

## Photoreactions of Diphosphines with Benzophenone

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Reactions of tetraphenyl- and tetraethyl-diphosphine with photoexcited benzophenone have been studied. In general, the products (after sulphurization with sulphur) are tetraphenylethylene, thiobenzophenone, and phosphinic acids. Diphenylmethyl(diphenyl)phosphine oxide, tetraphenyloxiran, tetraphenylthiiran, and phenyl triphenylmethyl ketone are also formed in amounts depending on the reaction conditions. A mechanism involving metathesis of the P-P bond by  $n-\pi^*$  triplet benzophenone is suggested.

IN continuation of our study on the reactions of diphosphines with free radicals,<sup>1</sup> we have investigated the reactions of diphosphines with photoexcited benzophenone. It is well established that the reactivity of  $n-\pi^*$  triplet benzophenone approximates to that of an alkoxy radical,<sup>2</sup> and an alkoxy radical easily reacts with trivalent phosphorus compounds.<sup>3</sup> Ingold *et al.* have recently reported the reaction of an alkoxy radical with

<sup>1</sup> R. Okazaki, Y. Hirabayashi, K. Tamura, and N. Inamoto, *J.C.S. Perkin I*, 1976, 1034.

<sup>2</sup> A. Padwa, *Tetrahedron Letters*, 1964, 3456; S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, 1965, **87**, 2996; C. Walling and M. J. Gibian, *ibid.*, p. 3361.

<sup>3</sup> W. G. Bentrude, 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, ch. 22.

tetra-alkoxydiphosphines.<sup>4</sup> We wished to discover whether it is possible for triplet benzophenone to attack the phosphorus atom of a diphosphine like an alkoxy radical. This reaction is also interesting in connection with the quenching mechanism of ketones by trivalent phosphorus compounds.<sup>5-7</sup>

### *Photoreactions of Tetraphenyldiphosphine (TPD) with*

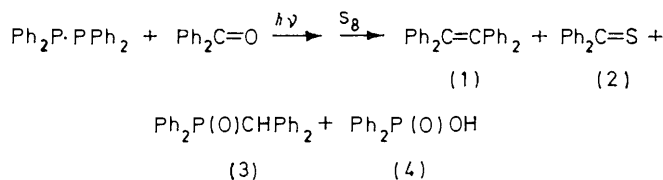
<sup>4</sup> D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 554.

<sup>5</sup> R. S. Davidson and R. F. Lambeth, *Chem. Comm.*, 1969, 1098.

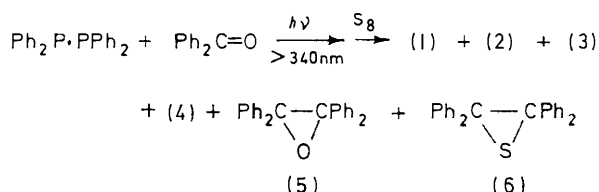
<sup>6</sup> L. D. Wescott, jun., H. Sellers, and P. Poh, *Chem. Comm.*, 1970, 586.

<sup>7</sup> R. H. Lema and J. C. Scaiano, *Tetrahedron Letters*, 1975, 4364.

*Benzophenone (Reactions I and II).*—A solution of TPD and benzophenone in benzene was irradiated with Pyrex-filtered light from a medium-pressure mercury arc to give, after sulphurization by sulphur, tetraphenylethylene (1) (40%), thiobenzophenone (2) (36%), diphenylmethyl(diphenyl)phosphine oxide (3) (13%), and diphenylphosphinic acid (4) (72%) (reaction I).

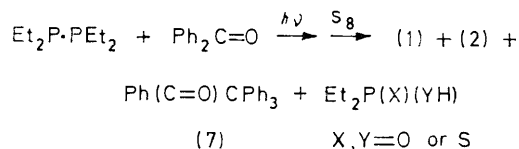


The same photoreaction was then carried out with light of wavelength  $>340$  nm, under conditions such that 95% of incident 366 nm light was absorbed by benzophenone, in order to avoid the possibility that the reaction proceeds *via* a diphenylphosphino radical ( $\text{Ph}_2\text{P}^\cdot$ ) formed by photolysis of TPD. The products (after sulphurization) were compounds (1) (44%), (2) (9%), (3) (2%), and (4) (43%), tetraphenylloxiran (5) (6%), and tetraphenylthiiran (6) (9%) (reaction II).



In addition to these products, there was formed a small amount of an unidentified compound (A) which gave the thiiran (6) during purification by silica gel chromatography. Since compound (6) was not detected in the initial reaction mixture by t.l.c., it seems to be a secondary product from the unknown (A). The mass spectrum of compound (A) showed a strong peak corresponding to (6) ( $m/e$  396) and the i.r. spectrum suggested the presence of a P=O group ( $1\ 200\ \text{cm}^{-1}$ ).

