

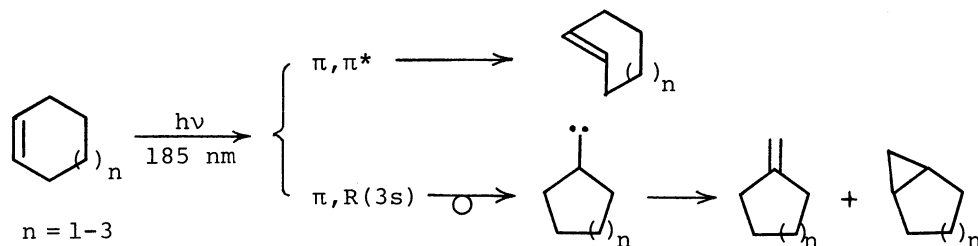
DIRECT PHOTOLYSIS AT 185 NM OF CYCLOPENTENE AND 2-NORBORNENE.
A NOVEL REACTION CHANNEL FOR π, π^* EXCITED SINGLET ALKENE

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Upon direct irradiation at 185 nm, the title compounds undergo hydrogen abstraction from the solvent via a π, π^* excited singlet state as well as skeletal rearrangement via a $\pi, R(3s)$ Rydberg excited state.

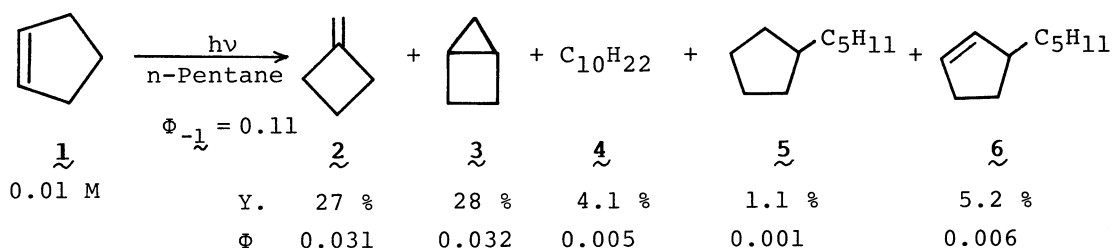
Photochemical behavior of simple alkenes upon direct irradiation in the liquid phase has been the subject of intensive investigations in recent years.¹⁻⁴⁾ Preceding reports from these laboratories¹⁾ revealed that the direct irradiation at 185 nm of a medium-sized cycloalkene (C_6-C_8) leads to cis-trans isomerization via a π, π^* excited singlet state as well as skeletal rearrangement to a carbene intermediate via a $\pi, R(3s)$ Rydberg excited state, as illustrated in the following scheme.



The photochemistry of smaller cycloalkenes is of our special interest, since cyclopentene, for example, is not compelled to be in a trans-form even as a transient species due to the geometrical requirement, and therefore new chemical and/or physical decay processes would emerge out from the π, π^* excited singlet state.

In this communication, we report the novel reaction channel for a π, π^* excited singlet alkene displayed upon direct irradiation of cyclopentene and 2-norbornene.

Cyclopentene (1). Direct irradiation at 185 nm⁵⁾ of a pentane solution of 1 (0.01 M) gave the rearrangement products, methylenecyclobutane (2) and bicyclo[2.1.0]pentane (3), as the major products along with smaller amounts of branched decanes (4), pentylcyclopentane (5), and pentylcyclopentene (6).⁶⁾ The chemical and quantum yields are shown below.⁷⁾ The products 2-4 were identified by comparison of the vpc reten-

