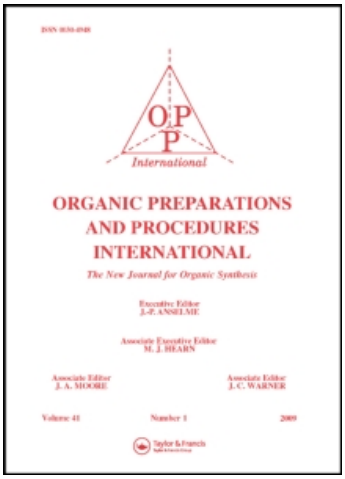

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SYNTHESIS OF 2-CHLORO- AND 2,5-DICHLOROBENZOPHENONES

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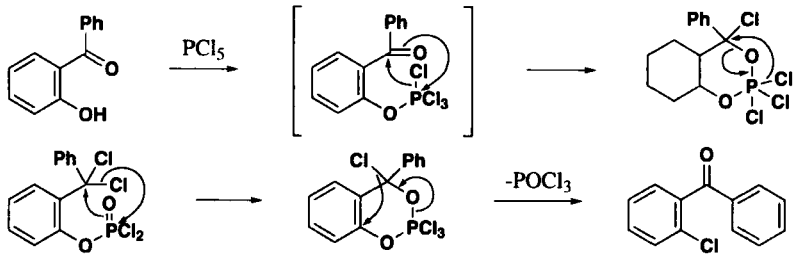
2-Chloro- and 2,5-dichlorobenzophenones (**3b** and **3a**) were required in connection with another project. The yields of the reported syntheses of 2,5-dichlorobenzophenone (**3a**) from the Friedel-Crafts reaction of *p*-dichlorobenzene with benzoyl chloride are either not reported[1] or low (20%[2] and 8%[3]) and these preparations involve long reaction times and vigorous conditions. In our own preliminary work, only a 17% yield of **3a** was obtained *via* the Friedel-Crafts reaction after 49 hrs. The low yields probably result from the ring-deactivating effect of the two chlorine substituents. The synthesis reported here produces **3a** from **1a** in two steps, each proceeding in high yields. The compound formed in the first step (**2a**) need not be isolated and may be heated directly after formation; it should be noted that both steps are new reactions (*Scheme 1*).

a) X = Cl b) X = H

Scheme 1

Possible rationalizations for the reaction of **1** with PCl_5 and for the elimination of phosphorus oxychloride from **2** on heating may be depicted as shown in *Scheme 2*.[4] An esr study of the pyrolysis reaction indicated that no detectable radicals were generated in the reaction.[5]



Scheme 2

Although *o*-chlorobenzophenone was obtained in good yield by the Friedel-Crafts reaction of *o*-chlorobenzoyl chloride with benzene, it could also be generated in good yield (80%) by use of the present procedure. It is evident that a wide number of compounds, otherwise difficulty

obtainable by other routes, could be accessed by the above sequence of reactions from the appropriate *o*-hydroxybenzophenones.

EXPERIMENTAL SECTION

Mps were obtained on a Thomas-Hoover Unimelt apparatus with T-H mps standards.and are uncorrected. *o*-Hydroxybenzophenone, mp. 37-78°C, was prepared by a Friedel-Crafts reaction of *o*-anisoyl chloride with benzene by the procedures of Ullman and coworkers.[6] Other compounds are commercially available. Carbon and hydrogen analyses were per-formed by Clark Microanalytical Laboratories, Urbana, IL; chlorine was determined by the silver thiocyanate-ferric alum method.

Synthesis of 2,5-Dichlorobenzophenone (3a).- Treatment of 5-chloro-2-hydroxybenzophenone with phosphorus pentachloride gave 5-chloro-2-(α,α-dichlorobenzyl)phenyl-phosphochloridate (**2a**) in 99% yield as previously described.[7] This compound (3.92 g., 9.69 mmol) was heated in a distilling flask (protected from moisture) and $POCl_3$ (1.25 g, 95%) distilled at about 109-120°C. Heating the residue under reduced pressure (ca. 1 mm) gave the product **3a** (0.93 g, 40%), bp. 240-260°C, as a colorless liquid which solidified upon cooling. Recrystallization from ethanol gave 0.93 g (40%) of 2,5-dichlorobenzophenone, mp. 88.5-89.5°C, *lit.*[1-3] 88°C, 85-86°C, 87°C. An IR spectrum of the residue showed that it consisted mainly (> 92%) of the expected product. Repetition of the reaction of **2a** with PCl_5 on a larger scale and without isolation of **2a** gave an 86% yield of **3a** and an 84% yield of $POCl_3$.[8]

Synthesis of *o*-Chlorobenzophenone (3b). Preparation of *o*-(α,α-Dichlorobenzyl)-phenylphosphochloridate (2b).- In a reaction vessel protected from moisture and arranged for trapping of HCl, a solution of *o*-hydroxybenzophenone (6.33 g, 31.9 mmol) in 60 mL of benzene was added over a period of 1 hr to PCl_5 (6.64 g, 31.9 mmol) covered with benzene (25 mL) at rt. After the addition was complete and further stirring for 30 min, the solvent was removed *in vacuo* to give a colorless liquid (11.7 g, 99%) which solidified on cooling, mp. 64-66°C. Recrystallization of a small sample from cyclohexane afforded colorless crystals, mp. 66-67°C.
IR (CCl_4): 1486, 1302, 1196, 940, 919 cm^{-1}. MW (cryoscopic): Calcd 370. Found 373.
Anal. Calcd for $C_{13}H_9Cl_4O_2P$: C, 42.19; H, 2.45; Cl, 38.33. Found: C, 42.08; H, 2.62; Cl, 38.21

The pyrolysis of **2b** was carried in an oil bath as described above, at 220°C to give an 80% yield of *o*-chlorobenzophenone (**3b**), mp. 46-47°C, *lit.*[9] 46°C (and 77% of $POCl_3$). An authentic sample of *o*-chlorobenzophenone, mp. 46-47°C, was prepared in 90% yield by the Friedel-Crafts reaction of *o*-chlorobenzoyl chloride with benzene.

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