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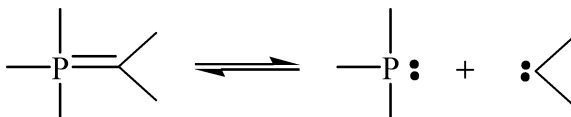
Ylides and Carbenes: the First Carbene Catalyzed Reaction

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The P=C ylidic bond of phosphorus ylides is able to dissociate with the formation of the appropriate phosphanes and carbenes.



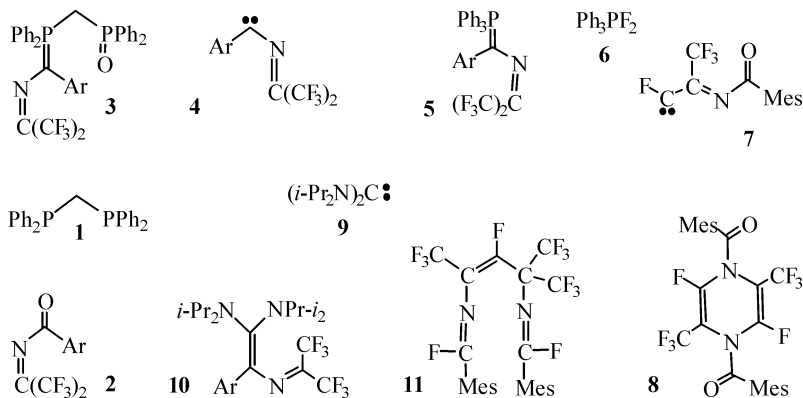
For example, ylide 3 obtained from diphosphane 1 and acyl imines 2 is capable of reversible cleavage of the P=C bond in solution to give carbene (nitrile ylide) 4 and the phosphane, respectively.¹ Carbene 4 can be trapped by Ph₃P to give ylide 5. Trying to obtain ylide 5 from Ph₃P and acyl imine 2 we found that under certain conditions the reaction leads to the formation of difluorophosphorane 6 and carbene 7. The latter can display not only carbene-like but also biradical-like properties to give dimer 8.

Ylides 3 and 5 can be used as a source of carbene (or nitrile ylide) 4 in different reactions under mild conditions. However, the interaction of ylide 5 with diaminocarbene 9 did not give the expected alkene 10, but led to a quantitative transformation into compound 11 which can be considered as an unsymmetrical dimer of carbene 4.² This is the first example of a reaction in which carbene acts as a catalyst.

Similarly to phosphanes, diaminocarbene 9 can react with acyl imine 2. Although this reaction should also include the intermediate

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formation of carbene 4, no traces of its dimer 11 were found in this case and the only product was alkene 10.



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