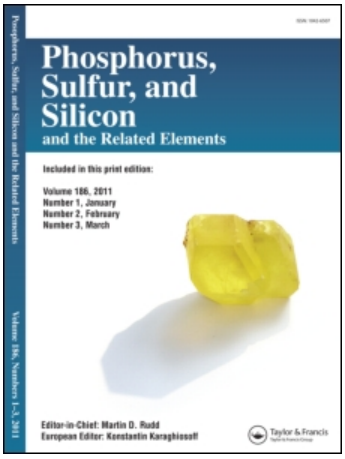

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GENERATION OF P-DIALKYLAMINO METHYLENEPHOSPHINE OXIDES BY THE PHOTOCHEMICAL FRAGMENTATION OF 2-DIALKYLAMINO-2-PHOSPHABICYCLO[2.2.2]-OCTA-5,7-DIENE 2-OXIDES

György Keglevich[a]; Kálmán Újszászy[b]; Gyöngyi S. Quin[c]; Louis D. Quin[c]
[a] Department of Organic Chemical Technology, Technical University of Budapest, Budapest, Hungary [b] Department of General and Inorganic Chemistry, Eötvös University of Sciences, Budapest, Hungary [c] University of Massachusetts, Amherst, MA, USA

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GENERATION OF P-DIALKYLAMINO METHYLENEPHOSPHINE OXIDES BY THE PHOTOCHEMICAL FRAGMENTATION OF 2-DIALKYLAMINO-2-PHOSPHABICYCLO[2.2.2]-OCTA-5,7-DIENE 2-OXIDES

GYÖRGY KEGLEVICH*
Department of Organic Chemical Technology, Technical University of Budapest, 1521 Budapest, Hungary

and

KÁLMÁN ÚJSZÁSZY
Department of General and Inorganic Chemistry, Eötvös University of Sciences, 1518 Budapest, Hungary

and

GYÖNGYI S. QUIN and LOUIS D. QUIN
University of Massachusetts, Amherst, MA 01003, USA

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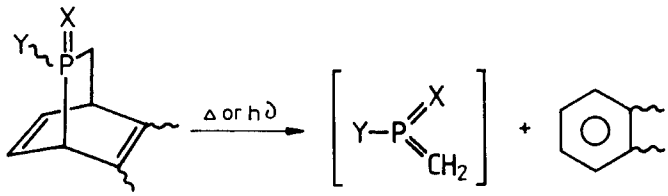
A new P-amino phosphabicyclooctadiene is described which together with a similar derivative can be utilized in the generation of dialkylamino methylenephosphine oxides by photolysis. Reaction of these so far unknown intermediates with ethanol gives rise to N,N-dialkyl-O-ethyl methylphosphonamidates. The latter species were also formed by the photolysis of a P-ethoxy phosphabicyclooctadiene carried out in the presence of secondary amines.

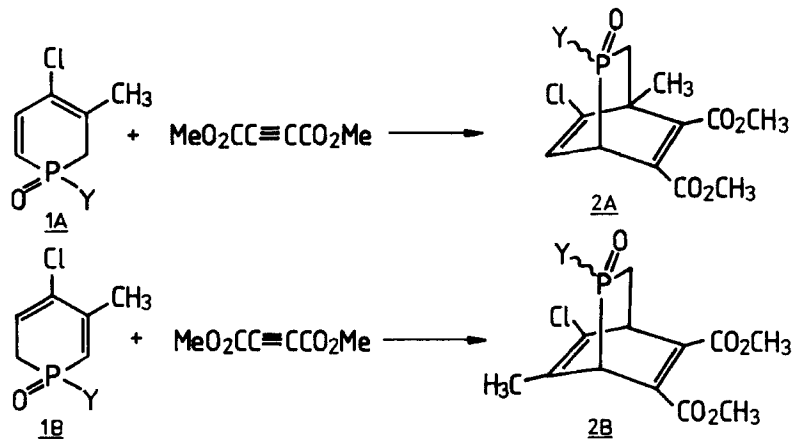
Key words: Phosphabicyclo[2.2.2]octadiene, methylenephosphine oxide, methylphosphonamidate.

