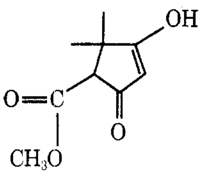
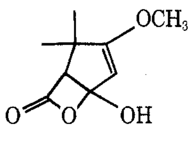
ments carried out in methanol-d_1 containing traces of acid (CF_3CO_2D) show no loss in intensity of the vinyl signal: the signal shows a change from δ 5.30 to δ 5.38 but the relative intensity of the signal to all other proton signals remains unity. Thus, equilibrium between **6** and **3** is the only one observed.

That the open form predominates in polar solvents is confirmed by the untraviolet spectrum: λ_{max} (95% ethanol) 239 mμ (ϵ 13,900). This absorbance is consistent with the chromophore $-C(OCH_3){=}C{-}C{=}O$ also found in **1** [λ_{max} (95% ethanol) 237 mμ (ϵ 13,900)], **2** [λ_{max} (95% ethanol) 237 mμ (ϵ 19,800)], and **4** [λ_{max} (95% ethanol) 240 mμ (ϵ 9900)].[1]

Two other structures, ester **9** and β-lactol **10**, may also be considered. However, compound **9** should show an ester absorption in the infrared spectrum as does compound **4**;[1] the absorption would not be expected to change with time in chloroform solution. Also, the ready loss of CO_2 on heating and on mass spectral analysis with formation of enol ether **2** would not be accommodated by **9**. While β-lactol formation to give **10** would parallel the observed behavior of phthalaldehydic acid,[6] one would expect infrared absorptions for the strained four-membered ring of structure **10** to be above ν 1800 cm^{-1}.[3] On this basis, the spectral and chemical evidence can be accommodated best by the γ-lactoenol **6**. This is a unique example of a stable enol[7] resulting from a Michael addition.



9



10

The γ-lactoenol forms by oxide attack on the δ carbon of the α,β-unsaturated cyclic ketone followed by H^+ addition to carbonyl oxygen. Survival of **6** results from the insolubility of **6** in aqueous acid medium and an equilibrium favoring **6** in the less polar organic solvents.[8] In more polar organic solvents strain relief derived by a retro-Michael is favored vs. keto–enol tautomerism.

Experimental Section[9]

Hydrolysis of 4,4-Dimethyl-3-methoxy-5-carbomethoxy-2-cyclopenten-1-one (1). Hydrolysis of compound **1** (0.50 g, 2.5 mmol) with 10 ml of 1% NaOH at 0° for 1 hr gave **6** (0.2 g, 50%) after acidification and extraction of the precipitated solid with ether. Recrystallization from 30–60° petroleum ether–ether solution gave white needles on cooling in Dry Ice–acetone, mp 102° dec.

Anal. Calcd for $C_9H_{12}O_4$: C, 58.68; H, 6.57; mol wt, 184. Found: C, 58.83; H, 6.49; mol wt, 184 (mass spectrometry).

Treatment of **6** with excess diazomethane in ether gave **1** quantitatively.

A sample of **6** (0.1 g) was decomposed at the melting point; the infrared spectrum of the oil which resulted was identical in all respects with the infrared spectrum of 4,4-dimethyl-3-methoxy-2-cyclopenten-1-one (**2**).[1]

Attempts to isolate **3** from chloroform solutions using standard poedures for unstable compounds only resulted in the recovery of **2** and **6**.

The principal peaks in the mass spectrum of **6** are as follows: MS (75 eV) *m/e* (rel intensity) 184 (1), 151 (2), 141 (8), 140 (57), 139 (25), 126 (9), 125 (100), 111 (5).

This contrasts to the principal peaks in the mass spectrum of **5**:[1] MS (75 eV) *m/e* (rel intensity) 184 (95), 169 (84), 154 (31), 153 (100), 152 (31), 137 (44), 126 (48).

Acknowledgment. We thank Mr. D. Kellner for some preliminary experiments.

Registry No.—**1**, 17037-96-6; **6**, 55681-96-4.

