

isolated as the hydrochloride by treating the dry ether solution with anhydrous hydrogen chloride to obtain the following compounds:

*2,3,4,5-Tetramethyl-β-phenethylamine hydrochloride* (30%); m.p. 246–248°; colorless platelets (ethanol-ether).

*Anal.* Calcd. for C<sub>12</sub>H<sub>20</sub>ClN: Cl, 16.6; N, 6.55. Found: Cl, 16.4; N, 6.49.

*2,3,4,6-Tetramethyl-β-phenethylamine hydrochloride* (69%); m.p. 283–285° (dec.); colorless platelets (ethanol).

*Anal.* Calcd. for C<sub>12</sub>H<sub>20</sub>ClN: Cl, 16.6; N, 6.55. Found: Cl, 16.3; N, 6.54.

*2,3,5,6-Tetramethyl-β-phenethylamine hydrochloride* (79%); m.p. 360–365° (subl.); colorless plates (ethanol-water).

*Anal.* Calcd. for C<sub>12</sub>H<sub>20</sub>ClN: Cl, 16.6; N, 6.55. Found: Cl, 16.3; N, 6.45.

*2,3,4,5,6-Pentamethyl-β-phenethylamine hydrochloride* (40%); m.p. 340° (subl.); colorless needles (ethanol-water).

*Anal.* Calcd. for C<sub>13</sub>H<sub>22</sub>ClN: Cl, 15.6; N, 6.15. Found: Cl, 15.7; N, 6.0.

*Acknowledgments.* This research was supported by Public Health Service Grants Nos. M-1588 and M-600.

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### Phosphinemethylenes. IV. Coupling of Triphenylphosphoniumcyclopentadienylide with *p*-Diethylaminobenzediazonium Chloride

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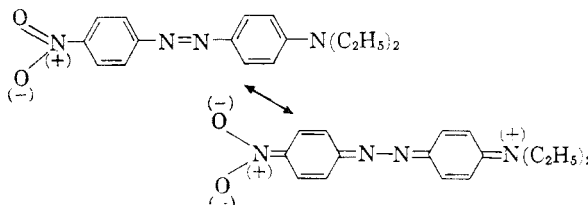
Received July 18, 1958

We described recently<sup>2a</sup> the preparation of the brightly colored phenylazophosphinemethylene (V) and *p*-nitrophenylazophosphinemethylene (VI), from the coupling reaction of triphenylphosphoniumcyclopentadienylide (I)<sup>2b</sup> with the corresponding diazonium halide, II and III. In these reactions, a methylene chloride solution of the phosphine methylene I was added to an aqueous solution of the diazonium chloride, buffered with sodium acetate. Using the same procedure, we have prepared triphenylphosphonium-[2-(*p*-diethylaminophenylazo)cyclopentadienylide] (VII), a stable, crystalline substance, m.p. 199–200°, which is green in the form of large crystals and red-orange when powdered.

The *p*-diethylaminophenylazophosphinemethylene (VII) formed a crystalline *dihydrobromide*, which, as previously discussed,<sup>2a</sup> has probably the structure of a cyclopentadienone phenylhydrazone (VIII).

It is of interest to compare the ultraviolet absorption spectra of the series of azophosphine-

methylenes having electron-attracting and electron-releasing groups in conjugation with the phosphorus. Table I shows the main absorption maxima of these substances in neutral and in acidic aqueous alcohol. In the azophosphinemethylenes (*neutral* medium), both types of groups exert a powerful bathochromic effect, although the *p*-nitro effect is considerably greater. We have suggested<sup>2a</sup> that these bands are due to electronic transitions from ground states of type  $a \leftrightarrow b$  (with little contribution from structures  $c$  and  $d$ ) to electronically excited states of type  $c \leftrightarrow d$ . It may well be that operation of *d*-orbital resonance in phosphorus permits a significant contribution of structure VIIe to the excited state. Some of the electronic features of 4'-nitro-4-diethylaminoazobenzene<sup>3</sup> can be recognized in the substituted azophosphinemethylenes VI and VII



Perhaps it is valid to regard the phosphoniumcyclopentadienylide moiety in the azophosphinemethylenes as both an electron-source and an electron sink, depending on the demands of the *p*-phenyl substituent X.

