The Photodeoxygenation of Benzophenone by Triphenylphosphine

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Summary Evidence is presented for the photodeoxygenation of benzophenone by triphenylphosphine.

A LIGHT-INDUCED reaction between benzophenone and triphenylphosphine, in the absence of oxygen, yields a red-brown air-sensitive solution. Differential i.r. spectroscopy, prior to exposure to air, with a sample of the unphotolysed material in the reference beam, reveals absorptions characteristic of triphenylphosphine oxide at 1432, 1195, 1110, 713, and 543 cm^{-1}, an absorption, which can be attributed to triphenylphosphinediphenylmethylene, at 1570 cm^{-1}, and another broad absorption centred at 660 cm^{-1}, attributable to triphenylphosphinediphenylmethylene. There are several shoulders which are also consistent with this argument. Negative absorptions at several frequencies characteristic of benzophenone *e.g.* 1650, 1300, 1270, 930, and 905 cm^{-1}, suggest that benzophenone has been depleted in the photolysed sample. There is a negative absorption, centred at 490 cm^{-1}, which can be attributed to the diminution of triphenylphosphine.

The visible spectrum of the red-brown solution has $\lambda_{max} = 727$ nm, compared to that of triphenylphosphinediphenylmethylene ($\lambda_{max} = 725$ nm).

When this red-brown solution is treated with acetaldehyde, the colour is discharged immediately.

We suggest that the first step is the photochemical deoxygenation of the $n \rightarrow \pi^*$ excited state of benzophenone to produce triphenylphosphine oxide and the red-brown, air-sensitive ylide, triphenylphosphinediphenylmethylene (I). In the subsequent dark reaction, the ylide reacts with acetaldehyde to yield a second molecule of triphenylphosphine oxide and one of 1,1-diphenylpropene according to the well-known Wittig reaction.

$$Ph_2CO + 2Ph_3P \xrightarrow{h\nu} Ph_3PO + Ph_3P{=}CPh_2 \text{ (I)}$$

$$Ph_3P{=}CPh_2 + MeCHO \rightarrow Ph_3PO + Ph_2C{=}CHMe$$

The presence of triphenylphosphine oxide in the final mixture was unequivocally proved by g.c.; the component corresponding to triphenylphosphine oxide had an identical i.r. spectrum to that of an authentic sample. We have tried to isolate 1,1-diphenylpropene but have been unable to separate it from unreacted triphenylphosphine. Neither have we been able to separate known mixtures of 1,1-diphenylpropene and triphenylphosphine by this method. T.l.c. (n-pentane or cyclohexane as eluents, on silica gel) however, yields spots with R_F values corresponding to those of authenic 1,1-diphenylpropene.

In another experiment, we exposed a solution of 2-hydroxy-4-methoxybenzophenone and triphenylphosphine to u.v. radiation but no reaction could be detected. Since this molecule undergoes a $\pi \rightarrow \pi^*$ transition instead of the usual $n \rightarrow \pi^*$ for ketones,[1] we have further support for our suggestion that the photochemical reaction is between the $n \rightarrow \pi^*$ excited state of the ketone and triphenylphosphine.

These observations are particularly timely in view of recent work on the quenching of excited states by arylamines and speculations on similar interactions between excited states and tervalent phosphorus compounds.[2] These deoxygenation reactions resemble the photodeoxygenation of nitro-compounds by triethyl phosphite[3] and the photorearrangement of dimethyl β-ketoethyl phosphites to dimethyl vinyl phosphates.[4]

All reactions were carried out in sealed Pyrex glass tubes after thorough outgassing of the samples on a high vacuum line, with benzene as solvent, and with long-wavelength u.v. light ($\lambda_{max} = 350$ nm). We feel that there can be no question that photodeoxygenation of benzophenone is occurring as shown by the differential i.r. spectral analysis, and it seems most likely that triphenylphosphinediphenylmethylene is formed.

Control experiments were carried out in which all operations were identical to those for the exposed tubes except that the control tubes were not exposed to u.v. light. No reactions could be detected.

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