

SYNTHESIS OF PHOSPHORANE HAVING KETENE GROUP AT α -POSITION

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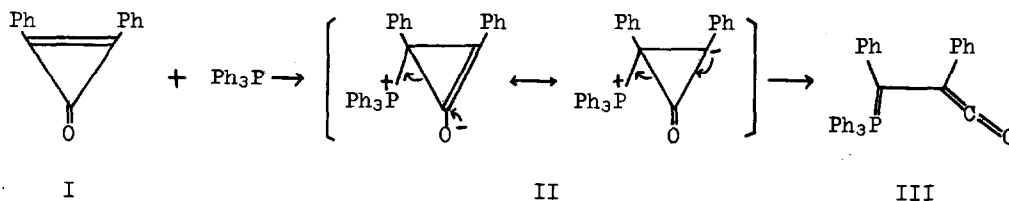
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(Received in Japan 17 March 1972; received in UK for publication 29 March 1972)

We wish to report the reaction of diphenylcyclopropenone(I) with triphenylphosphine to afford new type of phosphorane. The reaction of I with equivalent mole of triphenylphosphine in dry benzene at room temperature under nitrogen atmosphere for 3 hours gave α -triphenylphosphoranylidenediphenylketene(III)¹⁾ (orange crystals. m.p. 125-127°), which have been postulated as an intermediate²⁾ in the reaction of I with isonitrile, in 92% yield.

Anal. Found: C, 84.53; H, 5.52. Calcd. for $C_{33}H_{25}PO$: C, 84.61; H, 5.34%
Mol.wt. Found: 486 (by vapour pressure osmometer). Calcd. for $C_{33}H_{25}PO$: 468.
IR(KBr Tab): 2064(vs) ($\nu_{C=O}$), 1583(s), 1480(s), 1430(m), 1260(m), 1180(m),
1095(s), 690(s) cm^{-1} .

The reaction of I with triphenylphosphine may proceed via betaine intermediate(II) as illustrated below.

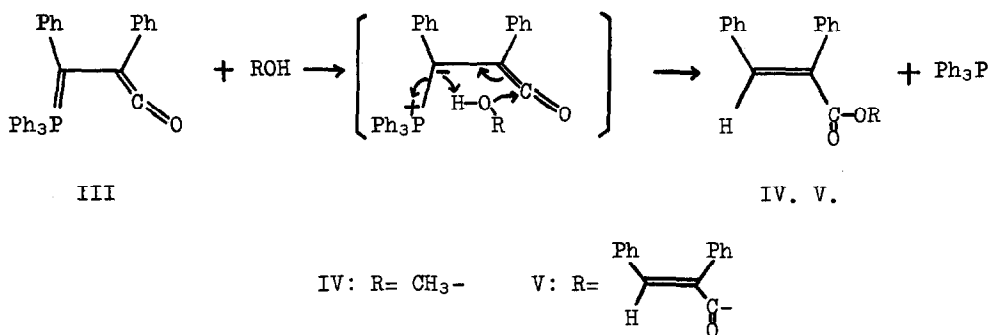


The compound III is the first example of isolated phosphorane possessing ketene group in a molecule, whose reactivity is of considerable interest.

Reactions of III with methanol and trans- α -phenylcinnamic acid in dry benzene at room temperature under nitrogen atmosphere gave methyl trans- α -phenylcinnamate³⁾ (m.p. 75.0-76.5°)(IV) and trans- α -phenylcinnamic anhydride(m.p. 118-120°)(V) in 100% and 89.5% yield, respectively. Similarly, 2,6-xylidine at 50°C gave trans-

N-(2,6-dimethylphenyl)- α -phenylcinnamoamide (m.p. 132-133°) (VI) in 97% yield. In these cases triphenylphosphine was obtained quantitatively. On the other hand III unlike usual ylides showed unreactivity to benzophenone and benzaldehyde.

These results indicate the nucleophilic attack would take place preferentially on ketene group rather than ylide group. The formations of IV and V may proceed through the concerted pathway involving ready elimination of triphenylphosphine as described below.



Similar mechanism would explain the formation of VI. The compound III easily reacted with 2,6-dimethylphenylisonitrile in dry benzene at room temperature under nitrogen atmosphere to afford 4-(2,6-dimethylphenylimino)-2,3-diphenylcyclobuten-1-one in 90% yield.

Studies on further reactivities of the novel ylide described above are in active progress.

References.

- (1) The compound III is sensitive to moisture but could be stored at room temperature in dry condition for a week without any detective decomposition.
- (2) N. Obata and T. Takizawa, Tetrahedron Letters, 2231(1970)
- (3) Christo G. Kratchanov and Gogdan J. Kurtev, Tetrahedron Letters, 3085(1965)