(14) P. Kovacic and S. S. Chudhary, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, N.Y., 1973, p 35.

(15) The IR stretching frequency of a double bond in conjugation with a carbonyl is very strong. See R. T. Conley, "Infrared Spectroscopy", Allyn and Bacon, Boston, Mass., 1966, p 99. The double bond stretching frequency was too weak to be observed at normal concentration in the 1,4-products where the carbonyl is not in conjugation.

(16) Bothner-By has investigated long-range coupling in a large number of butadienes and found that 1,4-vinyl protons in the trans,trans configuration show coupling constants ranging between 1.3 and 1.9 Hz, while cis,trans and cis,cis 1,4-vinyl protons show coupling between 0.5 and 0.9 Hz. Since the protons on the α,β carbons of **5** show a trans coupling (J = 14.2 Hz), the long range coupling of 0.6 Hz on the vinyl proton at δ 6.23 indicates a 1,4-cis,trans coupling in the trans,trans diene (**5**). See A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3445, 3451 (1965); A. A. Bothner-By and D. Jung, *ibid.*, **90**, 2342 (1968); A. A. Bothner-By and E. Moser, *ibid.*, **90**, 2347 (1968); A. A. Bothner-By and D. F. Koster, *ibid.*, **90**, 2351 (1968).

Liquid-Phase Photolysis of Dioxane

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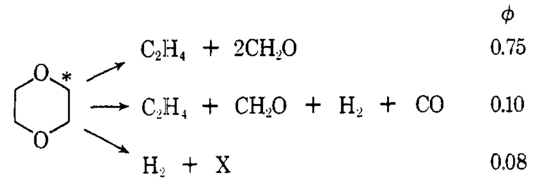
The photolysis of neat liquid-phase dioxane with a medium-pressure mercury lamp has been shown to give, in addition to gaseous products, a complicated mixture of liquid and solid products. The liquid product mixture has been partially separated, and evidence for the structures of nine previously unreported hydroxy ether and carbonyl containing components is presented. The products are postulated to result from initial CO bond scission followed by subsequent reactions of the radicals produced and from secondary photolyses. The photoproducts are not formed in any significant amount when either dioxane or dioxyldioxane is irradiated in ethanolic solution.

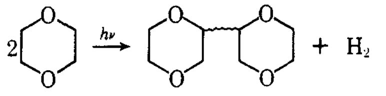
The photochemistry of simple aliphatic ethers in the gas phase has been studied by numerous workers, and a combination of radical and molecular processes reported.[1] In particular, the gas-phase photolysis of dioxane has been studied by Parrish and co-workers, both at 1470 Å[2] and with a megawatt ruby laser.[3] At 1470 Å, three processes were observed, and are given with their quantum yields in Scheme I. The laser-promoted decomposition yielded ethylene, CO, and H_2 in the ratio 1:2:2. It was postulated that these products were formed from a vibrationally excited ground state of dioxane, and that the hydrogen resulted from a molecular elimination, rather than via radical abstraction.

Scheme I



Considerably less attention has been given to the solution or neat liquid-phase photolysis of ethers, probably owing to the greater experimental difficulty of irradiating in the 200-nm region or below, where alcohols and ethers have their principal absorption band (n → σ^*). This is unfortunate because these compounds have often been used as solvents for photochemical reactions using low- and medium-pressure mercury lamps capable of emitting small to moderate amounts of radiation in this region.

Pfordte studied the neat liquid-phase photolysis of several aliphatic ethers,[4] and reported that dioxane, after irradiation for 24 h with a medium-pressure mercury lamp, yields gaseous, liquid, and solid products. The major gaseous products were identified as H_2, CO, CH_4, C_2H_4, and C_2H_6. Minor amounts of other saturated and unsaturated hydrocarbon gases were also detected. The liquid product was not analyzed, but the solids were shown to be the racemic and meso forms of dioxyldioxane (1), for which the following mechanism of formation was advanced (eq 1).

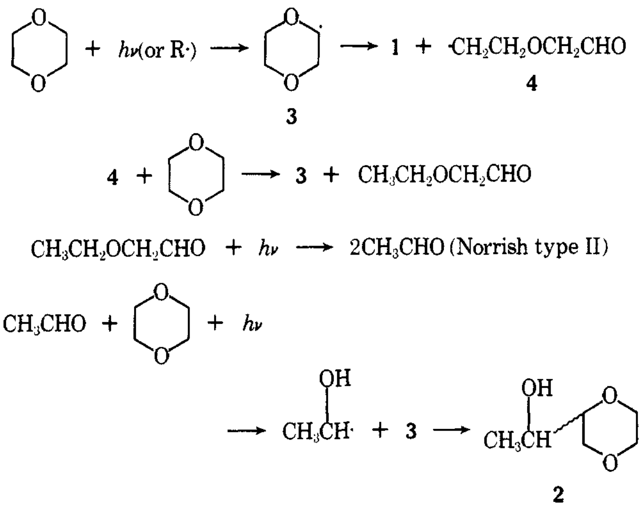


(1)

1

Mazzocchi and Bowen have recently reported[5] two additional products from the 200-h photolysis of neat dioxane, the meso and racemic forms of 1-hydroxyethyldioxane (2), which they rationalize as forming via Scheme II. There is precedent for the third step in Srinivasan's photolysis of methoxyacetone[6] which efficiently yields formaldehyde and acetone. The photoreduction of acetaldehyde in dioxane was demonstrated by Mazzocchi and Bowen to occur readily.