References and Notes

(1) J. M. Landesberg and D. Kellner, *J. Org. Chem.*, **33**, 3374 (1968).
(2) For examples see A. McKillop, M. E. Ford, and E. C. Taylor, *J. Org. Chem.*, **39**, 2434 (1974).
(3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Wiley, New York, N.Y., 1956.
(4) Band width at one-half peak height is 14 Hz.
(5) Band width at one-half peak height is 8 Hz.
(6) J. Kagan, *J. Org. Chem.*, **32**, 4060 (1967).
(7) (a) An example of a stable aliphatic enol is found in H. M. R. Hoffman and E. A. Schmidt, *J. Am. Chem. Soc.*, **94**, 1373 (1972). (b) E. A. Schmidt and H. M. R. Hoffman,, *J. Am. Chem. Soc.*, **97**, 7832 (1975).
(8) See E. S. Gould, "Mechanisn and Structure in Organic Chemistry", Henry Holt and Co., New York, N.Y., 1959, p 376 ff, for a discussion.
(9) General experimental details and procedures have been reported earlier.[1] Mass spectra were obtained on a Perkin-Elmer Hitachi Model RMU-6D mass spectrometer. The NMR spectra were determined on a Varian A-60 using tetramethylsilane as internal standard. All solvents for NMR determinations were obtained from Stohler Isotope Corp. and were used as received. Infrared spectra were recorded on a Perkin-Elmer Model 237 spectrophotometer using Ir transparent cells; bands in the carbonyl region were calibrated against the 1603 cm^{-1} band of polystyrene.

Photolysis of Dioxane

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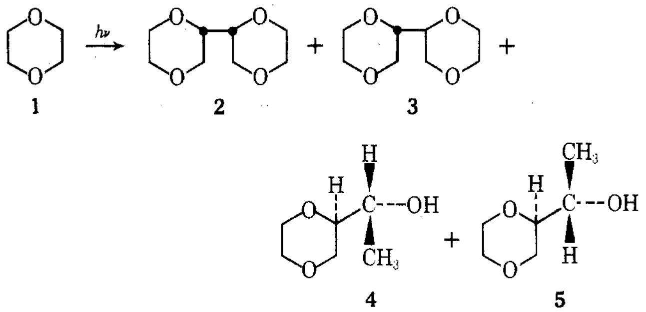
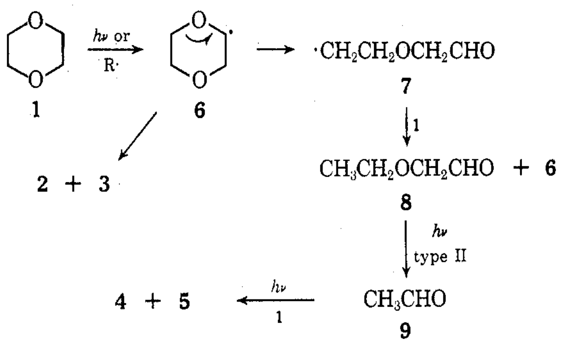
Dioxane has been a solvent of choice in many photochemical reactions owing to its excellent solvent properties and ultraviolet transparency. In the course of a series of photochemical reactions in dioxane we noted the presence of four products which were persistent in all of our photoreactions. In order to determine whether these products arose from irradiation of reactant, solvent, or both, we irradiated pure dioxane using a 450-W medium-pressure lamp through quartz in a nitrogen atmosphere. The reaction was monitored by GLC on a 20% Versmid column and indicated the slow formation of four products, in approximately equal amounts, over the period of irradiation.

Distillation, followed by preparative GLC, led to the isolation of the pair of diastereomeric dioxane dimers (**2** + **3**) which have been previously reported as products from the photolysis of dioxane,[1] and a pair of diastereomeric alcohols to which we assigned structures **4** and **5** on the basis of spectral and chemical evidence (vide infra).



