The Reaction of 2,4,6-Triphenylpyrylium Ion with Phenylphosphine. 1-Hydroxy-1,2,4,6-tetraphenylphosphorabenzene

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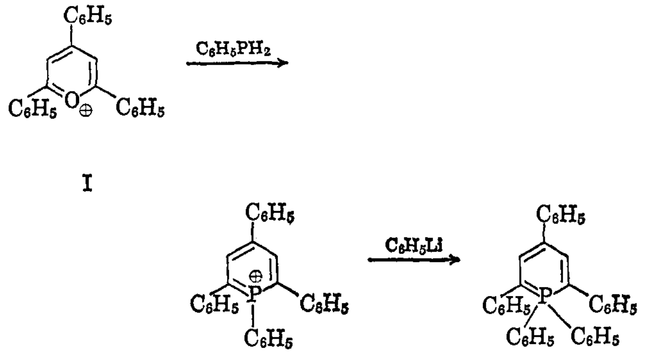
Abstract: Reaction of 2,4,6-triphenylpyrylium salts with phenylphosphine in pyridine produces a quantitative yield of two isomeric phosphorus heterocycles. The main product, an amorphous, yellow solid monoprotic acid, can be formulated as a hydrate of 1-hydroxy-1,2,4,6-tetraphenylphosphorabenzene (V). The crystalline isomer, to which it can be reversibly converted, has been identified as 2-hydroxy-1,2,4,6-tetraphenyl-2,3-dihydrophosphapyran oxide (IV).

The stability of many phosphorus ylids,[2,3] the possible aromatic character of phosphonitriles,[4] the aromatic character of 10-phenyl-9,10-dihydro-9,10-azaphosphaphenanthrene,[5] and the aromatic properties of several thiabenzenes[6] have stimulated our keen interest in preparing phosphorus analogs of the latter ("phosphorabenzenes").[7]

Since 2,4,6-triphenylpyrylium ion (and analogs) react readily with secondary amines to form pyridinium salts and with sulfide ion to form thiopyrylium ion,[8] the following procedure seemed of interest to explore.



I

II

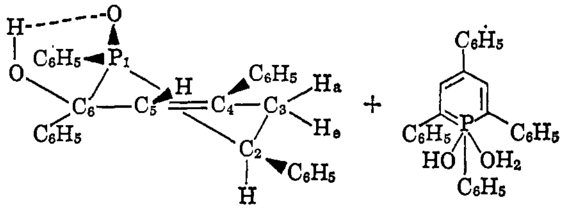
III

To date, the preparation of pentaphenylphosphorabenzene (III) by this procedure has been frustrated by the failure of the first step to produce the phosphorinium ion II. However, identification of the products formed in quantitative yield under the proper conditions has shed significant light on the failure to isolate the phosphorinium salts and on the properties of a phosphorabenzene.

Treatment of I (as fluoroborate) with excess phenylphosphine at 100° or in boiling methanol led to recovery of I in excellent yield. The trimethyl analog of I (as perchlorate) also failed to react with phenylphosphine in boiling methanol. A solution of dilithium phenylphosphide in tetrahydrofuran when treated with I perchlorate also led to a quantitative recovery of I perchlorate on acidification with 70% perchloric acid.

Reaction of I (as fluoroborate) with phenylphosphine in boiling pyridine rapidly led to a nearly quantitative conversion to a mixture of two isomers. We wish to suggest the following structures for the isomeric products, IV and V.

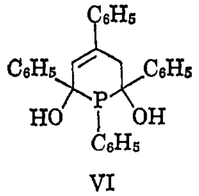
$$\text{I} + C_6H_5PH_2 \xrightarrow[\Delta]{C_5H_5N} C_5H_5\overset{\oplus}{N}H\ BF_4^{\ominus} +$$



IV, mp 257°

V, sp 70-80°

The elemental analyses of IV and V are identical and in agreement with II plus hydroxyl ion and water. We therefore first considered VI (and stereo or allylic isomers) as possible structures.



