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# Photolysis of Alcohols and Alkanones in Acetone Solutions. Photochemical [2+2]Cycloaddition Reaction between Acetone and Aliphatic Enols

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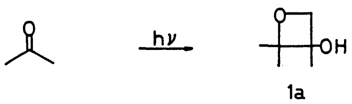
Transient enols including those of acetaldehyde, acetone, cyclopentanone, 3-pentanone, 2,4-dimethyl-3-pentanone, 2-butanone, and 2-methyl-3-pentanone were trapped photochemically with acetone via a [2+2]cycloaddition and isolated as corresponding 3-oxetanols in reasonable yields in the photolysis of six different secondary alcohols and two alkanones, 3-octanone and hexanal, in acetone solutions. The trapping experiments indicated the photodehydrogenation of unsymmetrical alcohols, 2-butanol and 2-methyl-3-pentanol, in acetone to be highly regioselective in preference for the formation of the less alkylated enol.

The chemistry of simple enols has received wide attention in recent years from structural and mechanistic interests.[1–4] A number of short-lived enols[1–3,5] have been prepared and characterized directly by spectral analyses including microwave,[6] IR,[7] and NMR.[2,8,9] CIDNP technique is particularly useful for identification of transient enol species which may often be involved in photochemical processes.[10,11] This method, however, does not always provide quantitative information on the formation of such species. In this connection, trapping experiments seem important. Although there have been extensive studies on ketonization of enols via protonation and halogenation,[3,12,13] works on reactions other than ketonization are surprisingly few. Cycloaddition reaction is especially attractive for chemical proof of transient enols. There have been reported several [2+4]-type cycloaddition reactions for some dienols such as photo enols of *o*-alkylated phenyl ketones,[14,15] however, successful trapping of simple enols like vinyl alcohol via a cycloaddition reaction is rare. An interesting observation, in this connection, is the formation of a small amount of 2,2,3-trimethyl-3-oxetanol (**1a**) in the photolysis of acetone in the liquid phase reported by Kagan et al.[16] Although mechanism for the formation of **1a** has not been established yet, a photocycloaddition between acetone and its enol would probably be involved.[17] Accordingly, an excited molecule of acetone seems to be a good candidate for a trapping agent for enol intermediates which are formed in photochemical reactions. We report here our results on the photolysis of eight different alcohols and two alkanones carried out in acetone solutions and show photochemical trapping of various enols with acetone.



## Results and Discussion

**Photocycloaddition of Acetone with Acetone Enol.** We first examined the photolysis of acetone in the liquid phase in the presence of a hydrogen-donating substrate with a view to understanding the mechanism for the formation of the oxetane **1a**. Table 1 shows the results of irradiation of acetone (100 cm$^3$) with or without a hydrogen-donating substrate (RH, 35 mmol) including cyclohexane, 2-propanol, 3-pentanol, 2-trimethylsiloxypropane, and triethylsilane under the same photolysis conditions (0—5 °C, 2 h under argon) using a 100 W low-pressure mercury lamp. In agreement with the earlier observation,[16] these photolysis reactions gave a mixture of **1a** and several other major compounds including 4-hydroxy-4-methyl-2-pentanone (**2**), pinacol (**3**), 2,5-hexanedione (**4**), and a coupling product **5** between acetone and RH as a low-boiling liquid distilling under vacuum. Obviously, **1a** is formed much more efficiently in the photolysis of acetone in the presence of a hydrogen donor than in the photolysis of pure acetone. For example, the yield of **1a** increased by a factor of more than nine when acetone was irradiated with 2-propanol instead of acetone alone. Cyclohexane shows a similar effect, although less pronounced. It is worth stating that the photolysis of acetone in cyclohexane has been reported to give a coupling product **5a** (R=cyclohexyl) but not **1a**.[18] The presence of a good hydrogen donor greatly favored the formation of **2** and **3** as well. In contrast, it little affected or in some cases reduced significantly the formation of 2,5-hexanedione. It is also informative that the irradiation of acetone containing 2-propanol and trace *p*-toluenesulfonic acid gave pinacol but not **1a** at all. Although **1a** readily rearranges to 4-hydroxy-3,3-dimethyl-2-butanone under acidic conditions,[19] we could not find the rearranged product either. Thus, the presence of trace acid completely prohibits the formation of **1a**. All these findings are consistent with a mechanism for the formation of **1a** outlined in Scheme 1. An excited molecule

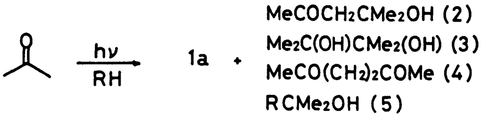
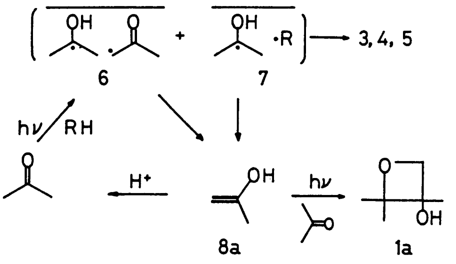


Table 1. Effects of a Hydrogen-Donating Substrate (RH) on the Liquid-Phase Photolysis of Acetone[a)]

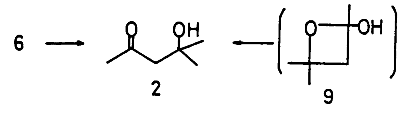
| Substrate (RH) | Low-boiling fraction/g[b)] | Products/mmol[c)] | | | | | |
|---|---|---|---|---|---|---|---|
| | | **1a** | **2** | **3** | **4** | **5** | Others |
| None | 0.094 | 0.41 | 0.19 | 0.08 | 0.18 | | |
| Cyclohexane | 0.584 | 1.89 | 0.86 | 0.59 | 0.20 | 1.13 | |
| 2-Propanol | 1.02 | 3.71 | 1.98 | 2.59 | 0.25 | | |
| 2-Propanol/*p*-TsOH | 0.303 | d) | d) | 2.58 | d) | | |
| 2-Trimethylsiloxypropane | 1.36 | 3.36 | 1.72 | 1.20 | 0.15 | 1.26 | e) |
| Triethylsilane | 3.75 | 3.80 | 0.85 | 3.39 | d) | | f) |
| 3-Pentanol | 4.52[g)] | 9.66 | 3.45 | 3.60 | d) | 4.38 | h) |

