# Substituent effects on decarbonylation: theoretical study of the interconversion of 1,2-bisketenes, cyclopropenones and alkynes

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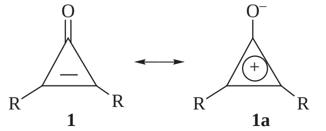
**The structures and energies of the stationary points for decarbonylation of substituted 1,2-bisketenes 14 forming cyclopropenones 1 which further decarbonylate to alkynes 16 have been calculated by *ab initio* and hybrid B3LYP methods. At the HF/6-31G* level ketenylcarbene intermediates 15 are formed from 14, but at the MP2/6-31G* and B3LYP levels the conversion of 14 to 1 becomes a one-step process. Decarbonylation of bisketenes 14 is favored by electronegative substituents, but decarbonylation of cyclopropenones 1 to alkynes 16 is favored by electropositive substituents, in agreement with experimental results. The stabilization of cyclopropenones by π-donor substituents ($NH_2$, OH and F) explains why OR and F, but not $Me_3Si$, substituted cyclopropenones have been observed as products from bisketene photolyses.**

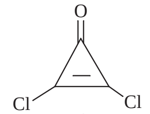
The first cyclopropenone was reported independently in 1959 by Vol'pin *et al.*[1a] and Breslow *et al.*,[1b] and the latter group reported the synthesis of the parent **1** in 1970.[1c] Interest in this family has continued unabated since, as summarized in reviews[2] and many recent publications.[3] The identification of the antibiotic penitricin as hydroxymethylcyclopropenone,[4a] the preparation of a cyclopropenone-containing amino acid derivative that was active as a proteinase inhibitor[4b] and a new general synthesis of cyclopropenones[4c] heighten interest in these compounds.

Despite the widespread study of cyclopropenones the factors which influence the stability of these species have not been completely understood. Because of the electron deficient character of cyclopropenones **1**, which may be represented by the resonance structure **1a**, electron donor substituents will tend to stabilize these species. However cyclopropenones such as dichlorocyclopropenone **2**, in which the chloro substituents are strong net electron acceptors, but which do have some π-donor character, also appear quite stable. Even difluoropropenone[3g] has been prepared and is sufficiently stable for a microwave structure determination, and although this compound is rather unstable at room temperature *ab initio* calculations suggest it has a resonance energy comparable to the parent.[3g] By contrast, bis(trimethylsilyl)cyclopropenone **3**, in which the trimethylsilyl groups are neither strong donors nor acceptors, has defied isolation, despite apparently being generated as a transient intermediate from the hydrolysis of the dichlorocyclopropene.[5a] The monosilylated cyclopropene **4a** has however been isolated in 22% yield as a minor product from oxidation of the corresponding cyclopropene,[5b] and **4b** was obtained in 24% yield by hydrolysis of the cyclopropenone acetal.[4c]

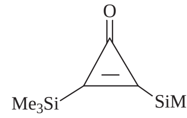
The photochemical decarbonylation of aryl amino-substituted cyclopropenones to give ynamines has also been reported,[5c,d] and a ketenylcarbene that can be trapped by $H_2O$ has recently been proposed[5e] as an intermediate in this reaction [eqn. (1)].



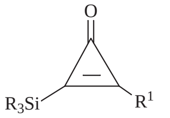
**1** **1a**



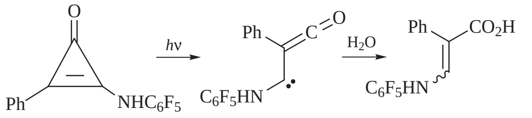
**2**



**3**



**4a**: R = Ph, $R^1$ = *i*–Pr
**4b**: R = Me, $R^1$ = H



(1)

In several cases photolysis or thermolysis of cyclobutenediones gave 1,2-bisketenes which led to cyclopropenone intermediates,[6] and in the case of **5** this was proposed[6a] to involve ring opening to the bisketene **6**, which underwent decarbonylation to the ketenylcarbene intermediate **7**, which then formed the cyclopropenone, as illustrated in eqn. (2).[6a] In other cases photolyses or thermolyses of cyclobutenediones have yielded not cyclopropenones but alkynes.[7,8] Formation of the cyclopropenone **3** might have been expected from the photolysis of the bisketene **9**, but only the alkyne **10** has been detected from this reaction [eqn. (3)].[8b] This result parallels the failure noted above to isolate **3** from dichlorocyclopropene hydrolysis.[5a] Photolyses of α-diazoketenes, generated from bis(diazoketones), form observed cyclopropenones [eqns. (4)–(6)],[9] and these reactions could conceivably involve ketenylcarbene intermediates.

Photolysis of fluoromaleic anhydride **11** under matrix isolation conditions gave a product tentatively identified as fluoro(ketenyl)carbene **12** on the basis of comparison of the calculated and observed spectra, together with fluorocyclopropenone **13** [eqn. (7)].[3i] Further irradiation led to the formation of fluoroacetylene. Calculations at the MP4(sdtq,fc)/6-311(2df,2p) level for *syn* and *anti* conformations of **12** revealed the latter was more stable by 0.9 kcal $mol^{-1}$, but there was a barrier for interconversion of 25 kcal $mol^{-1}$, while ring closure of *syn*-**12** to **13** had a barrier of 2.7 kcal $mol^{-1}$. Decarbonylation of *anti*-**12** had a barrier of 11.4 kcal $mol^{-1}$, while decarbonylation of **13** had a barrier of 49.7 kcal $mol^{-1}$. The ketenylcarbene **12** was suggested[3f] to have an important contribution from the structure **12a** with electron donation from the ketene oxygen to the carbene center.

The decarbonylation reaction of $CH_2$=C=O to give $CH_2$ and CO is a classical problem in chemical physics that is still avidly pursued.[10] Studies of decarbonylation of higher ketenes are

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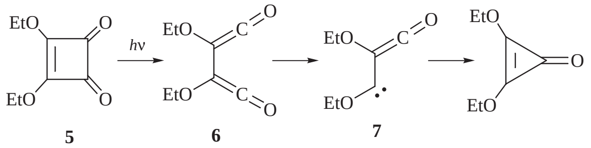
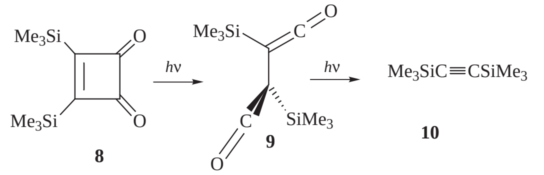
also continuing.[11a,b] A general theoretical study of thermal cheleotropic decarbonylation reactions has recently appeared,[11c] including the conversion of cyclopropanone to ethylene, and these reactions were classified as either pericyclic or pseudopericyclic processes. The low barrier for conversion of *syn*-**12** to **13** is typical of a pseudopericyclic process in which there is not continuous overlap of the orbitals in a closed loop.

