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ON THE PHOTOREDUCTION OF BENZOPHENONE IN SECONDARY ALCOHOLS*

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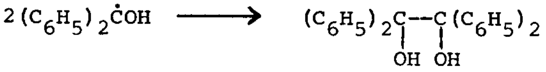
One of the most thoroughly studied photochemical reactions is the photoreduction of an aromatic ketone in 2-propanol or other secondary alcohol (1). The currently accepted mechanism, which comes from the work of several investigators, is outlined below.

$$(C_6H_5)_2CO \xrightarrow{h\nu} S_1 \longrightarrow T_1 \tag{I}$$

$$T_1 + RR'CHOH \longrightarrow (C_6H_5)_2\dot{C}OH + RR'\dot{C}OH \tag{II}$$

$$RR'\dot{C}OH + (C_6H_5)_2CO \longrightarrow RR'CO + (C_6H_5)_2\dot{C}OH \tag{III}$$



$$2(C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2\underset{OH}{C}-\underset{OH}{C}(C_6H_5)_2 \tag{IV}$$

Reaction (I) has been shown to occur with unit efficiency (1e,2). Hammond (3), as well as Walling and this author (4) have investigated step (II) and related reactions with a variety of hydrogen donors. The evidence that (III) and (IV) constitute the major (if not sole) pathway for formation of benzpinacol

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* Experiments similar to those described here have been performed by N. C. Yang and S. Murov. Their results are in qualitative and quantitative agreement with ours (N. C. Yang, personal communication).

and alcohol-derived ketone comes from the classic work of Pitts et. al., (1d) in which benzophenone was irradiated in (-)-2-butanol at low light intensity (10^{13} - 10^{14} quanta/min.). It was found that recovered solvent had not racemized and that a quantum yield of two obtained for loss of benzophenone. This eliminated from consideration the disproportionation reactions (V) and (VI).

$$2RR'\dot{C}\text{—}OH \longrightarrow RR'CHOH + RR'CO \qquad (V)$$

$$RR'\dot{C}OH + (C_6H_5)_2\dot{C}OH \longrightarrow RR'CHOH + (C_6H_5)_2CO \qquad (VI)$$

Reaction (VII) is eliminated because benzhydrol has never been found in either secondary alcohol or hydrocarbon photoreductions.*

$$Ph_2\dot{C}OH + RR'\dot{C}OH \longrightarrow Ph_2CHOH + RR'CO \qquad (VII)$$

However, it has been reported that the overall quantum yield for loss of benzophenone decreases from a maximum of two at low light intensity ($\leq 10^{15}$ quanta/min.) through unity (10^{17} quanta/min.) to as low as 0.37 (3×10^{18} quanta/min.) (5,6). Reasoning that this inverse relationship could arise from either 1) an inefficiency in the primary photochemical process or, 2) a free radical disproportionation reaction (e.g., V or VI) which reforms starting material due to higher radical concentrations at higher intensities, we have photolyzed benzophenone in d-2-octanol at very low and very high intensities. Recovered solvent was analyzed for optical activity and products were determined. The results indicate that the former effect is more likely operating, and that there is no qualitative difference in the reaction under the two sets of conditions.

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* Although benzhydrol is considerably more reactive toward T_1 than any other molecule in the system, it should be observed when secondary aliphatic alcohol is the solvent. The relative reactivity of benzhydrol is not sufficiently greater than that of solvent to kinetically compensate for the huge difference in concentrations.

