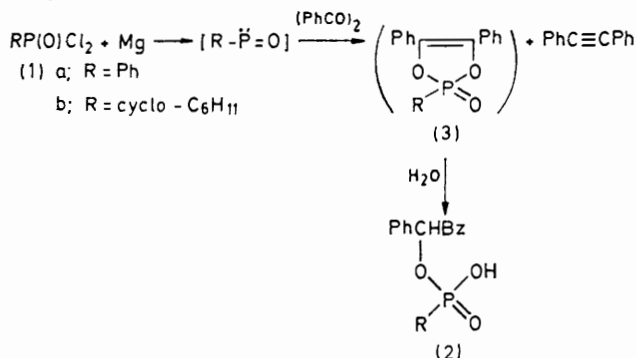


Phosphinidenes and Related Intermediates. Part II.¹ Reactions of Phosphonic or Phosphonothioic Dichlorides with Benzil in the Presence of an Excess of Magnesium. Formation of Diphenylacetylene

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Phenylphosphonic and phenylphosphonothioic dichlorides, when treated with benzil and an excess of magnesium, gave diphenylacetylene, diphenylmethyl phenyl ketone, and 1,2,2-triphenylethanol. The formation of these products is attributed to reduction of 1,3,2-dioxaphosphole 2-oxide and 2-sulphide, the adducts from phenylphosphinoylidene ($\text{Ph}-\ddot{\text{P}}=\text{O}$) and phenylphosphinothioylidene ($\text{Ph}-\ddot{\text{P}}=\text{S}$) intermediates with benzil, respectively, in the magnesium dichloride-magnesium system. The corresponding cyclohexyl derivatives similarly gave diphenylacetylene under similar conditions. A reaction mechanism involving the dianions of 1,3,2-dioxaphosphole 2-oxide and 2-sulphide is suggested.

In the preceding paper¹ we reported that reactions of phosphonic dichlorides (1) with a slight excess of magnesium and benzil gave α -benzoylbenzyl phosphonates (2), derived from 1,3,2-dioxaphosphole 2-oxides (3), together with a considerable amount of diphenylacetylene. We now suggest a mechanism for the formation of the acetylene.



When two equivalents of magnesium were used in the dechlorination of phenylphosphonothioic dichloride (4a) in the presence of benzil, 2,4,5-triphenyl-1,3,2-dioxaphosphole 2-sulphide (5a), the main product in the reaction with one equivalent of magnesium, was not obtained at all, but diphenylacetylene was obtained in 30% yield. In a similar reaction with cyclohexylphosphonothioic dichloride (4b), diphenylacetylene was obtained in 51% yield, together with 13% of the sulphide (5b).

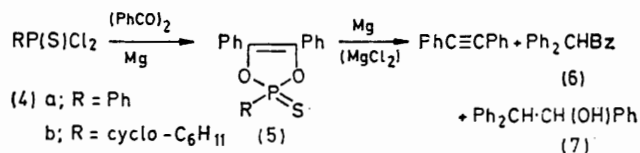
The reaction mixture of compound (4a) with benzil and one equivalent of magnesium, which contained 75% of the sulphide (5a), reacted again exothermically on addition of an equivalent of magnesium to afford diphenylacetylene (30%) and phenyl diphenylmethyl ketone (6) (12%). We therefore presume that the acetylene is formed from the sulphide (5a).

However, the sulphide (5a) did not react with magnesium alone, but reacted with magnesium in the presence of magnesium dichloride, which is produced in the reaction of the dichloride (4a) with magnesium, to give diphenylacetylene (48%), the ketone (6) (12%), and 1,2,2-triphenylethanol (7) (12%).

¹ M. Yoshifuji, S. Nakayama, R. Okazaki, and N. Inamoto, preceding paper.

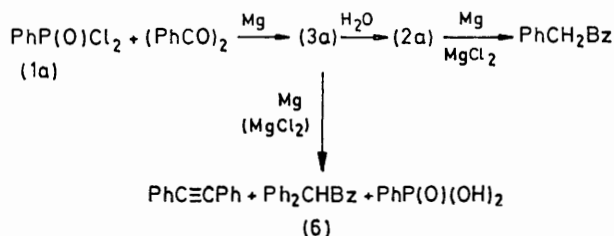
² M. Gomberg, *Rec. Trav. chim.*, 1929, **48**, 847.