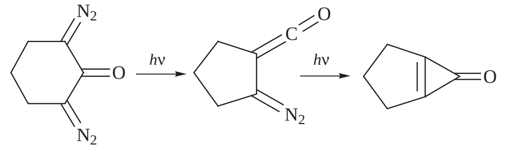
Recent theoretical work has included semiempirical studies of the structures and electronic configurations of cyclopropenone and some diaryl derivatives,[3j] and *ab initio* studies of cyclopropenone and analogues such as imino- and methylenecyclopropenone and their protonated derivatives to evaluate the aromaticity of these species.[3k] To further elucidate the problems associated with bisketene and cyclopropenone decarbonylation we have now carried out *ab initio* and hybrid DFT studies of these species and the mechanisms of their interconversion.



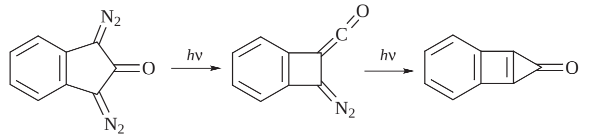
(2)[6a]



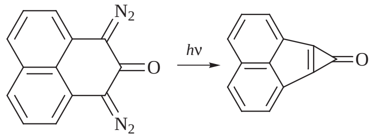
(3)[8b]



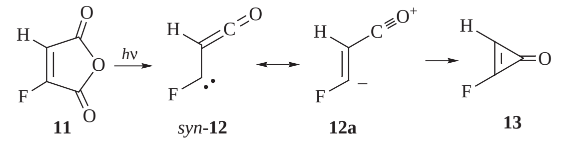
(4)[9a]



(5)[9b]



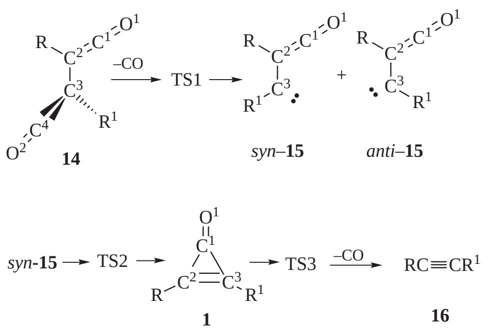
(6)[9c]



(7)

## Results

Structures and energies were calculated at the HF/6-31G*//HF/6-31G* level using Gaussian 94[12a] for the reactants and products as well as the transition states for interconversion of bisketenes **14**, cyclopropenones **1**, singlet ketenylcarbenes **15** and alkynes **16** (Scheme 1) with R = $R^1$ = H, $CH_3$, $NH_2$, OH, F and $SiH_3$, and for the pair of substituents H, $SiH_3$. For R = $R^1$ = H, $CH_3$, F and $SiH_3$ the structures and energies were also calculated at the MP2/6-31G*//MP2/6-31G* and Becke hybrid B3LYP/6-31G*//B3LYP/6-31G*[12b] levels. Zero-point vibrational energies (ZPVE) were calculated at the HF/6-31G*//MP2/6-31G* and B3LYP/6-31G*//B3LYP/6-31G* levels and were scaled by the factor 0.89. This choice of substituents provides a representative survey of several of the most important types encountered in practice. The MP2 and B3LYP calculated energy changes are summarized in Table 1, along with calculated energy, enthalpy, entropy and free energy changes at the B3LYP level and details of the energies are given in Table 2. Calculated bond distances and bond angles are given in Tables 3 and 4, respectively. The calculated structures found at the MP2 level for R = $R^1$ = $SiH_3$ are shown in Fig. 1.



**Scheme 1**

At the HF/6-31G* level transition structures for bisketene decarbonylation forming ketenylcarbenes *syn*-**15** were located, except for the $SiH_3$ derivative **15h**. At the MP2/6-31G* and B3LYP levels ketenylcarbene structures could not be found, and instead the transition structures found involved concerted decarbonylation with cyclization to give cyclopropenones **1**.

**Table 1** Comparative MP2 and B3LYP calculated energy and entropy changes in bisketene decarbonylations

| | Bisketene→TS1 | | | | | Bisketene $\xrightarrow{-CO}$ cyclopropenone | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| R, R | $E_{act}^{MP2\,a}$ | $E_{act}^{B3LYP\,a}$ | $\Delta H^{\ddagger\,b}$ | $\Delta S^{\ddagger\,b}$ | $\Delta G^{\ddagger\,b}$ | $\Delta E_o^{MP2\,a}$ | $E_o^{B3LYP\,a}$ | $\Delta H^b$ | $\Delta S^b$ | $\Delta G^b$ |
| H, H | 46.3 | 47.4 | 45.4 | −1.7 | 46.0 | 18.6 | 25.8 | 23.6 | 32.1 | 14.0 |
| $CH_3$, $CH_3$ | 37.5 | 39.6 | 37.6 | 0.1 | 37.5 | 7.9 | 13.1 | 11.1 | 35.3 | 0.6 |
| F, F | 27.9 | 32.4 | 30.7 | −0.1 | 31.0 | 1.1 | 11.1 | 9.6 | 33.8 | −0.5 |
| $SiH_3$, $SiH_3$ | 50.5 | 50.7 | 48.3 | 0.7 | 48.1 | 22.9 | 26.0 | 23.8 | 34.7 | 13.4 |
| R, R | Cyclopropenone→TS3 | | | | | Cyclopropenone $\xrightarrow{-CO}$ alkyne | | | | |
| H, H | 42.8 | 38.5 | 37.0 | 3.2 | 36.0 | −10.2 | 0.8 | −1.4 | 32.5 | −11.0 |
| $CH_3$, $CH_3$ | 34.9 | 27.8 | 26.1 | −2.2 | 26.8 | −5.8 | 1.8 | −0.3 | 37.9 | −11.6 |
| F, F | 35.0 | 38.2 | 36.6 | 3.8 | 35.8 | 19.5 | 26.9 | 25.0 | 34.8 | 14.6 |
| $SiH_3$, $SiH_3$ | 32.2 | 29.1 | 27.7 | 2.1 | 27.1 | −17.5 | −8.3 | −10.0 | 37.0 | −21.0 |

[a] From Table 2. [b] B3LYP.

**Table 2** Total energies (hartrees) for stationary points and relative energies (parentheses, kcal mol$^{-1}$)[a,b] in bisketene decarbonylation (Scheme 1)

