

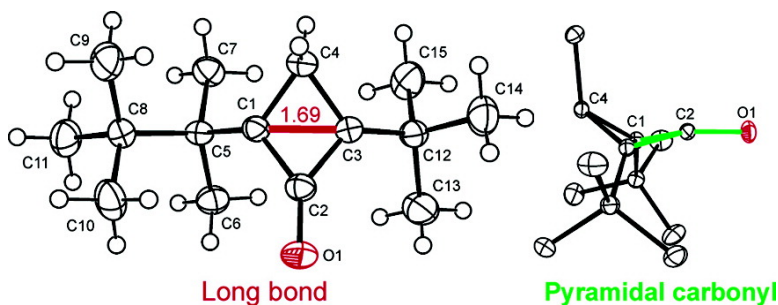
Communication

Preparation and Crystal Structure of Two Bicyclo[1.1.0]butan-2-ones: A Hybrid Oxyallyl–Cyclopropanone Motif

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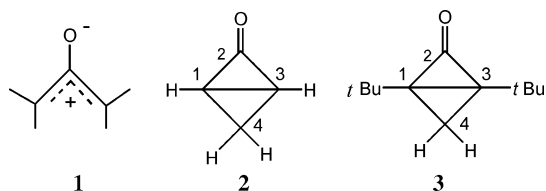
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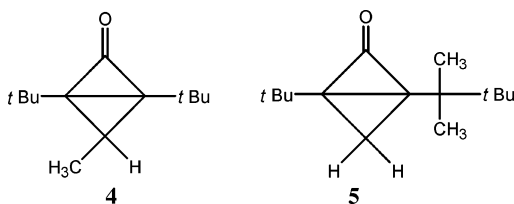
Oxyallyls **1** are proposed intermediates in a number of organic reactions.¹ However, only one report on the direct observation of an oxyallyl has appeared, involving low-temperature matrix photolysis generation and UV–visible detection.² However, we show in this communication that bicyclobutanones have a hybrid structure with some oxyallyl “character”, and in particular, that some bicyclobutanones can now be isolated as crystalline solids suitable for single-crystal X-ray diffraction study.

The preparation of bicyclo[1.1.0]butan-2-one (C_4H_4O) **2** has not yet been reported, but several 1,3-disubstituted analogues have previously been characterized in situ in this laboratory by low-temperature NMR methods.³ The most thermally stable of these was compound **3** and a *tert*-amyl analogue.



Attempts were made to obtain X-ray quality crystals, but a facile dimerization reaction forced one to work at quite low temperatures, and the solid formed from solutions under these conditions did not diffract.⁴ Two possible solutions to the above problems were to create a sterically modified **3** which might be less susceptible to dimerization or to create a less symmetrical molecule using substituents of different sizes.⁵

We now report the synthesis of two successful modifications, structures **4** and **5**, which have produced crystals suitable for X-ray study. Both ketones were fragile compounds to handle, but no identifiable dimerization products were noted. Both **4** and **5** were prepared from the corresponding 1,3-dibromocyclobutan-2-one precursors using a previously reported low-temperature method to debrominatively couple the 1–3 carbons.³ Crystallizations were carried out by low-temperature slow vacuum evaporation of solvent, THF for **4**, pentane for **5**.



Both **4** and **5** possess a very similar bicyclobutanone core structure, as shown in the ORTEP drawings in Figures 1 and 2. One advantage of having two structures available is that it helps suggest that the core structure is an inherent property of the system and not much related to the size and number of substituents on

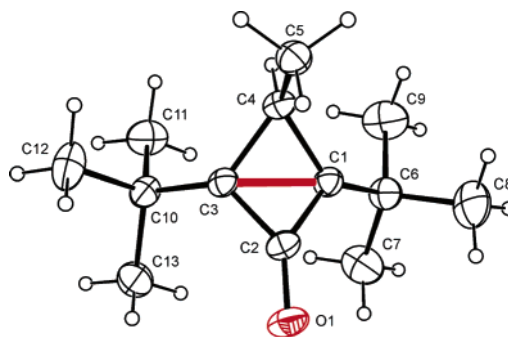


Figure 1. ORTEP plot of **4**.

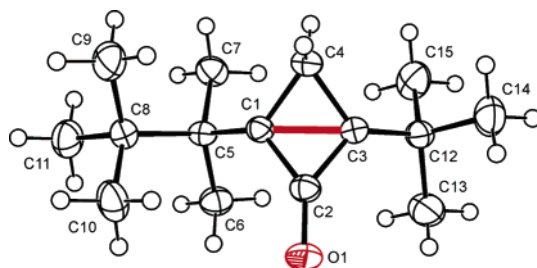


Figure 2. ORTEP plot of **5**.