VI

It would seem unlikely that trivalent phosphorus is present in either IV or V, however, since they are not oxidized by hydrogen peroxide or oxygen, are not attacked by sulfur in refluxing benzene, and are unreactive to methyl iodide with or without solvent. Infrared spectra indicate chelated hydroxyl in IV at 3150 cm^{-1}, and also contain a band at 1150 cm^{-1} in IV and 1190 and 1170 cm^{-1} in V which could be due to the PO bond. The close structural relationship

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[1] Supported in part by National Science Foundation Grant No. 6270.

[2] G. Wittig, *Experientia*, **12**, 41 (1956).

[3] F. Ramirez and S. Levy, *J. Org. Chem.*, **21**, 488 (1956).

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[7] Preliminary communication of this work appeared in *Chem. & Ind.* (Japan), **16**, 715 (1963), and of work by G. Markl on the synthesis of three phosphorabenzene analogs in *Angew. Chem.*, **25**, 168, 669, 1121 (1963).

[8] K. Dimroth, *ibid.*, **72**, 331 (1960); R. Wizinger and P. Ulrich, *Helv. Chim. Acta* **39**, 207 (1956).

of IV and V is indicated by their interconversion, as indicated.

$$\mathrm{IV}\ \underset{\text{long standing in solution}}{\overset{\text{1. }H_2SO_4\text{, 2. }H_2O}{\rightleftarrows}}\ \mathrm{V}$$

The conversion of IV to V by potassium *t*-butoxide in DMSO has also been confirmed not only by the change in color and solubility but by the characteristic nmr spectrum of V.

While the infrared and ultraviolet spectra of IV and V are very similar, the nmr spectra showed some notable differences which can be accounted for readily by the structures assigned above. The nmr spectrum of the amorphous compound (V) shows a single broad aromatic band at τ 2.7–3.0 in carbon tetrachloride or deuteriochloroform. The location of the three exchangeable hydrogens on oxygen within this band was demonstrated by addition of a small amount of acetic acid. The τ 2.7–3.0 band decreased in intensity with respect to TMS by about 15% (as expected) and the acetic acid band at τ -2.6 (OH) was considerably greater in intensity than one-third of the methyl band at τ 7.9 (CH_3).

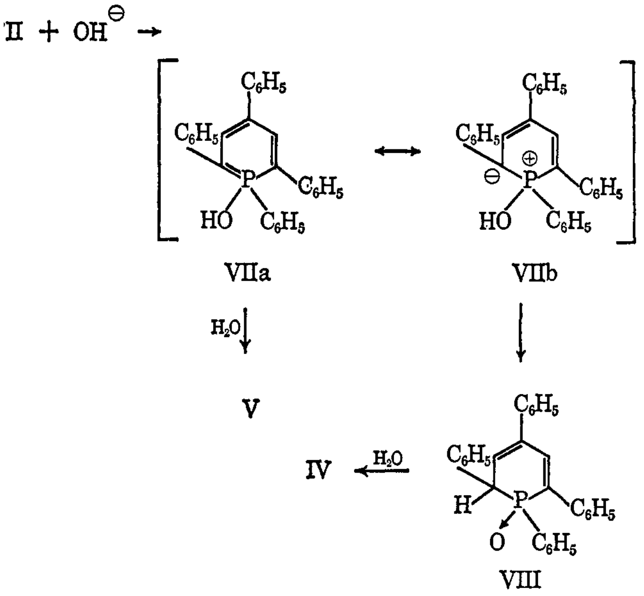
The insolubility of the crystalline isomer IV restricted the choice of solvents. In trifluoroacetic acid, the key features of the spectrum were a broad aromatic multiplet band at τ 2.65–2.9 (22 H), doublets at 3.8 (J = 22 cps), 4.95 (J = 12 cps), and 5.80 (J = 18 cps), and a triplet at 6.8 (J = 18 cps), each corresponding to one hydrogen atom. These bands, which have been checked by both 60- and 100-Mc nmr,[9] may be assigned to the hydrogens at carbons 5, 6, and 3, respectively. The large splitting constants may be ascribed to P^{31}, since it has been reported[10] that ($J_{P\text{-}\alpha H} \simeq$ 10–18 cps and $J_{P\text{-}\beta H} \simeq$ 15–30 cps. Weak hydrogen splitting may explain the breadth of these aliphatic hydrogen absorptions.