| R, R$^1$ | Level[c] | Bisketene **14** | TS1 | Carbene **15** + CO | TS2 + CO | Cyclo-propenone **1** + CO | TS3 + CO | Alkyne **16** + 2CO | Δ*E* (TS3 − **1**) − (TS1 − **14**) |
|---|---|---|---|---|---|---|---|---|---|
| H, H, (a) | HF | −302.244 92 | −302.173 51 | −302.194 03[d] | −302.190 83 | −302.230 14 | −302.160 13 | −302.257 48 | |
| | *f* | (0.0) | (44.81) | (31.93) | (33.94) | (9.27) | (53.21) | (−7.88) | −0.87 |
| | | | | −302.188 80[e] | | | | | |
| | MP2 | −303.088 33[c] | −303.014 51 | | | −303.058 66 | −302.990 53 | −303.074 86 | |
| | *f* | (0.0) | (46.31) | | | (18.62) | (61.37) | (8.45) | −3.57 |
| | B3LYP | −303.954 36 | −303.878 80 | | | −303.913 18 | −303.851 79 | −303.911 89 | |
| | *f* | (0.0) | (47.41) | | | (25.84) | (64.36) | (26.65) | −8.89 |
| $CH_3$, $CH_3$ (**b**) | HF | −380.261 76 | −380.192 35 | −380.220 10[d] | −380.220 39 | −380.270 12 | −380.186 05 | −380.294 47 | |
| | *f* | (0.0) | (43.56) | (26.14) | (25.96) | (−5.25) | (47.51) | (−20.53) | 9.20 |
| | | | | −380.212 28[e] | | | | | |
| | MP2 | −381.372 39 | −381.312 61 | | | −381.359 76 | −381.304 14 | −381.369 00 | |
| | *f* | (0.0) | (37.51) | | | (7.93) | (42.83) | (2.13) | −2.61 |
| | B3LYP | −382.537 25 | −382.474 06 | | | −382.516 37 | −382.472 13 | −382.513 58 | |
| | *f* | (0.0) | (39.65) | | | (13.10) | (40.86) | (14.85) | −11.89 |
| $NH_2$, $NH_2$ (**c**) | HF | −412.240 10 | −412.203 32 | −412.252 55[d] | −412.240 57 | −412.273 87 | −412.198 40 | −412.276 38 | |
| | *f* | (0.0) | (23.08) | (−7.81) | (−0.29) | (−21.19) | (26.17) | (−22.77) | 24.24 |
| | | | | −412.244 37[e] | | | | | |
| OH, OH (**d**) | HF | −451.906 80 | −451.863 41 | −451.910 27[d] | −415.901 25 | −452.928 37 | −451.847 92 | −451.927 94 | |
| | *f* | (0.0) | (27.23) | (−2.18) | (3.48) | (−13.54) | (36.95) | (−13.27) | 23.26 |
| | | | | −451.904 92[e] | | | | | |
| F, F (**e**) | HF | −499.909 71 | −499.864 01 | −499.900 00[d] | −499.892 48 | −499.922 04 | −499.831 22 | −499.911 31 | |
| | *f* | (0.0) | (28.68) | (6.09) | (10.81) | (−7.74) | (49.25) | (1.00) | 28.31 |
| | | | | −499.895 48[e] | | | | | |
| | MP2 | −501.096 24 | −501.051 77 | | | −501.094 42 | −501.038 66 | −501.063 38 | |
| | *f* | (0.0) | (27.91) | | | (1.14) | (36.13) | (20.62) | 7.08 |
| | B3LYP | −502.395 66 | −502.344 02 | | | −502.377 91 | −502.317 06 | −502.335 05 | |
| | *f* | (0.0) | (32.40) | | | (11.14) | (49.32) | (38.03) | 5.78 |
| H, $SiH_3$ (**f**) | HF | −592.319 21 | −592.239 72 | −592.263 31[d] | −592.263 39 | −592.303 29 | −592.244 09 | −592.339 18 | |
| | *f* | (0.0) | (49.88) | (35.08) | (35.03) | (9.99) | (47.14) | (−12.53) | −12.7 |
| | | | | −592.254 63[e] | | | | | |
| $SiH_3$, H (**g**) | HF | −592.319 21 | −592.244 66 | −592.263 71[d] | −592.261 11 | −592.303 29 | −592.244 09 | −592.339 18 | |
| | *f* | (0.0) | (46.15) | (34.83) | (36.46) | (9.99) | (47.14) | (−12.53) | −9.00 |
| | | | | −592.260 12[e] | | | | | |
| $SiH_3$, $SiH_3$ (**h**) | HF | −882.393 23 | −882.308 79 | −882.324 52[e] | *g* | −882.377 66 | −882.312 60 | −882.420 72 | |
| | *f* | (0.0) | (52.99) | (43.12) | *g* | (9.77) | (50.60) | (−17.25) | −12.16 |
| | MP2 | −883.398 34 | −883.317 86 | | | −883.361 80 | −883.310 51 | −883.389 74 | |
| | *f* | (0.0) | (50.50) | | | (22.93) | (55.11) | (5.40) | −18.32 |
| | B3LYP | −885.336 54 | −885.255 71 | | | −885.295 02 | −885.248 58 | −885.308 26 | |
| | *f* | (0.0) | (50.72) | | | (26.05) | (55.20) | (17.75) | −21.58 |

[a] *E*(CO) = −112.732 93 hartrees (HF/6-31G* + ZPVE//HF/6-31g*); −113.016 87 hartrees (MP2/6-31G* + ZPVE//MP2/6-31G*); −113.304 97 (B3LYP/6-31G* + ZPVE//B3LYP/6-31G*). [b] Including 0.89 zero-point vibrational energy correction calculated at the level of HF/6-31G*//MP2/6-31G* (for HF and MP2), or at the B3LYP/6-31G*//B3LYP/6-31G* level for B3LYP. [c] HF: HF/6-31G*//HF/6-31G*; MP2: MP2/6-31G*//MP2/6-31G*; B3LYP: B3LYP/6-31G//B3LYP/6-31G*. [d] *syn*. [e] *anti*. [f] Relative energy/kcal mol$^{-1}$. [g] No barrier located.

**Table 3** Bond distances (Å) calculated for bisketenes **14**, ketenylcarbenes **15**, cyclopropenes **1** and alkynes **16**, and transition states for their interconversion

