

TABLE VI  
CONDUCTANCE DATA IN 100% SULFURIC ACID, 25.000°

Solute	M	A	Solute	M	A
II	0.0491	308.4	III	0.0522	308.0
	.0992	197.5		.0520	306.9
	.1118	200.1		.0988	203.7
	.2017	162.2		.0991	212.3
				.1920	149.2
				.1933	151.8

Ultraviolet and visible spectra were determined in 1-cm. ground glass stoppered quartz cells using a Beckman DK2 or DU spectrophotometer; n.m.r. spectra were obtained on a Varian Associates 60 Mc instrument.

**Reaction of Trichloromethylpentamethylbenzene (I) with Boron Trifluoride-Trifluoroacetic Acid.**—A deep red solution was obtained when 2.65 g. (0.01 mole) of I was treated with 20 ml. of trifluoroacetic acid, 2 ml. of trifluoroacetic anhydride and excess boron trifluoride, all well protected from atmospheric moisture. Removal of the solvent and  $\text{BF}_3$  *in vacuo* left a dark red residue which, on hydrolysis, gave a 95% yield of pentamethylbenzoic acid.

Experiments on other samples of this red solid showed it to be insoluble in benzene, hexane, carbon tetrachloride, slightly soluble in chloroform and readily soluble in ether. Its visible and n.m.r. spectra in trifluoroacetic acid containing a little trifluoroacetic anhydride were nearly identical with solutions of I in 100% sulfuric acid.

A sample of this red solid, prepared from 5.0 g. of I, was heated *in vacuo*, whereupon a colorless liquid, b.p. 130–142° (5 mm.), which solidified in the receiver was obtained, m.p. 180–185°, 3.28 g. Recrystallization from anhydrous ether gave 1.97 g. (57.1%) of white crystals, m.p. 212–214°, of what was shown to be pentamethylbenzoic anhydride (VII). The ether filtrate had a strong odor of trifluoroacetic acid.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{30}\text{O}_3$ : C, 78.65; H, 8.25; mol. wt., 366.5. Found: C, 78.75; H, 8.40; mol. wt. (Rast, camphor), 350, 360.

The white solid, m.p. 180–185°, was easily hydrolyzed. In a separate experiment, 1.000 g. of this solid, dissolved in 25 ml. of acetone and 50 ml. of 0.2159 N sodium hydroxide, was heated on the steam-bath for 15 minutes. After cooling, the excess alkali was titrated (24.37 ml. of 0.1953 N hydrochloric acid required for phenolphthalein end-point). The solution consumed 6.04 meq. of sodium hydroxide (theory for the mixed pentamethylbenzoic trifluoroacetic anhydride (VI) is 6.4 meq.).

Pentamethylbenzoic anhydride (VII) was very resistant to alkaline hydrolysis (only an insignificant amount of base was consumed when an alkaline aqueous acetone solution was refluxed for 3 hours). Reduction with lithium aluminum hydride in tetrahydrofuran, by standard techniques, gave pentamethylbenzyl alcohol, m.p. 159–160° (lit. value<sup>7</sup> 160.5°), in 51% yield. Its m.p. and infrared spectrum were identical to samples prepared by hydrolysis of chloromethylpentamethylbenzene and by lithium aluminum hydride reduction of pentamethylbenzoic acid.

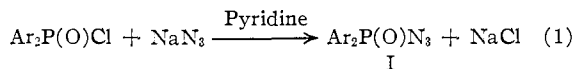
## COMMUNICATIONS TO THE EDITOR

### PREPARATION AND REACTIONS OF DIARYLPHOSPHONYL AZIDES

Sir:

In view of the recently reported reaction of sodium azide with trivalent phosphorus compounds to yield phosphinic nitrides<sup>1</sup> and the reaction of lithium azide with chlorobis(perfluoromethyl)phosphine to yield the sometimes stable azidobis(perfluoromethyl)phosphine,<sup>2</sup> we wish to report the synthesis and reactions of a series of new diarylphosphonyl azides having surprising thermal stability.

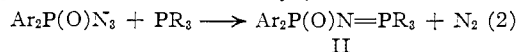
We have found that sodium azide reacts smoothly with diarylphosphonyl chlorides in anhydrous solvents such as pyridine, benzene, or acetonitrile to give the corresponding diarylphosphonyl azides (I) in good yields (Equation 1).



