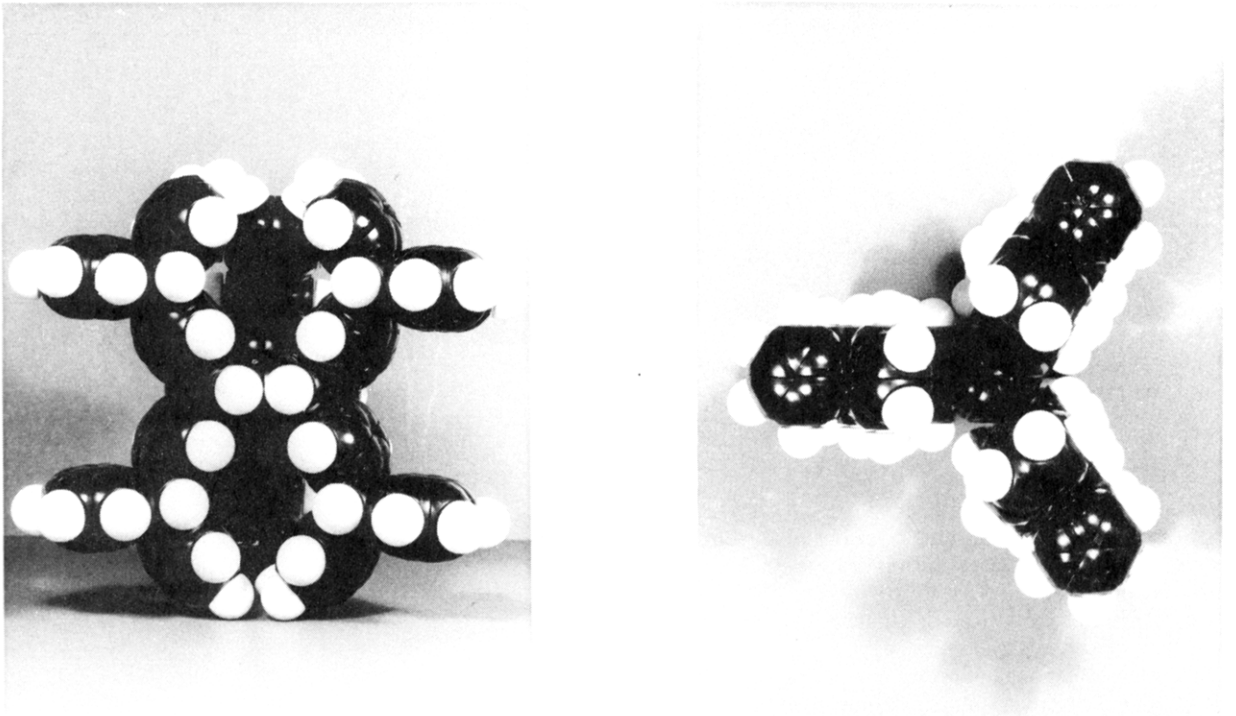

Figure 1. CPK model of **22**: side view showing cavities above and below the central benzene ring (left), and top view looking into one of the cavities, with the central benzene ring at the bottom of the cavity (right).

The mixture, which immediately turned brown, was stirred overnight, quenched with water (100 mL), and extracted with CH_2Cl_2. The organic layer was washed with water and saturated aqueous sodium chloride and dried. Removal of the solvent (rotavap) and recrystallization of the residue from hexanes–CH_2Cl_2 gave 1.03 g (87%) of **19**: mp 340 °C dec; ^{1}H NMR δ 4.72 (d, J = 2.18 Hz, 1 H), 4.82 (d, J = 6.4 Hz, 1 H), 5.24 (s, 2 H), 5.25 (s, 2 H), 6.59 and 6.61 (dd, J = 6.4, 2.18 Hz, 1 H), 6.83 (m, 4 H), 6.93 (m, 4 H), 7.21 (m, 4 H), 7.23 (s, 2 H), 7.28 (s, 2 H), 7.32 (m, 4 H); ^{13}C NMR δ 51.09, 53.88, 53.93, 58.33, 119.10, 119.35, 123.41, 124.97, 125.05, 132.85, 142.17, 142.70, 145.27, 145.67. Anal. Calcd for $C_{44}H_{27}Cl$: C, 89.40; H, 4.60. Found: C, 89.30; H, 4.55.

