Photoisomerization of 3,4-Dihydro-2H-pyrans

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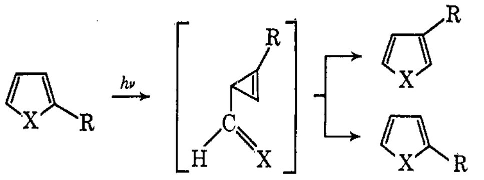
Mercury- ($^3P_1$) sensitized decomposition of 3,4-dihydro-2H-pyran in the vapor phase gave rise to ethylene, acrolein, and cyclobutane carboxaldehyde as the principal products. The molecular split which gave ethylene and acrolein had a maximum quantum yield of 0.14. The isomerization reaction had a quantum yield of 0.02 at *ca.* 50 Torr. In preparative runs at 1-atm pressure and 84.5°, there was a 20% yield of cyclobutanecarboxaldehyde. Photolysis of 2,5-dimethyl-3,4-dihydro-2H-pyran-2-carboxaldehyde in solution in cyclohexane with 300-nm radiation gave 2,5-dimethyl-2H-pyran, possibly by a free-radical process, and 1,2-dimethylcyclobutane-1,2-dicarboxaldehyde by a ring-contraction reaction. It is suggested that the photoisomerization of 3,4-dihydro-2H-pyrans to cyclobutanecarboxaldehydes is a general process that is analogous to the photochemical ring contraction that is known in 2,3-dihydrofurans and furans.

The photochemical reactions of five-membered-ring compounds which bear a heterocyclic atom have been extensively studied in recent years. A general scheme which seems to be applicable to the furan,[1,2] isoxazole,[3] thiophene,[4] and pyrazole[5] systems is given in eq 1.

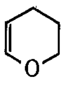


(1a)

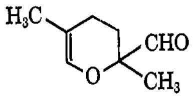
(1b)

The overall transformation from a 2-substituted to a 3-substituted compound has been observed in all these systems, but the intermediacy of a cyclopropene derivative has not been established in every instance. These reactions may be viewed as those of the 1,3-diene chromophore, which is present in all of these molecules,[6] but it seems equally valid—at least in the oxygen heterocyclics—to look upon reaction 1 as that of a cyclic vinyl ether. The photoisomerization of 2-methyl-4,5-dihydrofuran, which lacks the 1,3-diene system, gives cyclopropylmethyl ketone[1] just as vinyl ethers cleave photochemically to give aldehydes.[7]

The present study is one part of an attempt to extend these investigations to the six-membered heterocyclic compounds which bear an oxygen atom. Results on the photosensitized decomposition of 3,4-dihydro-2H-pyran (I) and the direct photolysis of 2.5-methyl-3,4-dihydro-2H-pyran-2-carboxaldehyde (II) are reported here.



I



II

Experimental Section

Materials.—Dihydropyran (I) from Aldrich Chemical Co. was fractionated in an annular spinning-band column. A narrow cut which boiled over a 0.1° range was collected, dried over Drierite, and used in all quantitative studies. By vapor phase chromatographic analysis it was found to be free from impurities. Dimethyl dihydropyrancarboxaldehyde (II) from Aldrich Chemical Co. was used as obtained.

Apparatus.—A spiral mercury resonance lamp (Ottawa-style) which was operated from a neon-sign transformer was used as the light source. The power supply was regulated by a Sola constant-voltage transformer. The lamp was calibrated with a potassium ferrioxalate actinometer.[8] Photolyses were conducted in a cylindrical quartz cell 18.3 cm long and 4.9 cm in diameter. It was flamed in air after each experiment to remove any polymeric deposit. A conventional vacuum line which was fitted with greaseless valves wherever possible was used to fill the cell and analyze for the products.

Analysis.—After preliminary distillations on the vacuum line at −190 and −150°, the high-boiling fraction of the photolysate was injected on a Ucon-550 X column (2 m) at 80° which was fitted to a Perkin-Elmer 154 D vapor fractometer. Quantitative analysis for the various products was effected by measuring the area under each curve. Calibrations for acrolein and the isomeric products were made with samples of authentic material. Analysis for cyclobutane was based on a calibration for an isomeric C_4 compound.

