was prolonged for 72 hr. but was discontinued for a few minutes every 4–8 hr. to permit removal of the cyclic disulfide. After 72-hr. heating, the amount of steam-distilled product that could still be collected was of the order of a few milligrams after several hours. The total amount of cyclic disulfide obtained was 963 mg. (80%) after drying. The product after sublimation (bath temperature 40° at 16–20 mm.) had m.p. 31–31.5°, lit.[5] m.p. 30.8–31.5°.

Anal. Calcd. for $C_4H_8S_2$: C, 39.96; H, 6.70; S, 53.34. Found: C, 39.84; H, 6.53; S, 53.24.

1,2-Dithiacyclohexane from disulfide **6** was obtained by the same procedure except that the system was heterogeneous throughout.

Disproportionation Procedures.—Solutions of 1 mmole of disulfide in 10 ml. of solvent were sealed in ampoules, dropped into a boiling water bath for the selected time, and then cooled as rapidly as possible in ice. Experiments in which 1,2-dithiacyclohexane was isolated by steam volatilization were carried out in flasks connected to condensers cooled with ice. Compounds formed or left unchanged routinely were characterized by melting point and mixture melting point and/or by the infrared spectrum.

Special modifications were the following.

A. 1,1-Biscycloalkylidene Disulfides 3 and 4.—After the heating period, ampoules were throughly cooled in Dry Ice, opened, quickly connected to an apparatus such that hydrogen sulfide could be flushed out with a slow stream of nitrogen into buffered (acetate) lead nitrate solution, and then allowed to warm to room temperature. Lead sulfide was collected and weighed. Ampoule contents were washed out and evaporated, solvent and volatiles being collected in a Dry Ice trap. Ketones were isolated from the trap contents as 2,4-dinitrophenylhydrazones. Acetylcystamine was extracted from the evaporation residues with ice cold water and was recrystallized from chloroform–ether. Unchanged starting materials were extracted with 2:3 alcohol–water mixture and crystallized by chilling. Sulfur was detected in the residues by insolubility in solvents other than carbon disulfide and was separated by vacuum sublimation.

B. Tetramethylene Bisdisulfides 5 and 6.—1,2-Dithiacyclohexane crystallized readily on ice cooling of the ampoules. It was isolated by filtration using a chilled funnel or better, with the salt **5**, by extraction into methylene chloride; despite the volatility of the dithiacyclohexane, it could be recovered and weighed reasonably satisfactorily by careful rapid evaporation of the dried extract. Evaporation of the aqueous layer or filtrate and consistency of the weight loss were used in several instances to substantiate the weight of dithiacyclohexane and thus provide assurance that only negligible amounts had escaped isolation. Water-soluble acetylcystamine was readily separated from insoluble **6**. Cystamine hydrochloride is readily soluble in ice-cold 2 *M* hydrochloric acid, but unchanged **5** is very slightly soluble, though soluble in water, thus permitting easy separation of these residues.

C. 1,2-Bisalkylene and -arylene Disulfides 7, 8, 9, and 10.—Disulfide **8** was reported previously.[2] Polymers which separated were removed by filtration using preweighed Celite and were estimated by drying to constant weight. Soluble products and unchanged starting materials were separated by solubility relationships obviously similar to those previously described and were recrystallized to purity.

Disproportionation of Disulfide 9 at Room Temperature.—The following experiment provides information on the speed at which disproportionation of this disulfide proceeds at room temperature in ordinary laboratory light. The disulfide **9** (379 mg.) was dissolved in 8 ml. of water and the solution was left to stand. Colloidal material separated slowly, and was removed repeatedly by filtration using preweighed Celite, which then was weighed after drying to constant weight. The total cumulative amount of colloidal polymer removed (in milligrams), and its per cent of total polymer theoretically possible were the following (after the number of days shown in parentheses): 59, 38 (7); 89, 58 (14); 119, 77 (21); 139, 90 (28), 152, 99 (37); 160, 104 (45).

