

Features of Electrophilic Substitution of Triphenylphosphonium Cyclopentadienylide

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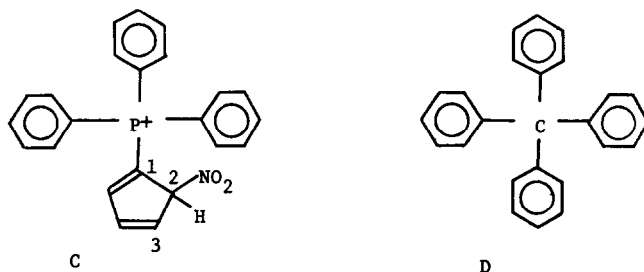
As reported in the previous paper,<sup>1</sup> phosphonium cyclopentadienylide as well as phosphonium methylide have been shown to have substantially the dipolar structure ( $\bar{C}-\overset{+}{X}$ ) as the ground state structure. This structural feature prompted us to attempt reactions of triphenylphosphonium cyclopentadienylide (I) with electrophiles, which have not been encountered except diazo-coupling<sup>2</sup> so far. The electrophilic reactions employed in this study are nitration, nitrosation, bromination and Vilsmeier reaction. Consequently we have found that the attacking position of electrophile and halosubstitution are quite strange compared with electrophilic aromatic substitution. The substitutions have been confirmed to take place on the cyclopentadienide ring and not on the phenyl ring from the nmr ( $CDCl_3$ ) spectra of the products. The nmr spectra of I appeared two multiplets centered at  $\tau$  2.2-2.6 (15H, phenyl) and at  $\tau$  3.7 (4H, cyclopentadienyl), on the other hand, those of the products appeared several multiplets (cyclopentadienyl proton) at  $\tau$  3.7 and somewhat downfield positions besides the multiplet at  $\tau$  2.2-2.6 (15H phenyl).<sup>3</sup> A preference for electrophilic attack at 2 (or 5) position over that at 3 (or 4) position of I has been confirmed by the chemical method.<sup>4</sup> The nmr spectra of cyclopentadienyl ring of the products have also been used for the determination of substitution position.

The reaction of I with ethylnitrate in the presence of aluminium chloride was attempted at 40° in chloroform under nitrogen atmosphere. After chromatography (adsorber: alumina, eluent: methylene chloride) of the reaction mixture, yellow crystal (recrystallized from methylene chloride-methanol) was obtained which was identified to be 2-nitroderivative (II). m.p. 243-244°. Yield 80%. ir (IBr)  $\nu_{as-NO_2}$  1465  $cm^{-1}$ ,  $\nu_{s-NO_2}$  1382  $cm^{-1}$ . nmr  $\tau$  2.85 (m. 1H), 2.90 (m. 1H), 3.7 (m. 1H), 2.2-2.6 (15H phenyl). uv (acetonitrile), 266 m $\mu$  (log  $\epsilon$  3.78), 372 (4.33). Nitration with nitronium fluoroborate also afforded 2-nitroderivative. That the stretching vibrations of  $NO_2$  showed lower values than the ordinary might be interpreted

