

funnel, and a reflux condenser which was protected with a calcium chloride drying tube was swept out with dry nitrogen. To the flask was added 1.5 g. (0.216 g.-atom) of clean lithium wire and 50 ml. of dry ether. To the stirred, cooled mixture was added dropwise, over 30 min., a solution of 15.5 g. (0.11 mole) of methyl iodide in 50 ml. of dry ether. After 1 hr., only traces lithium remained, and to the cold solution was added, dropwise, a solution of 5.0 g. (0.025 mole) of 4,5,7,8-tetramethyl-1-tetralone in 50 ml. of dry ether. Stirring was continued for 1 hr. and the solution was allowed to stand overnight at room temperature. The mixture was decomposed with cold, dilute hydrochloric acid and the layers were separated. The aqueous layer was extracted with ether and the ether extracts were combined and washed with dilute hydrochloric acid, dilute sodium bicarbonate, and with water. The extracts were dried over anhydrous magnesium sulfate, the ether was removed by distillation, and the residue was vacuum distilled at 162–176°/18 mm. The distillate showed a fairly strong infrared carbonyl band indicating that reaction was not complete.

The mixture was dehydrogenated with 5% palladium on

charcoal at 280–310° for 3 hr. Benzene was added to the cooled mixture and the solution was filtered to remove the catalyst, the solvent was removed by distillation, and the residual material was vacuum distilled. The distillate was crystallized from absolute alcohol to give 3.0 g. (61%) of colorless leaflets of 1,2,4,5,8-pentamethylnaphthalene, m.p. 58–59° (lit.,¹³ m.p. 60–61°). The infrared spectrum shows strong absorption at 11.65 and 12.35 μ , which is characteristic of a 1,2,4,5,8-structure.¹⁴

The picrate formed small dark red needles, m.p. 156–156.5° (lit.,¹⁰ m.p. 156–157°).

Acknowledgment.—This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

(13) L. Ruzicka, H. Schinz, and P. H. Müller, *Helv. Chim. Acta*, **27**, 195 (1944).

(14) Unpublished data in our laboratory.

Friedel-Crafts Reaction of Ferrocene with Phosphorus Trichloride. Formation of Triferrocenylphosphine¹⁻³

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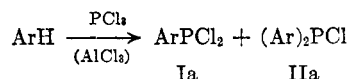
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The preparation of the first known compounds with phosphorus bonded to ferrocene carbon is described. The reaction of ferrocene with phosphorus trichloride in the presence of anhydrous aluminum chloride under conditions favoring monosubstitution gave rise to three products: ferrocenylphosphonous dichloride, diferrocenylphosphinous chloride, and triferrocenylphosphine. Formation of these compounds was demonstrated when the following derivatives were isolated: ferrocenylphosphinic acid; diferrocenylphosphinic acid and its hydrate; triferrocenylphosphine oxide, several of its hydrates, and a hydrogen chloride complex; and triferrocenylmethylphosphonium iodide. A tertiary phosphine was thus observed among the products of a Friedel-Crafts reaction for the first time. Infrared absorption bands were assigned to the ferrocenyl-phosphorus group. The possible existence of an interaction between phosphoryl and the ferrocene residues in the anhydrous phosphine oxide is discussed. Spectral evidence for ring hydration and ring hydrochlorination is presented.

Although ferrocene has been reported to undergo a wide variety of substitution reactions that are characteristically aromatic, including Friedel-Crafts acylation and alkylation,^{5,6} no investigation of its behavior towards phosphorus trichloride in a Friedel-Crafts reaction has heretofore been described. Indeed, no report of an attempt to introduce, by any other method, a phosphorus-containing function onto a cyclopentadiene ring of ferrocene has been located.⁷ Formation, *via* a Friedel-Crafts reaction, of compounds with phosphorus

bonded to ferrocene carbon is reported here in detail for the first time.

For more than a half century, aromatic hydrocarbons have been known to interact with phosphorus trichloride in a Friedel-Crafts reaction to give arylphosphonous dichlorides (Ia) and diarylphosphinous chlorides (IIa).⁸



In general, the reaction of an aromatic compound with phosphorus trichloride catalyzed by anhydrous aluminum chloride gives up to 80% yields of Ia in two to eight hours of refluxing.⁹ With reaction periods of the order of thirty hours, 30 to 50% yields of IIa are possible. Increasing alkyl substitution of the benzene ring leads to increased yields of com-

(8) A. Michaelis, *Ann.*, **293**, 193 (1896); *ibid.*, **293**, 261 (1896); *ibid.*, **294**, 1 (1897).

(9) For a review, see G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, pp. 43–46.

(1) Supported by the U. S. Army Research Office.

(2) Abstracted from a dissertation submitted to the Temple University Graduate Board in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Presented in part before the Division of Organic Chemistry, 3rd Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pennsylvania, February 25, 1960.

(4) (a) Frankford Arsenal; (b) Temple University.

(5) For a review, see P. L. Pauson, *Quart. Rev.* (London), **9**, 408 (1955).

(6) For a recent bibliography, see M. D. Rausch, E. O. Fischer, and H. Grubert, *J. Am. Chem. Soc.*, **82**, 76 (1960).

(7) Ferrocenylphosphonic acid has been synthesized in these laboratories from lithioferrocene.

