trichloride (2.3 g, 15.0 mmol) was weighed under dry nitrogen in a glove bag and placed under nitrogen in a 100-ml three-neck flask with 70 ml of dry glyme. $LiAlH_4$ (190 mg, 5.0 mmol) was quickly added to the stirred $TiCl_3$ slurry, and the resulting black suspension was stirred for 10 min before use. **B.** Alternatively, a 3:1 $TiCl_3$–$LiAlH_4$ premix (effective mol wt 167, 2.50 g, 15.0 mmol) was weighed under nitrogen in a glove bag and added to 70 ml of dry glyme under nitrogen. The resulting black suspension was stirred for 10 min before use.

The substrate alcohol (5.0 mmol) in several milliliters of glyme was then added, and the reaction mixture was refluxed for 16 hr. After cooling, the reaction mixture was quenched by addition of dilute aqueous hydrochloric acid, then diluted with water and extracted with ether. The ether extracts were combined, washed with brine, dried ($MgSO_4$), filtered, and concentrated at the rotary evaporator. Crude products were then purified either by crystallization or distillation. In this manner, the following reactions were run.

Benzyl alcohol gave **bibenzyl,** 78%, mp 51–51.5° (lit.[8] mp 52°).

α-Phenethyl alcohol gave a liquid mixture of meso and *dl* forms of **2,3-diphenylbutane,** 68%. Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.59; H, 8.67.

2-Phenyl-2-propanol gave **2,3-dimethyl-2,3-diphenylbutane,** 95%, mp 117–118° (lit.[9] mp 118–119°).

2-Cycloheptenol gave **3-(2-cycloheptenyl)cycloheptene,** 87%. Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.14; H, 11.76.

Farnesol gave a mixture of products which was separated by high-pressure liquid chromatography on Porosil A[10] (16 ft × 0.25 in.). The results are shown in Table I. Identifications were made on spectroscopic grounds (100-MHz NMR and mass spectra) and were unequivocal.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

Registry No.—Titanium trichloride, 7705-07-9; $LiAlH_4$, 16853-85-3.

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(1) E. E. van Tamelen and M. A. Schwartz, *J. Am. Chem. Soc.*, **87**, 3277 (1965).
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(8) "The Merck Index", 8th ed, Merck and Co., Rahway, N.J., 1968, p 147.
(9) P. E. Verkade, K. S. de Vries, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **82**, 637 (1963).
(10) Porosil A is a registered trademark of Waters Associates, Framingham, Mass.

Formation of a Stable Enol from a Michael Addition

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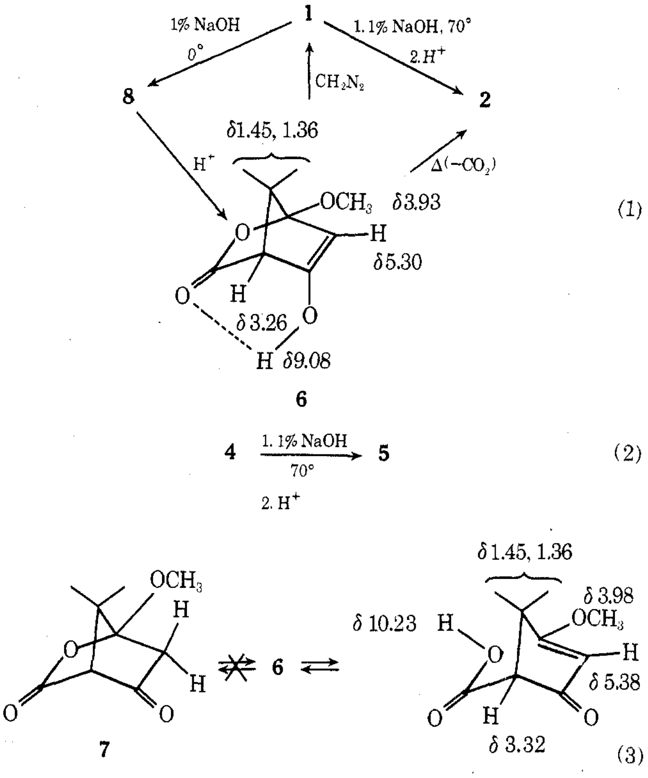
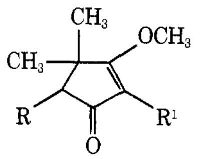
During the course of an earlier investigation,[1] difficulty was encountered in the hydrolysis of keto ester **1** (see Chart I). Base hydrolysis yielded only the enol ether **2** and not the corresponding acid **3**. This contrasted with the isomer **4**, which readily gave the acid **5** under similar conditions. Reinvestigation gave the γ-lactoenol **6**; evidence for the structure of this novel enol resulting from an internal Michael addition is presented here.

