1,6-Dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (18).
A mixture of 2,5-dihydroxy-7-methoxy-2-(2,4-dioxopentyl)-2,3-dihydro-4*H*-1-benzopyran-4-one (**12**; 0.197 g, 0.640 mmol), 0.7 mL of triethylamine, and 20 mL of THF was heated under reflux for 22 h. The 215 mg of orange residue remaining after evaporation of the solvent was subjected to chromatography (5 g of acidic silica gel, 0–80% ether/hexane) to give 140 mg (80%) of **18** as a yellow solid. Recrystallization (ethanol) gave 47 mg of light yellow crystals, mp 257–258 °C (lit.[9a] mp 255 °C), identical by TLC and NMR and mass spectroscopy with authentic material.

In a second synthesis of **18**, 0.126 g (0.39 mmol) of 1-(2,4-dimethoxy-6-hydroxyphenyl)-1,3,5,7-octanetetraone (**11c**) in 10 mL of methanol was added to excess sodium methoxide in methanol under nitrogen. The dark orange mixture was heated under reflux for 19.5 h, acidified (6 N HCl), and partitioned with water and ethyl acetate. After separation, the aqueous layer was extracted (2×, ethyl acetate), and the combined organic layers were dried ($MgSO_4$) and evaporated to give 102 mg (96%) of **18** as rust-orange crystals, identical by TLC and NMR and mass spectroscopy with authentic material. Recrystallization (ethanol/water) gave rust-orange crystals, mp 255–257 °C.

2-(2,4-Dioxopentyl)-2,5,7-trihydroxy-2,3-dihydrobenzopyran-4-one (19b). 1-(2,4,6-Tribenzoxyphenyl)-1,3,5,7-octanetetraone (**11e**; 0.723 g, 1.28 mmol) dissolved in 50 mL of 1:1 ethanol/THF was added to 70 mg of 10% Pd/C in a Brown hydrogenator and subjected to a H_2 atmosphere for 12 h. Filtration of the catalyst and evaporation of the solvent gave a yellow-brown residue which was partitioned between ethyl acetate and iced dilute HCl. After separation, the aqueous layer was extracted (2×, ethyl acetate), and the combined organic layers were washed (iced 5% $NaHCO_3$) and evaporated to give a yellow-brown oil which solidified in vacuo to give 0.38 g (100%) of crude **19a**, essentially pure by TLC, the NMR spectrum indicating a mixture of **19a** and **19b**. Chromatography (8 g of acidic silica

gel, 0–50% ether/hexane) gave **19b** as a yellow-orange oil which solidified in vacuo. Recrystallization (3×, ether/pentane) gave analytically pure off-white crystals: mp 139.5–141.5 °C (dried in vacuo to remove solvent trapped in crystals); ¹H NMR (CD₃CO-CD₃) δ 2.08 (s), 2.21 (s), 2.79 (d, *J* = 19 Hz), 2.80 (s), 2.99 (s), 3.22 (s), 3.25 (d, J = 19 Hz), 3.85 (br s), 5.82 (s), 5.91 (s), 5.93 (s), 12.02 (s); IR (CH₂Cl₂) 1637 (br) cm⁻¹; mass spectrum, *m/e* (relative intensity) 294 (6), 276 (4), 195 (34), 194 (36), 153 (31), 152 (43), 125 (17), 100 (30), 85 (34), 43 (100).

Anal. Calcd for $C_{14}H_{14}O_6$: C, 57.14; H, 4.80. Found: C, 57.45; H, 4.97.

1,3,6-Trihydroxy-8-methyl-9*H*-xanthen-9-one (20). Aqueous KOH (3 mL, 4 M) was added to a solution of 0.138 g (0.469 mmol) of 2-(2,4-dioxopentyl)-2,5,7-trihydroxy-2,3-dihydro-4*H*-1-benzopyran-4-one (**19b**) in 40 mL of ethanol in a system flushed throughly with nitrogen. The mixture was heated (70–90 °C) for 22.5 h and then acidified; evaporation gave a brown solid residue which was dissolved in ether, washed (dilute HCl, brine), and dried ($MgSO_4$) to give 123 mg (100%) of **20** [mp 280 °C (lit.[9a] mp 285–90 °C)], which gave a gray $FeCl_3$ test and had NMR and mass spectra and TLC identical with those of authentic material.

Photochemistry of 3-Oxacycloalkenes

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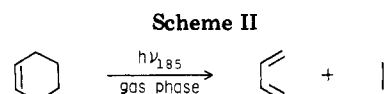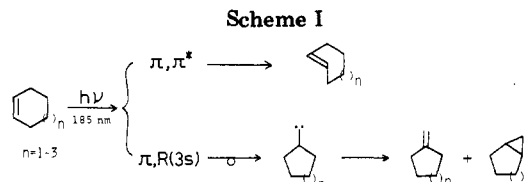
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Direct and sensitized photolyses of 3-oxacycloalkenes **1a–c** has been studied in *n*-pentane and in alcohols. In contrast to the photochemistry of cycloalkenes, the direct photolyses of **1a** and **1b** in pentane gave the products **2, 3,** and **4, 5,** respectively, which are derived from an allylic O–C bond cleavage. In addition, in the case of **1b**, a small amount of the carbene-derived product **6** was also obtained. The seven-membered oxacycloalkene **1c** gave no volatile product upon direct irradiation in pentane. Upon direct or sensitized photolyses in methanol, oxacycloalkenes **1b** or **1c** gave the adducts **7b,c** as major products. Irrespective of the method of excitation, the yield of the adduct in the photolyses in a series of alcohols decreased with decreasing pK_a value of the alcohol which can be explained in terms of the formation and subsequent trapping of the intermediate trans isomer **14** by the alcohol. These results can be rationalized in terms of the reactivities of the π,σ^* and π,π^* states and the increased stability of the Rydberg state.