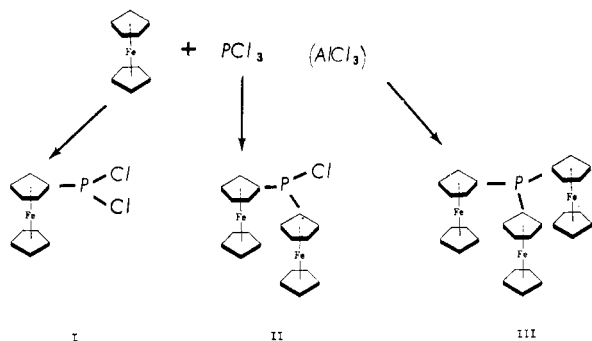
TABLE I
 PRODUCT YIELDS AND RATIOS IN THE FRIEDEL-CRAFTS REACTION

Reflux time, hr.	Yields, ^a %			Ratios		Recovered ferrocene, ^a %	Fe(OH) ₃ as ferrocene, ^a %
	ArP(O)H(OH)	Ar ₂ P(O)OH	Ar ₃ P ^b	Ar ₂ P	Ar ₃ P		
				ArP(O)H(OH)	Ar ₂ P(O)OH		
0.5	1.8	1.9	0.93 ^c	0.52	0.49	68.5	18.8
5.0	3.6	4.2	10.5 ^d	2.9	2.5	49.5	17.2

^a Based on 37.2 g. (0.2 mole) of ferrocene. ^b Derivatives calcd. as Ar₃P. ^c Only Ar₃PCH₃I and Ar₃PO were isolated. ^d Includes Ar₃PCH₃I, Ar₃PO, and HCl·Ar₃PO. Evidence points to the existence of other derivatives of Ar₃P in the reaction mixture, so that this figure should undoubtedly be larger.

pounds of type IIa and decreased amounts of type Ia.¹⁰ Formation of the tertiary phosphine (Ar₃P) by the replacement of all three chlorine atoms of phosphorus trichloride in a Friedel-Crafts reaction has never been reported.

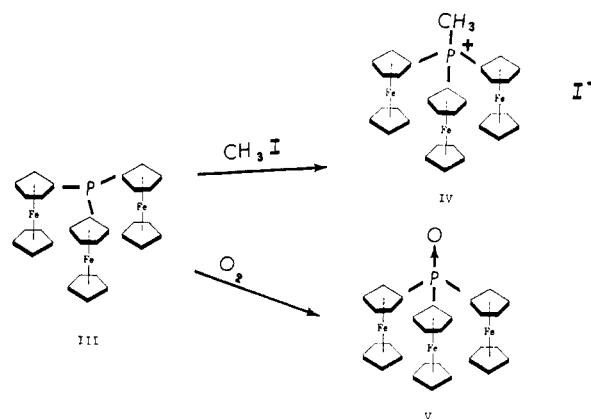
In the present investigation, when either reagent or technical grade anhydrous aluminum chloride was used as catalyst in the reaction of ferrocene with phosphorus trichloride, the trisubstituted compound, triferrocenylphosphine (III), was demonstrated to be present as a reaction product together with the expected mono- and disubstituted phosphorus compounds (I and II, respectively). The formation of compound III was quite unexpected.



Trisubstitution on phosphorus is even more unusual in view of the fact that a threefold excess of phosphorus trichloride was used, and the reaction mixture was refluxed for a period as short as one-half hour, conditions normally expected to favor monosubstitution.

The phosphine (III), apparently freed from a molecular complex by treatment with water, was converted to the quaternary salt, triferrocenylmethylphosphonium iodide (IV), on treatment with methyl iodide. Furthermore, the phosphine was converted unexpectedly to triferrocenylphosphine oxide (V) when no precautions were taken to exclude air during isolation and purification of products. This oxidation was surprising in view of the resistance of triphenylphosphine to air oxidation.¹¹

A water-insoluble hydrogen chloride complex of V was obtained from the reaction mixture and formulated as HCl·(C₁₀H₉Fe)₃PO. Hydrogen chlo-



ride, of course, had evolved profusely as a by-product of the Friedel-Crafts reaction, and had formed also upon treatment of the reaction mixture with water. Although trituration of the complex with water gave hydrated V, the same complex was unaffected by atmospheric moisture during storage for more than six months. The capacity of phosphine oxides to form addition compounds has been attributed to complexing *via* phosphoryl oxygen.^{12,13} Spectral evidence will be presented later, however, which indicates that in the case of the hydrogen chloride complex of V, cyclopentadieny' rings, rather than phosphoryl oxygen, are involved in complex formation. The complex could not be prepared by bubbling hydrogen chloride gas through solutions of V in benzene, or benzene and ethanol.

