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ORGANIC PHOTOCHEMISTRY WITH 6.7 eV PHOTONS: 4-VINYL CYCLOHEXENE

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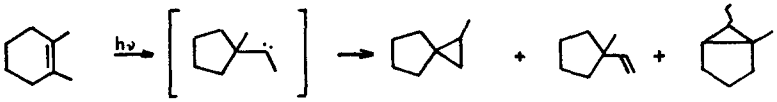
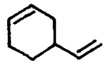
Irradiation of cyclic mono-olefins with 5-7 carbons in the ring has been shown to give rise to a variety of products which are best explained in terms of a carbene intermediate.[1-3] This mechanism which was first proposed by Fields and Kropp[1b] can be illustrated in the case of 1,2 - dimethyl cyclohexene as:





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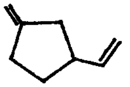
Evidence for this mechanism in the photochemistry of simple olefins at 185 nm (= 6.7 eV photons) has been obtained from studies on cycloheptene-1,2-d_2[2] and cyclohexene-3,3,6,6-d_4.[3]

The present work on the photolysis of 4-vinylcyclohexene (1) in solution at 185 nm is believed to be the first study of the photochemistry of a non-conjugated diolefin in the far-ultraviolet. It was undertaken to look for the existence of three effects which are: (1) interaction between the double bonds in the excited state, (2) stereochemistry of the carbene insertion, and (3) self-trapping of the carbene by addition to the vinyl group.

Photolyses were carried out in spectroscopic-grade pentane at a concentration of 4×10^{-2}M using the total radiation from a mercury resonance lamp. Since the path length of the irradiation cell was 1.5mm and 4-vinylcyclohexene has no significant absorption at $\lambda > 240$ nm,[4] the useful radiation was the resonance line at 185 nm. The products were separated by gas chromatography on a oxydipropionitrile column.

On photolysis of 4-vinyl cyclohexene to about 50% conversion, four products which were determined to be isomers of the starting material from their mass spectra were formed in 25% total isolated yield. The first of these was identified as 2:



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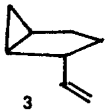

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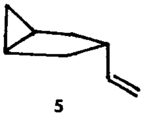

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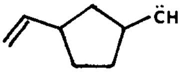

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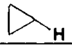
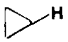
from its infrared ($>=CH_2$ at 6.02 and 11.35; $-CH=CH_2$ at 3.2, 6.08, 10.08, and 10.95μ) and nmr (δ, 5.8, 1H; 4.95, 2H; 4.82, 2H - singlet; 1.3 -2.6,7H) spectra. The remaining three products showed strikingly similar infrared spectra in which the absorptions of a $-CH=CH_2$ group (3.20, 6.10, 10.15 and 11.00μ) and a cyclopropane ring (9.78) were evident. The nmr spectrum at 60 MHz confirmed the presence of one vinyl group and a cyclopropyl ring in all three compounds. It appeared that all three of these products were isomeric vinyl bicyclo [3.1.0] hexanes. In order to resolve their structure and stereochemistry, their nmr spectra at 220 MHz were obtained. The salient features of these are shown in Table I.

Table I. 220 MHz SPECTRA OF PHOTOISOMERS 2, 3, and 4
(solvent: carbon tetrachloride; internal reference: chloroform)

	Chemical Shifts, δ					
Compound	-CH=C	$CH_2=C-$	C=C-CH	Ring Protons		
3	5.73	4.90	2.58	1.68, 1.32	0.32	0.14
4	5.69	4.91	2.72	2.1 --0.9	-- 0.27 --	
5	5.62	4.84	2.81	2.10, 1.60	0.42	0.14
	--	--	--	1.66, 1.17	0.25	0.14