Spin decoupling data showed that the doublet at τ 5.8 and the triplet at 6.8 were converted to a singlet and doublet, respectively. This behavior may be explained in terms of structure IV by the assumption that its preferred conformation places one of the hydrogens at C-3 in an axial position (τ 5.8) where it is split only by the *gem*-hydrogen whereas the equatorial C-3 hydrogen is split by both the *gem*-hydrogen and the phosphorus with nearly equal splitting constants. The splitting constant between the axial 3-H and the phosphorus should be low since the dihedral angle is approximately 90°.

Support for this interpretation comes from examination of the nmr spectrum of IV in perdeuteriodimethyl sulfoxide. The four aliphatic hydrogens noted in trifluoroacetic acid appear in virtually identical positions. The aromatic multiplet shifts to τ 2.4–2.7 and a new sharp doublet appears at 3.0 (J = 20 cps). These peaks may be assigned to the 2-hydroxyl hydrogen, an assignment confirmed by their disappearance on addition of a drop of D_2O. The protonation of the phosphorus oxygen by trifluoroacetic acid evidently chemically shifts this doublet under the aromatic band (where the hydroxyl hydrogens of V all appear).

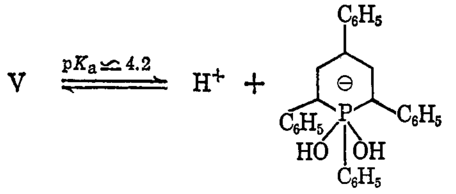
The considerable difference in the nature of phosphorus in IV and V is indicated by the shift of the P^{31} resonance ($\delta = -30$ ppm for IV in DMSO, $\delta = +22$ ppm for V in ethanol, both with respect to 85% phosphoric acid).[11] Ramirez has reported data for a number of phosphorane derivatives in the region of $\delta = +28$ to $+55$ ppm.[12]

It is of interest to speculate on the mechanism for formation of the PO bond. One intriguing possibility is that outlined as follows, involving coupling of transient intermediate II with hydroxyl ion to give the "phosphorabenzene" VII. Prototropic rearrangement of VII to VIII, followed by 1,4 addition[13] of water, would give IV.



The electron-attracting phosphine oxide group in VIII would seem likely to activate the addition of water to the conjugated diene system.

The coordination of a water molecule onto phosphorus in VII would lead to the amorphous isomer V. An interesting feature of the properties of V is the tenacity with which it holds the extra mole of water which we assign therefore to bonding to phosphorus. Phosphorus can assume a hexacovalent state and is believed to do so in crystalline PCl_5, which is assigned the structure of an ionic lattice of PCl_4^+ and PCl_6^-. Furthermore, bismuthic acid has six hydroxyls coordinated to pentavalent bismuth, so the acid is monoprotic. Titration of V in ethanol showed it to be a monoprotic acid easily titrated and with p$K_a \simeq$ 4.2. Association



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(9) We are greatly indebted to Dr. Fausto Ramirez, State University of New York, Stony Brook, for the 100-Mc spectra.

(10) T. H. Siddall, III, and C. A. Prohaska, *J. Am. Chem. Soc.*, **84**, 2502 (1962).

(11) We are indebted to Dr. Mildred Cohn and Dr. J. S. Leigh, Johnson Foundation, University of Pennsylvania, for the P^{31} spectra at 24.3 Mc.

(12) See, *e.g.*, F. Ramirez, A. N. Patwardhan, and S. R. Heller, *J. Am. Chem. Soc.*, **86**, 514 (1964).

(13) The 1,2 addition of water to give an isomer of IV with the 2-H and 6-OH transposed is an alternative possibility not excluded by our data.