a) All the photolysis reactions were carried out under the same irradiation conditions (0—5 °C, 2 h) using a 100 W low-pressure mercury lamp by taking 35 mmol of a substrate (RH) and 100 $cm^3$ of acetone. b) Amount of low-boiling liquid distilling below 70 °C at 0.5 Torr after fractionation of crude photolysate. c) Determined by GLC using appropriate internal standards. d) Could not be observed. e) 2,2,3-Trimethyl-3-trimethylsiloxyoxetane (**10**) was also formed. f) 2-Triethylsiloxypropane, 3-triethylsiloxy-2,2,3-trimethyloxetane, pinacol mono(triethylsilyl) ether, and triethylsilanol (**14**—**17**) were also formed. g) Irradiation for 4 h. h) 3-Ethyl-2,2,4-trimethyl-3-oxetanol (**1b**) and 3-ethyl-2-methyl-2,3-pentanediol (**20b**) were also formed.

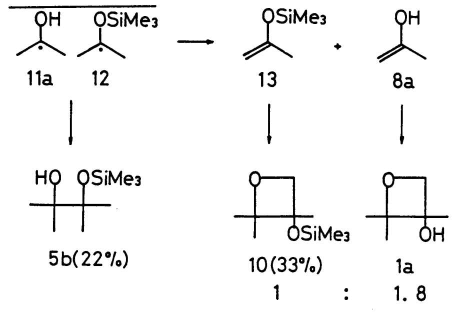


Scheme 1.

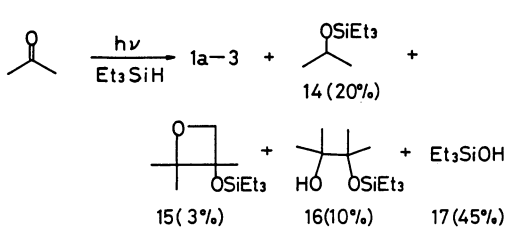
of acetone abstracts a hydrogen from solvent acetone or from a hydrogen donor RH yielding radical pairs **6** and **7** which can terminate to **3**—**5** via coupling reactions or to acetone enol **8a** via disproportionation.[20)] The enol thus generated can be trapped with another excited molecule of acetone as **1a** prior to complete ketonization. Under acidic conditions, the ketonization must be so rapid that **8a** cannot be trapped as oxetane. Table 1 clearly indicates that a hydrogen abstraction process leading to **6** which accounts for the formation of **4** does not contribute appreciably to the formation of **8a**, **2**, and **3** when a better hydrogen donor than acetone like 2-propanol is present. The product **2** may be formed directly from **6** or from **8a** via 2,4,4-trimethyl-2-oxetanol (**9**) which is a regioisomer of **1a**.[16,17)] The former is not the major route because such the pathway should yield **2** in proportion to the formation of **4** against the observation. Both fairly constant **2**/**1a** ratios irrespective of photolysis conditions and the fact that **2** as well as **1a** were not formed at all under acidic conditions are more in accord with the latter pathway.



The photolysis of acetone with 2-trimethylsiloxypropane gave pinacol mono(trimethylsilyl) ether **5b** and 2,2,3-trimethyl-3-trimethylsiloxyoxetane (**10**) in 22 and 33% yields based on the substrate added besides **1a**—**4**. The formation of these products is consistent with the intervention of a pair of radicals, 1-hydroxy-1-methylethyl radical (**11a**) and 1-trimethylsiloxy-1-methylethyl radical (**12**), which terminates to **5b** or disproportionates affording a mixture of **8a** and its trimethylsilyl ether **13**. Noteworthy is the fact that **1a** was formed predominantly over **10** (**1a**/**10**=1.8) in this photolysis reaction. Although the disproportionation step would give **8a** and **13** in comparable amounts, **8a** must remain in a very low concentration throughout the irradiation because of its short lifetime,[21)] while the concentration of **13** must accumulate during the irradiation. The preferential formation of **1a** therefore suggests that an enol can be trapped efficiently as oxetane as soon as it is generated.

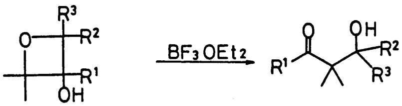


In the case of triethylsilane as a hydrogen donor, four major products, 2-triethylsiloxypropane (**14**), 3-triethylsiloxy-2,2,3-trimethyloxetane (**15**), pinacol mono(triethylsilyl) ether (**16**), and triethylsilanol (**17**) were obtained in 26, 10, 3, and 45% yields, respectively, besides **1**—**3**. Probably, the reaction involves the formation of 1-triethylsiloxy-1-methylethyl radical which accounts for the formation of **14**—**16**.[22)]

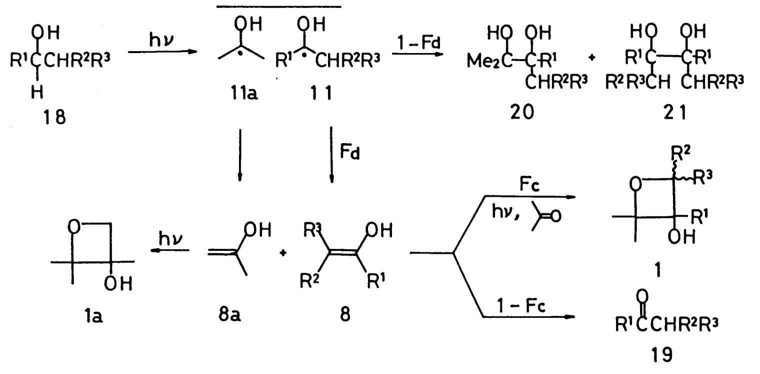


Mechanism for the formation of **17** is not clear.

