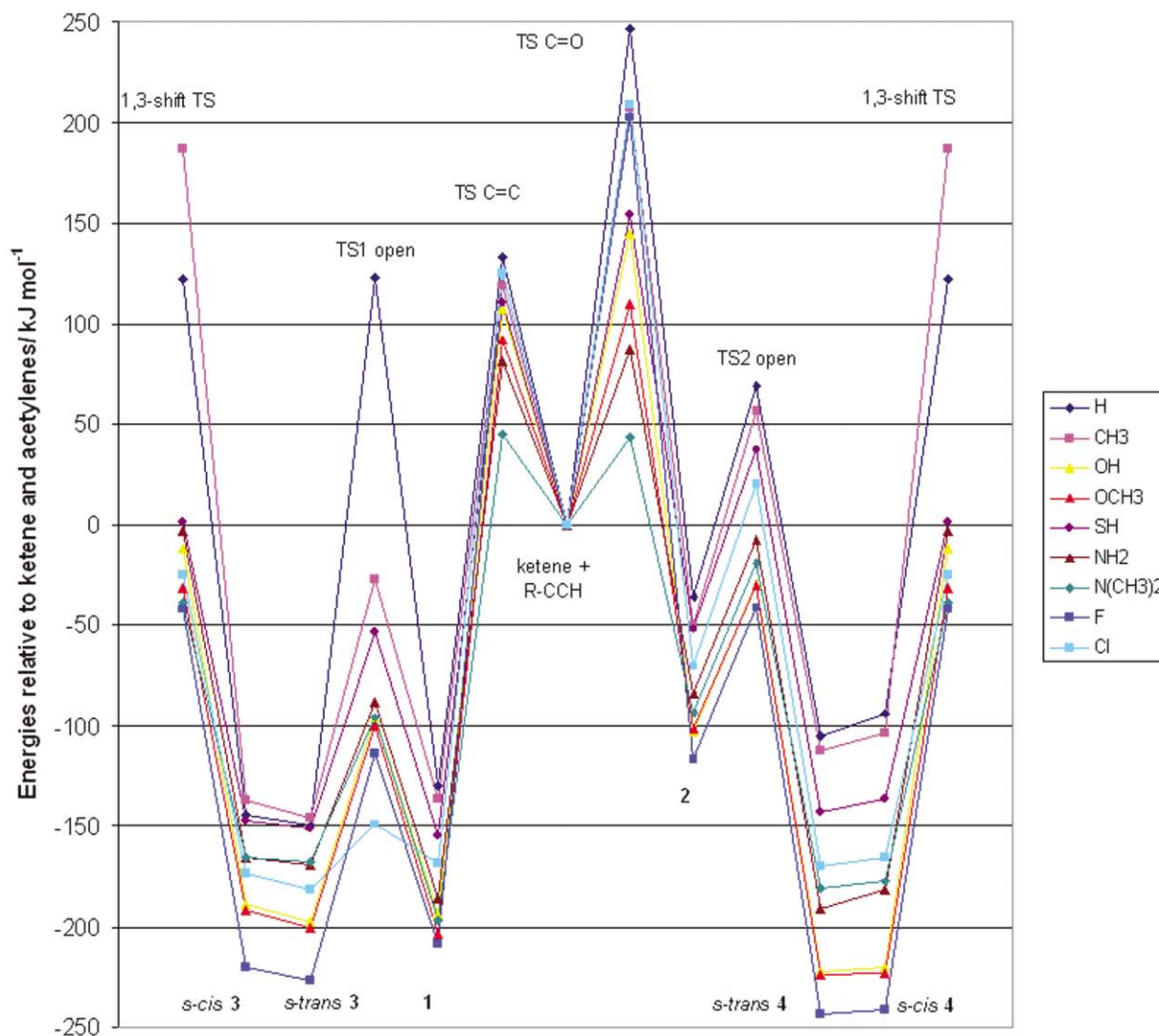
## Computational methods

Standard *ab initio* molecular orbital calculations<sup>28</sup> were carried out using the Gaussian 98 system of programs.<sup>29</sup> Geometry

**Table 2** G2(MP2,SVP)-calculated energies (kJ mol<sup>-1</sup>) of the complete reaction pathways relative to isolated ketene + substituted acetylene HCCX.

X	TS C=C <sup>a</sup>	1	TS1 open <sup>b</sup>	<i>s-cis</i> 3	<i>s-trans</i> 3	TS 1,3-shift	<i>s-trans</i> 4	<i>s-cis</i> 4	TS2 open <sup>b</sup>	2	TS C=O <sup>a</sup>
H	133	-130	123	-144	<b>-150</b>	122	-106	-94	69	-36	246
F	125	-209	-114	-220	-226	-42	<b>-243</b>	-241	-41	-117	202
Cl	125	-169	-67	-173	<b>-182</b>	-25	-170	-166	20	-70	209
CH <sub>3</sub>	119	-137	-27	-137	<b>-146</b>	187	-113	-104	56	-51	207
SH	110	<b>-155</b>	-54	-147	-151	1	-143	-137	37	-52	154
OH	107	-194	-96	-189	-197	-11	<b>-222</b>	-221	-29	-103	144
OCH <sub>3</sub>	92	-204	-100	-192	-200	-31	<b>-224</b>	-223	-30	-102	110
NH <sub>2</sub>	81	-186	-89	-165	-169	-3	<b>-191</b>	-182	-7	-84	87
N(CH <sub>3</sub> ) <sub>2</sub>	45	<b>-197</b>	-96	-165	-168	-39	-181	-178	-19	-93	43

<sup>a</sup> Transition states of the cycloaddition to C=C (C=O) bond. <sup>b</sup> Ring opening transition states of **1** and **2**. Bold numbers represent the most stable isomer, italic numbers represent the highest barriers for a given substituent X.

**Fig. 4** Energy profiles (kJ mol<sup>-1</sup>) for all calculated reactions, relative to ketene and acetylenes (center). the C=C addition pathway is shown on the left, C=O addition on the right.

optimisations were performed with the standard polarised split-valence 6-31G\* basis set at the Hartree-Fock (HF), second-order Møller-Plesset perturbation (MP2) and the hybrid density functional theory B3LYP levels. Harmonic frequencies were calculated at the HF/6-31G\* level in order to characterise the stationary points as minimum and transition state structures and to evaluate zero-point vibrational energies (ZVPEs). The directly calculated ZVPEs were scaled by 0.9135 to account for their overestimation at this level of theory.<sup>30</sup> Improved energies were obtained at the G2(MP2,SVP) level of theory.<sup>31</sup> This corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G\* energies together with zero-point energy 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 6-31Gd basis set. It has been shown<sup>31</sup> that the accuracy of the G2(MP2,SVP) method is comparable to that of the G2(MP2) theory<sup>32</sup> at a much lower computational cost. The frozen-core approximation was employed for all correlated calculations.

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