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PHOTOINDUCED ADDITION OF NUCLEOPHILES TO BICYCLO[2.2.1]HEPTA-2,5-DIENE

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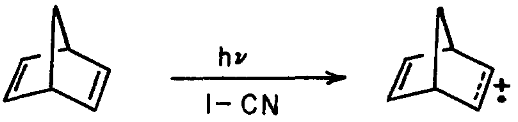
Summary: The 1-cyanonaphthalene photosensitized addition of water and methanol to the cation-radical of bicyclo[2.2.1]hepta-2,5-diene is described.

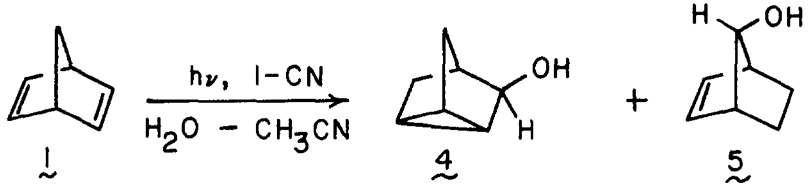
Recently, we demonstrated that nucleophiles could be added across strained carbon-carbon sigma bonds in photosensitized reactions which are readily interpreted in terms of the initial transfer of an electron from the strained sigma bond to the excited state of photosensitizers such as 1-cyanonaphthalene (1-CN).[2] In principle, electron transfer should occur from any species that has an $E_{\frac{1}{2}}$ for oxidation which is less than the $E_{\frac{1}{2}}$ for reduction of the excited state of the photosensitizer.[3] Bicyclo[2.2.1]hepta-2,5-diene (1), which has an $E_{\frac{1}{2}}$ for oxidation of 1.56 V,[4] should be susceptible to electron transfer to the excited state of 1-CN, which has an $E_{\frac{1}{2}}$ for reduction of 1.82 V.[5] Recently, Roth and Jones have demonstrated that 1 can be photochemically converted to the cation radical, 2. They have also shown that 2 and 3 are discrete species. We now wish to report the synthetically useful trapping of 2 by the nucleophiles, water and methanol. This represents an unusual example of the photoinduced addition of a nucleophile to a nonconjugated olefin.[6-8]



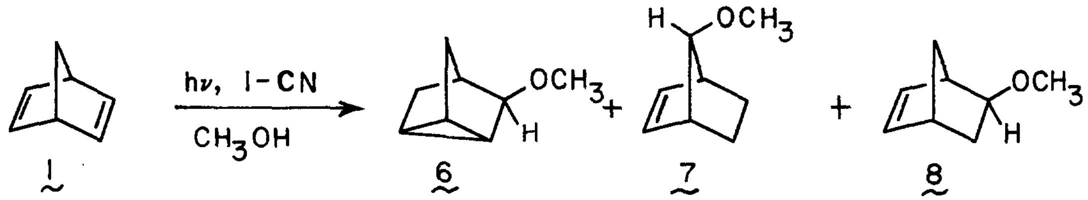
1 2

3

Irradiation of a solution of 1 and 1-CN (45 mol %) in 1:3 v/v water:acetonitrile for 12 h with 300 nm light (Rayonet reactor) gave 56% of 4 and 39% of 5. Similarly, irradiation of a solution of 1 (0.28 mmol) and 1-CN (0.13 mmol) in 0.5 g of methanol for 48 h with a Vycor filtered 450 Watt medium pressure Hanovia mercury vapor lamp gave 33% of 6, 33% of 7, and 10% of 8.[9] The structures of 4,[10] 5,[11] 6,[12] and 8[12] were established through comparison with authentic samples which were synthesized according to the literature procedures.[10-12] The structure of **7** was established through comparison with an authentic sample



which was prepared by the reduction of 7,7-dimethoxybicyclo[2.2.1]hept-2-ene[13] with triethylsilane - trimethylsilyl triflate.[14,15]



