C(CO2Me)Me2

## **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 photosensitized reaction of 1,1-diphenylethylene gave 2,2-diphenylethenyl(diphenyl)phosphine sulphide after sulphurization. We suggest that the triplet state of the ethylene behaves like a carbon radical in its attack on the phosphorusphosphorus 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 alkoxyl 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

bishchei Khim., 1968, 38, 193.
<sup>4</sup> W. G. Bentrude, 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, ch. 22.

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

$$Ph_{2}PPPh_{2} + R \cdot \longrightarrow Ph_{2}\dot{P} \longrightarrow PPh_{2}$$

$$R$$

$$(5)$$

$$(5) \longrightarrow Ph_{2}PR + Ph_{2}P \cdot R = C(CN)Me_{2}$$

$$(6) \qquad or$$

$$Ph_2P + R \rightarrow (6)$$

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 7 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>&</sup>lt;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>&</sup>lt;sup>3</sup> Yu. N. Shlyk, G. M. Bogolyubov, and A. A. Petrov, Zhur.

<sup>&</sup>lt;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.

this radical, since e.s.r. spectroscopy has shown the formation of phosphoranyl radicals from trivalent phosphorus compounds upon reaction with a radical.<sup>4</sup>

The attack of such stabilized radicals as 1-cyano- and 1-methoxycarbonyl-1-methylethyl upon the phosphorus of diphosphine is noteworthy in view of the reported inability of resonance-stabilized radicals to attack such trivalent phosphorus compounds as phosphinites<sup>8</sup> and chlorophosphines.9 The ease with which the present reactions proceed is probably due to the weakness of the P-P bond.

The anhydride (3) is presumably produced by oxidation of tetraphenyldiphosphine disulphide (formed from unchanged TPD by sulphurization) with air during work-up at high temperatures (see Experimental section); tetraphenyldiphosphine disulphide is reported to be oxidized with air in refluxing xylene to give  $(3).^6$  The mechanism of formation of the ester (4) is not clear.

The possibility that the phosphine (6) is formed by coupling between the radicals R. and Ph<sub>2</sub>P. generated by thermal cleavage of TPD can be ruled out, because cleavage of the P-P bond of TPD is reported to need temperatures higher than 180 °C.<sup>10</sup>

Reactions of 1-cyano-1-methylethyl radical with such polyphosphines as cyclopolyphosphine  $[(PhP)_n, n = 4 \text{ or }$ 5],<sup>11</sup> yellow phosphorus, and red phosphorus were carried out in the hope of obtaining the compounds PhPR<sub>2</sub> or  $R_{a}P [R = C(CN)Me_{2}]$ , but no reactions occurred under comparable conditions.

Photoreaction of TPD with 1,1-Diphenylethylene (DPE). —The reaction was carried out to discover whether photoexcited DPE can attack the diphosphine in a similar manner to the foregoing carbon radicals. Triplet DPE has been reported to have a reactivity similar to that of the  $n-\pi^*$  triplet state of benzophenone, and to behave like a carbon radical; it undergoes intra-12 or intermolecular <sup>13</sup> hydrogen abstraction, cycloaddition to isobutene,<sup>14</sup> and addition to benzene.<sup>15</sup> A solution of TPD, DPE, and xanthone in benzene was irradiated (>340 nm) under such conditions that about 95% of the incident light of 366 nm was absorbed by the xanthone. The products (after sulphurization by sulphur) were 2,2diphenylethenyl(diphenyl)phosphine sulphide (7) (34%), tetraphenyldiphosphine disulphide (8) (7%), and diphenylphosphinic acid (9) (18%). The facts that (i) 95%

$$\begin{array}{cccccc} Ph_2PCH = CPh_2 & Ph_2PPPh_2 & Ph_2POH \\ \| & & \| \| & & \cdot \| \\ S & SS & O \\ (7) & (8) & (9) \end{array}$$

of the 366 nm light is absorbed by xanthone and (ii) DPE is excited to the triplet state by photosensitization with

<sup>8</sup> R. S. Davidson, Tetrahedron, 1969, 25, 3383.

<sup>9</sup> L. Dulog, F. Nierlich, and A. Verhelst, Chem. Ber., 1972, 105.

874. <sup>10</sup> R. S. Davidson, R. A. Sheldon, and S. Trippett, J. Chem.