Results

Products.—Mercury- ($^3P_1$) sensitized decomposition of dihydropyran (I) in the vapor phase gave CO, ethylene, cyclobutane, acrolein, and cyclobutanecarboxaldehyde. The identities of the first four compounds were established from their infrared spectra and by a comparison of their retention times against those of authentic samples. The identification of cyclobutanecarboxaldehyde was based on the mass spectrum (parent peak at *m/e* 84), the infrared spectrum, which showed an aldehydic group [1725 (s) and 2700 (w) cm^{-1}], the nmr spectrum [τ 0.30 (d, 1 H), 6.8 (m, 1 H), and 7.8 (6 H)], and the melting point of its 2,4-dinitrophenylhydrazone [152.5–154.0° (lit.[9] mp 152–155°)]. There was a small quantity of a second isomer which was detected only in the reactions at pressures less than 50 Torr. It was not further identified.

Direct irradiation of dihydropyran (I) in the vapor phase with an unfiltered medium-pressure mercury arc also gave the same products. Photolysis in cyclopentane solution at 253.7 nm or with an unfiltered mercury arc gave no identifiable product.

In preparative-scale runs in which dihydropyran (I) was refluxed with mercury at 1 atm while the vapors were irradiated with the mercury resonance radiation at 253.7 nm, the isolated yield of cyclobutanecarboxaldehyde was 20%. In these runs, some secondary pho-

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[1] H. Hiraoka and R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 2720 (1968).

[2] E. E. Van Tamelen and T. H. Whitesides, *ibid.*, **90**, 3894 (1968).

[3] E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966).

[4] H. Wynberg, R. M. Kellogg, H. Van Driel, and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967), and references cited therein.

[5] H. Tiefenthaler, W. Dorschein, H. Goth, and H. Schmid, *Helv. Chim. Acta*, **50**, 2244 (1967).

[6] R. Srinivasan, *Pure Appl. Chem.*, **20**, No. 3 (1969).

[7] E. Murad, *J. Amer. Chem. Soc.*, **83**, 1327 (1961).

[8] The author thanks Dr. Stephan Boué for the actinometric measurements.

[9] B. C. Roquitte and W. D. Walters, *J. Amer. Chem. Soc.*, **84**, 4049 (1962).

TABLE I

MERCURY- ($^3P_1$) SENSITIZED DECOMPOSITION OF 3,4-DIHYDRO-2H-PYRAN[a]

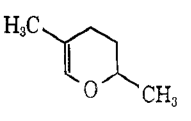
Dihydropyran, Torr	Time, min	Products, μmol/min						Remarks
		CO	C_2H_4	C_4H_8	Acrolein	Isomer	Cyclobutane-aldehyde	
29.5	8	1.53	0.90	0.46	1.95	0.04	0.15	
30.0	8	1.69	0.94	0.64	2.02	0.04	0.15	
30.5	4	0.89	0.12	0.76	2.21	0.05	0.18	
30.5	2	0.05	0.26	0.16	2.07	0.04	0.16	
30.2	1	0.37	0.11	0.96	2.64	0.05	0.19	Conversion 4%
9.6	2	2.01	3.34	0.25	0.80	0	Trace	
19.8	3	0.63	0.03	0.60	1.91	0.04	0.09	
39.3	4	0.46	b	0.83	2.66	0.05	0.27	
48.8	4	0.21	0.03	0.72	2.32	0.04	0.31	
59.3	5	0.66	0.03	0.09	0.71	0.03	0.30	
30.0	4	b	b	0.32	1.84	0.01	0.10	P_{O_2} = 22.7 Torr
30.2	4	b	b	0.81	2.18	0.21	0.15	P_{O_2} = 5.6 Torr
30.4	4	b	b	0.79	2.46	0.04	0.24	P_{O_2} = 52.8 Torr

[a] $I = 1.87 \times 10^{17}$ quanta/sec; cell volume = 172 ml; room temperature. [b] Not determined.

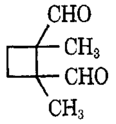
tolysis of the primary products was observed to occur. Under these conditions, two more volatile products were detected. The first of these had the formula $C_7H_{14}O$ [mol wt 114 (mass spectrum)] and its infrared spectrum showed a strong absorption at 1090 cm^{-1} (COC) and a medium absorption at 1375 cm^{-1} (CH_3). The nmr spectrum consisted of absorptions at τ 6.25 (q, 1 H), 7.0 (m, 2 H), 8.2–9.0 (complex, 8 H), and 9.3 (t, 3 H). The absence of any unsaturation in the molecule was indicated by the infrared and nmr spectra. The fact that the most intense peak in the mass spectrum was at *m/e* 85 suggested that the compound may possess a tetrahydropyranyl (C_5H_9O) ring. The remaining carbons and hydrogens can be accounted for by an ethyl group, the methyl part of which is identifiable in the infrared spectrum and in the nmr spectrum at τ 9.3. The compound was probably an ethyltetrahydropyran, but in the absence of more information it cannot be identified with certainty.