Recent reports from these laboratories[1,2] have shown that, upon direct irradiation in the liquid phase at 185 nm, medium-sized cycloalkenes (C_6–C_8) undergo cis–trans photoisomerization as well as skeletal rearrangements to give carbene intermediates as illustrated in Scheme I. A similar photochemical rearrangement has also been reported by Kropp and his co-workers[3] upon direct irradi-

(1) (a) Y. Inoue, S. Takamuku, and H. Sakurai, *J. Phys. Chem.*, **81**, 7 (1977); (b) *J. Chem. Soc., Perkin Trans. 2*, 1635 (1977); (c) *J. Chem. Soc., Chem. Commun.*, 423 (1976); (d) *ibid.*, 577 (1975).

(2) R. Srinivasan and K. H. Brown, *J. Am. Chem. Soc.*, **100**, 4602 (1978); *Tetrahedron Lett.*, 3645 (1978).

(3) P. J. Kropp, E. J. Reardon, Jr., E. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, Jr., *J. Am. Chem. Soc.*, **95**, 7058 (1973); T. R. Fields and P. J. Kropp, *ibid.*, **96**, 7559 (1974).

Scheme I

Scheme II

ation of some tri- and tetraalkylethylenes at longer wavelengths. The carbene formation, which appears to be a general reaction path in the direct photolysis of non-

Scheme III

$$\text{1a} \xrightarrow[\text{n-pentane}]{h\nu_{185}} \quad \text{2} \quad + \quad CH_3CH=CHCHO \;\; \text{3}$$

Scheme IV

$$\text{1b} \xrightarrow[\text{n-pentane}]{h\nu} \quad CH_2=CHCHO \;\; \text{4} \quad + \quad \text{5} \quad + \quad \text{6}$$

Scheme V

$$\text{1b} \xrightarrow[\text{MeOH}]{h\nu_{>200}} \quad CH_2=CH_2 \quad + \quad \text{6} \quad + \quad \text{7b}$$

Scheme VI

$$\text{1b} \xrightarrow[\text{ROH}]{h\nu(\text{sens})} \quad \begin{array}{l} \text{7b, R=Me} \\ \text{8b, R=Et} \\ \text{9b, R=i-Pr} \end{array}$$
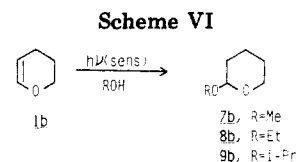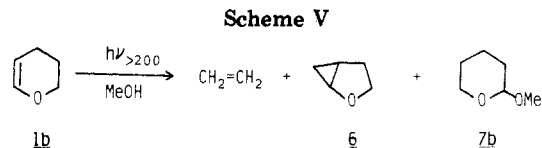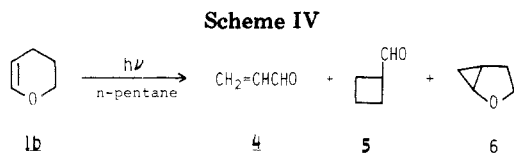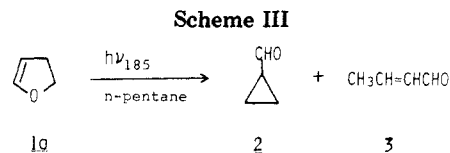
conjugated alkenes, has been accounted for in terms of the cation radical character of the π,R(3s) Rydberg excited state,[1,3] while the cis-trans isomerization may occur from a π,π^* excited state.

In direct photolysis in the gas phase at 185 nm, an additional process has been reported: cyclohexenes suffer photochemical retro-Diels–Alder reaction to give ethylenes and 1,3-butadienes[1b,4] (Scheme II), although this process is completely suppressed in the liquid phase. However, the presence of a nitrogen atom β to the double bond of cyclohexene enhances the reactivity: 1,2,5,6-tetrahydropyridines do undergo a retro-Diels–Alder reaction as the major process even in liquid-phase photolysis at 185 nm.[5]

The photochemistry of 3-oxacycloalkenes is of special interest, since the replacement of an allylic methylene group by an oxygen atom may cause substantial changes in the photochemical behavior and energetics of the C=C bond. Effects such as the stabilization of the highly strained trans isomers of medium-sized cycloalkenes by the flexible C–O–C linkage, resonance stabilization of the Rydberg state, and an enhancement of the photochemical retro-Diels–Alder reaction as in tetrahydropyridines are anticipated. A comprehensive photochemical study of 3-oxacycloalkenes has not been done so far, although one of us has reported the mercury-photosensitized reaction of 3,4-dihydro-2*H*-pyran in the gas phase.[6] We now report results on the direct photolyses at 185, 214, and >200 nm and the singlet- and triplet-sensitized photolyses of five- to seven-membered oxacycloalkenes.

