A New Organophosphorus Reaction involving Multiple Bond-breaking and -making

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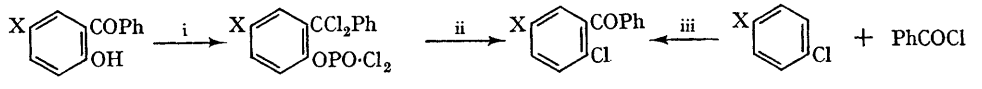
THE products from the reactions of phosphorus pentachloride with 5-chloro-2-hydroxybenzophenone and 2-hydroxybenzophenone were conclusively shown to have the substituted phenylphosphorodichloridate structures (I)[1] and (II)[2] respectively. Here we report a remarkable reaction that occurs on heating these compounds. On heating (I)[3] above the melting point at atmospheric pressure, a liquid shown by infrared spectral comparison to be phosphorus oxychloride (95% yield) distilled, leaving a solid residue. On distilling the residue under reduced pressure, b.p. 240—260°/ < 1 mm., a colourless liquid was obtained which solidified in the receiver. This compound, m.p. 88·5—89·5° (after recrystallization from 95% ethanol) was identified as 2,5-dichlorobenzophenone by mixed melting point and infrared spectral comparison with a sample prepared[4,5] by a

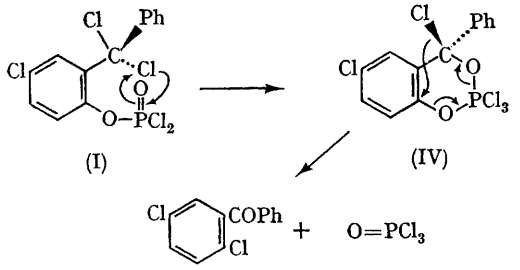


(i) PCl_5, $-HCl$; (ii) Heat, (iii) $-HCl, AlCl_3$

Friedel–Crafts reaction of benzoyl chloride and *p*-dichlorobenzene.

The yield of distilled product from (I) was 40%; infrared analysis on the residue from the vacuum distillation using the base-line technique showed *ca.* 92 ± 5% of 2,5-dichlorobenzene. A dark component of the residue was not investigated.

The reaction involves the breaking of at least four, and the formation of four, bonds. The following mechanism is presented as a working hypothesis for the reaction:



It is interesting that the postulated cyclic intermediate (IV) is the same as the one in a mechanism suggested[1,2] for the formation of (I) from the reaction of phosphorus pentachloride and 5-chloro-2-hydroxybenzophenone. It should be possible to test the suggested scheme for the reaction by the use of isotopic oxygen and/or chlorine.

The reaction also has synthetic utility. The yields of 2,5-dichlorobenzophenone from the Friedel–Crafts reactions are low and involve long reaction times.† The 40% yield obtained from (I) was a small-scale reaction [*ca.*, 3·9 g of (I)]. Much larger yields (*ca.* 80%) can be obtained in slightly larger scale reactions.[3b] Furthermore, in starting with the 2-hydroxybenzophenone, compounds (I) or (II) (which are formed quantitatively[1,2]) need not be isolated but can be converted directly into the 2-chlorobenzophenone.‡ Thus, the method has potential synthetic value for the preparation of 2-chlorobenzophenones which might be difficult to prepare by other means. Further studies on the scope and mechanism of the reaction are in progress.

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† 20% after one week (ref. 4); unspecified yield after 3 days (ref. 5); 16·5% in the present work after *ca.* 49 hr.
‡ Overall yields of *ca.* 85% for both steps were obtained for 2,5-dichlorobenzophenone (ref. 3b).

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[3] (a) Studies were carried out with (I) originally because of the commercial availability of 5-chloro-2-hydroxybenzophenone; (b) Similar results have been obtained with compound (II), A. G. Pinkus and T.-C. Chang, unpublished work.
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