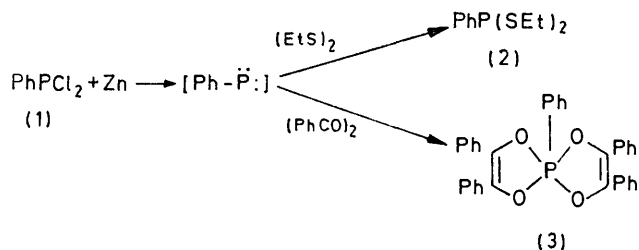


Phosphinidenes and Related Intermediates. Part I. Reactions of Phosphinoylidenes (R-P̄=O) and Phosphinothiylidenes (R-P̄=S) with Diethyl Disulphide and Benzil

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Organic phosphonic or phosphonothioic dichlorides were dechlorinated with an equimolar amount of magnesium in the presence of diethyl disulphide or benzil to give the corresponding SS-diethyl esters of phosphorus acids or 1,3,2-dioxaphosphole derivatives, respectively, but reactions of phosphonic dichlorides with magnesium in the presence of benzil gave products of hydrolysis of 1,3,2-dioxaphosphole derivatives. The results have been explained in terms of capture of reactive intermediates, phosphinoylidenes (R-P̄=O) or phosphinothiylidenes (R-P̄=S), by disulphide or benzil; similar results were obtained in the dechlorination reactions of phenylphosphonous dichloride.

PHOSPHINIDENES (R-P̄) are considered to be the phosphorus analogues of nitrenes. Schmidt *et al.*¹ have reported reactions of diethyl disulphide and benzil with phenylphosphinidene generated by thermal or photochemical decomposition of pentaphenylcyclopentaphosphane, and by dechlorination of phenylphosphonous dichloride (1) with zinc. Phosphinoylidenes (R-P̄=O) and



phosphinothiylidenes (R-P̄=S) would be expected to behave similarly to phosphinidenes.

Gallagher and Jenkins² have reported unsuccessful attempts to generate phenylphosphinoylidene. Phosphinothiylidene has been postulated as an intermediate in the formation of diphosphine disulphides by reactions of phosphonothioic dihalides with Grignard reagents.³ Very recently, Stille *et al.*⁴ have reported the generation of phenylphosphinoylidene in the thermal decomposition of 1,4-dihydro-1,2,3,4-tetraphenyl-1,4-(phenylphosphonyl)naphthalene.

We have studied the generation of phosphinoylidenes and phosphinothiylidenes, and their reactions with diethyl disulphide and benzil. We have also found that phosphinothiylidenes also behave as thionitroso-analogues towards 2,3-dimethylbuta-1,3-diene.⁵

Reactions with Diethyl Disulphide.—The dechlorination reactions of phosphonic (4) or phosphonothioic dichlorides (5) with magnesium gave SS-diethyl phosphonodithioates (6) or phosphonotrithioates (7) in the presence of diethyl disulphide. These results, and the physical properties of the products, (6) and (7), are summarised in Tables 1—3. The formation of the esters (6) and (7) suggests the occurrence of insertion of phosphinoylidenes or

phosphinothiylidenes into the S-S bond of diethyl disulphide, in analogy with the behaviour of phosphinidenes.¹

TABLE 1

Reactions of the dichlorides (4) and (5) with magnesium in diethyl disulphide

Dichloride	Reaction conditions Temp. (°C)	Time (h)	Product	Yield (%) †
(4a)	50—60	8	(6a)	41
(4b)	65	35	(6b)	35
(5a)	50	5	(7a)	41
(5b) ‡	50	11	(7b)	69

† Based on magnesium consumed. ‡ M. I. Kabachnik and N. N. Godovikov, *Doklady Akad. Nauk S.S.S.R.*, 1956, **110**, 217.