Disproportionation of the Free Base of Disulfide 5 at Room Temperature.—Three portions, each 0.1725 g. (0.5 mmole), of **5** were dissolved in (a) 4 ml. of water plus 1.0 ml. of 1 *M* aqueous sodium hydroxide, (b) 5 ml. of water, and (c) 5 ml. of 1 *M* hydrochloric acid. An oil rapidly separated from (a). After 13 days (a) was acidified with 2 ml. of 1 *M* hydrochloric acid; (b) and (c) were clear but (a) contained an oil which crystallized on ice cooling. All three were extracted with methylene chloride; the extracts were dried ($MgSO_4$) and evaporated. (b) and (c) gave no residue but (a) gave 55 mg. (theoretical 60 mg.). Residues on evaporation of the aqueous layers were (b) 0.173 g., (c) 0.171 g., and (a) 0.168 g.; the former two corresponded to no disproportionation and the last (allowing for 58.5 mg. of sodium chloride) to complete disproportionation.

The Preparation of Heterocyclic Organophosphorus Compounds by Cyclodehydrohalogenation[1]

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5-Chlorodibenzophosphole and 10-chlorophenoxaphosphine have been prepared in 6 and 24% yields, respectively, by dehydrohalogenation of 2-biphenylyl- and 2-phenoxyphenylphosphonous dichlorides. The phosphonous dichlorides were not isolated but underwent cyclization during the manipulations incident to their attempted isolation. 2-Benzylphenylphosphonous dichloride, however, could be isolated. It underwent cyclodehydrohalogenation to yield 5-chloro-5,10-dihydrodibenz[*b,e*]phosphorin when heated with anhydrous zinc chloride. The hydrolysis and oxidation of all three cyclic chlorophosphines yielded the corresponding cyclic phosphinic acids.

One method for preparing heterocyclic arsenic and antimony compounds is by cyclodehydration of appropriately substituted arylarsonic or arylstibonic acids. Thus phenazarsinic acid (I)[2] is readily prepared by heating *o*-arsonodiphenylamine with hydrochloric acid.[3] Freedman and Doak, however, have found that both 2-biphenylylphosphonic acid and 2-phenoxyphenylphosphonic acid fail to undergo cyclodehydration under a variety of experimental conditions.[4,5] Similarly, Campbell and Way have reported the failure of 2-biphenylylphenylphosphinic acid to cyclize when heated with polyphosphoric or sulfuric acids.[6] They were successful, however, in cyclizing the acid by heating with phosphorus pentachloride and nitrobenzene. In

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(1) Supported by Research Grant GM-09479 from the National Institutes of Health, U. S. Public Health Service.

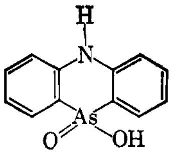
(2) In our previous papers on heterocyclic phosphorus compounds, we have employed the nomenclature of F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth, and Silicon," Interscience Publishers, Inc., New York, N. Y., 1950. At the suggestion of a referee and of the editor we have used Ring Index nomenclature in the present paper.

(3) C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 2499 (1927).

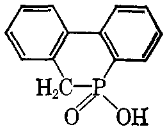
(4) This compound has previously been named phosphafluorinic acid; *cf.* L. D. Freedman and G. O. Doak, *J. Org. Chem.*, **21**, 238 (1956).

(5) L. D. Freedman, G. O. Doak, and J. R. Edmisten, *ibid.*, **26**, 284 (1961).

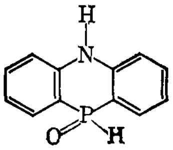
(6) I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 2133 (1961).


I

our laboratory this latter method has proved to be unsuccessful for the cyclization of several phosphonic acids. Lynch has recently obtained 5-hydroxy-5,6-dihydrodibenz[*b*,*d*]phosphorin 5-oxide (II) by the cyclodehydration of 2-phenylbenzylphosphonic acid.[7] In this case, however, the phosphono group was attached to a side chain rather than directly to the benzene ring.

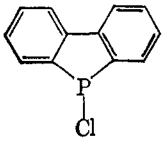

II

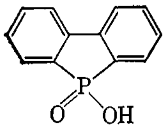
There is considerable evidence that cyclodehydrohalogenation might prove to be a better means of effecting cyclization of phosphorus compounds. This method has been used successfully for obtaining heterocyclic arsenic compounds where cyclodehydration failed. Thus 10-chlorophenothiarsine was readily obtained by cyclization of 2-dichloroarsinophenyl phenyl sulfide although 2-arsonophenyl phenyl sulfide could not be cyclized.[8] Phosphorus trichloride has been condensed with diphenylamine to yield, after hydrolysis, 5,10-dihydrophenophosphazine 5-oxide (III).[9–11] The initial attack probably occurs by electrophilic attack of phosphorus on a 2-position of a phenyl ring to form 2-dichlorophosphinodiphenylamine, which then loses hydrogen chloride to form the phosphazine. A similar mechanism very likely applies to the preparation of 2,8-dimethylphenoxaphosphinic acid through the condensation of phosphorus trichloride with *p*-tolyl ether.[5]