| | | R, $R^1$ | $C^1$=O | $C^1C^2$ | $C^2C^3$ | $C^1C^3$ | $C^3C^4$ | $C^4O^2$ | $C^2R$ | $C^3R$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **14** | HF | H, H | 1.144 | 1.312 | 1.483 | | 1.313 | 1.142 | 1.072 | 1.072 |
| | MP2 | | 1.180 | 1.328 | 1.478 | | 1.329 | 1.180 | 1.085 | 1.087 |
| | B3LYP | | 1.171 | 1.322 | 1.484 | | 1.324 | 1.168 | 1.091 | 1.084 |
| TS1 | HF | | 1.132 | 1.335 | 1.442 | 2.332 | 1.925 | 1.118 | 1.077 | 1.084 |
| | MP2 | | 1.209 | 1.376 | 1.412 | 1.548 | 1.714 | 1.164 | 1.084 | 1.086 |
| | B3LYP | | 1.200 | 1.366 | 1.405 | 1.563 | 1.768 | 1.148 | 1.084 | 1.085 |
| **15** | HF | *a* | 1.120 | 1.360 | 1.392 | 2.225 | | | 1.075 | 1.093 |
| | | *b* | 1.124 | 1.351 | 1.407 | 2.350 | | | 1.071 | 1.093 |
| TS2 | HF | | 1.134 | 1.361 | 1.361 | 1.912 | | | 1.076 | 1.085 |
| **1** | HF | | 1.190 | 1.412 | 1.327 | 1.412 | | | 1.071 | 1.071 |
| | MP2 | | 1.212 | 1.437 | 1.352 | 1.437 | | | 1.083 | 1.083 |
| | B3LYP | | 1.204 | 1.435 | 1.344 | 1.435 | | | 1.086 | 1.086 |
| TS3 | HF | | 1.113 | 1.785 | 1.273 | 2.400 | | | 1.064 | 1.076 |
| | MP2 | | 1.176 | 1.566 | 1.269 | 2.182 | | | 1.087 | 1.078 |
| | B3LYP | | 1.156 | 1.663 | 1.262 | 2.323 | | | 1.087 | 1.077 |
| **14** | HF | Me, Me | 1.148 | 1.308 | 1.491 | | 1.309 | 1.146 | 1.513 | 1.517 |
| | MP2 | | 1.184 | 1.328 | 1.486 | | 1.328 | 1.185 | 1.507 | 1.508 |
| | B3LYP | | 1.172 | 1.324 | 1.496 | | 1.325 | 1.170 | 1.515 | 1.514 |
| TS1 | HF | | 1.136 | 1.332 | 1.442 | 2.270 | 1.885 | 1.121 | 1.515 | 1.511 |
| | MP2 | | 1.210 | 1.378 | 1.425 | 1.555 | 1.683 | 1.712 | 1.482 | 1.502 |
| | B3LYP | | 1.205 | 1.367 | 1.420 | 1.569 | 1.721 | 1.152 | 1.490 | 1.506 |
| **15** | HF | *a* | 1.128 | 1.356 | 1.386 | 2.090 | | | 1.515 | 1.500 |
| | | *b* | 1.128 | 1.350 | 1.408 | 2.345 | | | 1.517 | 1.503 |
| TS2 | HF | | 1.132 | 1.356 | 1.377 | 2.023 | | | 1.512 | 1.499 |
| **1** | HF | | 1.196 | 1.407 | 1.328 | 1.407 | | | 1.486 | 1.486 |
| | MP2 | | 1.220 | 1.439 | 1.360 | 1.439 | | | 1.483 | 1.483 |
| | B3LYP | | 1.212 | 1.433 | 1.352 | 1.433 | | | 1.487 | 1.487 |
| TS3 | HF | | 1.116 | 1.738 | 1.271 | 2.310 | | | 1.488 | 1.494 |
| | MP2 | | 1.204 | 1.361 | 1.338 | 1.810 | | | 1.495 | 1.470 |
| | B3LYP | | 1.172 | 1.563 | 1.296 | 2.314 | | | 1.497 | 1.453 |
| **14** | HF | $NH_2$, $NH_2$ | 1.144 | 1.316 | 1.476 | | 1.318 | 1.146 | 1.423 | 1.430 |
| TS1 | HF | | 1.140 | 1.324 | 1.462 | 2.361 | 1.687 | 1.140 | 1.424 | 1.343 |
| **15** | HF | *a* | 1.132 | 1.340 | 1.433 | 2.287 | | | 1.425 | 1.318 |
| | | *b* | 1.136 | 1.329 | 1.451 | 2.420 | | | 1.426 | 1.318 |
| TS2 | HF | | 1.148 | 1.350 | 1.374 | 1.823 | | | 1.411 | 1.324 |
| **1** | HF | | 1.200 | 1.401 | 1.336 | 1.401 | | | 1.362 | 1.362 |
| TS3 | HF | | 1.119 | 1.842 | 1.399 | 2.490 | | | 1.344 | 1.327 |
| **14** | HF | OH, OH | 1.140 | 1.320 | 1.458 | | 1.318 | 1.141 | 1.379 | 1.380 |
| TS | HF | | 1.140 | 1.324 | 1.449 | 2.366 | 1.755 | 1.124 | 1.381 | 1.333 |
| **15** | HF | *a* | 1.128 | 1.344 | 1.413 | 2.267 | | | 1.371 | 1.320 |
| | | *b* | 1.128 | 1.341 | 1.424 | 2.404 | | | 1.373 | 1.323 |
| TS2 | HF | | 1.142 | 1.366 | 1.357 | 1.859 | | | 1.352 | 1.319 |
| **1** | HF | | 1.191 | 1.414 | 1.332 | 1.414 | | | 1.320 | 1.320 |
| TS3 | HF | | 1.112 | 1.944 | 1.291 | 2.415 | | | 1.302 | 1.351 |
| **14** | HF | F, F | 1.139 | 1.320 | 1.437 | | 1.320 | 1.139 | 1.347 | 1.347 |
| | MP2 | | 1.178 | 1.340 | 1.420 | | 1.342 | 1.177 | 1.371 | 1.377 |
| | B3LYP | | 1.170 | 1.332 | 1.422 | | 1.336 | 1.166 | 1.370 | 1.365 |
| TS1 | HF | | 1.134 | 1.330 | 1.436 | 2.343 | 1.811 | 1.116 | 1.341 | 1.330 |
| | MP2 | | 1.203 | 1.388 | 1.384 | 1.591 | 1.673 | 1.164 | 1.334 | 1.358 |
| | B3LYP | | 1.197 | 1.378 | 1.378 | 1.602 | 1.733 | 1.148 | 1.328 | 1.344 |
| **15** | HF | *a* | 1.120 | 1.356 | 1.396 | 2.260 | | | 1.332 | 1.316 |
| | | *b* | 1.124 | 1.350 | 1.411 | 2.409 | | | 1.331 | 1.329 |
| TS2 | HF | | 1.133 | 1.375 | 1.342 | 1.880 | | | 1.316 | 1.301 |
| **1** | HF | | 1.181 | 1.429 | 1.313 | 1.429 | | | 1.288 | 1.288 |
| | MP2 | | 1.204 | 1.467 | 1.344 | 1.467 | | | 1.324 | 1.321 |
| | B3LYP | | 1.196 | 1.462 | 1.336 | 1.462 | | | 1.312 | 1.312 |
| TS3 | HF | | 1.108 | 1.868 | 1.239 | 2.435 | | | 1.307 | 1.296 |
| | MP2 | | 1.168 | 1.841 | 1.278 | 2.608 | | | 1.313 | 1.303 |
| | B3LYP | | 1.148 | 1.920 | 1.260 | 2.636 | | | 1.299 | 1.300 |
| **14** | HF | H, $SiH_3$ | 1.141 | 1.315 | 1.498 | | 1.313 | 1.143 | 1.074 | 1.868 |
| TS1 | HF | | 1.131 | 1.340 | 1.432 | 2.316 | 1.953 | 1.118 | 1.079 | 1.874 |
| **15** | HF | *a* | 1.124 | 1.370 | 1.369 | 2.145 | | | 1.080 | 1.868 |
| | | *b* | 1.124 | 1.365 | 1.376 | 2.302 | | | 1.074 | 1.854 |
| TS2 | HF | | 1.130 | 1.366 | 1.359 | 2.009 | | | 1.078 | 1.867 |
| **1** | HF | | 1.192 | 1.398 | 1.338 | 1.424 | | | 1.072 | 1.880 |
| TS3 | HF | | 1.115 | 1.686 | 1.272 | 2.348 | | | 1.068 | 1.832 |
| **14** | HF | $SiH_3$, H | 1.143 | 1.313 | 1.498 | | 1.315 | 1.141 | 1.868 | 1.074 |
| TS1 | HF | | 1.130 | 1.335 | 1.460 | 2.315 | 1.948 | 1.116 | 1.873 | 1.086 |
| **15** | HF | *a* | 1.124 | 1.356 | 1.413 | 2.206 | | | 1.879 | 1.095 |
| | | *b* | 1.124 | 1.345 | 1.428 | 2.343 | | | 1.873 | 1.095 |
| TS2 | HF | | 1.134 | 1.361 | 1.383 | 1.905 | | | 1.880 | 1.087 |
| **1** | HF | | 1.192 | 1.424 | 1.338 | 1.398 | | | 1.880 | 1.072 |
| TS3 | HF | | 1.115 | 1.686 | 1.272 | 2.348 | | | 1.068 | 1.832 |
| **14** | HF | $SiH_3$, $SiH_3$ | 1.141 | 1.315 | 1.514 | | 1.315 | 1.141 | 1.869 | 1.869 |
| | MP2 | | 1.180 | 1.328 | 1.501 | | 1.327 | 1.179 | 1.861 | 1.865 |
| | B3LYP | | 1.168 | 1.324 | 1.511 | | 1.323 | 1.168 | 1.869 | 1.871 |