Gomberg² reported that the reduction of benzil in the magnesium-magnesium di-iodide system, in which magnesium monoiodide is formed *in situ*, gave the corresponding dianion, which afforded benzoin by hydrolysis.



The formation of the alcohol (7) is analogously attributable to further reduction of the ketone (6) with magnesium monochloride, and diphenylacetylene and the ketone (6), the latter of which is a reductive rearrangement product, are considered to be products of reduction of the sulphide (5a) by magnesium monochloride.

When phenylphosphonic dichloride (1a) was dechlorinated with an excess of magnesium in the presence of benzil, the oxide (2a) was not obtained at all; the products isolated were diphenylacetylene (63%) and the ketone (6) (0.4%). The reaction mixture of the dichloride (1a) with benzil and an equimolar amount of magnesium, from which the phosphonate (2a) (40%) and diphenylacetylene (10%) could be isolated, reacted again exothermically on addition of one equivalent of magnesium to give diphenylacetylene (55%), the ketone (6) (9%), and phenylphosphonic acid (24%).

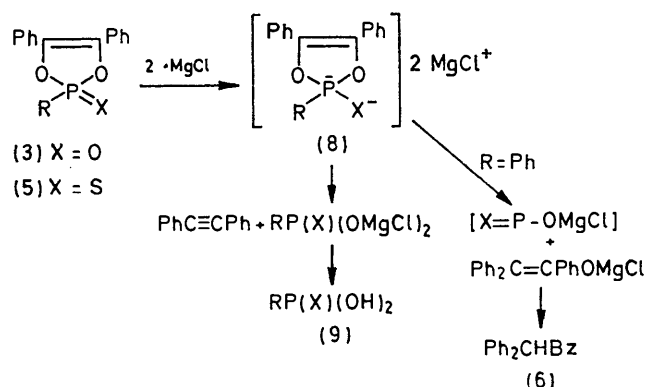
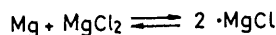
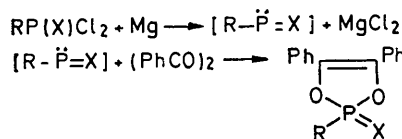


However, the phosphonate (2a) gave neither diphenylacetylene nor the ketone (6) but only benzyl phenyl ketone when treated with magnesium and magnesium dichloride. Therefore, the formation of the acetylene and the ketone (6) is attributable to the reduction of the oxide (3) with magnesium monochloride.

Similarly, the reaction of the dichloride (1b) with benzil and an excess of magnesium gave diphenylacetylene (52%) and the phosphonate (2b) (6%). It is noteworthy that the phosphonate (2b) was obtained in the

case of the dichloride (1b), in contrast to that of the dichloride (1a).

From the foregoing results, the formation of diphenylacetylene and the ketone (6) in the presence of an excess of magnesium can be probably explained by the illustrated reduction mechanism (Scheme). Two molecules of magnesium monochloride transfer two electrons to the oxide (3) or the sulphide (5) to form a dianion (8). Then follow two modes of electron shift (i) to afford diphenylacetylene and phosphonic or phosphonothioic acid (9),



SCHEME

and (ii) to afford the ketone (6) and polyphosphate* by 1,3-migration of the phenyl group. Phenylphosphonic acid was obtained in the case of the oxide (3a), but phenylphosphonothioic acid could not be isolated in the case of the sulphide (5a).

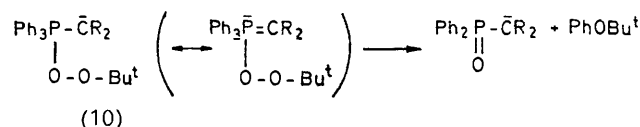
The fact that, even in the dechlorination with an equimolar amount of magnesium, a considerable amount of diphenylacetylene was obtained in the reaction of the dichlorides (1)¹ supports the suggested mechanism, since the oxide (3) is more liable to form the dianion (8) than the corresponding sulphide (5).

In the cases of the dichlorides (1b) and (4b), the phosphonate (2b) and the sulphide (5b) were isolated even in the presence of an excess of magnesium. These results can be also explained in terms of the foregoing mechanism, since the dianion (8) can be stabilised by conjugation with the phenyl group, but is not stabilised by a cyclohexyl group.

A mechanism involving a radical anion can also explain the observed results, but is considered less likely.