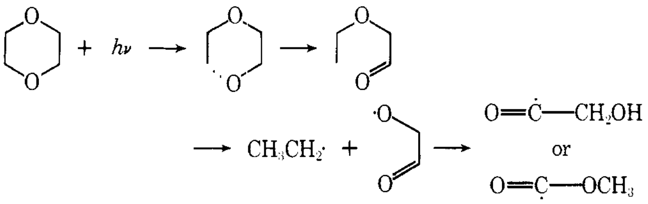
Scheme II



Both Pfordte and these later workers used medium-pressure mercury lamps which have an approximate lower wavelength limit of 190 nm. It seemed to us unlikely that a CH bond, which normally does not absorb above 150 nm (considering the absorption spectra of simple alkanes), could be broken in the primary step of this photolysis, as claimed, particularly since rupture of a CO bond in an n → σ^* process, occurring at slightly below 200 nm, is well documented.[7] Direct photochemical CH bond scission, in contrast to H *abstraction*, as occurs in the Norrish type II process or in Hg-sensitized decompositions, is usually limited to gas-phase or low-temperature matrix photoreactions where collisional deactivation of vibrationally excited species is less efficient.[8] Yang[9] has reported the cleavage of the α-CH bond in simple alcohols on photolysis at 185 nm with a low-pressure mercury lamp, through high-purity fused silica. We will discuss this report in more detail presently.

In an experiment very relevant to our work, McIntosh and Wan[10] conducted ESR studies on UV-irradiated dioxane and THF at 77 K. The resulting spectra showed none of the prominent triplet patterns which would have been attributable to splitting by the protons of the methylene group in a diradical derived from ring opening at the carbon–oxygen bond, but rather they suggest that both THF and dioxane produce ethyl radicals during photolysis. The sequence shown in Scheme III was proposed to account for the formation of ethyl radicals from dioxane. Subsequent abstraction of H· from dioxane by the ethyl radical could account for the ethane observed by Pfordte among the gaseous photoproducts. This scheme also provides an alternative, and, we think, preferable,[11] pathway for the formation of Mazzocchi and Bowen's ethoxyacetaldehyde.

Scheme III



The previous work, then, on the dioxane photolysis strongly suggested that low steady-state concentrations of carbonyl compounds and various radicals could be present when dioxane is used as a solvent in a photochemical reaction. In view of the well-known tendency of carbonyl compounds to act as triplet transfer agents, we decided to undertake a reexamination of the neat dioxane photolysis with particular emphasis on the liquid photoproduct. We found this product to be an exceedingly complex mixture, but high-resolution mass spectroscopy and GC/MS allowed us to deduce the structures, with varying degrees of certitude, of nine hitherto unreported products. Authentic samples of four of these, ethylene glycol, glycolaldehyde, dioxanone, and hydroxymethyldioxane, were obtained, and their spectral properties were completely consistent with those of the corresponding photoproducts. Attempts to synthesize the remaining five compounds were unsuccessful. We suggest that the photoproducts arise from a combination of radical and/or molecular fragmentations and secondary photolyses. Interestingly, when dioxane was irradiated in ethanol, only insignificant amounts of photoproducts were formed.

Results

Neat dioxane was irradiated through quartz with a 450-W medium-pressure mercury lamp. The complexity of the product mixture was found to be greatly dependent on the duration of the photolysis. Thirty minutes appeared to be the minimum irradiation time that would allow us to recover, by preparative gas chromatography, enough material for mass spectroscopic analysis, and all of the products reported herein were obtained from 30-min photolysates. The yield of dioxyldioxane (henceforth called dimer) increased steadily with irradiation time, and after 24 h, the dimer was the major nongaseous product.

Fifteen hundred milliliters of purified and degassed dioxane was divided into 30-mL portions placed in quartz tubes under nitrogen. The filled tubes, which because of the formation of gaseous products could not be sealed, were then irradiated under nitrogen, five or six at a time. The combined photolysate was distilled at atmospheric pressure, under nitrogen, to remove unchanged dioxane and gaseous photoproducts. A gas chromatogram of the remaining liquid (1.74 g) showed six or seven major, and approximately 50 minor, components. This mixture was separated by preparative gas chromatography into six fractions, numbered 1 through 6 in order of their increasing retention time. Fractions 2, 4, 5, and 6 were of sufficient volume to be analyzed spectroscopically as follows.

Table I. Mass Spectrum of Fraction 2 at Two Ionizing Voltages

70 eV		10 eV	
m/e	Rel intensity	*m/e*	Rel intensity
62	3	62	46
61	11	61	10
60	8	60	61
45	100	45	27
43	50	44	25
31	44	43	38
30	8	33	74
29	36	32	29
28	25	31	100