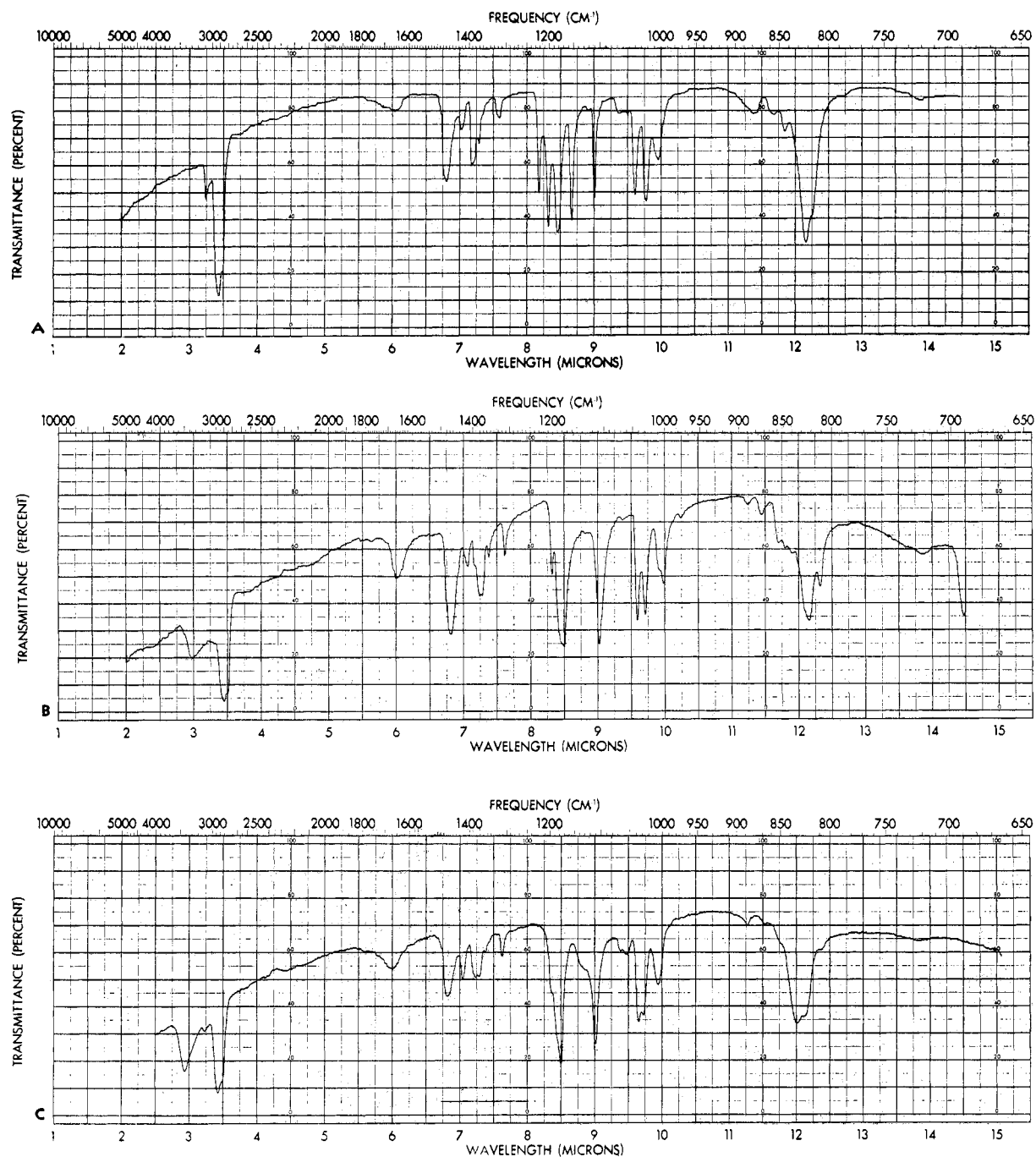
Hemi-, mono-, and dihydrates were either prepared directly from the phosphine oxide (V), or sometimes isolated from the reaction mixture which in the course of work-up had been treated with a large excess of water. V and its hydrates are water-insoluble and hydrophobic, and because of the heterogeneous nature of the reaction mixture, it would appear that the manner in which the reaction mixture is treated with water is a critical factor in the formation of a particular hydrate. The hemihydrate was converted to the dihydrate on exposure to the atmosphere over a period of two years, while anhydrous V showed no tendency to become hydrated during storage under the same conditions. Spectral evidence indicating ring

(10) A. W. Frank, *J. Org. Chem.*, **24**, 966 (1959).

(11) Ref. 9, p. 98; G. Revesz, M.A. thesis, Temple University, June, 1960.

(12) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 262 (1906).

(13) J. C. Sheldon and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1958).



hydration rather than hydrogen-bonding of water to phosphoryl oxygen will be presented later.

Two acids were isolated from the hydrolyzed reaction mixture. The first, water-soluble and relatively strong (pK 3.32), was identified as ferrocenylphosphinic acid (VI), which indicated the existence of the precursor I. The second acid, weak and water-insoluble, was identified as diferrocenylphosphinic acid (VII), which arose by the oxidative hydrolysis of II.

The discussion thus far tacitly assumes that substitution on phosphorus has occurred *via* a stepwise process, mono- to di- to tri-. Experimental evi-

dence has been assembled which tends to rule out the possibility that the mono- and disubstituted products arise *via* deferrocenylation of some molecular species containing "pentavalent" phosphorus.¹⁴ Table I summarizes this evidence.