III

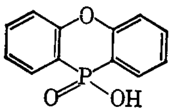
In the light of these considerations we have attempted the preparation of heterocyclic phosphorus compounds by cyclodehydrohalogenation of dichlorophosphines. In order to prepare the latter compounds we have used the excellent method recently introduced by Quin and Humphrey whereby the unisolated intermediate from the reaction of phosphorus trichloride and a diazonium salt is reduced with a metal.[12] Although Quin and Humphrey originally employed magnesium as the reducing agent, Quin[13] has informed us that aluminum is preferable for this purpose; in fact, Quin and Montgomery later employed aluminum for preparing diarylchlorophosphines.[14] For the preparation of the heterocyclic compounds described in the present paper we found that powdered aluminum was successful as a reducing agent, whereas in several attempts magnesium did not yield the desired compounds.

In the first reaction studied phosphorus trichloride was allowed to react with *o*-biphenyldiazonium fluoroborate, then the unisolated intermediate was reduced with powdered aluminum. Vacuum distillation of the reaction product, after removal of the solvent and lower boiling by-products, gave 5-chlorodibenzophosphole (IV) in 6% yield. This low yield was not unanticipated since it had previously been found that *o*-biphenylylphosphonic acid was obtained in only 9% yield from *o*-biphenyldiazonium fluoroborate and phosphorus trichloride.[15] This particular reaction was chosen, however, since the resulting 5-chlorodibenzophosphole, should be (and was) readily converted by hydrolysis and oxidation to the known 5-hydroxy-5H-dibenzophosphole 5-oxide[4] (V).

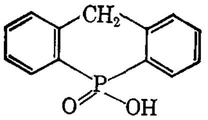

IV


V

We have also prepared 10-chlorophenoxaphosphine in 24% yield starting with *o*-phenoxybenzenediazonium fluoroborate. Hydrolysis and oxidation yielded the previously unknown phenoxaphosphinic acid (VI).


VI

In neither of the cases described above were we able to isolate the intermediate dichlorophosphines. These must have been formed but the high-temperature distillation, particularly in the presence of boron trifluoride and aluminum chloride, probably induced cyclodehydrohalogenation. Quite different results were obtained with *o*-benzylbenzenediazonium fluoroborate. Here we always obtained 2-dichlorophosphinodiphenylmethane as the principal phosphorus-containing product; in one case, however, a trace amount of 5-hydroxy-5,10-dihydrodibenz[*b*,*e*]phosphorin 5-oxide (VII) was isolated from the crude reaction mixture following hydrolysis and oxidation. The 2-dichlorophosphinodiphenylmethane was readily cyclized to the desired 5-chloro-5,10-dihydrodibenz[*b*,*e*]phosphorin (VIII) by heating with anhydrous zinc chloride. One attempt to bring about cyclization by heating the dichlorophos-


VII

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[7] E. R. Lynch, *J. Chem. Soc.*, 3729 (1962).

[8] E. Roberts and E. E. Turner, *ibid.*, 1207 (1926).

[9] A. Michaelis and A. Schenk, *Ann.*, **260**, 1 (1890).

[10] P. G. Sergeev and D. C. Kudryashov, *Zh. Obshch. Khim.*, **8**, 266 (1938).

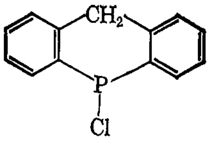
[11] M. Häring, *Helv. Chim. Acta*, **43**, 1826 (1960).

[12] L. D. Quin and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **83**, 4124 (1961).

[13] Personal communication from Dr. Quin.

[14] L. D. Quin and R. E. Montgomery, *J. Org. Chem.*, **27**, 4120 (1962).

[15] H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **76**, 1548 (1954).



VIII

phine with anhydrous aluminum chloride was not successful. Hydrolysis and oxidation of VIII yielded the phosphinic acid, VII.

The failure of 2-dichlorophosphinodiphenylmethane to undergo cyclodehydrohalogenation as readily as did the two 2-dichlorophosphino compounds derived from phenyl ether and biphenyl is not unexpected. The cyclization (at least under Friedel–Crafts conditions) must involve an electrophilic attack of phosphorus on the 2-position of the neighboring ring.[16] This position will be activated more by a phenoxy group or by a phenyl group than by a benzyl group.