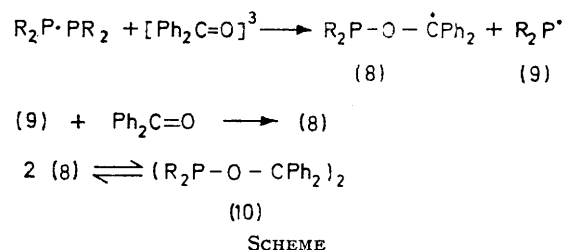
*Photoreaction of Tetraethyldiphosphine with Benzophenone (Reaction III).*—A mixture of tetraethyldiphosphine and benzophenone was irradiated in benzene with Pyrex-filtered light to afford compounds (1) (21%) and (2) (4%), phenyl triphenylmethyl ketone (7) (25%), and a mixture of diethylphosphinothioic and diethylphosphinic acids (54%).



*Reaction Mechanism.*—We have previously reported the reactions of carbon radicals and triplet 1,1-diphenylethylene with TPD involving an induced decomposition

<sup>8</sup> H. Hillgärtner, W. P. Neumann, and B. Schroeder, *Annalen*, 1975, 586; W. P. Neumann, B. Schroeder, and M. Ziebarth, *ibid.*, p. 2279.

(metathesis) of the P-P bond.<sup>1</sup> By analogy with these reactions, we consider that the photoreaction of benzophenone with TPD also begins with metathesis of the P-P bond by triplet benzophenone as shown in the Scheme. The reaction of benzophenone with the radical (9) is considered to be reasonable in view of the report of the reaction<sup>8</sup> of benzophenone with a silyl radical and the great affinity of a phosphorus atom for oxygen (like a silicon atom). Although we do not have enough data to delineate detailed reaction pathways, we consider that most of the products can be explained by further reactions of the oxyphosphine (10). Since reactions II and III gave essentially the same results as reaction I, and tetraethyldiphosphine has been reported to be inert to irradiation,<sup>9</sup> the formation of the radical (8) from a reaction between ground-state benzophenone and the



phosphino radical (9), generated by photolysis of the diphosphine seems less likely. However, this possibility cannot be eliminated completely, at least in the case of TPD, because it has been demonstrated by trapping diphenylphosphino radical with 1,1-diphenylethylene that photodissociation of TPD occurs to some extent, even upon irradiation at wavelengths  $>340$  nm.<sup>1</sup>

## EXPERIMENTAL

I.r. and u.v. spectra were recorded with Hitachi EPI-G2 and ESP-3 spectrophotometers, respectively, and n.m.r. spectra with Hitachi R-24 and JOEL JNM-C-60 spectrometers (tetramethylsilane as internal standard). Mass spectra were recorded with a Hitachi RMU-6L spectrometer. All reactions were carried out under nitrogen. The yields were calculated on the basis of benzophenone consumed for products without phosphorus and of diphosphines consumed for those with phosphorus.

*Photoreactions of Tetraphenyldiphosphine (TPD) with Benzophenone.*—(a) *Reaction I.* Benzophenone (14.0 g, 76.8 mmol) and TPD (5.44 g, 14.7 mmol)<sup>10</sup> dissolved in benzene (100 ml) and cooled in ice-water were irradiated with a 100 W medium-pressure mercury lamp (Rikosha) through a Pyrex filter for 48 h. After addition of sulphur (1.13 g, 35.3 mmol), the solution was refluxed for 1 h, then evaporated, and the residue was chromatographed on silica gel. The first fraction was a mixture of sulphur and tetraphenylethylene (1), the amount of the latter being determined by g.l.c. (4.7 mmol, 39%). The second fraction, a blue oil, was thiobenzophenone (2) (1.70 g, 8.6 mmol, 36%),  $M^+$  198. A solution of this fraction in benzene afforded benzophenone

<sup>9</sup> Y. N. Shlyk and G. M. Bogolyukov, *Doklady Akad. Nauk S.S.S.R.*, 1967, 176, 1327.

<sup>10</sup> H. Hoffmann and R. Grunewald, and L. Horner, *Chem. Ber.*, 1960, 93, 861.

upon irradiation with a tungsten lamp under oxygen,<sup>11</sup> and showed  $\lambda_{\max}$  605 nm.<sup>12</sup> The third fraction was unchanged benzophenone (9.6 g, 53 mmol). The fourth fraction was diphenylmethyl(diphenyl)phosphine oxide<sup>13</sup> (3) (1.40 g, 3.8 mmol, 13%), identical (i.r. spectrum; m.p. and mixed m.p. 300–301°) with an authentic sample. The fifth fraction was diphenylphosphinic acid (4) (0.93 g, 4.26 mmol, 72%), identical (i.r. spectrum) with an authentic sample.<sup>14</sup>

(b) A solution of benzophenone (14.0 g, 76.8 mmol) and TPD (4.83 g, 13.1 mmol) in benzene (100 ml) was irradiated under similar conditions and then divided into two parts. One half, after addition of butanal (0.8 g, 11.1 mmol), was refluxed for 1 h. Silica gel chromatography of the products gave the olefin (1), benzophenone, and the phosphinic acid (4), no g.l.c. peak being found corresponding to 1,1-diphenylpent-1-ene.<sup>15</sup> The other half of the mixture was evaporated and the residue left in air for a few days; a part was heated under reflux with sulphur in benzene, but no thiobenzophenone was obtained. The remainder was chromatographed on silica gel to give the olefin (1), benzophenone, and the phosphinic acid (4).