The second product had the formula $C_7H_{12}O$ [mol wt 112 (mass spectrum)] and showed infrared absorptions at 1725 (s) and 2700 cm^{-1} (aldehyde). The nmr spectrum showed an aldehydic proton at τ 0.05 (t) and the rest of the protons gave rise to a complex pattern at τ 7.2–8.6. Since there was no evidence for unsaturation in the molecule (and taking into account the aldehydic group), it had to have one carbocyclic ring. A strong peak in the mass spectrum at *m/e* 55 and the nmr absorption centered at τ 7.9 suggest a cyclobutyl ring. Once again, in the absence of detailed information, it is difficult to assign an unambiguous structure to the molecule, but 3-cyclobutylpropanal is a possibility.

Dimethyldihydropyrancarboxaldehyde (II) was irradiated in solution (2%) in cyclohexane at 300 nm. A gas was evolved and a considerable amount of a white polymer was formed. From the solution, two volatile products were isolated. One of these (10% yield) had the molecular formula $C_7H_{12}O$ [mol wt 112 (mass spectrum) and major peaks at *m/e* 97, 71, 69, 43, and 41)], and its infrared spectrum showed a strong absorption at 1160 cm^{-1} (COC) and medium absorptions at 1380 (CH_3) and 1670 cm^{-1} (C=C). The molecular weight suggested that this product was formed by the loss of CO from the starting material. Since the infrared spectrum indicated that the pyran ring was intact, a possible structure for the product will be 2,5-dimethyl-3,4-dihydro-2H-pyran (III). This was confirmed by the nmr spectrum, which showed absorptions at τ 3.76 (br, 1 H), 6.1 (m, 1 H), 8 (4 H), 8.30 (s, 3 H), and 8.62 (d, 3 H, J = 6.0 Hz). The last of these corresponds to the protons in a methyl group which is attached to a CH group. The second methyl group at τ 8.62 is unsplit and allylic. The single proton at τ 3.76 would correspond to an olefinic proton on a carbon that is α to an oxygen. The proton on the other carbon that is also α to an oxygen is presumably at τ 6.1. The remaining four protons, two of which are allylic, are in the broad absorption that is centered at τ 8.



III



IV

The second product was isolated only with difficulty (7% yield), since it decomposed even during the stripping of the solvent at its normal boiling point (81°). The mass spectrum indicated that it was an isomer of the starting material. In its infrared spectrum there were absorptions at 1725 (C=O), 2700 (aldehydic CH), and 1378 cm^{-1} (CH_3). The nmr spectrum showed a slightly broadened but unsplit peak at τ 0.32 which confirmed the presence of one or more aldehyde groups. All of the remaining protons were in a complex pattern at τ 7.2–9.1 in which a sharp, unsplit peak at τ 8.75 (*ca.* 6.5 H) was clearly discernible. By analogy to the photoisomerization of dihydropyran (I), it is reasonable to expect dimethyldihydropyrancarboxaldehyde (II) to isomerize to 1,2-dimethylcyclobutane-1,2-dicarboxaldehyde (IV). The complexity of the nmr spectrum as well as the slight broadening of the aldehyde proton absorption suggests that the product that was obtained was a mixture of the *cis* and *trans* forms of this compound. The crowding of the two methyl and the two CHO groups on adjacent carbon atoms may account for its thermal lability.

Rate Studies.—Quantitative data on the mercury-sensitized decomposition of dihydropyran (I) are summarized in Table I.

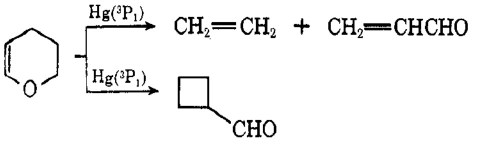
The maximum quantum yield for the formation of acrolein which was 0.14 was recorded at 39 Torr. The quantum yield for the formation of cyclobutanecarboxaldehyde was 0.02 at 49 Torr, but this may not be the maximum value, since the quantum yields were seen to increase with increasing pressure. The quantum yield for the disappearance of dihydropyran (I) was 0.7 at 30 Torr when the conversion was 4%.