These azides have been found to be surprisingly stable to heat and shock. In a typical experiment, 6.99 g. (0.0297 mole) of diphenylphosphonyl chloride and 2.09 g. (0.032 mole) of sodium azide in 20 ml. of pyridine (distilled from calcium hydride) were heated under reflux with stirring for 18 hr. The solids were removed from the reaction mixture by filtration under argon and the solvent was removed from the filtrate at reduced pressure. The residual dark oil was distilled in a simple bulb-to-bulb apparatus at about 0.05 mm. to yield

6.31 g. (87.4% yield) of colorless diphenylphosphonyl azide boiling at 137–140°. A small amount of decomposition was indicated by a slight pressure increase. *Anal.* Calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_3\text{OP}$ : N, 17.28; P, 12.74; mol. wt., 243. Found: N, 17.2; P, 12.88; mol. wt., 247. In a similar manner, bis-*p*-tolylphosphonyl, bis-*p*-chlorophenylphosphonyl, and diphenylthiophosphonyl azides have been prepared and characterized by elemental analysis and molecular weight. The infrared spectra showed strong azide absorption at about 4.65  $\mu$ .<sup>3</sup> The diphenylphosphonyl azide was characterized further by solvolytic conversion to diphenylphosphonic acid, isopropyl diphenylphosphonate, and diphenylphosphonanilide, and by the reactions here described.

The diarylphosphonyl azides were found to react with a variety of tertiary phosphorus compounds, such as triphenylphosphine, phenyldimethylphosphine, and trimethylphosphite in an easily controlled liberation of one mole of nitrogen<sup>4</sup> (Equation 2). The resulting diarylphosphonimido-phosphoranes (II) are readily purified white solids



and have been found to be rather stable to hydrolysis with dilute hydrochloric acid and with dilute ammonium hydroxide solution. In a typical experiment, 1.38 g. (0.00526 mole) of triphenyl-

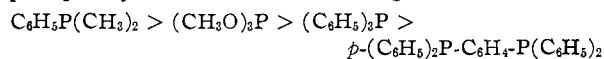
(3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 230.

(1) D. L. Herring, *Chem. and Ind.* (London), 717 (1960).  
(2) G. Thal, C. P. Haber and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).

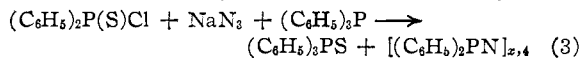
(4) The similar reaction of arylsulfonyl azides with trialkyl- and triarylsphosphites has appeared recently, J. Goardaler and H. Ullmann, *Ber.*, 94, 1067 (1961).

phosphine dissolved in 10 ml. of ether was added to 1.28 g. (0.00526 mole) of diphenylphosphonyl azide in 25 ml. of ether. When the mixture was heated under reflux for 4 hr., there was a slow precipitation of a white solid. The solid was removed by filtration, washed with ether and with dilute ammonium hydroxide solution and finally vacuum dried to yield white diphenylphosphonimidotriphenylphosphorane (75.7% yield), m.p. 150–151°, after recrystallization from isopropyl alcohol and water m.p. 170–171°. *Anal.* Calcd. for  $C_{30}H_{25}NOP_2$ : N, 2.93; P, 12.98; mol. wt., 477.5. Found: N, 2.92; P, 13.0; mol. wt., 480. In a similar manner, bis-*p*-tolylphosphonimidotriphenylphosphorane, m.p. 176–178°, bis-*p*-chlorophenylphosphonimidotriphenylphosphorane, m.p. 205–206°, diphenylphosphonimidotris-*p*-chlorophenylphosphorane, m.p. 135–140°, and diphenylthiophosphonimidotriphenylphosphorane, m.p. 179–179.5°, were prepared and fully characterized.