Trimerization of 19. To a stirred solution of **19** (0.60 g, 1 mmol) in 20 mL of THF under argon at −78 °C was added dropwise a hexane solution of butyllithium (1.1 equiv; 0.3 mL of a 2.5 M solution). After addition was complete, the mixture was allowed to slowly warm to room temperature, stirred for 2 h, and then heated at reflux for 30 min. The reaction was quenched with 1 mL of methanol. Solvent was removed (rotavap), the residue was extracted with CH_2Cl_2, and the extract was washed with water and saturated aqueous sodium chloride and dried. Removal of the solvent and chromatography of the residue over silica gel with CH_2Cl_2–hexanes (3:7) as eluent gave 0.13 g (22%) of recovered **19**, a trace of **17**,[10,11] 0.059 g (14%) of **20**, 0.11 g (25%) of **21**, and 0.009 g (2%) of **22**. For 5,18[1′,2′]:9,14[1″,2″]dibenzeno-7,16-etheno-5,7,9,14,16,18-hexahydroheptacene (**20**): mp 362 °C dec; ^{1}H NMR δ 4.91 (dd merged to a t, J = 3.2 Hz, 2 H), 5.23 (s, 4 H), 7.25 (s, 4 H), 6.82 (m, 6 H, 4 arom and 2 vinyl), 6.90 (m, 4 H), 7.21 (m, 4 H), 7.28 (m, 4 H); ^{13}C NMR δ 50.89, 53.85, 119.05, 123.27, 124.84, 139.79, 141.74, 143.52, 145.36, 145.63 (two arom overlapped); high-resolution mass spectrum calcd for $C_{44}H_{28}$ 556.30, found 556.22. For 20-chloro-5,5′,7,7′,9,9′,14,14′,16,16′,18,18′-dodecahydro-5,18[1′,2′]:9,14[1″,2″]:5′,18′[1‴,2‴]:9′,14′[1⁗,2⁗]tetrabenzeno-19,19′-bi(7,16-ethenoheptacene) (**21**); mp 358 °C dec; ^{1}H NMR δ 4.65 (s, 2 H), 4.84 (d, J = 6.1 Hz, 1 H), 5.10 (s, 2 H), 5.11 (s, 2 H), 5.17 (s, 2 H), 5.18 (s, 2 H), 5.48 (d, J = 1.4 Hz, 1 H), 6.78 (m, 8 arom H and 1 vinyl H), 6.80 (m, 8 H), 7.18 (m, 24 H); ^{13}C NMR δ 50.52, 51.42, 53.60, 55.35, 59.60, 118.56, 118.67, 119.02, 119.81, 123.08, 123.31, 124.69, 135.13, 139.05, 141.39, 141.56, 141.79, 141.91, 142.18, 142.76, 143.31, 145.10, 145.31, 145.41, 148.74. Anal. Calcd for $C_{88}H_{53}Cl$: C, 92.24; H, 4.66. Found: C, 92.16; H, 4.60. For 2,3:8,9:14,15:22,23:28,29:34,35-hexakis(9,10-dihydro-9,10-anthraceno)-5,6,11,12,17,18-hexahydro-5,18[1′,2′]:6,11-[1″,2″]:12,17[1‴,2‴]tribenzenotrinaphthylene (**22**): mp >400 °C; ^{1}H NMR (CD_2Cl_2) δ 5.17 (s, 12 H), 5.50 (s, 6 H), 6.80 (m, 24 H), 7.18 (m, 24 H), 7.24 (s, 12 H); ^{13}C NMR (CD_2Cl_2) δ 49.81, 53.79, 119.48, 123.45, 125.00, 134.86, 142.59, 142.96, 145.27, 146.01; high-resolution mass spectrum calcd for $C_{132}H_{78}$ 1662.61, found 1662.98.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE-87-12118) for a grant in support of this research.

