thermal relaxation time of the gas; so the operational mode can be treated as continuous. As a check, we verified that the amount of product produced was proportional to pulse duration, and, that at intermediate power levels, pulsed and CW operation gave consistent results.

Measurements were made first to determine the laser frequency giving the most efficient reaction. Figure 1 shows the optical absorption coefficient over the 966-cm^{-1} band (obtained from spectrophotometer measurements) and the reaction rate R for various laser frequencies (at fixed input power of 4.5 W into the cell with 200-Torr initial gas pressure). There is a gap in the R data because the CO_2 laser has no output in the 956-963-cm^{-1} range. We note that the reaction rate maximizes at a frequency ~7 cm^{-1} below the 966-cm^{-1} absorption band peak. This effect, termed "red shift", is observed in other compounds[6-9] and has been ascribed to vibrational anharmonicity and "hot-band" absorption.

On the basis of the rate data the laser frequency 953 cm^{-1} was used for measurements of the quantum requirement Q, defined as the number of photons absorbed per product molecule produced. This is identical with the ratio of the photon absorption rate to the reaction rate (in units of product molecules per second). Both of these quantities, it should be noted, are directly and easily measurable. The photon absorption rate comes simply from a measurement of the total power absorbed in the cell (corrected for window losses), while the rate of product molecule production is derived from the rate data using only the cell volume and the optical absorption coefficient of the CH_2CF_2 product at 1731 cm^{-1}.

Figure 2 shows the dependence of Q on laser power and initial CH_3CF_2Cl pressure. At 28 W and 600 Torr, Q reaches the value 5.6 photons per molecule dissociated, which is very close to the ΔH equivalent[3] of 5.2 photons per molecule (at 953 cm^{-1}) and which is nearly four times smaller than the activation energy equivalent[4] of 22 photons per molecule. In the high power, high pressure limit it appears that virtually all the energy $E_A - \Delta H$ released per reacting molecule is utilized by unreacted molecules in the beam, with negligible rate of energy loss due to thermal diffusion and convection or fluorescence.

Whereas the minimum Q value is set by ΔH in endothermic reactions, Q could approach 0 in exothermic reactions. The results of Basov et al.[10] support this conclusion. In studies of eight reactions, it was found that irradiation by a single 10^{-2}-s pulse at intensities above a threshold level produced nearly 100% conversion in the exothermic reactions, while for endothermic reactions the product yield was proportional to the number of pulses.

The reason why the "enthalpy limit" was not reached in the reported reactions of ethylene[1] and ethane[2] is not yet clear. The ethylene reaction mechanism is complicated, with numerous products, and appropriate values of E_A and ΔH are not clearly defined, while close inspection of the ethane data[2] indicates a limiting value of Q that is less than the claimed E_A equivalent. Perhaps the determining factor lies in having an efficient mechanism for feeding the released energy $E_A - \Delta H$ back to unreacted molecules. In the present case for example, most of $E_A - \Delta H$ may reside in vibrational excitation of the HCl product which is quickly transfered in collisions with CH_3CF_2Cl molecules.

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Product Control by Light Intensity. The Photoaddition of Aldehydes to α-Diketones

Sir:

The product(s) formed in a photochemical reaction can depend markedly on experimental variables such as wavelength of exciting light, concentration(s) of reactant(s), temperature, and solvent. Except for cases involving intense irradiation, variation in light intensity may affect quantum yield but is generally[1] not considered to be an important factor in determining products of reaction. We wish to report an example of a reaction in which product composition can be affected considerably by variation of light intensity over a moderate range readily accessible with conventional light sources.