**Photocycloaddition of Acetone with Other Aliphatic Enols.** Table 1 includes the result of the photolysis of acetone in the presence of 3-pentanol. From the discussion above mentioned, it is expected that irradiation of acetone in the presence of an alcohol (**18b**—**h**) may lead to formation of an enol (**8b**—**h**) derived from the alcohol added, hence a new 3-oxetanol (**1b**—**h**) according to Scheme 2, where Fd and Fc are fractions of enol formation from a hydroxyalkyl radical **11** and oxetane formation from the enol thus generated respectively. Indeed, 3-ethyl-2,2,4-trimethyl-3-oxetanol (**1b**) was obtained as a mixture of two stereoisomers (*E*/*Z*=1) in 24% yield on the basis of the consumed 3-pentanol together with 3-pentanone (**19b**, 18%) and 3-ethyl-2-methyl-2,3-pentanediol (**20b**, 25%) besides **1a**—**3**. Structure of **1b** was deduced from its spectral data (IR, NMR, and MS) and from its chemical property that either stereoisomer of **1b** gave 5-hydroxy-4,4-dimethyl-3-hexanone (**22b**) on treating with boron trifluoride etherate.[19,23] Provided **1b**, **19b**, and **20b** are the sole products from 3-pentanol and all **19b** is formed from an enol **8b**,[20] it follows from the result that a 63% fraction of 1-hydroxy-1-ethylpropyl



1a, b, e    22a, b, e



a) R1=Me; R2=R3=H, b) R1=Et; R2=Me; R3=H, c) R1=i-Pr; R2=R3=Me, d) R1, R2=-(CH$_2$)$_3$-R3=H, e) R1=Et, R2=R3=H, f) R1=i-Pr, R2=Me, R3=H, g) R1=R2=R3=H, h) R1=H, R2=R3=Me

Scheme 2.

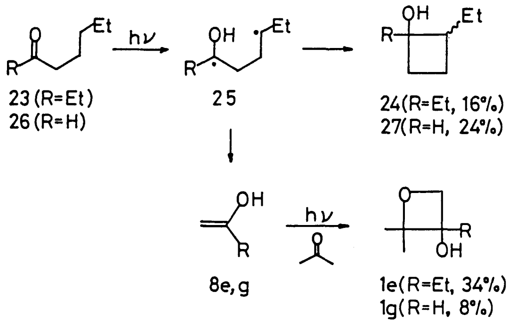
Table 2. Photolysis of Alcohols and Alkanones (RH) in Acetone Solutions[a)]

| Substrate (RH) | Conversion (%) | Enol trapped | Yield/%[b,c)] | | | | $F_d$[d)] (%) | $F_c$[e)] (%) | **1**/**1a** |
|---|---|---|---|---|---|---|---|---|---|
| | | | **1** | **19** | **20** | **21** | | | |
| 2-Propanol (**18a**) | f) | **8a** | 21[g)] | | 11[g)] | | | | |
| 3-Pentanol (**18b**) | 50 | **8b** | 24[h)] | 18 | 25 | | 63 | 57 | 0.45 |
| 2,4-Dimethyl-3-pentanol (**18c**) | 40 | **8c** | 18 | 23 | 14 | 4 | 69 | 44 | 0.33 |
| Cyclopentanol (**18d**) | 56 | **8d** | 5 | 20 | 12 | | 67 | 20 | 0.18 |
| 2-Butanol (**18e**) | 40 | **8e** | 15 | d) | 11 | 4 | | | 0.39 |
| 2-Butanol (**18e**) | 22[i)] | **8e** | 43 | d) | 5 | 1 | | | 0.68 |
| 2-Methyl-3-pentanol (**18f**) | 48 | **8f** | 21[h)] | 19 | 17 | | 70 | 53 | 0.34 |
| Ethanol (**18g**) | f,j) | | k) | f) | 13[g)] | | | | |
| Isobutyl alcohol (**18h**) | 40 | | k) | f) | 28 | 8 | | | |
| 3-Octanone (**23**) | 42[l)] | **8e** | 34 | f) | | | | | |
| Hexanal (**26**) | 96[m)] | **8g** | 8 | f) | | | | | |

a) All the phtolysis reactions were carried out under argon at 0—5 °C for 4 h with a 100 W low-pressure mercury lamp by taking 100 cm$^3$ of acetone and 35 mmol of a substrate RH. b) Determined by GLC. c) Based on the consumed substrate. d) (**1**+**19**)/(**1**+**19**+**20**+**21**). e) **1**/(**1**+**19**). f) Not determined. g) Based on the substrate added. h) As a mixture of two stereoisomers. i) At −70 °C for 2 h. j) 2-Methyl-3-butanone was also formded. k) Could not be detected. l) 1,2-Diethylcyclobutanol (16%) was also obtained. m) 2-Ethylcyclobutanol (24%) and 2-hydroxy-2-methyl-3-octanone (8%) were formed as well.

radical (**11b**) gave the enol **8b** and that a 57% fraction of **8b** was subsequently trapped as oxetane prior to complete ketonization to 3-pentanone. The results of the photolysis of eight different alcohols **18a—h** and two alkanones, 3-octanone (**23**) and hexanal (**26**), in acetone solutions are summarized in Table 2. Several interesting features are worth noting. First of all, a variety of ketone enols including a cyclic (**8d**) and acyclic ones with one (**8a** and **8e**), two (**8b** and **8f**), and three alkyl substituents (**8c**) were successfully trapped and isolated as corresponding oxetanes **1a—f** in the photolysis of secondary alcohols **18a—f** in fairly good yields, in most cases about 20% of the reacted alcohol. Fd and Fc values suggest that the radicals **11b—f** terminate preferentially via disproportionation to the enols and that the subsequent trapping with acetone proceeds with similar efficiencies about 50% irrespective of structure of enols except for **8d**. Since the photodehydrogenation of alcohols **18b—f** in acetone involves the formation of **8a** hence **1a** as a common side reaction, ratios of oxetanes **1b—f/1a**, which are listed in the last column in Table 2, also represent approximate relative efficiencies for the formation of the oxetane from each enol. The fairly constant ratios except for **1d** again suggest that the trapping efficiency does not vary appreciably with the structure of enols.