The ultraviolet absorption spectra of heterocyclic phosphinic acids has proved to be of value in establishing the structure for such compounds.[4,5,17] Table I lists the spectra of the three heterocyclic phosphinic acids described in the present paper together with the spectra of several closely related compounds. As indicated in the table, the spectra of phenoxaphosphinic acid and phenoxarsinic acid are virtually identical. The close resemblance of the spectra of the corresponding arsenic and phosphorus compounds has often been noted.[4,5,17–19] The spectrum of *o*-benzylphenylphosphonic acid is very similar to that of *o*-tolylphosphonic acid; the intensity of absorption of the benzyl compound is somewhat greater since it contains a second benzene ring. It is also seen that the spectrum of 5-hydroxy-5,10-dihydrodibenz[*b*,*e*]phosphorin 5-oxide is quite like the spectra of its nonheterocyclic analogs, *o*-benzylphenylphosphonic acid and diphenylphosphinic acid. This similarity is undoubtedly associated with the absence of appreciable resonance interaction between two benzene rings joined by either a methylene or a phosphinico (PO_2H) group.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA[a]

Compound	λ_{max}, mμ	ϵ_{max}
Phenoxaphosphinic acid	215	33,900
	241	13,000
	275[b]	2,300
	287[b]	4,120
	294	5,180
Phenoxarsinic acid[c]	214	32,200
	241	12,100
	274	3,450
	288[b]	4,600
	293	5,050
5-Hydroxy-5,10-dihydrodibenz[*b*,*e*]phosphorin 5-oxide	205	36,600
	227[b]	9,180
	264[b]	1,260
	268.5	1,630
	275.5	1,610
o-Benzylphenylphosphonic acid	218[b]	15,200
	263[b]	1,020
	269	1,370
	275.5	1,260
Diphenylphosphinic acid[c]	224	14,700
	255[b]	693
	259	958
	264	1,180
	272	933
o-Tolylphosphonic acid	215	7,330
	262	443
	267.5	573
	275	464

[a] The spectra of all compounds were determined in 95% ethanol with a Perkin-Elmer Model 350 spectrophotometer. [b] Shoulder. [c] The spectrum of this compound has been determined previously with a Beckman DU spectrophotometer; *cf.* ref. 4 and 5.

Experimental[20,21]

5-Chlorodibenzophosphole.—A 3-l. three-necked flask was equipped with a reflux condenser and sealed stirrer. On top of the reflux condenser was placed a drying tube connected to a large rubber balloon which could be filled with dry nitrogen. The flask was dried by flaming and sweeping with dry nitrogen. *o*-Biphenyldiazonium fluoroborate (80.4 g., 0.3 mole), 41.2 g. of phosphorus trichloride (0.3 mole), 6 g. of cuprous bromide, and 300 ml. of ethyl acetate, previously dried over phosphorus pentoxide and distilled, were added to the flask and stirring was started. The evolution of nitrogen started immediately and was complete in about 20 min. Stirring was continued for 1 hr. longer; then 5.4 g. (0.2 mole) of powdered aluminum (Mallinckrodt) was added and the mixture was refluxed for 2 hr. The mixture was then stirred overnight at room temperature.

The contents of the flask were then transferred in portions to a 500-ml. distilling flask without exposure to the atmosphere. This was accomplished with two bent adapters. One adapter had a 75° angle, the other a 105° angle, and both possessed standard-taper joints at both ends. This system of adapters was connected between the reaction flask and the distilling flask. By swiveling this system it was possible to pour the contents into the distilling flask without admitting air. The balloon filled with nitrogen maintained a positive nitrogen pressure during these manipulations. The solvent, excess phosphorus trichloride, and other low-boiling material were stripped by distillation at reduced pressure (water aspirator). A drying tube between the aspirator and flask prevented ingress of moisture. The high-boiling material remaining in the flask was distilled at about 5 μ. The distillate was then fractionated through a 6-in. Vigreux column. The principal fraction (17.5 g.) proved to be a mixture of *o*-chlorobiphenyl and *o*-fluorobiphenyl (identified by their infrared spectra). The higher boiling fraction (3.8 g.), b.p. 146–148 (5 μ), which crystallized in the condenser and receiver, was obtained as yellow crystals, m.p. 53–56°, yield 5.8%.