**Table 3** *Cont.*

| | | R, R$^1$ | C$^1$=O | C$^1$C$^2$ | C$^2$C$^3$ | C$^1$C$^3$ | C$^3$C$^4$ | C$^4$O$^2$ | C$^2$R | C$^3$R |
|---|---|---|---|---|---|---|---|---|---|---|
| TS1 | HF | | 1.132 | 1.341 | 1.448 | 2.273 | 1.981 | 1.116 | 1.881 | 1.875 |
| | MP2 | | 1.207 | 1.376 | 1.445 | 1.555 | 1.719 | 1.168 | 1.859 | 1.878 |
| | B3LYP | | 1.200 | 1.365 | 1.437 | 1.579 | 1.768 | 1.148 | 1.859 | 1.882 |
| **15** | HF | *b* | 1.124 | 1.361 | 1.400 | 2.320 | | | 1.880 | 1.886 |
| **1** | HF | | 1.192 | 1.407 | 1.344 | 1.407 | | | 1.880 | 1.880 |
| | MP2 | | 1.216 | 1.436 | 1.376 | 1.436 | | | 1.870 | 1.873 |
| | B3LYP | | 1.208 | 1.434 | 1.368 | 1.434 | | | 1.868 | 1.872 |
| TS3 | HF | | 1.116 | 1.666 | 1.293 | 2.287 | | | 1.871 | 1.833 |
| | MP2 | | 1.188 | 1.453 | 1.317 | 2.078 | | | 1.882 | 1.833 |
| | B3LYP | | 1.164 | 1.520 | 1.318 | 2.259 | | | 1.875 | 1.828 |

[a] *syn.* [b] *anti.*

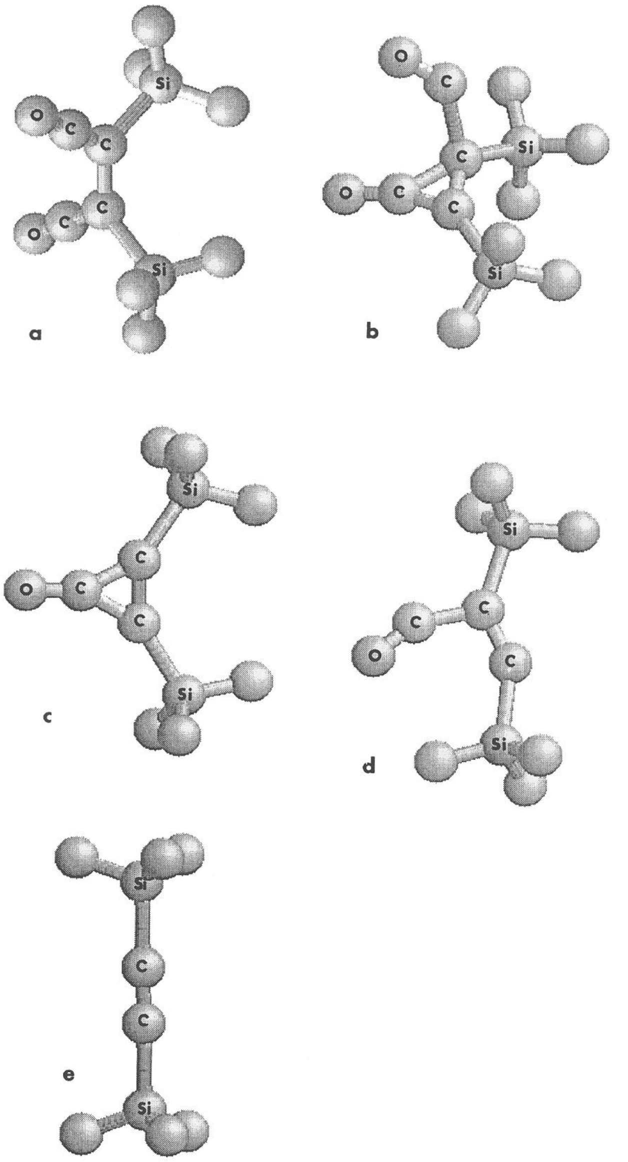


**Fig. 1** Calculated structures for decarbonylation of bis(SiH$_3$) substituted bisketene **14h**: (a) **14h**, (b) transition state for concerted decarbonylation of **14h**, (c) cyclopropenone **15h**, (d) transition state for decarbonylation of **15h**, (e) alkyne **16h**

Structures and energies were also calculated for the *anti*-ketenylcarbene structures *anti*-**15** at the HF/6-31G* level. These ranged in energy from 2.2 to 5.4 kcal mol$^{-1}$ higher in energy than the *syn*-isomers, and were not formed from decarbonylation of the bisketenes **14**. As noted above,[3f] the interconversion of *syn*- and *anti*-ketenylcarbenes has a high barrier, significantly higher than the barriers found here for cyclopropenone formation by the *syn*-ketenylcarbenes, and was not considered here.

## Discussion

In previous studies calculations at both the MP2/6-31G* and B3LYP levels have proven to be quite successful in predicting the energetics of many reactions involving ketenes[13a,b] and open shell molecules,[13c–e] whereas HF/6-31G* calculated energies have been less effective in quantitative predictions, although these have been useful to predict trends in reactivity. The H, H; CH$_3$, CH$_3$; F, F; and SiH$_3$, SiH$_3$ pairs of substituents are of major interest in our studies, and were examined at the higher levels of theory, and are the focus of the discussion, except as noted.

Comparing the MP2 and B3LYP calculations (Table 1) these give rather similar results for the activation energies, as values of $\Delta\Delta E_{\text{act}}$ for the transformations bisketene→TS1 and cyclopropenone→TS3 vary from 0.2 to 7.1 kcal mol$^{-1}$, with an average of 3.6 kcal mol$^{-1}$, whereas the differences in the energy changes $\Delta\Delta E°$ for the decarbonylations bisketene→cyclopropenone and cyclopropenone→alkyne vary from 3.1 to 11.0, with an average of 7.6 kcal mol$^{-1}$. Comparative experimental data for these conversions does not appear to be available, but it has been reported[13f] that DFT methods tend to overestimate the energies of alkynes relative to allenes, and this was attributed[13f] to the so-called 'self-interaction energy.'[13g] In our study the decarbonylations are more endothermic in every case at the B3LYP level, and the MP2 $\Delta E$ values are regarded as more reliable for these steps.