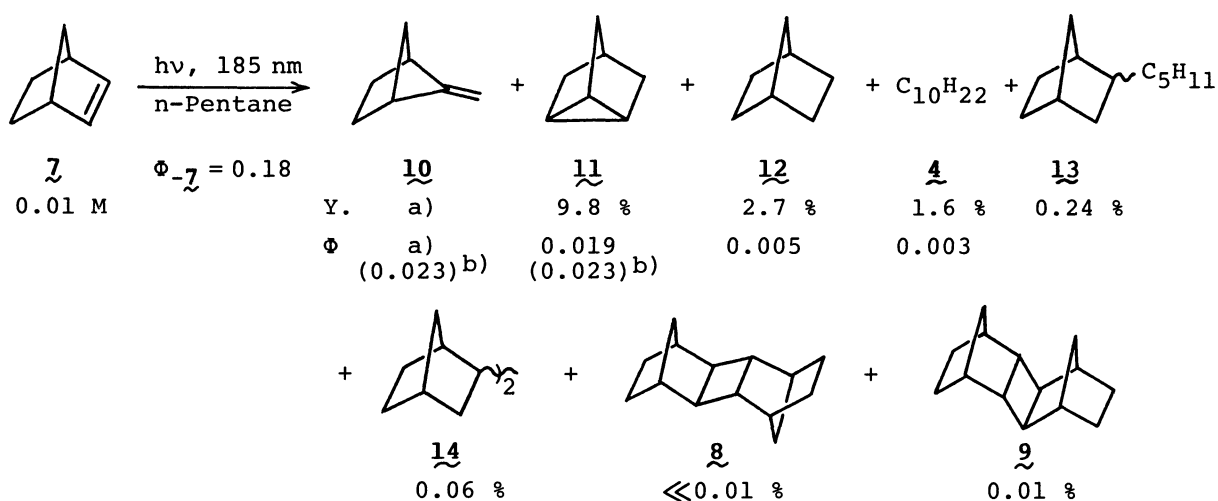


tion times on three different columns (PEG-300, ODPN, and DOP) and of mass spectra with those of the authentic specimens synthesized independently,⁸⁾ and 5 and 6 by the fragment patterns of their mass spectra and the chemical properties on hydrogenation over Pd/C.

The major products 2 and 3 are of common type observed in the direct photolysis of larger cycloalkenes mentioned above,¹⁾ and the origin should also be attributable to the rearrangement via a Rydberg excited state giving rise to a carbene. The similar product ratio of 2/3 from cyclobutylcarbene, generated thermally from the corresponding tosylhydrazone,⁹⁾ supports the intervention of the carbene intermediate. On the other hand, the nature of the products 4-6 suggests the involvement of radical intermediates in their formation, although similar products have never been reported in the direct photolysis of simple alkenes as yet.¹⁻⁴⁾ These products are inferred to arise via the initial abstraction of a hydrogen atom by an excited cyclopentene from the solvent and the subsequent chain reactions of cyclopentyl and solvent-derived pentyl radicals.

Norbornene (7). Apparently, little consent has been given to the direct photolysis of 2-norbornene. Arnold and Abraitys¹⁰⁾ reported that the direct irradiation at >200 nm of neat norbornene (10 M) gives exo-trans-exo and endo-trans-exo cyclo-dimers 8 and 9 in a ratio of 8:9 = >10:1, while the triplet photosensitization affords the same cyclodimers in reversed ratios of 1:2-9.¹¹⁾ More recently, Srinivasan and Brown^{2e)} have reported the sole formation of 5-methylenebicyclo[2.1.1]hexane (10) and nortricyclene (11) in quantum yields of 0.023 each¹²⁾ upon direct irradiation at 185 nm of 7 at 0.04 M concentration. However, no comprehensive study over a wide variety of norbornene concentrations has been presented, and the full feature of the photochemistry of norbornene upon direct irradiation remains unrevealed.

We started our work with the direct photolysis at 185 nm⁵⁾ of norbornene at 0.01 M concentration to obtain nortricyclene (11), norbornane (12), the branched decanes (4), 2-pentylnorbornane (13), and 2,2'-binorbornyl (14) in the yields shown below.^{6,13)} The cyclodimers 8 and 9 were however produced only in negligible yields less than 0.01 % at this concentration of 7.



- a) Not determined due to incomplete separation on vpc.
 b) Ref. 2e.

