copper was removed, the pH of the solution was adjusted to 3.7, whereupon the phosphonic acid crystallized from solution. The crystals were washed with cold alcohol and then dried *in vacuo*. The yield was 4.6 g. (49%), m.p. 213–215°.

Anal. Calcd. for $C_7H_{10}NO_3P$: N, 7.48; P 16.55. Found: N, 7.68; P, 16.60.

2-Amino-5-tolylphosphonic Acid.—2-Chloro-5-tolylphosphonic acid monohydrate[13] (11.2 g.) was treated with cuprous oxide and aqueous ammonia by the procedure described above. The copper complex of the amino acid was isolated, dissolved in 90 ml. of 4 *N* HCl, and then converted to the free acid. The yield was 4.4 g. (47%), m.p. 219–222°.

Anal. Calcd. for $C_7H_{10}NO_3P$: N, 7.48; P, 16.55. Found: N, 7.23; P, 16.21.

Acknowledgment.—The authors wish to acknowledge the invaluable technical assistance given by Mr. Austin C. Cooley.

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

Ferrocenylphosphonous Dichloride from Ferrocenylphosphinic Acid. The >PH(O) ⇌ >P(OH) Tautomerism[1]

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The conversion of phosphinic acids (I) to phosphonous dichlorides (III) by treatment with excess phosphorus trichloride has been considered by Frank[3] to be evidence for tautomerism involving form II. Recently, the existence of such an equilibrium was questioned by Quin and Dysart[4] who found only one inflection in the titration curves of several examples of I including those examined by Frank,[3] and that reaction of the acids with diazomethane failed to give the diesters. They suggested that, in the formation of III, the shift to tricovalent phosphorus involves not I, but the chloro derivative, ArPH(O)Cl.

$$\underset{\text{I}}{\mathrm{ArPH(O)OH}} \rightleftharpoons \underset{\text{II}}{\mathrm{ArP(OH)_2}} \longrightarrow \underset{\text{III}}{\mathrm{ArPCl_2}}$$

We have found that the method of Frank[3] is applicable to the conversion of ferrocenylphosphinic acid to ferrocenylphosphonous dichloride. The compound that we have used has an estimated electron density on phosphorus of such a magnitude[5] that Quin and Dysart's hypothesis[4] would predict failure to undergo the tautomeric shift. We suggest that our results, like those of Frank,[3] indicate an equilibrium involving form II, and that the results of Quin and Dysart are not inconsistent with the existence of II.[6]

It is significant that chemical and kinetic evidence point to the existence of a tautomeric equilibrium in a related system.[7,8]

$$\mathrm{(RO)_2P(O)H} \rightleftharpoons \mathrm{(RO)_2POH}$$

Ferrocenylphosphonous dichloride, a red-orange liquid decomposing on attempted distillation at 0.5 mm., was obtained in 53% yield. Its solubility in *n*-heptane distinguished it immediately from the phosphinic acid which was insoluble in the same solvent. The product was identified by its hydrolysis to the phosphinic acid and conversion to ferrocenylphosphonous dipiperidide, $C_5H_5FeC_5H_4P(NC_5H_{10})_2$. The air-stable dipiperidide, golden platelets with m.p. 106–107°, represents the first known phosphorus amide of ferrocene.

Experimental

Ferrocenylphosphonous Dichloride.[9]—Phosphorus trichloride (3.52 ml., 0.04 mole) was added dropwise over a period of 2 min. to a vigorously stirred slurry of 1.0 g. (0.004 mole) of ferrocenylphosphinic acid[10] in 20 ml. of benzene under nitrogen. The addition of only a few drops of phosphorus trichloride caused a sudden, complete solubilization of the acid. The solution was orange in color, no heat developed, and there was no gas evolution. Almost immediately, immiscible phosphorous acid began to appear as a dark greenish, viscous sirup adhering to the walls of the reaction flask. Stirring was continued for 0.5 hr. at room temperature.

After decantation of the orange solution, benzene and unreacted phosphorus trichloride were removed under reduced pressure (aspirator) on a steam bath. The residue, a red-orange liquid which decomposed on attempted distillation at 0.5 mm., was taken up in *n*-heptane. The orange heptane solution plus a small amount of insoluble yellowish solids were decanted from some red-orange, semisolid material adhering to the bottom of the flask. The solids, probably unreacted phosphinic acid, were removed by filtration. Sensitivity of the dichloride to hydrolysis was indicated when evaporation of films of the filtrate in air gave crystalline phosphinic acid. The solvent was evaporated from the filtrate under a stream of nitrogen leaving 0.6 g. (53%) of red-orange liquid product.

