From the product of the reaction described by Schaad[6] (77 g. of phenol, 20 g. of butadiene, 25 g. of U.O.P. polymerization catalyst #2, 200°, 4 hr.), there was obtained besides much unreacted phenol, 11 g. of a phenolic fraction, A, b.p. 65–130° (1 mm.), $n^{25}D$ 1.540; and 30 g. of dark, resinous material. The spectrum of A showed a strong band at 13.3 μ characteristic of *o*-substitution, only a weak band at 12.1 μ and no band at 10.35–10.40 μ, the position of one of the strongest bands of II, indicative of a symmetrically disubstituted *trans* double bond.

Acidity Functions.[19]—With anthraquinone as the Hammett indicator, the alkanesulfonic acid and polyphosphoric acid and the mixtures of 85% phosphoric acid and sulfuric acid and of polyphosphoric acid and phosphoric acid used as catalysts at 15–25° show acidity functions H_0 ranging from −6 to −7. The H_0 of 68–70% aqueous sulfuric acid is −5.0 to −5.2.

***p*-1-Butenylphenol** (I).—A mixture of 90 g. of II and 5 g. of 5% palladium-on-charcoal (Baker and Co., lot #785, activity 985) was refluxed under inert gas for 25 minutes when the reaction temperature had risen to 260°. The product was dissolved in ligroin and filtered, the solvent removed and the red, viscous oil (86 g.) distilled to yield a first fraction A (46 g.), b.p. 80–150° (0.5 mm.); a second fraction B (19 g.), b.p. 150–210° (0.5 mm.); and an orange resinous residue (18 g.). Crystallization of A from heptane yielded 5.5 g. of shiny, white platelets of the less soluble isomer I, identical with the compound prepared by alkali isomerization[1] of II. The infrared spectra of I and II in carbon disulfide are quite similar, except that I exhibits an intense band at 11.8 μ absent in the spectrum of II. The heptane mother liquor from I yielded 40 g. of unreacted II. Fraction B consisted largely of a colorless dimeric diphenol, b.p. 187–190° (0.4 mm.), which was accompanied by a fiery red impurity.

Anal. Calcd. $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.79; H, 8.13.

Butenylanisoles.—Anisole reacts much like phenol at 10–30°; mixed butenylanisoles were prepared in good yields with concd. sulfuric acid and with a 2:1 mixture of polyphosphoric acid and 85% phosphoric acid; b.p. 75–110° (10 mm.), $n^{25}D$ 1.519, strong bands at 12.1 and 13.3 μ, indicating *o*- and *p*-substitution.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.87; H, 9.00.

Acknowledgment.—I wish to thank Professors M. G. Ettlinger and C. D. Hurd for valuable advice.

MILWAUKEE, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

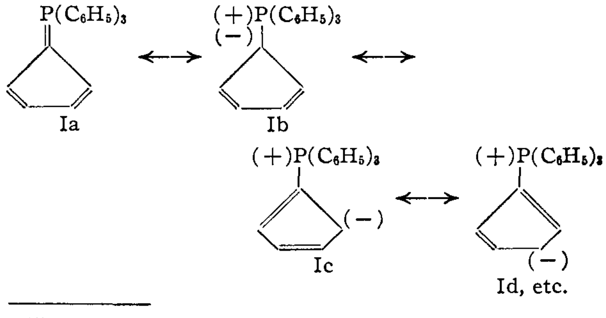
Phosphinemethylenes. III. A New Class of Azo Dyes Containing Phosphorus

BY FAUSTO RAMIREZ AND STEPHEN LEVY[1]

RECEIVED MAY 22, 1957

Triphenylphosphoniumcyclopentadienylide (I) couples readily with diazonium salts producing a new class of brightly colored azo dyes. The coupling reaction occurs at a position in the five-membered ring which preserves the stable cyclopentadienide system and which gives rise to the longest of the possible conjugated systems terminating at a phosphorus atom. The ultraviolet and infrared absorption spectra, and the dipole moment are described for the coupling products (VI and VII) from benzenediazonium chloride and *p*-nitrobenzenediazonium chloride. With hydrobromic acid, the azophosphinemethylenes VI and VII yield phenylhydrazones of a simple phosphonium derivative of cyclopentadienone (VIII and IX). The reaction of triphenylphosphine with pure *cis*-3,5-dibromocyclopentene leads, after alkaline treatment, to triphenylphosphoniumcyclopentadienylide (I) in yields comparable to those realized when the phosphine is added to the mixture of dibromides resulting from cyclopentadiene and bromine in chloroform solution.

Recent investigations in this Laboratory[2] have led to the preparation of several new types of phosphinemethylenes or phosphorus ylides[3] ($R_3P{=}CXY \longleftrightarrow R_3\overset{(+)}{P}{-}\overset{(-)}{C}XY$), and to the examination of their physical and chemical properties. Of particular interest is triphenylphosphoniumcyclopentadienylide[2a] (I), a remarkably stable, pale yellow, high melting (229–231°) substance with a dipole moment (6.99 *D*) which suggests roughly equal contributions from a homopolar structure, presumably Ia, and several dipolar forms (Ib-Id).



Ia Ib Ic Id, etc.

In line with recent views on non-benzenoid aromatic systems,[2a] it appeared of interest to explore the behavior of the phosphinemethylene I toward electrophilic reagents. This paper is concerned with the coupling reaction of I and diazonium salts.