It is clear that the tertiary phosphine arises from the mono- and disubstituted products rather than the reverse situation; that as the reflux period is lengthened, the quantity of tertiary phosphine formed assumes greater importance, overtaking and

(14) For reviews of the cleavage of the P—C bond, see ref. 9, pp. 70, 84–85; K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 247, 251 (1960).

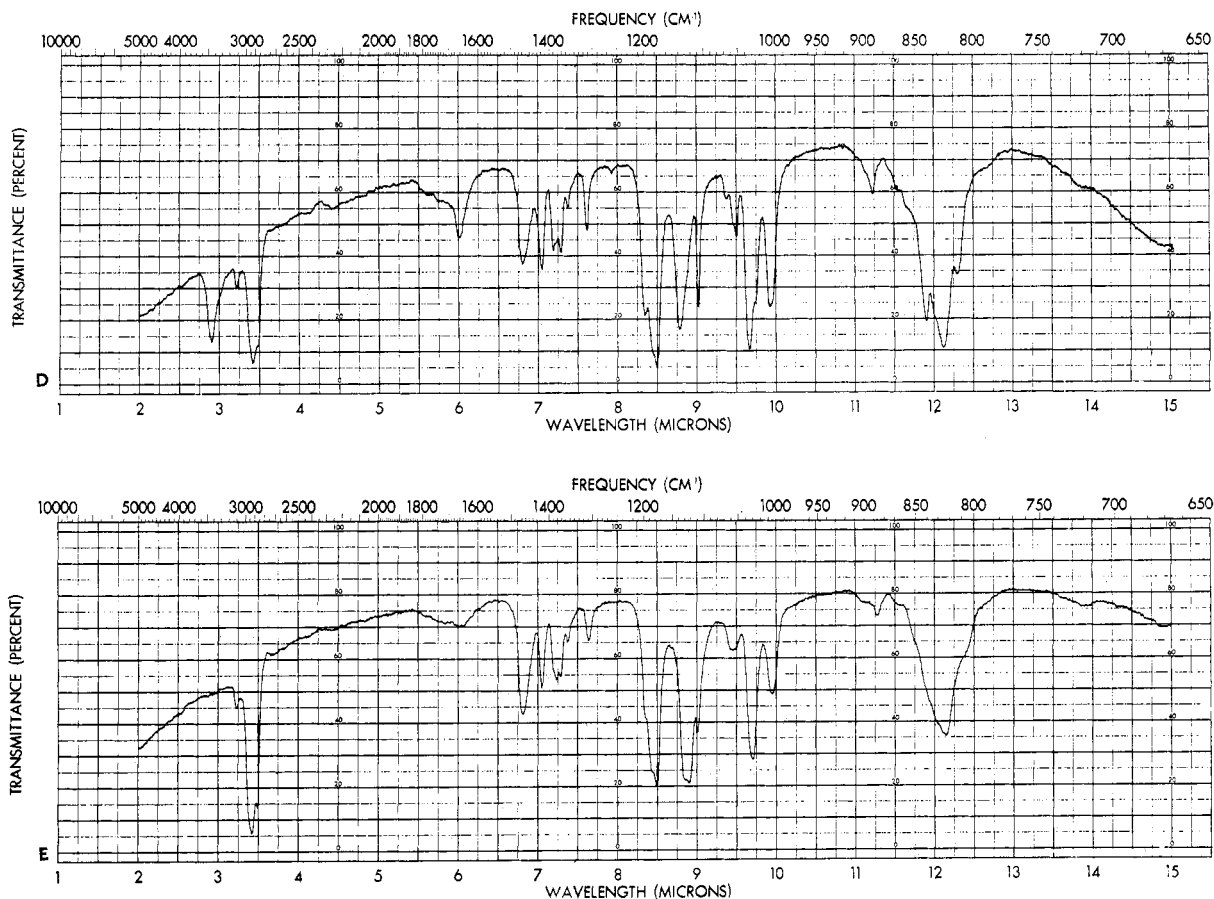
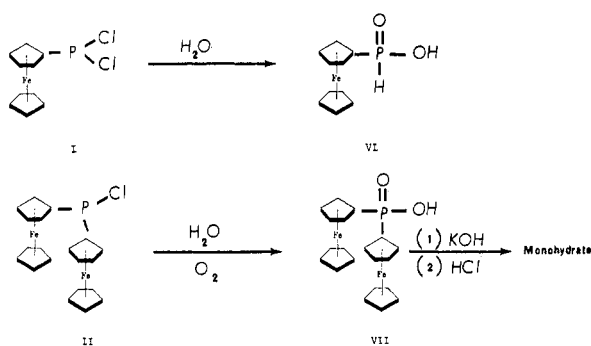


Fig. 1.—A, triferrocenylphosphine oxide; B, triferrocenylphosphine oxide hemihydrate; C, triferrocenylphosphine oxide monohydrate; D, triferrocenylphosphine oxide dihydrate; E, triferrocenylphosphine oxide-hydrogen chloride complex.



exceeding the amounts of primary and secondary products formed.

Table I also shows unchanged ferrocene recovered from the reaction mixtures, together with ferrocene decomposed to ferric hydroxide. Isolation of ferric hydroxide in like amounts in reactions utilizing reflux periods of one-half and five hours indicates that this substance arose not so much from the decomposition of products as from the decomposition of ferrocene itself, or a ferrocene complex.

