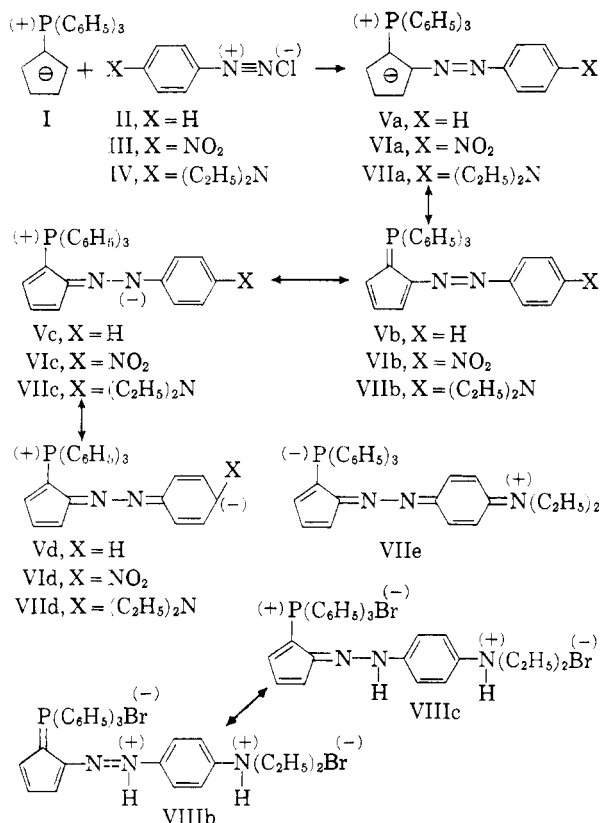


I with the diazonium salts can be carried out in a strongly acidic aqueous solution, in which I is soluble as its salt, without added organic solvent.



#### EXPERIMENTAL<sup>4</sup>

*Triphenylphosphonium-[2-(p-diethylaminophenylazo)-cyclopentadienyliide]* (VII). A solution of *p*-diethylaminobenzenediazonium chloride-zinc chloride-monohydrate, *p*-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-N<sub>2</sub>Cl·ZnCl<sub>2</sub>·H<sub>2</sub>O (3.89 g.) in water (50 ml.) was treated with sodium acetate (2 g.) and mixed with a solution of triphenylphosphoniumcyclopentadienyliide (I) (3.26 g.) in methylene chloride, at room temperature. The brown mixture was stirred 1 hr. and then treated with aqueous sodium hydroxide. The methylene chloride layer was concentrated *in vacuo* and the residue was dissolved in hot methanol. The azophosphinethylene VII (4.13 g., 83% yield, m.p. 194–196°) crystallized as orange-brown crystals, on cooling. It was recrystallized from benzene-methanol (3.4 g., m.p. 199–201°). The analytical sample was green in the form of large crystals and red-orange when powdered; bands (KBr) at 6.28(s), 6.70(w), 6.86(m), 7.02(m), 7.42(m), 7.60(s), 7.92(s), 8.42(m), 8.70(m), 9.02(m), 9.55(w) and 9.75(m) μ.

*Anal.* Calcd. for C<sub>33</sub>H<sub>32</sub>N<sub>3</sub>P: C, 79.0; H, 6.4; N, 8.4. Found: C, 78.9; H, 6.4; N, 8.8.

*Ultraviolet absorption spectra of the p-diethylaminophenylazophosphinethylene VII.* λ<sub>max</sub> in acetonitrile: 478 mμ (ε 34,000), maroon color. λ<sub>max</sub> in 95% ethanol: 483 mμ (ε 30,000) and inflections at 222 mμ (ε 52,300), 252 mμ (ε 18,000) and 345 mμ (ε 8,000). λ<sub>max</sub> in acid medium: (a) 423 mμ (ε 31,000), 1 ml. of a solution containing 12.1 mg. of the azophosphinethylene VII in 25 ml. of 95% ethanol, diluted to 25 ml. with 5% aqueous hydrochloric acid; (b) same spectra when dilution was performed with 0.1N and

with 0.01N hydrochloric acid; (c) ε = 24,000 at 423 mμ and no inflection at 483 mμ, when dilution was made with a buffer of pH ~ 5; (d) ε = 10,500 at 483 mμ and no inflection at 423 mμ when dilution was made with a buffer of pH ~ 6; turbidity was noticed; (e) solid precipitated when buffer of pH ~ 7 was employed for the dilution.

*Triphenylphosphonium-[2-(p-diethylaminophenylazo)-cyclopentadienyliide] dihydrobromide* (VIII). The *p*-diethylaminophenylazophosphinethylene VII (0.220 g.) was dissolved in 10 ml. of methanol containing ca. 7 drops of concentrated hydrobromic acid. Ethyl acetate was added and the dark yellow precipitate which formed was collected; weight: 0.255 g. The analytical sample was obtained from methanol-ethyl acetate and had m.p. 181–183° (Kofler, corr.); bands (KBr) 6.42 (m), 6.62 (m), 7.02 (m), 7.42 (s), 7.95 (s); 9.00 (s), 9.70 (m) μ.

