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Reaction of Phosphonium Cyclopentadienylide with Dichlorocarbene

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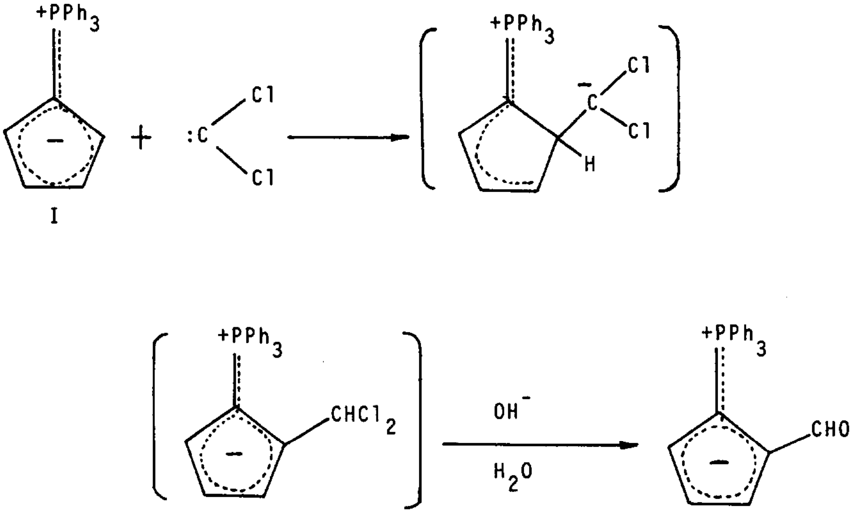
Previous publications[1,2] from our laboratory have demonstrated the reactions of triphenylphosphonium cyclopentadienylide (I) with various electrophiles and dienophiles. Our concern in the present paper has been directed to the reaction behaviour of I toward dichlorocarbene. Treatment of I in chloroform with potassium tert-butoxide at 0° yielded a dark red solution. After the mixture was allowed to stand for 2 hr at room temperature and poured into ice water, work-up of the organic layer gave white crystals (II), mp 221-222°. A small quantity of triphenylphosphine oxide was also obtained. The infrared spectrum of II in KBr disc shows a strong absorption at 1630 cm^{-1}, which is assigned to the strongly conjugated carbonyl stretching vibration. UV spectrum of II in acetonitrile shows the absorption maxima at 224 mμ (logε 4.42), 268 mμ (logε 4.00) and 302 mμ (logε 4.01). The nmr spectrum of II contains a formyl proton at τ 0.2 (d. 1H) besides the phenyl ring protons at τ 2.1-2.6 (m. 15H) and cyclopentadienyl ring protons at τ 3.2 (m. 2H) and τ 3.7 (m. 1H). The coupling constant of 1.5 Hz for the formyl proton in II is assigned to spin-spin coupling with phosphorus. These spectral data suggest that II is the monoformyl derivative of I. The authentic sample, 2-formyl derivative of I, was prepared from I and Vilsmeier reagent according to the procedure described in our previous communication.[1] The identity was confirmed by their spectral data and melting points. The reaction mechanism can be reasonably interpreted as shown in the following scheme.

It is noteworthy that the reaction behavior of I is quite different from those of triphenylphosphonium indenylide and fluorenylide with dichlorocar-



bene.[3] In the latter cases, the reaction gave triphenylphosphine oxide and the corresponding haloolefins, i.e. dichloromethylene-indene and -fluorene. These results are reasonably explained by the localization energies (Figure 1) calculated from Huckel MO method taking parameters; $\alpha_p = \alpha - 1.71\ \beta$, $\alpha_1 = \alpha - 0.1\ \beta$, $\beta_{p-c} = 0.87\ \beta$.[4] The localization energy at 2-position for I is the lowest among three positions 1,2 and 3 in I, whereas those at 1-position is the lowest for both phosphonium indenylide and fluorenylide, in accordance with experimental results.

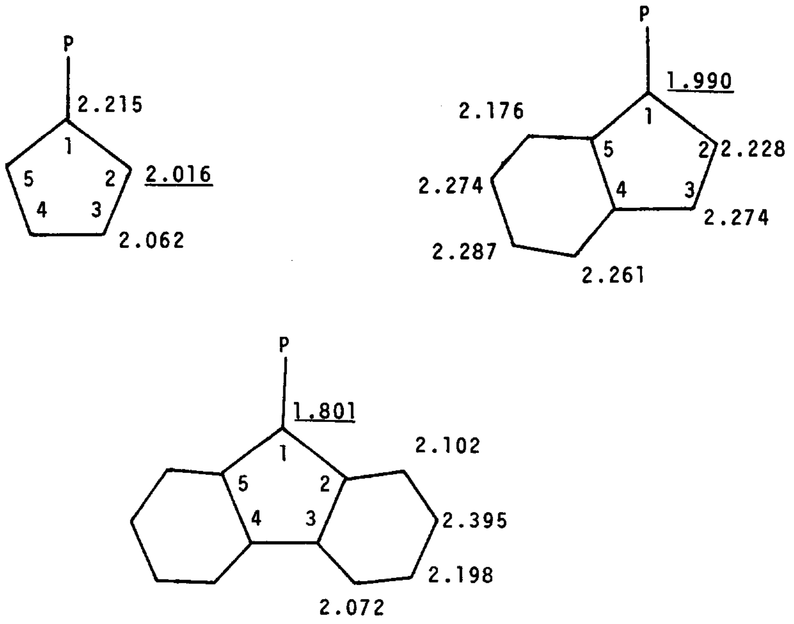


Figure 1. The localization energies (-β) for phosphonium cyclopentadienylide, indenylide and fluorenylide.

References

[1] Z. Yoshida, S. Yoneda, Y. Murata and H. Hashimoto, Tetrahedron Letters, 1523 (1971).

[2] Z. Yoshida, S. Yoneda, H. Hashimoto and Y. Murata, Tetrahedron Letters, 1527 (1971).

[3] M. Okano, Y. Ito and R. Oda, Tetrahedron Letters, 7 (1964).

[4] Coulomb integral for phosphorus atom (α_p) was determined from ionization potential for 3d-orbital by the use of equation $\alpha_p = I_p - 7.2/3.0$. Resonance integral (β_{p-c}) was estimated from Jaffe's table.[5]

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