Qualitatively, it appears that the rate of reaction of tertiary phosphorus compounds with diphenylphosphonyl azide to liberate nitrogen is in the order



There was no evidence of reaction during the attempted preparation of diphenylphosphonimidotriphenylphosphorane,  $(C_6H_5)_2PN=P(C_6H_5)_3$ , by the *in situ* reaction of chlorodiphenylphosphine, sodium azide, and triphenylphosphine in pyridine at 115°. However, when diphenylphosphonyl chloride was added to a mixture of triphenylphosphine and sodium azide in pyridine at 115°, there was a rapid evolution of nitrogen and diphenylphosphonimidotriphenylphosphorane was obtained in a quantitative yield. Unexpectedly, the *in situ* reaction with diphenylthiophosphonyl chloride did not yield the diphenylthiophosphonimidotriphenylphosphorane, but gave an 87% yield of triphenylphosphine sulfide and the same diphenylphosphinic nitride polymer mixture (Equation 3) previously reported by Herring<sup>1,5</sup> from



which diphenylphosphinic nitride tetramer has been isolated. The tetramer was characterized by comparison with authentic material.<sup>6</sup>

This unexpected reaction is being investigated further. In addition, the azides and corresponding phosphoranes of Groups III, IV, V, and VI are under active investigation.

**Acknowledgment.**—This research was supported in part by the United States Air Force under Contracts AF 33(616)-6913 and -7810, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

WHITTIER RESEARCH LABORATORY      ROGER A. BALDWIN  
AMERICAN POTASH AND CHEMICAL CORPORATION  
WHITTIER, CALIFORNIA      ROBERT M. WASHBURN  
RECEIVED AUGUST 18, 1961

(5) C. P. Haber, D. L. Herring, and E. A. Lawton, *J. Am. Chem. Soc.*, **80**, 2116 (1958).

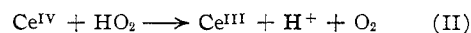
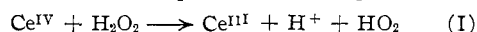
(6) We wish to thank Mr. D. L. Herring, U. S. Naval Ordnance Laboratory, Corona, Cal., for the sample of diphenylphosphinic nitride tetramer and its infrared spectrum.

## THE ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF THE $HO_2$ RADICAL IN AQUEOUS SOLUTION<sup>1</sup>

Sir:

In a recent note J. W. T. Spinks<sup>2</sup> reported an e.p.r. spectrum of what is believed to be the  $HO_2$  free radical in solid ice at liquid nitrogen temperature. We wish to support his findings by a similar e.p.r. spectrum obtained in an aqueous solution at room temperature.

The basis of our experiment is the generation of  $HO_2$  when ceric sulfate interacts with hydrogen peroxide in strong acid solutions. This reaction has been known in analytical chemistry for some time<sup>3</sup> and has been reinvestigated independently by Stein<sup>4</sup> and Anbar.<sup>5</sup> While Stein postulates that the reaction takes place in two steps



Anbar proposes as an intermediate the complex  $Ce^{III}\cdot OOH$ .

The set-up used in the present investigation consists of a flow-system with a mixing chamber located 0.5 cm. above the cavity of a Varian EPR Spectrometer. The mixed solutions flow through a quartz tube which passes through the center of the cavity. The flow velocity of the solutions can be varied over a wide range.

When a 0.001 *M* ceric sulfate solution is mixed with a 0.1 *M* solution of hydrogen peroxide, an e.p.r. spectrum is obtained as shown in Fig. 1.

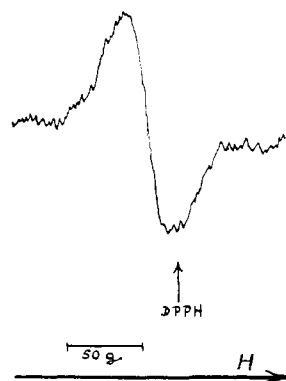


Fig. 1.—E.p.r. spectrum of the  $HO_2$  radical produced during the interaction of  $Ce(HSO_4)_4$  with hydrogen peroxide in 0.8 *N* sulfuric acid solution; vertical line indicates the position of DPPH signal.

The *g* for this species is 2,016 with a line width of 27 gauss. The magnitude of the spectrum is a function of the flow velocity as well as the concentration of solute in the solutions. When the flow of the solutions is stopped while in the cavity, the spectrum disappears rapidly. The individual solutions or an aged mixture of the two gave only background noise.

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. Kroh, B. C. Green and J. W. T. Spinks, *J. Am. Chem. Soc.*, **83**, 2201 (1961).

(3) Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 8th Ed., Vol. II, p. 752.

(4) S. Baer and G. Stein, *J. Chem. Soc.*, 3176 (1953).

(5) M. Anbar, *J. Am. Chem. Soc.*, **83**, 2031 (1961).