The 2-phosphabicyclo[2.2.2]octadiene derivatives are useful for the generation of 3-coordinate phosphorus species, methylenephosphine oxides and sulfides (Scheme I).[1–4] The fragmentation can be achieved either photochemically[2] or thermally.[3]



X = O, S
Y = Ph, Me, MeO, EtO, 1-PrO, 2-PrO

SCHEME I



Y = Ph(a), Me(b), MeO(c), EtO(d), 1-PrO(e), 2-PrO(f)

SCHEME II

The family of the methylenephosphine oxides and sulfides so far described includes P-phenyl-, P-methyl- and P-alkoxy derivatives.[2] The precursors of methylenephosphine derivatives (**2A** and **2B**) can be prepared by the Diels-Alder cycloaddition[1] of 1,2-dihydrophosphinine 1-oxides (**1A** and **1B**)[5–7] and dimethyl acetylenedicarboxylate (Scheme II).

In this paper, we show how dialkylamino methylenephosphine oxides can be generated from the corresponding phosphabicyclooctadienes, and how the 3-coordinate species can be used for phosphorylation.

RESULTS AND DISCUSSION

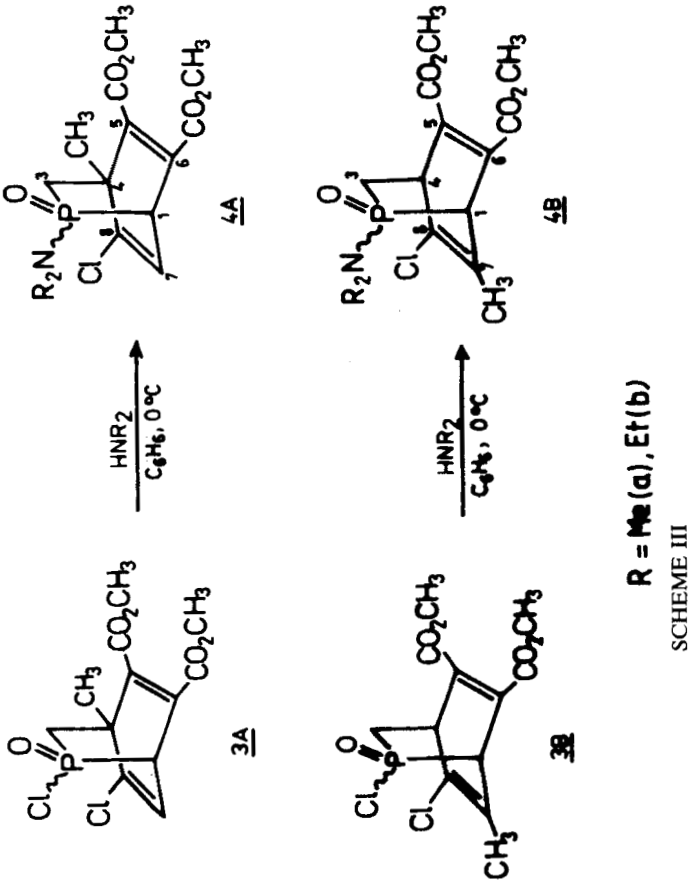
Synthesis and Characterization of P-diethylamino Cycloadduct **4b**

The title product (**4b**) was prepared from the P-ethoxy cycloadduct **2d**,[1] as it was described for the synthesis of **4a**.[3] The isomers (**A** and **B**) of phosphinic ester **2d** were transformed to chlorides **3A** and **3B** to give amides **4Ab** and **4Bb** by reaction with diethylamine. Similarly to the starting isomers (**2Ad** and **2Bd**), the double bond isomers (**A** and **B**) of amide **4b** also consisted of two diastereomers (Scheme III).

The four isomers were characterized by ^{31}P NMR spectroscopy, and the major diastereomer also by ^{13}C NMR spectral data (Table I). For comparison purposes, ^{13}C NMR parameters of the major isomer of starting ester **2Ad** were also included in Table I. Contrary to dimethylamino-cycloadduct **4a**,[3] the diethylamino-derivative (**4b**) did not give a detectable molecular ion in the mass spectrum.