The material balance in the runs in Table I was poor. Thus only 30% of the dihydropyran (I) that was lost was accounted for in the volatile products. The mass balance was worse when the conversion rose to 20%. It was independent of pressure in the range of 10–40 Torr. At pressures greater than 40 Torr, experimental difficulties in analyzing for a small change in the concentration of dihydropyran (I) prevented the collection of reliable data on the mass balance. However, the isolation of cyclobutanecarboxaldehyde in 20% yield from the preparative-scale run at 1 atm suggests that the mass balance did not improve significantly even at that pressure.

Discussion

The ultraviolet absorption spectrum of dihydropyran (I) in ethanol shows no maximum at wavelengths longer than 200 nm, the extinction coefficients at 220 and 210 nm being 250 and 2850 cm^2 mol^{-1}, respectively. There is no published report on the ultraviolet spectrum of a linear vinyl ether, but the fact that ethyl vinyl ether can be photolyzed by the radiation from an unfiltered medium-pressure mercury arc[7] suggests that the compound absorbs significantly above 200 nm. It is a reasonable assumption that the energies of the excited states of dihydropyran (I) are not much different from those of a cyclic olefin such as cyclohexene.

On sensitization by mercury ($^3P_1$) atoms, dihydropyran (I) may be excited to a triplet state as is the case in cyclic olefins. The present study indicates that two modes of decomposition occur on photoexcitation. These are given in eq 2 and 3.

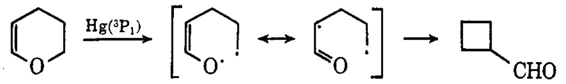


(2)

(3)

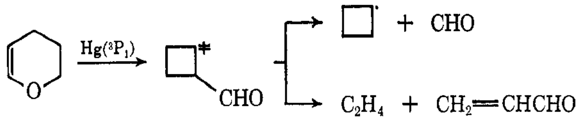
Since the formation of acrolein is not scavenged by the addition of oxygen, it probably arises from a molecular split according to eq 2. The fact that the yield of ethylene is invariably smaller than the yield of acrolein may be attributed to the difficulty in distilling off the ethylene from the photolysate. The yields of ethylene tended to be erratic and no quantitative significance can be attached to their magnitude. The formation of cyclobutanecarboxaldehyde was also unaffected by the addition of oxygen, suggesting that this is the intramolecular ring contraction that corresponds to eq 1 in the five-membered heterocyclics.

The detailed nature of the primary processes in this system is of interest. Reaction 3 may be written as a concerted process or as proceeding through a diradical intermediate (eq 3a) which does not lose its stereochemical integrity faster than its rate of closure to a cyclobutane product. The two pathways can be sorted out by the use of stereoisomeric 2,4-substituted dihydropyrans. Each isomer should give rise to two different cyclobutane carboxaldehydes if the reaction is concerted. Such studies are now in progress.



(3a)

The nature of the excited states of dihydropyran (I) which take part in reactions 2 and 3 is not clear. Assuming that only the ground singlet and the triplet states of the molecule are involved, reaction 3 may occur from the triplet state. If this results in a vibrationally excited product, further decomposition according to eq 4 and 5 may also occur. The formation of cyclobutane and CO can be explained by reaction 4.[10] There is no evidence for or against reaction 5 at present. The pyrolysis of cyclobutanecarboxaldehyde is known to proceed according to eq 5[9] but the photochemical decomposition of dihydropyran (I) to give the same products is by no means ruled out. In fact there is no evidence from this study that indicates that an electronically excited state of dihydropyran (I) is produced on sensitization by Hg ($^3P_1$) atoms.

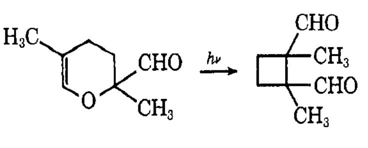


(4)

(5)

Cross sections for the quenching of Hg ($^3P_1$) atoms by dihydropyran (I), acrolein, and cyclobutanecarboxaldehyde are not available. Estimates from chemically similar molecules would suggest that all of these quenching cross sections are of the same order of magnitude. This would explain the occurrence of secondary decomposition reactions, *e.g.*, those that lead to products of the formulas $C_7H_{12}O$ and $C_7H_{14}O$, especially when the conversion of dihydropyran (I) exceeded 20%. At lower conversions, the disappearance of a large fraction of dihydropyran (I) must occur by a condensation process which is largely unexplained.