Fraction 2. The infrared spectrum of fraction 2 exhibited a strong absorption at 3330 cm^{-1}, suggesting multiple OH groups, a weak band at 2940 cm^{-1}, a broad band (ca. 22 cm^{-1} wide at its minimum) of only moderate intensity centered at about 1705 cm^{-1}, and other weak bands at 1200, 1090, 1050, and 890 cm^{-1}. The 1125-cm^{-1} band normally associated with the dioxane ring was missing. The NMR spectrum ($CDCl_3$) showed strong singlets at δ 2.75 and 3.75 (area ratio ca. 1:1.4), a pair of multiplets centered at δ 3.9 and 4.3 (each about equal in area to the δ 3.75 peak), and a singlet at δ 8.14 having an area about one-quarter of that of the δ 3.75 peak. When the probe temperature was raised to 75 °C, the δ 2.75 peak moved upfield to δ 2.15, suggesting an OH resonance, while the other peaks remained in their original positions. The mass spectrum of fraction 2 was recorded at ionizing voltages of 70 and 10 eV (Table I). The low voltage scan suggests that at least two components having nominal molecular weights of 62 and 60 are present in fraction 2. Mass measurements on these two peaks gave 62.0397 and 60.0217. The theoretical values for $C_2H_6O_2$ and $C_2H_4O_2$ are 62.0368 and 60.0211, respectively, and these compounds are postulated to be ethylene glycol and glycolaldehyde (**5**), $HOCH_2CHO$. The intense peaks at *m/e* 45 and 43, then, result from the loss of OH from the parent ions,[12] and the largest peak, at *m/e* 31, is due to CH_2OH^+. The presence of ethylene glycol was confirmed by comparison of the IR and NMR spectra and GC retention time with those of an authentic sample. The structure assignment of compound **5** is based partly on negative evidence and chemical intuition and partly on the NMR and mass spectra of an authentic sample. The only other plausible structures for $C_2H_4O_2$ are methyl formate and acetic acid. The former might have been considered to arise via H abstraction by the $O{=}\dot{C}CH_3$ radical postulated in Scheme III. The NMR spectrum of methyl formate exhibits an aldehyde resonance at δ 8.08 and a methyl resonance at δ 3.77, very near the methylene resonance of ethylene glycol (ca. δ 3.7). The infrared spectrum[13] of methyl formate shows C=O absorption at 1727 cm^{-1} which should have been distinguishable from the 1705-cm^{-1} peak observed in the spectrum of fraction 2. Finally, a large doublet at 1212, 1163 cm^{-1} in the spectrum of methyl formate is missing from the spectrum of fraction 2.

Table II. Mass Spectrum of Fraction 4 at Two Ionizing Voltages

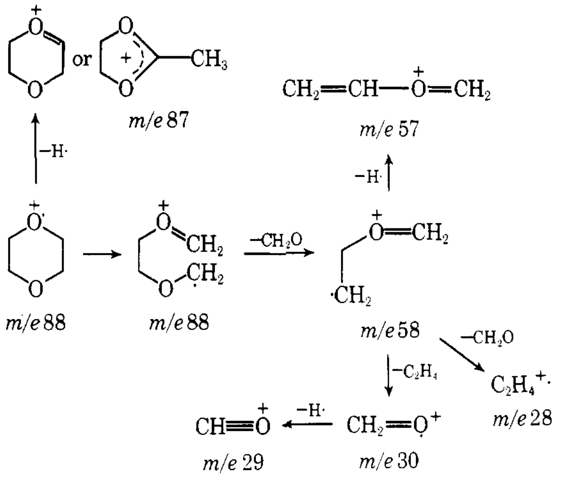
70 eV		8 eV	
m/e	Rel intensity	*m/e*	Rel intensity
130	4	172	5
118	11	148	5
104	37	130	14
102	17	118	31
87	86	104	43
86	17	102	33
74	41	87	69
73	92	86	18
60	17	74	45
59	47	73	29
58	100	58	100
45	72	45	18
44	50	30	6
43	85	28	20
31	85		
30	47		
29	59		
28	100		

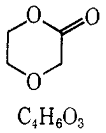
Acetic acid is excluded as a major component on the basis of its NMR and IR spectra.

Collins and George[14] studied the NMR spectrum of glycolaldehyde and reviewed the previously reported behavior of this compound. The monomeric aldehyde exists only in the gas phase. The solid compound exhibits no carbonyl absorption[13] and is most likely the symmetrical dimer, 2,5-dihydroxydioxane. In solution, glycolaldehyde exists as a highly solvent- and temperature-dependent mixture of the monomer, the symmetrical dimer, and an unsymmetrical dimer, 2-hydroxymethyl-4-hydroxy-1,3-dioxolane. The NMR spectra[14] of glycolaldehyde in Me_2SO-d_6 and in D_2O show multiplets in the region δ 3–5.2, but the spectra are different from each other and from the spectrum of fraction 2. An authentic sample of solid "glycolaldehyde" (Aldrich), dissolved in ethylene glycol, was shaken with $CDCl_3$ and the NMR spectrum of the $CDCl_3$ layer taken repeatedly over a period of several days. When the sample had come to equilibrium, the spectrum resembled much more closely that of fraction 2. The mass spectrum of solid "glycolaldehyde" (ionizing voltage 45 eV) showed major peaks (with the indicated relative intensities) at *m/e* 61 (21), 44 (99), 43 (41), 32 (100), and 31 (62). The P + 1 peak (*m/e* 61) was about four times as intense as the parent peak. It is presumed that this is due to hydrogen abstraction from a neutral molecule by the parent radical ion, $P^{+\cdot}$, to give PH^+, a process with ample precedent in the literature.[15]