Generation and Trapping of Amino- and Ethoxy-methylene-phosphine Oxides

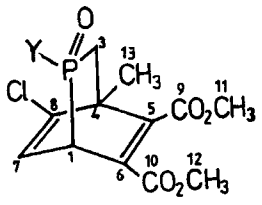
Two P-dialkylamino phosphabicyclooctadienes (**4a**[3] and **4b**) consisting of regio- (**A** and **B**) and stereoisomers were irradiated with ultraviolet light (254 nm) in aceto-



SCHEME III

TABLE I

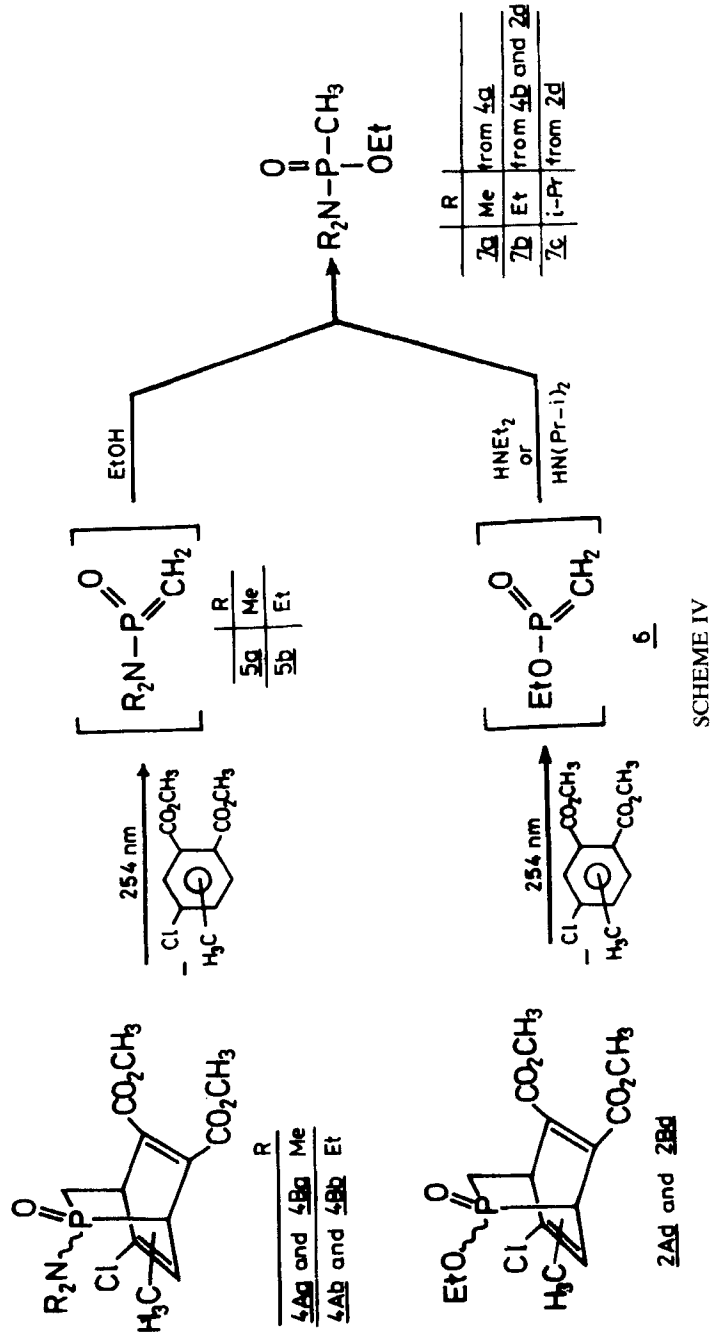
Selected NMR data for the major diastereomer of phosphabicyclooctadienes **2Ad** and **4Ab** in $CDCl_3$ solution



		15 14 **2Ad**, Y=CH_3CH_2O-	15 14 **4Ab**, Y=$(CH_3CH_2)_2N$
$\delta^{31}P$		+56.8	+60.7
	C_1	41.8(72.5)	46.3(61.2)
	C_3	27.6(131.0)	33.3(116.2)
	C_4	47.0(7.7)	47.7(10.3)
	C_7	124.1(10.4)	123.0(11.5)
$\delta^{13}C$	C_{11},C_{12}	52.3 52.4	52.6 52.7
(J_{PC})	C_{13}	20.0(12.2)	19.8(11.9)
	C_{14}	63.3(5.6)	39.8(5.2)
	C_{16}	15.8(6.7)	13.3(≈5)

nitrile solution in the presence of some ethanol. After a ca. 6 h irradiation, practically no starting material (**4a** or **4b**) remained in the mixture according to ^{31}P NMR. A new signal developed, however, at +27.9 ppm (CH_2Cl_2) and at +21.9 ppm ($CDCl_3$) due to trapped product **7a** and **7b**, respectively (Scheme IV).