Freeman, Grostic, and Raymond[5] have reported a useful correlation between the stereochemistry and the nmr absorptions of the cyclopropyl protons in 2- and 3- substituted bicyclo[3.1.0]hexanes. They observed that the trans-epimers exhibited an absorption area (at 60 MHz) for the C-6 hydrogens similar to that of the parent bicyclo[3.1.0]hexane, while in the cis series these absorptions were shifted downfield.[6] In the 220 MHz spectrum, this difference between the cis and trans epimers was even more striking. In bicyclo[3.1.0]hexane itself the protons of the $-CH_2-$ group in the cyclopropane ring are resolved as two separate absorptions 0.11 p.p.m. apart. Products 3 and 5 which showed a similar resolution of these absorptions were therefore identified as trans epimers, while 4 in which these absorptions were superimposed was identified as cis. In addition, the nmr spectrum of 5 showed proton absorptions occurring in pairs thus displaying an underlying plane of symmetry in the molecule. Such a pairing was absent in 3 or 4. It follows that 5 has the vinyl group at the 3 position and trans oriented while 3 and 4 are the 2-vinyl trans and cis isomers respec-

tively. The missing fourth member which would be *cis*-3-vinyl bicyclo[3.1.0] hexane (6) must have amounted to less that 5% of the total product mixture. The composition of the products was: 2, 27.6%; 3, 11.6%; 4, 37.8%; 5, 23.0%.
A quantitative study was made to compare the photochemistry of cyclohexene to that of 4-vinyl cyclohexene at 185 nm under identical experimental conditions and to low (< 10%) conversion. Data on the decomposition of the two compounds are listed in Table II.

Table II. PHOTOLYSES OF CYCLOHEXENE AND 4-VINYL CYCLOHEXENE AT 185 nm (Pentane solution; cell volume 150 ml; photon intensity: $2x10^{17}$/ml/min)

	Rates in μmole/min			
Compound	Concn (M)	disappearance	*exo* methylene	bicyclo[3.1.0] hexane
	$3.2x10^2$	16.6	2.7	4.6
	$2.6x10^2$	16.1	1.1	3.0

Discussion: The absorption spectrum of 4-vinyl cyclohexene[4] shows a greater intensity (ϵ=10800) at 185 nm than cyclohexene (ϵ=8100)[7] which can be attributed to the superimposition of an absorption of the vinyl group over that of cyclohexene. The absence of other features such as a secondary maximum and the close resemblance of the long wavelength end to cyclohexene itself indicates that there is little or no interaction between the double bonds in this excited state. The photochemistry is consistent with the absorption of the light by two non-interacting chromophores. Absorption by the vinyl group probably results in attack of the solvent as is the case in other terminal olefins.[8] The identical rates at which both cyclohexene and 4-vinyl cyclohexene disappear must be only a coincidence in view of what has been said above.

The total yield of the isomeric products which may come from a carbene intermediate, when corrected for the photons lost by absorption by the vinyl group come to 5.6 μ mole/min in 4-vinyl cyclohexene which compares favourably with the value of 7.3 μ mole/min in cyclohexene. The carbene from 4-vinyl cyclohexene would presumably have the structure (7). It can give rise to only one methylene cyclopentane and four isomeric vinyl bicyclo[3.1.0]hexanes. All but one of these have been realized. The absence of products which correspond to the internal addition of the carbene to the vinyl group may be attributed to the slowness in the rotation of the substituent group ($-CH=CH_2$) to a favorable geometry in the lifetime of the excited state.

It is also relevant to point out the absence of product(s) which correspond to the internal addition of one olefinic group to the other. Such cycloadditions which are well-known in the photochemistry of non-conjugated dienes at longer wavelengths can be observed at 185 nm in 1,5 dienes with a rigid geometry such as the *endo*-dimer of cyclopentadiene[10]. The lack of such a reaction in 4-vinyl cyclohexene once again suggests that the lifetime of the excited state that is formed at 185 nm is too short to allow any relaxation of the molecule.

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6. A second correlation that the same authors cite[5] is based on the splitting and chemical shift of the tertiary proton that is α to the substituent group. In the present instance, this is of less use since the splitting is more complex because the substituent group is a vinyl and not a methoxy as in ref. 5. However, it can be seen that between 3 and 4, the *trans* epimer has this absorption upfield to the *cis* epimer.
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9. This has been the subject of many reviews. See for example W. L. Dilling, Chem. Rev. 66, 373 (1966).
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