TABLE 2

Physical properties of the products (6) and (7)

Product	B.p. (°C)	Found (%)		Required (%)	
		C	H	C	H
(6a)	118 (0.1 mmHg), 163—165 (4 mmHg)	48.8	6.35	48.75	6.15
(7a)	109—117 (0.05 mmHg)	45.85	6.00	45.75	5.75
(6b)	149—150 (1.7 mmHg)	47.35	8.45	47.58	8.4
(7b)	132 (0.06 mmHg), 108 (0.02 mmHg)	44.85	7.65	44.75	7.9

TABLE 3

³¹P N.m.r. data for the products (2), (6), and (7)

Compound	δ _P (neat)	J _{PSCH} /Hz †	J _{PH_o} /Hz †	J _{PH_{m,p}} /Hz †
(2)	—76.0(sept)	8.1	8.1 ‡	§
(6a)	—52.5(sept × q)	14.1 (13.8)	14.1 (14.1)	3.2 §
(6b)	—100.0br(s) ¶	§	§	§
(7a)	—80.5(sept × q)	15.8 (15.7)	15.8 (15.7)	3.4 §
(7b)	—102.0br(s)	§	§	§

† Values in parentheses are from ¹H n.m.r. data. ‡ The phenyl signal was too complex to be analysed. § Could not be determined. ¶ In carbon tetrachloride.

The dichloride (1) gave diethyl phenylphosphonodithioite (2)¹ when treated with zinc in diethyl disulphide

³ H. J. Harwood and K. A. Pollart, *J. Org. Chem.*, 1963, **28**, 3430; P. C. Crofts and I. S. Fox, *J. Chem. Soc. (B)*, 1968, 1416.

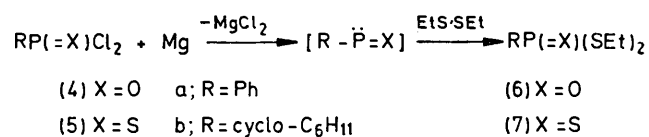
⁴ J. K. Stille, J. L. Eichelberger, J. Higgins, and M. E. Freeburger, *J. Amer. Chem. Soc.*, 1972, **94**, 4761.

⁵ S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Chem. Comm.*, 1971, 1186.

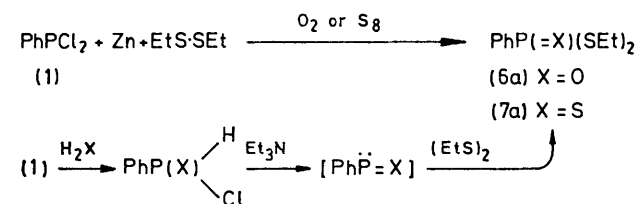
¹ (a) U. Schmidt and Ch. Osterroht, *Angew. Chem.*, 1965, **77**, 455; (b) U. Schmidt, I. Boie, Ch. Osterroht, R. Schröer, and H.-F. Grützmaier, *Chem. Ber.*, 1968, **101**, 1381.

² M. J. Gallagher and I. D. Jenkins, *J. Chem. Soc. (C)*, 1966, 2176.

under nitrogen, in 70% yield, but gave the ester (6a) or (7a) in 40% yield under oxygen or in the presence of

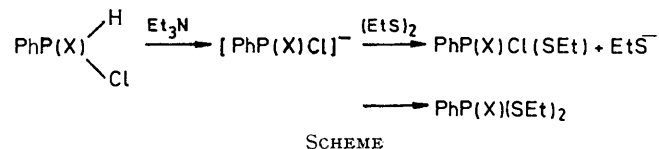


sulphur, respectively. However, the nature of the step where oxygen or sulphur is incorporated is obscure.

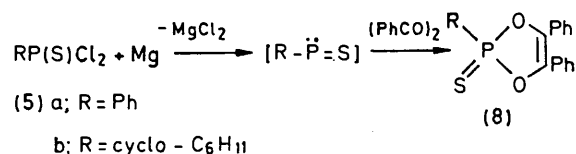


Partial hydrolysis of the dichloride (1) with an equimolar amount of water, followed by dehydrochlorination with triethylamine in diethyl disulphide at room temperature, gave the ester (6a) in 18% yield. A similar reaction with an equimolar amount of hydrogen sulphide instead of water gave the ester (7a) in 14% yield.

The low yields seem to be attributable to competition with intermolecular dehydrochlorination. In these cases, an ionic mechanism (Scheme) cannot be ruled out, by analogy with reactions of trivalent phosphorus compounds with disulphides.⁶



Reactions with Benzil.—The dichlorides (5) reacted with an equimolar amount of magnesium in the presence of benzil in tetrahydrofuran (THF) to give 1,3,2-dioxaphosphole 2-sulphides (8), suggesting the intermediacy of



phosphinoylidenes. The results of the reactions and the physical properties of the sulphides (8) are summarised in Tables 4 and 5.

The sulphide (8a) was also obtained by sulphurisation of 2,4,5-triphenyl-1,3,2-dioxaphosphole, which was prepared by the reaction of benzil with the dichloride (1) and magnesium,¹ along with 2,3,5,7,8-pentaphenyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nona-4,6-diene (3).

