Reactions of Cyclopentadienylidenetriphenylphosphorane (Phosphafulvene)

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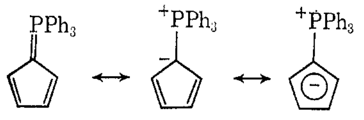
Attempts have been made to carry out the reactions of cyclopentadienylidenetriphenylphosphorane (phosphafulvene, I) with a number of dienophiles and electrophiles. From its reaction behavior toward the reagents, I has been found not to exhibit chemical properties expected for ylene and ordinary ylide compounds, but to have aromatic character in the cyclopentadienyl ring. The reactivity and the reaction position are discussed in terms of the results obtained from Hückel MO calculations.

The system investigated in this study is the dipolar mesomeric system, cyclopentadienylidenetriphenylphosphorane (I), whose skeleton is constructed of a cyclopentadienyl ring and an exocyclic phosphorus atom. This type of molecule is reminiscent of the carbon analog, fulvene. The dipole moment of dimethylfulvene is reported as only 1.44 D,[1] indicating that the nonpolar covalent structure dominantly contributes to its ground state. Actually, fulvenes act as both dienes and dienophiles in the Diels–Alder reaction, although some electrophilic substitutions of I are reported to occur.[2] On the other hand, since I shows a considerably large dipole moment of 7.0 D,[3] dipolar structures (Ib, Ic) other than covalent structure (Ia) might be important in the resonance hybrid of I.



Ia Ib Ic

Ramirez, *et al.*,[3] who first synthesized I, suggested its aromatic character from the experimental result[4] that diazo coupling took place on the cyclopentadienyl ring of I. They also described roughly equal contributions of ylene (Ia) and negative-charge delocalized ylide (Ic) structures, because its observed dipole moment (7.0 D)[3,5] corresponds to just the average value between the calculated moment 0.0 D for Ia and 14.0 D for Ic. In this prediction, however, only the π moment is taken into account, but the σ moment in the opposite direction is not. This situation prompted us to elucidate further the electronic structure of I. This could allow a better understanding of the nature of the d orbitals of I. In the first place, the electronic spectrum of cyclopentadienylidenetri-*n*-propylphosphorane (II), which was recently synthesized in order to simplify the spectrum, was measured in our laboratory and the observed intramolecular charge-transfer absorption band was theoretically treated by the semiempirical "molecules in molecule method."[6] Consequently, it was concluded that the polar ylide structure (Ib or Ic) dominantly contributes to the resonance hybrid of II in the ground state. As a next step, the reaction behavior of I toward a variety of reagents were studied. First, the reactions of I with dienophiles such as dialkyl acetylenedicarboxylate, tetracyanoethylene, and maleimide, and subsequently the reactions of I with various electrophiles, benzaldehyde and dichlorocarbene, were attempted. Here we wish to report the reaction behavior of I toward these reagents which are in marked contrast with those of fulvene. The reactivity of I is discussed in terms of the ionization potentials calculated by Hückel MO theory, and the reaction position predicted from electron transfer theory,[7] superdelocalizabilities,[8] and localization energies[9] are compared with the experimental results.

Results and Discussion

Reaction with Dienophiles.—The investigation of reaction behavior of I with dienophiles is interesting in comparison with those of fulvene, and also useful for determining whether I behaves as the ylene (Ia) or ylide (Ib, Ic). The reaction of I with electron-deficient unsaturated compounds such as dialkyl acetylenedicarboxylate, tetracyanoethylene,[10] and maleimide, which are known to be reactive dienophile as well as weak electrophile, was attempted. The reaction procedures and the spectral data of the products III, IV, and V (Figure 1) were described in our previous communication.[11] All the products were Michael addition reaction products by electrophilic attack on the cyclopentadienyl ring in I. No evidence for the Diels–Alder reaction was obtained. Even in the reaction of I with good dienophiles such as norbornadiene and 1,2-diphenylcyclopropene, Diels–Alder reaction did not take place.

Reactions with Electrophiles.—As mentioned above, since the reaction behavior of I with the dienophiles strongly supported the electron-rich 5C 6π aromatic character of the cyclopentadienyl ring of I, the reactions of I with several electrophiles have been carried out. The reaction products are summarized in Figure 1.

Discussion of nitration, nitrosation, bromination, and Vilsmeier reactions including structure proof were described in our previous communication.[12] The exclusive formation of 2-substituted derivatives was chemically proved in the case of nitrosation reaction.[12]

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(1) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1969).

