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DIRECT PHOTOLYSIS AT 185 nm OF SIMPLE CYCLOBUTENES. MOLECULAR ELIMINATION OF ACETYLENE

Yoshihisa INOUE,* Mitsuhiro SAKAE, and Tadao HAKUSHI
Department of Applied Chemistry, Himeji Institute of Technology,
2167 Shosha, Himeji, Hyogo 671-22

Direct photolyses at 185 nm of bicyclo[3.2.0]hept-6-ene and bicyclo[4.2.0]oct-7-ene in pentane afforded acetylene and the fragment cycloalkenes as the major photoproducts, whereas the Woodward-Hoffmann allowed ring-opening giving rise to 1,3-diene was a minor process.

The Woodward-Hoffmann allowed 1,3-diene$\rightleftarrows$cyclobutene interconversion has been well investigated theoretically and experimentally.[1] Thus the thermal conrotatory and photochemical disrotatory ring closure and opening processes have been exemplified extensively. Few photochemical ring opening has however been reported for simple cyclobutenes without conjugating chromophores, probably due to the lack of an absorption band in the accessible UV region. In the present communication, we report that yet another reaction channel predominates for the electronically excited simple cyclobutenes.

Direct irradiations at 185 nm of pentane solutions of bicyclo[3.2.0]hept-6-ene (**1a**) and bicyclo[4.2.0]oct-7-ene (**1b**)[2] were performed under nitrogen by using a mercury resonance lamp.[3] Acetylene (**2**) and the corresponding fragment cycloalkene, i.e. cyclopentene (**3a**) or cyclohexene (**3b**), were obtained as the major photoproducts along with a smaller amount of the ring-opening product, cyclic 1,3-diene (**4**), as shown in Scheme 1 and Table 1. At the early stages of reaction,

Scheme 1.

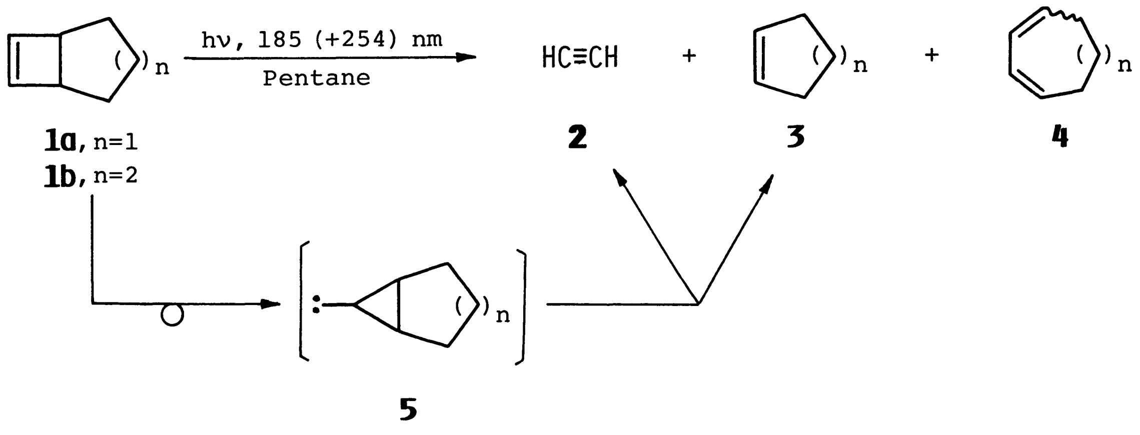


Table 1. Direct Photolyses of Bicyclo[3.2.0]hept-6-ene (**1a**) and Bicyclo[4.2.0]-oct-7-ene (**1b**)a)

Compd	Irradiation time/ min	Conversion/ %	Yield/ %b) (Φ)c)			
			2	**3**	cis,cis-**4**	cis,trans-**4**
1a	10	6.8	>23d) (0.054)	68 (0.16)	e)	e)
	25	17	>21	67	e)	e)
	50	31	>19	58	e)	e)
1b	10	7.8	f)	51 (0.15)	18 (0.053)	6.2 (0.018)
	15	12	f)	52	15	6.6
	30	20	f)	42	6.8	2.7

a) For experimental conditions, see Ref. 3. b) Yield based on consumed cyclobutene **1**, determined by VPC on a 2.25 m column of 25% β,β'-oxydipropionitrile. c) Quantum yield determined by the cyclooctene actinometry; H.-P. Schuchmann, C. von Sonntag, and R. Srinivasan, J. Photochem., 15, 159(1981). d) Only dissolved acetylene in pentane solution was measured. e) Formation not detected (yield<2%). f) Formation detected on VPC, but yield not determined.