Fraction 4. The major features of the infrared spectrum of fraction 4 were a strong OH stretching band at 3380 cm^{-1}, CH stretching absorption at 2900 cm^{-1}, a large C=O stretching band centered at 1740 cm^{-1}, and several peaks in the region 1250–1050 cm^{-1}, assumed to be CO stretching bands. The NMR spectrum lacked detail, but showed two broad regions of absorption at δ 3.5–4.0 and 4.0–4.7. The mass spectral data for this fraction appear in Table II. From the appearance of the spectra, we deduced that there were at least four major components, the parent ions of which had *m/e* values of 102.0303, 104.0456, 118.0610, and 130.0608, corresponding to the molecular formulas $C_4H_6O_3$ (102.0317), $C_4H_8O_3$ (104.0473), $C_5H_{10}O_3$ (118.0630), and $C_6H_{10}O_3$ (130.0630). The ions with nominal *m/e* values of 172 and 148 were considered to be contaminants from fraction 6. Because the molecular formulas of the major components suggest that the dioxane ring might be intact in each of them, it is of some interest to consider the fragmentation pattern for dioxane itself (Scheme IV). With the exception of *m/e* 57, peaks with all of the above *m/e* values appear in the spectrum of fraction 4. On the basis of the spectral data, then, the four major components of fraction 4 are presumed to be dioxanone (**6**), dioxanol (**7**), hydroxymethyldioxane (**8**), and hydroxyethylidenedioxane (**9**). The position of the double bond in **9** is not certain, though the mass spectrum of the trifluoroacetic anhydride derivatized product, to be described shortly, strongly suggests that **9** is an alcohol, rather than an aldehyde or a ketone.

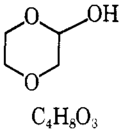
Scheme IV





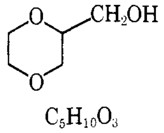
$C_4H_6O_3$

6



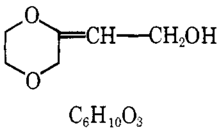
$C_4H_8O_3$

7



$C_5H_{10}O_3$

8

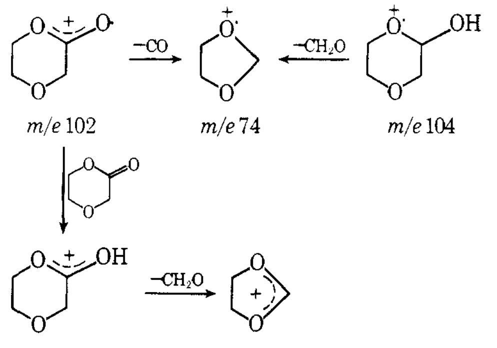


$C_6H_{10}O_3$

9

Authentic samples of **6** and **8** were prepared. The NMR spectrum of dioxanone exhibits a sharp singlet at δ 4.40 and two multiplets of equal intensity centered at δ 3.9 and 4.5. The infrared spectrum, taken neat, as was that of fraction 4, showed the following absorptions: CH stretching at 2900 cm^{-1}, C=O stretching at 1740 cm^{-1}, CH_2 bending at 1455 and 1432 cm^{-1}, CO stretching at 1200, 1130, and 1053 cm^{-1}, and other weaker bands at 876, 853, and 726 cm^{-1}. The mass spectrum of dioxanone, including parent, P + 1, and major peaks only, appears in Table III. The relatively large P + 1 peak is again attributed to hydrogen abstraction by the parent radical ion. The peaks at *m/e* 74 and 73 in the spectrum of fraction 4 can then be rationalized as shown in Scheme V.

Scheme V



The NMR spectrum of hydroxymethyldioxane shows only one very complex multiplet extending from δ 3.3 to 4.3. The major features of the infrared spectrum (neat) were absorptions attributable to OH stretching at 3378 cm^{-1}, CH

Table III. Mass Spectrum of Dioxanone at Two Ionizing Voltages

20 eV		45 eV	
m/e	Rel intensity	*m/e*	Rel intensity
103	18	103	6.6
102	18	102	9
101	12	101	10
87	22	87	18
86	12	75	12
75	12	73	34
73	31	61	11
58	10	60	11
57	16	59	10
45	44	58	10
44	16	57	30
43	29	55	11
42	10	45	75
32	100	44	21
		43	70
		42	21
		41	10
		40	11
		32	100
		31	33
		29	40

Table IV. Mass Spectrum of Hydroxymethyldioxane at 45 eV

m/e	Rel intensity	*m/e*	Rel intensity
118	8	57	27
87	100	45	27
86	12	44	15
75	15	43	47
74	12	41	12
73	11		
59	12		

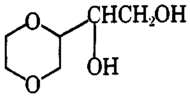
stretching at 2875 cm^{-1}, CH$_2$ bending at 1451 cm^{-1}, and numerous CO stretching peaks from 1302 to 1040 cm^{-1}. Peaks were also present at 980, 962, 944, 896, 864, 814, 625, and 588 cm^{-1}. Finally, the infrared spectrum of a mixture of roughly equal parts of dioxanone and hydroxymethyldioxane, except for some differences in peak intensities, is quite close to that of fraction 4, suggesting that **7** and **9** may be only minor components of this fraction. The mass spectrum of hydroxymethyldioxane is presented in Table IV. The base peak is at *m/e* 87, representing loss of $\dot{C}H_2OH$. The other major peaks are *m/e* 57, 45, and 43.

