Theoretical Evidence of a Singlet α-Oxocarbene Intermediate in the Retro-Wolff Rearrangement of Azafulvenone

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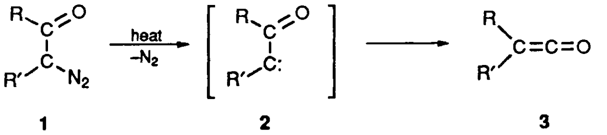
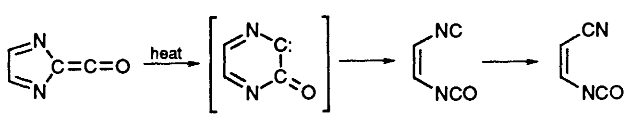
Ab initio MO calculations at the CISDQ/6-31G** level suggest that the transformation of azafulvenone yielding isocyanovinyl ketene involves a singlet cyclic α-oxocarbene intermediate.

The question of whether or not α-oxocarbenes **2** exist as discrete intermediates during the Wolff rearrangement (Scheme 1) converting diazoketones **1** to ketenes **3** continues to intrigue chemists. Although species **2** are commonly assumed to be involved in some way in the transformation, there is no kinetic, spectroscopic or theoretical evidence for their existence.[1,2] We have been interested in searching for such evidence in the reverse transformation, *i.e.* the rearrangement of ketenes. We found previously, by means of *ab initio* molecular orbital calculations, that in the retro-Wolff rearrangement of diazafulvenone **4** (Scheme 2) a singlet structure **5** having the form of a α-oxocarbene is involved as a transition structure for a concerted process connecting **4** to isocyanovinyl isocyanate **6** rather than a local equilibrium structure. Following pyrolysis of **4**, the cyanovinyl isocyanate **7** has been observed as the final product.[4]

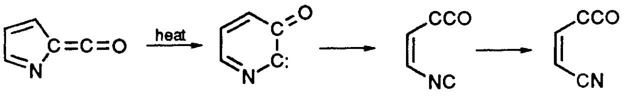


Scheme 1



Scheme 2

We report preliminary theoretical results suggesting that in the retro-Wolff rearrangement of azafulvenone **8** which is a carbon analogue of **4**, the corresponding singlet α-oxocarbene **9** (Scheme 3) exists as a local minimum on the potential energy surface.



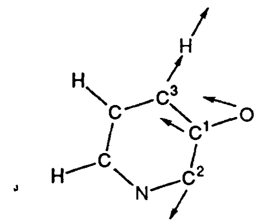
Scheme 3

For the purpose of comparison with previous results[3] on the rearrangement **4**→**7**, we have considered the sequence of reactions **8**→**9**→**10**→**11** (Scheme 3). Molecular geometries of the relevant stationary points were optimized at the Hartree-Fock level with the dp-polarized 6-31G** basis set. Harmonic vibrational wavenumbers were computed at this level in order to characterize stationary points as minima or transition structures and to estimate the zero-point vibrational contribution to relative energies. The identity of each transition structure has been confirmed by intrinsic reaction coordinate (IRC) calculations. Relative energies between stationary points were estimated from total energies calculated at the fourth-order Møller-Plesset perturbation theory (MP4SDTQ) and configuration interaction (CISDQ) using the 6-31G** basis set and HF/6-31G** optimized geometries. All calculations were performed using the GAUSSIAN 90 program.[5]

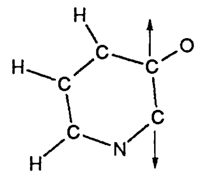
The selected geometrical parameters of the seven relevant stationary points determined with HF/6-31G** wavefunctions are displayed in Fig. 1. They include four minima, the reactant azafulvenone **8**, both intermediates oxocarbene **9** and isocyanovinyl ketene **10** and the final product cyanovinylketene **11**, and three transition structures TS **8/9**, TS **9/10** and TS **10/11** (**X**/**Y** denotes a transition structure connecting **X** and **Y**). Schematic potential energy profiles showing the molecular rearrangement are presented in Fig. 2.

