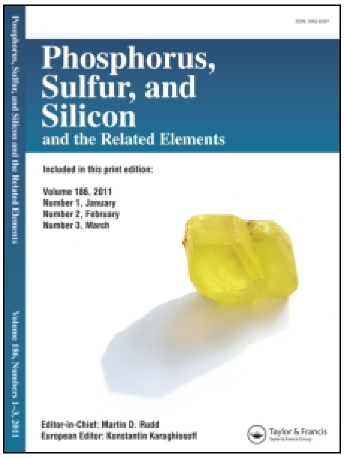

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A Novel Reaction between the P=O Group of Cyclic 2,4,6-Trialkylphenylphosphine Oxides and Dimethyl Acetylenedicarboxylate (DMAD)

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A NOVEL REACTION BETWEEN THE P=O GROUP OF CYCLIC 2,4,6-TRIALKYLPHENYLPHOSPHINE OXIDES AND DIMETHYL ACETYLENEDICARBOXYLATE (DMAD)

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The reaction of cyclic P-aryl phosphine oxides with DMAD affords ylides/phosphoranes via oxaphosphetes.

Keywords: Arylphosphine oxide; oxaphosphete; phosphorane/ylide

The Diels–Alder reaction of 1,2-dihydrophosphinine oxides (**1**) with suitable dienophiles furnished phosphabicyclo-octadienes (**2**) or phosphabicyclo-octenes (**3**) giving methylenephosphine oxides (**4**) on fragmentation, is useful in the phosphorylation of alcohols and amines (Figure 1).[1,2] An alternative mechanism was also substantiated that has never been observed earlier.[3]

During our efforts to prepare suitable precursors, novel phosphabicyclo-octenes, such as diaza derivative **6** and dimer **7**, were also synthesized.

Different approaches were explored to synthesize the P-trialkylphenyl phosphabicyclo-octenes (**9**). One possibility was the [4 + 2]

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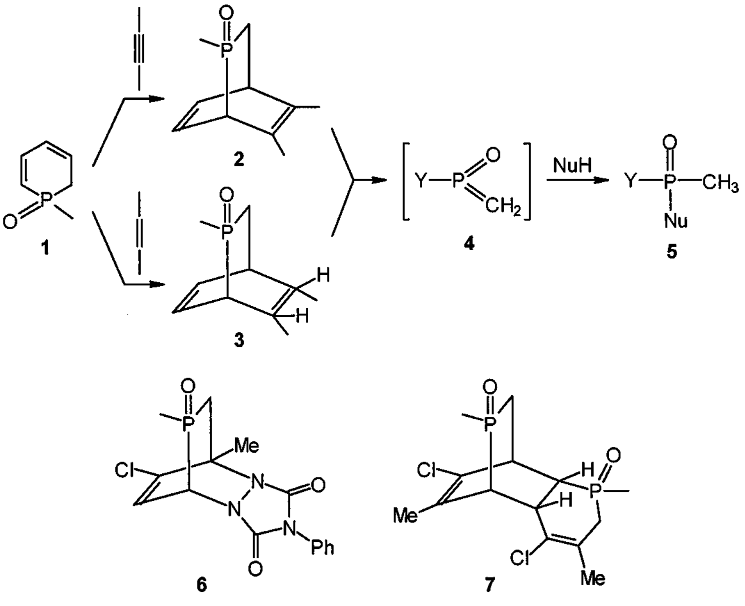


FIGURE 1

cycloaddition of the aryldihydrophosphinine oxide (**8**) with NPMI (Figure 2),[4] while another method comprised substitution at phosphorus of the already existing phosphabicyclo-octene skeleton. Experimental observations on the photolyses of compounds **9** were consistent with the involvement of a pentavalent pentacoordinate P-intermediate (**11**) (Figure 3).