⁶ M. Grayson and C. E. Farley, *J. Org. Chem.*, 1967, **32**, 236.

¹ T. H. Siddall, tert, and C. A. Prohaska, *J. Amer. Chem. Soc.*, 1962, **84**, 2502, 3467; M. J. Gallagher and I. D. Jenkins, *Topics Stereochem.*, 1968, **3**, 51.

The sulphide (8a) gave *O*- α -benzoylbenzyl *O*-ethyl phenylphosphonothioate (9) in ethanol in the presence of

TABLE 4

Reactions of the dichlorides (4) and (5) with magnesium and benzil

Dichloride [mmol †]	Mg (mg atom)	(PhCO) ₂ (mmol †)	Time (h)	Adduct [mmol(%)]	PhC:CPh (mmol)
(5a)[100]	110	110	3	(8a) [97(97)]	
(5b)[25(5·6)]	26	25 (3·7)	6	(8b) [12·7(65) ‡]	
(4a)[25]	31	27 (2)	1	(11a) [13·3(54)]	2·9
(4b)[25]	25	25 (6·4)	Over- night	(11b) [9·1(48) §]	1·9

† Value in parentheses shows recovered amounts. ‡ Based on dichloride consumed. § Based on benzil consumed.

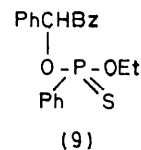
TABLE 5

Physical properties of the products (8), (9), and (11)

Product	M.p. (b.p.) (°C)	Analysis (%) †			
		C	H	S	δ_{P} (CHCl ₃)
(8a)	126·5—127	68·65 (68·55)	4·35 4·3	9·15 9·15)	—104(t, <i>J</i> _{PH₆} , 15·6 Hz)
(8b)	107·5—108·5	67·65 (67·4)	6·05 5·95	9·25 9·0)	—126br(s)
(9)	(202 at 0·6 mmHg)	66·8 (66·65)	5·5 5·35	8·1 8·1)	
(11a)	151—153	68·25 (68·15)	5·15 4·85)		
(11b)	111	66·9 (67·05)	6·55 6·45)		

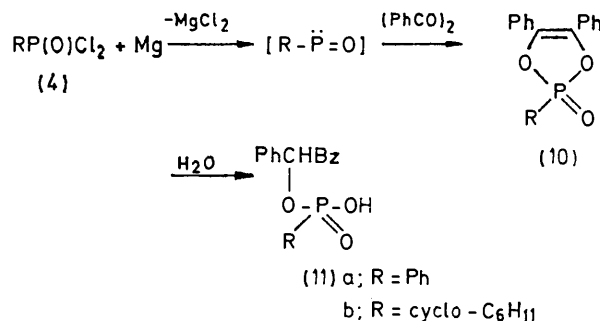
† Required values in parentheses.

a trace of hydrochloric acid in 80% yield (Table 5). The methyl n.m.r. signals of this compound consisted of a



doublet of triplets (see Experimental section) because of the presence of an asymmetric phosphorus atom.⁷

When the dichlorides (4) were dechlorinated with an equimolar amount of magnesium in the presence of

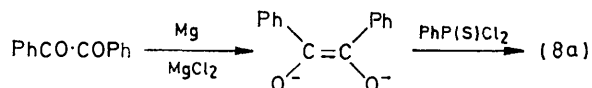


benzil, the isolated products were not the expected 1,3,2-dioxaphosphole 2-oxides (10), but the α -benzoylbenzyl phosphonates (11), obtained together with diphenyl-

acetylene (Table 4), the mechanism of formation of which is discussed in the following paper.⁸ The oxides (10) seem to be easily hydrolysed during isolation; the phosphonate (11a) was obtained instead of the oxide (10a) in the reaction of the sulphide (8a) with mercuric oxide.

In the reactions with benzil, a small amount of benzoin was always obtained, the formation of which is attributable to the reduction of benzil by magnesium monochloride formed in the reaction systems.⁹

The formation of the sulphide (8) may also be explicable in terms of the following mechanism. However,



this ionic reaction required more severe conditions and gave the sulphide (8a) in only low yield. Thus it seems most reasonable to postulate the intermediacy of phosphinoylidene or phosphinothioylidene in the reactions of the dichlorides (4) or (5) and magnesium.

The reactions did not occur in the absence of magnesium under the same conditions.

