NOVEL BRIDGED P-HETEROCYCLES FROM 1,2-DIHYDROPHOSPHININE 1-OXIDES

György Keglevich,[a*] János Kovács,[a] Krisztina Ludanyi[b] and László Tőke[c]

[a] Department of Organic Chemical Technology, Budapest University of Technology and Economics, H-1521 Budapest, Hungary. E-mail: keglevich@oct.bme.hu
[b] Hungarian Academy of Sciences, Chemical Research Center, H-1525 Budapest, Hungary
[c] Research Group of the Hungarian Academy of Sciences at the Department of Organic Chemical Technology, Budapest University of Technology and Economics, H-1521 Budapest, Hungary

Abstract: [4+2] cycloaddition of isomeric dihydrophosphinine oxides **1A** and **1B** gave novel 2-phosphabicyclo[2.2.2]octenes (**2**).

Introduction

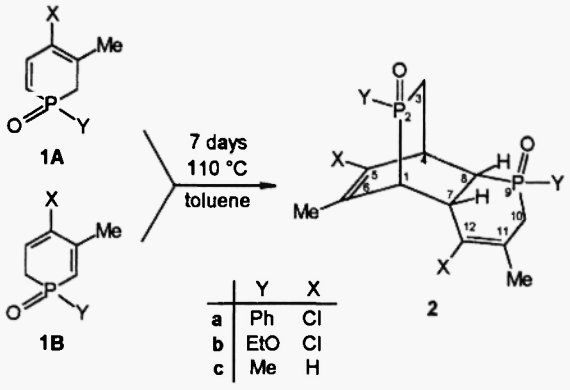
The 1,2-dihydrophosphinine 1-oxides are versatile intermediates in the synthesis of a variety of P-heterocycles.[1-3] The bridged heterocycles, such as 2-phosphabicyclo[2.2.2]octadiene and octene derivatives are of special interest, as they are precursors of low-coordinated fragments, methylenephosphine oxides used in phosphorylations.[4-6]

Results and discussion

In our project to explore new phosphabicyclooctenes, we wished to examine if the dihydrophosphinine oxides are dimerized in a Diels-Alder reaction. It was found that in boiling toluene, the double-bond isomers (**A** and **B**) of the dihydrophosphinine oxides (**1a-c**) entered into a [4+2] cycloaddition to furnish novel phosphabicyclooctenes (**2a-c**) in a selective manner (Scheme 1).

The P-phenyl and the P-ethoxy products (**2a** and **2b**, respectively) were obtained in ca. 30% yield after purification by column chromatography. Dihydrophosphinine oxides **1Ac** and **1Bc** were happen to be formed from the corresponding 4-chloro derivatives (**1A** and **1B**, where Y=Me and X=Cl) by dechlorination before the cycloaddition.

Although, assuming an endo fusion of the rings, as suggested by analogies,[7] and disregarding from the configuration of the phosphorus atoms, the combination of the double-bond isomers (**1A** and **1B**) may give eight structures (Figure 1), only one isomer (**2**) was found to have been formed in the cases studied.