Norrish II reaction of alkanones is another effective way to generate enols,[24] and it is interesting to see whether photolysis of alkanones in an acetone solution leads to formation of expected 3-oxetanols. Irradiation of 3-octanone (**23**) in acetone gave indeed 3-ethyl-2,2-dimethyl-3-oxetanol (**1e**) in 34% yield together with 1,2-diethylcyclobutanol (**24**) in 16% yield. The formation of **24** and **1e** hence its precursory enol **8e** is consistent with a conventional scheme for the photolysis of alkanones via an intermediate biradical **25**, although it is not clear whether excitation of 3-octanone is direct or sensitized by acetone under the present photolysis conditions. Photolysis of hexanal (**26**) in acetone was more complicated than that of 3-octanone but an expected vinyl alcohol could be isolated as the corresponding oxetanol **1g** in 8% yield along with several other products including 2-ethylcyclobutanol (**27**, 24%) and 2-hydroxy-2-methyl-3-octanone (**28**, 8%). In the photocycloaddition reactions between acetone and enols **8b—g**, regioisomeric 2-oxetanols like **9** might be formed but we could identify neither such compounds nor their decomposition products, presumably because of small amounts of their formation.



Photodehydrogenation of unsymmetrical alcohols such as 2-butanol (**18e**) and 2-methyl-3-pentanol (**18f**) is expected to produce a mixture of two regioisomeric enols **8** and **8′** which is more highly alkylated, hence thermodynamically more favorable than **8**. Indeed, the formation of **8e** and **8e′** has been confirmed by CIDNP experiments in the photochemical decomposition of *t*-butyl hydroperoxide in 2-butanol.[11] In the present experiments, however, only one of the regioisomers, i.e., the less highly alkylated isomer **8**, could be identified as oxetane in the photolyses of both alcohols **18e** and **18f**. For example, irradiation of **18e** in acetone gave **1e** in 15% yield or in 43% yield when the photolysis was carried out at −70 °C but not an isomeric oxetane **1e′** in detectable amounts. Since, as mentioned earlier, excited acetone would trap **8** and **8′** with similar trapping efficiencies, the above results strongly suggest that the formation of enols from unsymmetrical radicals **11e** and **11f** is highly regioselective in preference for the formation of **8e** and **8f** to their regioisomers **8e′** and **8f′**. Probably, in a disproportionation step, β-hydrogen abstraction from **11e** or **11f** by a partner radical **11a** would predominantly occur at the sterically less hindered site to yield a thermodynamically less favorable enol **8** as the major component in contrast to expectation from acid-catalyzed enolization of ketones.

Oxetanes **1b** and **1f** were obtained as two stereoisomeric mixtures in the ratios 1 : 1 and 4 : 1, respectively. These results appear interesting in relation to the stereochemical structure of the enols **8b** and **8f**; however, the stereochemistry of these oxetanes does not seem to provide meaningful information on the geometry of the enols in view of the fact that the

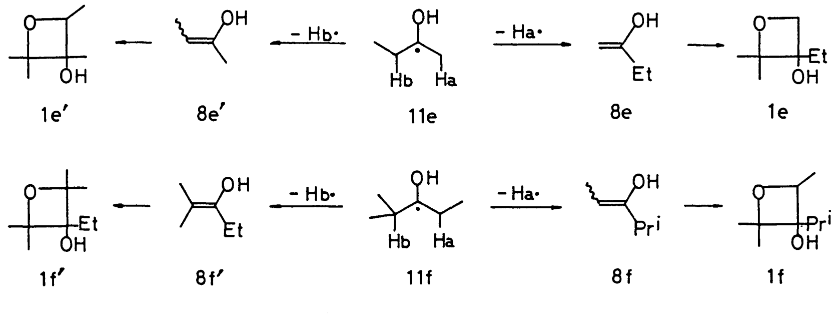
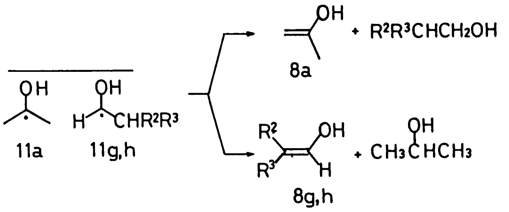


photo-oxetane formation between acetone and electron rich alkenes such as vinyl ethers is a nonstereospecific process.[25]

Temperature significantly affected the formation of oxetane and coupling products. Thus, irradiation of **18e** in acetone at 0—5 °C gave **1e**, **20e**, and **21e** in 15, 11, and 4% yields, while at −70 °C, in 43, 5, and 1% yields, respectively. A marked increase in the yield of the oxetane probably arises from retardation of the rate of ketonization of **8e** and partly from an increase in the fraction of disproportionation from **11e**.

Finally, in contrast to the photolysis of secondary alcohols, we could not detect the formation of aldehyde enols **8g** and **8h** as corresponding oxetanols in the photolysis of two primary alcohols, ethanol (**18g**) and isobutyl alcohol (**18h**), although CIDNP experiments indicate the formation of these enols under similar conditions.[26] In both cases, there were obtained considerable amounts of coupling products but not expected oxetanols **1g** and **1h** in detectable amounts. There seems to be no reason for that excited acetone traps aldehyde enols much less effectively than it does ketone enols. Indeed, vinyl alcohol could be trapped as **1g** in the photolysis of hexanal in acetone. It is therefore conceivable that aldehyde enols are formed in very low concentrations in the photolysis of primary alcohols in acetone solutions. Presumably, disproportionation of a pair of radicals such as **11a** and **11g** would preferentially occur in such a way that **11g** abstracts a hydrogen from **11a** affording acetone enol rather than it loses a $\beta$-hydrogen yielding vinyl alcohol, since **11g** is sterically less hindered and probably more reactive than its partner radical **11a**.



The present results indicate that aliphatic enols generated by photodehydrogenation of alcohols and by Norrish II reaction of alkanones can be isolated as corresponding 3-oxetanols when these photolysis reactions are carried out in acetone solutions, providing a rare example of [2+2]cycloadditions of simple enols.

## Experimental

IR spectra were recorded on a Hitachi R-215 spectrophotometer. NMR spectra were recorded in carbon tetrachloride on a Hitachi R-20B spectrometer. Mass spectra were taken with a Hitachi M-60 mass spectrometer or an ion cyclotron resonance (ICR) mass spectrometer.[27] GLC were performed with a Hitachi 163 gas chromatograph equipped with glass columns (6 mm×1.5, 2.0, and 3 m) packed with 10% Silicone oil SE-30 on Chamelite CS (SE-30), 25% silicon oil DC-550 on Chamelite CS (SIDC), 25% Apiezon grease L on Chromosorb W (AGL), 15% Carbowax 20M on Chamelite CS (CW), or 10% diethylene glycol succinate polyester on Chamelite CS (DGS). Acetone was purified by refluxing with potassium permanganate followed by fractionation.

