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Selective Formation of cis, trans-1,4-Cyclononadiene on Photochemical Decarbonylation of exo-Tricyclo[4.3.1.$0^{7,9}$]decan-10-one

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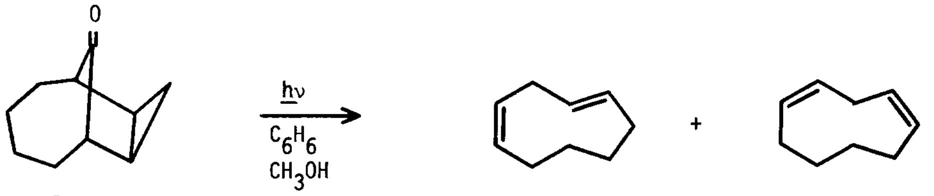
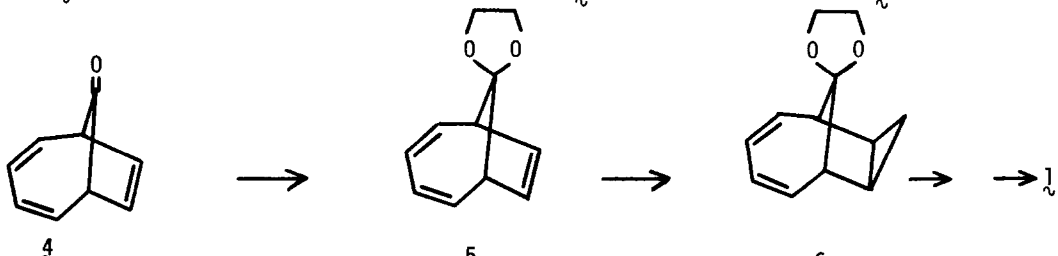
In the course of other work we have prepared the tricyclic ketone 1. Photolysis of this compound led to decarbonylation and opening of the cyclopropane ring to form a mixture of cyclononadienes 2 and 3 in which the previously unknown cis, trans-diene 2 predominates (2.3:1, eq. 1). The selective formation of this less stable product was initially surprising, and we offer here an explanation based on stereoelectronic control in fragmentation of an intermediate cyclopropylcarbinyl radical to the isomeric trans-homoallylic species.

The tricyclodecanone 1 was prepared from the readily available trienone 4.[1] Careful ketalization of 4 with glycol in the presence of a limited amount of p-toluenesulfonic acid furnished 5 (76%). Long reaction times or increased amount of catalyst led to formation of the ketal of 1-indanone through a known[1] acid-catalyzed process. Simmons-Smith reaction[2] of 5 provided the exo cyclopropane 6 as the major product (35%), and hydrogenation of 6 followed by deketalization gave ketone 1 (70% from 6). Structural assignments for these compounds are supported by analytical and spectroscopic data.[3] In particular, the



1 2 3 (1)



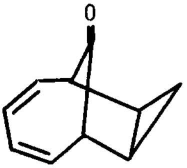
4 5 6

site of cyclopropanation of **5** is clear from both UV and NMR spectra, and the exo stereochemistry of the cyclopropane ring is indicated by deshielding of the endo geminal cyclopropane hydrogen atom in **6**.[4] Similarly, in lanthanide-shifted [Eu(fod)$_3$] NMR spectra of **7**,[3] which is available on deketalization of **6**, this endo proton is shifted rapidly downfield. In both **6** and **7** the appropriate signal can be independently assigned as the endo geminal proton by its smaller vicinal coupling constant (4 Hz) with the bridgehead cyclopropyl hydrogens. This exo stereochemistry of the cyclopropane ring is also consistent with the thermal stability of **1**, which is recovered (87%) unchanged after 8 h at ∿250°; this is expected for the exo compound, but the corresponding endo cyclopropyl ketone should decarbonylate readily under much milder conditions.[5,6]

Ketone **1** was irradiated in benzene containing 3% methanol through Pyrex (λ >2800 Å) using a 450-W Hanovia lamp.[7] Products **2** and **3** were separated and purified by gas chromatography. Diene **3** was identified by direct comparison with an authentic sample prepared by thermolysis of <u>cis</u>, <u>cis</u>-bicyclo[6.1.0]non-2-ene.[8] The new hydrocarbon **2** was identified by its spectroscopic properties, which require both bisallylic and allylic hydrogen atoms along with both a cis and trans disubstituted double bond.[3] Data on the time course of the reaction are presented in the table, and these indicate that both **2** and **3** are primary products of the photolysis.[9] This conclusion is buttressed by the observation that exposure of **2** to the reaction conditions led to only slow isomerization to **3** (**2**:**3** = 9.3:1 after 25 h). Added piperylene quenched the formation of both **2** and **3**.

