### PHOTOISOMERIZATION OF 4,5-DIHYDROOXEPIN

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We wish to record the photochemical behavior of the cyclic divinyl ether, 4,5-dihydrooxepin, I. Direct irradiation of dilute solutions of I<sup>4</sup> ( $\lambda_{max}^{n-heptane}$  216 nm ( $\varepsilon$  = 3720),  $\lambda_{max}^{n-heptane}$  231 nm ( $\varepsilon$  = 2000) at 253.7 nm results in the formation of three major photoproducts, 3-formylcyclopentene (II), <u>trans-2,5-hexadienal (III)</u>, and 5-hexynal (IV) in good overall conversion (<u>cf</u>. Table I).



The photoproducts, II, III, and IV were isolated from reaction mixtures by preparative glpc and identified by their spectral properties and comparison with authentic samples. II<sup>5</sup>: mass spectrum<sup>6</sup>, m/e (rel. intensity): 96 (18), 67 (100), 41 (39), 39 (30); ir<sup>6</sup>, 3050 w, 2805 m, 2710 m, 1720 s, 1604 w; nmr<sup>6</sup>, 9.44, d, J = 2.5 Hz, area 1, aldehyde H; 5.92, m, area 1, vinyl H; 5.66, m, area 1, vinyl H; 3.40, m, area 1, H  $\underline{\alpha}$  to carbonyl; 2.5 - 1.9, two m, area 4, methylene H's. III<sup>5</sup>: mass spectrum: 96(49), 67 (82), 41 (90), 39 (100); ir, 3080 w, 2810 w, 2730 w, 1689 s, 1627 m, 970 m; nmr, 9.45, d, J = 7.6 Hz, area 1, aldehyde H; 6.72, d of t, J = 16.0, 6.6 Hz, area 1, vinyl H at C-3; 6.00, d of d of t, J = 16.0, 7.6, 1.5 Hz, area 1, vinyl H at C-2; 5.8, m, area 1, vinyl H at C-5; 5.14 and 5.01, two m, area 2, terminal vinyl H's; 3.02, t of q, J = 6.6, 1.5 Hz, area 2, methylene H's at C-4. IV<sup>7</sup>: mass spectrum: 96 (10), 67 (65), 41 (55), 39 (100); ir, 3294 s, 2825 m, 2720 m, 2100 w, 1720 s; nmr, 9.72, t, J = 1.2 Hz, area 1, aldehyde H; 2.52, t of d, J = 7.1, 1.2 Hz, area 2, methylene H's <u>a</u> to carbonyl; 2.2 - 1.6, two groups of m, area 5, acetylenic and methylene H's.

## TABLE I

Exp. No.	<b>Composition</b> of Reaction Mixture				Conditions
	<b>%</b> I	% II	% III	% IV	(conc., solvent, temp., etc.)
1	88.7	5.0	3.2	3.1	0.15 M, ether, rm. temp.
	80.4	8.6	5.4	5.6	
	72.1	12.0	7.7	8.2	
	61.9	16.7	10.5	10.9	
	46.9	23.0	14.0	16.1	
	19.7	32.6	19.5	28.2	
	8.0	34.2	17.0	40.8	
2	51.0	19.2	15.6	14.2	0.1 M, ether, rm. temp.
3	53.0	18.8	15.6	12.6	0.1 M, ether, rm. temp., degassed <sup>C</sup>
4	66.6	18.0	9.8	5.6	0.1 M, methyl alcohol, rm. temp.
5	54.1	21.3	10.9	13.7	0.1 M, isopropyl alc., rm. temp.
6	52.0	12.0	22.0	14.0	0.1 M, ether, -100°C.
7	74.2	10.2	7.8	7.8	0.23 M in I and in piperylene,
	14.2	28.8	24.6	32.4	ether, rm. temp.
8	80.4	9.4	4.4	5.8	1:1 mole mixture of I and pipery- lene, rm. temp.

# Photoisomerization of 4,5-Dihydrooxepin<sup>a</sup>

<sup>a</sup> Irradiations were carried out in quartz tubes with unfiltered 253.7 nm. light. A typical experiment employed a merry-go-round apparatus equipped with four General Electric G875 lamps. Under these conditions, 3.5 hrs. irradiation sufficed to bring about ~50% conversion of I in a 0.15 M solution (Exp. 1).