(2) J. H. Day, *Chem. Rev.*, **53**, 167 (1953).

(3) F. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, **79**, 67 (1957).

(4) F. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, **79**, 6167 (1957).

(5) The dipole moment of I in benzene solution at 25° was also measured in our laboratory. Since the calculated molar reflection which is used to evaluate the observed dipole moment is dependent on atomic refractions, the difference of the atomic refractions for the ylide and for the ylene structures might affect the observed dipole moment values. Our observed values for I are 6.89 and 6.87 for the ylide and the ylene structures, respectively, both of which are nearly identical and in good agreement with that obtained by Ramirez, *et al.*

(6) (a) Z. Yoshida, K. Iwata, and S. Yoneda, *Tetrahedron Lett.*, 1517 (1971); (b) K. Iwata, S. Yoneda, and Z. Yoshida, *J. Amer. Chem. Soc.*, **93**, 6745 (1971).

(7) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 563 (1954).

(8) K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jap.*, **27**, 423 (1954); *J. Chem. Phys.*, **27**, 1247 (1957).

(9) G. W. Wheland, *J. Amer. Chem. Soc.*, **64**, 900 (1940).

(10) E. Lord, P. Naan, and C. D. Hall, *J. Chem. Soc. B*, 213 (1971).

(11) Z. Yoshida, S. Yoneda, H. Hashimoto, and Y. Murata, *Tetrahedron Lett.*, 1527 (1971).

(12) Z. Yoshida, S. Yoneda, Y. Murata, and H. Hashimoto, *Tetrahedron Lett.*, 1523 (1971).

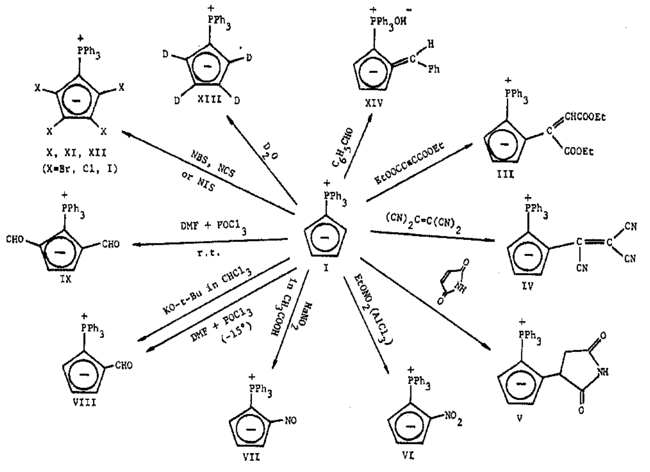


Figure 1.—Reactions of I with electrophiles and dienophiles.

The pmr data also supported the substitution of the 2 position. For instance, the pmr spectrum of the nitration reaction product (VI) showed three peaks of equal area centered at τ 2.85 (1 H), 2.90 (1 H), and 3.70 (1 H) besides the phenyl proton signal at τ 2.2–2.5 (15 H) as seen in Figure 2b. Among these three peaks (τ 2.85, 2.90, and 3.70), one peak at τ 3.70 is located within the signal due to the cyclopentadienyl ring protons of the parent compound (Figure 2a),[13] and the other two peaks shift downfield. This is readily interpreted if the nitro group is attached to the 2 position of I; *i.e.*, two electron-withdrawing substituents (phosphonium and nitro groups) should make the two protons at the 3 and 5 positions shift to lower field. Such interpretation might be applicable for III, IV, VII, and VIII.[16]

Tetrachloro and tetraiodo derivatives (XI and XII) were prepared by treatment of I with 4 mol of *N*-chloro- and *N*-iodosuccinimide at room temperature, respectively. It is noteworthy that the halogenation of I with even a small quantity of *N*-halosuccinimide exclusively afforded the tetrahalo derivatives.

Deuteration proceeded easily to give the tetradeuterio derivative (XIII), which was shown by the nmr spectrum. When deuterium oxide was added to a solution of I in deuteriochloroform, the multiplet at τ 3.4–3.8 corresponding to the cyclopentadienyl protons decreased gradually, and after 1 hr the signal was gone.