EXPERIMENTAL

¹H N.m.r. spectra were measured with Varian HA-100, JEOL JNM-4H-100, Varian T-60, JEOL JNM-C-60H and -3H-60, and Hitachi R-20B and R-24 spectrometers, with tetramethylsilane as internal standard at room temperature. ³¹P N.m.r. spectra were measured with a Hitachi R-20-R204-P spectrometer (24.3 MHz), with 85% phosphoric acid as external standard at 35°. Reactions were carried out under nitrogen unless stated otherwise.

Reactions of Phosphonic (4) and Phosphonothioic Dichloride (5) with Magnesium in Diethyl Disulphide.—A typical procedure is described for the reactions of phenylphosphonic dichloride (4a).

The dichloride (4a)¹⁰ (9.8 g, 50 mmol) was added dropwise with stirring to magnesium turnings (1.5 g, 62 mg atom) in diethyl disulphide (50 ml) and THF (10 ml), cooled with water, and the mixture was stirred for 8 h at 50–60°. Unchanged magnesium (0.4 g) was filtered off, the filtrate was washed with water, and the organic layer was distilled to afford SS-diethyl phenylphosphonodithioate (6a) (4.4 g, 18 mmol).

The results and the physical properties of the products are summarised in Tables 1–3.

The n.m.r. data (60 MHz; CCl₄) of the products are as follows: PhP(O)(SEt)₂: δ 1.32 (6H, t, *J* 7.5 Hz, CH₃), 2.87 (4H, sx, *J*_{HCOH} 7.5, *J*_{PSCH} 13.8 Hz, CH₂), 7.2–7.6 (3H, m, *H*_m and *H*_p), and 7.6–8.1 (2H, m, *J*_{PH₀} 14.1 Hz, *H*₀); PhP(S)(SEt)₂: δ 1.25 (6H, t, *J* 7.5 Hz, CH₃), 2.90 (4H, sx, *J*_{HCOH} 7.5, *J*_{PSCH} 15.7 Hz, CH₂), 7.2–7.7 (3H, m, *H*_m and *H*_p), and 7.7–8.3 (2H, m, *J*_{PH₀} 15.7 Hz, *H*₀); cyclo-C₆H₁₁P(O)(SEt)₂: δ 1.37 (6H, t, *J* 7.2 Hz, CH₃), 1–2.5 (11H, m, cyclo-C₆H₁₁), and 2.89 (4H, sx, *J*_{HCOH} 7.2, *J*_{PSCH}

13.8 Hz, SCH₂); cyclo-C₆H₁₁P(S)(SEt)₂: δ 1.33 (6H, t, *J* 7 Hz, CH₃), 1.2–2.5 (11H, m, cyclo-C₆H₁₁), and 2.86 (4H, sx, *J*_{PSCH} 14, *J*_{HCOH} 7 Hz, SCH₂).

Reactions of Phenylphosphonous Dichloride (1) with Zinc in Diethyl Disulphide.—(a) *Under nitrogen.* The dichloride (1)¹¹ (9.0 g, 50.3 mmol) was added dropwise during 1.5 h with stirring to activated zinc dust¹² (4 g, 60 mg atom) in diethyl disulphide (50 ml) and THF (10 ml). After stirring at room temperature for 2 h, distillation gave diethyl phenylphosphonodithioate (2) (8.5 g, 37 mmol, 74%), b.p. 135–139° at 2 mmHg (lit.¹⁰ 109–112° at 0.1 mmHg), δ (100 MHz; CCl₄) 1.32 (3H, t, *J* 7.5 Hz, Me), 1.33 (3H, t, *J* 7.5 Hz, Me), 2.4–3.1 (4H, m, CH₂), and 7.2–8.2 (5H, m, Ph).

(b) *Under oxygen.* A reaction on the same scale as that described in (a), with oxygen bubbled through the mixture at room temperature for 3 h gave the ester (6a) (4.9 g, 20 mmol, 40%).

(c) *In the presence of sulphur.* A reaction on the same scale as that described in (a) in the presence of sulphur (3.2 g, 100 mg atom) in carbon disulphide (5 ml) at room temperature for 1 day gave diethyl phenylphosphonotrithioate (7a) (4.9 g, 20 mmol, 40%).