Results

Direct Photolyses in *n*-Pentane. Three different light sources were employed to effect direct photolyses of 3-oxacycloalkenes in pentane. These were a mercury resonance lamp, a zinc resonance lamp, and a high-pressure mercury lamp, which have effective outputs at 185 (+254), 214 (+308), and >200 nm, respectively.

2,3-Dihydrofuran (1a). A pentane solution of 1a (0.01 M) was photolyzed with 185-nm light to give cyclopropanecarboxaldehyde (2) and crotonaldehyde (3) in the ratio of 1:1 (Scheme III). The combined chemical yield was less than 10%. When a solution of 1a was irradiated by the unfiltered light (>200 nm) of a high-pressure lamp, no volatile product was detected by VPC at conversions up to 50%, although a white precipitate due to a polymeric product (which was not characterized) was obtained.

3,4-Dihydro-2*H*-pyran (1b). Direct photolysis at 185 nm of a pentane solution of 1b (0.01 M) gave acrolein (4), cyclobutanecarboxaldehyde (5), and 2-oxabicyclo[3.1.0]-hexane (6) in the ratio of 17:5:1 (Scheme IV), while photolysis at 214 nm gave the same three products in a dif-

(4) Y. Inoue, S. Takamuku, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **48**, 3101 (1975).

(5) R. Srinivasan, J. Studebaker, and K. H. Brown, *Tetrahedron Lett.*, 1955 (1979).

(6) R. Srinivasan, *J. Org. Chem.*, **35**, 786 (1970).

Table I. Photolyses of Dihydropyran 1b and Tetrahydrooxepin 1c[a]

compd	excitation	% conversion	% yield of 7[b]
1b	direct (>200 nm)	47 (53)[c]	9.4 (14.4)[c]
	PhCO$_2$Me sens	51	12.7
	toluene sens	36	6.0
1c	direct (>200 nm)	43	37
	PhCO$_2$Me sens	48	54
	benzene sens	46	34

[a] Oxacycloalkene, 0.05 M; sensitizer, 0.2 M. [b] Yield of 2-methoxytetrahydropyran (7b) or 2-methoxyoxepan (7c) on the basis of the oxacycloalkene consumed. [c] The photolysis was performed in the presence of sulfuric acid at a concentration of 1.58×10^{-5} M, at which no acid-catalyzed addition of methanol was observed after 24 h at room temperature.

ferent ratio of 8:1:1. However, irradiation of a 0.05 M solution of 1b with a high-pressure mercury arc resulted in predominant formation of the oxabicyclohexane 6 in 6.5% yield, together with trace amounts of acrolein (4) and cyclobutanecarboxaldehyde (5). A white polymeric product was also formed upon prolonged irradiation.

2,3,4,5-Tetrahydrooxepin (1c). Only limited experiments on the photolysis at 185 nm and at >200 nm of the seven-membered oxacycloalkene 1c were carried out. It did not give any isomeric product in significant yield at these wavelengths, in contrast to the five- and six-membered cyclic compounds.

Photolyses in Alcohol. Direct and sensitized photolyses of the oxacycloalkenes were performed in a series of alcohols in order to find addition products with the alcohol.

2,3-Dihydrofuran (1a). Direct irradiation at >200 nm of 1a (0.05 M) in methanol merely resulted in consumption of the starting material without formation of detectable amounts of any product. Similar results were obtained in triplet and singlet photosensitizations of 1a (0.05 M) by using toluene (0.2 M) or methyl benzoate (0.2 M) as sensitizers.

3,4-Dihydro-2*H*-pyran (1b). Direct irradiation of 1b (0.05 M) at >200 nm in methanol gave rise to an adduct ether, 2-methoxytetrahydropyran (7b) in 20% yield at 13% conversion, along with ethylene and the oxabicyclohexane 6 in ~28% and 4.9% yields, respectively (Scheme V). The adduct yield on the basis of the alkene consumed decreased to 9.4% at a higher conversion of 47% (Table I).

Singlet and triplet photosensitizations of 1b by methyl benzoate or toluene also yielded the adducts 7b. The adduct yields at comparable conversions are shown in Table I.

The direct irradiation of dihydropyran in methanol, ethanol, and 2-propanol was performed in a merry-go-round apparatus in order to examine the effects of the acidity of the alcohol on the reaction. The corresponding

Table II. Relative Rates[a] of Adduct Formation in the Photolysis of Dihydropyran 1b[b] and Tetrahydrooxepin 1c[c]

compd	solvent (pK_a)	prod-uct	excitation		
			direct	$PhCO_2Me$ sens	toluene or benzene sens
1b	MeOH (15.5)	7b	1	1	1
	EtOH (15.9)	8b	0.64	0.84	0.75
	i-PrOH (~18)	9b	0.33	0.42	0.32
1c	MeOH (15.5)	7c	1	1	1
	EtOH (15.9)	8c	0.39	0.23	0.41
	i-PrOH (~18)	9c	0.08	0.03	0.07

