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LETTERS

Reaction of Dicarboethoxycarbene with 1,3-Cyclooctadiene.[1] Entry to the *trans*-Bicyclo[6.1.0]non-*cis*-2-ene System.

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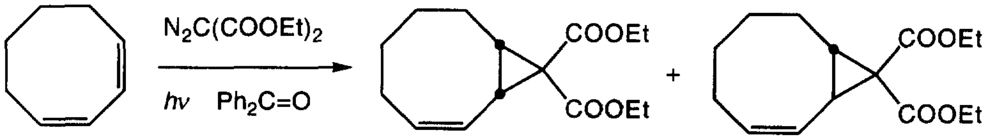
***Abstract*:** The benzophenone-photosensitized decomposition of ethyl diazomalonate in 1,3-cyclooctadiene led to *trans*-bicyclo[6.1.0]non-*cis*-2-ene, a new strained ring system. The function of the photosensitizer is to convert *Z,Z*-1,3-cyclooctadiene into the *E,Z*-isomer.

In the preceding Letter we showed that triplet dicarboethoxycarbene (DCC) added to cyclooctatetraene (COT) in both 1,2- and 1,4-fashion. By contrast, the photosensitized addition of DCC to 1,3-cyclooctadiene (COD) did not give 1,4-product, but only the conventional cyclopropane, **1**, and another compound, here shown to be **2**. For example, irradiation of a degassed solution of 158 mg of diethyl diazomalonate in 0.4 g COD and 16 mL pentane with 0.4 g added benzophenone led to 8% **1** and 38% **2**, which could be isolated by column chromatography on silica gel with 9:1 pentane:ether as eluent, in 20% yield.



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trans-Bicyclo[6.1.0]nonane is known,[2] as are derivatives,[3] including *trans*-bicyclo[6.1.0]nona-2,4,6-triene,[4] but, to our knowledge, **2** has not appeared. The structure of **2** was first suspected from its ^{1}H NMR spectrum,[5] but was definitively assigned by X-ray diffraction analysis of a single crystal of the related diacid **3**, produced by hydrolysis of **2**.[6] Diacid **3** lies on a crystallographic two-fold axis in the solid state, which requires that the molecule be disordered. This type of disorder is not unusual and was easily modelled and refined.[7] The cyclopropane ring is normal, with the two ring bonds to the carbon atom bonded to the two carboxylic acid groups at 1.526 (2) and 1.526 (2) Å, and the "back" ring bond at 1.470 (4) Å. These bonds are 1.531 (3), 1.538 (3), and 1.462 (3) Å in cyclopropane-1,1-dicarboxylic acid itself.[8] No substantial distortions were observed, and there is no evidence for significant slippage or twist in the cyclopropane bonds.[9] A figure comparing the X-ray structure to that obtained by an ab initio calculation at the HF/6-31G* level is shown below.[10] The largest differences between the experimental and calculated structures - chiefly bond angles and torsion angles near the cyclopropane - are likely manifestations of the crystallographic disorder.

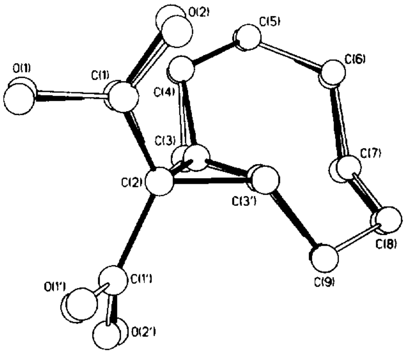
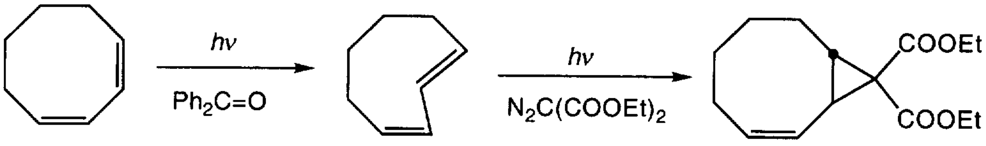


Figure 1. Superposition of the X-ray structure of **3** (solid bonds) and the HF/6-31G* geometry.