Table I. Major Infrared Absorption for Compounds IV and V (in KBr)

IV		V	
λ	Rel int[a]	λ	Rel int[a]
3420	S (br)	3430	S (br)
3150	S (br)		
3055	M	3055	M
3025	M	3025	M
1590	M	1585	M
1485	M	1480	M
1438	M	1437	M
1430	M	1427	M
1382	M	1190	S
1150	S	1170	S
1100	M	1100	M
1060	M	1060	M
1025	M	1020	M
1015	M		
935	M		
875	M		
865	M		
745	S	745	S
690	S	685	S

[a] S, strong; M, medium; W, weak; br, broad.

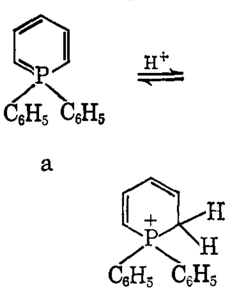
Table II. Reaction of I Fluoroborate with Phenylphosphine in Refluxing Pyridine

Time, min	15	30	60	120	210	120[a]	7200[b]
V, g	4.0	4.0	3.6	3.4	3.4	4.0	4.0
IV, g	0.27	0.35	0.64	0.8	0.85	0.05	0.02
$C_5H_5NH^+X^-$, g	1.55	1.65	1.6	1.65	1.65	1.6	1.6

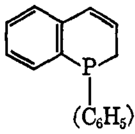
[a] Catalytic amount of pyridine in refluxing methanol. [b] Stirred at room temperature.

through the hydroxyls could explain the fact that the molecular weight in pyridine was about 30% greater than predicted for monomer.

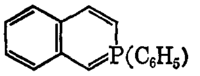
Markl[7] has presented preliminary reports of three analogous phosphorabenzene compounds, a, b, and c, indicating all three to be yellow or orange amorphous



a



b



c

solids which reversibly protonate to colorless, crystalline phosphonium salts as indicated for a. Since our compound V is formulated as a similar phosphorabenzene derivative and is found to be an acid as well, its rearrangement to IV may be initiated by shift of a proton to the α-carbon, VIIa to VIII, followed by addition of water to the unsaturation conjugated to the phosphine oxide.

The much lower stability of the phosphorabenzene ring system than that of thiabenzene is in accord with the view that the latter derives much of its stability from conjugation using a 3p orbital rather than by 3d–π bonding.[6]

Experimental Section

2,4,6-Triphenylpyrylium (I) fluoroborate was prepared by adding a solution of 80 g of I chloroferrate,[14] mp 278° (lit.[14] 277°), in 3.5 l. of boiling water to 125 ml of 40% fluoroboric acid. The precipitate (40 g) was recrystallized from acetone–ethanol as yellow needles, mp 252–253.5° (lit. mp 214–215°,[2] 225–226° [15]).

Anal. Calcd for $C_{23}H_{17}BF_4O$: C, 69.75; H, 4.33; F, 19.18. Found: C, 69.55; H, 4.54; F, 19.49.

Phenylphosphine was prepared by the method of Mann and Millar.[16] The infrared spectrum on sodium chloride showed a characteristic band at 4.4 μ.

Reaction of I with Phenylphosphine. A solution of 4 g (0.01 mole) of I fluoroborate and 1.55 g (0.015 mole) of phenylphosphine in 50 ml of dry, distilled pyridine was refluxed for 3 hr under nitrogen. The pyridine was removed by vacuum distillation and the resinous residue was extracted with benzene, leaving 2.4 g of nearly colorless solid. Water extraction of the latter gave 1.6 g (95%) of pyridinium fluoroborate, mp 212°, and 0.8 g of IV. The latter was recrystallized from *n*-butyl alcohol (or acetic acid) as pale white needles, mp 256–257°.

Anal. Calcd for $C_{29}H_{25}PO_2$: C, 79.80; H, 5.77; P, 7.10; mol wt, 436; active H, 4.00 (for one OH). Found: C, 79.62; 79.70; H, 5.77, 5.82; P, 7.11, 6.91; mol wt, 424 (vapor osmometer in pyridine); active H, 6.80 (by CH_3MgI).