Our attempts to prepare phosphabicyclo-octadienes with sterically demanding substituents on the phosphorus atom failed; the

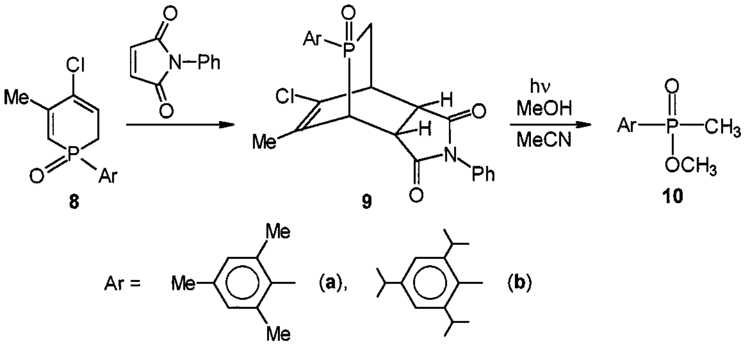


FIGURE 2

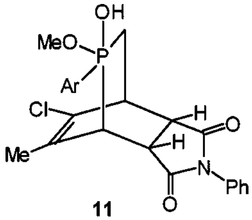


FIGURE 3

reaction of dihydrophosphinine oxides **8** with dimethyl acetylenedicarboxylate (DMAD) followed an unexpected protocol to give phosphorane/ylide **13**, presumably through spirocyclic oxaphosphete **12** (Figure 4).[5]

The novel reaction of P-heterocycles with DMAD proved to be general to afford products **15**, **17**, **19**, **21**, **23**, and **25** shown in Figure 5 and Table I.[4,6,7] The only criterion of the starting [2 + 2] cycloaddition is the presence of a trialkylphenyl substituent on the phosphorus atom.

Finally, it was found that the cycloaddition took also place with open-chained dialkyl arylphosphine oxides. The efficiency of these reactions was, however, rather poor.[7]

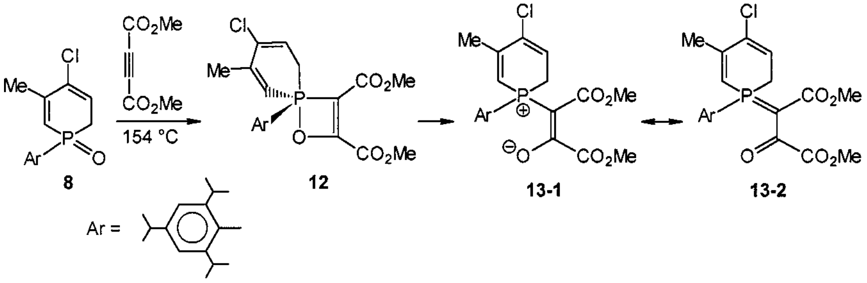


FIGURE 4

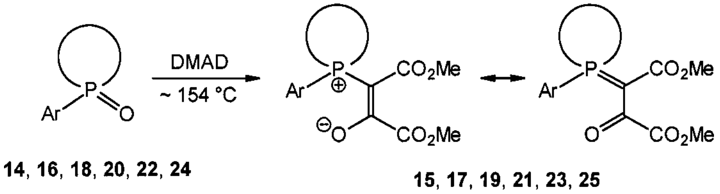
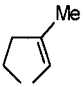
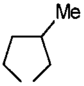
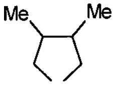
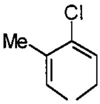


FIGURE 5 The substituents are shown in Table I.

TABLE I Substituents

	Ar	Starting material	Product	Reference
	2,4,6-triisopropylphenyl	**14**	**15**	6
	2,4-di-*tert*-butyl-6-methylphenyl	**16**	**17**	7
	2,4,6-triisopropylphenyl	**18**	**19**	6
	2,4-di-*tert*-butyl-6-methylphenyl	**20**	**21**	7
	2,4,6-triisopropylphenyl	**22**	**23**	6
	2,4,6-trimethylphenyl	**24**	**25**	4

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