Reactions of I with Benzaldehyde.—The resonance structure (Ib), in which the negative charge is localized on the carbon adjacent to the phosphorus atom, is also considered to be important in the resonance hydrid of I. If Ib is important in the transition state, the reaction expected of phosphorus ylides might take place. The reaction of I with benzaldehyde in tetrahydrofuran at ice temperature as well as at room temperature was carried out; in both cases, only a wine-red crystalline product (XIV, 185° dec) was obtained. The elemental analysis ($C_{30}H_{25}OP$) did not correspond to the Wittig reaction product (6-phenylfulvene) but to a compound represented as XIV. The nmr spectrum of XIV in DMSO-d_6 showed a singlet at τ 1.5 (1 H, methine) and two multiplets at τ 1.8–3.0 (20 H, phenyl) and at 3.1–3.6 (3 H, cyclopentadienyl). The existence of OH was confirmed by the observation of ν_{OH} (3500 cm^{-1}) and the displacement of OH with BF_4^- by the addition of HBF_4 to XIV. These spectral data support the structure given above. No evidence of the Wittig reaction was obtained. This is rather surprising, because, even fluorenylidenetriphenylphosphorane which is the dibenzo derivative of I easily reacts with benzaldehyde to give triphenylphosphine oxide and benzalfluorene in excellent yield.[17] This striking aspect of I can be interpreted as the reflection of the minor contribution of the negative-charge localized structure Ib to the resonance hybrid. The negative charge is considered not to be concentrated at the carbon adjacent to the phosphorus atom, but to be delocalized over the cyclopentadienyl ring of I. The formation of XIV clearly indicates a large contribution of the charge-delocalized resonance structure Ic. The difference between the reaction behavior of I and that of fluorenylidenetriphenylphosphorane might be explained by comparing

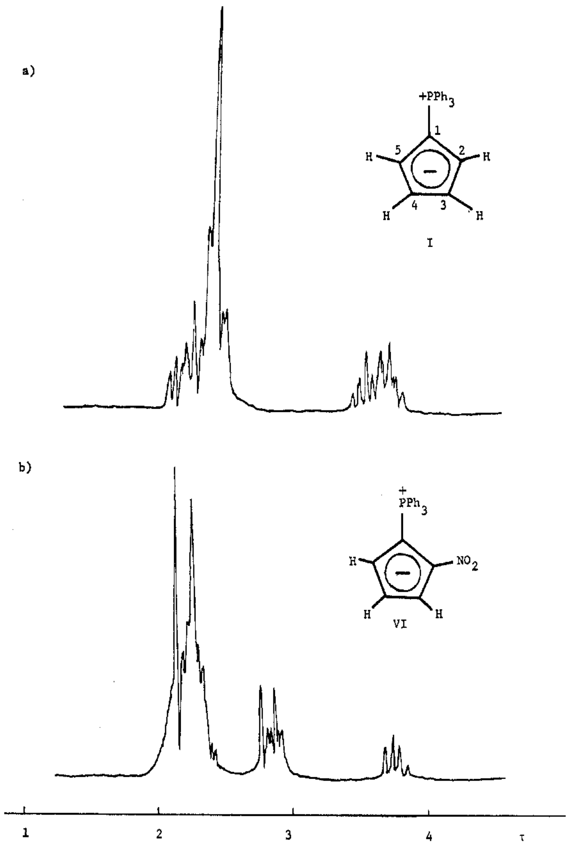
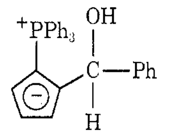


Figure 2.—The nmr spectra of I and VI.



XIV

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[13] The signal due to the cyclopentadienyl ring protons is expected to be an AA′BB′ pattern,[14] but it is very complicated[15] because of spin–spin coupling with phosphorus as shown in Figure 2a.

[14] In the pmr spectrum of dimethylsulfonium cyclopentadienylide, which is an analog of I, an AA′BB′ pattern was observed: Z. Yoshida, S. Yoneda, and M. Hazama, *Chem. Commun.*, 716 (1971).

[15] The pmr spectrum of the cyclopentadienyl ring of I has been completely analyzed: W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, **89**, 1438 (1967).

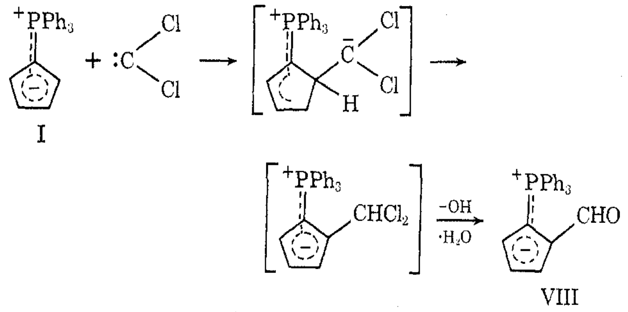
[16] These pmr data are in the Experimental Section.