The driving force for the formation of diphenylacetylene and the ketone (6) from the dianion (8) is probably the formation of both triple and P=X bonds. The phenyl

migration in the dianion (8) resembles phenyl migration to the β-oxygen atom of the peroxide (10).³



EXPERIMENTAL

All reactions were carried out under nitrogen.

Reactions of Phenylphosphonothioic Dichloride (4a) with an Excess of Magnesium.—(a) The dichloride (4a) (5.2 g, 25 mmol) was added dropwise to a stirred solution containing magnesium turnings (2.0 g, 83 mg atom), benzil (5.8 g, 28 mmol), and tetrahydrofuran (THF) (20 ml). The mixture was stirred at room temperature for 1 h, with occasional cooling (water). Filtration gave unchanged magnesium (0.82 g, 34 mg atom). The solvent was removed from the filtrate and the residue was dissolved in ether. The solution was evaporated and the residue was chromatographed on silica gel in carbon tetrachloride. Elution with carbon tetrachloride and with benzene gave diphenylacetylene (1.35 g, 7.6 mmol, 30%), m.p. 59–60° (lit.,⁴ 60–61°), and unchanged benzil (1.4 g, 6 mmol), respectively.

(b) The dichloride (4a) (10.4 g, 49 mmol) was added to a stirred mixture of magnesium (1.2 g, 50 mg atom), benzil (11.5 g, 55 mmol), and THF (30 ml). After stirring for 1 h, half the reaction mixture was removed and treated as described in (a). Chromatography on silica gel (elution with carbon tetrachloride) gave unchanged dichloride (4a) (0.1 g, 0.4 mmol) and 2,4,5-triphenyl-1,3,2-dioxaphosphole 2-sulphide (5a)¹ (6.1 g, 18 mmol, 75%), m.p. 126–127°, and elution with benzene gave unchanged benzil (1.8 g, 8.6 mmol).

Magnesium (1.5 g, 62 mg atom) was added to the other half of the reaction mixture. The exothermic reaction ceased within 1 h, and a similar treatment of the mixture gave unchanged magnesium (0.9 g, 38 mg atom). Chromatography gave diphenylacetylene (1.32 g, 7.4 mmol, 30%) (with carbon tetrachloride as eluant), phenyl diphenylmethyl ketone (6) (0.7 g, 2.9 mmol, 12%), m.p. 136–137° (from ethanol) (lit.,⁵ 137°), and unchanged benzil (0.2 g, 1 mmol) (with benzene), and benzoin (0.7 g, 3 mmol), m.p. 133.5–135° (with chloroform).

The yields were calculated based on the half quantity of the dichloride (4) consumed.

Reaction of 2,4,5-Triphenyl-1,3,2-dioxaphosphole 2-Sulphide (5a) with Magnesium–Magnesium Dichloride.—A mixture of anhydrous magnesium dichloride (0.56 g, 5.9 mmol) and magnesium (0.32 g, 13 mg atom) in THF (50 ml) was refluxed for 2 h after addition of a few drops of carbon tetrachloride to activate the magnesium surface. A solution of the sulphide (5a) (1.4 g, 4.5 mmol) in THF was then added and the mixture was refluxed for 1 week and treated as before. Chromatography gave diphenylacetylene (0.38 g, 2.1 mmol, 48%) (eluted with carbon tetrachloride), the ketone (6) (0.14 g, 0.51 mmol, 12%) (with benzene), and 1,2,2-triphenylethanol (7) (0.14 g, 0.51 mmol, 12%), m.p. 84–85° (from light petroleum) (lit.,⁶ 87°) (with benzene and chloroform).

Reactions of Phenylphosphonic Dichloride (1a) with an Excess of Magnesium.—(a) A mixture of the dichloride (1a) (4.7 g, 24 mmol), magnesium (2.0 g, 83 mg atom), and benzil

* Isolation of polyphosphate (HPOX)_n was not tried.

³ K. Yamada, K. Akiba, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1971, **44**, 2437.

⁴ H. Limpricht and H. Schwanert, *Annalen*, 1868, **145**, 330.

⁵ H. Ley and W. Manecke, *Ber.*, 1923, **56**, 777.

⁶ A. Gardeur, *Chem. Zentr.*, 1897(II), 661.

