Computational investigation of the mechanism of addition of singlet carbenes to bicyclobutanes

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Introduction

Single dichlorocarbene reacts with bicyclobutane to yield 1,1-dichloropenta-1,4-diene as well as C2 and C3 isomeric products. This reaction represents a substantial departure from other known reactions of carbenes. The analogous reaction of 1,2,3-trimethyldicyclotetras (TM122BCB) occurs with a pronounced regiochemical preference.

Computational methodology

- Gaussian software package (6-31G* for the gas phase and 6-31G* for the condensed system).
- BLYP-D3 6-31G* optimizations and frequencies, and IRC following.
- CBS-4 calculations (energies and thermodynamic quantities).
- QCISD 6-31G* optimizations and PES for unsubstituted system.
- QCISD 6-31G*//HF 6-31G* single point calculations for TM122BCB.
- QCISD 6-31G*//BLYP-D3 6-31G* potential energy surface for TM122BCB.

Results: concerted pathways

- Reaction pathways leading to 1,4-diene products were found.
- Pathways yielding (1,1) 1,1-diene products were also located, but had significantly higher barriers.
- For TM122BCB, seven distinct pathways were located. Six of these pathways, shown below, lead to five isomeric products (IRC reaction path following).

Mechanistic possibilities include a concerted pathway (VI) and a two-step mechanism involving a zwitterionic intermediate (VII). Intermediacy of a carbene (V) (Imine (VI) is unlikely, since the known product does not further react to yield pentadiene under the reaction conditions.

Mechanism 1: concerted

Mechanism 2: zwitterionic intermediate

Mechanism 3: intermediate bicyclobutane (unknown product)

The regiochemical preference of the reaction with TM122BCB has been taken as evidence against mechanism (VII). The intermediacy zwitterion would be expected to yield a mixture of products, with the mixture favoring the more substituted diene — the isomer that is not observed experimentally.

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Fig. 3. Proposed mechanisms for formation of 1,1-dichloro-1,4-pentadiene.

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Intermediates.

- Calculations suggest that no intermediate is involved for the parent system (B3LYP). Both the gas-phase and in the condensed phase of a solvent (PCD, cyclohexane), the energy of a zwitterionic intermediate results in collapse to products or starting materials.
- A shallow minimum corresponding to the zwitterion does exist for the same system (TM122BCB), in which it is without the positive charge.

Potential energy surfaces

A potential energy surface might shed additional light on this reaction. For instance, the regiochemistry might be driven in part by dynamic effects, since the energy barriers are very low, a full PES might help to elucidate such effects. Below, various results are defined, and potential energy surfaces in terms of these variables are illustrated for CC1, adding to TM122BCB.

Fig. 4. Six isomeric concerted pathways.

The three pathways that are calculated to be lowest in energy (3, 2, and I) lead to the two scenario products (1,1-dichloro-3,4-trimethylpentane-1,4-diene and 1,1-dichloro-5,6-dimethylhexane-1,4-diene). Of these products, only the former is observed experimentally.

- The calculations are in agreement that the barrier for direct formation of 1,1-dichloro-3,4-trimethylpentane-1,4-diene (I) is lower than the barrier for direct formation of 1,1-dichloro-5,6-dimethylhexane-1,4-diene (II).

However, the energy difference between these pathways is only about 1.0 kcal/mole or less, depending on the level of calculation — not enough to account for the experimental observation of extreme selectivity.

Furthermore, by a small margin, the very lowest barrier appears to be the one leading to the zwitterionic intermediate — which is expected to proceed preferentially to the unsubstituted (unknown substituted) product.

Table 1. Gas-phase transition-state energies relative to reactants.

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Gas-phase Energy (kcal/mol)</th>
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<tbody>
<tr>
<td>I</td>
<td>1.9</td>
</tr>
<tr>
<td>II</td>
<td>2.2</td>
</tr>
<tr>
<td>III</td>
<td>2.4</td>
</tr>
<tr>
<td>IV</td>
<td>2.6</td>
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<tr>
<td>V</td>
<td>2.8</td>
</tr>
<tr>
<td>VI</td>
<td>3.0</td>
</tr>
<tr>
<td>VII</td>
<td>3.2</td>
</tr>
<tr>
<td>VIII</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Fig. 5. 2-D potential energy surfaces for addition of CC1 to TM122BCB.

Literature cited


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