Chart I





	R	R^1
1	CO_2CH_3	H
2	H	H
4	H	CO_2CH_3
5	H	CO_2H
8	CO_2^-	H

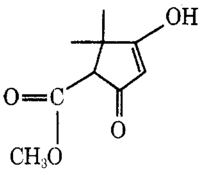
Saponification of **1** is effected by 1% sodium hydroxide at 0° and crystalline solid **6** precipitates on acidification. Treatment of this saponified product with diazomethane regenerates **1**. Elemental analysis shows that **6** is isomeric with **5**. On melting, mp 102° dec, **6** decomposes, a gas evolves, and oil **2** results (previously identified[1]).

The infrared spectrum indicates, however, that **6** is *not* the carboxylic acid **3** but the γ-lactoenol **6**. A freshly prepared chloroform solution of **6** shows a strong absorption at ν 1780 cm^{-1}. This is characteristic of the five-membered lactone ring.[2,3] A solution of **6**, on standing at room temperature or on heating, undergoes changes in the infrared spectrum: the absorption at ν 1780 cm^{-1} decreases while an absorption at ν 1725 cm^{-1} increases; this would correspond to the formation of keto acid **3** by a retro-Michael; prolonged standing or heating finally yields the infrared spectrum of **2**. A methanol solution of **6** has only infrared absorptions which would be characteristic of **3** [ν 1725 (acid C=O), 1675 (α,β-unsaturated C=O), 1600 cm^{-1} (C=C)]. Thus, in solution **6** opens to give **3**, which eventually gives off CO_2 and leads to **2**. Attempts to isolate **3** only yield mixtures of **6** and **2**.

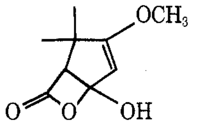
The nuclear magnetic resonance spectrum supports the above observations. In $CDCl_3$ **6** exhibits a chemical shift for the enolic proton at δ 9.08;[4] this is at higher magnetic field (δ 2.29 upfield) than the chemical shift of the carboxylic acid hydrogen of **5** (δ 11.37).[1] Heating the NMR solution (50°, 0.5 hr) brings about ring opening of **6** and the formation of **3**; a low-field absorption appears at δ 10.37[5] while the δ 9.08 signal decreases (and eventually disappears). No equilibrium with keto ester **7** is observed. NMR experiments 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 ab-



9



10

sorption 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.

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

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(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.
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(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, "Mechanism 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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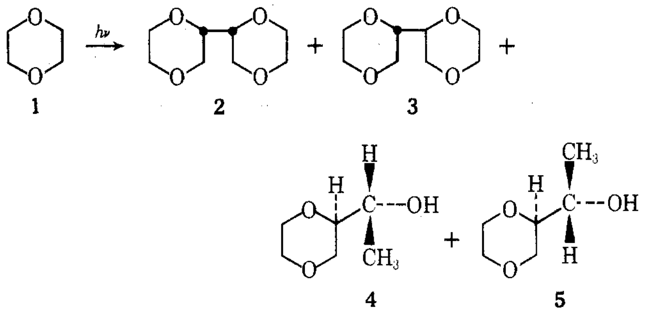
Dioxane has been a solvent of choice in many photochemical reactions owing to its excellent solvent properties and ultraviolet transparency. In the course of a series of photochemical reactions in dioxane we noted the presence of four products which were persistent in all of our photoreactions. In order 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]