[17] A. W. Johnson, *J. Org. Chem.*, **24**, 282 (1957).

the pK_a values of 4.69[18] for I with that of 7.5 for fluorenylidenetriphenylphosphorane.[19]

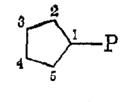
Reactions of I with Dichlorocarbene.—Treatment of I in chloroform with potassium *tert*-butoxide at 0° gave the monoformyl derivatives of I (VIII). This was confirmed by a mixture melting point (221–222°) method with an authentic sample prepared by the method previously described in this paper. No products other than VIII were detected on tlc of the reaction mixture. The reaction mechanism can reasonably be presented as shown in Scheme I. Again it should be noted that the reaction behavior of I with the electrophilic dichlorocarbene is quite different from that of indenylidene- and fluorenylidenetriphenylphosphorane. In the latter cases, the reaction yielded triphenylphosphine and the corresponding olefins, *i.e.*, dichloromethyleneindene and -fluorene.[20] Consequently, it could be concluded that the negative-charge delocalized ylide structure (Ic) displays a more important role than the negative-charge localized one (Ib) in the reaction of I.

SCHEME I



Hückel MO Treatment.—In the 6π-electron system (I) the Hückel MO calculation was carried out. The Coulomb integrals (α_P) and the resonance integrals (β_{C-P}) were taken as follows.

$$\alpha_p = \alpha + \delta_p\beta \qquad (1)$$



Here the coefficient δ_P was estimated from the ionization potential[6] (I_P) of the 3d orbital of phosphorus atom by using eq 2. The other Coulomb integrals are given in

$$\delta_P = I_p - 7.2/3.0 = 2.06 - 7.2/3.0 = -1.71 \qquad (2)$$

eq 3 and 4. The resonance integral for the C–P bond

$$\alpha_1 = \alpha - 0.1\beta \qquad (3)$$

$$\alpha_2 = \alpha_3 = \alpha_4 = \alpha_5 = \alpha \qquad (4)$$

is given in eq 5. The value of K_{C-P} was estimated by

$$\beta_{C-P} = K_{C-P}\beta \qquad (5)$$

Jaffe's table[21] using effective nuclear charges for the 3d orbital ($Z_p = 1.39$).[22] The resonance integrals for all the C–C bonds are taken to be β. Solving the secular equation by using the above parameters, energy levels and wave functions were obtained (Table I).

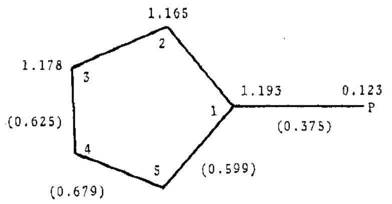


Figure 3.—The π-electron density and the π-bond order of I.

TABLE I

ENERGY LEVELS AND WAVE FUNCTIONS OF I

Energy level (β)	Wave function					
	P	1	2	3	4	5
−2.323	0.108	0.463	0.444	0.435	0.435	0.444
−1.618	0.223	0.618	0.151	−0.511	−0.511	0.151
−1.212	−0.000	−0.000	−0.602	−0.372	0.372	0.602
0.618	0.609	0.349	−0.459	0.207	0.207	−0.459
0.704	0.000	0.000	0.372	−0.602	0.602	−0.372
2.021	0.753	−0.531	0.263	−0.079	−0.079	0.263

The calculated ionization potential of -0.618β (8.60 eV) is an extremely small values. Therefore, the reaction of I with electrophilic reagents should easily take place. The molecular diagram of I is shown in the Figure 3. All the π-bond order values of 0.599 for the C_1–C_2 bond, 0.679 for the C_2–C_3 bond, and 0.625 for the C_3–C_4 bond are within the aromatic range (0.5–0.7) proposed by Streitwieser.[23] From the π-electron distribution, the π electron is shown to migrate from the cyclopentadienyl ring to phosphorus atom by only 0.123 which agrees with the prediction[6] that the ylide structure rather then the ylene structure is much important in the resonance hybrid of I. The remainder of the negative charge is delocalized almost homogeneously over the five-membered ring. The order of π-electron densities (q_r) is $q_1 > q_3 > q_2$. Therefore, electrophilic attack would be predicted to occur at the 1 position. However, the π-electron density is a reaction index in the unperturbed state of the molecule. More reliable reaction indices such as the superdelocalizabilities (S_E),[8] the localization energies (L_r),[9] and the free valences (F_r) of the reaction intermediate in electron-transfer theory[7] were evaluated and are given in Table II. The localization energy is the energy difference between the ground state (A) and the intermediate state (C) in Scheme II. The free valences of the intermediate (B) is one of the good reaction indices in a system where electron transfer easily takes place. The discussion in terms of electron transfer theory has been already described in more detail in our previous publication.[12] As seen in the Table II, all the reaction

