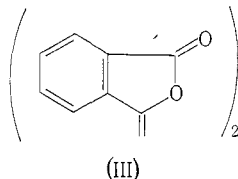
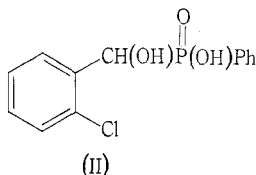
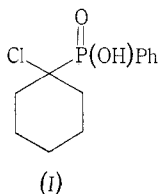


# ALUMINIUM CHLORIDE CATALYSED REACTION OF PHOSPHORUS(III) HALIDES AND CARBONYL COMPOUNDS\*

## II.† SCOPE OF THE REACTION

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We have previously described the ready reaction between benzophenone and phenylphosphonous dichloride or diphenylphosphinous chloride in the presence of partly hydrated aluminium chloride.<sup>1</sup> Attempted extension of this reaction to a wider range of carbonyl compounds has met with very limited success. Thus, cyclohexanone reacts smoothly with phenylphosphonous dichloride to give, after hydrolysis of the neutral reaction products,  $\alpha$ -chlorocyclohexylphenylphosphinic acid (I) (42%), and *o*-chlorobenzaldehyde similarly affords (*o*-chlorophenylhydroxymethyl)-phenylphosphinic acid (II) (69%) by acidification of the alkaline work-up. The latter reaction gives the same product as, and offers no advantages over, uncatalysed



addition;<sup>2</sup> so it was not pursued further. The isolation of the  $\alpha$ -hydroxy rather than the  $\alpha$ -chloro acid supports the contention<sup>1</sup> that the sluggish reactivity of the chlorodiphenylmethylphenylphosphinic chloride is steric in origin. Aralkyl ketones (e.g. acetophenone) and acyclic dialkyl ketones (e.g. nonan-5-one) gave high yields of neutral products, but these were shown (thin-layer chromatography, nuclear magnetic resonance spectra) to be complex mixtures containing as many as six components, which resisted all attempts at purification. This complexity is very probably a consequence of the known ability of aluminium chloride to promote aldol-type condensations<sup>3</sup> coupled with addition of the phosphorus halide to the resulting

\* Manuscript received May 10, 1968.

† Part I, *Aust. J. Chem.*, 1966, **19**, 2025.

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<sup>1</sup> Freeman, K. L., and Gallagher, M. J., *Aust. J. Chem.*, 1966, **19**, 2025.

<sup>2</sup> Michaelis, A., *Liebigs Ann.*, 1896, **293**, 193; Conant, J. B., and Wallingford, V. H., *J. Am. chem. Soc.*, 1924, **46**, 192, and previous papers in this series.

<sup>3</sup> Thomas, C. A., "Anhydrous Aluminium Chloride in Organic Chemistry." p. 634. (Reinhold: New York 1941.)

$\alpha,\beta$ -unsaturated ketones. An example of such a reaction has been reported in the formation of 4-methylpentan-2-one-4-phosphonic acid from acetone and phosphorus trichloride in the presence of aluminium chloride.<sup>4,5</sup>

Phthalic anhydride reacts readily, giving *trans*-biphtalyl (III) (10%) and an unstable acid fraction. The formation of biphtalyl is interesting since it occurs at a temperature substantially lower (100°, against 160°) than that required when phosphites are used as the deoxygenating agent.<sup>6</sup> Partly hydrated aluminium chloride is not necessary for this reaction and the anhydrous catalyst gives a higher yield (34%).

Finally, we investigated the reaction with anthraquinone and obtained a dark green amorphous acidic material in good yield. The very intractable nature of this product has prevented its adequate characterization. It gave a positive vat dye test suggesting a substituted anthraquinone. Its infrared spectrum closely resembled that of 2-anthraquinonylphenylphosphinic acid prepared from 2-aminoanthraquinone by the Doak-Freedman procedure, and it did not depress the melting point of the latter acid. Alkaline fusion<sup>7</sup> afforded anthraquinone. However, no pure derivatives were obtained despite many attempts and since good analytical figures could not be obtained its structure is still uncertain. The reaction is of interest, however, since Conant and his group<sup>8</sup> were unable to induce an uncatalysed reaction even under forcing conditions.