[a] The rate of 7b or 7c formation in methanol was taken as unity in each excitation method. [b] 1b, 0.05 M; sensitizer, 0.2 M; conversion rate <10%. [c] 1c, 0.05 M; sensitizer, 0.2 M; conversion rate <12%.
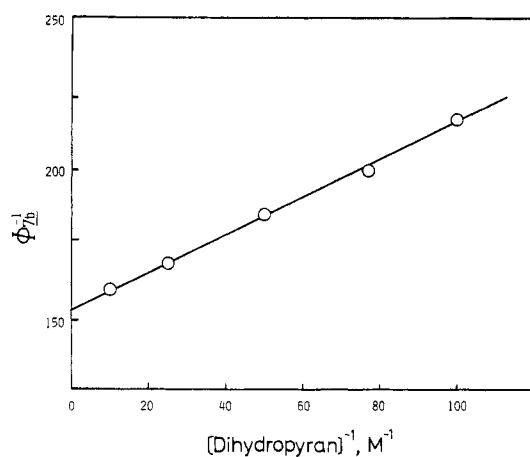
Table III. Methyl Benzoate Photosensitization of 1b and 1c in Methanol[a]

compd	ϕ_{-1}[b]	ϕ_7[c]
dihydropyran 1b	0.037	0.006
tetrahydrooxepin 1c	0.33	0.21

[a] 1b, 0.048 M; 1c, 0.042 M; methyl benzoate, 0.2 M; irradiation time, 35 min. [b] Quantum yield of disappearance of 1. [c] Quantum yield of production of adduct 7.

Table IV. $kq\tau$ Values and Limiting Quantum Yields (ϕ_7^∞) of the Adduct 7 in Methyl Benzoate Sensitization in Methanol

compd	$kq\tau$	ϕ_7^∞
dihydropyran 1b	240	0.0067
tetrahydrooxepin 1c	215	0.23
cis-cyclooctene[a]	130	0.42[b]

[a] Reference 7. [b] $\phi^\infty_{cis-trans}$.

Scheme VII

7c, R=Me
8c, R=Et
9c, R=i-Pr

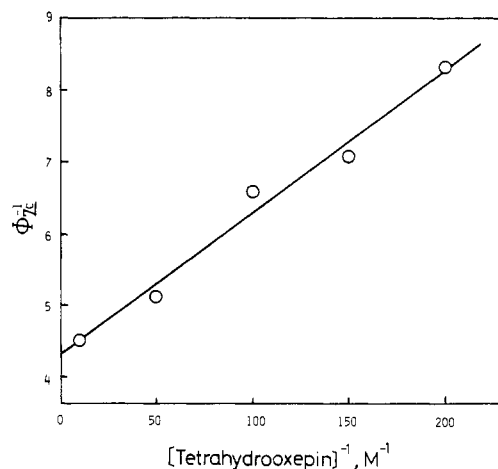**Figure 1.** Methyl benzoate sensitization of dihydropyran 1b in methanol.
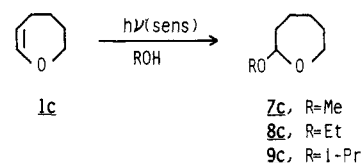
Figure 2. Methyl benzoate sensitization of tetrahydrooxepin 1c in methanol.

ethers **7b–9b** were obtained (Scheme VI). The product yields were proportional to the exposure time in the initial stages of reaction, indicating that the products are the primary photoproducts. The initial rate of adduct formation, however, differed substantially in each case even though the starting material was consumed at a comparable rate in every case. The singlet and triplet photosensitizations of dihydropyran in these alcohols were also performed in a similar manner. As can be seen from Table II, the relative rates of adduct formation in the initial states are quite similar in all three cases, viz., direct photolysis, methyl benzoate sensitization, and toluene sensitization.

The direct photolysis in methanol was run in the absence and in the presence of added sulfuric acid of 1.58 × 10⁻⁵ M concentration. An acid-catalyzed thermal addition of methanol to dihydropyran was not observed after the solution was left for 24 h at room temperature in the dark. The photolysis in acidic methanol solution produced the adduct ether **7b** in an improved yield as shown in Table I.

The singlet photosensitization by methyl benzoate (0.2 M)[7] in methanol was further investigated at a variety of

concentrations of dihydropyran. The quantum yields of disappearance of **1b** and formation of the adduct **7b** were measured (Table III). As can be seen from Figure 1, the plot of reciprocal quantum yield of **7b** against reciprocal concentration of **1b** gave a good linear relationship over the entire concentration range employed, which indicated the involvement of a single excited state of the benzoate in the present photolysis.

2,3,4,5-Tetrahydrooxepin (1c). Direct photolysis of **1c** (0.05 M) in methanol yielded 2-methoxyoxepan (**7c**) as the principal product in 37% yield (Scheme VII). Singlet and triplet photosensitizations by methyl benzoate (0.2 M) and benzene (0.2 M) also afforded the methoxyoxepan **7c** in 54% and 34% yields, respectively, at a comparable conversion. These yields are much better than those for the photolyses of dihydropyran **1b** (Table I).

The direct and sensitized photolyses were run in methanol, ethanol, and 2-propanol to give the corresponding ethers **7c–9c**, and the initial rates of ether formation were measured in every case. The relative rates shown in Table II are similar in all cases to those of the direct and sensitized photolyses.

(7) Y. Inoue, Y. Kunitomi, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 1024 (1978); *J. Chem. Soc., Perkin Trans. 2*, 1672, 1678 (1980).