Irradiation of benzene solutions of bicyclo[2.2.2]octane-2,3-dione (BOD) and aldehydes produces[2-5] mixtures of keto ester **1** and hydroxy diketone **2**. As part of an investigation of mechanism, the reaction with *p*-chlorobenzaldehyde was studied in detail. Both quantum yield and product ratio (**1**:**2**) were shown to vary with intensity of absorbed light for identical conversions (20%) of BOD. As shown in Table I, at the lowest light intensity used **1** constituted 94% of the reaction product, while at the highest intensity **2** was 71% of the total. This dramatic effect can be preparatively useful and is clearly of

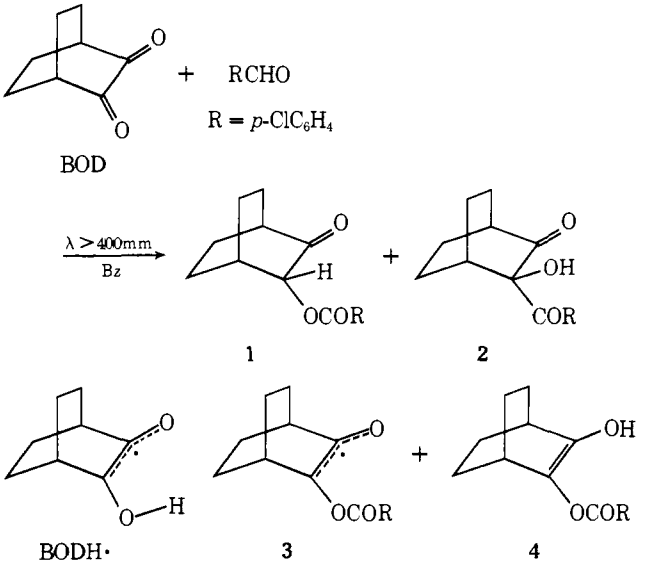

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Table I. Irradiations of Bicyclo[2.2.2]octane-2,3-dione (BOD) and *p*-Chlorobenzaldehyde at Different Light Intensities[a]

I_{abs}[b]	0.54	1.75	4.0	38.5	94.5	High[c]	Very high[d]
ϕ_{BOD}[e]	0.60	0.56	0.47	0.37	0.34		
Ratio[f] **1:2**	14.8	9.5	6.7	3.4	2.0	0.9	0.4

[a] Degassed benzene solution (3 ml), 2.7×10^{-2} M in BOD and 0.28 M in aldehyde, irradiated to 20% disappearance of BOD as determined by decrease of the maximum at 460 nm. [b] Total initial absorbed light intensity (einstein/min $\times 10^7$, determined by ferrioxalate actinometry) at 436 nm; light path 10 mm, unmasked area of cell, 9×27 mm. After 20% conversion, the absorbed light intensity was 92% of the initial value. [c] Total absorbed light, $\lambda > 425$ nm, from a 200-W high-pressure mercury lamp. [d] Total absorbed light, $\lambda > 425$ nm, from repeated flashing of a commercial photographic flash lamp. [e] Quantum yield for disappearance of BOD determined over the initial 5% of reaction. [f] Ratio of α-keto ester (**1**) to hydroxy diketone (**2**) as determined by high-pressure liquid chromatography on silica gel. Total yields of **1** + **2** were constant; both products were shown to be stable under the conditions of analysis. Identical values were obtained after 30% conversion.

mechanistic significance. It emphasizes the importance of including light intensity in detailed studies of photochemical reactions. In particular, the present results rule out the simple mechanism recently proposed[3e] for reaction of a closely related α-diketone with aldehydes. Equations 1-8 are proposed to account for the results observed.

$$\mathrm{BOD} \xrightarrow{h\nu} \mathrm{BOD}^{*1} \xrightarrow{\mathrm{isc}} \mathrm{BOD}^{*3} \qquad \phi_{\mathrm{isc}} \sim 1 \qquad (1)$$

$$\mathrm{BOD}^{*3} \rightarrow \mathrm{BOD} \qquad (2)$$

$$\mathrm{BOD}^{*3} + \mathrm{ArCHO} \rightarrow \mathrm{BODH}\cdot + \mathrm{Ar\dot{C}O}$$
$$\rightarrow \mathrm{BODH}\cdot + \mathrm{Ar\dot{C}O} \qquad (3)$$

$$\mathrm{BODH}\cdot + \mathrm{Ar\dot{C}O} \xrightarrow{k_4} \mathrm{BOD} + \mathrm{ArCHO} \qquad (4)$$

$$\xrightarrow{k_5} \mathbf{2} \qquad (5)$$

$$\xrightarrow{k_6} \mathbf{4} \rightarrow \mathbf{1} \qquad (6)$$

$$\mathrm{BOD} + \mathrm{Ar\dot{C}O} \xrightarrow{k_7} \mathbf{3} \qquad (7)$$

$$\mathbf{3} + \mathrm{BODH}\cdot \rightarrow \mathbf{4} + \mathrm{BOD} \rightarrow \mathbf{1} \qquad (8)$$