The formation of **2** and **3** may be easily rationalized[1] as a simple dimerization of dioxyl radical **6** formed by photoinitiated hydrogen abstraction from dioxane.[2] The most reasonable route to **4** and **5** involves a β bond cleavage in **6** to give radical **7**, which hydrogen abstracts from dioxane in a chain propagation step to afford ethoxyacetaldehyde (**8**).[3] The ultraviolet spectrum of **8** is such that under the conditions used it should be immediately exposed to light undergoing an efficient Norrish II reaction to give 2 mol of acetaldehyde.[4] Acetaldehyde would then be expected to undergo an efficient photoreduction in dioxane to afford **4** and **5**.[5,6]



Although the presence of **2–5** does cause some problems during the work-up of preparative photochemical reactions, a major objection to the use of dioxane in quantitative or mechanistic studies is the presence of small steady-state concentrations of **8** and **9**, which could cause troublesome sensitization and/or quenching reactions.

Experimental Section

Infrared spectra were obtained on a Beckman IR-8, NMR spectra on a Varian A-60D spectrometer, and gas chromatographic work was carried out on Varian 1200 (flame ionization) and A-90 (thermal conductivity) instruments.

Photolysis of Dioxane. A sample of 200 ml of spectrograde dioxane was purged with nitrogen for 1 hr and then irradiated with a 450-W Hanovia type L lamp for a period of 200 hr. Aliquots were removed during the course of the reaction and analysis on a 6 ft × 0.125 in. 20% Versmid on 60–80 Chromosorb W column at 140° indicated the slow generation of four products with retention times of 8 (A), 12.5 (B), 23, and 31 min. Dioxane was removed by distillation and the residue was distilled to give a fraction, bp 100–120° (17 mm), enriched in the two short retention time peaks. The residue was rich in the two long retention time components and these were separated via preparative GLC on a 6 ft × 0.25 in. 15% DC550 on 80–100 mesh Chromosorb W column at 125°. Melting points and spectral data (ir, NMR, MS) indicated that these were the dimers **2** and **3**.[1]

The two early retention time peaks were isolated from the distillation fraction by preparative GLC on a 6 ft × 0.25 in 20% Versmid on 60–80 Chromosorb W column at 110°.

The material corresponding to peak A was identified as **4** (or **5**) on the basis of the following data: ν_{max} ($CDCl_3$) 3600, 2870, 2980, and 1120 cm^{-1}; NMR ($CDCl_3$) τ 8.87 (d, J = 6 Hz, 3 H, CH_3), 7.27 (broad s, 1 H, OH), 6.0–6.7 (broad m, 8 H, HCO); MS m/e (rel intensity) 132 (P, 4), 87 (100), 45 (98).

The material corresponding to peak B was identified as **5** (or **4**) on the basis of the following data: ν_{max} ($CDCl_3$) 3600, 2865, 2970, 1115 cm^{-1}; NMR ($CDCl_3$) τ 8.83 (d, J = 6.5 Hz, 3 H, CH_3), 7.72 (broad s, 1 H, OH), 5.9–6.6 (broad m, 8 H, HCO); MS m/e (rel intensity) 132 (P, 6), 87 (100), 45 (52).

Acknowledgment. We wish to thank the Center for Materials Research of the University of Maryland for partial support of this work.

Registry No.—**1**, 123-91-1; **4**, 55759-33-6; **5**, 55759-34-7.

References and Notes

(1) K. Pfordte, *Justus Liebigs Ann. Chem.*, **625**, 30 (1959).

(2) Although we would normally expect it to result from hydrogen abstraction processes, in the present case **6** probably arises via excitation of dioxane with 185-nm light. The formation of similar radicals in alcohols has been reported: N. C. Yang, D. P. C. Tang, D. M. Thap, and J. S. Sallo, *J. Am. Chem. Soc.*, **88**, 2851 (1966).

(3) N. L. Drake, H. M. Duvall, T. L. Jacovs, H. T. Thompson, and H. M. Sonnicksen, *J. Am. Chem. Soc.*, **60**, 73 (1938).

(4) The photochemistry of methoxyacetone has been studied. This material undergoes efficient Norrish II cleavage (quantum yield = Φ = 0.32) to give acetone and formaldehyde: R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 2475 (1962).