TABLE II

REACTION INDICES OF I

	q_r	f_r[a]	S_E	F_r	$L(-\beta)$
P	0.123	0.000	0.152		
C_1	1.193	0.000	1.297	0.159	2.215
C_2	1.165	0.724	1.431	0.678	2.016
C_3	1.178	0.276	1.377	0.513	2.062
C_4	1.178	0.276	1.377	0.513	2.062
C_5	1.165	0.724	1.431	0.678	2.016

[a] Frontier electron density.

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(18) The pK_a values of I was determined by the potentiometric titration in 50 vol. % methanol solution.

(19) A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

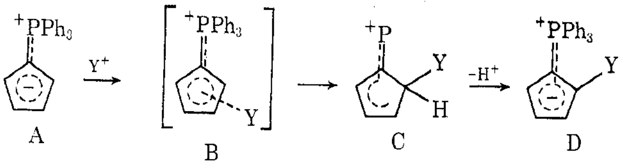
(20) M. Okano, Y. Ito, and R. Oda, *Tetrahedron Lett.*, 6 (1964).

(21) H. H. Jaffe, *J. Chem. Phys.*, **21**, 258 (1953).

(22) D. W. J. Cruickshank and B. C. Webster, *J. Chem. Phys.*, **40**, 3733 (1964).

(23) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 172.

SCHEME II



indices which do not involve π-electron density indicate that the electrophilic attack should take place at the 2 or 5 position, in good agreement with the experimental results.

The fact that the reaction of I with most electrophilic reagents such as NO_2^+, NO^+, etc, gave monosubstituted or, at most, disubstituted derivatives of I (only the halogenation afford tetrasubstituted ones) can be rationalized by ionization potentials calculated from Hückel MO method. The calculated ionization potentials (E_{ho}, energy of the highest occupied MO) of several substituted derivatives are listed in Table III.

TABLE III

IONIZATION POTENTIALS OF THE DERIVATIVES OF I

Substituent	NO_2	NO	Cl	Br
Unsubstituted	0.618	0.618	0.618	0.618
5	0.694	0.697	0.577	0.582
2,5	0.721	0.742	0.540	0.550
2,3,5			0.522	0.535
2,3,4,5			0.511	0.526

In the case of attack by NO_2^+ or NO^+, the ionization potentials are shown to increase with increasing substitution. This indicates that the subsequent electrophilic substitution become difficult. On the other hand, the ionization potential decreases with halogen substitution and this accounts for the fact that the tetrahalo derivative is exclusively obtained in the halogenation.

Experimental Section

Spectra.—Ultraviolet spectra were taken on Hitachi EPS-3T photometer. Infrared spectra were recorded on a Hitachi grating infrared spectrophotometer Model-215. Nmr spectra were recorded on a Jeolco C-60H nmr spectrometer.

Cyclopentadienylidenetriphenylphosphorane (I).—I was prepared by the method of Ramirez[3] and had mp 230–231° (lit. 229–231°).

Triphenylphosphonium-α,β-carboethoxyvinylcyclopentadienylide (III).—To a stirred solution of 1.94 g (0.006 mol) of I in 30 ml of methylene chloride was added dropwise a solution of 1.0 g (0.006 mol) of diethyl acetylenedicarboxylate in methylene chloride at room temperature. The solution was yellow and immediately turned to reddish orange. The reaction mixture was allowed to stand for an additional 30 min at room temperature and poured with stirring into 50 ml of *n*-hexane. The yellow precipitate which deposited was collected by filtration, washed with ethanol, and recrystallized from methylene chloride–ethanol to afford III as yellow crystals in almost quantitative yield: mp 224–225°; ir (KBr) $\nu_{C=O}$ 1687, 1725 cm^{-1}; uv max (MeOH) 225 mμ (log ε 4.56), 269 (4.04), 394 (4.23); nmr ($CDCl_3$) τ 2.1–2.6 (m, 1.5 H, phenyl), 3.2, 3.7, 4.0 (each m, 1 H, cyclopentadienyl), 5.28 (s, 1 H, vinyl), 5.10 (q, 2 H, methylene), 6.15 (q, 2 H, methylene), 8.15 (t, 3 H, methyl), 9.05 (t, 3 H, methyl).