The structure of the N,N-dialkyl-O-ethyl methylphosphonamidates was confirmed by mass spectroscopy: for **7a** m/z = 151, while for **7b** m/z = 179 was detected. Product **7b** was formed (and could be isolated) in a low yield (15%). This can be explained by the sensitivity of precursor **4b**, or by the polymerization of intermediate **5b**. Dialkylamino methylenephosphine oxides **5a** and **5b**, intermediates of the above transformations, are the first examples of this kind of 3-coordinate reactive species. So far, only the P-phenyl- and the P-methyl methylenephosphine oxides and P-alkoxy methylenephosphine oxides have been described.[2] In an experiment, the THF solution of cycloadduct **4a** was irradiated at −75°C without any trapping agent for 4.5 h. Then some ethanol was added to the mixture. The ^{31}P NMR spectrum obtained later, revealed the presence of some unreacted starting material (**4a**) and that of trapped product **7a** (δ_p = +28.1 (THF, EtOH)). From this experiment the conclusions can be drawn that methylenephosphine oxide **5a** is indeed the intermediate of the fragmentation and that species **5a** has a certain life-time at low temperature.



SCHEME IV

Methylphosphonamidate **7b** (described above) and another product (**7c**) were also prepared by another approach, by the photolysis of the P-ethoxy phosphabicyclooctadiene oxide isomers (**2Ad** and **2Bd**) in the presence of diethylamine and diisopropylamine as trapping agents. The intermediate of this transformation, ethoxy methylenephosphine oxide **6** reacted immediately with the secondary amine at room temperature to give phosphonamidates **7b** ($\delta p = +21.8$ ($CDCl_3$), m/z = 179) and **7c** ($\delta p = +19.4$ ($CDCl_3$), m/z = 207) (Scheme IV).

Completion of the photolysis required a period of 12 h irradiation, and ^{31}P NMR revealed that the products (**7b** and **7c**) were formed in about 65% yield; the remaining 35% represented side products of uncertain nature and origin.

Both methods shown in Scheme IV for the preparation of methylphosphonamidates **7a–c** are new, but, unfortunately, their use is limited by the low yields due to decomposition of the starting material (**4a** and **4b**) and/or side reactions.

EXPERIMENTAL

FT ^{31}P NMR spectra were recorded with an IBM NR-80 spectrometer using 85% H_3PO_4 as external standard with $CDCl_3$ as solvent and internal lock. Downfield shifts have positive signs. ^{13}C and ^1H NMR spectra were recorded with Varian XL-300 and Bruker AW-80 spectrometers, respectively, with Me_4Si as internal standard. Coupling constants are given in Hertz. Mass spectra were obtained on a MS 25-RFA spectrometer at 70 eV.

Photolyses were conducted in an Ace Glass quartz, water-cooled immersion well with a 450 W Hanovia medium-pressure lamp (nominally 254 nm). The substrates were placed in 5 mm EPR precision quartz tubes that were attached to the outer wall of the Ace immersion well. The reactions were followed by ^{31}P NMR to the disappearance of the starting material.

Phosphabicyclooctadiene **2d** was prepared as described earlier.[1]

4- and 7-Methyl-8-chloro-2-diethylamino-5,6-di(methoxycarbonyl)-2-phosphabicyclo[2.2.2]octa-5,6-diene 2-oxide (**4Ab** and **4Bb**) were synthesized from **2Ad** and **2Bd** through **3A** and **3B** as described for the preparation of amide **4a**.[3] Yield: 26%; ^{31}P NMR ($CDCl_3$) δ +60.7 (53%), +57.0 (27%), +62.6 (10%) and +61.2 (10%); ^1H NMR, δ 1.23 (t, J = 5.3, 6H, $CH_2\underline{CH_3}$), 3.0–3.67 (m, 4H, $\underline{CH_2}CH_3$), 3.88 (s, 6H, $COCH_3$); ^{13}C NMR for the major isomer of **4Ab**, Table I; MS, m/z (relative intensity) 211 (M^+, 100); IR (film) 1276, 1436, 1729, 2979 cm^{-1}.