(5) Ketones are known to undergo photoreduction in the presence of dioxane: K. Shima and S. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **36**, 121 (1963); G. O. Schenck, H. D. Becker, K. H. Schutte-Elte, and C. H. Krauch, *Chem. Ber.*, **96**, 510 (1963); W. Droste, H. D. Scharf, and F. Korte, *Justus Liebigs Ann. Chem.*, **724**, 71 (1969).

(6) We have carried out the photoreduction of acetaldehyde in dioxane and it does afford **4** and **5** efficiently.

Conformational Aspects of 1,4-Oxathiane *S*-Oxide by Carbon Magnetic Resonance Spectroscopy

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Recently, considerable discussion has focused on the conformational preferences of the sulfinyl oxygen atom (S–O) in a variety of six-membered rings. For example, *trans*-1,4-dithiane 1,4-dioxide, possessing a diaxial oxygen conformation in the solid state,[1] appears to exist preferentially in the same conformation in solution.[2] This axial preference of the S–O group has been established for thiane *S*-oxide (**1**) by low-temperature ^{1}H NMR techniques[3] while an equilibrium mixture of anancomeric *cis*- and *trans*-4-*tert*-butylthiane *S*-oxides (**2** and **3**) exhibits a predominance of the cis isomer bearing the axial oxygen.[4] In contrast, the sulfinyl oxygen atom of 3,3-dimethylthiane *S*-oxide prefers the equatorial conformation (>95%).[5] The equatorial preference in the 3,3-dimethyl derivative is undoubtedly due to the repulsive 1,3-syn–axial methyl–sulfinyl oxygen atom interaction while the axial preference in **1** has been ascribed to an attractive interaction between the axial sulfinyl oxygen atom and the syn-axial C–H atoms.[6] In 1,3-dithiane *S*-oxide[7] and 1,3-oxathiane *S*-oxide[8] the sulfur oxygen atom favors the equatorial conformation in the former and the axial position in the latter. In view of the growing concern for those factors which influence (and possibly control) the conformations of sulfoxides in cyclic systems, we wish to report our results and conclusions regarding the conformations of 1,4-oxathiane *S*-oxide (**4**).

We have examined the conformational equilibria of 1,4-oxathiane *S*-oxide and the corresponding 3,3,5,5-tetradeuterio derivative **5** using ^{13}C NMR spectroscopy.

At −80° in CD_2Cl_2, two absorptions are observed for **5** while in a separate experiment four absorptions were visible for **4**. The carbons α to the ring oxygen and the ones α to the sulfinyl group were easily assigned since deuteration served to "mask"[9] only carbons adjacent to the sulfinyl group. Inspection of the low-temperature spectrum of **4** revealed two low-field absorptions of unequal intensity (δ 57.66 and 64.68 ppm) which exhibited a chemical shift difference of 7.02 ppm. A similar result was obtained for the high-field carbons α to the S–O group ($\Delta\delta$ = 7.42 ppm = 51.67 − 44.25). The conformer assignments for the two forms were made by comparison with the appropriate carbon shifts of other systems with established conformations as shown in Table I.

In all cases, it is apparent that the axial (sc) sulfinyl oxygen atom in a *chair conformation* engenders an upfield shift on the β carbons as compared to the equatorial (ap) sulfinyl oxygen atom.[10,11] From these data we conclude that the high-intensity absorptions (most populous conformer) correspond to the one with the *axial sulfinyl oxygen* atom (**4a**). This conclusion is in harmony with the one arrived at by Szarek et al.[15] from an examination of the ^{1}H NMR couplings and proton chemical shifts of **4** at ambient temperature. Calculation of the corresponding conformational free energy ($\Delta G°$) gave the data in Chart I.[16] The data on the conformational equilibrium of thiane *S*-oxide[3] are included for comparison.

It is especially noteworthy that the $\Delta G°$ for **4** is more than three times that observed for thiane *S*-oxide under similar conditions ($\Delta G°_{-80°}$ = 0.68 ± 0.07 kcal/mol for **4** and $\Delta G°_{-90°}$ = 0.17 ± 0.03 kcal/mol[3] for **1**). Dreiding mo-