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The Use of a Cyclopropylcarbinyl Radical Rearrangement as a Singlet Diradical Probe
Phyllis A. Leber, Franklin & Marshall College, Lancaster PA 17604-3003

Rate constants for overall decomposition (k_d) for a series of *exo*-7-alkylbicyclo[3.2.0]hept-2-enes are relatively invariant (Table 1). For the alkyl substituents ethyl, propyl, butyl, isopropyl, and *t*-butyl, the ratio of the rate constant for [1,3] sigmatropic rearrangement to the rate constant for fragmentation, k_{13}/k_f , is significantly lower than $k_{13}/k_f = 150$ observed for *exo*-7-methylbicyclo[3.2.0]hept-2-ene.

Table 1. Experimental Rate Constants and Exit Channels for *exo*-7-Alkylbicyclo[3.2.0]hept-2-enes @ 275 °C

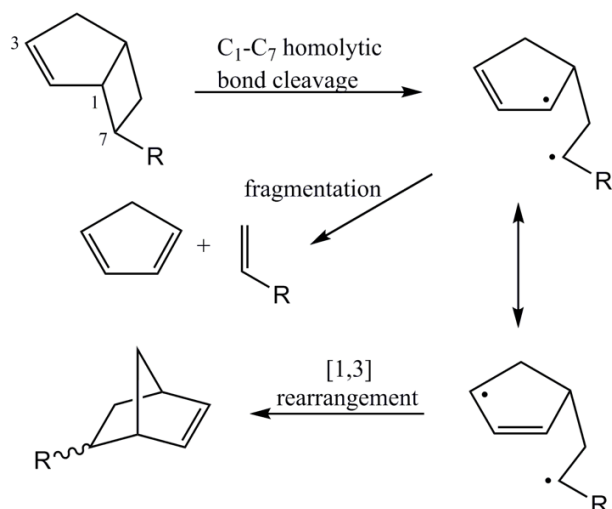
| R- | k_d @ 275 °C | k_{rel} | k_{13}/k_f | % [1,3] | % epim | % frag |
|---------------|--|-----------|--------------|---------|--------|--------|
| Pr- | $2.0(\pm 0.1) \times 10^{-5} \text{ s}^{-1}$ | 1.8 | 3.2 | 76 | 0 | 24 |
| Bu- | $1.9(\pm 0.1) \times 10^{-5} \text{ s}^{-1}$ | 1.7 | 1.8 | 64 | 0 | 36 |
| Et- | $1.6(\pm 0.1) \times 10^{-5} \text{ s}^{-1}$ | 1.5 | 5.4 | 84 | 0 | 16 |
| Me- | $1.5(\pm 0.2) \times 10^{-5} \text{ s}^{-1}$ | 1.4 | 150 | 95 | 4 | 0.6 |
| <i>t</i> -Bu- | $1.4(\pm 0.1) \times 10^{-5} \text{ s}^{-1}$ | 1.3 | 2.9 | 74 | 0 | 26 |
| <i>i</i> -Pr- | $1.1(\pm 0.1) \times 10^{-5} \text{ s}^{-1}$ | 1.0 | 1.9 | 65 | 0 | 35 |

The rates of retro Diels-Alder reactions for all *exo*-5-alkylnorbornenes were comparable as were those for the *endo*-5-alkylnorbornenes. In all cases, the reactivity of the *endo*-5-alkylnorbornenes exceeded that of the corresponding *exo*-5-alkylnorbornenes by a factor greater than 2 (Table 2).