The Reaction of Triphenylphosphoniumcyclopentadienylide (I) with Diazonium Salts. Coupling Reaction with Benzenediazonium Chloride (II).—The course of this reaction and the proof of structure of the product are formulated in Chart I. When a methylene chloride solution of the phosphinemethylene I was added to an aqueous solution of benzenediazonium chloride (II), buffered with sodium acetate, an immediate reaction occurred. The reddish-orange substance, m.p. 239–240°, which was isolated in 88% yield, had the formula $C_{29}H_{23}N_2P$ and was shown to be triphenylphosphonium-(2-phenylazo)-cyclopentadienylide (VI). This structure was established as follows. (1) The coupling product or azophosphinemethylene VI was converted by hydrobromic acid into an orange **hydrobromide** VIII of m.p. 236–237° and formula $C_{29}H_{24}N_2PBr$. (2) This hydrobromide VIII had the structure of a cyclopentadienone-phenylhydra-

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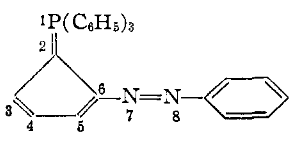
[1] Texas Co. Fellow, 1956–1957. From part of the Ph.D. Thesis of S. Levy.

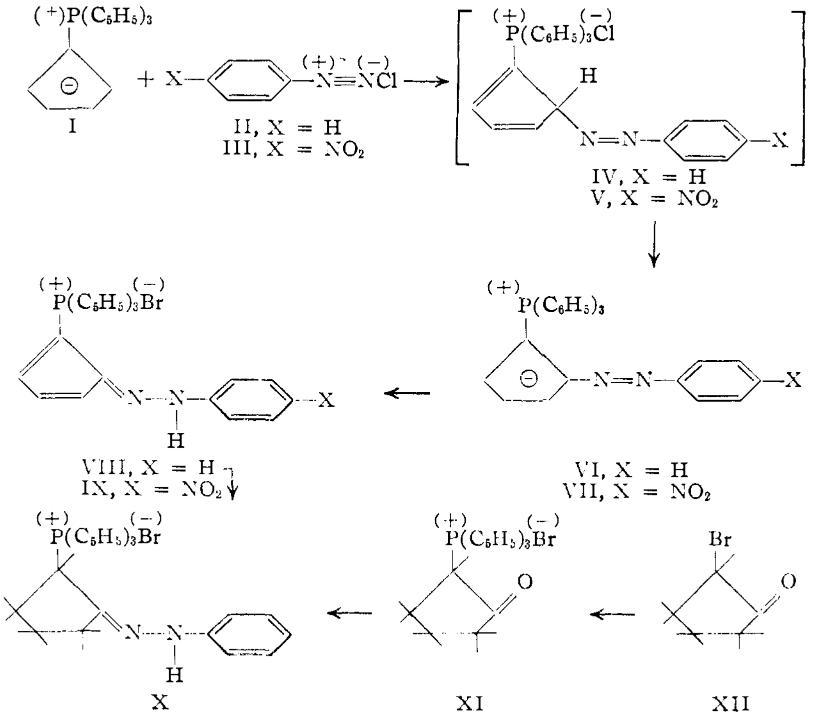
[2] (a) F. Ramirez and S. Levy, THIS JOURNAL, **79**, 67 (1957); (b) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957); (c) THIS JOURNAL, **78**, 5614 (1956).

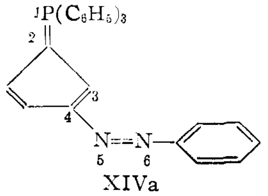
[3] For the nomenclature of these compounds, see ref. 2b, footnote 1. References to past and current work on phosphinemethylenes are found in ref. 2 and in G. Wittig, *Experientia*, **12**, 41 (1956).



VIa

CHART I





XIVa

zone and not that of the phenylazo tautomer (such as IV of Chart I, with bromine in place of chlorine), since the infrared spectrum of the solid in KBr-pellet or of a solution in chloroform had a band in the NH region and a very strong band at 6.4 μ. The latter is presumably due to the conjugated C=N group of a phenylhydrazone.[4] (3) Catalytic hydrogenation of the hydrobromide VIII afforded the colorless (2-phenylhydrazonocyclopentyl)-triphenylphosphonium bromide (X). (4) An authentic sample of the alicyclic phenylhydrazone X was prepared from (2-oxocyclopentyl)-triphenylphosphonium bromide (XI) and phenylhydrazine. (5) The oxophosphonium bromide XI was made, in turn, from 2-bromocyclopentanone (XII) and triphenylphosphine.

An examination of the charge distribution in triphenylphosphoniumcyclopentadienylide (I) as given by the resonance structures Ib, Ic and Id, reveals three possible sites for the attack of the electrophilic diazonium cation. The sequence of reactions outlined above establishes that the coupling took place at a position in the five-membered ring which is *adjacent* to the phosphorus-bearing ring position (attack as on structure Ic). The resulting azophosphinemethylene would thus possess the longest of the possible conjugated systems involving the nitrogen and phosphorus atoms, as can be seen from formulas VIa and XIVa, the latter corresponding to coupling according to structure Id. It also should be noticed that coupling according to structure Ib would destroy the stable cyclopentadienide system.