Anal. Calcd for $C_{31}H_{29}O_4P$: C, 74.98; H, 5.88. Found: C, 74.88; H, 6.04.

Triphenylphosphonium-2-tricyanovinylcyclopentadienylide (IV).—To a suspension of 2.55 g (0.0098 mol) of I in tetrahydrofuran (60 ml) was added at 10° a solution of 1.0 g (0.0098 mol) of tetracyanoethylene in tetrahydrofuran (10 ml). The reaction mixture immediately turned orange and gradually become reddish orange. The reaction mixture was allowed to stir for 3 hr at the same temperature, concentrated by evaporation, and chromatographed on alumina using methylene chloride as the eluent. The solvent was removed under reduced pressure from the reddish orange colored eluate, and the residue was recrystallized from chloroform–*n*-hexane to afford IV as reddish orange crystals in 40% yield: mp 218–219°; ir (KBr) $\nu_{C≡N}$ 2220 cm^{-1}; uv max (MeOH) 223 mμ (log ε 4.55), 267 (4.02), 462 (4.63); nmr ($CDCl_3$) τ 2.1–2.6 (m, 16 H, phenyl and cyclopentadienyl), 3.2 (m, 1 H, cyclopentadienyl), 3.7 (m, 1 H, cyclopentadienyl).

Anal. Calcd for $C_{28}H_{18}N_3P$: C, 78.67; H, 4.24; N, 9.82. Found: C, 78.30; H, 4.54; N, 9.83.

The above reaction in the presence of triethylamine gave IV in quantitative yield.

Preparation of V.—A solution of 2.0 g (0.0061 mol) of I and 0.3 g (0.0031 mol) of maleimide in dioxane (40 ml) was refluxed for 15 hr and chromatographed over cellulose powder using benzene as the eluent. Solvent was removed from the eluate, and the residue was repeatedly recrystallized from methanol–benzene to give V in 50% yield: mp 195–196°; ir (KBr) $\nu_{C=O}$ 1700, 1770 cm^{-1}; uv max (methylene chloride) 269 mμ (log ε 4.04), 295 (3.83), 475 (1.30); nmr ($CDCl_3$) τ 1.7 (s, 1 H, NH), 2.0∼2.6 (m, 1.5 H, phenyl), 3.5–3.8 (m, 3 H, cyclopentadienyl), 5.85 (t, J = 6.8 Hz, 1 H, methyne), 6.90 (d, J = 6.8 Hz, 2 H, methylene).

Anal. Calcd for $C_{27}H_{22}NO_2P$: C, 79.61; H, 5.65. Found: C, 79.52; H, 5.43.

Reaction of I with Norbornadiene (or 1,2-Diphenylcyclopropene).—Following the procedure employed in the preparation of III, IV, and V, the reaction of I with norbornadiene (or 1,2-diphenylcyclopropene) was carried out. After work-up of the mixture, I was quantitatively recovered.

Triphenylphosphonium-2-nitrocyclopentadienylide.—To a stirred solution of 1.0 g (0.0031 mol) of I in 30 ml of chloroform was added 2.0 g of aluminum chloride and 0.56 g (0.0061 mol) of ethyl nitrate at room temperature under nitrogen atmosphere, and the mixture was stirred for 3 hr at 40°. The reaction mixture was chromatographed on alumina using methylene chloride as an eluent, the solvent was removed from the eluate, and the residue was recrystallized from methylene chloride–ethanol to yield triphenylphosphonium-2-nitrocyclopentadienylide (VI) in 80% yield: mp 243–44°; ir (KBr) $\nu_{as\text{-}NO_2}$ 1465 cm^{-1}, $\nu_{s\text{-}NO_2}$ 1382 cm^{-1}; uv max (acetonitrile) 222 mμ (log ε 4.59), 266 (3.78), 372 (4.33); nmr ($CDCl_3$) τ 2.2–2.6 (m, 15 H, phenyl), 2.85 (m, 1 H, cyclopentadienyl), 2.90 (m, 1 H, cyclopentadienyl), 3.7 (m, 1 H, cyclopentadienyl).

Anal. Calcd for $C_{23}H_{18}O_2NP$: C, 74.39; H, 4.89; N, 3.78. Found: C, 74.22; H, 5.11; N, 3.50.