Chains of hydrogen-bonded diacid **3** molecules running parallel to the crystallographic *c*-axis are observed, with both carboxylic acid hydrogen atoms participating in intermolecular hydrogen bonding. In contrast, only one of the two acidic hydrogens in cyclopropane-1,1-dicarboxylic acid is involved in intermolecular hydrogen bonding. These contrasting hydrogen bonding patterns may be designated as **C(6) [R^2(8)]** and **C(6)**, respectively.[11]

Compound **2** is not formed from photolysis of **1**, nor is it the product of addition of the triplet carbene to the *Z,Z*-diene. Molecular mechanics calculations (MMFF)[12] and semiempirical MO calculations (AM1)[13] find that compound **1** is more stable than compound **2** by 3.1 kcal/mol and 3.7 kcal/mol respectively; thus the more highly strained compound **2** is formed preferentially in the photolysis.

Photolysis of COD and related cycloheptyl systems, is known to produce the *E,Z*-isomer from the much more stable *Z,Z*-isomer in reasonable amounts.[14] We find that benzophenone-photosenstized irradiation of *Z,Z*-COD for 14 h leads to about 10% of the *E,Z*-isomer (isolated yield). Direct irradiation of ethyl diazomalonate in the *E,Z*-diene led to **2** and minor amounts of isomeric compounds, but not **1**. Thus, it appears that the function of the sensitizer is to produce substantial amounts of the *E,Z*-diene. The singlet carbene then adds in a straightforward 1,2-fashion, "selecting" the more reactive trans double bond in the otherwise routine addition reaction. Indeed the selectivity must be very great, as there cannot be large amounts of the *E,Z*-diene present because of the slow approach of the starting material to the photostationary state. Although the addition may be routine, the results are not; this route should allow easy entry to this new strained ring system.



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1. This work was supported by the National Science Foundation through Grants CHE-9702823 (MJ) and CHE-9707958 (RAP).

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5. ^{1}H NMR (CDCl$_3$): **1**: δ 5.78 (m, 1H), 5.62 (m, 1H, J = 11.5 Hz), 4.18 (dq, 4H), 2.35 (m, 2H), 2.04 (m, 1H), 2.00 (m, 1H), 1.94 (m, 2H), 1.72, (m, 1H), 1.64 (m, 1H), 1.44 (m, 1H), 1.28 (dt, 6H), 1.14 (m, 1H). **2**: δ 5.8 (m, 1H), 5.6 (m, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 2,58, (m, 1H), 2.30 (m, 1H), 2.15 (m, 1H), 2.06, m, 1H), 1.98 (m, 1H), 1.94 (m, 1H), 1.72 (m, 1H), 1.64 (m, 1H), 1.54 (m, 1H), 1.08 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H).
^{13}C NMR (CDCl$_3$): **1**: δ 14.3, 14.4, 24.3, 25.1, 29.9, 30.1, 30.2, 32.9, 36.4, 61.1, 61.8, 121.0, 136.4, 168.9, 171.1. **2**: δ 14.4, 14.5, 24.1, 26.5, 31.3, 32.2, 32.6, 34.5, 39.6, 61.5, 61.5, 123.2, 137.9, 168.3, 168.7.

6. Crystal data: $C_{11}H_{14}O_4$: monoclinic, space group *C2/c*; a = 9.516 (2) Å, b = 9.616 (2) Å, c = 11.647 (2) Å, β = 90.99 (2), V = 1065.6 (3) Å^3, Z = 4, D_{calcd} = 1.310 gcm^{-1}; $R(F)$ = 0.041, $wR(F^2)$ = 0.088, and S = 1.06 for 639 reflections with $I > 2\sigma(I)$; $R(F)$ = 0.088, $wR(F^2)$ = 0.099 and S = 0.83 for 1236 unique relections and 99 variables.

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