Coupling Reaction with *p*-Nitrobenzenediazonium Chloride (III).—The reaction of the phosphinemethylene I with *p*-nitrobenzenediazonium chloride (III) proceeded smoothly and afforded triphenylphosphonium-[2-(*p*-nitrophenylazo)-cyclopentadienylide] (VII). This azophosphinemethylene was green when in the form of large crystals and deep purple-red when finely pulverized or in solutions. It formed an orange hydrobromide, formulated as a cyclopentadienone *p*-nitrophenylhydrazone (IX).

Dipole Moments and Ultraviolet Absorption Spectra. Dipole Moments of the Azophosphinemethylenes.—The dipole moment[5] of the phenylazophosphinemethylene VI is 6.52 *D* and that of the *p*-nitrophenylazophosphinemethylene VII is 9.09 *D*, both in benzene at 25°. These values should be compared with the previously reported one[2a] of 6.99 *D* for the parent phosphinemethylene I.

For the azophosphinemethylenes, a number of resonance structures can be written. Some of them, such as VIa (or VIIa), VIb (or VIIb) and VIc (or VIIc) have their equivalent in the parent phosphinemethylene I. The additional structures, such as VIe (or VIIe) and VIf (or VIIf) would imply greater charge separation and an enhanced dipole moment (relative to I) if they contributed appreciably to the ground state of the molecule. One possible explanation for the slight reduction actually observed in the dipole moment of the phenylazophosphinemethylene VI, relative to that of the phosphinemethylene I, would be that in the former the homopolar structure VIa makes a greater contribution to the hybrid ground state, reflecting possibly the increased conjugation. On the other hand, it seems conceivable that the electric properties of the molecule could be significantly altered by an approach of the charged centers, as in structure

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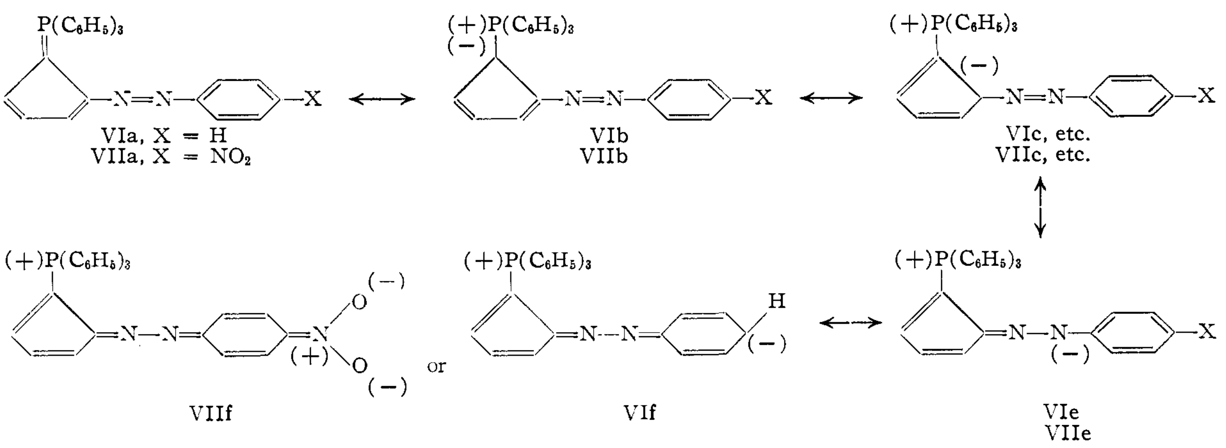
[4] (a) F. Ramirez and A. Kirby, This Journal, **75**, 6026 (1953); (b) **76**, 1037 (1954).

[5] We thank Dr. M. T. Rogers of Michigan State University for the data on dipole moments.



VIa, X = H
VIIa, X = NO_2

VIb
VIIb

VIc, etc.
VIIc, etc.

VIIf

VIf

VIe
VIIe

VIe.[6] It should be noted also that the stable closed system of six π-electrons characteristic of the cyclopentadienide ring would be offset in structures such as VIe and VIf.

Ultraviolet Absorption Spectra of the Azophosphinemethylenes.—Figure 1 discloses the remarkable bathochromic effect exerted by the **phenylazo** group (curve 1) and by the *p*-**nitrophenylazo** group (curve 2) in conjugation with the parent phosphinemethylene (curve 3).

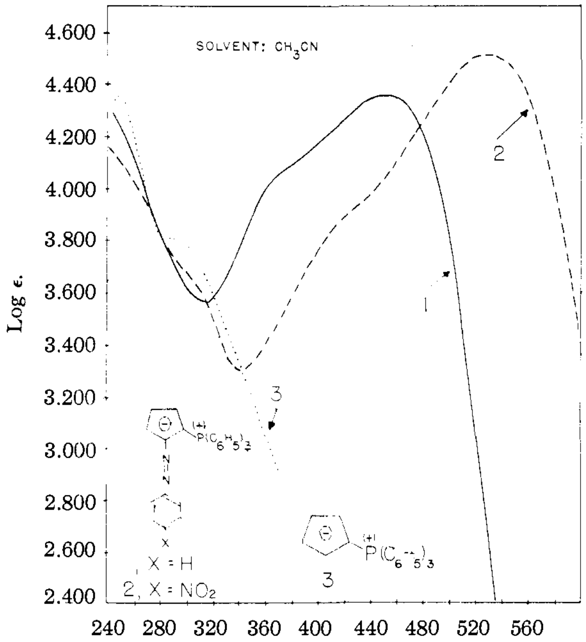


Fig. 1.

