

Short communication

Synthesis of 1,2,3,4,5,6-Hexahydrophosphinine 1-Oxides by Catalytic Hydrogenation of 3-Phosphabicyclo[3.1.0]hexane 3-Oxides*

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Abstract: Synthesis of 1,2,3,4,5,6-hexahydrophosphinine 1-oxides by catalytic hydrogenation of 3-phosphabicyclo[3.1.0]hexane 3-oxides was reported in this communication.**Keywords:** Phosphabicyclohexane, hexahydrophosphine, hydrogenation, monodechlorination, mechanism.

6,6-Dichloro-3-phosphabicyclo[3.1.0]hexanes (**1**) easily available from 3-phospholene 1-oxides by the addition of dichlorocarbene to the double bond [1, 2] are useful intermediates for the preparation of 1,2,3,4,5,6-hexahydrophosphinine 1-oxides (**3**). In the first method, the dichlorocarbene adducts (**1**) were transformed to the isomeric mixtures (**A**) and (**B**) of the dihydrophosphinine oxides (**2**) by thermolysis [2], that were then hydrogenated catalytically to give hexahydrophosphinine oxides (**3**) [3] (Scheme 1).

It was also possible to convert the dichlorocarbene adducts (**1**) to the hexahydrophosphinines (**3**) in one pot: catalytic hydrogenation of starting materials **1** till the absorption of three equivalents of hydrogen afforded products **3** [4] (Scheme 1).

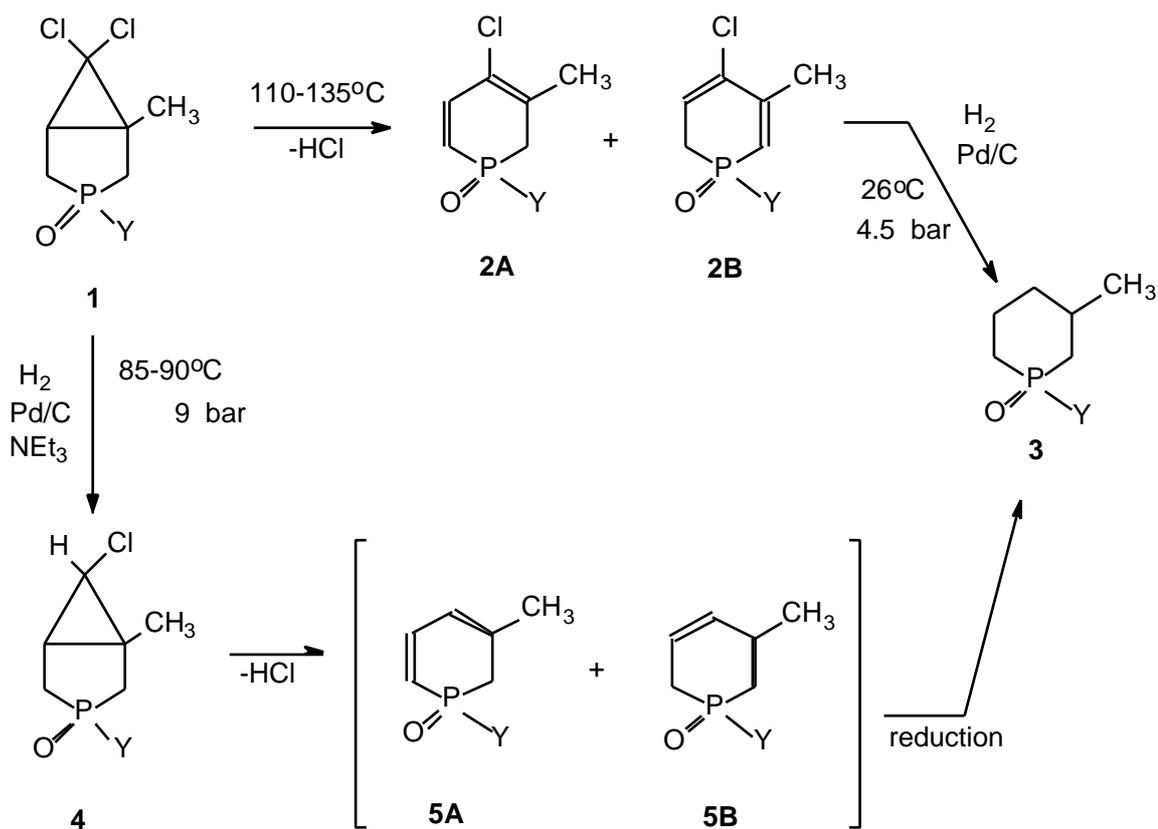
As can be seen from Table 1, yields of the *p*-alkoxy hexahydrophosphinine oxides (**3c-e**) are better by the one-