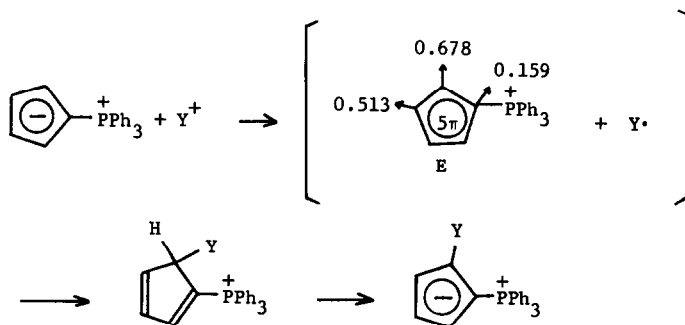
in terms of larger conjugation of cyclopentadienyl ring with nitro group. Reaction of I with sodium nitrite in aq. acetic acid at 0-5°, and the subsequent work-up afforded green 2-nitroso derivative (III) in almost quantitative yield. m.p. 210° (dec). The substitution position of III was confirmed as follows. The product obtained by the treatment of III with aniline in glacial acetic acid was identified with the phenylazo derivative, which was already prepared and proved to be 2-substituted one by Ramirez et al.<sup>5</sup> nmr  $\tau$  2.0-2.8 (16H, phenyl 15H + cyclopentadienyl 1H), 3.4-3.9 (m. 2H, cyclopentadienyl), ir (KBr)  $\nu_{\text{NO}}$  1492  $\text{cm}^{-1}$ . uv ( $\text{CH}_3\text{OH}$ ) 268  $\text{m}\mu$  (log  $\epsilon$  3.67), 360 (3.94). Although nitration and nitrosation of I at 0-40° afforded only 2-substituted derivative, Vilsmeier reaction of I gave 2-formyl and 2,5-diformyl derivatives depending on the reaction temperature. To phosphorus oxychloride and N,N-dimethyl formamide mixture was added I below -15° and stirred until room temperature. After work-up, soft-pink 2-formyl derivative (IV) was obtained in 70% yield. m.p. 221-222° (dec), ir (KBr);  $\nu_{\text{C=O}}$  1630  $\text{cm}^{-1}$ . nmr,  $\tau$  0.35 (s. 1H, formyl), 2.2-2.6 (m. 15H, phenyl) 3.1 (m. 1H cyclopentadienyl), 3.6 (m. 2H cyclopentadienyl). uv (acetonitrile) 224  $\text{m}\mu$  (log  $\epsilon$  4.42), 268 (4.00) and 372 (4.31). On the other hand, the reaction of I with Vilsmeier reagent at room temperature afforded 2,5-diformyl derivative (V) in 90% yield. m.p. 225-227° (dec). ir (KBr);  $\nu_{\text{C=O}}$  1640  $\text{cm}^{-1}$ . nmr,  $\tau$  0.2 (d. 2H, formyl), 2.0-2.5 (m. 15H, phenyl), 2.95 (d. 2H, cyclopentadienyl). As the coupling constants, 1.5  $\text{H}_2$  for the formyl protons and 5.0  $\text{H}_2$  for the cyclopentadienyl protons were observed, which are due to coupling with phosphorus. uv ( $\text{CH}_3\text{CN}$ ), 226  $\text{m}\mu$  (log  $\epsilon$  4.29), 268 (4.21), 302 (4.01). Quite a different behavior of electrophile was found in the reaction of I with N-bromosuccinimide (NBS) or bromine. Treatment of I with four mole of NBS in the presence of potassium t-butoxide in acetonitrile at room temperature afforded white 2,3,4,5-tetrabromo derivative (VI) in quantitative yield. m.p. 224-225° (dec). Bromine gave also the same result. It is noteworthy that even equimolar NBS at room temperature gave the same product. No peaks corresponding to the cyclopentadienyl proton was observed in the nmr spectra of VI in  $\text{CDCl}_3$ . uv 225  $\text{m}\mu$  (log  $\epsilon$  4.50) 265 (4.15). From these result, it seems that apparent behavior of I toward electrophile is quite strange compared with electrophilic substitution of benzene derivatives. Because nitration, nitrosation and Vilsmeier reaction have occurred at 2-position of cyclopentadienide ring, on the other hand bromination easily has afforded the tetrasubstituted derivative.

It is surprising that the electrophilic substitution occurred at 2-position which is

stereochemically unfavorable for the reaction as shown in C. For instance, nitration of tetraphenylmethane (D) takes place at 4 position.<sup>6</sup> This means that the electrophilic reaction of I is strongly controlled by the electronic factor. From HMO calculation, total  $\pi$  electron density of each position is in the order 1- (1.193) > 3- (1.178) > 2-positions (1.165), suggesting that 2-position is not favorable for attack of electrophile from the total  $\pi$  electron density. Moreover, the reaction behavior of I with NBS (or  $\text{Br}_2$ ) indicates



that bromination more easily takes place with increasing bromo-substitution. These strange reaction behaviors of I is rationalized by the application of "electron transfer theory" to this reaction system shown in scheme 1.



From the electron transfer theory,<sup>7</sup> cyclopentadienide ring having lower ionization potential (8.6 eV) is understood to react more easily with an electrophile ( $\text{Y}^+$ ) than benzene ring (ionization potential 9.24 eV), and free valences of electron transfer intermediate (E, cation radical) by which orientation of electrophile is decided are indicated in E. The free valence value at 2 position is highest in the intermediate (E), rationalizing that the

electrophilic substitution takes place at 2-position. On the other hand, ionization potential ( $E_{ho}$ : energy (-8) of highest occupied MO) is shown to decrease with increasing bromo-substitution (e.g.  $E_{ho}$ : I 0.618, 2-bromoderivative 0.476, 2,5-dibromoderivative 0.382), explaining that tetrabromo derivative exclusively forms in the bromination.

#### References

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- (3) PMR spectra of I and mono- (or di) substituted derivatives of I were complicated due to H-P coupling.
- (4) Detail on the identification will be published later.
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