The difference in the λ_{max} for the two azophosphinemethylenes, VI and VII, indicates that *the nitro group is involved in the electronic transitions responsible for the absorption.* The ground state of these transitions could be pictured as a hybrid of structures VIa (or VIIa), VIb (or VIIb), VIc or VIIc), etc. (around the ring), with little contribution of structures VIe (or VIIe) and VIf (or VIIf). The latter would be of significance in the electronically excited state. The bathochromic effect of the *p*-nitro group in the azophosphinemethylenes then reflects the enhanced contribution of structure VIIf to the excited state.

The similarities between curve 1 of Fig. 1 and curve 1A of Fig. 2, and between curve 2 of Fig. 1 and curve 2A of Fig. 2, are significant and indicate practically no protonation of the phosphinemethylenes or phosphorus ylides in the hydroxylic solvent. Curves 1A and 2A of Fig. 2 remained essentially unchanged upon addition of alkali.

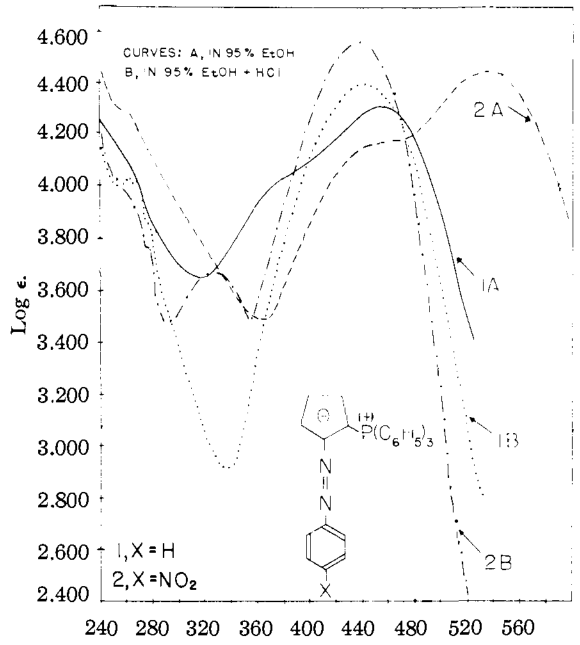


Fig. 2.

Ultraviolet Absorption Spectra of the Hydrobromides VIII and IX (Cyclopentadienonearylhydrazones).—Curves 1B and 2B of Fig. 2 represent, respectively, the spectra of the phenylazophosphinemethylene VI and of the *p*-nitrophenylazophosphinemethylene VII *in strong acid medium.* In other words, curves 1B and 2B correspond to the spectra of the cyclopentadienone-arylhydrazonephosphonium cations of VIII and IX. This is con-

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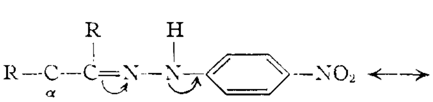
(6) There seems to be no reason, so far, to invoke covalency formation between the nitrogen and the phosphorus (as could be derived from VIe), even if the unknown steric demands of pentacovalent organophosphorus could be met.

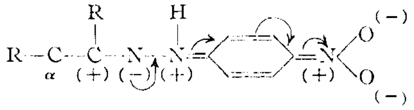
firmed by the exact correspondence of curve 1B with that of the hydrobromide VIII in 95% ethanol (no added acid) and the correspondence of curve 2B with that of the hydrobromide IX, in the same solvent.

The striking feature of curves 1B and 2B is the similarity in their $\lambda_{\max}$ *at ca. 440 mμ.* This similarity arises from a small hypsochromic shift upon addition of mineral acid to the phenylazophosphinemethylene (VI) and a large hypsochromic shift upon addition of acid to the *p*-nitrophenylazophosphinemethylene (VII). It can be seen that in the hydrobromides (*i.e.*, arylhydrazones) *the p-nitro group is not involved in the electronic transitions responsible for the absorption.*

Ordinarily, the $\lambda_{\max}$ of the *p*-nitrophenylhydrazone of a given carbonyl compound appears at a considerably longer wave length than that of the phenylhydrazone.[7] This has been interpreted[4,7] in terms of the contribution of resonance structures of type XVI to the excited state. These take into account also the effect of the structure of the ketone on the $\lambda_{\max}$ (*e.g.*, the bathochromic effect in derivatives of α,β-unsaturated ketones or phenyl ketones)

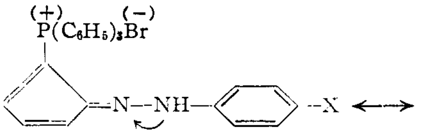


XV

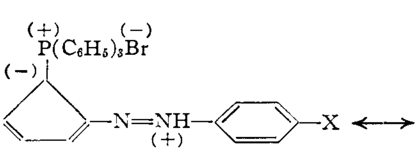


XVI, etc.