In several other modifications of reaction conditions, no further increase in product yields was obtained. These modifications included extending the reflux period to twenty-five hours, increasing the

amounts of aluminum chloride catalyst and phosphorus trichloride, running the reaction in benzene as solvent, and employing phosphorus oxychloride as an aluminum chloride complexing agent.¹⁵ In the last modification the expected precipitation of phosphorus oxychloride-aluminum chloride complex did not occur. No method was devised capable of breaking the aluminum chloride complex of I without simultaneous hydrolysis of I.

Infrared bands of significance are summarized in Table II. Bands appearing in the regions 1015–1045 cm^{-1} (strong intensity) and 1310–1320 cm^{-1} (weak-to-medium intensity) in all spectra are assigned to the ferrocenyl-phosphorus group. (Cf. assignment of bands near 1000 and 1440 cm^{-1} to phenyl-phosphorus.¹⁶) All spectra show bands near 1110 and 1005 cm^{-1} in accordance with the “9–10- μ rule”¹⁷ for ferrocenes having an unsubstituted cyclopentadiene ring.

Spectral Interpretations.—Although the infrared spectrum of triferrocenylphosphine oxide (V; Fig. 1A) exhibits four sharp peaks at 1220, 1200, 1180,

(15) W. T. Dye, Jr., *J. Am. Chem. Soc.*, **70**, 2595 (1948); B. Buchner and L. B. Lockhart, Jr., *Org. Syn.*, **31**, 88 (1951).

(16) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(17) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

TABLE II
SIGNIFICANT INFRARED BANDS (CM.⁻¹) OF PHOSPHORO-FERROCENE COMPOUNDS^a

Compound	Fig.	Bonded O—H(H ₂ O) stretching	Ferrocenyl-phosphorus group	P—O stretching ^b	Ring complexing	Asym-metric ring breathing ^c	Ferrocenyl-phosphorus group	In-plane C—H bending ^c	P—OH Deform. ^d	Out-of-plane C—H bending ^e	Others ^f
IV			1313			1111	1035	1007		828	1202
V	1A		1316	1180		1108	1038; 1021 ^f	1002		822 (817) ^g	1188; 1182 ^h
V·1/2H ₂ O	1B	3370	1315	1177		1109	1043; 1030 ^f	1003		823	1200
V·H ₂ O	1C	3410	1311	1177	(1130) ^g	1110	1037; 1029 ^f	1006		833	1202
V·2H ₂ O	1D	3450	1313	1177	1139	1109	1035 (1027) ^f	1007		840	(1183) ^g
V·HCl	1E		1310	1178	1130; 1123 ^f	1110	1030	1005		825	(1182) ^g
VI			1319	1199		1110	1036	(996)-977-(962) ^h		823	1199
VII			1312	1186		1110	1034; 1019 ^f	1000		835	(1198) ^g
VII·H ₂ O		3200	1314	1192	1139	1108	1038	1004	986	834	1208 ⁱ

^a All spectra were obtained on Nujol mulls (Perkin-Elmer Model 321). ^b Assigned¹⁸ frequency, 1170–1310 cm.⁻¹ ^c Bands corresponding to assigned¹⁸ ferrocene bands. CH and CC stretching bands¹⁸ in the regions, 3060–3100 cm.⁻¹ and 1410–1430 cm.⁻¹, respectively, are common to all spectra. ^d Assigned¹⁹ frequency within the region, 900–1055 cm.⁻¹; those in the assigned¹⁸ region, 2550–2700 cm.⁻¹, are relatively weak. ^e Possibly due to in-plane C—H bending. ^f A doublet. ^g A shoulder. ^h A single, broad band extending from 962 to 996 cm.⁻¹, believed to be a combination of C—H and P—OH absorption bands. ⁱ Possibly part of a phosphoryl doublet.

and 1152 cm.⁻¹ in the phosphoryl stretching region, the spectra of the hydrates of V (Fig. 1B, 1C, 1D) show a single, strong band at 1177 cm.⁻¹ with residual peaks near 1200 and 1183 cm.⁻¹. In contrast, both triphenylphosphine oxide and its hemihydrate show single bands in the phosphoryl stretching region at practically identical frequencies (1202 and 1201 cm.⁻¹, respectively, for carbon tetrachloride solutions).²⁰ Of the four bands between 1225 and 1150 cm.⁻¹ in the spectrum of V, phosphoryl stretching is considered to give rise primarily to the one at 1180 cm.⁻¹.

The three additional bands may arise *via* phosphoryl doubling, or belong to in-plane C—H bending vibrations which are either infrared-inactive, or weakly absorbing in ferrocene itself.^{18,21,22} The appearance of these additional bands in the spectrum of the anhydrous oxide suggests the existence of an interaction between phosphoryl oxygen and the ferrocene residues, which is removed when the molecule is hydrated.