The results in Table 1 indicate that for each of the pairs H, H; CH$_3$, CH$_3$; F, F; and SiH$_3$, SiH$_3$ there are substantial barriers for the initial decarbonylation of the bisketene, but there is a much higher barrier for the bisketene with the SiH$_3$, SiH$_3$ substituents, which strongly stabilize the ketene, in contrast to the lower barrier for the F, F substituents, which destabilize the ketene. The low stability and tendency to decarbonylation of the fluoro-substituted monoketenes FCH=C=O and CF$_2$=C=O are well-documented.[8a] The lower barrier for decarbonylation of the bisketene with CH$_3$, CH$_3$ compared to H, H substituents is also consistent with the greater ketene stabilizing ability of H compared to CH$_3$.

The calculated values of $\Delta E$ for formation of the cyclopropenones are also less favorable for the H, H and SiH$_3$, SiH$_3$ substituents compared to CH$_3$, CH$_3$ and F, F, and this is as expected with the greater ketene stabilizing ability of the former two pairs, and the greater ability of the latter two to stabilize the electron-deficient cyclopropenone ring by electron donation. As shown in **1a** the cyclopropenone ring is electron deficient, and is known to be stabilized by π-donor substituents.[3g] There is a high barrier for the decarbonylation of the parent bisketene **14a** and the formation of the cyclopropenone **1a** is substantially endothermic (Table 1), but nevertheless this process has been reported upon photolysis in an Ar matrix at 10 K, and the cyclopropenone was observed by its IR band.[6c]

For decarbonylation of the cyclopropenones the SiH$_3$, SiH$_3$ substituents give the lowest barrier and the most favorable overall process for conversion to the alkyne. These results may

**Table 4** Bond angles (°) and dipole moments $\mu$ (Debye) calculated for bisketenes **14**, ketenylcarbenes **15**, cyclopropenones **1** and alkynes **16**, and transition states for their interconversion