*Anal.* Calcd. for the monohydrobromide C<sub>33</sub>H<sub>32</sub>N<sub>3</sub>PBr: C, 67.9; H, 5.8; for the dihydrobromide C<sub>33</sub>H<sub>34</sub>N<sub>3</sub>PBr<sub>2</sub>: C, 59.6; H, 5.1. Found: C, 58.8; H, 5.4.

*Coupling of triphenylphosphoniumcyclopentadienyliide (I) with benzenediazonium chloride (II) in aqueous mineral acid solution.* A benzenediazonium chloride solution was prepared in the usual manner from 0.186 g. of aniline, 0.5 ml. of concd. hydrochloric acid, 3 g. of ice, and 0.138 g. of sodium nitrite (in 3 ml. of water). This cold solution (0–5°) was quickly added to a solution containing 0.652 g. of triphenylphosphoniumcyclopentadienyliide (I) in 50 ml. of 10% aqueous hydrobromic acid, kept at 10°. An immediate red-orange precipitate appeared. After 40 min., the solid was collected; weight: 0.951 g., m.p. 221–228°. This solid, which is triphenylphosphonium-(2-phenylazo)-cyclopentadienyliide hydrobromide,<sup>2a</sup> was dissolved in methanol (25 ml.). The filtered solution was treated with 5% aqueous sodium hydroxide and the precipitate thus formed (0.65 g., crude m.p. 226°) was recrystallized from benzene-methanol. The yield of triphenylphosphonium-(2-phenylazo)cyclopentadienyliide<sup>2a</sup> (V) was 0.46 g. (71%), m.p. 238–240°.

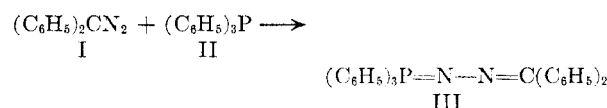
DEPARTMENT OF CHEMISTRY  
COLUMBIA UNIVERSITY  
NEW YORK 27, N. Y.

### Reaction of Diazocyclopentadiene with Triphenylphosphine

FAUSTO RAMIREZ AND STEPHEN LEVY<sup>1</sup>

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The reaction of aliphatic diazo compounds with tertiary phosphines has been studied by Staudinger and his co-workers.<sup>2,3</sup> Diphenyldiazomethane (I) was said<sup>2</sup> to react with triphenylphosphine (II) to give a "phosphazine" III, a yellow crystalline substance which decomposed at 173°. When the phosphazine III was heated to 185° *in vacuo*, triphenylphosphine-diphenylmethene IV was obtained as red crystals, m.p. 170–172°.

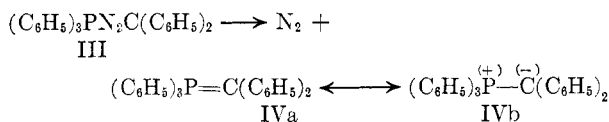


(1) Texas Co. Fellow, 1956–1957

(2) (a) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 2, 619 (1919); *Helv. Chim. Acta*, 2, 635 (1919).

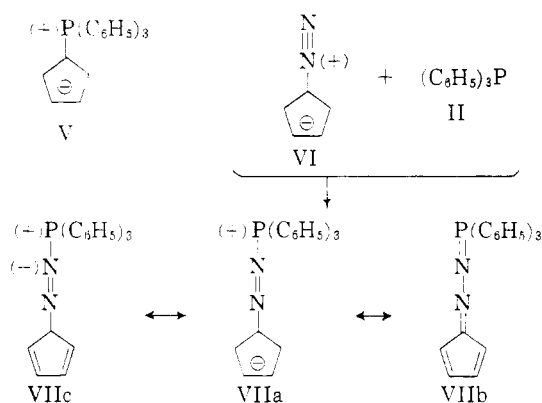
(3) Cf. G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc. New York, N. Y. 1950; pp. 28, 297.

(4) Analyses by Micro-Tech. Laboratories, Skokie, Ill.; melting points are corrected.



We have recently described<sup>4</sup> the preparation of triphenylphosphoniumcyclopentadienylide (V) from triphenylphosphine and the dibromocyclopentenes. It was therefore of interest to investigate the reaction of triphenylphosphine (II) with diazocyclopentadiene<sup>5</sup> (VI) as a new route to the phosphinemethylene V.

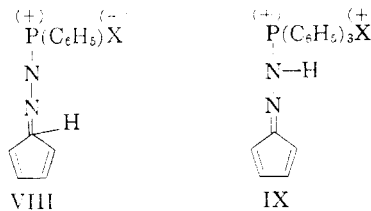
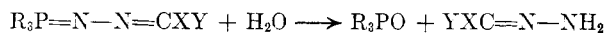
The orange phosphazine VII, m.p. 122–124° was obtained readily and in good yield, but all attempts to effect its thermal decomposition to the phosphinemethylene V have failed.



