

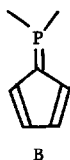
Reactions of Phosphonium Cyclopentadienylide with Dienophiles

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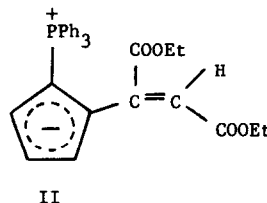
It has been shown that the ylide structure (A) predominantly contributes to the phosphonium cyclopentadienylide in the ground state¹ and the electrophilic substitutions at cyclopentadienyl ring easily take place in the reactions of triphenylphosphonium cyclopentadienylide with various electrophiles.²



The investigation of reaction behavior of phosphonium cyclopentadienylide with dienophile is another useful examination for determining whether phosphonium cyclopentadienylide behaves as the ylide (A) or as the ylene (B). The

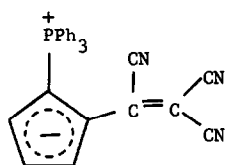
electron-deficient unsaturated compounds such as dialkyl acetylene dicarboxylate and tetracyanoethylene are known to be a reactive dienophile³ as well as to be a weak electrophile.⁴ The present investigation was directed toward answering whether triphenylphosphonium cyclopentadienylide (I) is undergone Diels-Alder reaction or electrophilic reaction.

To a solution of I in methylene chloride was added diethyl acetylene dicarboxylate, then the reaction mixture was stirred at room temperature for 30 min. After work-up, yellow material ($C_{31}H_{29}O_4P$) (II) was almost quantitatively obtained. m.p. 224-225°. The nmr of II in $CDCl_3$ showed a complex multiplet (15 H) at τ 2.1-2.6 (phenyl protons), three multiplets of equal area (1H) centered at τ 3.2, 3.7 and 4.0 (cyclopentadienyl protons), a singlet (1H) at τ 5.28 (a vinyl proton), two quartets of equal area (2H) centered at τ 5.10 and 6.15



(methylene protons) and two triplets of equal area (3H) at τ 8.15 and 9.05 (methyl protons). The infrared spectrum of II (KBr disc) showed an existence of two strong $C=O$ stretching absorptions at 1687 cm^{-1} and 1725 cm^{-1} . The UV spectrum of II in methanol exhibited maxima

at 225 mμ (log ε 4.56), 269 mμ (log ε 4.04) and 394 mμ (log ε 4.23). The compound II is not Diels-Alder product but Michael addition product. Even in the presence of benzophenone as a carbonyl compound, the reaction did not afford triphenylphosphine oxide as well as the Wittig reaction product which should form from Diels-Alder product (reactive ylide compound). To a suspension of I in tetrahydrofuran was added a solution of tetracyanoethylene in tetrahydrofuran at 10° and the mixture was stirred at room temperature for 3 hrs. After work-up, orange material ($C_{28}H_{18}N_3P$) (III) was obtained as the major product. m.p. 218-

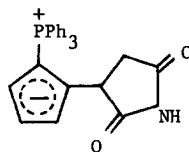


III

219° (decomp).

The nmr spectrum of III in deuterochloroform showed a multiplet (16 H) at τ 2.1-2.6 and two multiplets of equal area centered at τ 3.2 (1H) and at τ 3.7 (1H). One proton of cyclopentadienyl ring proton of III might be included in aromatic regions (τ 2.1-2.6). IR (KBr disk); ν_{CN} 2220 cm^{-1} . $\lambda_{max}^{CH_3OH}$; 223 mμ (log ε 4.55), 267 mμ (log ε 4.02) and 462 mμ (log ε 4.63). This product was confirmed to be the same as Rigby's product⁵ obtained by the reaction in the presence of excess triethylamine. Tricyanovinyl derivative (III) is sure to be formed via the Michael addition, then subsequent elimination of hydrogen cyanide.

Reaction of I with maleimide was also attempted in dioxane under nitrogen atmosphere. After keeping 15 hrs. at reflux temperature, the reaction mixture was chromatographed on cellulose powder using benzene as an eluent. Thus we got white solid (IV) ($C_{27}H_{22}NO_2P$) as a major product. m.p. 195°. In the nmr spectrum of IV, one broad proton in the lowest magnetic field is assigned to N-H proton, because this peak disappears by addition of deuterium oxide. Two multiplets at τ 2.0-



IV

2.6 (15 H) and at τ 3.5-3.8 (3H) are assigned to aromatic and cyclopentadienyl protons, respectively. A triplet centered at τ 5.85 (1H) and a doublet centered at τ 6.90 (2H) are well interpreted as the protons of five-membered ring containing nitrogen atom. IR (KBr disc); $\nu_{C=O}$ 1700 and 1770 cm^{-1} . $\lambda_{max}^{CH_2Cl_2}$; 269 mμ (log ε 4.04), 295 mμ (log ε 3.83) and 475 mμ (log ε 1.30). Further we attempted to react I with maleic anhydride in the presence of benzophenone, however no formation of triphenylphosphine oxide was observed, being one

of the products formed by the Wittig reaction of the Diels-Alder product with benzophenone.

On the other hand, norbornene, good hydrocarbon dienophile, did not react with I in the presence or absence of a carbonyl compound such as benzophenone.

From the attempted reactions, I is clear to form the Michael addition product by the electrophilic attack of electron-deficient unsaturated compounds. No evidence for Diels-Alder reaction was obtained. Such a reaction behavior of I toward the dienophiles strongly supports the $5C6\pi$ aromatic character of cyclopentadienyl ring of I, giving a proof for the previous prediction.¹

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