Excitation of BOD to the singlet state[6] followed by intersystem crossing to the triplet[7] and hydrogen atom transfer from aldehyde affords a radical pair in a solvent cage. Diffusion from the cage will then give free semidione (BODH·) and aroyl radicals.[8] Subsequent encounters between radicals can result either in back transfer of hydrogen to regenerate ground state starting materials[10] and thereby reduce the overall quantum yield or in radical coupling to give predominantly (or exclusively[11]) **2**. As an alternative to radical coupling, encounters between aroyl radicals and BOD will result in formation (possibly reversibly) of the new radical **3**[12] which then reacts with BODH· to afford **1** via it enol (**4**).[14,15]

The primary effect of light intensity on this system should be to determine the steady-state free radical concentrations. At high light intensities and concomitant high radical concentrations, radical coupling will predominate resulting in an increased rate of formation of **2** (via reaction 5) and in reduction of the quantum yield for disappearance of BOD (via reaction 4). At lower light intensities and correspondingly lower free radical concentrations, formation of the addition product **3** (via reaction 7) will become more important resulting in a higher fraction of **1** in the products and higher quantum yield. Similar effects of light intensity would thus be predicted for any system in which radical-radical reactions and radical-molecule reactions are in competition.

The scheme suggested above also predicts that product composition should depend upon the concentration of BOD present; this prediction was borne out by experiment. The results of a series of experiments in which benzene solutions containing different concentrations of BOD were irradiated at identical initial absorbed light intensity are presented in

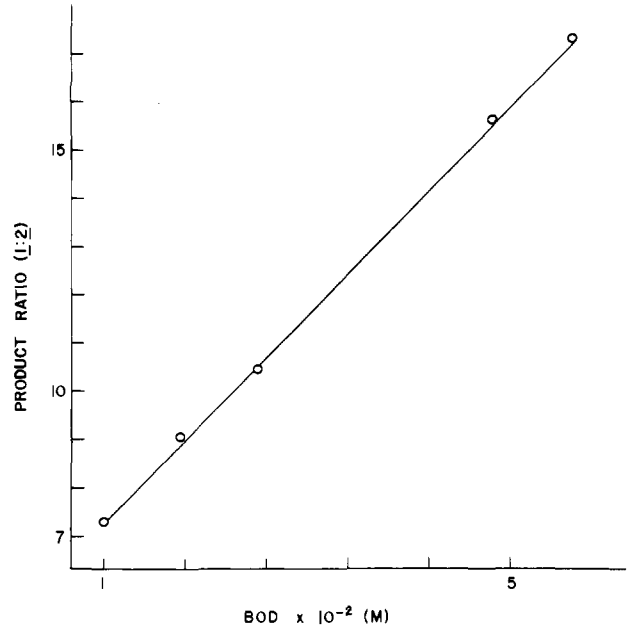

Figure 1. Plot of product ratio vs. concentration of BOD from irradiations at 436 nm of degassed benzene solutions of 0.28 M *p*-chlorobenzaldehyde. Initial absorbed light intensity $1.0 \pm 0.1 \times 10^{-7}$ einstein/min.

Figure 1. The ratio **1:2** increased linearly as a function of BOD concentration.

Results similar to those described above have been obtained[1,16] with camphorquinone. The formation of products of types **1** and **2** in reactions of 1,1,4,4-tetramethyltetralin-2,3-dione[3e,16] and 2,2,5,5-tetramethyltetrahydrofuran-3,4-dione[2] suggest that these diketones may also react via the mechanism suggested above.

Acknowledgment. We wish to acknowledge a stimulating discussion with Professor G. S. Hammond as well as the cooperation of Professor M. Cocivera in determination of the ESR spectra.