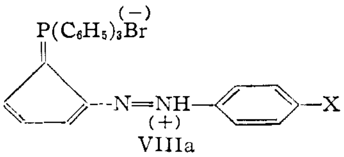
The apparent anomaly in the spectra of the hydrobromides VIII and IX is understood if one realizes the virtual impossibility of effecting the polarization shown in formula XV when the parent carbonyl compound is of a cyclopentadienone type. In this case the electronic transition is between a ground state essentially represented by VIIIe (or IXe) and an excited state to which structures VIIIb, etc. (around the ring) (or IXb, etc.) and VIIIa (or IXa) make appreciable contributions.[4] The operation of d-orbital resonance in phosphorus is implicit in structure VIIIa (or IXa).



VIIIe, X = H
IXe, X = NO₂



VIIIb, etc.
IXb, etc.



VIIIa
IXa

From the above discussion it can be seen that the electronic transition in the *phenylazophosphine methylene*, abbreviated as VIb → VIe is not very different in magnitude from the electronic transition in the corresponding *hydrobromide*, abbreviated as VIIIe → VIIIb. In the *p*-nitro case, the transitions would be, respectively, VIIb → VIIf and IXe → IXb. These considerations would explain the observed shifts in $\lambda_{\max}$ in Fig. 2, namely, 1A to 1B and 2A to 2B.

A point worth mentioning is that the introduction of two conjugated double bonds into the five-membered ring of the alicyclic phenylhydrazone X, connecting the phosphonium group and the azo methine group (as in VIII) results in the very considerable bathochromic shift of 165 mμ. This shift is possibly an indication of d-orbital resonance in phosphorus.

Note on the Preparation of Triphenylphosphoniumcyclopentadienylide (I).—The action of triphenylphosphine on pure *cis*-3,5-dibromocyclopentene was investigated. The yield of the phosphinemethylene I was comparable to that realized when the phosphine was added to the mixture of dibromides resulting from cyclopentadiene and bromine in chloroform solution.

Although the exact composition of the cyclopentadiene dibromide mixture is not known,[8] *cis*-3,5-dibromocyclopentene seems to be an important direct product of the bromination, together with the *trans*-3,5-isomer. Obviously, the reaction of triphenylphosphine with the dibromides[9] may take several paths (for example, S_N2 followed by S_N2'). Probably, under the experimental conditions used (excess phosphine) only bis-phosphonium bromides of *trans*-configuration need be considered; these may be 3,4- as well as 3,5-cyclopentene derivatives.[10]

The formation of the desired phosphinemethylene I by the action of alkali on the phosphonium bromides is only one of several possible reactions. Removal of a proton by the base would lead, either from 3,4- or from 3,5-cyclopentene derivatives, to: (i) the phosphinemethylene I and one mole of recovered triphenylphosphine or (ii) to highly unstable phosphinevinylmethylene structures $C{=}C{-}\underset{(-)}{C}{-}\underset{(+)}{P}(C_6H_5)_3$. On the other hand, in the alkaline medium, the phosphonium bromides could undergo their characteristic decomposition into phosphine *oxides* and unstable cyclopentene derivatives. Triphenylphosphine *oxide* and triphenylphosphine were indeed isolated in the experiments

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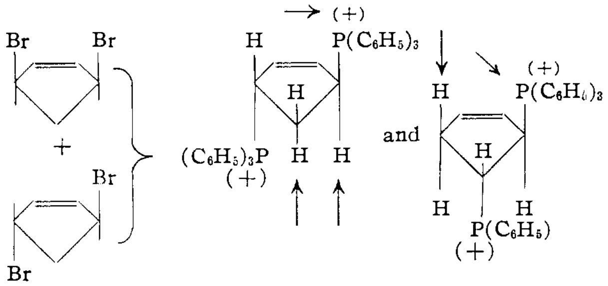
[7] F. Bohlmann, *Chem. Ber.*, **84**, 490 (1951).

[8] W. G. Young, H. K. Hall, Jr., and S. Winstein, THIS JOURNAL, **78**, 4338 (1956).

[9] For a discussion of the action of dimethylamine on the cyclopentadiene dibromides see ref. 8 and 10. D. Lloyd and J. Sneezum (*Chemistry & Industry*, 122 (1953)) have reported the action of pyridine on the crude dibromide mixture.

[10] A. C. Cope, L. L. Estes, Jr., J. R. Emery and A. C. Haven, Jr., THIS JOURNAL, **73**, 1199 (1951).

producing the phosphinemethylene I (over-all yield of I: 46% from cyclopentadiene).



Experimental[11]

Triphenylphosphoniumcyclopentadienylide (I).—(a) The following modified procedure was found convenient: bromine (53.3 g.) was rapidly added to a solution of cyclopentadiene (22 g.) in chloroform (30 ml.) at −40 to −30°, under nitrogen. After 1 hour at this temperature, the solution was treated with triphenylphosphine (175 g.) in chloroform (600 ml.). The mixture was allowed to reflux for 14 hours, the chloroform was removed under reduced pressure and the glassy residue was dissolved in methanol. Addition of aqueous sodium hydroxide (45 g. in 175 ml.) precipitated the phosphinemethylene I, which was collected, washed with hot methanol and pet. ether and dried; yield of I: 49.9 g. (46%), m.p. 213–218°; after two recrystallizations from chloroform–ethanol: 39.7 g. (37%), m.p. 225–227°.