(5.8 g, 27 mmol) in THF (18 ml) was stirred at room temperature for 1 h. Treatment as before gave diphenylacetylene (2.6 g, 15 mmol, 63%), the ketone (6) (27 mg, 0.099 mmol, 0.4%), benzoin (0.24 g, 1.1 mmol), unchanged benzil (0.55 g, 2 mmol), and unchanged magnesium (0.84 g, 35 mg atom).

(b) A mixture of the dichloride (1a) (9.8 g, 50 mmol), magnesium (1.2 g, 50 mg atom), and benzil (11.4 g, 54 mmol) in THF (50 ml) was stirred at room temperature for 1 h, with occasional cooling (water). Half of the reaction mixture was removed, and treated with ether and then chloroform to give α -benzoylbenzyl phenylphosphonate (2a) (2.7 g) as the insoluble fraction. The soluble product was chromatographed to give diphenylacetylene (0.45 g, 2.5 mmol, 10%), unchanged benzil (1.4 g, 6.5 mmol), and the phosphonate (2a) (0.8 g). The total amount of the phosphonate (2a),¹ m.p. 150—152°, was 3.5 g (10 mmol, 40%).

To the other half of the reaction mixture, magnesium (0.98 g, 40 mg atom) was added at room temperature with stirring. The exothermic reaction ended within 1 h. Unchanged magnesium (0.44 g, 18 mg atom) was recovered. The solvent was evaporated off and the residue was treated with ether to give phenylphosphonic acid (insoluble) (0.95 g, 6.0 mmol, 24%), m.p. 158—162° (lit.,⁷ 165—166°), and the ethereal extracts were chromatographed on silica gel to give diphenylacetylene (2.5 g, 14 mmol, 55%), the ketone (6) (0.49 g, 2.3 mmol, 9%), and benzoin (0.34 g, 1.6 mmol).

Reaction of α -Benzoylbenzyl Phenylphosphonate (2a) with Magnesium-Magnesium Dichloride.—Anhydrous magnesium dichloride (0.32 g, 3.4 mmol) was dissolved in refluxing THF (50 ml) and magnesium (0.16 g, 6.7 mg atom) was added. A few drops of carbon tetrachloride were added to activate the surface of the magnesium. The phosphonate

(2a) (1.1 g, 3.1 mmol) was then added and the mixture was refluxed for 92 h with stirring. Treatment as before gave benzyl phenyl ketone (0.20 g, 1.0 mmol, 33%), m.p. 55—56° (from ethanol) (lit.,⁸ 57°), and no diphenylacetylene.

Reaction of Cyclohexylphosphonothioic Dichloride (4b) with an Excess of Magnesium.—At room temperature, the dichloride (4b) (5.5 g, 25 mmol) in THF (10 ml) was added dropwise to a stirred mixture of magnesium (1.6 g, 66 mg atom) and benzil (5.8 g, 27 mmol) in THF (30 ml). The mixture was stirred with occasional cooling (water) for 1 h. Treatment as before gave diphenylacetylene (2.3 g, 13 mmol, 51%), the sulphide (5b)¹ (1.2 g, 3.3 mmol, 13%), m.p. 107—108.5°, unchanged benzil (1.2 g, 5.7 mmol), and benzoin (1.2 g, 5.6 mmol).

Reaction of Cyclohexylphosphonic Dichloride (1b) with an Excess of Magnesium.—The dichloride (1b) (5.4 g, 27 mmol) was added dropwise with stirring to a suspension containing magnesium (1.5 g, 62 mg atom), benzil (5.8 g, 28 mmol), and THF (25 ml) during 1.5 h with cooling (water). To complete the reaction, the mixture was heated at 50° for 5 h, but small amount of magnesium (0.16 g, 11%) was recovered. The THF was removed, and the residual material was extracted with ether. The extracts were dried (MgSO₄) and chromatographed on silica gel to give diphenylacetylene (2.5 g, 14 mmol, 52%) and α -benzoylbenzyl cyclohexylphosphonate¹ (0.55 g, 1.5 mmol, 6%), together with unchanged benzil (0.19 g, 3%).

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⁷ H. Z. Lecker, T. H. Chao, K. C. Whitehouse, and R. A. Greenwood, *J. Amer. Chem. Soc.*, 1954, **76**, 1045.

⁸ C. Graebe and H. Bunzener, *Ber.*, 1879, **12**, 1079.