Photolysis of the isomeric mixture of P-dimethylamino phosphabicyclooctadiene **4a**: A 24.5 mg (0.07 mmol) sample of **4a** as a mixture of four isomers[3] in 1 ml of dry acetonitrile containing 0.4 ml of dry ethanol was irradiated for 4.5 h. Evaporation of the volatile components left **7a** as a brown oil (ca. 20%); ^{31}P NMR ($CDCl_3$) δ +27.9 (CH_2Cl_2); GC-MS, m/z: 151 (M^+), 137 (M-15+H).

Photolysis of the isomeric mixture of P-diethylamino phosphabicyclooctadiene **4b** was carried out as that of amide **4a** shown above. Quantity of the starting cycloadduct (**4b**): 32 mg (0.0852 mmol), time of irradiation 6.5 h. The crude product obtained by concentration in vacuo was purified by flash column chromatography (silica gel, 3% methanol in chloroform) to give 2.3 mg (15%) of **7b**. ^{31}P NMR ($CDCl_3$) δ +21.9 (Reference 8, δ +28.0 (no solvent provided)); CI-MS, m/z: 180 (M+H), 164 (M-15).

Photolysis of the isomeric mixture of P-dimethylamino phosphabicyclooctadiene **4a** *at* −75°: A 12.0 mg (0.34 mmol) sample of **4a** in 0.6 ml of THF was irradiated at −75° for 4.5 h. Then, 0.2 ml of ethanol was added and the mixture was allowed to warm slowly to room temperature. ^{31}P NMR showed the presence of **7a** (δ +28.1) and some starting material.

Photolysis of the isomeric mixture of P-ethoxy phosphabicyclooctadiene **2d**: a) using diethylamine as the trapping agent: 70.0 mg (0.201 mmol) of the mixture of isomeric **2d**[1] (^{31}P NMR ($CDCl_3$) δ +57.3, +56.8, +55.6 and +53.8) was photolyzed in 0.7 ml of dry acetonitrile and 0.3 ml of diethylamine for 12 h. The sample obtained after evaporating the volatile components was purified by flash column chromatography as above to give 12 mg of an oil containing ca. 60% of **7b** (^{31}P NMR ($CDCl_3$) δ +21.8; GC-MS, m/z: 179 (M^+), 164 (M-15); CI-MS, 180 (M+H)) and ca. 40% of unidentified side products having $\delta p = -0.99$ and +11.3. b) using diisopropylamine as the trapping agent: The experiment was

performed as above to give an oil containing ca. 63% of **7c**. ^{31}P NMR ($CDCl_3$) δ +19.4; CI-MS, m/z: 208 (M+H), 192 (M-15); HRMS, M^{+}_{found} = 207.1411, $C_9H_{22}NO_2P$ requires 207.1388.

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REFERENCES

1. L. D. Quin, J-S. Tang and Gy. Keglevich, *Heteroatom Chem.*, **2,** 283 (1991).
2. L. D. Quin, J-S. Tang, G. S. Quin and Gy. Keglevich, *Heteroatom Chem.*, **4,** 189 (1993).
3. Gy. Keglevich, K. Újszászy, L. D. Quin and G. S. Quin, *Heteroatom Chem.*, **4,** 559 (1993).
4. L. D. Quin, S. Jankowski, G. S. Quin, A. Sommese, J-S. Tang and X-P. Wu, ACS Symposium Series 486, 115 (1992).
5. Gy. Keglevich, B. Androsits and L. Tőke, *J. Org. Chem.*, **53,** 4106 (1988).
6. Gy. Keglevich, J. Brlik, F. Janke and L. Tőke, *Heteroatom Chem.*, **1,** 419 (1990).
7. Gy. Keglevich, L. Tőke, A. Kovács, G. Tóth and K. Újszászy, *Heteroatom Chem.*, **4,** 61 (1993).
8. V. E. Bel'skii, L. A. Kudryavtseva, E. I. Gol'dfarb and B. E. Ivanov, *Zh. Obshch. Khim.*, **39,** 2658 (1969); C. A., **72,** 121628 f (1975).