Products from Photolysis of **1**

Time (h)	Conversion (%)	Yields (%) **2**	Yields (%) **3**	Yields (%) Total	**2**:**3**
1.01	≤5	69 (rel.)	31 (rel.)	-	2.2
2.00	8	50	24	74	2.1
6.00	21	61	24	85	2.5
11.00	39	52	22	74	2.4
19.52	54	48	19	67	2.5
25.00	61	50	21	71	2.4
29.00	68	58	26	84	2.2
44.00	81	56	25	81	2.2



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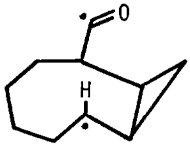

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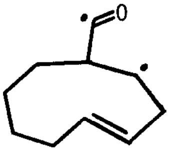

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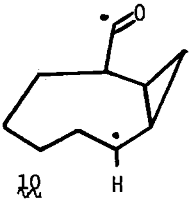

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Previous studies on the equilibration of 1,2-, 1,3- 1,4-, and 1,5-cyclononadienes[10a] in which diene **3** but not **2** was observed, as well as examination of molecular models, indicate that the *cis*, *trans*-diene **2** is thermodynamically less stable than *cis*, *cis*-diene **3**. In the related monoalkenes it is known from heats of hydrogenation that *cis*-cyclononene is more stable ($\Delta\Delta H$) than the trans isomer by 2.9 kcal/mol.[10b] In addition we have found that irradiation of **2** in acetone leads to its complete destruction with formation of **3** as the only monomeric product. These observations suggest that photolysis of **1** does not proceed by way of long-lived biradical intermediates, and that some detailed explanation for the selective formation of **2** is required. It also appears inappropriate that the results be ascribed to a combination of linear and non-linear (and therefore both conrotatory and disrotatory) concerted pathways,[11] such as have been invoked in the decarbonylation of substituted 3-cyclopenten-1-ones,[12] since the exo stereochemistry of the cyclopropane ring is unfavorable for the occurrence of such processes.[6] In this connection the thermal stability of **1** mentioned above is noteworthy.

We suggest that although the structural constraints of **1** disfavor concerted processes, they permit a biradical mechanism to operate with selective formation of the trans double bond of **2**. Initial α-cleavage in **1** should lead to the acyl cyclopropylcarbinyl biradical **8** in which the initial geometry, as shown, is quite favorable for stereoelectronically controlled fragmentation[13] with formation of the *trans*-homoallyl acyl biradical **9**; decarbonylation of **9** would then give **2** directly. Rotation about carbon-carbon bonds in **8** to provide the geometry necessary (see **10**) for fragmentation to the *cis*-homoallyl system that leads to **3** should be hindered by transannular interactions in the eight-membered ring, thus permitting preferential, kinetically controlled cleavage to **9** and formation of the observed major product **2**.[14,15]

Footnotes and References

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(3) Spectroscopic data (in CCl_4 except as noted) for **1**, **2**, **5**, **6**, **7**, and the ethylene ketal of **1** follow. These new compounds all gave satisfactory elemental analyses ($\pm \leq 0.23\%$) for carbon and hydrogen. For **1**: IR 3060 (w), 1745 (s), 1025 (m), 1010 (w) cm^{-1}; NMR δ -0.058 (m, 1 H), 0.58-1.00 (m, 1 H), 1.00-2.11 (m, 10 H), 2.33 (m, 2 H). For **2**: IR 3010 (s), 1665 (w), 1625 (w), 975 (s), 700 (s) cm^{-1}; IR (CS_2) 785 (m), 735 (m) cm^{-1}; NMR δ 0.67-3.27 with major absorptions at 1.08, 1.37, 1.78, 1.92, 2.27, and 2.77 (m, 10 H), 5.52 (m, 4 H). For **5**: IR 3050 (m), 3020 (s), 2930 (s), 2875

(s), 845 (s), 665 (s) cm^{-1}; NMR δ 2.72 (m, 2 H), 3.83 (s, 4 H), 5.23 (m, 2 H), 5.72 (m, 4 H). For **6**: 3025 (m), 680 (s) cm^{-1}; NMR δ -0.25 (dt, *J* = 5.5, 8 Hz, 1 H), 0.70 (dt, *J* = 5.5, 4 Hz, 1 H), 1.45 (dd, *J* = 8, 4 Hz, 2 H), 2.02 (m, 2 H), 3.78 (m, 4 H), 5.57 (m, 4 H); UV (95% C_2H_5OH) λ_{max} (ε) 287 (1565), 276 (3100), 266 (3330), 260 sh (2790) nm. For **7**: 3065 (w), 1755 (s), 1595 (w) cm^{-1}; NMR δ -0.32 (dt, *J* = 6.5, 4 Hz, 1 H), 0.28 (dt, *J* = 6.5, 7.5 Hz, 1 H), 1.85 (dd, *J* = 7.5, 4 Hz, 2 H), 2.62 (m, 2 H), 5.63 (m, 4 H); UV (95% C_2H_5OH) λ_{max} (ε) 318 (550), 277 (3795), 266 (3975), 257 (2595) nm. For ketal of **1**: IR 3005 (m), 1115 (s), 1080 (m) cm^{-1}; NMR δ 0.37 (m, 1 H), 0.90 (m, 3 H), 1.10-2.13 (m, 10 H), 3.73 (s, 4 H).

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(9) Yields were determined by gas chromatography on a 15 ft x 0.25 in. column of 25% DEGS on Chromosorb P 60/80, using response factors and internal standards (*o*-methylacetophenone for **1** and *p*-xylene for **2** and **3**). For the first entry in the table (≤5% conversion) yields are relative; for later points they are based on converted **1**.

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(14) For a related example of unusual product specificity due to restricted rotation in a twelve-membered ring biradical intermediate formed on Type II hydrogen abstraction see J. J. Hemperly, S. Wolff, and W. C. Agosta, *J. Org. Chem*., **40**, 3315 (1975).

(15) This investigation was supported by the National Science Foundation through grant No. CHE74-21436.