Of particular interest are the carbene **9** and both TSs **8/9** and **9/10**. In **9**, the C'-2^2-N bond angle around the carbenic centre is quite opened, approaching linearity (144°), while the C^2–N distance is relatively short (1.19 Å). Apparently the molecular structure of **9** is similar to that of benzyne with a characteristic C≡N triple bond.

The TS **8/9** is confirmed by IRC calculations to be the TS connecting **8** to **9** rather than to the isocyanide **10**, in contrast with the situation in diazafulvenone.[3] The normal coordinates of the imaginary vibrational mode are displayed in **8/9a**. The largest components of the transition vector **8/9a** are situated on the O, C^1, C^2 and C^3 atoms and correspond essentially to the displacement of the C^1O group in **8** from the C^2 to C^3 atom accompanied by cleavage of the existing C^2–C^3 bond (1.86 Å in **8/9**) and a formation of the new C^1–C^3 bond (1.62 Å in **8/9**). During the C^1O displacement, C^1 remains bonded to C^2 and the C^1–C^2 distance is not particularly stretched. The transformation **8**→**9** is thus clearly a retro-Wolff rearrangement.



8/9a



9/10a

The C^1–C^2 distance in the transition structure **9/10** is in fact significantly stretched (1.75 Å). The identity of this TS is confirmed by transition vector **9/10a** in which the C^1–C^2 stretching is found to be the only important vibrational mode. Concerning the isocyanide **10** and cyanide **11** molecules and the TS **10/11** linking them, their geometrical features are quite similar to those of various substituted vinyl isocyanide–cyanide systems.[3,6]

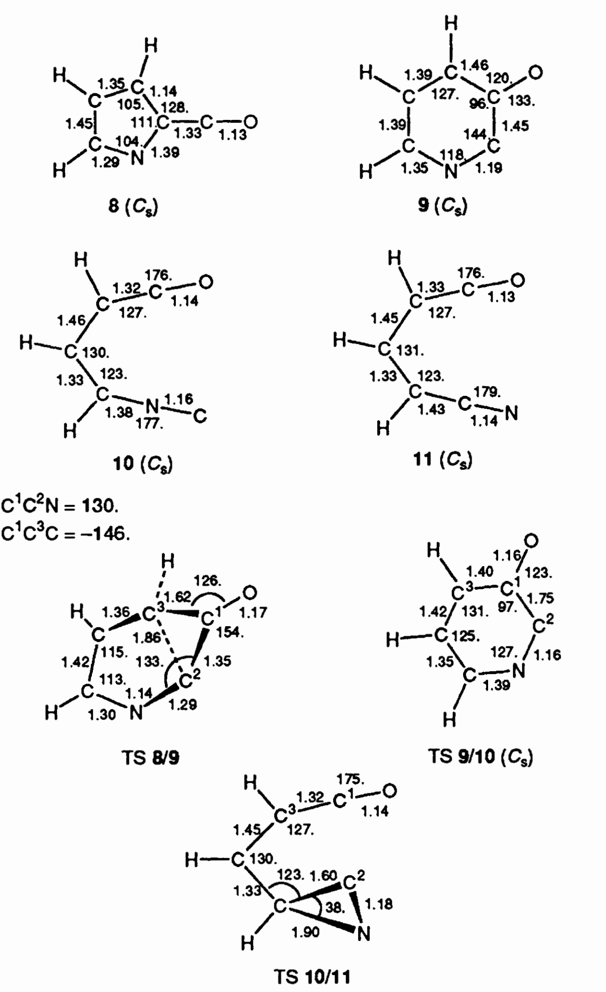


Fig. 1 Selected HF/6-31G** optimized geometries of stationary points on the azafulvenone→cyanovinyl ketene pathway. Bond lengths are given in Å and angles in degrees.

