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PHOTOPHYSICS AND PHOTOCHEMISTRY OF P-BENZOYLPHENYLDIPHENYLMETHYL IN SOLUTION

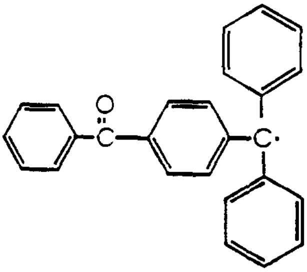
by D. C. Neckers*, S. Rajadurai, O. Valdes-Aguilera, A. Zakrzewski and S. M. Linden[1]

Center of Photochemical Sciences
Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

ABSTRACT: The photochemistry and photophysics of p-benzoylphenyldiphenylmethyl (I) is reported in benzene at room temperature. This report is the first of the photochemical properties of a stable radical conjugated with an n-π* carbonyl group.

Shortly after the discovery of triphenylmethyl[2], Gomberg reported it decomposed in sunlight[3]. Some years later, the photoproducts were identified as triphenylmethane and 9-phenylfluorene dimer[4]. Letsinger confirmed these results but isolated 9-phenylfluorene in basic dioxane[5]. Lewis first reported the absorption spectrum and fluorescence of triphenylmethyl in an EPA glass at 90°K[6]. Several recent reports on the photophysics of triphenylmethyl and its analogs are contradictory[7].

We view p-benzoylphenyldiphenylmethyl (I) as a benzophenone substituted at the para position with a stable radical center. Obviously this radical raises many interesting questions among which is what is the interaction between the radical and the n-π* chromophore of the carbonyl function. We report the results of spectroscopic and product investigations herein.



I

I was prepared in purified benzene[8] by Wittig's method[9]. The absorption spectrum of the red radical [λ_{max} = 340 nm (5700 $M^{-1}cm^{-1}$), 395 nm (3500 $M^{-1}cm^{-1}$), 544 nm (540 $M^{-1}cm^{-1}$) and 586 nm (690 $M^{-1}cm^{-1}$), Figure 1a] compares with triphenylmethyl: [λ_{max} = 335 nm, 478 nm, 498 nm and 521 nm]. In contrast to a previous report we find that the spectrum follows Beer's law over a concentration range from .3 mM to 3.5 mM and that there is no effect on the spectrum of temperature from 293°K to 313°K. I fluoresces with a maximum at 616 nm (τ = 15 ns; $Ø_f$ = 0.14)[10]. The fluorescence spectrum, Figure 2, is independent of the wavelength of excitation and the absorption spectrum superimposes the excitation spectrum, Figure 1 b [3.0 mM]. Thus the concentration of the dimer is not significant at room temperature.

Further evidence that the concentration of dimer is not significant at room temperature (3mM) results from a study of p-benzoyl-p',p"-t-butyltriphenylmethyl. The absorption spectrum of this radical shows maxima 10 nm red shifted from I at 400 nm, 554 nm and 596 nm and the emission spectrum shows a maximum at 630 nm which is independent of the wavelength of excitation. When red I is cooled (77°K) in benzene the sample becomes colorless and develops the typical benzophenone phosphorescence, Figure 3, ($\tau = 3.9$ msec). This phosphoresence is that of the quinoid dimer[11].

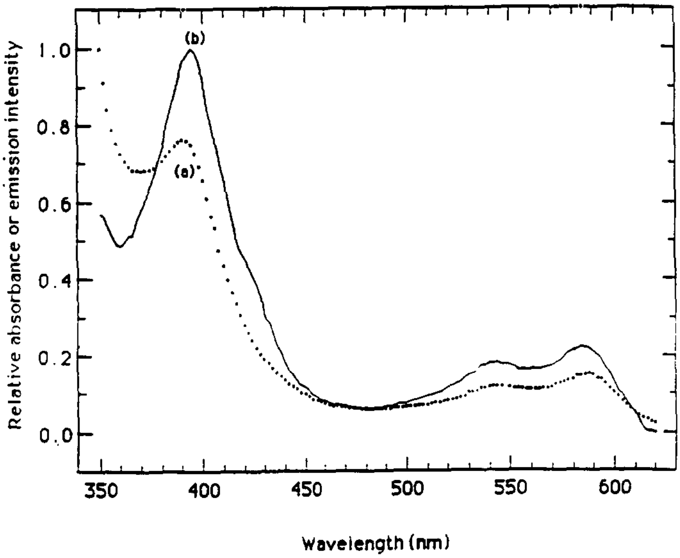


Figure 1: Absorption spectrum (a) and excitation spectrum (b) monitored at 612 nm of I in benzene at 298°K.

The absorption spectrum of I in CH_3CN is similar to that in benzene whereas the emission spectrum is decidedly red shifted (λ_{max} = 648 nm; shoulder 692 nm) indicating that the excited state of I is much more polar than the ground state and that the p-benzoyl function is extending charge delocalization to oxygen. The radical has no reactivity with 2-propanol in the ground state. Fluorescence quenching of I by 2-propanol gives a nonlinear Stern-Volmer plot indicating some interaction of the solvent with both the ground and excited state. In 2-propanol the emission maximum is similarily shifted showing the same effect 2-propanol has as CH_3CN, thus suggesting reaction is at the oxygen atom to which the radical center may be delocalized (1).