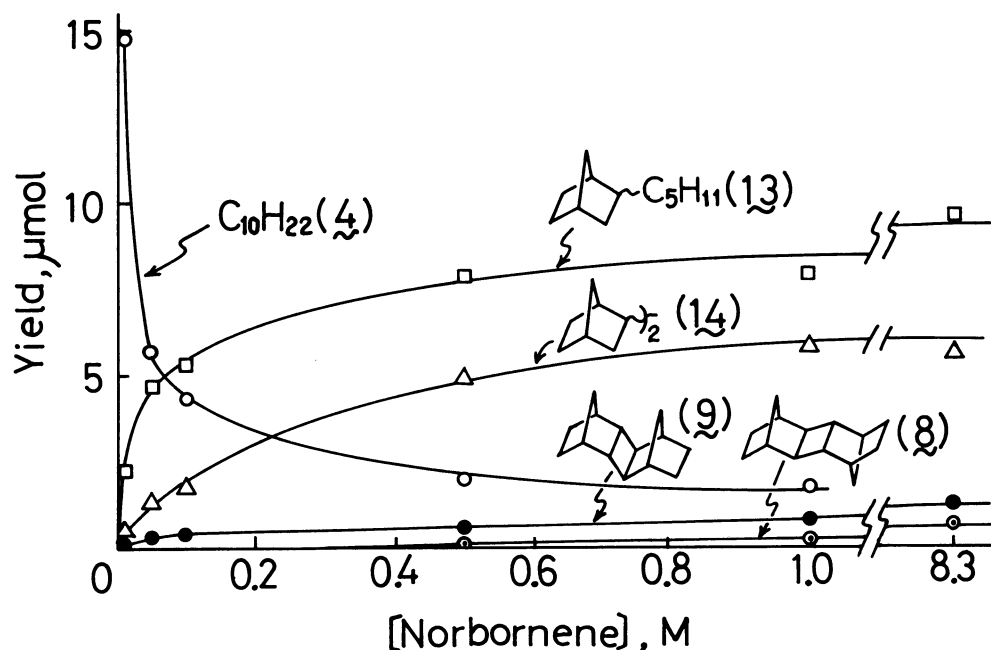


Figure. Effects of norbornene concentration on product yields

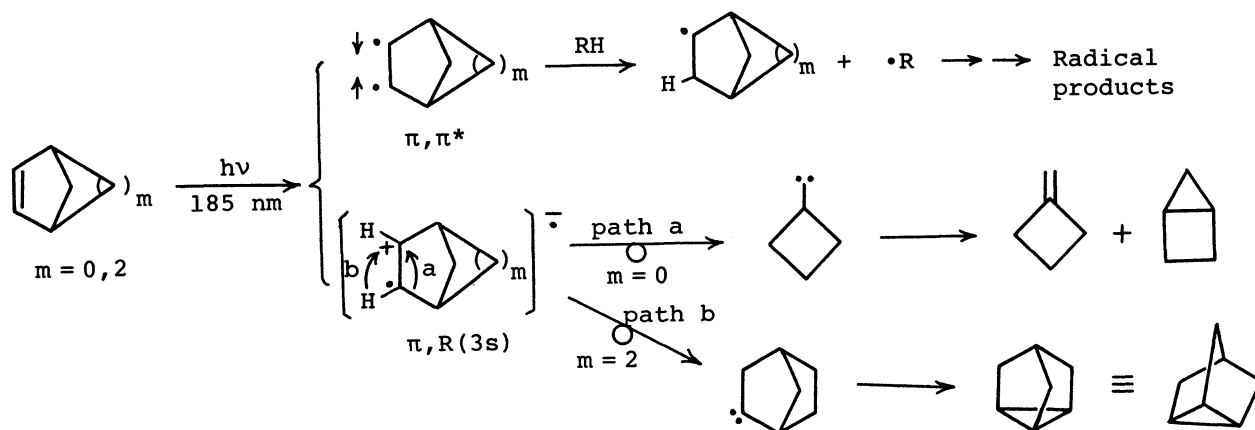
The photochemical behavior of norbornene parallels to that of cyclopentene 1 except the cyclodimerization; the rearrangement to a carbene and the hydrogen abstraction well account for the products. Effects of norbornene concentration on the product yields were further examined over a concentration range of 0.01-8.3 M under equivalent conditions. As can be seen from Figure, with increasing norbornene concentration, the yields of 13 and 14 increase dramatically at the expense of the branched decanes 4. This is most probably due to scavenging of the initially-produced pentyl and norbornyl radicals by norbornene at high concentrations. Important is that the cyclodimers 8 and 9 are still just the minor products even at 8.3 M of 2 and, contrary to the previous result,¹⁰⁾ the ratio of 8/9 is similar to that for the triplet sensitization. This apparent discrepancy was eliminated by examining the vpc column employed by Arnold et al.¹⁰⁾ an SE-30 column was found not to separate 8 and 14, and their combined yield must be reported as that of 8. The definitive ratios of 8, 9, and 14 were obtained by using a PEG-20M column; see Table.