**2,2,3-Trimethyl-3-(trimethylsiloxy)oxetane (10).** A solution of 2-(trimethylsiloxy)propene (4.61 g) in acetone (100 cm³) was irradiated with a 100 W low-pressure mercury lamp under argon for 2 h, during which period 56% starting material was consumed. Fractionation of crude photolysate gave **10** as a colorless oil (1.68 g, 55%): bp 66—68 °C (22 Torr; 1 Torr=133.3 Pa); IR (neat) 1255, 1025, and 845 cm⁻¹; ¹H NMR $\delta$=0.09 (9H, s), 1.18 (3H, s), 1.30 (3H, s), 1.43 (3H, s), 3.94 (1H, d, $J$=6.0 Hz), and 4.32 (1H, d, $J$=6.0 Hz). Found: C, 57.25; H, 10.70%. Calcd for $C_9H_{20}O_2Si$: C, 57.40; C, 10.71%. A foregoing fraction, bp 35—58 °C (28 Torr) contained another component which was shown to be 4-hydroxy-4-methyl-2-pentanone (**2**). GLC analysis (SE-30, 100 °C) of the crude photolysate indicated the formation of **10** and **2** in the ratio 86 : 14. **10** gave quantitatively 2,2,3-trimethyl-3-oxetanol (**1a**) on treatment with methanol.

**Photolysis of Acetone in the Presence of a Hydrogen-Donating Substrate. General Procedure.** Acetone (100 cm³) was directly irradiated under argon with or without a hydrogen donating substrate (35 mmol) using a 100 W low-pressure mercury lamp (Eikosha Halos PIH-100) in a 200 cm³ photolysis vessel which was immersed in an ice bath. After irradiation, acetone was first removed by distillation under reduced pressure (ca. 120 Torr) and resulting oil was fractionated under vacuum from 6 to 0.5 Torr. Each fraction was analyzed directly by GLC using an appropriate internal standard. In most cases, products were isolated by GLC and characterized from their spectral data.

**Photolysis of Acetone.** Irradiation of acetone (100 cm³) for 2 h gave 0.094 g of an oil, bp 42—58 °C (6 Torr), besides high-boiling material (0.212 g) after fractionation of photolysate. The former oil was shown to be a mixture of 2,2,3-trimethyl-3-oxetanol (**1a**), 4-hydroxy-4-methyl-2-pentanone (**2**), pinacol (**3**), and 2,5-hexanedione (**4**) in the ratio 51 : 23 : 9 : 17 in agreement with the earlier observation.[16]

**Photolysis of Acetone with 2-Propanol (18a).** Irradiation of acetone (100 cm³) containing 2-propanol (2.19 g, 35.5 mmol) for 2 h gave a mixture of **1a**—**4** in the ratio 42 : 23 : 31 : 3 [1.016 g, bp 48—58 °C (6 Torr)] besides 0.246 g of a high boiling material.

**Photolysis of Acetone with 2-Propanol in the Presence of *p*-Toluenesulfonic Acid.** A solution of 2-propanol (2.14 g), *p*-toluenesulfonic acid (99 mg), and acetone (100 cm³) was irradiated for 2 h. Most acetone was removed by distillation at 110 Torr. Residue was dissolved in ether, washed with aq. $NaHCO_3$, and dried. Solvent was removed to give a solid (303 mg) which was shown to be almost pure pinacol hydrate.

**Photolysis of Acetone with Cyclohexane.** Irradiation of an acetone solution of cyclohexane (2.99 g) for 2 h gave 0.583 g of an oil, bp 49—53 °C (6 Torr), besides 0.381 g of a high-boiling material. The former oil consisted of **1a**—**4** and another major component which was shown to be 2-cyclohexyl-2-propanol (**5a**) by comparison with an authentic sample: IR 3400 cm⁻¹; ¹H NMR $\delta$=1.08 (6H, s), 0.9—2.0 (11H, m). GLC analysis of the crude photolysate indicated the formation of **1a**—**4** and **5a** in the ratio 40 : 18 : 13 : 4 : 24.

**Photolysis of Acetone with 2-Trimethylsiloxypropane.** Irradiation of an acetone solution of 2-trimethylsiloxypropane (4.73 g) for 2 h led to 16% consumption of 2-trimethylsiloxypropane to give 1.361 g of an oil distilling below 49 °C at 2 Torr besides 0.136 g of a high-boiling material. GLC analysis (2 m, SE-30, 80 °C) indicated the former oil to be a mixture of **1a**—**4** and two other major components ($t_R$=10.7 and 11.4 min), which were isolated by GLC and assigned to 2,3-dimethyl-3-(trimethylsiloxy)-2-butanol (**5b**) and **10**, respectively. **5b**: $^1$H NMR $\delta$=0.13 (9H, s), 1.08 (6H, s), 1.21 (s, 6H). On treatment with methanol **5b** cleanly gave pinacol. GLC analysis indicated the formation of **5b** and **10** in 22 and 33% yield, respectively on the basis of 2-trimethylsiloxypropane consumed. The relative yields of **1a**—**4**, **5b**, and **10** were 36 : 19 : 11 : 1 : 13 : 20.

**Photolysis of Acetone with Triethylsilane.** An acetone solution of triethylsilane (2.35 g) was irradiated for 2 h. Distillation of photolysate gave two fractions, I (2.22 g) distilling below 90 °C at 17 Torr and II (1.51 g), bp 123—135 °C (3 Torr). The fraction I contained **1a**—**3** and two other components. They were identified as triethylisopropoxysilane (**14**) and triethylsilanol (**17**) by comparison with authentic specimens. The fraction II consisted of two major components and they were assigned to 3-triethylsiloxy-2,2,3-trimethyloxetane (**15**) and 2,3-dimethyl-3-triethylsiloxy-2-butanol (**16**) from their spectral data. **15**: $^1$H NMR $\delta$=0.4—1.1 (15H, m), 1.18 (3H, s), 1.32 (3H, s), 1.42 (3H, s), 3.95 (1H, d, $J$=6.0 Hz), 4.29 (1H, d, $J$=6.0 Hz). On treatment with methanol **15** cleanly gave **1a**. **16**: IR 3430, 1020, and 740 cm$^{-1}$; $^1$H NMR $\delta$=0.45—1.1 (15H, m), 1.09 (6H, s), 1.22 (6H, s), 1.97 (1H, s, disappeared on adding $D_2O$). GLC analysis indicated the formation of **14**, **15**, **16**, and **17** in 26, 3, 10, and 45% yields, respectively. The relative yields for **1a**—**3**, **14**, **15**, **16**, and **17** were 15 : 3 : 14 : 21 : 2 : 8 : 36, respectively.