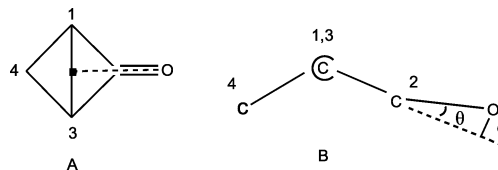


Figure 3. Bond angle θ in (B) is the angle given by O–C2 with the extension of the C1–C3 bisector point in (A) and C2.

C1, 3, and 4. Previously reported MO calculations also support this conclusion.⁶

The remarkable geometric features in **4** and **5** are an extremely long C1–C3 bond, 1.691(5) and 1.692(2) Å, respectively, a distinctly pyramidal ketone functionality as defined by the angle θ in Figure 3, 12.5 and 12.2°, respectively, or 0.265 and 0.26 Å out of the plane of the three carbons as defined by “d” in Figure 3B. To put these numbers in perspective, one notes that the planar carbonyl is among the most rigid functional groups in organic chemistry, and out-of-plane pyramidalizations of only 0.074 Å have been noted as unusually large.⁷

Finally, there are short C1–C2, C2–C3 bonds, 1.428(5), 1.437(5) Å, and 1.434(2), 1.441(2) Å, respectively. These numbers can be compared to reported general average values of about 1.51 Å for carbonyl– C_α bonds;⁸ however, for the few reported data sets available for cyclopropanones, shorter values are found, 1.469⁹ and 1.47 Å.¹⁰ A consequence of the long C1–C3 bond and these short C1–C2, C2–C3 bonds is a widened 72.4 and 72.1° angle at the carbonyl center.

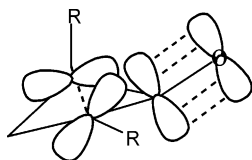


Figure 4. Schematic representation of the proposed orbital overlaps in bicyclobutanones.

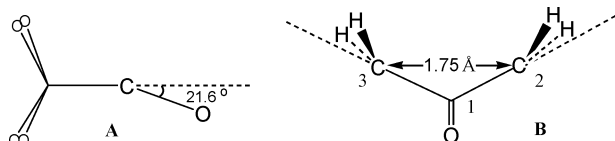


Figure 5. Two schematic views of a reaction coordinate along the potential energy surface for the cyclization of oxyallyl to cyclopropanone where the carbonyl pyramidal distortion is at a maximum (A). At this point, as sketched in (B), the dihedral angle H–H–C2–C1 (H–H–C3–C1) is 161.0°.

These unusual structural parameters can be rationalized using the simple bonding model shown in Figure 4.³ The long C1–C3 bond is visualized as a mainly p_z – p_z (σ – π)-type overlap. The carbonyl pyramidalization helps create a better (σ – π) overlap between C2 and C1–C3, and the short carbonyl–C $_{\alpha}$ bond distances are then a natural consequence of the C2 overlaps (some double bond “character” in the C1–C2, C2–C3 bonds).

This qualitative picture and the title suggestion of a hybrid oxyallyl–cyclopropanone structure for **4** and **5** can be given additional credence using a simple computational approach. This model (B3LYP/6-31G*) involves coordinate following of the disrotatory cyclization of parent oxyallyl to cyclopropanone.¹¹ As one proceeds downhill in energy, the planar oxyallyl evolves a distinctly pyramidal carbonyl which reaches a maximum bend of 21.6° (defined in the same way as in Figure 3), and where the forming “bond” is still 1.75 Å. In the end, of course, the carbonyl (cyclopropanone) is again planar (C2–C3 bond 1.57 Å). Two views of this intermediate structure (Figure 5) illustrate the carbonyl distortion (5A) and the still mainly p-orbital character of the forming 2–3 bond in cyclopropanone (5B). During this process, the carbonyl and carbonyl–C $_{\alpha}$ bonds do not change much. The analogy between this Figure 5 structure and real structures **4** and **5** is only approximate because of ring constraints in the latter, but it does illustrate that carbonyl pyramidalization is associated with an intermediate oxyallyl–cyclopropanone structure.¹²

The bicyclo[1.1.0]butane skeleton is noted for the presence of a relatively short transannular bond, mostly ca. 1.51 Å, as shown in a number of X-ray structure determinations.¹⁴ However, this distance is strongly correlated with the interflap angle of the two cyclopropane planes and becomes shorter as this angle decreases.¹⁵ The interflap angles in the bicyclobutanones **4** and **5** are 157.7 and 157.9°, respectively, much larger than those reported for the hydrocarbon skeleton, which have angles of 110–130° in most cases. With the larger interflap angles in **4** and **5**, one would expect longer transannular bonds, but even so, the bicyclobutane hydrocarbon and ketone have remarkably dissimilar transannular bond lengths.¹⁶

In conclusion, we have presented here the first X-ray diffraction structures of the bicyclobutanone ring system, and we show that several of the unique bonding features can be attributed to a hybrid oxyallyl–cyclopropanone structural motif.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Crystallographic data for **4** and **5**, experimental preparation details and NMR data for **4** and **5** and for the precursors of these, and coordinates for the MO calculations reported in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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