Two types of interaction may be postulated: (1) interaction between oxygen and the ring carbons as depicted in Fig. 2, which is reasonable if some canting of the rings is permitted²³; (2) orbital overlap between oxygen and iron, which implies an electrophilic character for the iron. We prefer the first mode of interaction, and would eliminate the second on the basis of the known nucleophilic character of the iron atom in ferrocene.^{24–27}

The proposed interaction may be destroyed by hydrogen-bonding of water or hydrogen chloride to phosphoryl oxygen or to the rings. Evidence that water and hydrogen chloride are not bonded to phosphoryl oxygen lies in the fact that the phosphoryl stretching band remains fixed at 1177–1178 cm.⁻¹ in the spectra of the hydrates and hydrogen chloride complex of V (Fig. 1B, 1C, 1D, 1E). If bonding were to phosphoryl oxygen, some variation in the phosphoryl stretching frequency would be expected. Evidence that hydrogen-bonding of water and hydrogen chloride is to the rings is the

(18) E. R. Lippincott and R. D. Nelson, *J. Am. Chem. Soc.*, **77**, 4990 (1955).

(19) L. C. Thomas and R. A. Chittenden, "Correlation of Infrared Absorption Spectra of Organo-Phosphorus Compounds with Molecular Structure. Part III. The P—O—X Bonds." Porton Technical Paper No. 689, Chemical Defense Experimental Establishment (Great Britain), June 25, 1959. (Tech. Abstract Bull. -ASTIA-No. U59-24-Dec. 15, 1959, p. 6474; AD-226-954).

(20) M. Halmann and S. Pinchas, *J. Chem. Soc.*, 3264 (1958).

(21) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).

(22) R. D. Nelson, W. G. Fateley, and E. R. Lippincott, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

(23) K. L. Rinehart, Jr., A. K. Frerichs, P. A. Kittle, L. F. Westman, D. H. Gustafson, R. L. Pruett, and J. E. McMahon, *ibid.*, **82**, 4111 (1960).

(24) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *ibid.*, **82**, 5249 (1960).

(25) D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. 13, 1–8 (1960); *Chem. Abstr.*, **54**, 22539g (1960).

(26) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, **81**, 3484 (1959).

(27) A. Berger, W. E. McEwen, and J. Kleinberg, *ibid.*, **83**, 2274 (1961).

appearance of bands near 1130 cm.^{-1} . In the case of the hydrates of V, band intensities are related to the extent of hydration of V. The absorption is not shown by the hemihydrate. These bands are interpreted as indicating some kind of ring vibration arising from ring-complexing of water or hydrogen chloride, as opposed to complexing of these by the iron atom.²⁴ This is suggested by the close proximity of the absorptions to a band near 1105 cm.^{-1} which in ferrocene itself has been assigned¹⁸ to asymmetrical ring breathing.

Although the phosphoryl-ring interaction is presumed to be intramolecular in nature (Fig. 2), the possibility of an intermolecular interaction should not be disregarded. Distinguishing between the two via dilution effects is precluded, inasmuch as V is insoluble in non-hydrogen-bonding solvents such as cyclohexane, *n*-heptane, and carbon tetrachloride.

In the case of the secondary phosphinic acid (VII), the appearance of a band at 1139 cm.^{-1} in the spectrum of the hydrate but not in the spectrum of the anhydrous form is again suggestive of ring hydration.

Work done in connection with triphenylphosphine oxide^{20,28,29} and ferrocene³⁰ is largely in agreement with our findings here.

Experimental³¹

Friedel-Crafts Reaction Employing 5-Hr. Period of Reflux. Step 1.—A slurry consisting of 20.1 g. (0.15 mole) of anhydrous aluminum chloride and 41.2 g. (0.3 mole) of phosphorus trichloride was stirred under nitrogen in a flask fitted with a stirrer and condenser. A slurry of 37.2 g. (0.2 mole) of ferrocene in 41.2 g. (0.3 mole) of phosphorus trichloride was added over a 3-min. period through a powder funnel which was then replaced by a stopper. The reaction mixture immediately turned greenish black with formation of a dark green insoluble complex. (In one case, the momentary application of heat was necessary to initiate the reaction.) An exothermic reaction occurred, but no external cooling was required. The mixture was heated at reflux for 5 hr., allowed to cool to room temperature, and the yellow-orange phosphorus trichloride phase decanted under a blanket of nitrogen through a sintered-glass filter under suction. Five 100-ml. phosphorus trichloride extracts of the solids remaining in the reaction flask were added through the filter. The phosphorus trichloride solution was retained.

The solids in the reaction flask were treated cautiously with 200 ml. of water with external cooling. The inky blue aqueous solution and solids were extracted with 300 ml. of benzene, and the mixture poured onto a filter under suction. Fresh water was used to flush any material remaining in the reaction flask onto the filter, and the brownish orange filter cake (A) was washed free of the blue aqueous solution. The orange benzene extract (B) was separated from the inky water phase (C). Solution B was reserved for treatment in step 3, and aqueous phase C for treatment in step 7.

Step 2. Isolation of Triferrocenylmethylphosphonium Iodide (IV).—Solids A were extracted with four 100-ml. portions of boiling benzene, and the orange extracts were

(28) R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, **65**, 1132 (1961).

(29) A. L. Geddes, *ibid.*, **58**, 1062 (1954).

(30) D. S. Trifan, J. L. Weinmann, and L. P. Kuhn, *J. Am. Chem. Soc.*, **79**, 6566 (1957).