Scheme VIII

Scheme IX
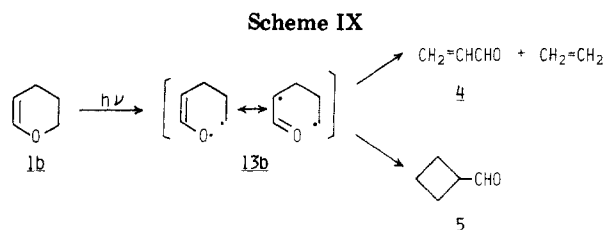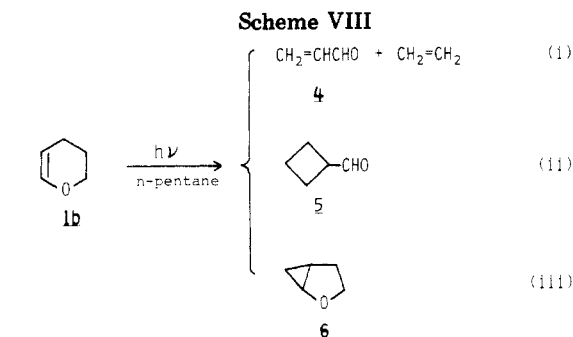
The quantum yields of disappearance of 1c and formation of 7c were measured in the methyl benzoate sensitization of 1c in methanol (Table IV). Upon methyl benzoate sensitization, a Stern–Volmer study was performed by changing the concentration of tetrahydrooxepin 7c. The result is shown in Figure 2.

Discussion

When a pentane solution of dihydropyran 1b is photolyzed with 185- or 214-nm light, three processes are observed (see Scheme VIII). However, when radiation from a high-pressure mercury lamp is used to photolyze dihydropyran in pentane or in methanol, only the carbene-derived product 6 (and ethylene)[8] is obtained in significant yield. It is obvious that, due to the large output of the lamp at longer wavelengths, both acrolein (4) and cyclobutanecarboxaldehyde (5) are quickly decomposed, while oxabicyclohexane 6 builds up.

The process i is formally a retro-Diels-Alder reaction which has been reported in the liquid-phase direct photolysis of 1,2,5,6-tetrahydropyridines[5] but only in the *gas-phase* photolysis of cyclohexenes.[1b,4] Processes i and ii may go through the same intermediate 13b generated by an allylic O–C bond cleavage (Scheme IX). It is interesting to note the similarity between the direct photolysis in the liquid phase and mercury-sensitized photolysis of 1b in the gas phase,[6] although the excited state responsible for the cleavage and the spin state of the resulting biradical 13b would be different in these two instances.

Similar allylic O–C bond cleavage and the subsequent recombination and hydrogen shift of the resulting biradical 13a may lead to the photoisomerization of dihydrofuran 1a as illustrated in Scheme X.

A smaller bond-dissociation energy for the allylic O–C bond (68 kcal/mol)[9] compared to that of the allylic C–C bond (72 kcal/mol)[9] and resonance stabilization of the biradical 13 may account for the facile photochemical

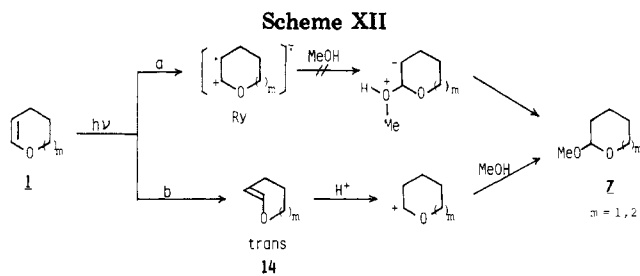**Scheme X**

Scheme XI
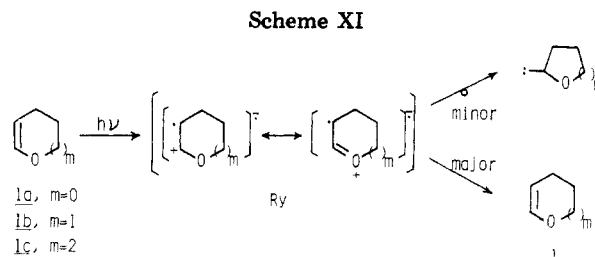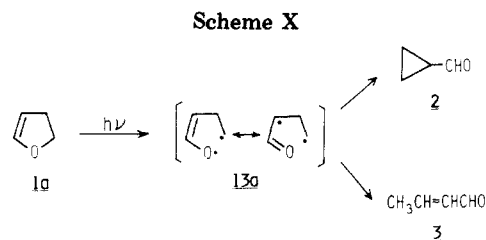
allylic O–C bond cleavage of 1a,b in the liquid phase. The excited state responsible for this process might be the π,π^* excited singlet state by analogy to the gas-phase photolysis of cyclohexenes.[1b,4] However, when an oxygen atom is placed adjacent to the double bond, the lone pairs of electrons on the oxygen do interact with the π system of the double bond. Rossi[10] has carried out INDO-S calculations on methyl vinyl ether to reveal the excited states and energy levels in the vinyl ether system for a geometry that approximates that of the cyclic molecules that have been investigated here. It was found that in regions from 220 to 185 nm there are at least two transitions which correspond to π,π^* and π,σ^* excitations. The π,σ^* transition can lead to the break of an allylic O–C single bond which is seen as the important process in the photolysis of dihydropyran 1b at 185 nm. Further support for the π,σ^* excited state may be found in the fact that a π,π^* singlet state of 1b generated in the benzoate photosensitization described below does not give the retro-Diels-Alder reaction but undergoes only cis–trans isomerization. Rossi has also found that the energies of these transitions and their intensities are a sensitive function of the geometry of the C=C—O—C group. This would mean that the size of the ring in which the unsaturated ether group is present, and therefore its geometry, would affect the spectroscopy significantly. The effect would also explain the poor yields of the allylic cleavage in the photolyses of the five- and seven-membered rings, 1a and 1c.