Partial Hydrolysis of the Dichloride (1) Followed by Dehydrochlorination in Diethyl Disulphide.—Water (1.1 g, 62 mmol) in THF (10 ml) was added drop by drop to the dichloride (1) (10.2 g, 57.2 mmol) in THF (10 ml) with stirring at room temperature during 30 min, and the mixture was stirred for 30 min. After removal of the solvent and the hydrogen chloride evolved, the product was dissolved in diethyl disulphide (30 ml), and triethylamine (7.3 g, 72 mmol) was added dropwise during 1.5 h with vigorous stirring at room temperature. The mixture was stirred for an additional 4 h and filtered, and the filtrate was treated as described previously to give the ester (6a) (2.6 g, 10 mmol, 18%).

Reaction of the Dichloride (1) with an Equimolar Amount of Hydrogen Sulphide Followed by Dehydrochlorination in Diethyl Disulphide.—Hydrogen sulphide (1.9 g, 56 mmol) in THF (32 ml) was added dropwise with stirring during 1 h to a solution of the dichloride (1) (10.0 g, 56 mmol) in THF (10 ml) at room temperature, and the mixture was stirred for an additional 4 h. The solvent was removed, the residue was dissolved in diethyl disulphide (50 ml), and triethylamine (14.5 g, 0.14 mol) was added dropwise during 1.5 h at 0° with vigorous stirring. After stirring for an additional 4 h at room temperature, the mixture was washed thoroughly with water and extracted with ether; the extracts were dried (MgSO₄) and distilled to give the ester (7a) (2.0 g, 7.6 mmol, 14%).

Reactions of the Dichlorides (5) with Magnesium in the Presence of Benzil.—A typical procedure is described for the reaction of phenylphosphonothioic dichloride (5a).

The dichloride (5a)¹³ (21.2 g, 0.10 mol) was added dropwise over 30 min to a stirred solution containing magnesium (2.7 g, 0.11 g atom), benzil (23.0 g, 0.11 mol), and THF (70 ml). The mixture was stirred for 3 h with occasional cooling (water). The solvent was removed and the residue was extracted with warm ether to leave an ether-insoluble material including benzoin (1.5 g, 7 mmol), m.p. 129–131°.

¹¹ B. Buchner and L. B. Lockhart, jun., *Org. Synth.*, 1963, Coll. Vol. IV, p. 784.

¹² E. Le Goff, *J. Org. Chem.*, 1964, **29**, 2048.

¹³ W. L. Jensen, U.S.P. 2,662,917/1951 (*Chem. Abs.*, 1954, **48**, 13,711h).

⁸ S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, following paper.

⁹ M. Gomberg, *Rec. Trav. chim.*, 1929, **48**, 847.

¹⁰ A. D. F. Toy, *J. Amer. Chem. Soc.*, 1948, **70**, 186.

Evaporation of the extracts gave 2,4,5-triphenyl-1,3,2-dioxaphosphole 2-sulphide (8a) (34 g, 97 mmol, 97%), m.p. 126.5—127° (from ether), δ (100 MHz; CDCl₃) 7.1—7.35 (6H, m, H_m and H_p), 7.35—7.6 (7H, m, H_m, H_p, and H_o), and 8.0 (2H, octet, H_o); J_{PH_o} 15.5, J_{PH_m} 7.5, and $J_{\text{H}_o\text{H}_p}$ 2 Hz (primes refer to the C-phenyl ring).

Generally, after removal of the ether from the extracts, the residue was chromatographed on silica gel in carbon tetrachloride.

The results and the physical properties of the products are in Tables 4 and 5.

Ethanolysis of the Sulphide (8a).—Concentrated hydrochloric acid (1 drop) was added to the sulphide (8a) (0.94 g, 2.7 mmol) in ethanol (4 ml), and the solution was refluxed for 2 h. The usual treatment gave O- α -benzoylbenzyl O-ethyl phenylphosphonothioate (9) (0.85 g, 2.1 mmol, 80%), δ (60 MHz; C₂Cl₄) 0.99 (1H, t, J 7.2 Hz, Me), 1.20 (2H, t, J 7.2 Hz, Me), 3.3—4.4 (2H, m, CH₂), and 6.6—8.2 (16H, m, Ph and >CH-).

Preparation of the Sulphide (8a).—(a) *By reaction of the dichloride (1) with magnesium in the presence of benzil, followed by sulphurisation.* A solution of the dichloride (1) (4.5 g, 25 mmol) and benzil (5.3 g, 27 mmol) in THF was added dropwise to magnesium (0.75 g, 31 mg atom) in THF at room temperature with stirring. A solution of sulphur (1 g, 31 mg atom) in carbon disulphide (15 ml) was then added. After heating for 4.5 h at 60° and removal of the solvent, the product was extracted with benzene and the extracts were chromatographed on silica gel to give the sulphide (8a) (0.80 g, 2.3 mmol, 9%) and the spiro-compound (3) (1.2 g, 2.3 mmol, 9%), m.p. 204—208° (lit.,^{1b} 216—218°).