(31) Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

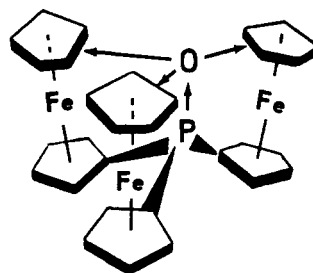


Fig. 2.—Triferrocenylphosphine oxide.

combined and filtered. The remaining solids (D) were reserved for step 4. When methyl iodide was added to the benzene solution, immediate clouding developed. After several minutes, the powdered, orange product was removed by filtration; yield 2.0 g. (4.1%). The filtrate (E) was reserved for treatment in step 3. Crystallization of the product from ethanol afforded orange crystals; infusible, soluble in hot water.

Anal. Calcd. for $C_{31}H_{30}IPFe_3$: C, 51.14; H, 4.15; I, 17.43; P, 4.26; Fe, 23.02. Found: C, 50.43, 50.64; H, 4.60, 4.40; I, 17.65, 17.92; P, 4.00, 4.25; Fe, 23.67, 23.56.

Addition of methyl iodide to a benzene extract of the phosphorus trichloride-insoluble solids (step 1) prior to washing with water gave no precipitation of quaternary salt.

Step 3. Isolation of Triferrocenylphosphine Oxide (V).—Evaporation of combined solutions B and E, from steps 1 and 2, respectively, gave a solid residue which was triturated and boiled, twice, with dilute aqueous potassium hydroxide. The alkaline extract (F) was reserved for step 6. The alkali-insoluble solids (G) were extracted with boiling *n*-heptane, and the heptane solution held for step 7. The heptane-insoluble solids from G were extracted with boiling benzene to give on concentrating and cooling, three times, a total of 0.9 g. of V. (The crystalline solids consisted of varying mixtures of V and its dihydrate. Washing with hot acetone converted the dihydrate to anhydrous V.) The benzene filtrate was evaporated to dryness, and the solid residue extracted first with boiling acetone, then with boiling benzene. Addition of petroleum ether to the extracts caused 0.2 g. of V to separate from each. (Note: Pure V is insoluble in acetone.) The heptane- and benzene-insoluble solids from G were extracted with ethanol and the insoluble brown solids removed by filtration and discarded. Evaporation of the ethanolic solution to dryness gave 0.2 g. of the dihydrate of V; combined yield (including V isolated in step 4) 2.0 g. (5.0%) as compound V. Recrystallization of either V or its dihydrate from benzene-petroleum ether afforded a light yellow anhydrous powder (cotton-like); infusible, and insoluble in water.

Anal. Calcd. for $C_{30}H_{27}OPFe_3$: C, 59.85; H, 4.52; P, 5.15; Fe, 27.83; mol. wt., 602. Found: C, 59.80, 60.16; H, 4.60, 4.72; P, 4.89, 4.87; Fe, 27.19, 27.29; mol. wt. by freezing point depression of camphor, 578, 591.

Step 4. Isolation of the Hydrogen Chloride Complex of Triferrocenylphosphine Oxide (V·HCl)—Solids D (step 2) were extracted with four 100-ml. portions of boiling chloroform. The insoluble brown solids, evolving hydrogen chloride, were removed by filtration and discarded, and the chloroform filtrate evaporated to dryness. The residue was extracted with three 50-ml. portions of boiling benzene, and the combined yellow-green filtrates concentrated. After removal of insoluble brown solids by filtration, the filtrate was concentrated further and cooled, affording grayish green crystalline product; yield 0.6 g. (1.4%). The infusible, water-insoluble product was purified by recrystallization from benzene. Trituration with water caused conversion to the monohydrate of V, the water becoming acidic with dissolved hydrogen chloride.

Anal. Calcd. for $C_{30}H_{25}OClPFe_3$: C, 56.43; H, 4.42; O, 2.51; P, 4.85; Fe, 26.24; neut. equiv., 638.5. Found:

C, 56.05, 56.10; H, 4.29, 4.51; O, 1.77, 2.06; P, 4.45, 4.46; Fe, 25.98, 25.86; neut. equiv., 622 (by back-titration from an excess of alkali).

The filtrate, after crystallization of the hydrogen chloride complex, was concentrated again and the yellow-green solids collected on a filter. The infrared spectrum of these solids indicated a mixture of V and its complex. Prolonged trituration with water, and drying for 1 hr. at 100° *in vacuo* gave 0.3 g. of V. The remaining filtrate was concentrated once more to give 0.2 g. of V.

Step 5. Isolation of Ferrocenylphosphinic Acid (VI).—Phosphorus trichloride was removed from the phosphorus trichloride phase (step 1) by distillation at slightly reduced pressure (aspirator). The reddish orange, semisolid residue was washed with two 25-ml. portions of water, and the greenish washings discarded. The remaining yellow solids were then boiled with five 75-ml. portions of water, and the resulting orange solids removed each time by filtration. Each of the orange filtrates was concentrated and cooled, after removal of small quantities of brown solids whenever they separated, to afford golden platelets (VI); yield 1.8 g. (3.6%). (The addition of hydrochloric acid during concentration of aqueous solutions of VI appeared to suppress the formation of insoluble, brown products; prolonged heating caused an increase in the amount formed. See Note, step 6.) For analysis, the product was recrystallized from water to give golden platelets, m.p. 137–138°.

