# The Formation of Ylids by the Addition of Phosphines to Activated Olefins

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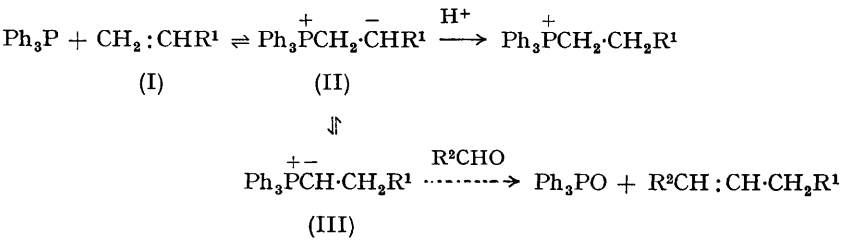
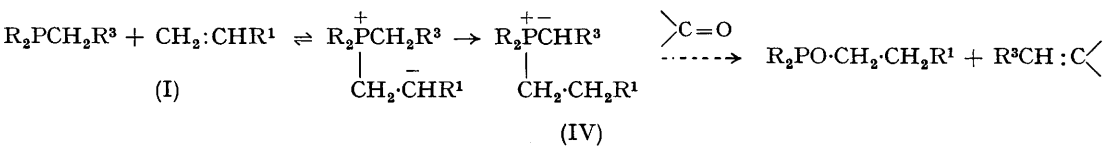
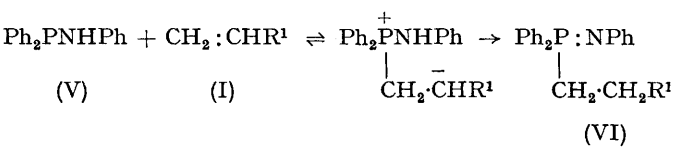
TRIPHENYLPHOSPHINE adds to activated olefins, *e.g.*, (I; $R^1$ = CN, $CONH_2$, $CO_2Et$) to give the betaines (II), although the equilibrium position is largely on the side of the reactants. Hoffmann[1] showed that the betaines can be protonated to give phosphonium salts, and Oda, Kawabata, and Tanimoto[2] showed that the betaines give rise to the corresponding ylids (III) which can be captured by aldehydes in Wittig olefin syntheses.

We have shown that when the phosphines $R_2PCH_2R^3$, where $R^3$ is a group capable of stabilising an adjacent carbanion, are treated with the activated olefins (I; $R^1$ = CN, $CONH_2$, $CO_2Et$) the intermediate betaines transfer a proton to give the ylids (IV) which can be used *in situ* in Wittig olefin syntheses. The reactions proceed under mild conditions with or without a hydroxylic solvent. Some typical results are given in the Table.

Aminophosphines react with activated olefins in







(V) (I) (VI)

TABLE

| Phosphine | $R^1$ | Solvent (reflux) | Carbonyl compound | Olefin (%) |
|---|---|---|---|---|
| $PhP(CH_2Ph)_2$ | CN | EtOH | PhCHO | 18 (*cis*) 79 (*trans*) |
| $PhP(CH_2Ph)_2$ | CN | –/100° | Fluorenone | 42 |
| $PhP(CH_2Ph)_2$ | CN | –/90° | $MeCH_2$·CHO | 13 (*cis*) 64 (*trans*) |
| $Ph_2PCH_2$·$CO_2Et$ | CN | EtOH | PhCHO | 69 (*trans*) |
| $Ph_2PCH_2$·$CO_2Et$ | $CO_2Et$ | –/130° | Cyclohexanone | 54 |
| $Ph_2PCH_2Ph$ | CN | MeOH | PhCHO | 17 (*cis*) 53 (*trans*) |
| $Ph_2PCH_2Ph$ | $CONH_2$ | EtOH | PhCHO | 13 (*cis*) 37 (*trans*) |

a similar way, *e.g.* the aminophosphine (V) on warming with the olefins (I; $R^1$ = CN, $CONH_2$) gives the stable iminophosphoranes (VI; $R^1$ = CN, $CONH_2$) in >87% yield, the structures being shown by their reactions with benzaldehyde at 100° to give benzylideneaniline (>95%) and phosphine oxides.

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[1] H. Hoffmann, *Chem. Ber.*, 1961, **94**, 1331.
[2] R. Oda, T. Kawabata, and S. Tanimoto, *Tetrahedron Letters*, 1964, 1653.