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(5) The facile isomerization **2** → **1** will be reported separately. It was responsible for the earlier failure[3c] to detect products of type **2** in reactions of camphorquinone with *p*-chlorobenzaldehyde.
(6) Light of $\lambda > 400$ nm was used in all experiments ensuring exclusive initial excitation of BOD (λ_{max} 460 nm).
(7) Intermediacy of the triplet state of BOD in these reactions is supported by sensitization and quenching experiments. Efficient intersystem crossing

is assumed by analogy.[4] A Stern–Volmer treatment (plot of $1/\phi$ vs. concentration of anthracene quencher) at initial absorbed light intensity of 3×10^{-7} einstein min gave a reasonable straight line over the range 1.5–10 $\times 10^{-5}$ M anthracene with a slope of 7×10^4 M^{-1}. However, it should be emphasized that this result may be fortuitous. In the present case, the effect of quencher in reducing the instantaneous concentration of triplet states is comparable to reducing light intensity and thus increasing quantum yield. The observed result will be the sum of this effect plus the usual effect of the quencher in reducing quantum yield.

(8) The intermediacy of these radicals is supported by a number of experimental results including ESR spectra, CIDNP experiments,[3d,e] and minor products observed in special cases. No CIDNP effect could be detected with aromatic aldehydes.[9] It might be noted that the transient reported[3d] in the CIDNP spectrum of camphorquinone and acetaldehyde has been shown[9] to be acetyl chloride presumably formed via reaction of intermediate acetyl radicals with carbon tetrachloride, the solvent employed in these experiments.

(9) M. Cocivera, personal communication.

(10) Unequivocal support for the occurrence of reaction 4 derives from the observation that irradiation of BOD and benzaldehyde in the presence of deuterium oxide to partial completion afforded recovered benzaldehyde enriched in deuterium. From kinetic analysis, k_4 is suggested to be three to four times larger than k_5.

(11) The results presented in Table I establish that $k_5 > k_6$; extrapolation to even higher light intensities suggests that reaction 6 may be unimportant.

(12) The feasibility of addition of aroyl radicals to BOD was established by experiments in which cyclobexane solutions containing benzoin isopropyl ether, a known[13] precursor of benzoyl radicals, and BOD were irradiated at 366 nm (>99% of light absorbed by the benzoin ether). The only addition product formed was keto ester 1. A similar result was obtained using benzoyl radicals generated by thermolysis of di-*tert*-butyl peroxide in the presence of benzaldehyde and BOD. The reversibility of this addition reaction is suggested but has not been established experimentally.

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(14) Formation of 1 via its enol 4 is energetically reasonable and consistent with stereochemistry observed in reactions of camphorquinone.[3c]

(15) An alternative reaction of 3, abstraction of hydrogen from aldehyde, would produce 1 plus an aroyl radical resulting in a chain reaction. This is not consistent with the data presented in Table I.

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Organofluorosilicates in Organic Synthesis. 2. A Convenient Procedure for Preparing Primary Alcohols from Olefins. A Novel Facile Oxidative Cleavage of Carbon–Silicon Bonds by *m*-Chloroperoxybenzoic Acid[1]

Sir:

It has long been recognized that "silicon–alkyl and, particularly, silicon–aryl bonds are fairly resistant to oxidative cleavage, and appropriately substituted organic groups attached to silicon may be oxidized without cleavage of the silicon–carbon bonds".[2]

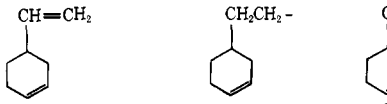
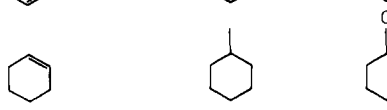
However, we have found that silicon–carbon bonds in organopentafluorosilicates[3] are easily cleaved by the action of *m*-chloroperoxybenzoic acid (MCPBA) to afford the corresponding alcohols in high yields. This reaction provides the first method for the direct introduction of an oxygen functionality into an organic group via cleavage of the silicon–carbon bond,[4] and makes possible a simple and practical procedure for the conversion of olefins into primary alcohols.[7]

$$RCH{=}CH_2 + HSiCl_3 \xrightarrow{H_2PtCl_6} RCH_2CH_2SiCl_3$$

$$\xrightarrow{KF} K_2[RCH_2CH_2SiF_5] \xrightarrow{MCPBA} RCH_2CH_2OH$$

In contrast to reactions with NBS,[1] reactions of organopentafluorosilicates with MCPBA were greatly dependent upon the nature of the reaction media. Thus, yields of 1-octanol produced in the reaction of $K_2[C_8H_{17}SiF_5]$ with MCPBA varied with solvent as follows: THF, trace; EtOH, MeCN, dioxane, ~30%; benzene, 45%; diglyme, 60%; DMF, 82%.