Three times recrystallized benzophenone was dissolved (~.1 *M*) in distilled (b.p. 73°/10 mm.) *d*-2-octanol (Aldrich Chemical Co.) after the rotation of the pure solvent had been measured, and the solution was thoroughly degassed in a Pyrex tube with a 6 mm. thick cylindrical sidearm. After sealing off, the solution was allowed to flow into the cell sidearm, and was irradiated either at the focal point of a lens in front of a Bausch & Lomb SP-200 mercury lamp (high intensity) or about one foot away from a tungsten 60 watt light bulb (low intensity). A sample of pure d-2-octanol was also run through the same procedure and irradiated at high intensity. Reactions were carried essentially to completion as evidenced by loss of benzophenone (absorbance in the near UV) and formation of benzpinacol (gravimetric). From the concentration of benzophenone, the dimensions of the cell, and the time necessary to produce complete reaction, there is no question that the two sets of reactions are in the $\Phi_{Ph_2CO} = 2$ and $\Phi_{Ph_2CO} < 1$ intensity ranges respectively. Since it was important to keep the benzophenone concentration fairly low (approximately 0.1 *M*),* and since we wanted to be able to observe solvent racemization if it occurred, the solvent was recycled several times. This meant carefully distilling off solvent, analyzing, and irradiating it with benzophenone again. This recycling was done twice for the irradiations with the mercury lamp (meaning three photolyses, designated High III) and once with the tungsten source (two photolyses, designated Low II). The only material codistilling with solvent was some 2-octanone, a major product of the reaction. The mole ratio of ketone to alcohol was determined by gas chromatography with a calibrated 5'x 1/8" didecyl phthalate column at 120°C, 30 ml. He per minute.**

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* There has been a report of a concentration dependence of the quantum yield. (7) The experiments performed here were at constant concentration. The benzophenone dependence is currently being studied.

** The yields of 2-octanone are in accord with what would be predicted from earlier work (4) on the relative reactivity of methylene CH_2 versus α-hydroxy C-H.

TABLE I.

Chemical and Optical Purity of the 2-octanol.

	Sample of Alcohol			
	Non-irradiated pure	Irradiated pure	Low II[a]	High III[a]
Purity[b] (%)	100	100	96.6 ±2.0	94.7 ±2.4
Observed[c] rotation $\alpha_D^{25^\circ}$	+15.18±.04°	+15.20±.06°	+14.88±.05°	+14.57±.06°
Calc'd rotation based on Steps I,II,III,IV (any Φ)	----+15.19°----		+14.67±.31°	+14.38±.36°
Calc'd rotation based on Φ = 1, Steps I,II,V,IV	----+15.19°----		+14.16±.30°	+13.56±.34°

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a) See text. b) Chemical purity based on g.c. analysis. c) In a two decimeter cell.

Table I tabulates the data from one triplicate set of experiments. Rotations were taken on both a Zeiss Photoelectric Polarimeter at 546 and 578 mμ and in a thermostatted two decimeter cell on a Rudolph polarimeter, the latter data at the sodium D line being reported in the table. The other wavelength data were in thorough agreement with these. Essentially all the error in the calculated rotations arises from the determination of alcohol/ketone ratios on gas chromatography. The fourth line of entries was calculated by assuming that the sole operating mechanism consists of reactions (I-II) and (IV-V). This would produce a quantum yield of unity, and each mole of ketone produced leads to one of racemized alcohol. If (VI) is included, one must also consider some aliphatic ketone-producing reaction such as (III) or (V). For the Φ = 1 case, the maximum rotation would be the same as for the (I,II,IV,V) mechanism if (III) were the step competing with (VI). At lower quantum yields (where our high intensity experiments are probably operating) the calculated rotations decrease in a parallel manner with the quantum yield.

It is clear that well outside experimental error, the high intensity rotations are in agreement with the low intensity ones after correction for relative purity. Furthermore, both are within experimental error of the calculated rotations based on the mechanism containing steps I, II, III, and IV, but cannot be rationalized if any of the disproportionation reactions and included. Both (V) and (VI) produce starting secondary alcohol from its semipinacol radical, and would be expected to cause racemization of solvent to the extent that they occur. Only a few special radicals are known to retain their stereochemistry, and it would be surprising indeed if an aliphatic semipinacol free radical were not to racemize in solution.

In all probability the same mechanism obtains at high and low intensities, leaving Yang's proposal of paramagnetic quenching of benzophenone triplets by radicals (6) (reactions VIII and IX) as a quite attractive explanation for the intensity effect.

$$T_1 + RR'\dot{C}OH \longrightarrow (C_6H_5)_2CO + RR'\dot{C}OH \qquad (VIII)$$

$$T_1 + (C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2CO + (C_6H_5)_2\dot{C}OH \qquad (IX)$$

This conclusion may have fairly broad implications for many other photochemical studies, in that the possibility of direct quenching of paramagnetic states should be considered if moderate steady state radical concentrations (or fairly long-lived radicals) are being produced in a system.

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