(c) *Reaction II.* A solution of TPD (1.09 g, 2.96 mmol) and benzophenone (2.72 g, 14.8 mmol) in benzene (180 ml) was irradiated for 12 h with a 100 W medium-pressure mercury lamp through a filter solution (1 cm) of copper sulphate [ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (250 g) in distilled water (1 l)].<sup>16</sup> After addition of sulphur (194 mg, 6.1 mmol), the solution was refluxed for 1 h. The yield of thiobenzophenone (2) (9%) was estimated by electronic spectroscopy ( $\lambda_{\max}$  604 nm) by use of a reported  $\epsilon$  value.<sup>12</sup> The solution was shaken with 5% sodium carbonate solution to remove diphenylphosphinic acid (4) (560 mg, 2.54 mmol, 43%). The neutral products were subjected to dry column chromatography (silica gel) with carbon tetrachloride–chloroform (9 : 1) to

give tetraphenylethylene (1) (510 mg, 1.56 mmol, 44%), tetraphenyloxiran (5) (70 mg, 0.20 mmol, 6%), tetraphenylthiiran (6) (118 mg, 0.32 mmol, 9%), an unidentified compound (A) (125 mg), and diphenylmethyl(diphenyl)phosphine oxide (3) (36 mg, 0.10 mmol, 2%). Compounds (5) and (6) had i.r. spectra identical with those of authentic samples,<sup>17,18</sup> and their mass spectra showed molecular ions. Attempted purification of (A) always resulted in partial formation of (6), and the mass spectrum of (A) showed a fairly intense peak at  $m/e$  364.

*Photoreaction of Tetraethyldiphosphine with Benzophenone (Reaction III).*—A solution of benzophenone (9.2 g, 50.5 mmol) and tetraethyldiphosphine<sup>19</sup> (1.82 g, 10.2 mmol) in benzene (100 ml) was irradiated with a 100 W medium-pressure mercury lamp through a Pyrex filter for 48 h. The solution, after addition of sulphur (0.724 g, 22.6 mmol) and subsequent refluxing for 1 h, was chromatographed on silica gel to give five fractions. The first, third, and fourth were tetraphenylethylene (1) (0.65 g, 1.95 mmol, 21%), thiobenzophenone (2) (4% by u.v.), and benzophenone (5.78 g, 31.7 mmol), respectively, and were identified as described for reaction I. The second, m.p. 179° (lit.,<sup>20</sup> 181–182°), was identified as phenyl triphenylmethyl ketone (7) (817 mg, 2.34 mmol, 25%) by i.r., n.m.r., and mass spectra, and molecular weight (350 by Rast method; calc. 348). The fifth was identified as a mixture of diethylphosphinic and diethylphosphinothioic acids on the following basis: (i) the mass spectrum showed  $m/e$  138 ( $\text{Et}_2\text{POSH}$ ), 123 ( $\text{Et}_2\text{PSH}_2$  or  $\text{Et}_2\text{PO}_2\text{H}_2$ ), 110 ( $\text{EtPSOH}_2$ ), 94 ( $\text{EtPSH}_2$  or  $\text{EtPO}_2\text{H}_2$ ), and 93 ( $\text{EtPSH}$  or  $\text{EtPO}_2\text{H}$ ); (ii) the multiplet at  $\delta$  0.8–2.2 in the n.m.r. spectrum due to the ethyl group was very similar to that of an authentic sample of diethylphosphinic acid;<sup>21</sup> and (iii) the mixture could be titrated with aqueous sodium hydroxide (54%, 11.0 mmol as a mono-basic acid).

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<sup>11</sup> G. Oster, L. Citarel, and M. Goodman, *J. Amer. Chem. Soc.*, **1962**, **84**, 703.

<sup>12</sup> W. A. Lees and A. Burawoy, *Tetrahedron*, **1964**, **20**, 1527.

<sup>13</sup> I. M. Downie and G. Morris, *J. Chem. Soc.*, **1965**, 5771.

<sup>14</sup> L. R. Ocone, C. W. Schaumann, and B. P. Block, *Inorg. Synth.*, **1966**, **8**, 71.

<sup>15</sup> W. Schlenk and E. Bergmann, *Annalen*, **1930**, **479**, 42.

<sup>16</sup> S. L. Murov, 'Handbook of Photochemistry,' Dekker, New York, **1975**, p. 99.

<sup>17</sup> J. Lévy and R. Lagrave, *Bull. Soc. chim. France*, **1928**, **43**, 437.

<sup>18</sup> A. Schönberg and E. Frese, *Chem. Ber.*, **1962**, **95**, 2810.

<sup>19</sup> H. Niebergall and B. Langenfeld, *Chem. Ber.*, **1962**, **95**, 64.

<sup>20</sup> H. L. Bradlow and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **1947**, **69**, 1254.

<sup>21</sup> W. Kuchen, K. Strolenberg, and H. Buchwald, *Chem. Ber.*, **1962**, **95**, 1703.