

## Reactions of Tetraphenyldiphosphine with Carbon Radicals

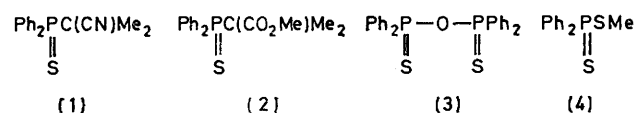
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1-Cyano-1-methylethyl and 1-methoxycarbonyl-1-methylethyl radicals reacted with tetraphenyldiphosphine to afford, after sulphurization, 1-cyano-1-methylethyl-(1) and 1-methoxycarbonyl-1-methylethyl-(diphenyl)phosphine sulphides (2), respectively. A mechanism involving metathesis of the P-P bond is suggested. The photo-sensitized reaction of 1,1-diphenylethylene gave 2,2-diphenylethyl(diphenyl)phosphine sulphide after sulphurization. We suggest that the triplet state of the ethylene behaves like a carbon radical in its attack on the phosphorus-phosphorus bond.

ALTHOUGH extensive studies have been reported concerning ionic reactions of diphosphines and polyphosphines, there have been few reports on the reactions of radicals with these compounds.<sup>1,2</sup> Shlyk *et al.*<sup>3</sup> have described briefly some photochemical reactions of diphosphines with hydrazines, disulphides, diselenides, and ditellurides but the mechanism remains obscure.<sup>4</sup> More recently, Ingold *et al.* have reported the reaction of an alkoxy radical with tetra-alkoxydiphosphines.<sup>5</sup> These results are in sharp contrast with the well known metathesis of oxygen-oxygen and sulphur-sulphur bonds.

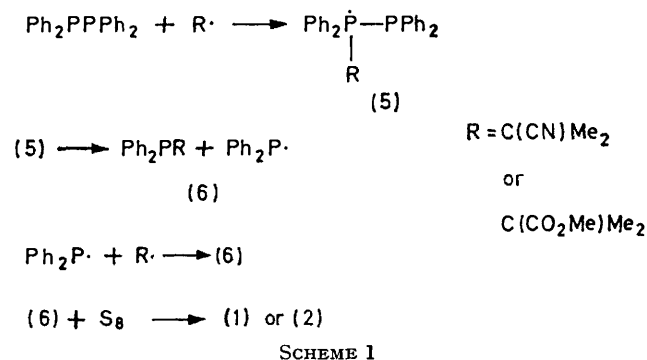
As a continuation of our work on diphosphine derivatives,<sup>6</sup> we describe here the reactions of carbon radicals with tetraphenyldiphosphine.

*Reactions of Tetraphenyldiphosphine (TPD) with Carbon Radicals.*—The reaction of TPD with 1-cyano-1-methylethyl radicals generated from azobisisobutyronitrile (AIBN) in refluxing benzene followed by sulphurization with sulphur gave 1-cyano-1-methylethyl(diphenyl)phosphine sulphide (1) in 82% yield. In the reaction



with 1-methoxycarbonyl-1-methylethyl radicals generated from the corresponding azo-compounds the products

were 1-methoxycarbonyl-1-methylethyl(diphenyl)phosphine sulphide (2) (43%), diphenylphosphinothioic anhydride (3) (14%), and methyl diphenylphosphinodithioate (4) (13%).



The formation of the products (1) and (2) can be explained in terms of Scheme 1, involving an induced decomposition (metathesis) of the P-P bond by the radical R·. This represents the first unambiguous example of metathesis of the P-P bond by a carbon radical, although a few workers<sup>7</sup> have postulated such a metathesis in reactions with a conjugated olefin. Although we have no experimental evidence for the existence of the phosphoranyl radical (5), we consider that the initial step of the reaction is the formation of

<sup>1</sup> A. H. Cowley, *Chem. Rev.*, 1965, **65**, 617.

<sup>2</sup> L. Maier, 'Organic Phosphorus Compounds,' ed. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, vol. 1, ch. 2.

<sup>3</sup> Yu. N. Shlyk, G. M. Bogolyubov, and A. A. Petrov, *Zhur. obshchei Khim.*, 1968, **38**, 193.

<sup>4</sup> W. G. Bentrude, 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, ch. 22.

<sup>5</sup> D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 554.

<sup>6</sup> T. Emoto, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 898.

<sup>7</sup> R. Brandon, R. N. Haszeldine, and P. J. Robinson, *J.C.S. Perkin II*, 1973, 1301; W. Hewertson and I. C. Taylor, *J. Chem. Soc. (C)*, 1970, 1990.



24 mmol) in benzene was gradually heated to reflux over 2 h and refluxing was continued for 5 h. After addition of sulphur (0.90 g, 28 mmol), the mixture was refluxed for 1 h. After evaporation of the benzene, tetramethylsuccinonitrile was removed by vacuum sublimation and the residue was chromatographed on silica gel. 1-Cyano-1-methylethyl-(diphenyl)phosphine sulphide (**1**) was eluted with benzene-ether and recrystallized from ethanol; yield 5.48 g, 82%; m.p. 121—121.5° (lit.,<sup>18</sup> 123—125°);  $\nu_{\max}$  (KBr) 2 220  $\text{cm}^{-1}$  (C≡N);  $\tau$  (CCl<sub>4</sub>) 8.50 (6 H, d,  $^3J_{\text{PH}}$  15 Hz), 2.4—2.6 (6 H, m), and 1.6—2.0 (4 H, m).