Triphenylphosphonium-2-nitrosocyclopentadienylide.—To a solution of 1.0 g (0.0031 mol) of I in acetic acid was added dropwise aqueous sodium nitrite (0.214 g, 0.0031 mol) for 10 min at 0–5°. After stirring an additional 20 min at the same temperature, the reaction mixture was neutralized with aqueous sodium hydroxide at 0°. A green precipitate deposited, which was separated by filtration, washed several times with water, and chromatographed on alumina to give triphenylphosphonium-2-nitrosocyclopentadienylide (VII) in almost quantitative yield as dark green crystals: mp 210° dec; uv max (MeOH) 268 mμ (log ε 3.67), 360 (3.94); nmr ($CDCl_3$) τ 2.3–2.8 (m, 15 H phenyl), 3.0 (m, 1 H, cyclopentadienyl), 3.5 (m, 1 H, cyclopentadienyl), 3.8 (m, 1 H, cyclopentadienyl).

Anal. Calcd for $C_{23}H_{18}ONP$: C, 77.75; H, 5.35, N, 3.94, P, 8.72. Found: C, 77.60; H, 5.32, N, 3.88, P 8.74.

The position of substitution was confirmed as follows. To a mixture of aniline (1 ml) and glacial acetic acid (3 ml) was added dropwise a solution of 1.0 g of VII in ethanol at room temperature. After stirring for 12 hr at 90–100°, the reaction mixture was poured into water, and the brown precipitate that separated was filtered and chromatographed on silica gel to give orange crystals: mp 238–240°; uv max (EtOH) 220 mμ (log ε 4.70), 4.55 (4.25). This compound was identified as triphenylphosphonium-2-phenylazocyclopentadienylide[4] by a mixture melting point method, its uv spectrum, and R_f value.

Triphenylphosphonium-2-formylcyclopentadienylide (VIII).—The Vilsmeier reagent was prepared as follows. To 40 ml (0.52 mol) of *N*,*N*-dimethylformamide was added 16.1 ml (0.18 mol) of phosphorus oxychloride at −15 to −10° under nitrogen atmosphere, and the mixture was kept at the same temperature for 10 min. To this solution, 26.1 g (0.080 mol) of I was slowly added maintaining the temperature at −15 to −10°. The mixture was allowed to stand until room temperature. The reddish orange reaction mixture was poured into ice–water, and the precipitate was collected and chromatographed on alumina to give an orange solid (VIII) in 70% yield: mp 221–222° dec; ir (KBr) $\nu_{C=O}$ 1630 cm^{-1}; uv max (acetonitrile) 224 mμ (log ϵ 4.42), 268 (4.00), 372 (4.31); nmr (CDCl$_3$) τ 0.35 (s, 1 H, formyl), 2.2–2.6 (m, 15 H, phenyl), 3.1 (m, 1 H, cyclopentadienyl), 3.6 (m, 2 H, cyclopentadienyl).

Anal. Calcd for $C_{24}H_{19}OP$: C, 81.35; H, 5.40; P, 8.74. Found: C, 81.01; H, 5.17; P, 9.18.

Triphenylphosphonium-2,5-diformylcyclopentadienylide (IX).—Phosphorus oxychloride, 40.4 ml (44.0 mmol), was added dropwise at 0–5° to a stirred solution of 6.52 g (20 mmol) of I in 40 ml of *N*,*N*-dimethylformamide under a nitrogen atmosphere. After the reaction proceeded for 2 hr at room temperature, the mixture was poured into ice–water and neutralized with aqueous sodium hydroxide. The light orange precipitate which deposited was collected by filtration, washed with water, and purified by reprecipitation from methylene chloride–methanol to give IX as a light pink solid in 80% yield: mp 225–227° dec; ir (KBr) $\nu_{C=O}$ 1640 cm^{-1}; uv max (acetonitrile) 220 mμ (log ϵ 4.29), 268 (4.21), 310 (4.01); nmr (CDCl$_3$) τ 0.2 (d, J = 1.5 Hz, 2 H, formyl), 2.0–2.5 (m, 15 H, phenyl), 2.95 (d, J = 5.0 Hz, 2 H, cyclopentadienyl).

Anal. Calcd for $C_{25}H_{19}O_2P$: C, 78.53; H, 5.01. Found: C, 78.31; H, 5.28.

Triphenylphosphonium-2,3,4,5-tetrabromocyclopentadienylide (X). **A.**—Bromine, 3.52 g (0.022 mol), was added dropwise to a stirred suspension of potassium *tert*-butoxide in acetonitrile at room temperature. After stirring additional 2 hr, the reaction mixture was poured into water, and the brown precipitate which separated was collected by filtration, washed with methanol, and recrystallized from methylene chloride–benzene to afford X (40% yield) as white crystals: mp 224–225° dec; uv max (acetonitrile) 225 mμ (log ϵ 4.51), 268 (4.15), 310 (sh); nmr (CDCl$_3$) τ 2.1–2.7 (m, 15 H, phenyl).