The most abundant ion in the mass spectrum of fraction 4 is that with *m/e* 58. This ion makes only a very minor contribution to the spectra of dioxanone and hydroxymethyldioxane, but a major one to the spectra of dioxane and dioxene. We are unable to explain this anomaly at present.[16]

Fraction 5. The infrared spectrum of fraction 5 shows a strong OH absorption at 3570 cm^{-1}, a weak to moderate C═O absorption at 1730 cm^{-1}, and strong C–O absorption in the 1163–1053-cm^{-1} region. The NMR spectrum shows peaks at δ 2.95 (broad singlet), 3.5–4.2 (broad multiplet), 4.5–4.7 (broad multiplet), and 8.1 (singlet), with the approximate area ratios 15:25:3:1. The mass spectral data (Table V) suggest at least three possible molecular ions at *m/e* 118.0617, 148.0750, and 174.0909, corresponding to $C_5H_{10}O_3$ (118.0630), $C_6H_{12}O_4$ (148.0736), and $C_8H_{14}O_4$ (174.0892). In the absence of evidence to the contrary, we have assumed that the $C_5H_{10}O_3$ component is the same as that found in fraction 4, namely, hydroxymethyldioxane (**8**). Owing to the large number of components in the photolysate, the separation into fractions was somewhat arbitrary, and some overlap of fractions on repeated collections probably was unavoidable. The NMR and IR spectra provide some evidence for the presence of an aldehyde in fraction 5, but as $C_5H_{10}O_3$, $C_6H_{12}O_4$, and $C_8H_{14}O_4$ all possess one degree of unsaturation, if the dioxane ring is intact in all three compounds as suggested by the fragmentation pattern, they must be alcohols or ethers. Thus, the aldehyde is regarded as a minor component, about which there is little structural information. Our postulated structures for the major components of fraction 5 are **10** and **1**. Structure **1** is advanced because it is a known reaction product. Structure **10** is chosen from among its possible isomers, such as **11** and **12**, on the grounds that the introduction of both a hydroxyl and a β- (or α-) hydroxyethyl group or two hydroxymethyl groups on the dioxane ring would involve further radical attacks on species such as **7**, **8**, or **9**. This we consider to be statistically improbable within an irradiation time of only 30 min.

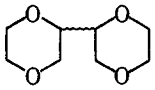
Table V. Mass Spectrum of Fraction 5 at Two Ionizing Voltages

70 eV		10 eV	
m/e	Rel intensity	*m/e*	Rel intensity
174	4	174	22
148	27	148	38
118	25	118	38
103	4	103	67
91	31	90	28
88	8	89	28
87	100	88	17
86	24	87	100
74	13	86	72
73	98	73	89
60	16	60	44
59	13	58	28
58	16	45	44
57	13	28	11
45	93		
44	26		
43	41		
31	48		
30	73		
29	28		
28	76		



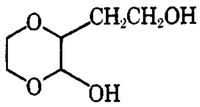
$C_6H_{12}O_4$

10

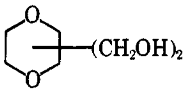


$C_8H_{14}O_4$

1



11



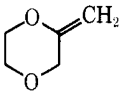
12

Fraction 6. The infrared spectrum of fraction 6 is of rather low intensity, but shows absorption bands at 3390, 2857, 1724, 1136–1030, and 877–870 cm^{-1}, suggesting, in addition to CH, the presence of OH, C═O, and CO bonds. The NMR spectrum shows only two regions of absorption, a broad singlet at δ 2.8 and a broad multiplet at δ 3.5–4.0, with approximate relative areas of 2.3:1. The mass spectral data for fraction 6 are listed in Table VI. The spectrum at both ionizing voltages was quite weak, and only two peaks could be mass measured

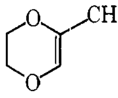
Table VI. Mass Spectrum of Fraction 6 at Two Ionizing Voltages

70 eV		10 eV	
m/e	Rel intensity	m/e	Rel intensity
190	<1	190	5
148	2	186	7
146	2	161	10
145	2	159	13
131	2	149	10
119	15	148	3
117	10	146	7
101	8	145	10
100	1	131	13
89	5	119	10
88	6	117	51
87	100	103	30
86	33	101	20
73	31	100	20
60	3	89	15
59	9	88	20
58	9	87	100
57	16	86	48
45	53	73	70
44	9	60	5
43	25	59	10
41	13	58	15
31	26	57	20
29	13	45	25
28	10	44	8
		43	8
		31	3

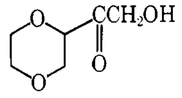
with certainty, *m/e* 146.0572 and 100.0539. These correspond to $C_6H_{10}O_4$ (146.0579) and $C_5H_8O_2$ (100.0524). We have no evidence whatever to allow us to choose among the numerous isomers of $C_5H_8O_2$. Structures **13** and **14**, as well as various ring-opened and ring-contracted compounds are possibilities.



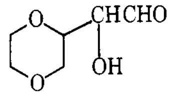
13



14



15



16

For the $C_6H_{10}O_4$ component, we propose either structure **15** or **16**, or a mixture of the two, since they may be interconverted through a common enediol. Here again, we prefer a structure with a single side chain over a multiply substituted dioxane or ring-opened product because these imply further attack on an initial photoproduct which is present only in low concentration. Attempts to synthesize authentic **15** or **16** met with failure.

GC/MS Analysis of Trifluoroacetate-Derivatized Photolysate. Because the mass spectral analysis of the dioxane photolysate suggested that the majority of the photoproducts are alcohols, and since alcohols are known to give weak, if any, molecular ion peaks, the product mixture was derivatized with trifluoroacetic anhydride. The crude photolysate, after removal of excess dioxane, was subjected to GC/MS analysis before and after treatment with trifluoroacetic anhydride. The mass spectrum of the underivatized photolysate exhibited all of the molecular ions discussed previously, except those at *m/e* 62 and 60, corresponding to ethylene glycol and glycolaldehyde. These two compounds had previously been separated from the other components using a Porapak Q column, whereas a Dexsil 300 column was employed in the GC/MS system. On this column, these two compounds show approximately the same retention time as dioxane itself, and were therefore eluted with the solvent and not leaked to the mass spectrometer. When the trifluoroacetate-derivatized photolysate was analyzed in the GC/MS system, it was found that the molecular ions previously attributed to the nonalcoholic components (**6** and **1**) were still present. On the other hand, the parent peaks attributed to the alcoholic components were either missing or greatly attenuated. New peaks, corresponding to the molecular ions of the trifluoroacetate esters of all of these alcohols, were observed with the exception of compound **7**. Since compound **7**, as postulated, is a hemiacetal, it may be that it did not survive the derivatization process.