### Experimental

All reactions involving trivalent phosphorus compounds were carried out in an atmosphere of dry purified nitrogen. All compounds are colourless unless otherwise stated.

#### General Procedure

This was the same as described previously.<sup>1</sup>

#### $\alpha$ -Chlorocyclohexylphenylphosphinic Acid (I)

Cyclohexanone (1.96 g) gave only neutral products (3.04 g), presumably the acid chloride and unchanged ketone. Boiling under reflux with aqueous ethanolic hydrochloric acid afforded the  $\alpha$ -chloro acid (I), 2.1 g (42%), m.p. 149–150° from ethyl acetate (Found: C, 55.85; H, 6.3; Cl, 12.9; P, 12.2; equiv. wt., 259.  $C_{12}H_{16}ClO_2P$  requires C, 55.7; H, 6.2; Cl, 13.7; P, 12.0%; equiv. wt., 259).  $\nu(P=O)$  1220  $cm^{-1}$ .

#### (*o*-Chlorophenylhydroxymethyl)phenylphosphinic Acid (II)

*o*-Chlorobenzaldehyde (1.4 g) yielded the acid (1.94 g; 69%) by acidification of the alkaline work-up, m.p. 283–284° from ethanol–water (9 : 1) (Found: C, 55.5; H, 4.1; Cl, 12.6; equiv. wt., 293. Calc. for  $C_{13}H_{11}ClO_3P$ : C, 55.4; H, 3.9; Cl, 12.6%; equiv. wt., 282). P.m.r. ( $CF_3COOH$ ) showed benzylic and aromatic protons in the ratio 1 : 10.

#### Phthalic Anhydride Reaction

In this instance chloroform was used instead of benzene in the work-up. Anhydride (1.48 g) gave phthalic acid (0.26 g) and a yellow oil by acidification of the alkaline work-up. The neutral

<sup>4</sup> Michaelis, A., *Ber. dt. chem. Ges.*, 1884, 17, 1273.

<sup>5</sup> Drake, L. R., and Marvel, C. S., *J. org. Chem.*, 1937, 2, 387.

<sup>6</sup> Ramirez, F., Yamanaka, H., and Basedow, O. H., *J. Am. chem. Soc.*, 1961, 83, 173.

<sup>7</sup> Freeman, K. L., and Gallagher, M. J., *Aust. J. Chem.*, 1966, 19, 2159.

<sup>8</sup> Conant, J. B., MacDonald, A. D., and Kinney, A. McB., *J. Am. chem. Soc.*, 1921, 43, 1928.

layer afforded yellow crystals of *trans*-biphthalyI (0.12 g; 10%), m.p. 352–354° from xylene (lit.<sup>6</sup> 352–354°) (Found: C, 72.75; H, 3.4. Calc. for  $C_{16}H_8O_4$ : C, 72.7; H, 3.05%).  $\nu(C=O)$  1780  $cm^{-1}$ .

#### *Anthraquinone Reaction*

The ketone (2.1 g) gave recovered starting material (0.53 g) and a dark green amorphous acidic solid (2.66 g), m.p. c. 220–230°. It was insoluble in all common solvents. It dissolved with difficulty in dimethylformamide and could be recovered unchanged on dilution with water. Equivalent weights were 20% low for an anthraquinone-phenylphosphinic acid. Attempted reduction, methylation, or salt formation afforded equally intractable solids. Alkaline fusion afforded anthraquinone.

*2-Anthraquinonylphenylphosphinic acid* was prepared from 2-aminoanthraquinone by the Doak–Freedman procedure,<sup>9</sup> m.p. 252–254° from ethanol (Found: C, 68.0; H, 4.2. Calc. for  $C_{20}H_{13}O_4P$ : C, 69.0; H, 3.8%). The melting point was undepressed by admixture with the reaction product and the infrared spectra of the two substances were similar.

<sup>9</sup> Doak, G. O., Freedman, L. D., and Pettit, E. L., *J. org. Chem.*, 1960, **25**, 140.