Ferrocenylphosphonous Dipiperidide.—The ferrocenylphosphonous dichloride (0.0021 mole) was dissolved without further purification in 20 ml. of *n*-heptane. The solution, which became somewhat cloudy on standing (probably as a result of some hydrolysis), was added dropwise over a period of 5 min. to a vigorously stirred solution of 0.85 ml. (0.0086 mole) of piperidine in 20 ml. of benzene protected against atmospheric moisture. Cooling was applied with an ice-bath during the addition. The orange solution in the reaction flask soon became cloudy with formation of piperidine hydrochloride. After the addition, the mixture was stirred 2 hr. at room temperature, and then filtered. The filtrate was evaporated to dryness on a steam bath. The residue, a dark orange viscous liquid which became brown-orange in color as it solidified, was extracted three times with boiling heptane, and the insoluble, brown-orange, viscous liquid was discarded. After filtration of the combined orange heptane extracts, evaporation of the solvent under an air stream gave orange crystals together with a yellow viscous liquid which gradually solidified on standing; the yield (crude) was 0.32 g. (39.5%). The product was taken up in boiling ethanol, and the solution was filtered, concentrated, and cooled to give 0.1 g. of product in the form of golden platelets, m.p. 106–107° (uncor.).

Anal.[11] Calcd. for $C_{20}H_{29}FeN_2P$: C, 62.51; H, 7.61; Fe, 14.53; N, 7.29; P, 8.06. Found: C, 62.10; H, 7.52; Fe, 14.52; N, 6.75; P, 7.93.

Further concentration and cooling of the mother liquor yielded no more product. After removal of solvent by evapora-

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[1] Abstracted in part from the Ph.D. Dissertation of G. P. Sollott, Temple University, Jan., 1962. For previous publication based on this work, *cf.* ref. 10.

[2] (a) Frankford Arsenal; (b) Temple University.

[3] A. W. Frank, *J. Org. Chem.*, **26**, 850 (1961).

[4] L. D. Quin and M. R. Dysart, *ibid.*, **27**, 1012 (1962).

[5] The electron donor ability of the ferrocenyl group appears to be greater than that of *p*-methoxyphenyl; *cf.* E. M. Arnett and R. D. Bushick, *ibid.*, **27**, 111 (1962).

[6] Quin and Dysart's argument against tautomerism has now been questioned by J. Reuben, D. Samuel, and B. L. Silver, *J. Am. Chem. Soc.*, **85**, 3093 (1963).

[7] G. O. Doak and L. D. Freedman, *Chem. Rev.*, **61**, 31 (1961).

[8] D. Samuel and B. L. Silver, *J. Org. Chem.*, **28**, 2089 (1963).

[9] The method was based on A. W. Frank's procedure A, ref. 3.

[10] G. P. Sollott and E. Howard, Jr., *J. Org. Chem.*, **27**, 4034 (1962).

[11] The analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

tion, an odor of piperidine was detected in the residue. Moistened indicator paper turned blue on contact with the residue, indicating that alcoholysis had occurred. Crystallization of phenylphosphonous dipiperidide from ethanol has been reported with no indication that alcoholysis occurs, except that the product possesses a piperidine-like odor.[3]

Infrared Spectra of Ferrocenylphosphonous Dichloride and Ferrocenylphosphonous Dipiperidide.—Infrared spectra were obtained from a liquid smear of the dichloride and from a Nujol mull of the dipiperidide, employing a Perkin-Elmer Model 321 spectrophotometer.

Both compounds show asymmetric ring breathing near 1110 cm.$^{-1}$, and in-plane C–H bending near 1005 cm.$^{-1}$,[12] which are characteristic of monosubstituted ferrocenes.[13] The compounds also show ferrocene C–H stretching and out-of-plane C–H bending bands in the regions 3060–3100 and 810–835 cm.$^{-1}$, respectively.[12] A C–C stretching band appears near 1410 cm.$^{-1}$,[12] in the spectrum of the dichloride, but is absent from this region in the spectrum of the dipiperidide. Both compounds absorb near 1310 and 1025 cm.$^{-1}$ in the regions assigned earlier[10] to the ferrocenylphosphorus group. Bands shown by the dichloride at 1164 and 1199 cm.$^{-1}$ and by the dipiperidide at 1150, 1160 (doublet), and 1212 cm.$^{-1}$ are due possibly to ferrocene in-plane C–H bending.[10,14] Other bands appear in the spectrum of the dipiperidide at 850, 890, 932, 1050, and 1115 (doublet with ferrocene band at 1108) cm.$^{-1}$. Bands attributable to P=O or P—O—H are not present in either spectra.

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

(13) M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958).

(14) G. P. Sollott, H. E. Mertwoy, S. Portnoy, and J. L. Snead, *J. Org. Chem.*, **28**, 1090 (1963).

Dehydro-1,1′-trimethyleneferrocene[1]

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As part of a study of the chemistry of bridged ferrocenes we were led to examine the transformation of α-keto-1,1′-trimethyleneferrocene tosylhydrazone (2) under conditions of the Bamford–Stevens reaction.[2] This base-catalyzed reaction has been shown to give initially a diazo compound, which may undergo cationic decomposition in the presence of proton-donor solvents, or in their absence decompose to carbenic intermediates and thence products of hydrogen migration, skeletal rearrangement, or insertion reactions.[3] We were principally interested in the latter mode of this reaction since the action of carbenes on metallocenes has not been widely explored,[4] and the possibility existed that an insertion reaction might lead to a cyclopropane-bridged ferrocene.