Solution Photolysis of Dioxane and Dioxyldioxane. The previously described photoproducts were obtainable only when neat dioxane was photolyzed. When dioxane was irradiated for 30 min as 1.5, 3.0, and 6.0 M ethanolic solutions, only negligible amounts of photoproducts were formed. Furthermore, to investigate the possibility that the products were actually arising from secondary photoreactions of the dimer, dioxyldioxane was prepared and irradiated for 30 min as a 0.1 M ethanolic solution. Gas chromatographic analysis of the resulting photolysate again showed only minor amounts of photoproducts. Hirayama[17] has investigated the fluorescence of neat dioxane, and has found that dilution of the dioxane with isooctane causes a hypsochromic shift in the fluorescence, and reduces its quantum yield. In addition, the absorption spectrum of dioxane shows an inverse dependence of extinction coefficient on solvent viscosity. Finally, no fluorescence could be detected from dioxane in the gas phase. It was thus concluded that monomeric dioxane does not fluoresce, and that dioxane is strongly associated in the excited state. The lack of significant amounts of products from our solution photolysis of dioxane supports this conclusion.

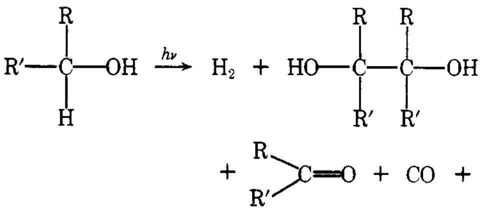
Discussion

We propose, then, that the dioxane photoproducts arise largely from the coupling of α-hydroxy and α-oxy radicals not produced in the primary step, though some, such as **2**, **8**, and **10**, could have resulted from the photoreduction of aldehydic intermediates. Plausible mechanisms for the formation of most of the products are detailed in Scheme VI.

An alternative explanation for the formation of **8**, **10**, and **15** has been proposed to us,[18] namely, that since the dioxyl radical would be expected to disproportionate to dioxane and dioxene, as well as to couple, **8**, **10**, and **15** could result from radical addition of, respectively, methanol, ethylene glycol, and glycolaldehyde to dioxene. To test this possibility, we refluxed mixtures of dioxene and benzoyl peroxide in methanol and in ethylene glycol. In neither case were detectable amounts of addition products obtained. It may be, however, that benzoyl peroxide is not the optimum initiator for these reactions, so they cannot be ruled out in the photolysis of dioxane.

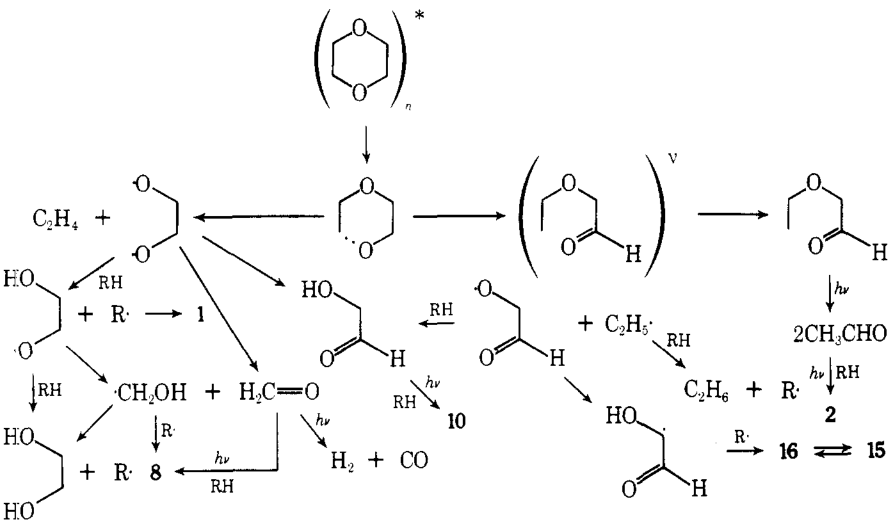
We still consider it unlikely that the primary process is the cleavage of a CH bond in dioxane, primarily because ethers, and dioxane in particular, have been shown in numerous cases to fragment on photolysis via CO bond scission.

As mentioned above, Yang has found[9] that methanol, ethanol, and 2-propanol, when irradiated neat at 185 nm, react according to eq 2. Hydrogen is the major gaseous product, and it is difficult to imagine a pathway, other than the cleavage of



$$R'{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{-}OH \xrightarrow{h\nu} H_2 + HO{-}\overset{\displaystyle R}{\underset{\displaystyle R'}{C}}{-}\overset{\displaystyle R}{\underset{\displaystyle R'}{C}}{-}OH + RR'C{=}O + CO + \text{other minor products} \quad (2)$$

Scheme VI



RH = dioxane; R· = 3

the α-CH bond of the alcohol, whereby it and the pinacol could be formed together. However, at 185 nm, it is likely that the chromophore responsible is the oxygen. Two facts are germane to the photolysis of dioxane with a medium-pressure lamp. First, with this lamp, the output in the region of 185 nm is blanked out due to self-absorption. Secondly, Yang reports that the impurities in ordinary quartz absorb strongly at 185 nm, and that high-purity fused silica is a requirement for studies at that wavelength.