Table I. Oxidative Cleavage of $K_2[RSiF_5]$ by MCPBA in DMF[a]

Olefin	R in $K_2[RSiF_5]$	Product	Yield, %[b]
n-$C_6H_{13}CH{=}CH_2$	n-C_8H_{17}-	n-$C_8H_{17}OH$	82
n-C_8H_{16}[c]	n-C_8H_{17}-	n-$C_8H_{17}OH$	68
n-$C_{10}H_{21}CH{=}CH_2$	n-$C_{12}H_{25}$-	n-$C_{12}H_{25}OH$	75
$MeO_2C(CH_2)_8$-$CH{=}CH_2$	MeO_2C-$(CH_2)_{10}$-	$MeO_2C(CH_2)_{10}$-OH	77
			54
			22
	C_6H_5-[d]	C_6H_5OH	64[e]

[a] Carried out on a 3-mmol scale in the same manner as described in the text. [b] Isolated yield by distillation, based on the silicate, unless otherwise noted. [c] An isomeric mixture of internal and terminal olefins. [d] Prepared from commercial $C_6H_5SiCl_3$. [e] Determined by GLC.

Interestingly, the yield of 1-octanol was improved up to 70% by the addition of an equimolar amount of 18-crown-6 to a reaction mixture in benzene. However, the most convenient and practical solvent is still DMF. It should also be mentioned that the presence of extra lithium or potassium fluoride almost completely inhibits the oxidation reaction, the reason for which is not clear. Other peroxides examined, such as peroxyacetic acid in acetic acid and *tert*-butyl hydroperoxide in diglyme or hydrogen peroxide, gave mainly octyltrifluorosilane rather than the octanol.

A typical procedure is given for the preparation of methyl 11-hydroxyundecanoate from methyl 10-undecenoate. $K_2[MeO_2C(CH_2)_{10}SiF_5]$ was prepared by the platinum-catalyzed hydrosilylation of methyl 10-undecenoate with trichlorosilane followed by treatment with potassium fluoride in water.[3] The silicate (1.20 g, 3.0 mmol), MCPBA (80% pure) (0.81 g, 3.6 mmol as active oxygen), and dry DMF (10 mL) were combined and stirred at room temperature for 6 h. The mixture changed gradually to an almost homogeneous solution. After the addition of ether, the mixture was washed successively with water (once), 20% sodium bisulfite (twice), and saturated sodium bicarbonate (twice), dried over sodium sulfate, and evaporated. Bulb-to-bulb distillation of the residue gave 0.50 g (77% yield based on the silicate) of pure methyl 11-hydroxyundecanoate.[8]

Representative results summarized in Table I were obtained under similar conditions. Primary alcohols were obtained in high yields, the secondary alcohol yield being much lower. The phenyl–silicon bond in $K_2[PhSiF_5]$ is also cleaved to form phenol. While many advantages mentioned in the previous paper[1] also apply to the present reaction, the following particular points deserve further comment. (1) The MCPBA cleavage of, at least, the primary alkyl–silicon bond in silicates proceeds much faster than the epoxidation of double bonds, as indicated by the selective preparation of 4-(2-hydroxyethyl)cyclohexene from 4-vinylcyclohexene. This opens a new route to unsaturated primary alcohols from various polyenes. (2) Since the platinum-catalyzed hydrosilylation of internal olefins forms primary alkyl–silicon compounds exclusively,[9] the present procedure provides a novel route to primary alcohols from a mixture of positional isomers of olefins. This is exemplified by the result given for n-C_8H_{16} in Table I.

Mechanistic studies and additional synthetic applications of the present oxidation reaction are now in progress.

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