

Equilibration of 2*H*-Azirine with Vinylnitrene

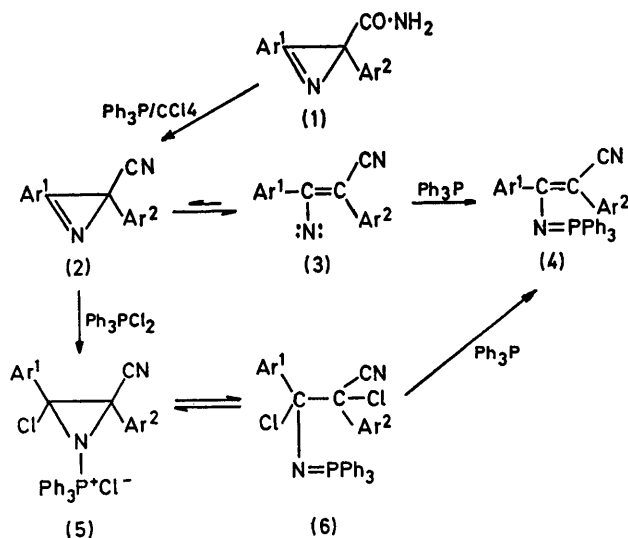
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Summary Treatment of 2,3-diaryl-2*H*-azirine-2-carboxamide with triphenylphosphine and carbon tetrachloride affords the triphenyliminophosphorane (4).

THE postulated¹ equilibration of 7-azabicyclo[4,1,0]hepta-2,4,6-triene (bicyclic 2*H*-azirine) with phenylnitrene, especially the change to the nitrenoid species, has not been examined even for monocyclic 2*H*-azirines. We report here results for 2,3-diaryl-2-cyano-2*H*-azirine.

Reaction of the carboxamides² (1; Ar¹ = Ar² = Ph), (1; Ar¹ = Ph, Ar² = *p*-ClC₆H₄), and (1; Ar¹ = *p*-MeC₆H₄, Ar² = Ph) with triphenylphosphine (3 mol. equiv.) and carbon tetrachloride³ (excess) in tetrahydrofuran at 50—60° under nitrogen for 2 h afforded triphenylphosphine oxide and the iminophosphoranes (4; Ar¹ = Ar² = Ph), m.p. 178—179° (from CCl₄) (20%), (4; Ar¹ = Ph, Ar² = *p*-ClC₆H₄), m.p. 208—209° (from benzene–light petroleum) (20%), and (4; Ar¹ = *p*-MeC₆H₄, Ar² = Ph), m.p. 197—198° (from CCl₄–light petroleum) (14%), respectively, which were characterized by analysis, molecular weight, and



spectroscopy. In particular, the presence of a very strong $\nu(\text{P}=\text{N})$ band⁴ (CHCl_3) ($1385\text{--}1390\text{ cm}^{-1}$) and the low $\nu(\text{C}\equiv\text{N})$ frequency ($2200\text{--}2180\text{ cm}^{-1}$) support the proposed structures.

The 2*H*-azirine (**2**) was not isolated but detected by i.r. spectroscopy. Electrophilic attack on the azirine (**2**) by dichlorotriphenylphosphorane⁵ to give an aminophosphonium salt (**5**) followed by equilibration⁶ with the isomer (**6**) and dechlorination⁷ by triphenylphosphine is unlikely since reaction of the azirine (**1**; $\text{Ar}^1 = \text{Ar}^2 = \text{Ph}$) with

dibromotriphenylphosphorane⁸ afforded neither the azirine (**2**) nor the iminophosphorane (**4**). Our observations can be rationalized in terms of equilibration of (**2**) with the vinyl-nitrene (**3**), which probably favours markedly the very reactive nitrene species. Rapid coupling with tervalent phosphorus compounds⁹ would assist this shift in the equilibrium.

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