**Photolysis of Acetone with 3-Pentanol (18b).** Irradiation of 3-pentanol (3.10 g) in acetone (100 cm$^3$) for 2 h resulted in 46% consumption of 3-pentanol to give an oil (3.18 g) distilling below 60 °C at 2 Torr besides a high-boiling residue (0.51 g). The distilled oil was shown to be a mixture of three major components besides **1a**—**3**, unchanged **18b**, and 3-pentanone (**19b**). They were assigned to (*E*)- and (*Z*)-stereoisomers of 3-ethyl-2,2,4-trimethyl-3-oxetanol (**1b**) and 3-ethyl-2-methyl-2,3-pentanediol (**20b**) from their spectral data. (*E*)-**1b** (tentative stereochemical assignment): MS (ICR) *m/z* 145 ($M^+$ +1); IR 3420, 1150, 1055, 1010, and 905 cm$^{-1}$; $^1$H NMR $\delta$=0.84 (3H, t, $J$=7.2 Hz), 1.19 (3H, d, $J$=6.6 Hz), 1.24 (3H, s), 1.28 (3H, s), 1.65 (2H, q, $J$=7.2 Hz), 1.85 (1H, s, OH), and 4.30 (1H, q, $J$=6.6 Hz). On treatment with boron trifluoride etherate in dichloromethane (−15 °C, 30 min), this compound was smoothly converted into a single product which was shown to be 5-hydroxy-4,4-dimethyl-3-hexanone (**22b**): IR 3460 and 1700 cm$^{-1}$; $^1$H NMR $\delta$=0.99 (3H, t, $J$=7.2 Hz), 1.03 (3H, d, $J$=6.6 Hz), 1.10 (6H, s), 2.46 (2H, q, $J$=7.2 Hz), 2.32 (1H, OH), 3.80 (1H, q, $J$=6.6 Hz). Found: C, 66.50; H, 11.25%. Calcd for $C_8H_{16}O_2$: C, 66.68; H, 11.18%. (*Z*)-**1b** (tentative stereochemical assignment): MS (ICR) *m/z* 145 ($M^+$ +1); IR 3450, 1060, and 1015 cm$^{-1}$; $^1$H NMR $\delta$=0.89 (3H, t, $J$=7.2 Hz), 1.18 (3H, d, $J$=6.6 Hz), 1.20 (3H, s), 1.30 (3H, s), 1.69 (2H, q, $J$=7.2 Hz), and 4.35 (1H, q, $J$=6.6 Hz). On treatment with boron trifluoride etherate, this isomer also gave **22b** as a single product. An attempt at isolation of **1b** by GLC (3m, DGS) at 130 °C resulted in collection of **22b**. **20b**: IR 3450, 1380, 1125, and 950 cm$^{-1}$; $^1$H NMR $\delta$=0.77—1.5 (10H, m), 1.16 (s, 6H), and 1.63 (2H, s, disappeared on adding $D_2O$). GLC analysis of crude photolysate indicated the formation of **1a**—**3**, **1b**, **19b**, and **20b** in the ratio 34 : 12 : 13 : 15 : 11 : 15. The yield of the last three products were shown to be 24 (*E*/*Z*=1.0), 25, and 18%, respectively, based on 3-pentanol reacted.

**Photolysis of Acetone with 2,4-Dimethyl-3-pentanol (18c).** Irradiation of a solution of **18c** (4.14 g) in acetone (100 cm$^3$) for 4 h resulted in 40% consumption of **18c** to give two fractions, I [2.524 g, bp 25—46 °C (6 Torr)] and II [2.364 g, bp 52—64 °C (1 Torr)], besides a high-boiling residue (0.378 g) after fractionation of photolysate. The fraction I contained mainly **1a**—**3** (in the ratio 61 : 24 : 15), unchanged **18c**, and 2,4-dimethyl-3-pentanone (**19c**). The fraction II contained two major components and three minor ones besides small amounts of **1a**—**3**. The former two were shown to be 3-isopropyl-2,2,4,4-tetramethyl-3-oxetanol (**1c**) and 3-isopropyl-2,4-dimethyl-2,3-pentanediol (**20c**) by their spectral data. **1c**: mp 99—100 °C; MS (ICR) *m/z* 173 ($M^+$ +1); IR (Nujol) 3440, 1020 cm$^{-1}$; $^1$H NMR $\delta$=0.82 (6H, d, $J$=6.0 Hz), 1.20 (6H, s), 1.37 (6H, s), 1.60 (1H, s, OH), and 1.88—2.63 (m, 1H). **20c**: IR 3420 cm$^{-1}$; $^1$H NMR $\delta$=1.05 (12H, d, $J$=6.0 Hz), 1.27 (6H, s), 1.8—2.4 (2H, m), and 1.80 (2H, broad s, disappeared on adding $D_2O$). One of the three minor components in II was assigned to 3,4-diisopropyl-2,5-dimethyl-3,4-hexanediol (**21c**) from its spectral properties: IR 3470 cm$^{-1}$; $^1$H NMR $\delta$=0.93 (24H, d, $J$=6.6 Hz), 1.7—2.3 (2H, m), and 2.0 (2H, broad s, OH). The rest two components were not identified yet. GLC analysis (1.5 m, AGL, 130 °C) of crude photolysate indicated the formation of **19c**, **1c**, **20c**, and **21c** in 23, 18, 14, and 4% yields, respectively.