The tosylhydrazone (2) was readily prepared from the bridged ketone (1) by treatment with toluenesulfonylhydrazine under normal reaction conditions. Irradiation of 2 in dimethoxyethane solution in the presence of sodium methoxide failed to give any well-defined products. When decomposition was carried out thermally in dimethoxyethane solution with sodium methoxide, the products were α-methoxy-1,1′-trimethyleneferrocene and the ketone (**1**), while with dimethyl sulfoxide as solvent 1,1′-trimethyleneferrocene (**4**) in addition to **1** was isolated. However, when the tosylhydrazone was subjected to thermal decomposition in cyclohexane solution in the presence of sodium methoxide or preferably sodium hydride, moderate yields of dehydro-1,1′-trimethyleneferrocene (**3**) were obtained. The structural assignment for this substance is supported by its elemental analysis and by its n.m.r. spectrum (peaks at τ 3.96, 6.05, and 7.23, relative intensity 2:8:2),[5] and is confirmed by its conversion to **4** on catalytic hydrogenation. The new compound is the simplest member of a class of ferrocene derivatives possessing an unsaturated three-carbon bridge linking the two rings.[6]

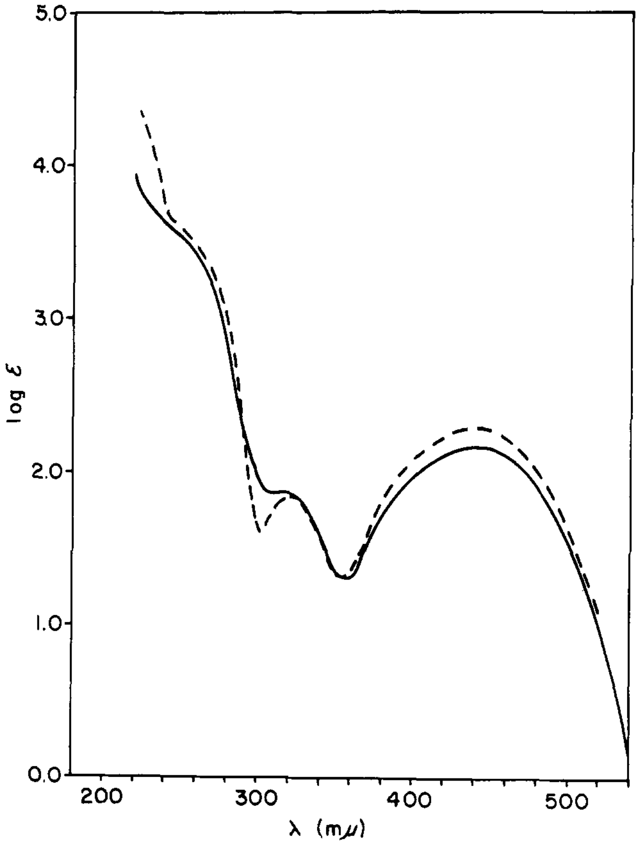

Fig. 1.—Ultraviolet and visible absorption spectra, taken in 95% ethanol: ......, 1,1′-trimethyleneferrocene (**4**); ———, dehydro-1,1′-trimethyleneferrocene (**3**).

Although the aprotic reaction conditions under which **3** is produced are those favoring the generation of a carbenoid intermediate, no products such as **5** or **6**, which might be expected to be formed from such an intermediate, were detected. In this respect the reaction of **2** more closely resembles the behavior of cyclohexanone and cyclopentanone tosylhydrazones

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(1) This research was supported by a grant (RG-5978) from the National Institutes of Health, U. S. Public Health Service.

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(3) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960). (b) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959). (c) P. Clarke, M. C. Whiting, G. Papenmeier, and W. Reusch, *J. Org. Chem.*, **27**, 3356 (1962).

(4) J. H. Richards, K. Plesske, and H. Werner, Abstracts, Symposium on Current Trends in Organometallic Chemistry, University of Cincinnati, Cincinnati, Ohio, June, 1963, p. 77.

(5) Determined in CDCl$_3$ solution at a concentration of approximately 60 mg./ml. and recorded at 60 Mc. with a Varian Model V-4300 spectrometer. Peak positions were calibrated against tetramethylsilane as internal standard by side banding.

(6) For other such compounds, *cf.* M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Am. Chem. Soc.*, **85**, 316 (1963); W. Mock and J. H. Richards, *J. Org. Chem.*, **27**, 4050 (1962). K. L. Rinehart, *et al.* [*J. Am. Chem. Soc.*, **84**, 3263 (1962)] had earlier attempted, without success, to prepare dehydro-1,1′-trimethyleneferrocene by dehydration of α-hydroxy-1,1′-trimethyleneferrocene.