In the photolysis of dimethyldihydropyrancarboxaldehyde (II), the formation of 1,2-dimethylcyclobutane-1,2-dicarboxaldehyde (eq 6) is a ring contraction entirely similar to eq 1 in the five-membered heterocycles. It is noteworthy that in this instance the reaction was initiated by irradiating in the n → π* region of the aldehyde group, which must then have activated the adjacent ether bond. This example also shows that the ring contraction is by no means peculiar to the gas-phase or the mercury-sensitized system.



(6)

The formation of 2,5-dimethyl-3,4-dihydropyran (II) can be explained by a free-radical process of the kind commonly observed in the irradiation of alde-

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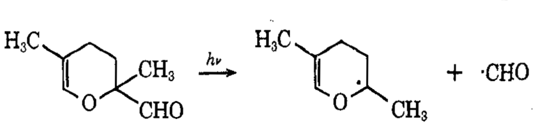
[10] This decomposition may also occur by the secondary excitation of cyclobutanecarboxaldehyde, but at low conversions of dihydropyran (I) such a possibility can be discounted.

hydes.[11] A primary split to give two radicals (eq 7) would set up a chain (eq 8 and 9), the products



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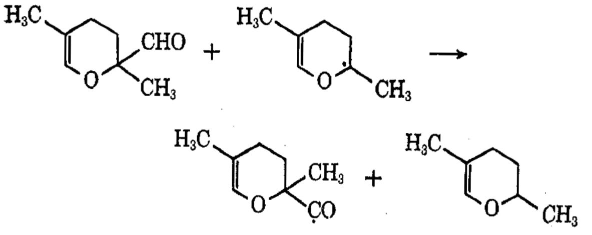

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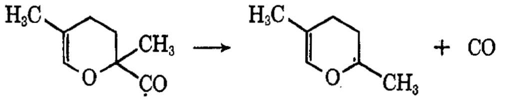
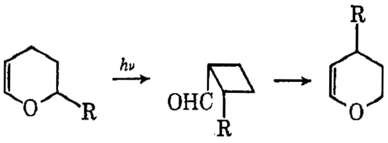


(9)

of which would be CO and dimethyldihydropyran (III). The former undoubtedly was the gas that was evolved in the reaction.

In the 2,3-dihydrofuran system, the photochemical ring contraction is not reversible either thermally or photochemically.[1] This is probably due to the large activation energy that is required to open the cyclopropane ring.[12] In the dihydropyran (I) system the reversal of the ring contraction would regenerate another 2,3-dihydropyran, but with a possible reshuffling of the carbon atoms (eq 10). Since the activation energy for the opening of a cyclobutane ring is almost as large as for a cyclopropane,[12] it is doubtful that this reaction will occur. However, in a search through the literature, the analog of eq 10 is seen in the pyran (V).[13]



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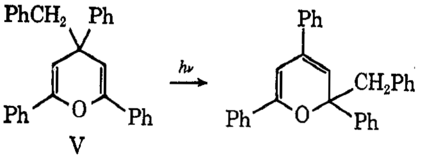
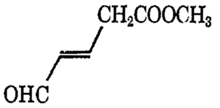
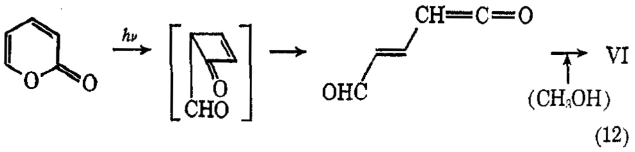


(11)

A ring contraction similar to eq 4 has been reported to occur in 3,4-dihydro-2-pyrones.[14] The formation of a ketene intermediate and the acid VI[15] in the photolysis of 2-pyrone in the presence of methanol may also proceed through a ring contraction mechanism (eq 12).



VI



(12)

Such a process would serve to explain the exclusive formation of the *trans* product, since 3-methylcyclobutene is known to open to *trans*-1,3-pentadiene.[16]

Registry No.—I, 110-87-2; II, 1920-21-4; III, 15990-85-9; *cis*-IV, 23061-80-5; *trans*-IV, 23061-81-6.

Acknowledgment.—The author thanks Mrs. Jane Picone for her skillful technical assistance. The nmr spectra were recorded by Mr. John Powers.

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[11] C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 278.

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[16] R. Srinivasan, *ibid.*, **84**, 4141 (1962).