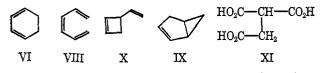
and subsequent cyclization for 1,3-cyclohexadiene (VII) itself. Thus prolonged irradiation of VII in solution has been reported to give only trienes VIII and polymer.^{4,9} In the hope of providing some basis for understanding the influence of structural variations on photochemical reaction patterns, we have reexamined the solution photochemistry of this parent compound, with the results described below.

Ethereal solutions (1%) of VII were irradiated with a Hanovia high-pressure mercury lamp through a Vycor filter. Initial ring opening to a mixture of 1,3,5hexatrienes (VIII) was evidenced by a large increase in ultraviolet absorption (λ 256 m μ) which was paralleled by the appearance of a new glpc peak.

Continued irradiation led to the appearance of two



additional glpc peaks, of shorter retention times, whose intensity increased as those of VII and VIII decreased. These new components (ca. 12% each as estimated by glpc) could be isolated by fractionation of the reaction mixture and were proven to be bicyclo-[3.1.0]hex-2-ene (IX)¹⁰ and 3-vinylcyclobutene (X) on the basis of the following evidence.

The mass spectrum of IX showed its parent peak at m/e 80 in accord with the molecular formula C₆H₈. The nmr spectrum showed resonances at τ 4.0, 4.7, 7.65, 8.35, 9.25, and 10.25 as reported recently for authentic IX prepared by the action of bis(iodomethyl)zinc on cyclopentadiene.¹⁰ The infrared spectrum of IX showed maxima at 3100 (s), 2920 (s), 1360 (m), 1020 (s), 910 (s), 800 (s), 780 (m), 765 (s), and 715 cm⁻¹ (s).

The mass spectrum of X again had its parent peak at m/e 80. In the nmr it showed a typical ABX pattern at τ 6.6, 7.2, and 7.8, a sharp singlet at τ 4.0 (cyclobutene protons), and multiplets at τ 4.2 and 5.0 (vinyl protons). The infrared spectrum showed absorption at 3100 (s), 2940 (s), 1820 (w), 1640 (w), 1440 (w), 990 (s), 910 (s), 770 (s), and 685 cm^{-1} (s). Pyrolysis at 200° gave quantitative conversion to trans-1,3,5-hexatriene, in accord with expectations for structure X.¹¹ Under the pyrolysis conditions chosen, IX was completely unchanged. Chemical support for the assignment of structure X to this product was obtained by ozonolysis followed by an oxidative work-up using hydrogen peroxide. Under the conditions used, succinic acid (identified as its dimethyl ester) was the only isolable product, in accord with the expected facile decarboxylation of the initially formed carboxysuccinic acid XI.

Photochemical formation of IX in this reaction shows that the 1,3-cyclohexadiene \rightarrow bicyclo[3.1.0]hex-2-ene transformation, which probably proceeds via 1,3,5-hexatriene, is an important reaction for the parent compound, as is the case for I and V. The simultaneous formation of a cyclobutene (X) finds its simplest analogy in the observation that 1,3-butadiene itself can yield cyclobutene upon irradiation^{11,12}

and suggests that analogous vinylcyclobutenes might be found in the more complex cases of 1,3-cyclohexadiene or 1,3,5-hexatriene irradiation if the reaction mixtures were examined closely enough.

The influence of substituents on the preferred course of these reactions, the factors controlling their stereochemistry, the role of the 1,3,5-hexatrienes as intermediates in the production of monocyclic and bicyclic photoproducts, and the nature of the excited states involved in these transformations all remain to be analyzed. We hope to be able to contribute to some of these questions in a continuation of the present work.

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Liquid Phase Photolysis of Simple Alcohols

Sir:

Because of the lack of suitable light sources, photochemical reactions of organic compounds in the liquid phase with light from the vacuum ultraviolet region have not been extensively investigated, especially with respect to detailed product analyses.¹ Although lowpressure mercury discharge lamps emit at 185 m μ as well as at 254 m μ , the former line is strongly absorbed by the impurities in fused quartz. Recently, the quality of fused quartz has been improved to such an extent that light at 185 m μ is transmitted at an appreciable intensity. The current communication deals with photochemistry of simple alcohols in the liquid phases.¹⁻⁷

The reactions were carried out in a fused quartz apparatus as previously described.⁸ The apparatus has a volume of 170 ml and an emission surface of approximately 190 cm². External heating is provided by means of a heating tape. The reactions were completely inhibited by a Vycor filter. No attempts were made to isolate the $185\text{-m}\mu$ line from other emissions of mercury. The alcohols used were reagent grade, fractionated through a 50-plate column and analyzed by vps before use. The alcohols were flushed with high purity nitrogen and the photolyses were performed at the reflux temperatures of the alcohols to exclude air from the reactions. The reactions were carried out to about 2-3% completion. The gas evolution was fairly rapid at the beginning (150-220 ml/hr) and slowed down to a steady rate (75-100 ml/hr) after the second hour. The gaseous products were analyzed by vpc with a Molecular Sieve 5-A column at 100°, and higher boiling products were analyzed by vpc and fractional distillation. The results of photolyses of methanol, ethanol,

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2-propanol, and 2-methyl-2-propanol are summarized below, and the products are expressed in units of mmoles per hour: methanol: H_2 , 2.97; CO, 0.098; CH₄, 0.012; HCHO, 0.32; (CH₂OH)₂, 1.92; glycerine, 0.26; ethanol: H_2 , 2.54; CO, 0.75; CH₄, 0.81; CH₃CHO, 0.10; 2,3-dihydroxybutane, 1.63; 2-propanol: H_2 , 1.72; CO, 0.68; CH₄, 1.27; C₂H₆, 0.05; acetone, 0.23; pinacol, 1.52; 2-methyl-2propanol: CH₄, 5.10; CO, 0.42; acetone, 0.35; pinacol, 1.25; 3-hydroxy-3-methyl-2-butanone, 0.33; 2,5-dihydroxy-2,5-dimethylhexane, 1.74.

