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PHOTOCHEMISTRY OF BENZOCYCLOBUTENE

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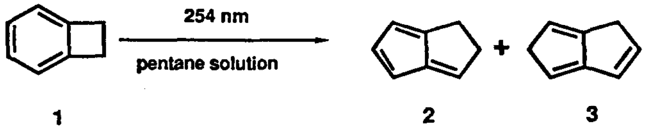
Abstract: Photolysis of benzocyclobutene (1) in pentane solution at 254 nm yields 1,1-dihydropentalene (2) and 1,5-dihydropentalene (3) as the major isomeric products; formation of 2 and 3 is consistent with a "prebenzvalene"-carbene rearrangement mechanism.

The chemistry of benzocyclobutene (1) and of the dihydropentalenes are topics of current interest.[1,2] Pyrolysis of benzocyclobutene produces styrene by a mechanism involving arylcarbene-cycloheptatetraene interconversions.[1b] Although the photochemical reactions of substituted benzocyclobutenes have been known for some time,[1d] we are unaware of reports of photochemical investigations of the parent hydrocarbon, benzocyclobutene itself. We report here that the photolysis of benzocyclobutene in pentane solution at 254 nm yields two dihydropentalenes, 2 and 3 as the dominant products.



Solutions of benzocyclobutene (1) in pentane were purged with Ar and photolyzed in a Rayonet reactor equipped with sixteen 254 nm low pressure mercury lamps. Reaction products were analyzed on a Hewlett Packard 5890 GC-MS spectrometer. ^{1}H NMR spectra were recorded on an IBM/Bruker 250 MHz spectrometer, and preparatory GC was used to separate products from unreacted starting material. A sample of α,α-dideuteriobenzocyclobutene (1-d_2) was synthesized according to a literature method.[1e] The deuterium content of 1-d_2 was determined by mass spectrometry and found to contain no less than 90% deuterium.

In a typical experiment, 10^{-3}M solution of benzocyclobutene in pentane was photolyzed at 254 nm. The GC-MS spectrum of reaction products indicated that the major course of reaction is the production of two C_8H_8 isomers (2 and 3) of benzocyclobutene ($M^+/e = 104$, C_8H_8). In addition, hydrogen abstraction products ($M^+/e = 104 + 72 = 176$, presumably the source of hydrogen is the solvent pentane) and a trace amount of benzene (less than 2%) was formed (Table 1). The ratio of the two isomers of benzocyclobenzene, (2 and 3), did not change significantly with conversion, i.e., 4.6 ± 0.2 with 20% conversion vs. 4.2 ± 0.2 with 30% conversion. After hydrogenation of a mixture of the two isomers (2 and 3), only a single hydrogenation product was formed and was identified as bicyclo[3.3.0]octane by comparison with an authentic sample by GC-MS analysis. The positions of double bonds in the dihydropentalenes were established by ^{1}H NMR: the spectrum of the major dihydropentalene is consistent with that of 1,2-dihydropentalene (2) reported in the literature.[2,3,4] [($CDCl_3$): δ 2.64 (2H), 3.01 (2H), 5.90 (1H), 6.12 (2H)]; the spectrum of the minor dihydropentalene is consistent with that of 1,5-dihydropentalene (3) reported in the literature[2,4] [($CDCl_3$): δ 3.01 (2H), 3.33 (2H), 5.83 (2H), 6.45 (2H)].

The photolysis of 1-d_2 in pentane solution at 254 nm was investigated to provide information concerning the reaction mechanism of conversion of 1 to 2 and 3. All products formed in the photolysis of 1-d_0 were found in comparable quantities in the photolysis of 1-d_2. From GC/MS analysis, there was no deuterium lost in the formation of the dihydropentalenes. After preparatory GC separation, the ^{1}H NMR spectrum of the major deuterio-1,2-dihydropentalene was recorded. The intensities of peaks at higher field [δ 2.64, δ 3.01] decreased by half relative to those of 1-d_0, while the intensities of remainder of the peaks were unchanged. The two higher field peaks are assigned to the 1,2-dihydro positions of 1,2-dihydropentalene (2), which were originally located on the four-membered ring of benzcyclobutene. This result establishes that deuterium atoms of 1-d_2 do not migrate from one ring to the other in the formation of 2.

TABLE 1. Photolysis of Benzocyclobutene in Pentane Solution at 254 nm.