Anal. Calcd. for $C_{12}H_8ClP$: C, 65.93; H, 3.59; P, 14.17. Found: C, 65.65; H, 3.69; P, 13.97.

5-Hydroxy-5H-dibenzophosphole 5-Oxide.—The oxidation of 0.52 g. of 5-chlorodibenzophosphole suspended in alkaline solution with 20 ml. of 30% hydrogen peroxide gave a 94% yield of the crude acid after acidification of the alkaline solution. After recrystallization from aqueous alcohol the compound proved to be identical (melting point and mixture melting point) with a sample of this compound prepared by a different method.[4]

10-Chlorophenoxaphosphine.—*o*-Aminophenyl phenyl ether was readily prepared by reduction of *o*-nitrophenyl phenyl ether (Eastman Kodak No. 3425) with Raney nickel and hydrogen at 50 lb. pressure. The yield of amine after recrystallization from aqueous alcohol was 96%, m.p. 46.5°. *o*-Phenoxybenzenedi-

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[16] Similar conclusions were reached by E. Roberts and E. E. Turner [*J. Chem. Soc.*, **127**, 2004 (1925)] and by J. D. C. Mole and E. E. Turner [*ibid.*, 1720 (1939)].

[17] L. D. Freedman and G. O. Doak, *J. Org. Chem.*, **24**, 638 (1959).

[18] H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

[19] L. D. Freedman, *J. Am. Chem. Soc.*, **77**, 6223 (1955).

[20] Melting points were determined on a Fisher-Johns apparatus with a thermometer calibrated against U. S. P. reference standards as previously described; *cf.* G. O. Doak and L. D. Freedman, *ibid.*, **73**, 5658 (1951).

[21] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Model 421 spectrophotometer.

azonium fluoroborate was readily prepared in 73% yield by diazotization in fluoroboric acid solution.

The reaction of this diazonium fluoroborate with phosphorus trichloride, reduction, and isolation of the 10-chlorophenoxaphosphine was carried out in the same manner as described above for 5-chlorodibenzophosphole. The reaction was run on a 0.5-mole scale; the yield of the yellow crystalline solid, m.p. 62–64°, was 28.2 g., 24%.

Anal. Calcd. for $C_{12}H_8ClOP$: C, 61.43; H, 3.44; P, 13.20. Found: C, 60.81; H, 3.51; P, 12.59.

Phenoxaphosphinic Acid.—The oxidation of 10-chlorophenoxaphosphine suspended in alkaline solution with 30% hydrogen peroxide gave, after acidification of the alkaline solution, the acid in 99% yield. It was recrystallized from alcohol, m.p. 231–234°.

Anal. Calcd. for $C_{12}H_9O_3P$: C, 62.08; H, 3.91. Found: C, 61.81; H, 3.84.

***o*-Benzylphenylphosphonous Dichloride.**—*o*-Aminodiphenylmethane[22] was converted to the diazonium fluoroborate in 83% yield by diazotization in fluoroboric acid. The reaction of this salt (113 g., 0.4 mole) with phosphorus trichloride and reduction with powdered aluminum was carried out as described above for 5-chlorodibenzophosphole. The high-boiling material that was obtained was finally fractionated through a 21-in. spinning band column. The yield of *o*-benzylphenylphosphonous dichloride was 6.9 g. (6.4%), b.p. 132–137° (0.2 mm.).

Anal. Calcd. for $C_{13}H_{11}Cl_2P$: Cl, 26.35; P, 11.51. Found: Cl, 26.10; P, 11.55.

5-Chloro-5,10-dihydrodibenz[*b,e*]phosphorin.—*o*-Benzylphenylphosphonous dichloride (2.04 g.) and 1.1 g. of anhydrous zinc chloride were heated together in a nitrogen atmosphere for 24 hr. The liquid was then distilled at 10 μ. The compound was obtained as yellow crystals, 25% yield, m.p. 78–86°.

Anal. Calcd. for $C_{13}H_{10}ClP$: C, 67.11; H, 4.33; P, 13.31. Found: C, 66.86; H, 4.59; P, 13.49.

5-Hydroxy-5,10-dihydrodibenz[*b,e*]phosphorin 5-Oxide.—5-Chloro-5,10-dihydrodibenz[*b,e*]phosphorin suspended in alkaline solution was oxidized with 30% hydrogen peroxide. The free acid was obtained in 81% yield when the alkaline solution was acidified. It decomposed on heating above 225°.