| | | R, R$^1$ | C$^2$C$^1$O | C$^3$C$^4$O | C$^1$C$^2$R | C$^1$C$^2$C$^3$ | C$^2$C$^1$C$^3$ | C$^2$C$^3$R$^1$ | C$^1$C$^2$C$^3$C$^4$ | C$^1$C$^2$C$^3$R$^1$ | $\mu$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **14** | HF | H, H | 179.6 | 179.5 | 116.8 | 120.6 | | 122.6 | 84.9 | −97.4 | 1.91 |
| | MP2 | | 179.2 | 179.1 | 118.2 | 118.8 | | 123.2 | 82.1 | −99.1 | 2.33 |
| | B3LYP | | 179.5 | 179.4 | 117.6 | 119.8 | | 122.6 | 78.3 | −102.7 | 1.82 |
| TS1 | HF | | 179.5 | 140.8 | 116.4 | 114.4 | 34.3 | 110.4 | 89.8 | −165.1 | 2.50 |
| | MP2 | | 158.4 | 133.9 | 147.1 | 67.5 | 57.4 | 130.1 | 90.0 | −127.9 | 4.91 |
| | B3LYP | | 159.4 | 135.6 | 146.4 | 68.7 | 56.8 | 131.1 | 91.7 | −130.0 | 3.61 |
| **15** | HF | *a* | 178.5 | | 118.4 | 107.9 | 36.5 | 109.3 | | 180.0 | 2.78 |
| | | *b* | 176.1 | | 118.1 | 116.8 | 32.3 | 109.4 | | 0.0 | 2.62 |
| TS2 | HF | | 176.8 | | 129.6 | 89.2 | 45.2 | 119.6 | | 180.0 | 2.67 |
| **1** | HF | | 151.8 | | 152.9 | 61.9 | 56.2 | 145.1 | | 180.0 | 4.69 |
| | MP2 | | 151.9 | | 154.0 | 61.9 | 56.1 | 144.3 | | 180.0 | 2.75 |
| | B3LYP | | 152.1 | | 153.8 | 62.1 | 55.8 | 144.1 | | 180.0 | 4.01 |
| TS3 | HF | | 157.3 | | 103.9 | 102.1 | 31.3 | 121.6 | | 180.0 | 2.58 |
| | MP2 | | 151.5 | | 114.1 | 100.2 | 34.9 | 147.2 | | 180.0 | 1.92 |
| | B3LYP | | 147.1 | | 108.7 | 104.3 | 31.8 | 144.0 | | 180.0 | 1.47 |
| **14** | HF | Me, Me | 179.6 | 179.5 | 120.9 | 117.5 | | 121.7 | 79.3 | −102.9 | 2.65 |
| | MP2 | | 179.0 | 179.2 | 122.4 | 115.5 | | 122.0 | 78.2 | −104.1 | 3.14 |
| | B3LYP | | 179.2 | 179.3 | 122.1 | 115.7 | | 122.3 | 76.5 | −105.0 | 2.52 |
| TS1 | HF | | 179.4 | 138.6 | 120.5 | 109.8 | 36.7 | 115.4 | 83.9 | −157.7 | 3.02 |
| | MP2 | | 158.4 | 134.1 | 148.6 | 67.4 | 57.7 | 129.6 | 87.7 | −127.1 | 5.45 |
| | B3LYP | | 159.0 | 137.1 | 147.5 | 68.5 | 57.3 | 130.6 | 89.6 | −127.2 | 4.21 |
| **15** | HF | *a* | 179.8 | | 124.6 | 99.3 | 40.9 | 118.4 | | 180.0 | 2.73 |
| | | *b* | 176.9 | | 119.7 | 116.5 | 32.5 | 119.8 | | 0.0 | 1.63 |
| TS2 | HF | | 179.0 | | 127.0 | 95.5 | 42.6 | 120.3 | | 180.0 | 2.77 |
| **1** | HF | | 151.8 | | 151.3 | 61.8 | 56.3 | 146.9 | | 180.0 | 5.28 |
| | MP2 | | 151.8 | | 152.3 | 61.8 | 56.4 | 145.9 | | 180.0 | 5.55 |
| | B3LYP | | 151.9 | | 152.2 | 61.9 | 56.3 | 146.0 | | 180.0 | 4.68 |
| TS3 | HF | | 156.7 | | 109.9 | 99.1 | 32.9 | 132.1 | | 180.0 | 2.30 |
| | MP2 | | 175.3 | | 139.2 | 84.2 | 47.4 | 150.4 | | 0.0 | 2.11 |
| | B3LYP | | 137.9 | | 115.9 | 107.9 | 32.3 | 139.9 | | 0.0 | 0.82 |
| **14** | HF | NH$_2$, NH$_2$ | 178.4 | 178.2 | 121.3 | 117.8 | | 120.6 | 76.8 | −107.9 | 1.70 |
| TS1 | HF | | 178.7 | 134.9 | 121.3 | 115.8 | 33.9 | 113.6 | 74.0 | −152.4 | 4.20 |
| **15** | HF | *a* | 180.0 | | 116.1 | 111.1 | 35.8 | 114.3 | | −179.9 | 4.15 |
| | | *b* | 175.0 | | 115.5 | 121.0 | 30.9 | 117.5 | | 0.0 | 1.72 |
| TS2 | HF | | 171.7 | | 132.7 | 84.0 | 48.6 | 130.0 | | −179.8 | 5.45 |
| **1** | HF | | 151.5 | | 151.0 | 61.5 | 56.9 | 147.5 | | 180.0 | 5.92 |
| TS3 | HF | | 146.6 | | 113.6 | 99.6 | 33.6 | 114.4 | | −178.3 | 3.73 |
| **14** | HF | OH, OH | 178.9 | 178.6 | 118.6 | 119.4 | | 121.8 | 72.0 | −106.8 | 3.03 |
| TS1 | HF | | 178.8 | 139.7 | 119.7 | 117.1 | 33.0 | 113.4 | 80.4 | −158.1 | 3.59 |
| **15** | HF | *a* | 178.6 | | 118.4 | 110.6 | 35.7 | 110.0 | | −177.3 | 2.05 |
| | | *b* | 177.8 | | 116.9 | 120.7 | 30.6 | 109.8 | | −0.3 | 1.82 |
| TS2 | HF | | 171.9 | | 130.3 | 86.1 | 46.7 | 124.6 | | −176.9 | 2.79 |
| **1** | HF | | 151.9 | | 148.0 | 61.9 | 56.2 | 150.0 | | 180.0 | 7.46 |
| TS3 | HF | | 161.5 | | 104.8 | 94.4 | 32.2 | 120.9 | | 178.4 | 2.11 |
| **14** | HF | F, F | 177.3 | 177.3 | 117.5 | 121.0 | | 121.3 | 85.3 | −98.3 | 0.68 |
| | MP2 | | 176.6 | 176.5 | 118.4 | 118.3 | | 123.1 | 86.6 | −97.5 | 0.48 |
| | B3LYP | | 177.1 | 176.8 | 118.8 | 118.0 | | 123.2 | 80.9 | −100.3 | 0.50 |
| TS1 | HF | | 179.1 | 143.6 | 117.9 | 115.8 | 33.4 | 110.6 | 97.7 | 150.5 | 1.03 |
| | MP2 | | 158.8 | 137.0 | 145.9 | 70.0 | 54.9 | 130.3 | 93.3 | −125.8 | 3.36 |
| | B3LYP | | 159.8 | 137.4 | 144.7 | 71.1 | 54.5 | 131.4 | 93.9 | −127.3 | 2.27 |
| **15** | HF | *a* | 179.5 | | 117.8 | 110.4 | 35.3 | 110.5 | | 180.0 | 2.16 |
| | | *b* | 177.3 | | 117.0 | 121.5 | 29.9 | 106.9 | | 0.0 | 2.48 |
| TS2 | HF | | 172.1 | | 128.5 | 87.5 | 45.5 | 125.1 | | 180.0 | 0.89 |
| **1** | HF | | 152.6 | | 150.8 | 62.6 | 54.8 | 146.6 | | 180.0 | 2.94 |
| | MP2 | | 152.7 | | 151.7 | 62.7 | 54.5 | 145.7 | | 180.0 | 2.74 |
| | B3LYP | | 152.8 | | 151.5 | 62.8 | 54.4 | 154.7 | | 180.0 | 2.51 |
| TS3 | HF | | 157.1 | | 98.9 | 101.2 | 29.9 | 136.5 | | 180.0 | 1.94 |
| | MP2 | | 120.1 | | 109.8 | 112.2 | 27.0 | 135.0 | | 0.0 | 0.83 |
| | B3LYP | | 123.8 | | 107.5 | 110.3 | 26.6 | 137.7 | | 0.0 | 0.24 |
| **14** | HF | H, SiH$_3$ | 180.0 | 178.7 | 116.4 | 121.4 | | 122.2 | 86.4 | −95.8 | 1.59 |
| TS1 | HF | | 178.8 | 141.7 | 116.8 | 113.5 | 34.5 | 119.3 | 84.7 | −158.9 | 2.04 |
| **15** | HF | *a* | 177.0 | | 121.3 | 114.2 | 38.4 | 122.8 | | 180.0 | 2.53 |
| | | *b* | 175.0 | | 118.4 | 114.2 | 33.0 | 132.2 | | 0.0 | 2.54 |
| TS2 | HF | | 179.3 | | 126.6 | 95.0 | 42.3 | 127.2 | | 180.0 | 2.31 |
| **1** | HF | | 150.7 | | 152.2 | 60.7 | 56.6 | 152.2 | | 180.0 | 4.71 |
| TS3 | HF | | 156.5 | | 107.7 | 104.2 | 31.6 | 143.9 | | 180.0 | 2.75 |
| **14** | HF | SiH$_3$, H | 178.7 | 180.0 | 119.7 | 117.9 | | 122.1 | 86.4 | −96.4 | 1.59 |
| TS1 | HF | | 179.0 | 141.7 | 120.4 | 111.8 | 35.8 | 109.9 | 91.8 | −164.6 | 1.99 |
| **15** | HF | *a* | 179.5 | | 122.9 | 103.1 | 38.1 | 109.1 | | 180.0 | 2.35 |
| | | *b* | 178.0 | | 123.9 | 115.3 | 33.4 | 110.4 | | 0.0 | 2.18 |
| TS2 | HF | | | 176.5 | 132.7 | 87.9 | 46.3 | 117.3 | | 180.0 | 2.53 |
| TS3 | HF | | | 156.5 | 107.7 | 104.2 | 31.6 | 138.2 | | 180.0 | 2.75 |
| **14** | HF | SiH$_3$, SiH$_3$ | 178.7 | 178.7 | 119.3 | 118.2 | | 122.5 | 92. 0 | −89.1 | 1.22 |
| | MP2 | | 178.3 | 178.0 | 119.6 | 118.7 | | 121.6 | 95.5 | −86.2 | 1.52 |
| | B3LYP | | 178.4 | 178.0 | 118.8 | 119.1 | | 122.1 | 92.0 | −88.6 | 1.11 |