The ultraviolet spectrum of the phosphazine VII in 95% ethanol exhibits a strong and symmetrical band with maximum at 345 m $\mu$  ( $\epsilon$  20,000). This band is absent in the phosphinemethylene V and probably arises from conjugation of the cyclopentadienylide and the phosphonium groups through the azo-function  $-\text{N}=\text{N}-$ , by operation of *d*-orbital resonance in phosphorus (VIIa $\longleftrightarrow$ VIIb).

In 95% ethanol solution containing hydrochloric acid, the phosphinemethylene<sup>4</sup> V has well defined maxima at 263 m $\mu$  ( $\epsilon$  10,300), 269 m $\mu$  ( $\epsilon$  12,100), and 276 m $\mu$  ( $\epsilon$  11,200). Similar maxima are observed in the spectrum of the phosphazine VII in the same medium. These bands probably correspond to the triphenylphosphonium absorption superimposed on the cyclopentadiene absorption,<sup>4</sup> as in formula VIII for one of the possible tautomeric forms of the protonated phosphazine. The spectrum of the phosphazine VII in acid medium exhibits also a maximum at 295 m $\mu$  ( $\epsilon$  13,000) not present in the spectrum of the phosphinemethylene V. Interpretation of this spectrum is complicated by the possibility of other tautomeric forms such as the interesting phosphoniumhydrazone IX. It seems clear, however, that no significant hydrolysis of the phosphazine in the acidic aqueous alcoholic medium

took place. Staudinger<sup>2</sup> has called attention to the hydrolysis of other phosphazines to the hydrazone and the tertiary phosphine oxide:



#### EXPERIMENTAL<sup>6</sup>

*Diazocyclopentadiene* (VI) was prepared as described by Doering and DePuy<sup>5</sup> and collected at 47–49° (45–48 mm.). All operations with diazocyclopentadiene should be carried out cautiously. During one preparation, a violent explosion took place after distillation.

*Reaction of diazocyclopentadiene* (VI) with triphenylphosphine (II). A solution of diazocyclopentadiene (VI) (0.90 g.) in petroleum ether (b.p. 30–60°) (3 ml.) was mixed with a solution of triphenylphosphine (II) (2.65 g.) in anhydrous ether (20 ml.). An orange solid separated after a few minutes and was collected after 2 hr., washed with ligroin and dried. Crude weight: 29 g., m.p. ca. 117°; the infrared spectrum was identical with that of the analytical sample, m.p. 117–119° (corr.) obtained from methylene chloride–petroleum ether. The phosphazine VII has bands (KBr) at 6.60 (s), 6.75 (m), 6.90 (w), 7.00 (s), 7.45 (m), 9.0 (vs. broad), 10.27 (vs), 10.92 (s), 11.30 (vs), 11.80 (s), and 12.95 (vs)  $\mu$ . The ultraviolet spectrum in 95% ethanol had  $\lambda_{\text{max}}$  345 m $\mu$  ( $\epsilon$  20,000), a broad band centered at ca. 300 m $\mu$  ( $\epsilon$  8,000), three slight maxima at 262, 268, and 275 m $\mu$  ( $\epsilon$  6,000) and a shoulder at 220 m $\mu$  ( $\epsilon$  36,600). The spectrum in 95% ethanol containing hydrochloric acid had  $\lambda_{\text{max}}$  295 m $\mu$  ( $\epsilon$  13,600), 278 m $\mu$  ( $\epsilon$  15,200), 270 m $\mu$  ( $\epsilon$  15,200), 268 m $\mu$  ( $\epsilon$  13,000; inflexion), and 225 m $\mu$  ( $\epsilon$  30,000).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{15}\text{N}_2\text{P}$ : C, 78.0; H, 5.4; Found: C, 78.3; H, 5.7.

The phosphazine VII was heated to 165–175° alone and in the presence of copper powder. The thermal decomposition was also attempted in boiling xylene. No triphenylphosphoniumcyclopentadienylide V could be detected among the tarry decomposition products.

DEPARTMENT OF CHEMISTRY  
COLUMBIA UNIVERSITY  
NEW YORK 27, N. Y.

(6) Analysis by Microtech Laboratory, Skokie, Ill.

### Detection of Thiocarbonyl Groups by Infrared Spectroscopy

E. SPINNER

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Until recently only meagre and contradictory information was available concerning the position of thiocarbonyl bands in the infrared,<sup>1</sup> but it has now

(4) (a) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 67 (1957); (b) *J. Am. Chem. Soc.*, **79**, 6167 (1957).

(5) W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

(1) J. I. Jones, W. Kynaston, and J. L. Hales, *J. Chem. Soc.*, 614 (1957).