Ultraviolet absorption in ethanol occurred at λ_{max} 205 mμ (log ε 4.56), with a shoulder at 250 mμ (log ε 4.08); major infrared bands are summarized in Table I.

The benzene extract above left a yellow residue which was purified by repeated dissolution in benzene and precipitation with petroleum ether to give 3.5 g of V as amorphous solid, mp 70–80°. It can also be purified by dissolving the residue in ethanol and pouring into a large volume of water. The semicolloidal suspension formed was either salted out or centrifuged.

Anal. Found: C, 79.75; H, 5.83; P, 6.76; mol wt, 570; active H, 6.60.

Ultraviolet absorption in ethanol occurred at λ_{max} 210 mμ (log ε 4.83) with a shoulder at 252 mμ (log ε 4.72); major infrared bands are summarized in Table I. The total yield of IV and V, 4.3 g, is over 95% of theory. Results of the study of reaction conditions are summarized in Table II.

The reaction of I perchlorate, mp 274–275° (lit.[17] mp 271°), and I iodide, mp 222° (lit.[18] mp 222°), with phenylphosphine in boiling pyridine also gave IV and V.

Interconversion of IV and V. IV dissolved in 80–100% sulfuric acid to give solutions which changed from purple to blue to green to brown. On pouring into cold water, material identical with V in solubility, melting point, and infrared spectra was obtained. V, on prolonged standing in methanol, ethanol, or benzene, gave precipitates which, on recrystallization, were found to be identical with IV.

Reaction of IV with Potassium *t*-Butoxide. It is reported[19] that phosphine oxides containing a C–H group adjacent to P react with aldehydes and ketones in the presence of potassium *t*-butoxide with the formation of olefins and phosphinic acids. When 0.56 g of IV, 0.15 g of acetophenone, and 0.16 g (excess) of potassium *t*-butoxide were refluxed in dry, distilled toluene for 8 hr, the whole reaction mixture turned bright red in 10 min. After 8 hr of refluxing, the reaction mixture was cooled and diluted with water. The water layer, after acidification, gave no diphenylphosphinic acid. The toluene layer, after evaporation, gave 0.30 g of starting material and a resinous mass which could not be solidified. Without acetophenone, however, IV gave quantitative yields of V with potassium *t*-butoxide in boiling toluene or *t*-butyl alcohol.

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Determination of pK_a of V. pH measurements were made at 26° using a glass electrode with a Beckmann G Model pH meter in 90% ethanol (standardized against aqueous buffer). The titration curve gave a sharp break at 1 equiv of base. The pH at half-neutralization was 4.2 on titration with either sodium hydroxide or potassium ethoxide.

D_2O Exchange Experiment. A saturated solution of compound IV in perdeuteriodimethyl sulfoxide was prepared in a 4-mm nmr tube. A few microliters of D_2O was added to this solution and the spectrum was recorded at intervals using a HR-60 nmr spectrometer. The doublet at τ 3.0 started disappearing and completely disappeared after 2 hr. No change in any other aliphatic hydrogen peaks was noted.

Spin Decoupling.[20] A Howlett-Packard audio frequency oscillator (200J) and counter (5512A) were used with a Varian integrator utilizing the field-sweep technique. The spectra were recorded for 5% solution of IV in trifluoroacetic acid, and the chemical shift of each proton was measured by the usual side-band technique. The integrator operated in conjunction with a 2-kc field modulator using a modulation index of 1989 cps. The chemical shift between the doublet at τ 5.8 and 6.8 was approximately 105 cps. The triplet at τ 6.8 completely collapsed to form a doublet at the irradiation frequency 1877 cps. The doublet at τ 5.8 collapsed to form a single peak at the irradiation frequency 2088 cps. The modulation frequency differences were 110 and 100 cps for the first and second irradiations, respectively, in agreement with the measured chemical shifts.

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(20) We are grateful to Dr. Kermit C. Ramey, Research and Development Department, Atlantic Refining Co., for these data.