(b) **From Pure *cis*-3,5-Dibromocyclopentene.**—To a solution of triphenylphosphine (7.81 g.) in chloroform (100 ml.) was added *cis*-3,5-dibromocyclopentene (3.36 g., m.p. 35–40°, prepared as described),[8] under nitrogen. After 14 hours at its reflux temperature, the chloroform solution was shaken with aqueous sodium hydroxide (2 g. in 30 ml.). The chloroform layer was evaporated under reduced pressure and the residue was treated with methanol (100 ml.). The yield of triphenylphosphoniumcyclopentadienylide (I) of m.p. 217–222° was 2.69 g. (55%).

Ultraviolet Absorption Spectra of Phosphinemethylene I.—λ_{max} *in acetonitrile:* 222 mμ (ε 39,200), 250 mμ (ε 22,300) and *ca.* 295 mμ (ε 6,100) with tailing above 300 mμ (ε at 375 mμ < 100). λ_{max} in 95% *ethanol:* 224 mμ (ε 36,200), shoulders at 250 mμ, 267 mμ (ε 9,500) and 278 mμ (ε 6,900) with tailing into longer wave lengths. λ_{max} in 95% *ethanol saturated with hydrogen chloride:* 224 mμ (ε 27,400), 263 mμ (ε 10,300), 269 mμ (ε 12,100) and 276 mμ (ε 11,200); no absorption above 300 mμ.

Triphenylcyclopentadienylphosphonium Bromide (XIII) or **Triphenylphosphoniumcyclopentadienylide Hydrobromide.**—To a suspension of triphenylphosphoniumcyclopentadienylide (I) (0.200 g.) in dimethylformamide (10 ml.) was added 8 drops of a 10% aqueous hydrobromic acid solution. The resulting clear solution was filtered into 400 ml. of anhydrous ether. The colorless hydrobromide XIII precipitated out (0.167 g., 67%) and had m.p. 198–200°. Upon drying at 100° (0.1 mm.) for analysis, the sample became slightly pink and the m.p. dropped somewhat (191–194°) but the analysis was satisfactory. Bands in KBr at: 6.32(m), 6.80(vs), 7.02(vs), 7.45(m), 7.65(m) and 9.05(vs) μ.

Anal. Calcd. for $C_{23}H_{20}PBr$: C, 67.8; H, 4.9. Found: C, 68.1; H, 4.8.

The ultraviolet spectrum of the hydrobromide XIII in 95% *ethanol* was very similar to that of the phosphinemethylene I in alcohol containing dilute *hydrochloric acid*. The small absorption at 300 mμ and above indicates some dissociation to the phosphinemethylene.

Triphenylphosphonium-(2-phenylazo)-cyclopentadienylide (VI).—A benzenediazonium chloride solution was prepared in the usual manner from 1.40 g. of aniline, 3.8 ml. of concd. hydrochloric acid, 17 g. of ice and 1.05 g. of sodium nitrite (in 25 ml. of water). Addition of *ca.* 7 g. of sodium acetate raised the *p*H to 5–6 and produced a yellow precipitate. To this mixture was added, with stirring, a solution of triphenylphosphoniumcyclopentadienylide (I) (4.89 g.) in methylene chloride (150 ml.); the temperature was kept at 0–5° during the rapid addition. The methylene chloride phase became orange immediately. After 30 minutes at 0°, the mixture was treated with 5% aqueous sodium hydroxide (15 ml.), the methylene chloride layer was separated and the aqueous layer was extracted with methylene chloride. The combined methylene chloride solutions were evaporated to dryness *in vacuo* and the residue was treated with methanol (200 ml.); the insoluble, orange azophosphinemethylene VI was collected and dried; yield 5.64 g. (88%), m.p. 225–230°; after one recrystallization from benzene–methanol, 5.0 g. of m.p. 238–240°. The analytical sample (from ethyl acetate–ethanol) was deep orange and had m.p. 239–240°; bands in KBr at 6.32(w), 6.78(m), 7.00(s), 7.22(s), 7.42(m), 7.65(vs), 7.90(vs), 8.24(ms), 8.45(s), 8.80(s), 9.02(s), 9.45(s), 9.80(ms) and 10.02(m) μ. The infrared spectrum was not altered significantly by solution in chloroform.

Anal. Calcd. for $C_{29}H_{23}N_2P$: C, 80.9; H, 5.4; N, 6.5; P, 7.2; mol. wt., 430. Found: C, 80.7; H, 5.8; N, 6.8; P, 7.5; mol. wt., 413 (isothermal distillation in chloroform); dipole moment, 6.52 *D* at 25° in benzene.

Ultraviolet Absorption Spectra of the Phenylazophosphinemethylene VI.—λ_{max} in *acetonitrile:* 220 mμ (ε 49,700) and 452 mμ (ε 23,500) (very broad); slight inflection at *ca.* 250 mμ. λ_{max} in 95% *ethanol:* 219 mμ (ε 42,900), 255 mμ (ε 13,700) (inflection) and 455 mμ (ε 20,600) (very broad); this spectrum was not affected by addition of aqueous sodium hydroxide. λ_{max} in 95% *ethanol saturated with hydrogen chloride:* 226 mμ (ε 10,700), 267 mμ (ε 10,500), 275 mμ (ε 7,300) (these three peaks correspond to the resolution of the 255 mμ-inflection in the conjugate base) and 440 mμ (ε 25,300) (very broad and symmetrical).