In sharp contrast to the direct photolysis of cycloalkenes,[1,2] the photorearrangement via a carbene intermediate is apparently a minor process in the direct photolysis of oxacycloalkenes. It is unlikely that the Rydberg bands of oxacycloalkenes lie at wavelengths shorter than 185 nm, since the replacement of an allylic methylene group of cycloalkene by an oxygen atom is believed to decrease the energy of the Rydberg state. We conclude that the direct irradiation even at 214 nm does generate a Rydberg state of oxacycloalkenes as well as π,π^* and π,σ^* excited singlet states. The question is why the Rydberg state of oxacycloalkenes, unlike those of cycloalkenes, does not give rise to rearrangement products in significant yield. This distinctive result could possibly be attributed to resonance stabilization of the Rydberg state of oxacycloalkenes, which is not available for cycloalkenes. The resonance stabilization of the Rydberg state diffuses the positive charge on the carbon atom over the adjacent ox-

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(8) It is evident that the direct photolysis of 1b gives ethylene along with acrolein 4, although the formation of ethylene was confirmed only in the photolysis in methanol but not in pentane due to incomplete separation on VPC from the solvent peak.

(9) R. T. Sanderson, "Chemical Bond and Bond Energy", Academic Press, New York, 1976, p 163.

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(10) A. R. Rossi, private communication.

Scheme XII

Scheme XIII

$$Bz \xrightarrow{h\nu} {}^1Bz \tag{1}$$

$$^1Bz \rightarrow Bz, {}^3Bz \tag{2}$$

$$^1Bz + 1 \rightarrow Ex \tag{3}$$

$$Ex \rightarrow {}^1p + Bz \tag{4}$$

$$Ex \rightarrow 1^+\cdot + Bz^-\cdot \tag{5}$$

$$Ex \rightarrow 1 + Bz \tag{6}$$

$$^1p \rightarrow 1 \tag{7}$$

$$^1p \rightarrow 14 \tag{8}$$

$$14 + MeOH \rightarrow 7 \tag{9}$$

ygen atom, diminishing the cation radical character of the Rydberg state, as illustrated in Scheme XI. This stabilization in turn reduces the reactivity of the Rydberg state to regenerate the starting oxacycloalkenes instead of giving the carbene-derived products.

Direct photolysis with unfiltered radiation from a high-pressure mercury lamp was carried out in methanol in order to trap a highly strained trans isomer of the oxacycloalkenes. Upon direct irradiation in methanol, only six- and seven-membered oxacycloalkenes gave the adduct ethers **7b,c** as principal products. The adduct formation is comparable to the allylic bond cleavage for six-membered oxacycloalkene **1b** and is predominant for the seven-membered **1c**. On the other hand, direct photolysis of five-membered oxacycloalkene **1a** in methanol merely resulted in consumption of the starting material without formation of adduct ether, which suggests that the C–O–C linkage is not sufficiently flexible to allow the generation of trans-oxacyclopentene **14a** (see Scheme XII).

As can be seen from Table II, the direct irradiations of **1b** and **1c** in a series of alcohols show that the initial rate of adduct formation increases with increasing acidity of the alcohol. The irradiation in acidic methanol also enhances the product yield as shown in Table I. Contrary to the idea that the adducts might be attributable to the nucleophilic addition[3,11] of alcohol to the electron-deficient double bond of the Rydberg state (path a in Scheme XII), the above-mentioned ring-size dependence of reactivity and the effects of acidity of the medium clearly rule out the incorporation of path a and, rather, indicate the intermediacy of the trans isomer **14** as a precursor to the adduct; the trans isomer is highly strained and therefore easily trapped by protonation as is demonstrated in the photochemistry of cycloalkenes.[1,2]

Sensitized photolyses of **1b,c** in methanol also yielded the adduct ethers **7b,c** although the sensitized photolyses in pentane resulted in the loss of 1 and the formation of uncharacterized polymers. Singlet sensitization by methyl benzoate gives a higher adduct yield than direct and triplet-sensitized photolyses do. As shown in Table II, the relative rates of adduct formation in the sensitized photolyses are comparable to those in the direct photolysis. This strongly suggests the presence of a trans isomer as a common intermediate in both the direct and the sensitized photolyses.

