Equilibration of 2*H*-Azirine with Vinylnitrene

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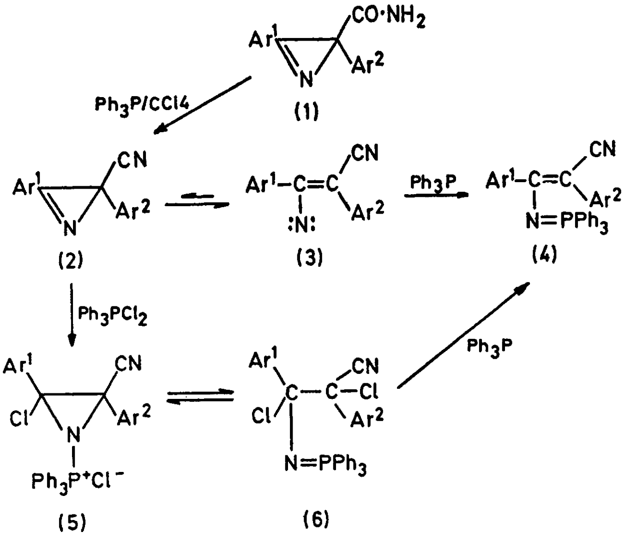
Summary Treatment of 2,3-diaryl-2*H*-azirine-2-carboxamide with triphenylphosphine and carbon tetrachloride affords the triphenyliminophosphorane (**4**).

THE postulated[1] 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 carboxamides[2] (**1**; $Ar^1 = Ar^2 = Ph$), (**1**; $Ar^1 = Ph$, $Ar^2 = p\text{-}ClC_6H_4$), and (**1**; $Ar^1 = p\text{-}MeC_6H_4$, $Ar^2 = Ph$) with triphenylphosphine (3 mol. equiv.) and carbon tetrachloride[3] (excess) in tetrahydrofuran at 50—60° under nitrogen for 2 h afforded triphenylphosphine oxide and the iminophosphoranes (**4**; $Ar^1 = Ar^2 = Ph$), m.p. 178—179° (from CCl_4) (20%), (**4**; $Ar^1 = Ph$, $Ar^2 = p\text{-}ClC_6H_4$), m.p. 208—209° (from benzene–light petroleum) (20%), and (**4**; $Ar^1 = p\text{-}MeC_6H_4$, $Ar^2 = Ph$), m.p. 197—198° (from CCl_4–light petroleum) (14%), respectively, which were characterized by analysis, molecular weight, and



spectroscopy. In particular, the presence of a very strong $\nu(P{=}N)$ band[4] ($CHCl_3$) (1385—1390 cm^{-1}) and the low $\nu(C{\equiv}N)$ frequency (2200—2180 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 dichlorotriphenylphosphorane[5] to give an aminophosphonium salt (**5**) followed by equilibration[6] with the isomer (**6**) and dechlorination[7] by triphenylphosphine is unlikely since reaction of the azirine (**1**; $Ar^1 = Ar^2 = Ph$) with dibromotriphenylphosphorane[8] afforded neither the azirine (**2**) nor the iminophosphorane (**4**). Our observations can be rationalized in terms of equilibration of (**2**) with the vinylnitrene (**3**), which probably favours markedly the very reactive nitrene species. Rapid coupling with tervalent phosphorus compounds[9] would assist this shift in the equilibrium.

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