The gas evolutions in these photolyses were inhibited by cyclohexene and were completely suppressed by the presence of 5% of cyclohexene (0.6 M) In all cases, cyclohexene only absorbs a minor portion of the light. In the case of photolysis of 2-propanol in the presence of 5% of cyclohexene, the following products were obtained in units of millimoles per hour: acetone, 2.0; pinacol, 0.09; cyclohexane, 0.60; cyclohexyldimethylcarbinol, 0.51; cyclohexenyldimethylcarbinol, 0.40; bicyclohexyl, 0.12; cyclohexenylcyclohexane, 0.05; high boiling residue (0.04 g/hr).

The principal gaseous product is hydrogen in all cases except 2-methyl-2-propanol and the principal higher boiling products are the corresponding carbonyl compounds and the glycol. When the results of photolysis of 2-propanol in the presence of cyclohexene, a radical scavenger, were compared with the results of photolysis of pure 2-propanol, it is interesting to note that the evolution of hydrogen, methane, and carbon monoxide was completely suppressed and the yield of acetone became much higher. On the basis of the above observations, hydrogen is most likely formed from a radical process such as indicated by reactions 1 and 2 and acetone is not formed directly from 2-propanol by a molecular elimination of hydrogen. One possible

$$R \xrightarrow{\mu} C \xrightarrow{\mu} OH \xrightarrow{\mu} R'$$

$$\begin{array}{c}
\mathbf{R}' \\
\mathbf{R} - \mathbf{C} - \mathbf{OH} + \mathbf{H} \cdot \longrightarrow \mathbf{R}' \\
\overset{}{\longrightarrow} \mathbf{C} - \mathbf{OH} + \mathbf{H}_2 \quad (2)
\end{array}$$

$$\begin{array}{cccc}
H & & R \\
R' & & R' R' \\
2 & & & & \\
C & -OH \longrightarrow R - C - C - R \\
R & & & OH OH
\end{array}$$
(3)

$$\begin{array}{ccc} R' & R' \\ \hline C & -OH \longrightarrow & C = O + H \cdot \text{ or other products} & (4) \\ R & R \\ \text{vibrationally} \\ \text{excited} \end{array}$$

explanation is that the 2-hydroxy-2-propyl radical formed in reaction 1 may be vibrationally excited. The light at 185 m μ is very energetic and is equivalent to 6.5 ev or 148.7 kcal/einstein. After the initial cleavage of the α -C-H bond in photoexcited 2-propanol, which has a bond energy estimated at about 85 kcal, the excess energy may remain preferably in the form of vibrational energy in the 2-hydroxy-2-propyl radical rather than in the form of kinetic energy of the hydrogen atom. The vibrationally excited 2-hydroxy-2-

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propyl radical thus generated may differ in its behavior from the normal 2-hydroxy-2-propyl radical which usually dimerizes to give pinacol (reaction 3) or is scavenged by cyclohexene. It is probable that the vibrationally excited 2-hydroxy-2-propyl radical may disproportionate, dissociate, or react with cyclohexene to give acetone prior to its deactivation (reaction 4). The accumulation of acetone in the photolysis of 2propanol in the presence of cyclohexene may be attributed to the quenching effect of cyclohexene on the secondary decomposition of acetone by the 254-m μ emission of the light source.

The α -C-C bond in 2-propanol has a bond energy comparable to that of the α -C-H bond. An initial cleavage of photoexcited 2-propanol will give a methyl radical and a 1-hydroxyethyl radical (reaction 5). The products which may be derived from these radicals are conspicuously absent in the photolysis of 2-propanol in the presence of cyclohexene or among the higher boiling products in the photolysis of pure 2propanol. Therefore, the formation of methane and carbon monoxide in the photolysis of 2-propanol is probably derived from the secondary photolysis of acetone. This fact was readily demonstrated by photolyzing acetone in 2-propanol.^{5,9}

$$(CH_3)_2CH \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow (5)$$

We wish to suggest that the principal primary process in the liquid phase photolysis of simple primary and secondary alcohols is the cleavage of an α -C-H bond, while the primary process for tertiary alcohols is the cleavage of an α -C-C bond. Our preliminary investigations indicate that photochemical reactions in the liquid phase with 185 m μ light might be quite selective and the investigations are being extended to other organic compounds.

Acknowledgment. The authors wish to thank the Atomic Energy Commission for the support of this work.

(9) A detailed analysis of gas evolved from the photolysis of 2-propanol at 60-min intervals indicated that the gas evolved earlier is considerably richer in hydrogen, but we are not able as yet to obtain a sample completely free of methane. Acetaldehyde, if formed, would have been detected under the reaction conditions.

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Dependence of the Quantum Yield of Photoreduction of Benzophenone in 2-Propanol on Light Intensity. Possibility of Triplet Quenching by the Radical Intermediates in Solution

Sir:

The photoreduction of benzophenone in 2-propanol has been extensively investigated.¹ The reaction is

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