The hydrogen abstraction upon direct photolyses of 1 and 2 is tentatively attributed to the π, π^* excited singlet state, since the quantum yields of the carbene-derived products 2 and 3 or 10 and 11, which arise from Rydberg state, are not affected significantly by reducing the ring size from seven to five through six.¹⁴⁾ Thus the direct photolysis of cyclopentenes may be summarized as follows.

Table. Dimer distribution upon photolyses of 2

Excitation	[<u>2</u>], M	Product		
		<u>14</u>	<u>8</u>	<u>9</u>
Direct (>200 nm) ^{a)}	10	-	>10	: 1
Direct (185 nm) ^{b)}	8.3	4.2	: 0.57	: 1
	1.0	7.5	: 0.25	: 1
	0.5	8.3	: 0.17	: 1
Acetone-sens. ^{b)}	0.5	0.13	: 0.15	: 1

a) Ref. 10. b) This work.



The 1,2-hydrogen shift in $\pi, R(3s)$ state giving rise to the cyclic carbene (path b) is considered to be particular to rigid cycloalkenes,¹⁵⁾ since the ratio of alkyl shift to hydrogen shift, i.e. path a to b, has been shown as 14:1 in the direct photolysis at 185 nm of cyclohexene-3,3,6,6-d₄.^{2e)}

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- 5) The light source and the procedures employed were similar to those reported previously.¹⁾ The direct excitation at 185 nm leads to the simultaneous formation of a π, π^* singlet and a $\pi, R(3s)$ excited states of the cyclopentenes **1** and **2**: M.B. Robin, "Higher Excited States of Polyatomic Molecules," Academic Press, New York (1975), Vol. 2, ch. 4.
- 6) The branched decanes **4** have been shown to be a mixture of dimers of 2- and 3-pentyl radicals.^{8c)} The formation of cyclopentane could not be confirmed due to the overlap of the solvent peak on vpc.
- 7) The chemical yields were based on the alkene consumed and the quantum yields were determined by means of the cyclooctene actinometer.^{1,3)}
- 8) For the syntheses of **2**, **3**, and **4**, see a) J.D. Roberts and C.W. Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949), b) P.G. Gassman and K.T. Mansfield, *Org. Synth.*, Coll. Vol. **5**, 96 (1973), and c) Y. Inoue, Y. Ueda, and T. Hakushi, *J. Am. Chem. Soc.*, **103**, 1806 (1981), respectively.
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- 11) The formation of the same two products in a similar ratio was also reported by Kropp upon xylene-photosensitization of **2**: *J. Am. Chem. Soc.*, **91**, 5783 (1969).
- 12) The quantum yields adopted here have been amended according to the recent report.³⁾
- 13) The products **4**, **8**, **9**, **11**, **12**, and **14** were identified by direct comparison with the authentic specimens synthesized independently.
- 14) Compare the present results with those in reference 2e.
- 15) In this context, a part of bicyclo[2.1.0]pentane **3** may arise via the 1,2-hydrogen shift (path a), as judged from the 2:3 ratios. The ratio obtained here is somewhat different from that reported for a thermally generated cyclobutylcarbene.⁹⁾

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