Diaryl Sulfone Anion Radicals[1,2]

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Abstract: The anion radicals of diphenyl sulfone and *p,p'*-ditolyl sulfone possess epr spectra which are closely related to those of the corresponding hydrocarbons, biphenyl and *p,p'*-bitolyl. This indicates that a strong conjugation mechanism is operating between the two aromatic rings of the sulfone radicals. Gas chromatographic analysis shows that the spectra of the reduced diaryl sulfones are not due to the presence of biphenyl or *p,p'*-bitolyl impurities. The spin densities observed at the ring positions of the diphenyl sulfone anion radical have been accounted for by means of a Hückel calculation assigning $\alpha_{SO_2} = \alpha_C - 2.60\beta_{C-C}$ and $\beta_{C-SO_2} = 0.99\beta_{C-C}$ as Hückel parameters for the sulfone $d_{(3z^2-r^2)}$ orbital which has the correct symmetry to combine with the two aromatic rings. The spin density on the sulfone group is not large.

Previous work on anion radicals produced by the alkali metal reduction of a variety of aromatic sulfones has demonstrated that these species tend to possess considerably narrower epr (electron paramagnetic resonance) spectra than those formed from the corresponding sulfides as illustrated in Table I.[2a–c] These observations have been interpreted to indicate that the total spin density located on the aromatic rings of the sulfone anion radicals is lowered by the concentration of spin density on the sulfonyl groups. In this paper we report that the anion radicals of diphenyl sulfone and *p,p'*-ditolyl sulfone provide a contrasting situation; relatively little spin density appears to be withdrawn from their aromatic rings by the sulfonyl groups.

Table I

Compound	Spectral width of anion radical, gauss
Thiaxanthone	17.3
Thiaxanthone sulfone	14.5
Dibenzothiophene	25.4
Dibenzothiophene sulfone	10.7

Experimental Section

Commercial samples of the sulfones were recrystallized before use. Formation of the anion radicals of the sulfones was accomplished by reduction of the parent compounds over potassium mirrors in 1,2-dimethoxyethane at −70°.[4–6] Spectra were taken at that temperature since at higher temperatures the resolution attained was inferior, and the anion radicals were unstable. Measurements of the epr spectra were carried out on Varian spectrometers.[7]

Since the epr spectrum observed when diphenyl sulfone was reduced by potassium was found to have some resemblance to that of the well-known biphenyl anion radical, it was felt important to exclude the possibility that biphenyl might be formed during the reduction of the sulfone. Accordingly, after the metallic reduction of a sample of the sulfone was complete, the solution was opened to air and analyzed by vapor phase chromatography by the procedure previously described by Britt and Kaiser.[8,9] This analysis showed that biphenyl was not formed in a detectable amount.

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(1) Grateful acknowledgment is made to the Donors of the Petroleum Research Fund for support of this research. M. M. U. thanks the National Science Foundation for a Predoctoral Fellowship.

(2) Previous publications in the series on Conjugative Effects of Sulfur in Aromatic Anion-Radicals include (a) E. T. Kaiser and D. H. Eargle, Jr., *J. Am. Chem. Soc.*, **85**, 1821 (1963); (b) E. T. Kaiser and D. H. Eargle, Jr., *J. Chem. Phys.*, **39**, 1353 (1963); (c) D. H. Eargle, Jr., and E. T. Kaiser, *Proc. Chem. Soc.*, 22 (1964); (d) E. T. Kaiser and D. H. Eargle, Jr., *J. Phys. Chem.*, 69, 2108 (1965).

(3) To whom inquiries regarding this paper should be addressed at the University of Chicago.

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(7) A spectrometer at the U. S. Naval Research Laboratory was used with the kind consent of Dr. William B. Moniz of that laboratory.

(8) A. D. Britt and E. T. Kaiser, *J. Phys. Chem.*, **69**, 2775 (1965).

(9) The authors wish to thank Mr. P. L. Hall for performing the vapor phase chromatographic analysis.