Preparation of Aryl Chlorides from Phenols

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Stauffer Chemical Company, Eastern Research Center, Livingstone Avenue, Dobbs Ferry, New York 10522

Received March 3, 1988

Very few methods have been reported in the literature for converting phenols directly into arylhalides. To our knowledge, only two such processes are available to accomplish this transformation. Bestmann and Schnabel[1] have found that chlorobenzene can be prepared from phenol via a phenylchloroformate intermediate produced by reaction with phosgene. This material can then be treated with triphenylphosphine, producing chlorobenzene in 67% yield by elimination of carbon dioxide. Unfortunately, triphenylphosphine remains with the product and must be deliberately removed.

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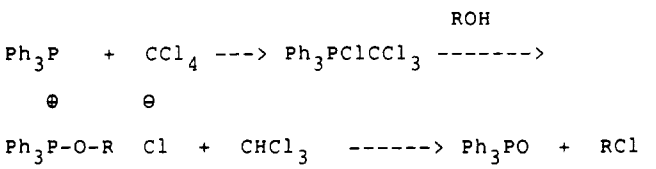
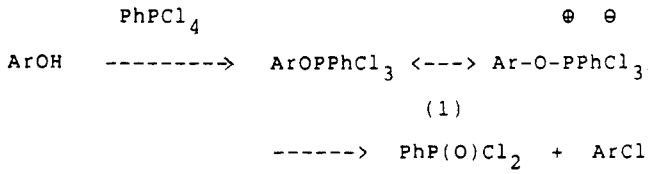
0022-3263/90/1955-3415$02.50/0

Scheme I



Scheme II



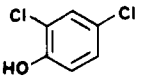
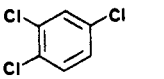
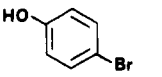
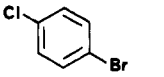
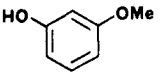
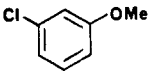
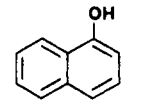
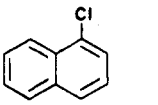
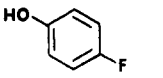
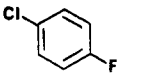
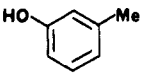
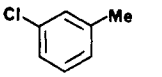
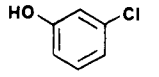
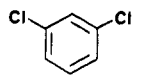
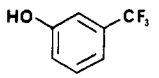
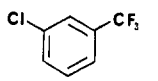
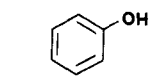
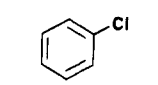
Wiley and co-workers[2] produced bromobenzene by heating a mixture of phenol and triphenylphosphine dibromide at 200 °C until the evolution of hydrogen bromide stopped. Bromobenzene was obtained in 92% yield. In this case, triphenylphosphine oxide was formed as a by-product and, again, a separation step was needed. Our continued work in the area of organophosphorus chemistry has led us to the discovery that phenylphosphorus tetrachloride (PPTC) is an excellent reagent for converting phenols into chlorobenzenes. The byproducts are hydrogen chloride and phenylphosphonic dichloride. The former bubbles out of the reaction mixture, and the latter can be removed simply by aqueous extraction.

Prior to our work, PPTC wa almost unknown as a reagent for organic synthesis. Timohkin et al.[3] reported the reaction of cyclohexene with PPTC to give *trans*-1,2-dichlorocyclohexane and 3-chlorocyclohexene. Mitrasov et al.[4] found that treatment of aliphatic aldehydes and ketones with PPTC produced geminal dichlorides. PPTC has also been used to form tetrazines from hydrazides.[5] Recently, we have used PPTC to convert nitro aromatics to chloro aromatics.[6] Now we report further extension of the utility of this reagent to include reaction with phenols to produce aryl chlorides. Thus, phenol can be heated to 160 °C in molten PPTC to give chlorobenzene in 76% yield after distillation.

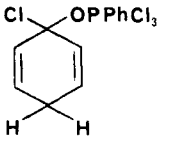
Our reaction conditions were tested on a variety of substrates, and our results are recorded in Table I. These data show that substituted phenols will readily undergo hydroxyl displacement.

From a mechanistic point of view, we feel that this reaction may be compared to a similar halogenation of alkanols using triphenylphosphine and carbon tetrachloride.[7] Appel[7a] suggests that this reaction proceeds in three steps as shown in Scheme I. The triphenylphosphine–carbon tetrachloride complex reacts with an alcohol to produce chloroform and a triphenylalkoxychlorophosphorane intermediate. The latter then decomposes to give triphenylphosphine oxide and the desired alkyl chloride.