(b) *By reaction of the dichloride (5a) with the dianion of benzil.* A mixture of magnesium (0.64 g, 26 mg atom) and anhydrous magnesium dichloride (2.4 g, 26 mmol) in THF (50 ml) was refluxed until the magnesium had almost disappeared.⁹ After addition of benzil (5.5 g, 26 mmol) in THF (30 ml), the mixture was refluxed overnight, then the dichloride (5a) (5.6 g, 26 mmol) was added dropwise at room temperature, and stirring was continued for 5 h. THF was replaced with ether, and from the ethereal solution, the sulphide (8a) (0.70 g, 2.0 mmol) was obtained in 18% yield [based on dichloride (5a) consumed; 2.2 g of the dichloride (5a) was recovered].

Reaction of the Dichloride (4a) with Magnesium in the Presence of Benzil.—The dichloride (4a) (4.9 g, 25 mmol) was added dropwise to a suspension of benzil (5.7 g, 27

mmol) and magnesium (0.76 g, 31 mg atom) in THF (40 ml), and the mixture was stirred at room temperature for 1 h. After removal of the solvent, the product was extracted with ether; the extracts slowly deposited α -benzoylbenzyl phenylphosphonate (11a) (0.75 g). The filtrate was evaporated and the residue was dissolved in carbon tetrachloride and chromatographed on silica gel to afford diphenylacetylene (0.52 g, 2.92 mmol, 11%) (m.p. 59.5—60.5°; eluted with carbon tetrachloride), benzil (0.49 g, 2 mmol) (eluted with benzene), benzoin (6 mg, 0.03 mmol), and the phosphonate (11a) (1.6 g, 4.6 mmol) (eluted with chloroform).

Ether-insoluble material was extracted with chloroform to give the phosphonate (11a) (2.4 g, 6.7 mmol; total 4.7 g, 13.3 mmol, 54%), δ (100 MHz; CDCl₃) 6.63 (1H, d, J_{POCH} 9 Hz, >CH-), 7—8 (15H, m, Ph), and 10.74 (1H, s, OH).

Attempt to Prepare 2,4,5-Triphenyl-1,3,2-dioxaphosphole 2-Oxide (10).—A solution of the 2-sulphide (8a) (1.0 g, 2.9 mmol) in benzene (60 ml) was stirred with mercuric oxide (0.94 g, 4.3 mmol) at 40° for 41 h. After filtration and removal of the solvent, the product was extracted with ether to give the phosphonate (11a) (0.51 g, 1.5 mmol), together with starting material (0.41 g, 1.2 mmol).

Reaction of Cyclohexylphosphonic Dichloride (4b) with Magnesium in the Presence of Benzil.—The dichloride (4b)¹⁴ (5.0 g, 25 mmol) was added dropwise during 30 min to a stirred solution containing magnesium (0.61 g, 25 mg atom), benzil (5.3 g, 25 mmol), and THF (30 ml). The mixture was cooled with water during the exothermic reaction, and stirred overnight at room temperature after the magnesium had been consumed. It was then washed with water, extracted with benzene, and dried (MgSO₄). The material obtained after evaporation of the solvent was chromatographed on silica gel to give α -benzoylbenzyl cyclohexylphosphonate (11b) (3.3 g, 9.1 mmol), and diphenylacetylene (0.33 g, 1.9 mmol), together with unchanged benzil (1.3 g, 25%). The yields of the phosphonate (11b) and diphenylacetylene were 48 and 9% based on the benzil consumed; the phosphonate showed δ (60 MHz; CCl₄) 0.9—2.2 (11H, m, cyclo-C₆H₁₁), 6.49 (1H, d, J_{POCH} 8.3 Hz, >CH-), 7.1—8.1 (10H, m, Ph), and 11.0 (1H, s, OH).

We thank Dr. Hiromichi Akiyama, International Christian University, Tokyo, for measuring the ³¹P n.m.r. spectra.

[3/303 Received, 12th February, 1973]

¹⁴ R. Graf, *Chem. Ber.*, 1952, **85**, 9.