We did not specifically observe the 1-hydroxyethyldioxane (**2**) reported by Mazzocchi and Bowen, though it is entirely possible—even likely—that it was present in one of our GC fractions, probably either 5 or 6. These workers reported that the mass spectra of the diastereomeric alcohols **2** showed a parent peak at *m/e* 132 (4 or 6% of base intensity), a base peak at *m/e* 87, and a peak at *m/e* 45 (52 or 98% of base intensity). The spectrum of each photolysate fraction, except fraction 2 which lacked the *m/e* 87 peak, contained intense peaks at *m/e* 87 and 45, and since the parent peak of **2** is so small, no special importance would be attached to it in the spectrum of a mixture of compounds which were also substituted dioxanes but ones having a higher molecular weight than that of **2**. Finally, Mazzocchi and Bowen isolated **2** after a 200-h photolysis of dioxane, so it is perhaps not to be expected that it would be a major component after only 30 min.

Three photoproducts are not obviously accommodated by our reaction scheme, namely, **6**, **7**, and **9**. The structure of compound **9** is known with less certainty from the experimental evidence than are the structures of the other photoproducts. However, traces of acid and water in the photolysate could catalyze the dehydration of compound **10** to yield **9**. Compounds **6** and **7** are not major components of the photolysate, and could have been formed by the reaction of dioxyl radicals with small amounts of oxygen not removed from the solution.

In summary, dioxane should be used with caution as a solvent in photochemical reactions in the 200-nm region, since even after relatively short periods of irradiation, it produces a multiplicity of products—including carbonyl compounds which can function as triplet transfer agents.

Experimental Section

Purification of Dioxane. Reagent grade dioxane was percolated through a column of acid-washed alumina into a flask containing KOH pellets, and the mixture stirred for 12 h. The upper layer was decanted, dried over fresh KOH pellets, filtered, and refluxed over sodium for 12 h. It was then distilled from the sodium and stored under nitrogen in an airtight amber bottle.

Photolysis of Dioxane. The dioxane, in 200-mL batches, was degassed in a round-bottom flask, using three freeze–pump–thaw cycles, and was transferred under nitrogen into a glove bag. Aliquots (30 mL) were transferred under nitrogen to 1 × 51 cm quartz tubes which were then closed with stopcocks. Five or six tubes were fastened with rubber bands to the outside of a Hanovia water-jacketed quartz dipping well, and were connected to a manifold which supplied a common nitrogen atmosphere to all tubes. Gaseous photoproducts and nitrogen were vented through a water bubbler. Irradiations were performed with a Hanovia 450-W medium-pressure mercury lamp.

Analysis of Photoproducts. Excess dioxane was distilled from the crude photolysate under nitrogen at atmospheric pressure, while the pot temperature was maintained at the boiling point of dioxane by means of an oil bath. The product mixture was analyzed and partially separated by gas chromatography on a Hewlett-Packard 5700A chromatograph, employing a 10 ft × 0.125 in. column packed with 10% Carbowax 20M on 60–80 mesh Gas Chrom W DCMS AW, maintained at a temperature of 180 °C, with an injection temperature of 250 °C, and a flow rate of 10 mL/min. The mass spectra of the four trapped fractions were recorded on a Du Pont 21-110C high-resolution mass spectrometer. Mass measurements were obtained using an electronic peak matching apparatus with perfluorokerosene as a reference. Low-resolution spectra were obtained on a Finnigan 1015 S/L quadrupole mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer, and NMR spectra on Varian A-60 and EM-360 instruments.

Preparation and Photolysis of Dioxyldioxane. Dioxyldioxane was recovered from the 24-h photolysis of dioxane, and the racemic and meso forms recrystallized from hexane and methanol, respectively, mp 131–134 °C (lit.[4] 131 °C); mp 153–156 °C (lit.[4] 157 °C). A 0.1 M solution of dioxyldioxane (24 mL) (mixture of diastereomers) was irradiated in a quartz tube under nitrogen for 30 min. The solvent was removed by distillation, and the photolysate analyzed by gas chromatography on a 6 ft × 0.125 in. column packed with 10% UCW 98 on 80–100 mesh Chromosorb W. The column temperature was programmed from 100 to 300 °C at 8 °C/min. The injection temperature was 250 °C, and the flow rate 70 mL/min.

The Solution Photolysis of Dioxane. Ethanolic dioxane solutions, 1.5, 3.0, and 6.0 M, were irradiated for 30 min in quartz tubes under nitrogen. After removal by distillation of most of the solvent, the remaining liquid was analyzed using the same column and conditions as for the dioxyldioxane photolysis.

Preparation of Dioxene and Dioxanone. Dioxene was prepared according to the method of Moss and Paige.[19] in which diethylene glycol is cyclodehydrated–dehydrogenated by refluxing with copper chromite and $NaHSO_4$. When the bisulfate is omitted, dioxanone is the major product. Physical constants: dioxene, bp 92–93 °C, reported 93–95 °C; dioxanone, bp 109–110 °C (22 mm) (ca. 220 °C at 760 Torr), reported (Beilstein) bp 213–214 °C (747 mm).