Anal. Calcd. for $C_{13}H_{11}O_2P$: C, 67.83; H, 4.82. Found: C, 67.51; H, 4.69.

***o*-Benzylphenylphosphonic Acid.**—*o*-Benzylphenylphosphonous dichloride was suspended in aqueous alkali and oxidized with 30% hydrogen peroxide. The acid was obtained in 92% yield by acidification of the alkaline solution. It was recrystallized from aqueous alcohol, m.p. 186–188°.

Anal. Calcd. for $C_{13}H_{13}O_3P$: C, 62.91; H, 5.28. Found: C, 62.70; H, 5.34.

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[22] J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Am. Chem. Soc.*, **78**, 3819 (1956).

Reactions of Organometallics with Fluoroaromatic Compounds[1]

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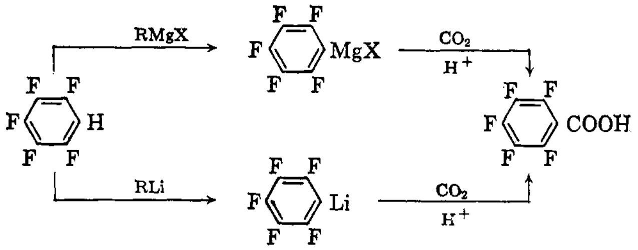
Nucleophilic displacement reactions of Grignard reagents on hexafluorobenzene in tetrahydrofuran have been studied. In general the reaction becomes more facile with the change from aryl to alkyl to allyl Grignard reagents. If the fluoroaromatic ring contains a hydrogen moiety, an acid–base reaction becomes predominant. This is true whether a Grignard or alkyllithium reagent is employed. In this manner mono- or di-Grignard and mono- or dilithio reagents of highly fluorinated benzene compounds have been prepared and converted to the corresponding acids by carbonation.

The nucleophilic substitution reactions of alkyl- and aryllithium reagents on fluoroaromatic compounds have been previously reported.[2] The reaction proceeds to give good yields of the desired alkyl fluoroaromatic compounds. Disubstitution is also possible with the second group substituting *para* to the original

$$RLi + C_6F_6 \longrightarrow RC_6F_5 + LiF$$

alkyl group. For Grignard reagents the published information is more limited. Thus, Pummer and Wall[3a] have reported that 2,3,4,5,6-pentafluorotoluene is formed in 3% yield by the reaction of methylmagnesium iodide with hexafluorobenzene. Harper and Tamborski[3b] have reported the preparation of 1,4-dibenzyl-2,3,5,6-tetrafluorobenzene in 54% yield by the reaction of benzylmagnesium chloride with hexafluorobenzene in tetrahydrofuran.

In addition to reporting further information on the substitution of Grignard reagents on hexafluorobenzene, we wish to report a new series of metalation reactions between organometallic reagents and hydrofluoroaromatic compounds. With hydrofluoroaromatics, the nucleophilic displacement of fluoride ion frequently becomes secondary to an acid–base type reaction as illustrated by the preceding equations.



Nucleophilic Displacement of Fluorine with Grignard Reagents.—The action of Grignard reagents on hexafluorobenzene in tetrahydrofuran have been studied. The reactivity of the Grignard reagents with hexafluorobenzene decreases in the following order: allyl or benzyl > alkyl > aryl. While allylmagnesium chloride reacts vigorously with hexafluorobenzene, the yield of allylpentafluorobenzene is only 26%, as a result of secondary side reactions. The reaction of benzylmagnesium chloride with hexafluorobenzene is similarly vigorous and yields 1,4-dibenzyltetrafluorobenzene in 54% yield. The reaction of 1 equiv. of ethylmagnesium bromide with hexafluorobenzene is moderate and gives ethylpentafluorobenzene in 37% yield. When the mole ratio of Grignard reagent to hexafluorobenzene is increased to 2:1, ethylpentafluorobenzene is produced in 62% yield. Based upon gas–liquid chroma-

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[1] This work was reported at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] (a) A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 808 (1961); (b) J. M. Birchall and R. N. Haszeldine, *ibid.*, 3719 (1961); (c) J. M. Birchall, T. Clarke, and R. N. Haszeldine, *ibid.*, 4977 (1962).

[3] (a) W. J. Pummer and L. A. Wall, *Science*, **127**, 643 (1958); (b) R. J. Harper and C. Tamborski, *Chem. Ind.* (London), 1824 (1962).