**Photolysis of Acetone with Cyclopentanol (18d).** Irradiation of a solution of cyclopentanol (3.10 g) in acetone for 4 h resulted in 34% consumption of the alcohol to yield two liquid fractions, I (1.23 g, distilling below 48 °C at 1 Torr) and II [0.36 g, bp 63—70 °C (0.5 Torr)], besides a high-boiling residue (1.09 g) after fractionation of crude photolysate. The fraction I contained mainly **1a**—**3**, cyclopentanol, and cyclopentanone (**19d**). The fraction II contained mainly two components. They were isolated by GLC and assigned to 1-hydroxy-7,7-dimethyl-6-oxabicyclo[3.2.0]heptane (**1d**) and 1-(2-hydroxyprop-2-yl)cyclopentanol (**20d**). **1d**: MS (ICR) *m/z* 143 ($M^+$ +1); IR 3430 cm$^{-1}$; $^1$H NMR $\delta$=1.17 (3H, s), 1.38 (3H, s), 1.5—2.1 (m, 6H), 2.36 (1H, disappeared on adding $D_2O$), and 4.62 (1H, d, $J$=2.5 Hz). **20d**: IR 3500 cm$^{-1}$; $^1$H NMR $\delta$=1.19 (6H, s), 1.47—1.87 (8H, m), and 2.35 (2H, disappeared on adding $D_2O$). GLC analysis (1.5 m, AGL, 130 °C) of crude photolysate indicated the formation of **1a**—**4**, **19d**, **1d**, and **20d** in the ratio 31 : 12 : 14 : 3 : 21 : 6 : 13. The yields of the last three components were 20, 5.2, and 12%, respectively, based on the consumed **18d**.

**Photolysis of Acetone with 2-Butanol (18e).** Irradiation of a solution of 2-butanol (2.71 g) in acetone for 4 h resulted in 37% consumption of 2-butanol to give two liquid fractions, I (1.1 g, distilling below 62 °C at 6 Torr) and II [0.89 g, bp 80—88 °C (2 Torr)], besides a high-boiling residue (0.3 g). I contained mainly **1a**—**4** (in the ratio 48 : 20 : 23 : 9). GLC analysis (2 m, SE-30, 130 °C) showed II to be a mixture of three major components ($t_R$ 4.7, 5.1, and 7.8 min). They were assigned to 3-ethyl-2,2-dimethyl-3-oxetanol (**1e**), 2,3-dimethyl-2,3-pentanediol (**20e**), and 3,4-dimethyl-3,4-

hexanediol (**21e**) from their spectral data. **1e**: MS (ICR) $m/z$ 131 (M+1); IR 3420 cm$^{-1}$; $^1$H NMR $\delta$=0.90 (3H, t, $J$=6.0 Hz), 1.26 (3H, s), 1.33 (3H, s), 1.44—1.91 (2H, m), and 4.16 (2H, almost s). On treatment with boron trifluoride etherate, **1e** was converted into 1-hydroxy-2,2-dimethyl-3-pentanone (**22e**): $^1$H NMR $\delta$=1.00 (3H, t, $J$=7.2 Hz), 1.11 (6H, s), 1.81 (1H, disappeared on addition of D$_2$O), and 3.43 (2H, s). The NMR spectrum was in agreement with that reported.[28] **22e** was also obtained when **1e** was passed through a 3 m DGS column at 130 °C. **20e**: IR 3430 cm$^{-1}$; $^1$H NMR $\delta$=0.92 (3H, t, $J$=6.6 Hz), 1.07 (3H, s), 1.15 (6H, s), 1.43 (2H, q, $J$=6.6 Hz), and 1.65 (2H, OH). The IR spectrum was superimposable with that reported.[29] The NMR spectrum of **21e** [$\delta$=0.91 (6H, complicated), 1.06 (6H, s), 1.8 (2H, OH)] was in agreement with that reported.[30] GLC analysis of crude photolysate indicated the formation of **1a—4**, **1e**, **20e**, and **21e** in the ratio 36 : 15 : 17 : 14 : 8 : 3. The yields of the last three components were 15, 11, and 4%, respectively, based on 2-butanol reacted.

**Photolysis of Acetone with 2-Butanol at Low Temperature.** Irradiation of 2-butanol (2.71 g) in acetone (100 cm$^3$) at Dry Ice temperature for 2 h resulted in 14% consumption of 2-butanol to give 1.18 g of an oil distilling below 57 °C at 3 Torr. GLC analysis indicated the oil to be a mixture of **1a—4**, **1e**, **20e**, and **21e** in the ratio 38 : 16 : 4 : 10 : 26 : 3 :1. The yields of the last three components were 43, 5, and 1%, respectively, on the basis of 2-butanol consumed.

**Photolysis of Acetone with 2-Methyl-3-pentanol (18f).** Irradiation of 2-methyl-3-pentanol (3.63 g) in acetone for 4 h resulted in 42% consumption of the alcohol to give two liquid fractions, I (3.13 g, distilling below 48 °C at 2 Torr) and II [1.0 g, bp 55—70 °C (1.5 Torr)]. Fraction I contained mainly **1a—3**, unchanged **18f**, and 2-methyl-3-pentanone (**19f**). GLC analysis (1.5 m, SIDC, 130 °C) indicated the fraction II to be a mixture of two major components ($t_R$ 15.2 and 28 min) together with two minor ones ($t_R$ 17.2 and 18.8 min) besides small amounts of **1a—3**. The major two products were shown to be 3-isopropyl-2,2,4-trimethyl-3-oxetanol (**1f**) and 3-ethyl-2,4-dimethyl-2,3-pentanediol (**20f**). **1f**: MS (ICR) $m/z$ 159 (M$^+$+1); IR 3430 cm$^{-1}$; $^1$H NMR $\delta$=0.76 (3H, d, $J$=7.2), 0.80 (3H, d, $J$=7.2 Hz), 1.15 (3H, d, $J$=6.0 Hz), 1.21 (3H, s), 1.35 (3H, s), 1.97 (1H, disappeared on addition of D$_2$O), 1.9—2.4 (1H, m), and 4.40 (1H, q, $J$=6.0 Hz). **20f**: IR 3440 cm$^{-1}$. $^1$H NMR $\delta$=0.93 (3H, d, $J$=6.6 Hz), 0.99 (3H, d, $J$=7.2 Hz), 0.8—1.0 (3H), 1.21 (6H, s), 1.4—2.1 (2H, m), and 2.2 (2H, disappeared on addition of D$_2$O). One of the two minor products was assigned to a stereoisomer of **1f** from the following spectral data: IR 3430 cm$^{-1}$; $^1$H NMR $\delta$=0.82 (3H, d, $J$=6.6 Hz), 0.85 (3H, d, $J$=6.6 Hz), 1.16 (3H, d, $J$=7.2 Hz), 1.22 (3H, s), 1.36 (3H, s), 1.9—2.4 (1H, m), and 4.24 (1H, q, $J$=7.2 Hz). The rest one components was not identified yet. GLC analysis indicated the formation of **1a—3**, **19f**, **1f** (4 : 1 mixture of stereoisomers), and **20f** in the ratio 39 : 17 : 11 : 12 : 13 : 11. The yields of the last three products were 19, 21, and 17%, respectively, on the basis of 2-methyl-3-pentanol consumed.