The photosensitization by methyl benzoate was further investigated, since aromatic carboxylic esters have recently been demonstrated to lead to singlet sensitization of cyclooctene[7] to activate the cyclooctene nonvertically via an exciplex to a twisted singlet state, which in turn decays into cis- or trans-cyclooctene in the same decay ratio as that observed in the direct photolysis of cyclooctene at 185 nm. The sequence shown in Scheme XIII can be written
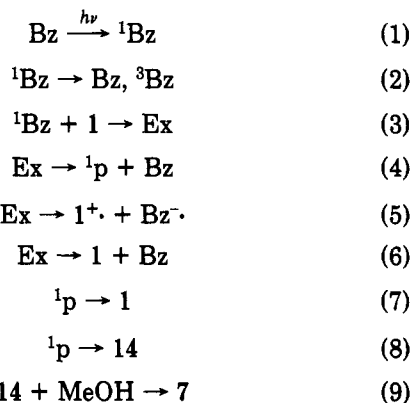
for the singlet sensitization of oxacycloalkenes, where Bz, Ex, and ¹p represent methyl benzoate, exciplex, and the twisted singlet state of oxacycloalkene, respectively, and the superscript refers to the spin state. Electron-transfer process 5 is added to the standard scheme for singlet sensitization,[7] since oxacycloalkenes have lower ionization potentials than cycloalkenes, and a polar solvent is used. The resulting cation radical $1^+\cdot$ may initiate cationic polymerization of oxacycloalkenes.

A steady-state treatment of the above sequence gives the expression shown below for the reciprocal quantum yield

$$1/\Phi_7 = \left(\frac{k_4 + k_5 + k_6}{k_4}\right)\left(\frac{k_7 + k_8}{k_8}\right)\left(1 + \frac{k_2}{k_3[1]}\right)$$

of the adduct 7. From the intercepts (I) and the slope (S) in Figures 1 and 2, the ratio I/S is calculated to give the k_3/k_2 or, more conventionally, the $k q\tau$ values for **1b** and **1c**. The results are shown in Table IV along with the $k q\tau$ value for the methyl benzoate sensitization of cyclooctene in methanol.[7] The $k q\tau$ values for **1b** and **1c** are comparable to each other and are much higher than that for cis-cyclooctene, a typical dialkylethylene. This higher quenching efficiency should be attributed to the facile interaction of the electron-rich oxacycloalkenes 1 with methyl benzoate in its excited singlet state, since the presence of charge-transfer interaction has been demonstrated in the methyl benzoate photosensitization of simple alkenes.[7]

The inverses of the intercepts in Figures 1 and 2 give the limiting quantum yield of 7, i.e., Φ_7^∞. As can be seen from Table IV, the limiting quantum yield for **1b** is surprisingly low in comparison with that for **1c**. Table III also reveals a similar tendency of the quantum yield of the adduct 7 at a finite concentration of 1. A part of the smaller quantum yield of disappearance of **1b** can be interpreted in terms of the decay processes 6 and/or 7 which regenerate the starting oxacycloalkene 1. Even when the smaller quantum yield of the disappearance of the starting material in the photolysis of **1b** is taken into account, the chemical yield of **7b** amounts to only one-sixth of the dihydropyran **1b** that disappeared, while the yield of **7c** goes up to two-thirds of the tetrahydrooxepin **1c** that is used up. These lower quantum and chemical yields of the adduct **7b** upon singlet sensitization of **1b** can be understood in the framework of the competitive energy-transfer process 4, electron-transfer process 5, and decay process 6 in the exciplex. The greater strain in the twisted singlet ¹p of **1b** decelerates the energy transfer to render the electron-transfer and decay processes dominant. Cationic polymerization of **1a,b** initiated by the cation radical $1^+\cdot$ accounts for the low chemical yield of the adduct 7 and the formation of some polymeric products.

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In conclusion, the photochemistry of 3-oxacycloalkenes may be summarized as follows: (1) the π,σ^* excited singlet state which is revealed to be characteristic of the vinyl ether system leads to an allylic O–C bond cleavage; (2) the Rydberg excited state is much less reactive than that of cycloalkenes due to resonance stabilization; (3) the π,π^* excited singlet and triplet states give rise to the trans isomers as principal products in the six- and seven-membered oxacycloalkenes.

Experimental Section

Materials. **2,3-Dihydrofuran (1a)** was synthesized by the α-benzoyloxylation of tetrahydrofuran with *tert*-butyl perbenzoate in the presence of copper(I) chloride[12] and the subsequent thermal decomposition of the resulting 2-tetrahydrofuranyl benzoate in a distillation apparatus.[13] Redistillation over potassium carbonate gave the dihydrofuran of >98% purity.

3,4-Dihydro-2*H*-pyran (1b) was obtained commercially (Tokyo Kasei Co. or Aldrich Chemical Co.) and was fractionally distilled prior to use.

2,3,4,5-Tetrahydrooxepin (1c) was prepared in a three-step process starting from 1,6-hexanediol.[14] Activated alumina (60 g) and 1,6-hexanediol (100 g) were placed in a distillation apparatus fitted with a heating mantle, and the mixture was heated up to 250–270 °C until distillation ceased (4 days) to give 90 g of distillate. The organic layer was separated from the distillate, dried over potassium carbonate, and then distilled over sodium hydride to give 44 g (52%) of oxepan. The tetrahydrooxepin (1c) of 96% purity was prepared from the oxepan according to the same procedures[11,12] employed in the synthesis of 1a.

All the products were characterized by means of IR, ^{13}C NMR, and mass spectra.

