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

György Keglevich^a; Henrietta Forintos^a; Helga Szelke^a; Annamária Tamás^a; Ágnes Gyöngyvér Vaskó^a; János Kovács^a; Tamás Körtvélyesi^b; László Kollár^c; László Tőke^a

^a Department of Organic Chemical Technology, Budapest University of Technology and Economics, Budapest, Hungary ^b Department of Physical Chemistry, University of Szeged, Szeged, Hungary ^c

Department of Inorganic Chemistry, University of Pécs, Pécs, Hungary

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

György Keglevich,^a Henrietta Forintos,^a Helga Szelke,^a
Annamária Tamás,^a Ágnes Gyöngyvér Vaskó,^a János Kovács,^a
Tamás Körtvélyesi,^b László Kollár,^c and László Tóke^a
Department of Organic Chemical Technology, Budapest
University of Technology and Economics, Budapest, Hungary;^a
Department of Physical Chemistry, University of Szeged,
Szeged, Hungary;^b and Department of Inorganic Chemistry,
University of Pécs, Pécs, Hungary^c

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

Keywords: Arylphosphine oxide; oxaphosphete; phosphorane/ylyde

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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Address correspondence to György Keglevich, Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary. E-mail: keglevich@oct.bme.hu

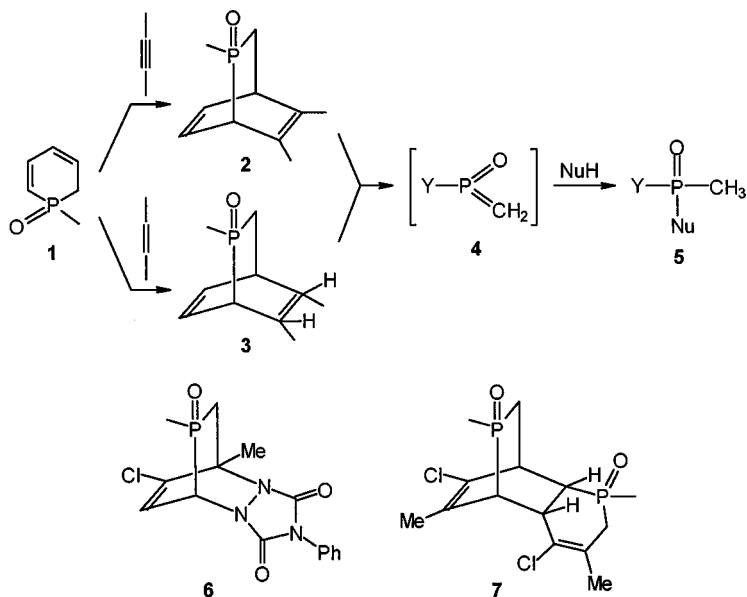


FIGURE 1

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

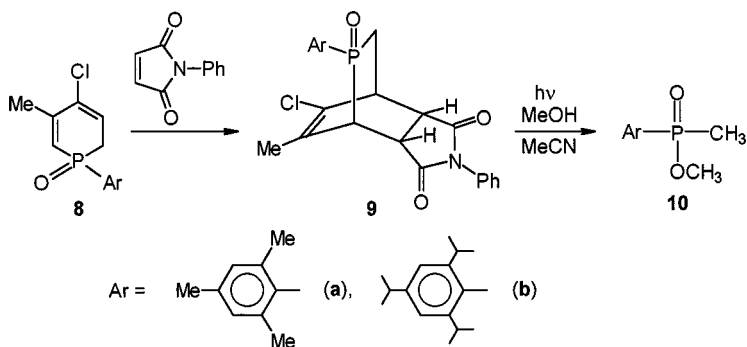


FIGURE 2

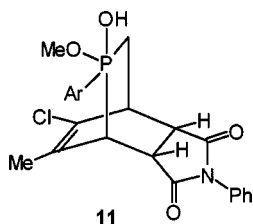


FIGURE 3

reaction of dihydroposphinine oxides **8** with dimethyl acetylenedicarboxylate (DMAD) followed an unexpected protocol to give phosphorane/ylide **13**, presumably through spirocyclic oxaphosphate **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

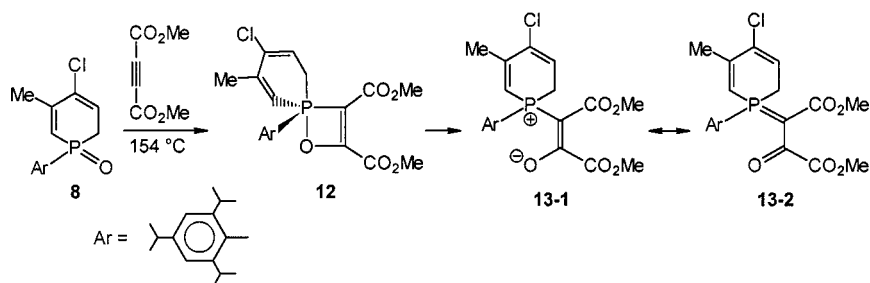


FIGURE 4

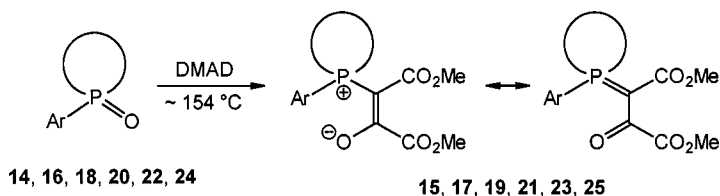









FIGURE 5 The substituents are shown in Table I.

TABLE I Substituents

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

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