*Reaction of TPD with Dimethyl Azobisisobutyrate (MAIB).*—TPD (5.39 g, 14.6 mmol) and MAIB<sup>19</sup> (3.8 g, 18 mmol) dissolved in benzene (50 ml) were refluxed for 2 h. More MAIB (3.0 g, 12 mmol) was added to the solution, which was refluxed for 5 h. After addition of sulphur (1.12 g, 35 mmol), the solution was refluxed for 1 h. The benzene was evaporated off and the viscous residue was distilled under reduced pressure to give low boiling (b.p. 60—125° at 0.6 mmHg) and high boiling (b.p. 205—210° at 0.6 mmHg) fractions. The former was dimethyl tetramethylsuccinate (i.r. and n.m.r.) and the latter was chromatographed on silica gel to give methyl diphenylphosphinodithioate (**4**) (1.0 g, 13%), m.p. 82—83° (lit.,<sup>20</sup> 82—83°);  $\tau$  (CCl<sub>4</sub>) 7.8 (3 H, d,  $^3J_{\text{PH}}$  14.6 Hz), 2.5—2.8 (6 H, m), and 1.9—2.3 (4 H, m), and 1-methoxycarbonyl-1-methylethyl(diphenyl)phosphine sulphide (**2**) (3.95 g, 43%), m.p. 84.5—85° (from petroleum) (Found: C, 63.8; H, 6.05; S, 9.7. C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>PS requires C, 64.1; H, 6.0; S, 10.1%),  $\nu_{\max}$  (KBr) 1 710 (C=O) and 1 250  $\text{cm}^{-1}$  (C—O—C),  $\tau$  (CCl<sub>4</sub>) 8.5 (6 H, d,  $^3J_{\text{PH}}$  15.8 Hz), 6.6 (3 H, s), 2.5—2.7 (6 H, m), and 1.8—2.2 (4 H, m). The distil-

lation residue was chromatographed on silica gel to give diphenylphosphinothioic anhydride (**3**) (0.92 g, 14%), m.p. 200.5—201° (lit.,<sup>21</sup> 201.5—202°),  $\nu_{\max}$  (KBr) 1 100 (P—Ph) and 910  $\text{cm}^{-1}$  (P—O—P),  $m/e$  450 ( $M^+$ , 90%) and 139 (100).

*Photoreaction of TPD with DPE.*—A solution (180 ml) of TPD (1.08 g, 2.92 mmol), DPE (2.12 g, 11.8 mmol), and xanthone (1.16 g, 5.90 mmol) in benzene was irradiated for 12 h with a 100 W high-pressure mercury lamp (Rikosha) through a filter solution (1 cm) of copper(II) sulphate [CuSO<sub>4</sub>·5H<sub>2</sub>O (250 g) in distilled water (1 l)].<sup>22</sup> After addition of sulphur (183 mg, 5.84 mmol), the solution was refluxed for 1 h, then shaken with 5% sodium carbonate solution to remove diphenylphosphinic acid (0.23 g, 18%), which was identified by comparison of the i.r. spectrum with that of an authentic sample. The neutral product was submitted to dry column chromatography (silica gel) with carbon tetrachloride-chloroform (3 : 1) to give tetraphenyl-diphosphine disulphide (**8**) (87 mg, 7%), 2,2-diphenyl-ethenyl(diphenyl)phosphine sulphide (**7**) (392 mg, 34%), and unchanged xanthone (82%); compound (**8**) was identified by comparison of spectral data (i.r., n.m.r., and mass spectra) with those of an authentic sample,<sup>23</sup> and (**7**) by comparison of the spectral data with those reported<sup>24</sup> and by mass spectrum [ $m/e$  396 ( $M^+$ , 24%), 217 (50), and 140 (100)].

A solution (180 ml) of TPD (10.8 g, 2.92 mmol) and TPE (2.07 g, 11.4 mmol) in benzene was irradiated for 12 h under identical conditions and the product was worked up in a similar manner to give compounds (**7**) (515 mg, 23%) and (**8**) (371 mg, 30%).

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<sup>18</sup> H. Low and P. Tavs, *Tetrahedron Letters*, 1966, 1357.

<sup>19</sup> J. Thiele and K. Heuser, *Annalen*, 1896, **290**, 35.

<sup>20</sup> T. Robert, T. R. Hopkins, and P. W. Vogel, *J. Amer. Chem. Soc.*, 1956, **78**, 4447.

<sup>21</sup> T. A. Mastryukova, T. A. Melenteva, and M. I. Kavachnik, *Zhur. obshchei Khim.*, 1965, **35**, 1197.

<sup>22</sup> S. L. Murov, 'Handbook of Photochemistry,' Deckker, New York, 1975, p. 99.

<sup>23</sup> W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, **91**, 2871.

<sup>24</sup> D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.