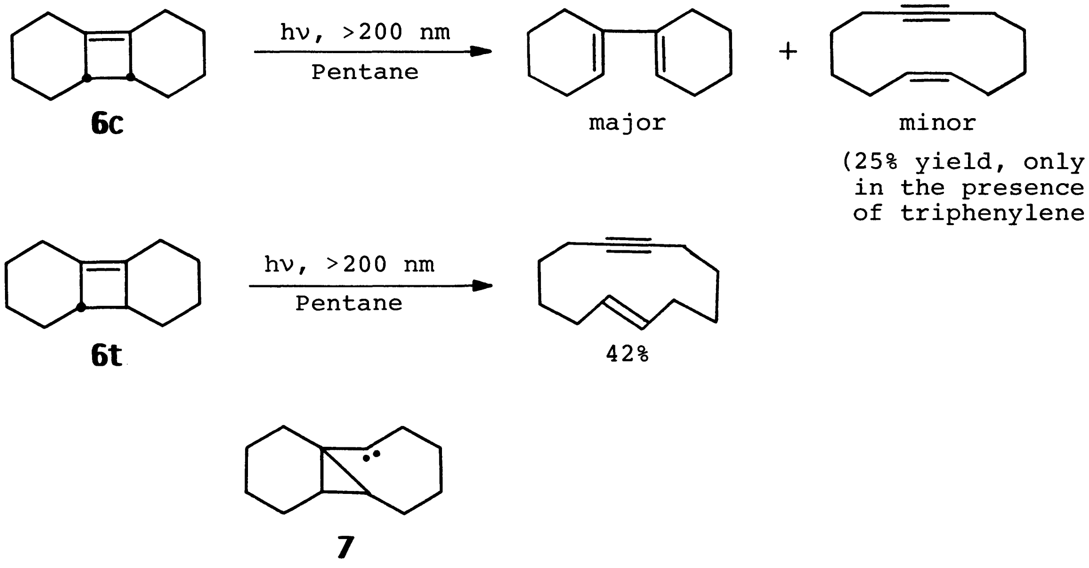
the yields of **3** and/or **4** increased as linear functions of irradiation time, indicating that these are the primary photoproducts. However, the formation of cis,trans-**4b** may be attributable to the secondary cis→trans photoisomerization of the initially formed cis,cis-isomer by the 254 nm resonance line which is radiated simultaneously from the light source.3)

Triplet photosensitization of **1b**(0.01 M) with benzene(0.1 M) as a sensitizer gave rise to a complex mixture of volatile products containing **3b** and unknown compounds in lower yields (<3%); no **4b** was detected on VPC in a significant yield. This is due to the spin-forbidden concerted cyclobutene→1,3-diene transformation; calculations show larger energy barrier for this transformation in the triplet.1c,d) Cyclodimerization would be the major decay path of the triplet cyclobutenes.4)

It should be noted that, in the direct photolyses at 185 nm, the major photochemical process actually occurred is not a ring opening but a molecular elimination of acetylene to give the cycloalkene **3** as a fragment. This result may not be necessarily unexpected or unreasonable, being contrary to the anticipation of the Woodward-Hoffmann rule.1a) While the electrocyclic interconversion between cyclobutenes and 1,3-dienes is closely related to the π,π^* excitation,1) recent investigations5a-d) demonstrate amply that excited singlet states other than π,π^* are involved in the direct photolyses of simple alkenes. In the present case, the excited state proposed is a π,3s Rydberg state, which gives a carbene intermediate **5** through 1,2-shift of a vinyllic alkyl group as shown in Scheme 1.6) Since the carbene formation upon direct irradiation of simple cycloalkenes is widely exemplified5) and the cyclopropylcarbenes, including **5**, generated independently in thermal decomposition of the corresponding tosylhydrazones are known to yield acetylene and the fragment alkenes,7) the above stepwise mechanism via carbene sounds fairly reasonable, although a concerted [$2\sigma+2\sigma$] cycloreversion process may not be strictly ruled out from the present data.

In this context, the "pretty" example8) of the photochemical [$\sigma 2_s+\sigma 2_s$] cycloreversion, observed for heavily substituted cyclobutenes **6**,9) would rather be interpreted in terms of our stepwise mechanism via carbene **7**, since the lowest excited singlet state of tetrasubstituted alkenes is believed to be π,3s Rydberg in nature10) and this excited state has been shown to give a carbene.5) The carbene also accounts for the stereospecific formation of the product alkenynes, although the stereospecificity was taken as support for the Woodward-Hoffmann allowed [$\sigma 2_s+\sigma 2_s$] cycloreversion.

Scheme 2.



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References

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3) The light source at 185 nm was a 30-W mercury resonance lamp fitted with a Suprasil envelope; no filter was used to eliminate the another major resonance line at 254 nm, since the cyclobutenes **1** are totally transparent at the wavelength. A pentane solution of **1** (0.01 M) charged in a Suprasil tubing (10 mm o.d.) was purged with nitrogen at -10°C and was irradiated externally at room temperature, the light path being flushed with nitrogen.

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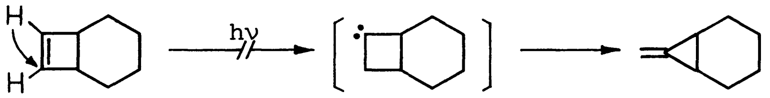
6) Although, in the direct photolyses of cyclopentenes,5d,e) 1,2-shift of a vinyllic hydrogen as well as alkyl group has been reported to occur in similar efficiencies, cyclobutenes **1** seems to undergo the alkyl shift predominantly to give cyclopropylcarbenes **5**. Indeed, 7-methylenenorcarane (**8b**), which might be formed via 1,2-shift of a vinyllic hydrogen and the subsequent rearrangement of the resulting cyclobutylidene **9b**,7) could not be detected on VPC by the retention time comparison with the authentic specimen synthesized independently; R. G. Salomon, A. Sinha, and M.F. Salomon, J. Am. Chem. Soc., 100, 520(1978).



1b **9b** **8b**

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