TABLE I  
ULTRAVIOLET SPECTRA OF TRIPHENYLPHOSPHONIUM-[2-(X-PHENYLAZO)]CYCLOPENTADIENYLIDES

X	Neutral $\lambda_{\max}$ , M $\mu$ ( $\epsilon$ )	Acid $\lambda_{\max}$ , M $\mu$ ( $\epsilon$ )
<i>p</i> -H	455 (20,600)	440 (25,300)
<i>p</i> -N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	483 (30,000)	423 (31,700)
<i>p</i> -NO <sub>2</sub>	537 (28,300)	436 (36,300)

In the hydrobromides, or in the azophosphinemethylenes in *acid* medium, both types of groups exert a weak hypsochromic effect, but now the *p*-diethylamino effect is somewhat greater. The bands in acid medium can be interpreted<sup>2a</sup> in terms of electronic transitions from a ground state of type VIIc to an electronically excited state of type VIIIb. In this anomalous<sup>2a</sup> phenylhydrazone absorption, the nature of the group X in the *p*-phenyl position is not very significant. In acid medium, the diethylammonium group is, as the nitro-group, strongly electron attracting, affecting adversely the stability of structure VIIIb.

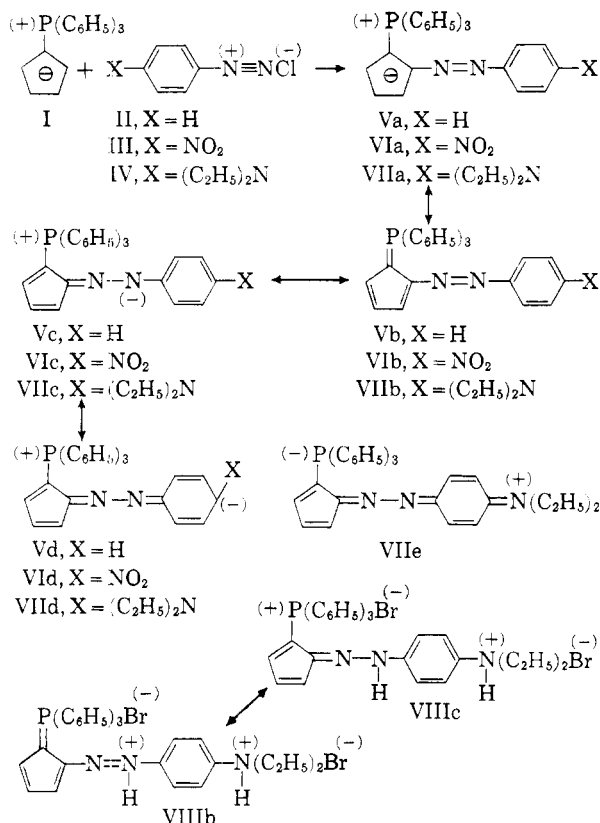
It may be pointed out that, at least in some cases, the coupling reaction of the phosphinemethylene

(1) Texas Co. Fellow, 1956–1957.

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

(3) (a) E. Sawicki, *J. Org. Chem.*, **21**, 605 (1956); (b) W. S. McGuire, T. F. Izzo, and S. Zuffanti, *J. Org. Chem.*, **21**, 632 (1956).

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)  $\mu$ .

*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.*  $\lambda_{\max}$  in acetonitrile: 478  $m\mu$  ( $\epsilon$  34,000), maroon color.  $\lambda_{\max}$  in 95% ethanol: 483  $m\mu$  ( $\epsilon$  30,000) and inflections at 222  $m\mu$  ( $\epsilon$  52,300), 252  $m\mu$  ( $\epsilon$  18,000) and 345  $m\mu$  ( $\epsilon$  8,000).  $\lambda_{\max}$  in acid medium: (a) 423  $m\mu$  ( $\epsilon$  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)  $\epsilon$  = 24,000 at 423  $m\mu$  and no inflection at 483  $m\mu$ , when dilution was made with a buffer of pH  $\sim$  5; (d)  $\epsilon$  = 10,500 at 483  $m\mu$  and no inflection at 423  $m\mu$  when dilution was made with a buffer of pH  $\sim$  6; turbidity was noticed; (e) solid precipitated when buffer of pH  $\sim$  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)  $\mu$ .

*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°.

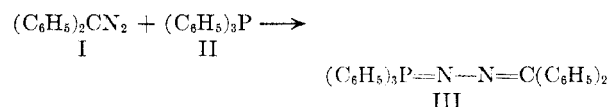
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### Reaction of Diazocyclopentadiene with Triphenylphosphine

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Received July 18, 1958

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.