Triphenyl-(2-phenylhydrazono)-cyclopentadienylphosphonium Bromide (VIII) or **Triphenylphosphonium-(2-phenylazo)-cyclopentadienylide Hydrobromide.**—To a solution of 0.200 g. of the phenylazophosphinemethylene VI in warm tetrahydrofuran (15 ml.) was added 15 drops of 10% aqueous hydrobromic acid. The clear solution was filtered into diethyl ether. The hydrobromide VIII precipitated and was collected (0.200 g., 84%) and dried 2 hours at *ca.* 140° (0.001 mm.) for analysis. The sample, before and after drying, had m.p. 236–237°. Bands in KBr 2.90–2.95 μ (broad; NH), 6.25(w), 6.45(vs; C=N?), 6.72(s), 6.98(m), 7.10(s), 7.45(s), 8.00(vs), 9.02(vs) and 6.95(vs) μ. The spectrum is essentially identical in chloroform solution.

Anal. Calcd. for $C_{29}H_{24}N_2PBr$: C, 68.1; H, 4.7. Found: C, 67.8; H, 4.8.

The hydrobromide VIII retained water tenaciously. Thus, when the sample prepared above was dried 24 hours at *ca.* 56° (0.1 mm.) the analysis was: C, 66.9; H, 4.6; the m.p. was 236–237°. (Calcd. for $C_{29}H_{24}N_2PBr \cdot {}^1/_2H_2O$: C, 66.9; H, 4.8.) The same hydrobromide can be prepared as follows: a suspension of the azophosphinemethylene VI in methanol or ethanol is treated with 10% aqueous hydrobromic acid. The clear solution is evaporated to dryness and the residue is recrystallized from ethanol–water. Under these conditions, after drying at 100° (0.1 mm.) the hydrobromide still contains water of crystallization and melts at 232–235°.

Ultraviolet Absorption Spectrum of Hydrobromide VIII.—λ_{max} in 95% *ethanol:* 225 mμ (ε 37,000), 259 mμ (ε 12,800), 266 mμ (ε 12,000), 274 mμ (ε 8,100) and 442 mμ (ε 28,200). The spectrum was very similar to that of the azophosphinemethylene VI in *alcohol containing dilute hydrochloric acid* or *saturated with hydrogen chloride.*

(2-Oxocyclopentyl)-triphenylphosphonium Bromide (XI).—A solution of freshly distilled 2-bromocyclopentanone (9.5 g.), and triphenylphosphine (15.2 g.) in chloroform (40 ml.) was kept in the ice-box overnight. The solution was filtered onto 500 ml. of diethyl ether. The oil which precipitated crystallized on cooling and was collected (11 g.). This material was washed thoroughly with hot benzene and the benzene-insoluble residue (2 g., m.p. 263–270°) was used to prepare the analytical sample of the ketophosphonium bromide XI. Recrystallization from methanol–ethyl acetate gave the phosphonium bromide XI as white crystals, m.p. 270–272°; λ_{max} in ethanol: 217 mμ (ε 38,500),

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[11] Analyses by Micro-Tech. Laboratories, Skokie, Ill., and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., m.p.'s are corrected.

225 mμ (ε 37,000), 257 mμ (ε 10,100), 266 mμ (ε 9,200) and 275 mμ (ε 6,700). Bands (KBr) at 3.73 (w, C—H), 5.82 (s, C═O), 6.30 (w), 7.00 (s), 9.00 (s) and 10.1 (w) μ.

Anal. Calcd. for $C_{23}H_{22}OBrP$: C, 65.0; H, 5.2. Found: C, 65.3; H, 5.5.

(2-Phenylhydrazonocyclopentyl)-triphenylphosphonium Bromide (X).—A solution of phenylhydrazine hydrochloride (2 g.) in water was treated with 5% aq. sodium hydroxide. The solution was saturated with sodium chloride and extracted with ether. The ether extract was treated with concd. hydrobromic acid and the phenylhydrazine hydrobromide (1.9 g.) was collected. A solution of the hydrobromide in water (25 ml.) was treated with sodium acetate (3 g.) followed by a solution of (2-oxocyclopentyl)-triphenylphosphonium bromide (XI) (1.00 g.) in hot water (20 ml.). The mixture was kept on the steam-bath for 2 hr. The solid which separated was filtered, washed with dilute hydrobromic acid, cold methanol and ether; yield 0.62 g., m.p. 190–197°. Recrystallization from methanol–ethyl acetate (or from dilute aq. ethanol) gave colorless crystals of X, m.p. 204–205°. λ_{max} in ethanol: 217 mμ (ε 45,400), 225 mμ (ε 40,600), 269 mμ (ε 20,200) and 277 mμ (ε 20,600). Bands (KBr) at 2.9–3.0(w; NH), 6.28(s, C═N); 6.65 (mw), 6.75(mw), 7.00(s), 9.05(s) and 10.08(w) μ.

Anal. Calcd. for $C_{29}H_{28}N_2BrP$: C, 67.6; H, 5.5; N, 5.4; Br, 15.5. Found: C, 67.4; H, 5.8; N, 5.8; Br, 16.0.

