from light. The solution was cooled to 20°. Upon adjusting to pH 3 with concentrated hydrochloric acid, pteroic acid separated as a bright yellow solid. This was centrifuged at 3000 rpm and washed thoroughly by suspension and centrifugation with three to five 10-ml portions of water. The moist solid was freeze-dried to give 263 mg of pteroic acid (84%). The nmr spectrum in deuterated trifluoroacetic acid showed a singlet at δ 4.90 (2 H, bridge CH_2), doublet at 7.49 (2 H, $J = 9$ cps, benzene CH), doublet at 7.85 (2 H, $J = 9$ cps, benzene CH), and a singlet at 8.54 (1 H, pteridine CH).

Anal. Calcd for $C_{14}H_{12}N_6O_3$: C, 53.85; H, 3.88; N, 26.92. Found: C, 53.7; H, 4.2; N, 26.8.

Paper chromatography (0.10 *N* ammonium bicarbonate) showed R_f 0.17 (quench), pteroic acid, free of all fluorescent compounds.

The sample of pteroic acid was acylated with trifluoroacetic anhydride and converted to folic acid by the mixed anhydride method as previously described.[15] Upon reduction to the dihydro form with sodium dithionite, the sample showed full activity with the two enzymes listed above.

Registry No.—Pteroic acid, 119-24-4; N^2-acetylpteroic acid ethyl ester, 27345-61-5.

Acknowledgment.—I wish to thank Miss E. J. Crawford for the enzyme assays.

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Effects of 4-Alkyl Substitution on the Photoreduction of Benzophenone

NICOLAE FILIPESCU,* LEE M. KINDLEY,[1]
AND FREDRICK L. MINN

Department of Chemistry, The George Washington University, Washington, D. C. 20006

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We recently investigated the photoreduction of benzophenone[2] (B) and its di-*p*-*tert*-butyl derivative[3] (TBB) in isopropyl alcohol. Both the photoreduction of TBB and the reactions of its long-lived intermediates with coreactants were surprisingly more complex than those of B. Therefore, it was of interest to examine the analogous reactions of symmetrical benzophenones with gradually increasing size of the alkyl substituent. Here we report on a similar spectroscopic investigation of the photolysis of di-*p*-methylbenzophenone (MB), di-*p*-ethylbenzophenone (EB), and di-*p*-isopropylbenzophenone (IPB) in degassed isopropyl alcohol.[4] The experimental methods, the designation of intermediates, and methods of calculation of extinction coefficients, stoichiometry, and rate constants were described previously.[2,3]

Successive short irradiations of degassed ketone solutions indicated formation of an intermediate species In_1 with λ_{max} between 330 and 350 nm. That this transformation was free of side reaction was shown by the isosbestic points at 237 and 298 nm (MB), 238 and 299 nm (EB), and 237 and 302 nm (IPB). The dark reaction of MB paralleled that of B; namely, the absorption band characteristic of In_1 decreased gradually to complete disappearance (for initial photoconversion less than 50%) or to an unchanging concentration (for conversion in excess of 50%). The spectral changes in the dark indicated that In_1 reacted bimolecularly with the residual benzophenone until one or the other was consumed. The plot of the second-order rate expression gave an excellent fit with the rate constant given in Table I. Product analysis identified only acetone and the tetramethyl-substituted benzopinacol. As for B, In_1 was oxygen sensitive and reverted to MB on exposure to air, as shown by both the uv absorption and reappearance of the characteristic ketone phosphorescence in the emission spectrum of refrozen samples at 77°K.