Preparation of Hydroxymethyldioxane. Using the method of Wojtowicz et al.,[20] allyl alcohol was chlorinated in ethylene glycol to give $ClCH_2CH(CH_2OH)OCH_2CH_2OH$, which yielded hydroxymethyldioxane on refluxing with aqueous NaOH, bp 98–99.5 °C (16 mm); reported[20] bp 100–105 °C (18 mm).

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Registry No.—*dl*-**1**, 3333-27-5; *meso*-**1**, 3443-36-5; **5**, 141-46-8; **6**, 3041-16-5; **7**, 22347-47-3; **8**, 29908-11-0; **9**, 62005-92-9; **10**, 62005-93-0; **15**, 62005-94-1; **16**, 62005-95-2; dioxane, 123-91-1; ethylene glycol, 107-21-1.

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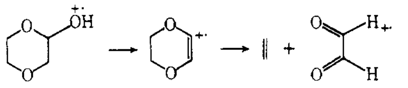
(15) See, for example, Hamming and Foster, "Interpretation of Mass Spectra of Organic Compounds", Academic Press, New York, N.Y., 1972, p 104.

(16) A referee has suggested the following scheme for the production of an ion with *m/e* 58.



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Stereoselectivity in Synthesis and Nucleophilic Displacement Reactions of *cis*- and *trans*-2,3-Dichlorotetrahydropyrans

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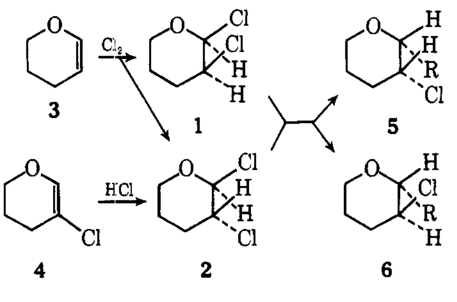
The stereochemistry of addition of chlorine to 3,4-dihydro-2*H*-pyran was reinvestigated and found to depend importantly on solvent polarity. In nonpolar solvents (e.g., pentane) stereoselective syn addition occurred yielding a mixture of *cis*- and *trans*-2,3-dichlorotetrahydropyrans in a ratio of 4:1. In polar solvents (e.g., dichloromethane) the cis:trans product ratio obtained was 1:2. Synthesis of *trans* 2,3-dichlorotetrahydropyran was accomplished by stereospecific syn addition of hydrogen chloride to 5-chloro-3,4-dihydro-2*H*-pyran. A general mechanism for the addition of chlorine to enol ethers which is consistent with the observed solvent dependence is discussed. The stereochemistry of nucleophilic displacement reactions at C-2 of *cis*- and *trans*-2,3-dichlorotetrahydropyrans and *trans*-2,3-dichlorotetrahydrofuran was studied using a variety of nucleophiles including NaSPh, NaOMe, NaN_3, and KOAc in dimethylformamide solution. *cis*-2,3-Dichlorotetrahydropyran yielded exclusively trans products with inversion at C-2. *trans*-2,3-Dichlorotetrahydropyran and -tetrahydrofuran yielded only cis products with C-2 inversion in reactions with NaSPh; with less effective nucleophiles mixtures of cis and trans products were obtained.

In connection with a synthetic program, we required *cis*- and *trans*-2,3-dichlorotetrahydropyran, **1** and **2**, respectively. It was thought by early workers[1] (owing to assumptions about the reaction mechanism) that addition of chlorine to 3,4-dihydro-2*H*-pyran (**3**) yielded only *trans*-2,3-dichlorotetrahydropyran (**2**). In 1965 Lemieux and Fraser-Reid[2] showed the product of this addition in carbon tetrachloride solution to be a 1:1 mixture of cis and trans dichloro compounds **1** and **2**. We have reinvestigated the addition reaction of chlorine to 3,4-dihydro-2*H*-pyran (**3**) and have found reaction conditions whereby the addition occurs with high (4:1) stereoselectivity, yielding largely *cis*-2,3-dichlorotetrahydropyran (**1**). The trans isomer[3] (**2**) was obtained by stereospecific syn addition of hydrogen chloride to 5-chloro-3,4-dihydro-2*H*-pyran (**4**). Using 2,3-dichlorotetrahydropyran and similar 2,3-dichlorotetrahydrofuran preparations of known stereochemical compositions, we have studied the stereochemical consequences of reactions of **1** and **2**, and those of *trans*-2,3-dichlorotetrahydrofuran (**7**), with selected nucleophiles.



Results

Chlorine Addition to 3,4-Dihydro-2*H*-pyran (3). Effects of variation of solvent and other reaction conditions on the stereoselectivity of addition of chlorine to 3,4-dihydro-2*H*-pyran (**3**) are recorded in Table I. When the addition reaction is carried out in polar solvents (e.g., dichloromethane or tetrahydrofuran) the product mixtures obtained exhibit a cis:trans isomer ratio little different from that observed at thermodynamic equilibrium,[2] i.e., 35% cis (**1**). As the reaction solvent polarity decreases the cis isomer (**1**) content of the product mixture increases to a maximum of about 80% when the addition reaction is carried out in pentane. Variation of reaction temperature from −78 to 25 °C has little effect; at higher temperatures equilibration of **1** and **2** occurs.[2] The concentration of 3,4-dihydro-2*H*-pyran (**3**) is important when nonpolar solvents are used; concentrations of **3** greater than