Table 2. Experimental Rates of Retro Diels-Alder Reactions for *exo*- (k_{RDA}) and *endo*- (k'_{RDA})-5-Alkylnorbornenes @ 275 °C

| R- | k_{RDA} | k'_{RDA} | k'_{RDA}/k_{RDA} |
|---------------|--|--|--------------------|
| Et- | $2.5(\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ | $5.5(\pm 0.3) \times 10^{-4} \text{ s}^{-1}$ | 2.2 |
| Me- | $2.0(\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ | $4.7(\pm 0.2) \times 10^{-4} \text{ s}^{-1}$ | 2.3 |
| Pr- | $2.5(\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ | $6.0(\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ | 2.4 |
| <i>i</i> -Pr- | $1.7(\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ | $4.6(\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ | 2.7 |
| Bu- | $1.8(\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ | $5.0(\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ | 2.8 |
| <i>t</i> -Bu- | $9.4(\pm 0.8) \times 10^{-5} \text{ s}^{-1}$ | $6.1(\pm 0.2) \times 10^{-4} \text{ s}^{-1}$ | 6.5 |

The rate constants for the overall rate of decomposition (k_d) for a series of *exo*-7-alkylbicyclo[3.2.0]hept-2-enes are listed in Table 1 from the most reactive *exo*-7-propylbicyclo[3.2.0]hept-2-ene to the least reactive *exo*-7-isopropylbicyclo[3.2.0]hept-2-ene. Given that all of the *exo*-7-alkylbicyclo[3.2.0]hept-2-enes afford a secondary alkyl-allyl diradical upon homolytic cleavage of the C1-C7 bond (Scheme 1), it is not surprising that the k_d values for the most reactive entry is less than a factor of two greater than the least reactive entry (Table 1).



Scheme 1. Bifurcation of 2° Alkyl-Allyl Diradical between Rearrangement and Fragmentation

The larger the alkyl mass, the greater the extent of fragmentation at the expense of [1,3] rearrangement. The absence of a global trend related to how the resultant non-equilibrated singlet diradicals bifurcate between rearrangement and fragmentation (Scheme 1) suggests multiple operative factors once the initial transition structure is reached and the intermediate begins to sample the available conformational space. Regardless of the size or mass of the alkyl group, the [1,3] rearrangement process dominates fragmentation by a factor of ca. 2:1 or greater, so that $k_{13} > k_f$ for all alkyl substituents.

Regardless of the size and mass of the alkyl group, the stereoselectivity of the [1,3] carbon migration appears to be quite stable at 80-89% suprafacial inversion (*si*), as seen in Table 3, an observation consistent with conservation of angular momentum but not conservation of orbital symmetry. This global result comports with the phenomenon of “dynamic matching” espoused by Carpenter and collaborators for [1,3] sigmatropic rearrangements in general.

Table 3. Stereoselectivity of [1,3] Carbon Shifts in *exo*-7-Alkylbicyclo[3.2.0]hept-2-enes

| R- | k_{si} | k_{sr} | si/sr | % <i>si</i> | % <i>sr</i> |
|---------------|-------------------------------------|-------------------------------------|---------|-------------|-------------|
| Et- | $1.2 \times 10^{-5} \text{ s}^{-1}$ | $1.5 \times 10^{-6} \text{ s}^{-1}$ | 8.0 | 89 | 11 |
| <i>i</i> -Pr- | $6.5 \times 10^{-6} \text{ s}^{-1}$ | $8.1 \times 10^{-7} \text{ s}^{-1}$ | 8.0 | 89 | 11 |
| Me- | $1.2 \times 10^{-5} \text{ s}^{-1}$ | $1.9 \times 10^{-6} \text{ s}^{-1}$ | 6.8 | 87 | 13 |
| Pr- | $1.3 \times 10^{-5} \text{ s}^{-1}$ | $2.2 \times 10^{-6} \text{ s}^{-1}$ | 5.9 | 86 | 14 |
| Bu- | $9.7 \times 10^{-6} \text{ s}^{-1}$ | $1.8 \times 10^{-6} \text{ s}^{-1}$ | 5.4 | 84 | 16 |
| <i>t</i> -Bu- | $8.3 \times 10^{-6} \text{ s}^{-1}$ | $2.1 \times 10^{-6} \text{ s}^{-1}$ | 4.0 | 80 | 20 |

This project has resulted in a new collaboration with Professor Alex Davis, a computational chemist. Katie Kidder was able to obtain undergraduate research experience in both experimental and computational chemistry and is now pursuing a Ph.D. in computational chemistry at Penn State University.