Table I. Chloroaromatics from Phenols Using PPTC

starting material	product	yield
		49%
		78%
		80%
		82%
		81%
		42%
		71%
		70%
		76%

An analogous mechanism can be proposed for the reaction of phenols with PPTC. Scheme II shows initial formation of an intermediate 1 which then undergoes elimination of phenylphosphonic dichloride, giving the aryl chloride product. It is not clear at this point whether 1 decomposes by direct displacement of phenylphosphinic dichloride by chloride as illustrated in Scheme II or if a hydroquinoid species like 2 is involved. We know that



(2)

2 is not essential for our chlorination reaction to occur because PPTC will also chlorinate nonaromatic alcohols. Table II lists a variety of alcohols that are not phenols but do undergo hydroxide replacement by chloride upon treatment with PPTC. The reactions described by Table II occur more readily than their phenolic counterparts, and a general method for these processes follows. Chlorine gas (10 mM) is bubbled into a solution of phenylphosphorus dichloride (10 mM) in chloroform (20 mL). External cooling is sometimes necessary to keep the reaction temperature below 35 °C throughout the chlorine addition. The alcohol (10 mM) is then added at or below room temperature (Table II), and the reaction mixture is maintained at the conditions specified in Table II. When the reaction is complete, the mixture is poured onto ice/water (50 mL) and neutralized with 50% aqueous sodium hydroxide. The layers are separated, and the aqueous portion is extracted with two 30-mL portions of chloroform. The combined organic extracts are washed with brine, dried over anhydrous magnesium sulfate, and

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(2) Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964.
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(4) Mitrasov, Y. N.; Vladyko, E. D.; Kormachev, V., USSR SU 1,051,097 and 1,051,096.
(5) (a) Yagupol'skii, L. M.; Matyshecheva, G. I.; Mikhailov, V. S.; Bulygina, L. A. USSR SU 498,300. (b) Matyshecheva, G. I.; Mikhailov, V. S.; Yagupol'skii, L. M. *Zh. Org. Khim.* **1974**, *10*, 124.
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Table II. Chlorides from Alcohols Using PPTC

$$ROH \xrightarrow[CHCl_3]{PhPCl_4} RCl$$

R	conditions	% yield
n-hexyl	25 °C, 6 h	77
benzyl	25 °C, 6 h	100
s-pentyl	50 °C, 12 h	80
i-pentyl	25 °C, 12 h	44
neopentyl	25 °C, 12 h	55
(R)-(−)-2-octyl	25 °C, 5 min	85 (94% ee inversion)
tert-butyl	50 °C, 12 h	97
norbornyl	25 °C, 12 h	60
cyclopropylmethyl	0 °C, 5 min	98

distilled to give the desired product in good yield (Table II).

With this discovery, we have broadened the scope of reactivity of PPTC. We feel that continued studies on PPTC itself and other similar organophosphorus compounds could potentially contribute a variety of new synthetic methodologies to the organic chemist.

Experimental Section

All products were identified by comparison to authentic samples. A typical procedure is given for the preparations of the aryl chlorides listed in Table I. The chlorides listed in Table II were prepared in the same manner using the conditions specified in Table II.

General Procedure. Chlorine gas (10 g, 142 mM) is bubbled into phenylphosphorus dichloride (18.6 mL, 142 mM) at such a rate as to maintain the reaction temperature at 70–80 °C. After the chlorine addition is complete, the resulting molten PPTC is a clear yellow liquid. Phenol (13.4 g, 142 mM) is added on one portion, and the reaction mixture is heated to 160 °C overnight. The cooled reaction mixture is then poured onto crushed ice/water (200 mL) and neutralized with 50% aqueous sodium hydroxide. After extraction with ether, the combined ether extracts are dried and distilled to give chlorobenzene (12.1 g, 76%) as a colorless liquid.