**Photolysis of Acetone with Ethanol (18g).** Irradiation of ethanol (1.67 g) in acetone for 4 h gave 2.134 g of an oil distilling below 63 °C at 2 Torr besides a high-boiling residue (0.323 g). GLC analysis (1.5 m, SIDC, 100 °C) indicated the oil to be a mixture of two major products ($t_R$ 3.6 and 6.0 min) besides **1a—3**. They were shown to be 3-hydroxy-3-methyl-2-butanone and 2-methyl-2,3-butanediol (**20g**) by comparison with the authentic specimens. **20g**: IR 3420 cm$^{-1}$; $^1$H NMR $\delta$=1.13 (6H, s), 1.14 (3H, d, $J$=7.2 Hz), 3.50 (1H, q, $J$=7.2 Hz), and 3.61 (2H, disappeared on addition of D$_2$O). GLC analysis showed the formation of **1a—3**, 3-hydroxy-3-methyl-2-butanone, and **20g** in the ratio 38 : 17 : 18 : 5 : 22.

**Photolysis of Acetone with Isobutyl Alcohol (18h).** Irradiation of isobutyl alcohol (2.70 g) in acetone for 4 h resulted in 40% consumption of the alcohol to give 1.85 g of an oil distilling below 53 °C at 2 Torr besides a high-boiling residue (0.467 g). GLC analysis (2 m, SE-30, 80 °C) indicated the oil to be a mixture of two major components ($t_R$ 10.6 and 26 min) besides **1a—4**. They were assigned to 2,4-dimethyl-2,3-pentanediol (**20h**) and 2,5-dimethyl-3,4-hexanediol (**21h**, mostly as meso form) from their spectral data which were in agreement with those reported.[29] GLC analysis indicated the formation of **1a—4**, **20h**, and **21h** in the ratio 32 : 14 : 13 : 7 : 27 : 8. The yields of the last two products were 28 and 8%, respectively, based on isobutyl alcohol consumed.

**Photolysis of Acetone with 3-Octanone (23).** Irradiation of 3-octanone (4.66 g) in acetone (100 cm$^3$) for 4 h resulted in 42% consumption of 3-octanone to give, after fractionation of crude photolysate, two liquid fractions, I (4.04 g, distilling below 33 °C at 0.5 Torr) and II [0.67 g, bp 42—64 °C (0.5 Torr)], besides a high-boiling residue (1.09 g). Fraction I contained mainly **1a** and **2** other than **23**. Fraction II contained two major components which were assigned to **1e** and 1,2-diethylcyclobutanol (**24**) from their spectral properties. **24**: MS $m/z$ 129 (M$^+$+1); IR 3430 cm$^{-1}$; $^1$H NMR $\delta$= 0.87 (6H, complicated), 1.2—2.07 (9H, m), 1.17 (1H, disappeared on adding D$_2$O). GLC analysis (2 m, SE-30, 80 °C) indicated the formation of **1a**, **2**, **1e**, and **24** in the ratio 46 : 19 : 24 : 11. The yields of the last two products were 34 and 16%, respectively, on the basis of 3-octanone consumed.

**Photolysis of Acetone with Hexanal (26).** Irradiation of hexanal (3.64 g) in acetone (100 cm$^3$) for 4 h resulted in 96% consumption of hexanal to give, after fractionation of photolysate, two liquid fractions, I (1.54 g distilling below 30 °C at 0.5 Torr) and II [0.80 g, bp 54—67 °C (0.5 Torr)], besides a high-boiling residue (0.26 g). GLC analysis (1.5 m, SIDC, 70 °C) indicated the fraction I to contain three major components ($t_R$ 27.6, 32.8, and 40.4 min) other than **1a** and **2** ($t_R$ 44.4 and 35.2 min, respectively). They were characterized as ($E$)- and ($Z$)-stereoisomers of 2-ethylcyclobutanol (**27**) and 2,2-dimethyl-3-oxetanol (**1g**) from their spectral properties. ($E$)-**27** (tentative stereochemical assignment): IR 3350 and 1105 cm$^{-1}$; $^1$H NMR $\delta$=0.87 (3H, t, $J$=6.6 Hz), 1.08—2.27 (7H, m), 2.07 (1H, disappeared on adding D$_2$O), and 3.69 (1H, m). ($Z$)-**27** (tentative stereochemical assignment): IR 3330 and 1120 cm$^{-1}$; $^1$H NMR $\delta$=0.87 (3H, t, $J$=6.6 Hz), 1.06—2.6 (7H, m), 1.54 (1H, disappeared on adding D$_2$O), and 4.27 (1H, m). These NMR spectra were in agreement with those reported.[31] **1g**: MS $m/z$ 103 (M$^+$+1), 72, and 59; IR 3400, 1150, 1120, 1045, 975, 955, and 825 cm$^{-1}$; $^1$H NMR $\delta$=1.29 (3H, s), 1.32 (3H, s), 4.0—4.62 (3H, m). Fraction II contained two major components. One of them was assigned to 2-hydroxy-2-methyl-3-octanone (**28**): IR 3450 and 1715 cm$^{-1}$; $^1$H NMR $\delta$=0.91 (3H, t, $J$=6.5 Hz), 1.29 (6H, s), 1.07—1.64 (6H, m), 2.46 (2H, t, $J$=6.6 Hz), and 3.4 (1H, OH). GLC analysis indicated the formation of **1a**, **2**, **27** (2 : 1 stereoisomeric mixture), **1g**, and **28** in the ratio 14 : 6 : 48 : 16 : 16. The yields of the last three products were 24, 8, and 8%, respectively, on the basis of hexanal consumed.

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