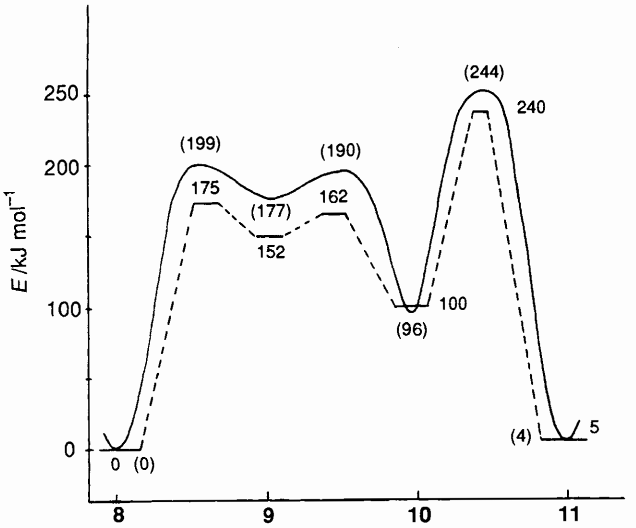


Fig. 2 Schematic energy diagram for the azafulvenone→cyanovinyl ketene transformation at two levels of theory: (——), CISDQ + ZPE; (- - -), MP4SDTQ + ZPE

The relative energy ordering between seven stationary points remains unchanged at all levels of theory considered. For the structures **9**, **8**/**9** and **9**/**10**, the CISDQ values, relative to **8**, are systematically larger than the MP4SDTQ values (about 25 kJ mol^{-1}) whereas for the structures **10**, **11** and **10**/**11**, both levels yield similar values. Unless otherwise noted, the values mentioned hereafter refer to the CISDQ/6-31G** + ZPE values. A number of points are noteworthy. (i) Azafulvenone **8** is surprisingly the most stable isomer, lying about 4 kJ mol^{-1} below cyanovinylketene **11**. Earlier calculations[3] at a similar level indicated that diazafulvenone **4** is about 140 kJ mol^{-1} higher in energy than cyanovinylisocyanate **7** (Scheme 2). (ii) A consequence of the high stability of azafulvenone **8**, compared with diazafulvenone **4**, is the emergence of the cyclic α-oxocarbene **9** as an equilibrium structure. At all levels of theory employed, **9** persists as a local minimum being about 177 kJ mol^{-1} above **8**. Nevertheless, the potential well associated with the oxocarbene **9** is not sufficiently deep; the barrier heights separating **9** from **8** and **10** are only 22 and 13 kJ mol^{-1}, respectively. The TS **8**/**9** is consistently found to be slightly higher in energy than the TS **9**/**10**. It is well known that a singlet carbene is better represented by two reference wavefunctions comprising both possible configurations of the carbenic lone pair. This implies that oxocarbene **9** could actually lie somewhat lower in energy than the position suggested in Fig. 2 by single reference calculations in this work. (iii) Isocyanide **10** is calculated to be 96 kJ mol^{-1} above azafulvenone **8** and 92 kJ mol^{-1} above its cyanide isomer **11**.[7] In spite of its high energy, isocyanide **10** is predicted to be separated from oxocarbene **9** and cyanide **11** by substantial energy barriers of 94 and 148 kJ mol^{-1}, respectively. More importantly, the TS **10**/**11** lies definitely much higher in energy than both TSs **8**/**9** and **9**/**10**. The isocyanide–cyanide rearrangement is no doubt the rate-determining step of the entire process. In this context, the isocyanide **10** could eventually be detectable following, *e.g.* a thermolysis at high temperature of azafulvenone **8**. For its part, the oxocarbene **9** can hardly be detectable due to its low kinetic and thermodynamic stability.

Our preliminary results, obtained from *ab initio* MO calculations, suggest that the retro-Wolff rearrangement converting azafulvenone **8** to cyanovinylketene **11** involves a singlet cyclic α-oxocarbene **9** as the reaction intermediate. The existence of a high energy α-oxocarbene equilibrium structure apparently arises from a peculiarly high stability of azafulvenone **8**. Because the isocyanide **10**–cyanide **11** conversion is by far the rate-determining step of the whole transformation, it is unlikely that the α-oxocarbene **9** could be detected upon pyrolysis of azafulvenone **8**.

Acknowledgements

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