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NEW OBSERVATIONS ON THE PHOTOPINACOLIZATION OF BENZOPHENONE IN ALIPHATIC ALCOHOLS

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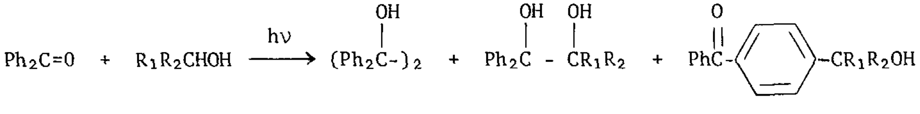
Abstract: Irradiation of benzophenone in alcohol solutions produces unsymmetrical pinacols and para-coupled products as well as benzpinacol; the product composition depends on light intensity.

The formation of benzpinacol (1) by irradiation of solutions of benzophenone (BP) in aliphatic alcohols was correctly interpreted by Ciamician[1] in 1900 and the first report of a mechanistic study appeared in 1920[2]. Since that time, this reaction has been the subject of an enormous number of investigations employing almost every conceivable technique. In connection with an interest in effects of light intensity on product formation in photochemical reaction[3], we have reexamined the reaction of BP in methanol, ethanol, and 2-propanol taking advantage of the availability of high performance liquid chromatography (HPLC) as a mild and powerful analytical method.

Irradiation of BP in methanol had previously been shown[4] to yield 1 (30%) and 1,1-diphenyl-1,2-ethanediol (2a, ∿ 70%), the product of coupling between intermediate benzophenone ketyl (BPH•) and hydroxymethyl radicals. HPLC analysis[5] of reaction mixtures using refractive index and ultraviolet (254 nm) detectors in series indicated the presence of an additional minor product having intense absorption at 254 nm. This was shown to be 4-hydroxymethylbenzophenone[6] (3a) by comparison of HPLC and GC retention times with those of an authentic sample[7] and finally by isolation of 3a (1%) from the reaction mixture[8]. Similar results were obtained with ethanol and 2-propanol where unsymmetrical pinacols 2b and 2c were isolated[9] and the presence of para-substituted benzophenones (3a, 3b) established by the HPLC technique.



BP 1 2a,b,c 3a,b,c

a, $R_1 = R_2 = H$ b, $R_1 = H$, $R_2 = CH_3$ c, $R_1 = R_2 = CH_3$

Availability of the convenient HPLC method for analysis allowed determination of the product composition at differing light intensities. Degassed solutions of BP (0.019 M) in the appropriate alcohol were irradiated at 366 nm to low conversion[11], opened to the air for at least 5 hours, the amount of benzophenone reacted determined by measurement of the decrease in its absorption spectrum, and the product composition determined by HPLC analysis. The quantum yields for disappearance of BP and the product compositions obtained in this way are summarized in Table I below:

Table I

Quantum Yields and Mole Fractions of Products from Irradiations (366 nm) of Degassed Solutions of Benzophenone (0.019 M) in Aliphatic Alchohols.

	Methanol				Ethanol				2-Propanol			
I_{abs}[a]	ϕ_{-BP}[b]	1	2a	3a	ϕ_{-BP}[b]	1	2b	3b	ϕ_{-BP}[b]	1	2c	3c
High[c]	-	0.30	0.62	0.07	-	0.50	0.30	0.20	-	0.91	0.06	0.03
1x10^{-5}	0.45	0.36	0.57	0.07	0.5	0.63	0.21	0.16	0.9	0.95	0.03	0.02
2x10^{-6}	0.55	0.50	0.44	0.06	0.7	0.74	0.14	0.12	1.1	0.97	0.02	0.01
2x10^{-7}	0.9	0.58	0.35	0.06	1.3	0.87	0.05	0.08	1.7	0.99	0.01	0.005
2x10^{-8}	1.4	0.82	0.14	0.04								
4x10^{-9}	1.7	0.89	0.08	0.03								

a. Absorbed light intensity (einstein/min) using the benzophenone-benzhydrol actinometer. b. Quantum yield for disappearance of benzophenone determined after 5% conversion. Values were corrected for absorption by 3. c. Full spectrum from a 200 w high pressure mercury lamp.

The decrease in quantum yield with increasing light intensity observed previously[12,13] in the reaction of benzophenone with isopropyl alcohol is shown to occur with ethanol and methanol as well. This effect is due in part to increased formation of 4, the so-called "light absorbing transient" (LAT), which acts as an internal filter and a quencher of benzophenone triplets[14]. In addition, while the limiting quantum yield (ϕ_{lim}) for formation of 1 is two, ϕ_{lim} for formation of 2 and 3 is unity leading to lower quantum yields at higher light intensities where these products constitute a larger proportion of the product. Disproportionation of radicals (reaction 5 below) to regenerate BP and alcohol, shown to be unimportant at low light intensity[15], may occur at high intensities providing an additional factor which reduces quantum yields.

The obvious effect of a change in light intensity is to change the rate of formation of excited states and thereby the steady state concentrations of reactive intermediates. A similar effect can be achieved by addition of a quencher. Thus, addition of naphthalene, which reduces quantum yields in benzophenone photoreactions by diffusion-controlled triplet quenching, should have the same effect as reducing light intensity. This was checked in the benzophenone-methanol system with the results shown in Table II where it can be seen that the expected effect on product composition was indeed observed.

Table II

Product Ratios from Irradiation (366 nm) of Benzophenone (0.019 M) in Degassed Methanol Containing Naphthalene at 1 x 10^{-5} einstein/min.

Naphthalene (M)	0	2×10^{-3}	5×10^{-3}	1×10^{-2}
Molar Ratio 2a:1	1.70	1.54	1.32	0.99

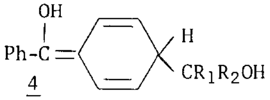
The accepted explanation for $\phi_{lim}=2$ and exclusive formation of 1 and acetone in benzophenone-isopropyl alcohol reactions is the assumption that the fast equilibrium[16,17] between ground state BP and alcohol-derived radicals (reaction 1) lies, for all practical purposes, completely to the right so that the only products are 1 and oxidized alcohol. This approximation is correct for the special case of high BP concentration and low light intensity. However, the results in Table I clearly indicate that radical-radical reactions become increasingly important with increasing light intensity. At least three additional reactions between BPH• and $R_1R_2\dot{C}OH$ need to be considered, as shown above. Obviously, the rates of these reactions will increase faster than the rate of reaction (1) as radical concentrations increase. The differences between the three alcohols investigated presumably reflect steric effects on reaction rates and possibly electronic effects on equilibrium (1) as well. The results are completely inconsistent with a cage effect[18].

(1) $Ph_2CO + R_1R_2\dot{C}OH \rightleftharpoons Ph_2\dot{C}OH + R_1R_2C{=}O$

(2) $2\ Ph_2\dot{C}OH \longrightarrow$ 1

(3) $Ph_2\dot{C}OH + R_1R_2\dot{C}OH \longrightarrow$ 2

(4) " + " $\longrightarrow$



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(5) " + " $\longrightarrow$ $BP + R_1R_2CHOH$

Similar light intensity effects have also been observed in reactions of 4,4'-dimethoxybenzophenone with alcohols.

Finally, we note that care is necessary in comparing results obtained at low light intensities (e.g. quantum yield determinations; quenching, and sensitization studies) with those obtained at high intensities (e.g. flash photolysis, esr studies) in mechanistic investigations unless it is demonstrated that light intensity effects are unimportant.

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