Sensitizers, i.e., benzene, toluene, and methyl benzoate, were fractionally distilled prior to use. Methanol used as a solvent was refluxed over magnesium turnings and distilled. *n*-Pentane was shaken with concentrated sulfuric acid, washed with water, dried over potassium carbonate, and then distilled.

Direct Photolyses. Irradiations were carried out in *n*-pentane solution (10^{-2} M) at 185 (+254) nm with a hot cathode mercury resonance lamp (35 W), at 214 nm with a Phillips Zn resonance lamp, and at >200 nm with Hanovia 450-W, high-pressure, Hg lamp. Following photolysis, the solvent was removed on a spinning-band distillation column, and the residue was distilled bulb-to-bulb in a vacuum. The distillate which contained all of the unreacted material and the volatile products was separated into its components by preparative VPC.

Photolysis of 2,3-Dihydrofuran (1a). A 0.6-g sample of 1a in 150 mL of pentane was irradiated for 96 min. The conversion was ca. 50%. Following the workup, separations were carried out on a Carbowax column (12 ft × 0.25 in.) at 60 °C. Two isomeric products (*m/e* 70) were collected in ca. 5% yield each. They were identified as 2 and 3 from a comparison of their infrared spectra with those of authentic samples.[15,16]

Photolysis of 3,4-Dihydro-2*H*-pyran (1b). A 0.6-g sample of 1b in 150 mL of pentane was irradiated for 120 min. Considerable gas evolution was noted. Following the workup, separation was carried out on a temperature-programmed Carbowax column (12 ft × 0.25 in.) at 80–130 °C. The major product *before* workup was found to be lost during distillation. This was identified as acrolein by comparison of its spectral properties with

those of an authentic sample. The second product, which was a major constituent (40 mg) in the worked up sample, was cyclobutanecarboxaldehyde (5) as shown by comparison of its infrared and NMR spectra with those of an authentic sample made by mercury photosensitization.[6] A third product (6 mg) which was isomeric with 1b (*m/e* 84) has infrared absorptions at 1120 (vs, C–O–C) and 3030 (m, cyclopropyl) cm⁻¹ and NMR absorptions (complex) from δ 4 to –0.2. Since the material had no unsaturation, it had to be bicyclic. The ether absorption in the infrared indicated that the oxygen was located in a cyclopentane rather than a three- or four-membered ring. A comparison of the spectrum to that of 2-oxa[4.1.0.0³,⁵]tricycloheptane[17] showed striking similarities between the two compounds. The structure 6 was assigned to the product on this basis. The compound tended to rearrange even in a gas chromatograph to carbonyl compounds.

Photolysis of 1b at 214 nm indicated that the distribution of products was 8:1:1 4/5/6.

Throughout the direct photolyses in methanol, an unfiltered, high-pressure, Hg lamp was used as a light source. A methanol solution of 3-oxacycloalkene (0.05 M) containing cyclooctane (2 × 10⁻³ M) as an internal standard was charged into a quartz tube, flushed with nitrogen gas at –10 °C, and then irradiated at room temperature in a merry-go-round apparatus. The product yields following irradiation were determined by periodic analysis of aliquots on VPC over a 5-ft column of Apiezon L grease. The FID responses on VPC were calibrated for each compound.

The preparative-scale photolyses of 1b and 1c were carried out in order to obtain the adduct ethers 7. A methanol solution (80 mL) containing 0.1 M dihydropyran 1b was placed in an annular vessel, flushed with nitrogen gas, and then irradiated for 20 h by using a 300-W, high-pressure, Hg lamp. The photolysate was poured into saturated aqueous sodium chloride solution and extracted three times with *n*-hexane. The combined extracts were dried and distilled fractionally to give 2-methoxytetrahydropyran (7b) in 10% yield. The product showed identical IR, ^{13}C NMR, and mass spectra with those of an authentic sample synthesized independently. The direct irradiation of tetrahydrooxepin 1c in methanol and a similar subsequent treatment gave 2-methoxyoxepan (7c) in 40% yield, the spectra of which were exactly identical with those of an authentic sample.

Sensitized Photolyses. Photosensitizations were carried out in methanol or in *n*-pentane in the presence of sensitizer (0.2 M). The apparatus and the procedures were similar to those employed in the direct photolyses in methanol.

The chemical actinometer used was the methyl benzoate sensitized cis–trans photoisomerization of cyclooctene,[7] the quantum yield of which has been calibrated by a potassium ferrioxalate actinometer.[18]

Independent Syntheses of Authentic Samples. 2-Methoxy-, 2-ethoxy-, and 2-isopropoxytetrahydropyrans (7b–9b) were prepared from 3,4-dihydropyran in an acid-catalyzed addition of the corresponding alcohol in the dark. To an equimolar mixture of dihydropyran (2 g) and an alcohol was added 1 drop of hydrochloric acid, and the mixture was allowed to stand for 24 h at room temperature. The reaction mixture was distilled over potassium hydroxide to give the corresponding alkyl 2-tetrahydropyranyl ether. The yields of the adduct ethers 7b–9b were 67, 82, and 82%, respectively. The products were spectroscopically identified by IR, NMR, and mass spectra.

2-Methoxyoxepan (7c) was prepared in a similar manner from tetrahydrooxepin 1c and methanol. The product was identified by IR, NMR, and mass spectra.

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(17) R.S. thanks Professor Harold Shechter of The Ohio State University for these spectra.
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