**Table 4** *Cont.*

| | | R, R$^1$ | C$^2$C$^4$O | C$^3$C$^4$O | C$^1$C$^2$R | C$^1$C$^2$C$^3$ | C$^2$C$^1$C$^3$ | C$^2$C$^3$R$^1$ | C$^1$C$^2$C$^3$C$^4$ | C$^1$C$^2$C$^3$R$^1$ | $\mu$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| TS1 | HF | | 179.1 | 142.7 | 119.5 | 109.1 | 37.0 | 123.3 | 85.6 | −157.7 | 4.41 |
| | MP2 | | 159.4 | 132.1 | 149.0 | 66.9 | 58.7 | 129.1 | 82.8 | −130.6 | 4.55 |
| | B3LYP | | 160.4 | 135.5 | 147.1 | 68.6 | 57.9 | 131.1 | 85.3 | −131.0 | 3.15 |
| **15** | HF | *b* | 177.5 | | 123.7 | 114.3 | 33.4 | 131.0 | | 0.0 | 2.06 |
| **1** | HF | | 151.5 | | 152.3 | 61.5 | 57.1 | 146.3 | | 180.0 | 4.63 |
| | MP2 | | 151.4 | | 153.6 | 61.4 | 57.3 | 145.1 | | 180.0 | 4.80 |
| | B3LYP | | 151.5 | | 152.3 | 61.5 | 57.0 | 146.2 | | 180.0 | 3.84 |
| TS3 | HF | | 158.3 | | 114.3 | 100.5 | 33.8 | 136.0 | | 180.0 | 2.41 |
| | MP2 | | 159.4 | | 126.7 | 97.1 | 39.0 | 147.1 | | 0.0 | 1.49 |
| | B3LYP | | 150.9 | | 120.6 | 105.3 | 34.3 | 145.2 | | 0.0 | 0.77 |

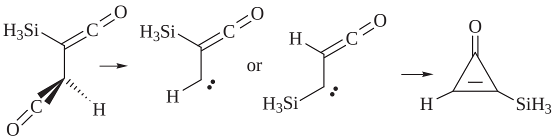
[a] *syn.* [b] *anti.*

be attributed to the relative lack of a stabilizing influence of $SiH_3$ on the cyclopropenone, and a strong stabilization by $SiH_3$ of the developing alkyne in the transition state and product. By contrast formation of the F, F substituted alkyne is highly unfavorable, as expected for the destabilizing interaction of the electronegative fluorine with the sp hybridized alkyne. For the parent cyclopropenone **1a** there is a high barrier for decarbonylation, of 42.8 and 38.5 kcal mol$^{-1}$ at the MP2 and B3LYP levels, respectively, and this barrier is reflected in the known[1c,6c] stability of **1a**. Interestingly these barriers are almost identical to MP2 and MP4(SDTQ) barriers of 43.0 and 39.3 kcal mol$^{-1}$, respectively, calculated for cyclopropanone decarbonylation.[11c] These high barriers were attributed[11c] to the cyclopropanone decarbonylation being 'effectively forbidden' because of the antiaromatic character of this transition state, and the same stricture applies to the decarbonylation of cyclopropenone.

The HF barriers for the initial decarbonylation of $NH_2$, $NH_2$ and OH, OH substituted bisketenes resemble those of the F, F case, and in all three examples minimum energy structures for singlet ketenylcarbenes are found, but with low barriers for decarbonylation (Table 2). Decarbonylation of these bisketenes to form ketenylcarbenes requires much less energy than for those with the other substituents, and this is expected for these groups, which can stabilize the carbenes by π-donation. Similarly at the HF level the energetics for conversion of the OH, OH; $NH_2$, $NH_2$; and F, F substituted bisketenes to cyclopropenones are more favorable, as expected for these groups which destabilize the ketene[8a,b] and stabilize the product cyclopropenones. The well documented[6] photochemical conversion of the dialkoxy 1,2-bisketenes to the corresponding cyclopropenones is consistent with these calculations.

For decarbonylation of the di($SiH_3$) substituted bisketene **14h** the ketenylcarbene *syn*-**15h** is not a stationary point on the reaction path and is predicted to form the cyclopropenone **1h** with no barrier, even at the HF level. At the MP2 and B3LYP levels the cyclopropenone **1h** is predicted to have barriers of 32.2 and 29.1 kcal mol$^{-1}$ for decarbonylation to give the alkyne, and these are 18.3 and 21.6 kcal mol$^{-1}$ less than those for formation of the cyclopropenone from the bisketene. The lower stability of **1h** compared to its precursor **14h** could prevent observation of the former from **14h** under thermal conditions where **1h** is formed with excess vibrational energy, or where further photolysis occurs, and this agrees with the experimental observation that cyclopropenone **3** has not yet been observed upon photolysis of bisketene **9**.[8]

The initial decarbonylation of the mono ($SiH_3$) substituted bisketene **14f** could occur with loss of one or the other CO group, and the HF barriers differ by 3.8 kcal mol$^{-1}$ [eqn. (8)]. The preferred ketenylcarbene is that with the silyl substituent stabilizing the ketene (**15g**), and this reacts by a low barrier to form the minimum energy cyclopropenone **1f**, which reacts by a 37.1 kcal mol$^{-1}$ barrier to form the alkyne **16f**. As the latter barrier is less than that of 46.2 kcal mol$^{-1}$ for decarbonylation of the bisketene it may be difficult to prepare monosilylated cyclopropenes by pyrolysis of monosilylated bisketenes, and these cyclopropenones may also be labile to photolysis conditions.



**14f** **15g** **15f** **1f** (8)

The exothermic decarbonylation of the disilyl cyclopropenone **1h** reflects the strong stabilization of the disilyl alkyne **16h**. At the HF/6-31G* level successive replacement of hydrogen in the alkyne HC≡CH by $SiH_3$ groups results in stabilization by 4.6 and 4.7 kcal mol$^{-1}$ relative to the bisketene, showing additivity of substituent effects, and a stabilization of the alkyne by $SiH_3$ even greater than that for the ketene.

As depicted in Fig. 1, the concerted formation of the cyclopropenones upon decarbonylation of the bisketenes involves in-plane nucleophilic attack on the LUMO concentrated at $C_\alpha$ of the ketenyl moiety by the lone pair of the developing carbenic carbon. The contrast between the proposed[3f] observation of the monofluoro ketenylcarbene *syn*-**12** [eqn. (7)] and our finding that decarbonylation of the difluoro bisketene **14e** does not lead to a ketenylcarbene **15e** is not unreasonable, as fluoroketenes are strongly destabilized, and so cyclopropenone **1e** is formed directly.[8a] A ketenylcarbene intermediate was also proposed as an unobserved intermediate in the reaction shown in eqn. (1).[5e]

Difluoro-1,2-bisketene **14e** has the lowest barrier for decarbonylation, while difluorocyclopropenone **1e** has the most unfavorable product forming step. These differences are reflected in the geometries, as the bond distance changes in reaching TS1 for **14e** are the smallest, while those for reaching TS3 are the largest of the group.

The calculated entropy changes (Table 1) show very small changes for the transition states for the bisketene decarbonylations, consistent with the occurrence of concerted bond breaking and formation, but with a large positive change for cyclopropenone formation. The entropy changes for reaching the second decarbonylation transition state are also rather small, and are again quite large for the second decarbonylation.

A referee has asked about possible Hammett correlations of the data, but in our experience[6e,8a–c] ketene reactivities can usually not be interpreted in these terms, and we have not found such correlations of the data in Tables 1 and 2.

In summary bisketene decarbonylation is predicted to serve as a facile preparative route to cyclopropenones only for those derivatives with strong π-donor substituents. For silyl substituted cyclopropenones the barriers for their decarbonylation are significantly less than the barriers for decarbonylation of the initial bisketene, and so the cyclopropenones may not survive at the conditions of their generation.

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