Anal. Calcd for $C_{23}H_{15}Br_4P$: C, 43.03; H, 2.33. Found: C, 43.04; H, 2.28.

B.—A solution of 7.74 g (0.044 mol) of *N*-bromosuccinimide in acetonitrile (10 ml) was added to a suspension of 3.26 g (0.01 mol) of I at room temperature. After stirring for 30 min and work-up afforded X in 90% yield.

Triphenylphosphonium-2,3,4,5-tetrachlorocyclopentadienylide (XI).—The reaction of I with *N*-chlorosuccinimide was carried out by the same procedure as above and worked up to afford XI as a white solid in 82% yield: mp 234–235°; uv max (acetonitrile) 268 mμ (log ϵ 3.89); nmr (CDCl$_3$) τ 2.1–2.7 (m, 15 H, phenyl).

Anal. Calcd for $C_{23}H_{15}Cl_4P$: P, 6.68; Cl, 30.55. Found: P, 6.35; Cl, 30.29.

Triphenylphosphonium-2,3,4,5-tetraiodocyclopentadienylide (XII).—The reaction of I with *N*-iodosuccinimide was carried out by the same procedure as above, and worked up to afford XII as white yellow solid in 87% yield: mp 204–205°; uv max (acetonitrile) 260 mμ (log ϵ 4.25), *ca.* 300 (sh).

Anal. Calcd for $C_{23}H_{15}I_4P$: P, 3.73. Found: P, 3.60.

Reaction of I with Benzaldehyde.—To a cooled solution of 3.26 g (0.01 mol) in tetrahydrofuran was added dropwise a solution of 1.06 g (0.01 mol) of benzaldehyde at room temperature. After reaction for 3 hr, the reddish violet solution was evaporated under reduced pressure, and the residue was chromatographed on polyamide using methylene chloride as an eluent. After removal of the solvent under reduced pressure from the eluate, the residue was recrystallized from methanol–ether to yield wine-red crystals (XIV), which decomposed at 185°: uv max (MeOH) 267 mμ (log ϵ 3.6), 315 (3.4), 520 (2.8); ir (KBr) ν_{OH} 3500 cm^{-1}; nmr (DMSO-d_6) τ 1.5 (s, 1 H, methyne), 1.8–3.0 (m, 20 H, phenyl), 3.1–3.6 (m, 3 H, cyclopentadienyl).

Anal. Calcd for $C_{30}H_{25}OP$: C, 83.31; H, 5.82; P, 7.16. Found: C, 84.13; H, 6.09; P, 6.45.

Reaction of I with Dichlorocarbene.—When 5.0 g (0.04 mol) of dry powdered potassium *tert*-butoxide was slowly added to a solution of 4.0 g (0.012 mol) of I dissolved in 200 ml of chloroform at 0–5° under a nitrogen atmosphere, the original yellow color of solution changed to dark red. After 2 hr at room temperature, the reaction mixture was poured into ice–water, and the organic layer was collected, dried over magnesium sulfate, and evaporated under reduced pressure. The oily residue was chromatographed on alumina to yield a light pink solid in 3.2% yield, mp 221–222°. This product was identical with triphenylphosphonium-2-formylcyclopentadienylide (VIII). A trace of triphenylphosphine oxide (mp 156–157°) and the starting material (I) were also obtained.

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Registry No.—I uncharged form, 2224-32-0; I charged form, 29473-30-1; III uncharged form, 34411-82-0; III charged form, 33356-41-1; IV uncharged form, 15924-42-2; IV charged form, 33356-42-2; V uncharged form, 34411-84-2; V charged form, 33356-43-3; VI uncharged form, 41172-19-4; VI charged form, 41172-20-7; VII uncharged form, 41265-38-7; VII charged form, 41172-21-8; VIII uncharged form, 34299-42-8; VIII charged form, 41172-23-0; IX uncharged form, 33082-53-0; IX charged form, 41172-25-2; X uncharged form, 33082-54-1; X charged form, 41172-27-4; XI uncharged form, 41172-28-5; XI charged form, 41172-29-6; XII uncharged form, 41172-30-9; XII charged form, 41172-31-0; XIV uncharged form, 41172-32-1; XIV charged form, 41172-33-2.