	Y	X
a	Ph	Cl
b	EtO	Cl
c	Me	H

Scheme 1

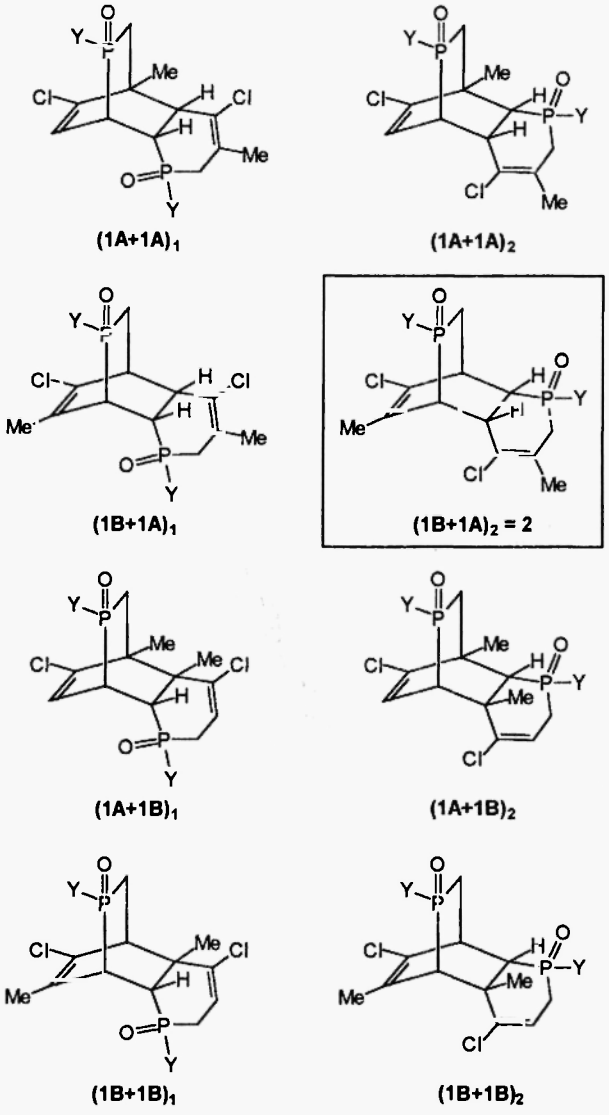


Figure 1

The most favourable isomer (**2**) may be formed from dihydrophosphinine oxide **1B** as the diene and from double-bond isomer **1A** as the dienophile. Formation of the other isomers (**1A+1A**, **1A+1B** and **1B+1B**) is not so advantageous due to the position of the skeletal methyl groups. Stereostructure of the dimers (**2a-c**) was supported by ^{31}P NMR, and in the case of product **2a** also by ^{13}C and ^{1}H NMR data. The lack of the J_{PP} coupling in the ^{31}P NMR spectrum was in accord with the four-bond distance of the P_2 and the P_9 atoms. For product **2a**, the ^{13}C and ^{1}H NMR data suggested that all the four olefinic carbon atoms (C_5, C_6, C_{11} and C_{12}) were quaternary. The $^{3}J_{PC}$ coupling of ca 11Hz detected on C_{12} was in accord with the endo ring fusion assumed.[7] Elemental composition of the cycloadducts (**2a-c**) was confirmed by high resolution EI or FAB-MS.

^{31}P NMR analysis of the crude reaction mixtures showed the presence of some other minor cycloadducts. Separation and identification of these components will be attempted.

It is worthy of mention that the dimerization of the dihydrophosphinine oxides (**1A** and **1B**) could be catalysed by secondary amines; in the presence of catalytic amount (up to 20%) of diisopropylamine, the cycloaddition of isomers **1A**a and **1B**a was much faster.

Stability of the new phosphabicyclooctenes (**2**) and their applicability in UV light mediated phosphorylations will be soon explored. The mechanism of the fragmentation is also a major point of interest.[10]

Conclusion

The above examples together with earlier experiences[7] demonstrate that the 1,2-dihydrophosphinine oxides are versatile starting materials in the synthesis of bridged P-heterocycles; the Diels-Alder reaction of two isomeric units of the dihydrophosphinine oxides affords phosphabicyclooctenes that may be precursors of low-coordinate fragments, methylenephosphine oxides useful in phosphorylations.

Experimental

The starting dihydrophosphinine oxides were prepared as described earlier.[11,12]

General procedure for the preparation of cycloadducts 2a-c

The 10 ml toluene solution of 1.70 mmol of dihydrophosphinine oxide (**1a-c**) consisting of 30% of the **A**, and 70% of the **B** isomer was stirred at the boiling point for 7 days. The solvent was evaporated and the residue so obtained purified by repeated column chromatography (silica gel, 3% methanol in chloroform) to give the dimer (**2a-c**).

2a: Yield 34% (based on **1A**a); δ_P ($CDCl_3$) 37.5 (P_2), 28.6 (P_9); δ_C ($CDCl_3$) 19.6 (C_6–Me), 24.6 (J'=7.4, C_{11}–Me), 31.0 (J'=63.4, C_{10}), 32.0 (J=76.0, J'=10.9, C_3), 39.7 (J=5.9, C_7[a]), 40.0 (J=67.2, J'=13.5, C_1), 45.1 (C_4[a]), 47.7 (J=63.6, C_8), 127.6 (C_6[b]), 127.7 (C_{11}[b]), 129.0, (J=12.0, $C_{2'}$[c]), 129.1 (J'=11.9, $C_{2'}$[c]), 129.3 (J'=12.1, C_{12}[d]), 130.1 (J=9.6, $C_{3'}$[e]), 130.2 (J=10.0, C_5[d]), 131.3 (J=11.8, $C_{3'}$[e]), 131.5 (J=95.9, $C_{1'}$[f]), 132.1 (J'=100.9, $C_{1'}$[f]), 132.6 ($C_{4'}$, $C_{4'}$), J: coupled by P_2, J': coupled by P_9, [a–f]may be reversed; δ_H ($CDCl_3$) 1.58 (s, 3H, Me),

1.85 (s, 3H, Me), 7.46–7.76 (m, 5H, Ar); MS, *m/z* (rel. int.) 476 (M^+, 20), 441 (M–35, 19), 337 (M–PhPO–15, 55), 125 (PhPO+H, 100), 77 (Ph, 72); M^+_{found}=476.0527, $C_{24}H_{24}Cl_2O_2P_2$ requires 476.0629 for the ^{35}Cl isotopes.

2b: Yield 26%; δ_P ($CDCl_3$) 56.6 (P_2), 45.5 (P_9); $(M+H)^+_{found}$=413.0537, $C_{16}H_{25}O_4P_2Cl_2$ requires 413.0605 for the ^{35}Cl isotopes.

2c:Yield 11%; δ_P ($CDCl_3$) 43.1 (P_2), 33.9 (P_9); $(M+H)^+_{found}$=285.1112, $C_{14}H_{23}O_2P_2$ requires 285.1173.

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