<sup>b</sup> Analysis by gipc on a column (10 ft. x 1/4 in.) of 15% diisodecyl phthalate on Gas-Chrom-P with n-octane as an internal standard. The percentages given are normalized for the mixture of isomers I - IV but, in view of the good material balance, are reasonable measures of the product yields through ~50% reaction (see text). That glpc analysis did not alter the nature or proportions of the isomers produced was demonstrated by direct mar analysis of a photoreaction mixture after irradiation at room temperature.

c Degassing was accomplished by repeated <u>in vacuo</u> bulb-to-bulb transfers of the ethereal solution.

As the experimental results summarized in Table I reveal, the course of the photoreaction is relatively insensitive to the solvent (Exp. 1, 4 and 5), the temperature (Exp. 2 and 6), the presence of oxygen (Exp. 2 and 3), and the presence of a piperlylene quencher (Exp. 1, 7 and 8). Attempts to sensitize the reaction by conducting it in benzene solution ( $E_{T_1} = 85$ kcal/m) or in the presence of acetophenone ( $E_{T_1} = 76$  kcal/m) or benzophenone ( $E_{T_1} = 69$  kcal/m) failed. Under these conditions, none of the three photoproducts formed and I could be recovered in good yield.

A quantum yield<sup>8</sup> for the disappearance of I of  $1.1 \pm 0.2$  indicates a high efficiency in the photoconversion. The material balance, also, is quite good through the first 50% of the reaction, better than 90% of the starting material being accounted for by the mixture of isomers, I - IV. Thereafter, substantial material losses ensue via polymerization and/or secondary reactions of III, and, to a lesser extent, of II (cf. Exp. 1). At least three other volatile products are formed in minor amounts (less than 10%) during the photoreaction. The most abundant of these is tentatively identified as cis-2,5-hexadienal by its nmr spectral characteristics. Its concentration relative to its trans isomer, III, appears to remain fairly constant at ca. 1:4.5 throughout the reaction. Direct irradiation of ethereal solutions of each of the major photoisom ers, II, III, and IV, failed to implicate any one of them as the precursor of the others, although a small amount of cis-2,5-hexadienal was detectable in the irradiation of III.

The information assembled thus far suggests that II, III, and IV (and possibly the <u>cis</u> isomer of III) are all primary photoproducts and that the reaction proceeds through the excited singlet state of I.

Recent reports on the photochemistry of cyclic vinyl ethers include examples in the 2,3-dihydrofuran system<sup>9</sup>, the 3,4-dihydro-2H-pyran system<sup>10</sup>, and the furan system<sup>11</sup>. In all of these, a ring contraction leading to cyclic carbonyl valence isomers has been observed. The formation of the photoisomer, II, in the present investigation, parallels this general observation and may most simply be viewed as a 1,3 shift over the enolyl system of I. In principle, this transformation could occur in a concerted manner or through a diradical species, V (process a). The formation of III as a primary product requires a bond rotation as well as a hydrogen transfer to achieve the observed <u>trans</u> geometry, a condition which seems

most easily met in the diradical (process b). The acetylenic aldehyde, IV, to our knowledge, is a novel type of photoproduct. Its formation, also, may be rationalized by the species V, and requires a transfer of the C-6 vinyl hydrogen to the oxygen (or carbon) of the enolyl portion of the diradical (process c).



Investigations of the dihydrooxepin and related vinyl ether systems are continuing in

### our laboratories.

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- Nmr and ir data for II and III reported by A. Viola and J. H. MacMillan, J. Amer. Chem. Soc., 92, 2402 (1970) correspond well with the values found in this work.
- 6. Mass spectral data were obtained at 70 eV with a Varian-Matt CH-5 instrument. Ir spectra were run on thin films on a Perkin-Elmer 621 spectrophotometer and are recorded in cm<sup>-1</sup>. Nmr spectra were measured with a Varian HA-100 MHz instrument as solutions in CCl<sub>4</sub>. Chemical shifts are given in  $\underline{\delta}$  units.
- 7. An authentic sample of IV, prepared by manganese dioxide oxidation of 5-hexynol (Farchan Research Laboratories), possessed spectral properties identical with those reported for the photochemically produced compound.
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