Registry No. PPTC, 4895-65-2; $PhPCl_2$, 644-97-3; PhOH, 108-95-2; *p*-BrC_6H_4OH, 106-41-2; *m*-HOC_6H_4OMe, 150-19-6; *p*-HOC_6H_4F, 371-41-5; *m*-HOC_6H_4Me, 108-39-4; $Me(CH_2)_5OH$, 111-27-3; $PhCH_2OH$, 100-51-6; $Me(CH_2)_2CH(Me)OH$, 6032-29-7; $HOCH_2CH_2CHMe_2$, 123-51-3; $HOCH_2C(Me)_3$, 75-84-3; (*R*)-$MeCH(OH)(CH_2)_5Me$, 5978-70-1; t-BuOH, 75-65-0; PhCl, 108-90-7; *p*-ClC_6H_4Br, 106-39-8; *m*-ClC_6H_4OMe, 2845-89-8; *p*-ClC_6H_4F, 352-33-0; *m*-ClC_6H_4Me, 108-41-8; $Me(CH_2)_5Cl$, 544-10-5; $PhCH_2Cl$, 100-44-7; $MeCH_2CH_2CH(Me)Cl$, 29593-35-9; $ClCH_2CH_2CHMe_2$, 107-84-6; $ClCH_2C(Me)_3$, 753-89-9; (*R*)-$Me(CH_2)_5CH(Cl)Me$, 18651-57-5; t-BuCl, 507-20-0; *m*-HOC_6H_4Cl, 108-43-0; *m*-$HOC_6H_4CF_3$, 98-17-9; *m*-ClC_6H_4Cl, 541-73-1; *m*-$ClC_6H_4CF_3$, 98-15-7; 2,4-dichorophenol, 120-83-2; α-naphthol, 90-15-3; bicyclo[2.2.1]heptan-1-ol, 51566-98-4; cyclopropylmethyl alcohol, 2516-33-8; 1,2,4-trichlorobenzene, 120-82-1; 1-chloronaphthalene, 90-13-1; 1-chlorobicyclo[2.2.1]heptane, 765-67-3; cyclopropylmethyl chloride, 5911-08-0.

Precursors to Carbon-13-Labeled Reactive Intermediates: Preparation and NMR Characterization of Two Double Label Isomers of Methyl Cyclopropene-3-carboxylate

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Received November 29, 1989

Bond distances can be determined with about 1% accuracy in orientationally disordered solids by use of a recently developed nutation NMR technique.[1] This method has provided important structural data in several systems,[2] and it seems particularly promising as a means of determining bond lengths and local geometries in reactive intermediates, substances which are difficult to prepare as X-ray quality single crystals.

Reactive carbocation salts represent a class of reactive intermediates that have been resistant to direct structural study. An enormous amount of structural and dynamic information about carbocations has been deduced from NMR studies, but there is very little *direct* information available concerning bonding distances and geometries of these reactive intermediates. This is not from lack of effort. Major programs have been mounted in several laboratories to do diffraction studies on reactive carbocation salts, but only a few structures have been solved successfully.[3a,4] The kinds of problems encountered are noted in some published reports.[3]

These diffraction studies are major achievements that have provided important data. However, a critical evaluation indicates that all had rather special features: strategically placed methyl group substituents,[3a,4a] donor heteroatoms,[4b,5] or extended π-systems.[4a,5] These special features tend to minimize crystal lattice disorder problems, problems which appear repeatedly in unsuccessful X-ray studies of carbocation salts.

While not without difficulties, nutation NMR appeared to be a more generally applicable method of gaining direct structural data about reactive intermediates. We have initiated a program that makes use of this technique to study some carbocations of particular interest. Nutation NMR involves the use of a pulse train that efficiently suppresses chemical shift information while retaining the dipolar coupling information.[1] After Fourier transformation, this dipolar coupling information, extracted from an amorphous or polycrystalline solid, is presented in the form of a Pake doublet.[6] Since the magnitude of a dipolar coupling constant is inversely proportional to the cube of the internuclear separation, distances between proximate atoms and localized geometries may be determined in a fairly direct manner.[1,2e] The application of this method to a carbon compound requires that the reactive intermediate be labeled with carbon-13 at *two* specific sites. Further, those sites in the labeled intermediate should be enriched to the 99% level in order to minimize the number of monolabeled molecules in the system.[7] Unlike diffraction methods, a "complete" structure determination can only be projected for the most simple or symmetrical carbocations.[2e] However, key features of the carbon framework can be determined by judicious synthetic design.

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0022-3263/90/1955-3417$02.50/0