0.62 g. of precipitate was obtained, with a melting range of 135–180°. One recrystallization from ethylene chloride yielded 9% of product melting at 205–208°.

The product recrystallized three times from ethylene chloride was used as an analytical sample and dried for 1.5 hr. at 108°, which did not affect the weight or the melting point. Neutralization equivalent and elementary contents suggested formulation as an anhydride. An attempt was made to obtain the acid by recrystallization from acetone and water, in the ratio of 1 ml. of acetone and 3.5 ml. of water per 0.1 g. of product, followed by drying at room temperature in the open for 3 hr.: however, although the melting point decreased to 194–195°, the neutralization equivalent remained unchanged.

Anal. Calcd. for $C_6H_4BBrO_2$: C, 36.23; H, 2.03; Br, 40.19; neut. equiv., 198.86. Found: C, 36.02; H, 2.26; Br, 40.34; neut. equiv., 199.0; 195.8, 196.2.

***o*-Trifluoromethylbenzeneboronic Acid.**—To a stirred solution of 23.0 g. (0.10 mole) of tri-*n*-butyl borate in 20 ml. of ether 0.05 mole of *o*-trifluoromethylphenyllithium, prepared by refluxing equimolar amounts of α,α,α-trifluorotoluene and *n*-butyllithium for 6 hr.,[7] was added slowly while cooling at −70°. The mixture was left overnight at this temperature, then hydrolyzed with 30 ml. of 8% hydrochloric acid, and the ether layer extracted with 50 ml. of 15% sodium carbonate and 60 ml. of 8% sodium hydroxide in five portions. Upon acidification to pH 3 and subsequent extraction with ether, the carbonate extracts did not yield any significant amount of product, whereas 4.60 g. (48.5%) of a crystalline material, melting range 50–85°, was obtained from the sodium hydroxide solution. It is worth noting that the etheral extraction of the carefully acidified solution was particularly necessary in this case, since the precipitate was small and appeared to be soluble in excess acid. The crude material was recrystallized from petroleum ether (b.p. 60–80°), to yield 1.80 g. (19%) of crystals melting at 86–94°. Another recrystallization from the same solvent and then from ethylene chloride raised the melting point to 106–107°.

In another experiment, employing the same amounts, the reaction mixture was hydrolyzed with water and the ether layer evaporated to yield 4.54 g. of crude material. Another 0.20 g. was obtained by acidification and ether extraction of the aqueous layer. One recrystallization from petroleum ether yielded a 16% of product melting at 92–98.5°.

Anal. Calcd. for $C_7H_6BF_3O_2$: neut. equiv., 189.95. Found: neut. equiv., 187.2.

***o*-Trifluoromethylbenzeneboronic Anhydride.**—The anhydride was obtained by recrystallizing the acid twice from anhydrous ethylene chloride, and had a melting point of 136.5–141°. Heating at 108° for over 1 hr. failed to attain a constant weight, but the melting point and neutralization equivalent were practically unaffected.

Anal. Calcd. for $C_7H_4BF_3O$: C, 48.89; H, 2.35; F, 33.15; neut. equiv., 171.94. Found: C, 48.95; H, 2.66; F, 32.75; neut. equiv., 172.5.

Grignard Route to 4,4′-Dichlorobenzophenone

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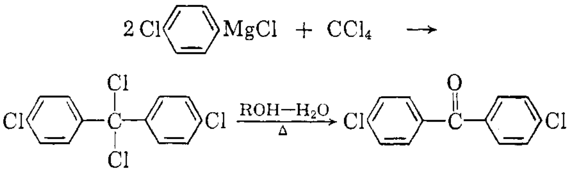
Literature references to the reaction of Grignard reagents with carbon tetrachloride are relatively few. Binaghi[2] isolated triphenylmethyl peroxide, hexaphenylethane, and triphenylcarbinol from the reaction of carbon tetrachloride with phenylmagnesium bromide. Kinney and Spliethoff[3] obtained 1,1,1-trichloropentane from the reaction of butylmagnesium chloride with carbon tetrachloride.

Satisfactory yields of 4,4′-dichlorobenzophenone were obtained in our laboratory by the following sequence of reactions:



The Grignard reagent[4] was added to solutions of carbon tetrachloride in tetrahydrofuran, benzene, pentane–benzene, and toluene over wide temperature ranges without gross differences in yield. Thickening was observed with hydrocarbon solvents. Extensions of the above reaction are under investigation.

Experimental

To a solution of 34 g. (0.222 mole) of carbon tetrachloride in 200 ml. of tetrahydrofuran was added 0.45 mole of *p*-chlorophenylmagnesium chloride[4] over a period of 30 min. with vigorous stirring. The temperature was maintained at 10° utilizing a Dry Ice–acetone bath. The reaction mixture was stirred for 30 min. and then hydrolyzed by the cautious addition of 150 ml. of 10% sulfuric acid at room temperature. The organic phase was separated and the aqueous phase was extracted twice with 100-ml. portions of diethyl ether. Solvents were distilled from the combined organic fractions under reduced pressure leaving a dark brown residue. Hydrolysis of the intermediate 4,4′-dichlorobenzophenone dichloride was effected by adding the residue to 300 ml. of 50% ethanol and refluxing the mixture for 90 min. with stirring. Following cooling to room temperature and decantation of the liquid portion, the tan product was slurried with 100 ml. of petroleum ether. The crude ketone was then filtered and washed with petroleum ether. A crude yield of 23.0g. (41%) melting at ca. 134° was obtained. Recrystallization from absolute ethanol gave white plates melting at 149–150°. Recrystallization from isomeric heptanes did not change the melting point. Admixture with authentic 4,4′-dichlorophenzophenone showed no depression. The 2,4-dinitrophenylhydrazone melted at 237.5–239.5° (lit.,[5] m.p. 238–240°).

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