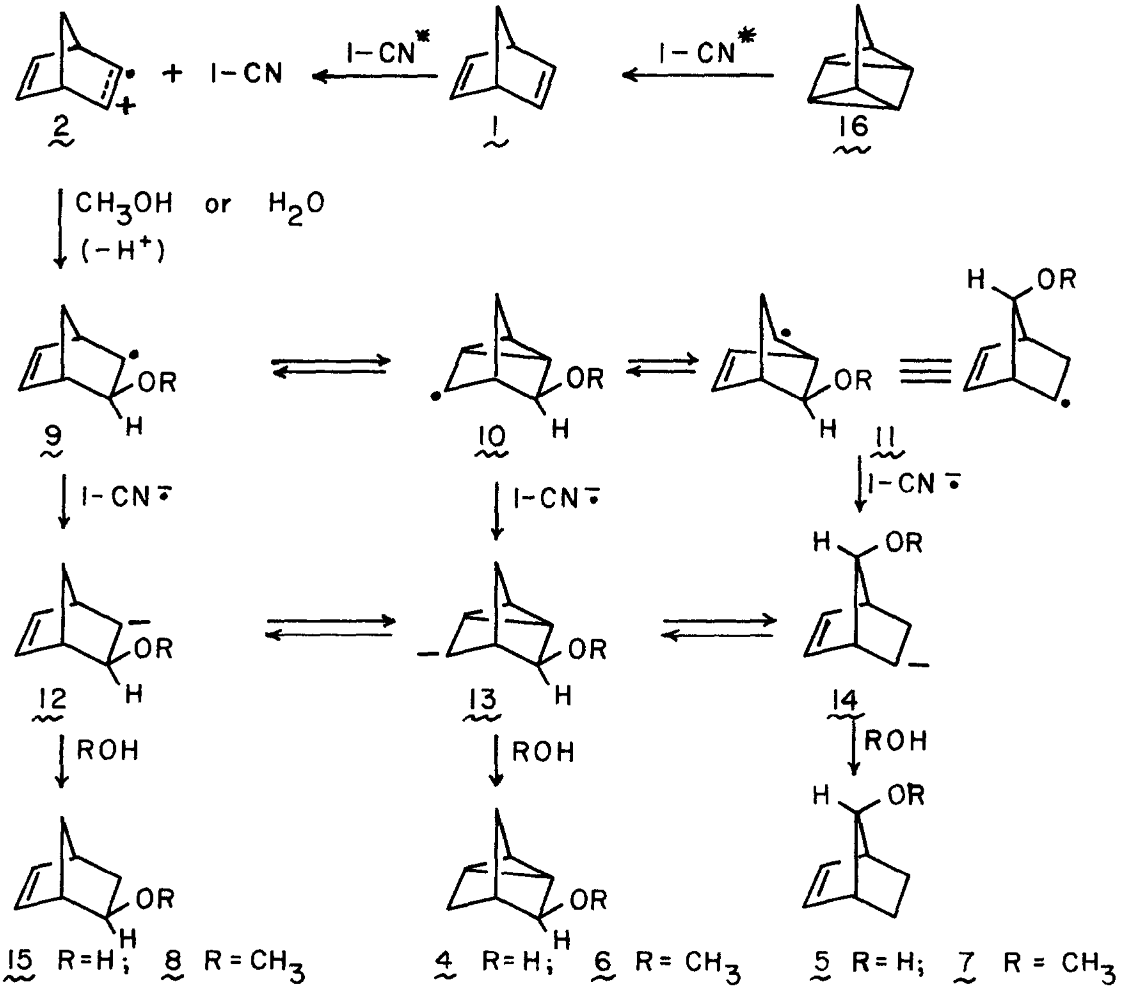
From a mechanistic point of view, we believe that **1** reacts with the excited state of 1-CN to give the singlet ion pair consisting of **2** and the 1-CN anion radical.[5] In the presence of methanol, **2** should undergo nucleophilic attack to produce **9**, as shown in Scheme 1. The bicyclo[2.2.1]hept-5-en-2-yl radical has been extensively studied and is known to be in rapid equilibrium with the tricyclo[2.2.1.$0^{2,6}$]hept-3-yl radical and the isomeric bicyclo[2.2.1]hept-5-en-2-yl radical.[16] Thus, **9** should be in rapid equilibrium with **10** and **11**. Back electron transfer from the 1-CN anion radical to **9**, **10**, and/or **11** would give **12**, **13**, and/or **14**, respectively. Exactly to which radical back electron transfer occurs is not consequential since **12**, **13**, and **14** are either resonance structures or they are in rapid equilibrium as indicated in Scheme 1.[17] Quenching of the carbanion(s) by proton transfer would give the observed products.

The significant difference in product ratios between the water - acetonitrile system and methanol indicates that there is either a significant solvent effect on the protonation step or that the contributions made by **12**, **13**, and **14** differ considerably when R is hydrogen versus when R is methyl. When R was hydrogen, no trace of **15**[18] could be detected. Thus, the process which produced **8** in methanol was completely absent in water - acetonitrile.

When tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (**16**) was irradiated in methanol containing 1-CN, the rapid conversion of **16** to **1** was observed. In addition, extremely trace amounts of methyl ethers were formed. Because of the propensity for the formation of **1** from **16**, it could not be determined whether all of the ether products were derived directly from **1** *via* **2** or whether trace amounts of products were resulting from the capture of **3** by solvent.[19]

In conclusion, we have established that nucleophiles can be added to **1** in a synthetically satisfactory fashion in a photoinitiated electron transfer process involving the intermediacy of the cation radical, **2**.

Scheme 1



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15. This reduction gave a 62% yield of a 1:1 mixture of the *syn*- and *anti*-7-methoxybicyclo[2.2.1]hept-2-enes. Since a sample of the syn methyl ether was now available, we could unequivocally demonstrate that this isomer was absent in the photochemical addition of methanol to **1**.

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