The m.p. of X is somewhat affected by the rate of heating.[4]

(2-Phenylhydrazonocyclopentyl)-triphenylphosphonium Bromide (X) from Triphenyl-(2-phenylhydrazono)-cyclopentadienylphosphonium Bromide (VIII).—To a prereduced suspension of PtO_2-catalyst (0.489 g.) in moist methanol was added a solution of the bromide VIII (0.107 g.) in methanol. The mixture was hydrogenated under ambient conditions. About 70% of the theoretical amount of hydrogen was taken up during the first 3 minutes; hydrogenation was discontinued after 10 minutes. The light yellow solution was filtered and concentrated at low temperature and reduced pressure. The remaining solid (0.108 g.) had m.p. 200–204°. One recrystallization from methanol–water raised the m.p. to 204–205°, alone and mixed with authentic (2-phenylhydrazonocyclopentyl)-triphenylphosphonium bromide (X). The identity was confirmed by infrared spectra.

Similar results were obtained when solutions of triphenylphosphonium-(2-phenylazo)-cyclopentadienylide (VI) in hydrobromic acid were hydrogenated directly (*i.e.*, without isolation of bromide VIII).

Triphenylphosphonium-[2-(*p*-nitrophenylazo)-cyclopentadienylide] (VII).—A *p*-nitrobenzenediazonium chloride solution was prepared from *p*-nitroaniline (2.07 g.), concd. hydrochloric acid (3.9 ml.), water (3 ml.) and sodium nitrite (1.05 g. in 2.5 ml. of water). To the cold solution (0–5°) was added sodium acetate (5 g.) (*p*H *ca.* 5–6) and then a solution of triphenylphosphoniumcyclopentadienylide (I) (4.89 g.) in methylene chloride (150 ml.). The mixture was stirred for 30 minutes at 0–5° and then was treated with 15 ml. of 5% aqueous sodium hydroxide. The methylene chloride layer was separated, the aqueous layer was extracted with methylene chloride and the combined organic solution was evaporated under reduced pressure. The insoluble solid (5.53 g., 78%) which remained after treatment of the residue with methanol (200 ml.) had m.p. 218–226° and was fairly pure *p*-nitrophenylazophosphinemethylene VII. One recrystallization from benzene–methanol raised the m.p. to 240–242°. The analytical sample had the same m.p. Bands in KBr at 6.30(s), 6.70(s), 6.95(s), 7.22(m), 7.52(s), 7.65(vs), 8.1–8.2(vs), 8.45(s), 8.86(s), 9.02(s), 9.15(vs), 9.42(s), 9.75(s), 10.05(s) and 11.15(m). The spectrum was essentially identical in chloroform.

Anal. Calcd. for $C_{29}H_{22}O_2N_3P$: C, 73.3; H, 4.7; N, 8.8. Found: C, 73.3; H, 4.5; N, 9.3; dipole moment: 9.09 *D* at 25° in benzene.

Ultraviolet Absorption Spectra of the *p*-Nitrophenylazophosphinemethylene VII.—λ_{max} in *acetonitrile:* 222 mμ (ε 44,600) and 528 mμ (ε 32,700) (very broad); inflection at *ca.* 250 mμ. λ_{max} in 95% *ethanol:* 222 mμ (ε 53,400); *ca.* 253 mμ (ε 20,100) (inflection), *ca.* 460 mμ (ε 15,300) (inflection) and 537 mμ (ε 28,300) (broad); the position of the maxima was not affected by addition of aq. sodium hydroxide to the ethanol solution. λ_{max} in 95% *ethanol saturated with hydrogen chloride:* 224 mμ (ε 36,600), 260 mμ (ε 9,100), 268 mμ (ε 7,800), 275 mμ (ε 5,600), 326 mμ (ε 4,700) and 436 mμ (ε 36,300).

Triphenyl-[2-(*p*-nitrophenylhydrazono)-cyclopentadienyl]-phosphonium Bromide (IX) or Triphenylphosphonium-[2-(*p*-nitrophenylazo)-cyclopentadienylide] Hydrobromide.—A suspension of the azophosphinemethylene VII (0.500 g.) in 95% ethanol (50 ml.) was treated with 10% aqueous hydrobromic acid (10 ml.) at 50°. The clear solution was concentrated (*in vacuo*) somewhat until crystals appeared. The yellow hydrobromide (0.482 g., 83%) obtained on cooling had m.p. 192–195°. Recrystallization from 95% ethanol containing some hydrobromic acid furnished the analytical sample of m.p. 194–196°. After drying at 100° (0.1 mm.) the hydrobromide appeared to retain water of crystallization. Bands in chloroform solution: 6.25(w), 6.43(vs), 6.57(vs), 6.73(vs), 7.05(s), 7.52(vs), 8.02(vs), 9.02(vs) and 9.70(s) μ.

Anal. Calcd. for $C_{29}H_{23}O_2N_3PBr\cdot{}^1/_2H_2O$: C, 61.6; H, 4.3. Found: C, 61.5; H, 4.6.

Ultraviolet Absorption Spectrum of Hydrobromide IX.—λ_{max} in 95% *ethanol:* 226 mμ (ε 29,100), 253 mμ (ε 13,300), 267 mμ (ε 9,700), 275 mμ (ε 7,100), 322 mμ (ε 4,500) and 437 mμ (ε 40,800). The spectrum was very similar to that of the azophosphinemethylene VII in alcohol saturated with hydrogen chloride.

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