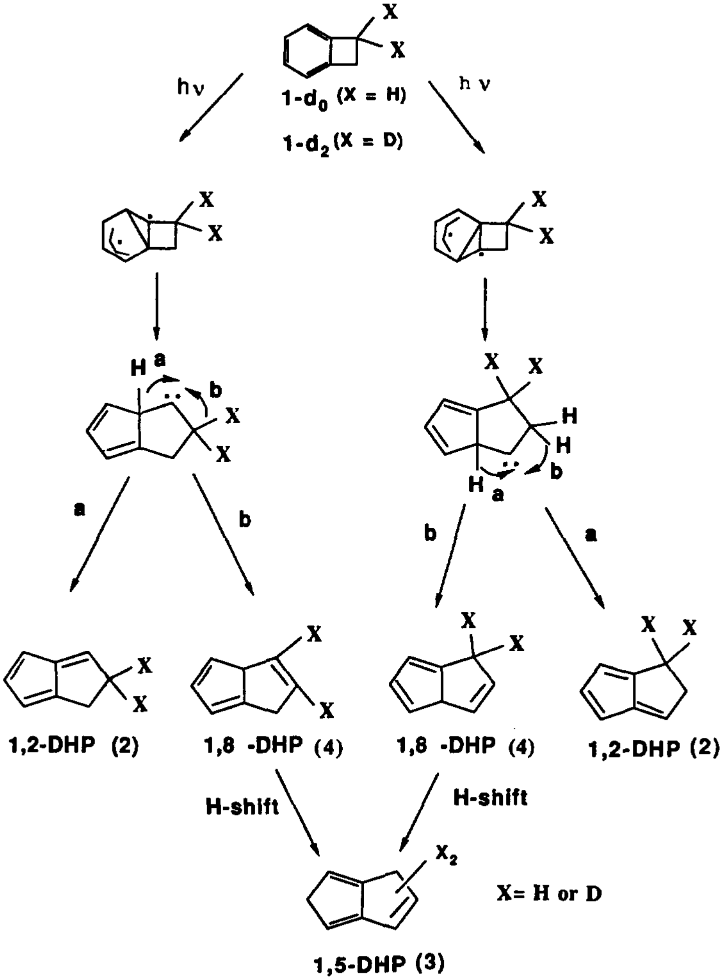
Photolysis time (hr)	2	3	Hydrogen Abstraction Products	Conversion
0.5[(a)]	71 ± 1%	16 ± 1%	13 ± 1%	21 ± 0%
3.5[(b)]	58 ± 1%	14 ± 1%	28 ± 1%	32 ± 2%

(a) Mass balance is 87 ± 5%

(b) Mass balance is 50 ± 2%

The results of our investigation differ from those observed from the photolysis of substituted benzocyclobutenes for which electrocyclic ring opening to o-quinodimethanes is the major reaction pathway.[1d] We propose a mechanism shown in Scheme 1 to explain the formation of 2 and 3 in the photolysis of 1. In analogy to the photochemistry of benzene and benzene derivatives,[5] we suggest the "prebenzvalenes" shown as primary photochemical intermediates. This species can yield a secondary carbene intermediate by breaking one of the three-membered ring bonds, as shown in Scheme 1. Subsequent 1,2-hydrogen shifts in this carbene yield the observed dihydropentalenes 2 and 3. Pathway a showing the transfer of a more reactive allylic hydrogen yields 1,2-dihydropentalene (2), the major product of reaction. The 1,2-hydrogen shift in pathway a does not involve the movement of hydrogen atoms in the four-membered ring of benzocyclobutene, so that no deuterium scrambling is expected in this

Scheme I


X
X
hν
hν
1-d$_0$ (X = H)
1-d$_2$ (X = D)
X
X
X
X
H a
b
X
X
X X
H
H
H a
b
a
b
b
a
X
X
X
X
X
X
X X
1,2-DHP (2)
1,8 -DHP (4)
1,8 -DHP (4)
1,2-DHP (2)
H-shift
H-shift
X$_2$
X= H or D
1,5-DHP (3)

pathway. The 1,2-hydrogen shift shown in pathway b yields 1,8-dihydropentalene (4), which is thermally unstable[2,6] and is not observed. We speculate that 4 is formed, but rearranges to the observed minor product 3 by successive 1,5-hydrogen shifts.

Conclusion

In conclusion, photolysis of benzocyclobutene in pentane solution at 254 nm yields 1,2-dihydropentalene and 1,5-dihydropentalene as the major isomeric products. A "prefulvene"-carbene mechanism is consistent with the results of a deuterium labelling experiment. The difference between the photochemistry observed with the parent and the ring opening reactions of the small ring substituted derivative is attributable to the decreased stability of the bis-allylic cyclobutane bond in the latter.

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