Anal. Calcd. for $C_{10}H_{11}O_2PF_2$: C, 48.04; H, 4.43; P, 12.39; Fe, 22.34; neut. equiv., 250. Found: C, 47.16, 47.38; H, 4.54, 4.30; P, 12.14, 12.16; Fe, 21.63, 22.10; neut. equiv., 251; pK 3.32.

Step 6. Isolation of Diferrocenylphosphinic Acid (VII).—The water-insoluble solids remaining after extraction of VI with water (step 5) were taken up in aqueous potassium hydroxide, and the insoluble orange solids (H) removed by filtration, and reserved for step 7. To the orange filtrate was added the alkaline extract F (step 3). Dropwise acidification of the combined solutions with concentrated hydrochloric acid caused the monohydrate of VII to precipitate as a light yellow, water-insoluble, infusible powder; yield 1.9 g. (4.2%). The product was purified by re-dissolving in aqueous potassium hydroxide, filtering the solution, and precipitating with hydrochloric acid.

Anal. Calcd. for $C_{20}H_{19}O_2PF_2 \cdot H_2O$: C, 53.14; H, 4.68; P, 6.85; Fe, 24.71. Found: C, 53.26, 53.23; H, 4.73, 4.67; P, 6.60, 6.50; Fe, 23.39, 23.05.

(N. B. Early isolation of the acids from their solutions was necessary; when solutions of the acids were allowed to stand overnight, color changes occurred, and insoluble, brown solids separated.)

The hydrate was converted to the anhydrous acid without visible change by drying at 100° for 1 hr. *in vacuo*.

Anal. Calcd. for $C_{20}H_{19}O_2PF_2$: C, 55.34; H, 4.41; P, 7.14; Fe, 25.74. Found: C, 55.39, 55.12; H, 4.66, 4.68; P, 7.40, 7.23; Fe, 25.54, 24.90.

Step 7. Recovery of Unchanged Ferrocene and Isolation of Ferric Hydroxide.—From aqueous phase C (step 1), from the *n*-heptane extract of solids G (step 3), and from solids H (step 6), a total of 18.4 g. of ferrocene (49.5%) was recovered. In the work-up of aqueous phase C, 3.7 g. of ferric

hydroxide was also obtained, which corresponds to 6.4 g. (17.2%) ferrocene.

Friedel-Crafts Reaction Employing 0.5-Hr. Period of Reflux.—The reaction and isolation steps for the Friedel-Crafts reaction employing a 0.5-hr. reflux period were essentially the same as those described in detail above for the 5-hr. reaction. One notable difference was failure to isolate the hydrogen chloride complex of V. Product yields for this reaction are recorded in Table I.

Procedure for Formation and Isolation of Triferrocenylphosphine Oxide Hemihydrate ($V \cdot \frac{1}{2}H_2O$).—In a Friedel-Crafts reaction employing a 5-hr. period of reflux, the solids remaining after decantation of the phosphorus trichloride phase were extracted repeatedly with benzene, and then alternately with benzene and water. The remaining solids were extracted with chloroform, the extract was evaporated to dryness, and the residue was extracted with benzene at room temperature. From this extract anhydrous V was isolated by addition of petroleum ether. Further extraction of the above residue with boiling benzene yielded 1.2 g. of product which recrystallized from benzene as an infusible, water-insoluble, yellow powder.

Anal. Calcd. for $(C_{30}H_{27}OPFe_3)_2 \cdot H_2O$: C, 58.96; H, 4.62; P, 5.07; Fe, 27.42. Found: C, 58.35, 58.58; H, 5.19, 5.27; P, 4.56, 4.53; Fe, 28.18, 28.43.

The infrared spectrum of the yellow solid remaining upon drying the hemihydrate 1 hr. at 100° *in vacuo* was identical to that of V obtained from the original 5-hr. reaction.

Preparation of Triferrocenylphosphine Oxide Monohydrate ($V \cdot H_2O$).—The hydrogen chloride complex of V was trituated with water, and the yellow, insoluble, infusible solid collected on a filter, washed with water, and air-dried. The infrared spectrum of this substance was identical to the spectrum of the yellow solid which separated upon addition of excess water to an ethanolic solution of V.

Anal. Calcd. for $(C_{30}H_{27}OPFe_3) \cdot H_2O$: H_2O , 2.90. Found: H_2O , 2.74 (by weight loss).

The infrared spectrum of the yellow solid remaining after drying the monohydrate 1 hr. at 100° *in vacuo* was identical to the spectrum of V obtained from the original 5-hr. reaction. An attempted crystallization of the hydrate from benzene caused conversion to anhydrous V.

Preparation of Triferrocenylphosphine Oxide Dihydrate ($V \cdot 2H_2O$).—A solution of V in 95% ethanol was evaporated to dryness under an air stream, and the residue crystallized from benzene to give a yellow, water-insoluble, infusible powder.

Anal. Calcd. for $(C_{30}H_{27}OPFe_3) \cdot 2H_2O$: H_2O , 5.64. Found: H_2O , 5.04 (by weight loss).

The infrared spectrum of the yellow solid obtained by drying the dihydrate 1 hr. at 100° *in vacuo* was identical to that of V obtained from the original 5-hr. reaction.

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