Soc. (C), 1966, 722. <sup>11</sup> W. Kuchen and W. Grunewald, Chem. Ber., 1965, **98**, 480. 1973, 52 <sup>12</sup> E. Scully and H. Morrison, J.C.S. Chem. Comm., 1973, 529; A. C. Pratt, ibid., 1974, 182.

xanthone <sup>12-15</sup> suggest Scheme 2, involving triplet DPE. for the formation of (7), which is similar to that for the reactions with carbon radicals discussed above.

$$Ph_{2}PPPh_{2} + [Ph_{2}C = CH_{2}]^{3} \longrightarrow Ph_{2}\dot{P} - PPh_{2}$$

$$Ph_{2}PCH_{2}\dot{C}Ph_{2} + Ph_{2}P^{*}$$

$$(10)$$

$$Ph_{2}P^{*} + Ph_{2}C = CH_{2} \longrightarrow (10)$$

$$(10) \longrightarrow Ph_{2}PCH = CPh_{2} \xrightarrow{s_{8}} (7)$$

$$SCHEME 2$$

This is a new reaction mode of triplet DPE. The possibility that the P-P bond cleavage takes place via energy transfer from xanthone to TPD can be ruled out by the observation that benzophenone reacts efficiently with TPD under similar photolytic conditions to give tetraphenylethylene as major product.<sup>16</sup> Although it is considered that xanthone should behave similarly, no reaction products derived from xanthone were found, and the xanthone was recovered in high yield in the present reaction, suggesting that its triplet energy was efficiently transferred to TPE.

However, we cannot completely eliminate the possibility that the product (7) was formed, at least in part, by the reaction of DPE with diphenylphosphino-radical generated by photochemical cleavage of TPD, because irradiation of TPD and DPE in the absence of xanthone under otherwise identical conditions also gave (7), although the yield was lower (23%). This result suggests that TPD is photolytically very labile, and is decomposed into diphenylphosphino-radicals by 366 nm light in spite of the low extinction coefficient (ca. 30) at this wavelength. The phosphino-radical thus formed should react with ground state DPE to give (10) and then (7) in view of the known reactivity of phosphino-radicals with olefins.4

The disulphide (8) is considered to be formed by sulphurization of unchanged TPD.

## EXPERIMENTAL

I.r. spectra were recorded with a Hitachi EPI-G2 spectrophotometer, n.m.r. spectra with Hitachi R-24 and JEOL JNM-C-60H spectrometers (tetramethylsilane as internal standard), and mass spectra with a Hitachi RMU-6L spectrometer. All reactions were carried out under nitrogen.

Reaction of TPD with Azobisisobutyronitrile (AIBN).---A solution (40 ml) of TPD (3.9 g, 12 mmol)  $^{17}$  and AIBN (4.0 g,

<sup>13</sup> H. M. Rosenberg and P. Serve, J. Amer. Chem. Soc., 1970, 92, 4745.

<sup>14</sup> T. S. Cantrell, Chem. Comm., 1970, 1633.

- <sup>15</sup> M. Kawanishi and K. Matsunaga, J.C.S. Chem. Comm., 1972, 418
- <sup>16</sup> R. Okazaki, K. Tamura, Y. Hirabayashi, and M. Inamoto, unpublished results. <sup>17</sup> H. Hoffmann, R. Grunewald, and L. Horner, *Chem. Ber.*,
- 1960, 93, 861.

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 benzeneether 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 cm<sup>-1</sup> (C=N);  $\tau$  (CCl<sub>4</sub>) 8.50 (6 H, d,  ${}^{3}J_{PH}$  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 19 (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., 20 82-83°);  $\tau$  (CCl<sub>4</sub>) 7.8 (3 H, d,  ${}^{3}f_{PH}$ 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.  $84.5-85^{\circ}$  (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 cm<sup>-1</sup> (C=O-C),  $\tau$  (CCl<sub>4</sub>) 8.5 (6 H, d,  ${}^{3}J_{PH}$  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-

18 H. Low and P. Tavs, Tetrahedron Letters, 1966, 1357.

J. Thiele and K. Heuser, Annalen, 1896, 290, 35.
 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.

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°),  $v_{max}$  (KBr) 1 100 (P–Ph) and 910 cm<sup>-1</sup> (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  $[CuSO_4, 5H_2O$  (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 tetraphenyldiphosphine disulphide (8) (87 mg, 7%), 2,2-diphenylethenyl(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 24 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>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.