Steady state irradiation at 586 nm, 544 nm and 360 nm respectively of the intensely red color solution of I in the absence of oxygen in benzene leads to irreversible bleaching and the formation of p-benzoylphenyldiphenylmethane (54.0%) as the predominant volatile product with minor amounts of 4-(9-fluorenyl)benzophenone (4.5%), benzophenone (2.5%), 4-phenylbenzophenone, (10.0%), tetraphenylethylene (7.9%) and 9,10-diphenylphenanthrene (5.8%)[12]. The quantum efficiency of photobleaching with 360 nm irradiation is 7 times greater than that with 586 nm. When irradiated in deuterated benzene the radical gives no deuterated hydrocarbon, nor is biphenyl formed, but photobleaching of I (3.5 mM) in the presence of decafluorobenzophenone (6.8 mM) gives decafluorophenylmethanol as well as tetrafluorophenyl pentafluorophenyl ketone with the subsequent decrease in the yield of p-benzoylphenyldiphenylmethane[13]. Irradiation of decafluorobenzophenone in benzene in the absence of I yields none of the hydrogenated product mentioned above thus we conclude reduction of the partner ketone is deriving from reaction intermediates formed bimolecularly. Quenching experiments show that I also does not abstract hydrogen from toluene. These experiments show that the hydrogen source for the formation of p-benzoylphenyldiphenylmethane must be either another radical or photoproducts and not the solvent. Since a reducing intermediate can be intercepted by perfluorobenzophenone, hydrogen atom transfer to the ketone is suggested. Both 360 nm and 586 nm photolysis also give tetraphenylethylene and 360 nm irradiation also produces 9,10-diphenylphenanthrene. The absence of the formation of 9,10-diphenylphenanthrene during 586 nm irradiation shows that it is a secondary photoproduct of tetraphenylethylene at UV irradiation[14].

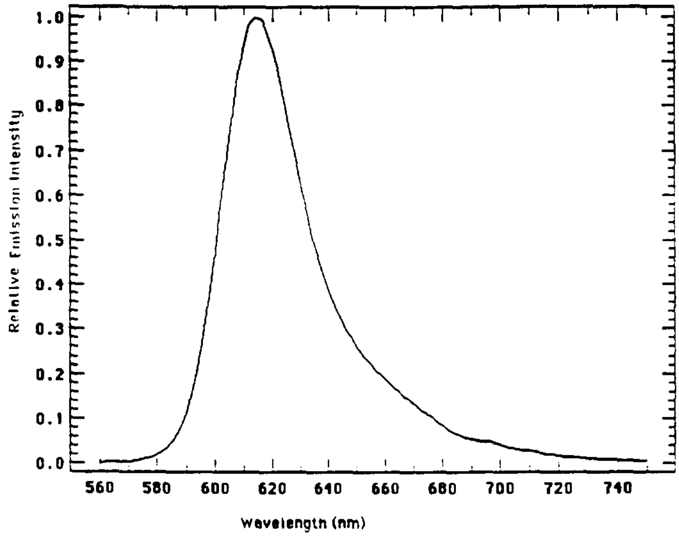


Figure 2: Emission spectrum of I in benzene at 298°K.
Monitored at 544 nm.

I is thus rich in both spectral information and photochemistry. Its photochemistry parallels that of the triphenylmethyl radical itself in that p-benzoylphenyldiphenylmethane is by far the major volatile product. This product must come from bimolecular reactions of the parent radical because the solvent is not involved. We have measured E_0red in acetonitrile (0.396 v) and this suggests that carbanion formation from the emitting excited state ($\Delta E = 46.1$ kcal/mol) is likely. Fluorescence from I is relatively long lived and has the structure of that reported for triphenylmethyl by Lewis[5]. It is, however, very much affected by solvent and shifts to significantly longer wavelength in both acetonitrile and 2-propanol. Studies on other systems clearly show that the emission properties of triphenylmethyl radicals with substituents para are distinct from those with substituents in other positions either on an aromatic ring, or in other parts of the molecule. Our studies are continuing with.systems related to these in order to assess the effect of chromophores of known spectroscopy and photochemistry on a stable triarylmethyl radical center and they will be reported in a full report later.

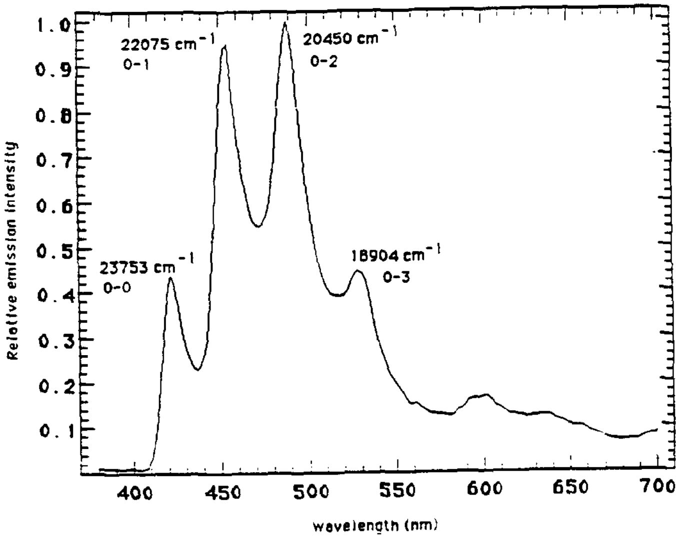


Figure 3: Phosphorescence spectrum of colorless frozen solution of I in benzene at 77°K; benzophenone emission from the dimer.

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