The dark reactions of the In_1 intermediates of EB and IPB paralleled those of B and MB only when the initial photoconversion was less than 50% but resembled that of TBB for higher conversions. The rate constants for the former reaction, derived again from excellent second-order fits, are listed in Table I. For high initial photoconversions, another slower dark reaction, competing with the In_1 + ketone reaction, was detected which converted the In_1 intermediates to yellow species designated In_2. The $In_1 \rightarrow In_2$ dark reaction of EB and IPB proved to be first order (see Table I). The yellow In_2 species were stable indefinitely (months) in the absence of oxygen but reacted rapidly on admission of air. Multicomponent absorption spectroscopy allowed calculation of the extinction coefficients of In_1 as a symmetrical broad band with λ_{max} at 333 (MB), 338 (EB), and 348 nm (IPB) and of In_2 again as an unstructured band with λ_{max} 382 nm for both EB and IPB.

Elementary molecular orbital calculations of expected electronic absorption,[5] ionic-like reaction with $(CH_3)_2CHONa$ (see below) accompanied by corresponding bathochromic shift in uv absorption, oxygen sensitivity, absence of paramagnetism,[6-11] and analogy with other unsymmetrical coupling reactions of radicals[12] suggest enol structure **1** for In_1 intermediates. Such a configuration has been proposed by several independent investigators.[2,13,14] An attempt was made to obtain direct confirmation of the nature of In_1 by recording nmr spectra of photolyzed solutions of TBB in degassed perdeu-

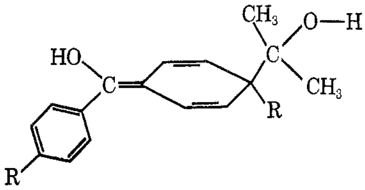

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TABLE I

RATE CONSTANTS FOR DARK PROCESSES

Dark reaction	Ketone B	 MB	 EB	 IPB	 TBB
In_1 + ketone, l./(mol sec)	2.75×10^{-3}	1.75×10^{-3}	1.12×10^{-3}	1.22×10^{-3}	2.50×10^{-3}
$In_1 \rightarrow In_2$, sec^{-1}			2.35×10^{-7}	2.63×10^{-7}	1.5×10^{-7}

terated isopropyl alcohol. The sharp singlet at δ 1.4 ppm, corresponding to methyl protons, decreased upon irradiation with concomitant increase of a new signal at 1.2 ppm, indicating changes in the chemical environment of the *tert*-butyl groups in In_1. Although the aromatic signal at 7.6 ppm decreased with photolysis, the expected vinyl proton absorption around 6.0 ppm could not be observed because of masking signals from solvent impurities. Within its sensitivity limitations, this experiment seems to confirm proposed structure **1**.

From the data in Table I, one can see that the rate constant for the dark reaction of In_1 with residual ketone changes gradually with increasing size of the alkyl substituent, with maxima for B and TBB and minimum for EB. Although the variation is relatively small, it seems to suggest coexistence of two opposing effects or a change in mechanism reminiscent of SN2–SN1 alkyl-dependent solvolysis reactions. Although the significance of this minor variation is not well understood, the absence of a pronounced substituent effect on the In_1 + ketone reaction suggests that the substituent R probably does not interfere with the alcoholic OH, the presumed reaction site.[2]

Upon mixing with isopropoxide, irradiated solutions of the ketones generated yellow metastable species, presumably enolates of **1**. The rate constants for the subsequent complex dark transformation[3] could be estimated only for EB and IPB and were comparable to those of TBB.

We found that the characteristic uv absorption of In_1 continued to increase slightly in the dark for periods up to 10 min following the initial irradiation of IPB, EB, and much less for MB. Low-temperature emission spectra of samples frozen immediately after irradiation failed to reveal the presence of a transient precursor to In_1. This behavior contrasts with that of TBB where a fluorescent precursor was detected and also with that of B where no increase in In_1 absorption was observed once photolysis ended. Despite this precursor's lack of absorption in the 275–340 nm region, the reactive short-lived intermediate is not a ketyl or other radical[6–11] with increased stability from the substituent, since such species have subsecond lifetime in liquid solution.[15] Except for TBB, its concentration never builds high enough for spectroscopic detection in any substituted ketone investigated.

Registry No.—MB, 611-97-2; EB, 21192-56-3; IPB, 21192-57-4.

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[15] Esr measurements confirmed the absence of paramagnetic species.