pot method (60-78%), than those by the two-step conversion (25-40%).

Table 1. Yields of hexahydrophosphinine oxides **3a-e** by the two methods (Scheme 1).

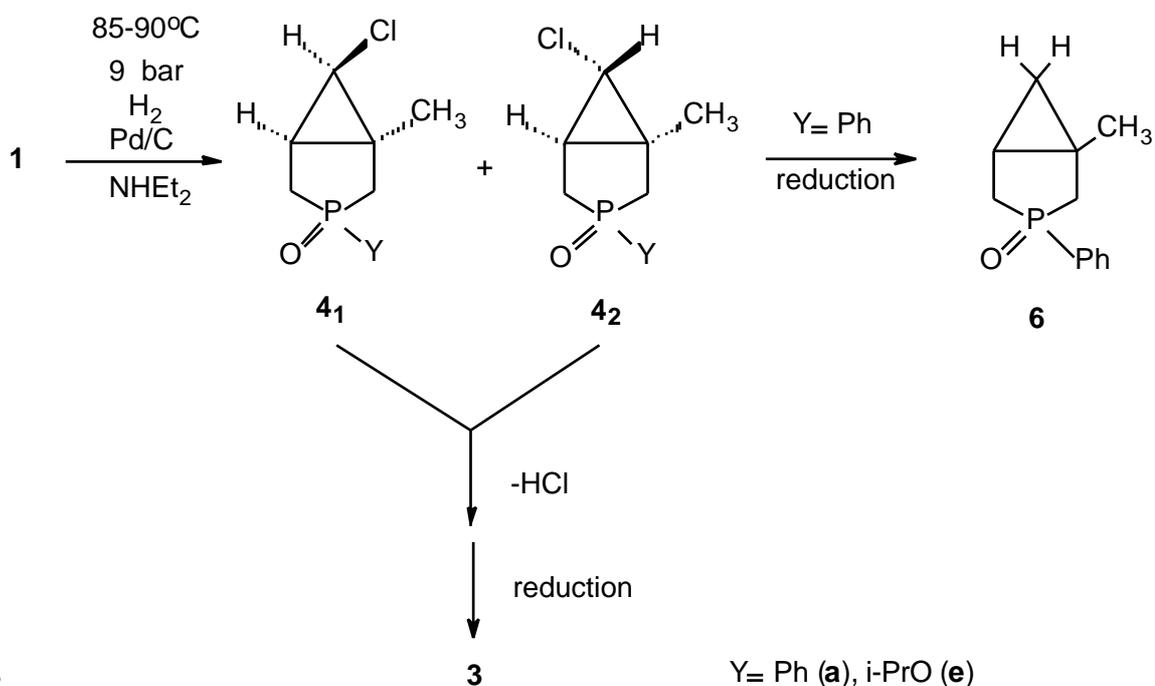
Y	1	2	3	1	4	5	3
				Yield (%)			
Ph (a)	-						70
n-Bu (b)	-						58
EtO (c)	25						73
n-PrO (d)	28						60
i-PrO (e)	40						78

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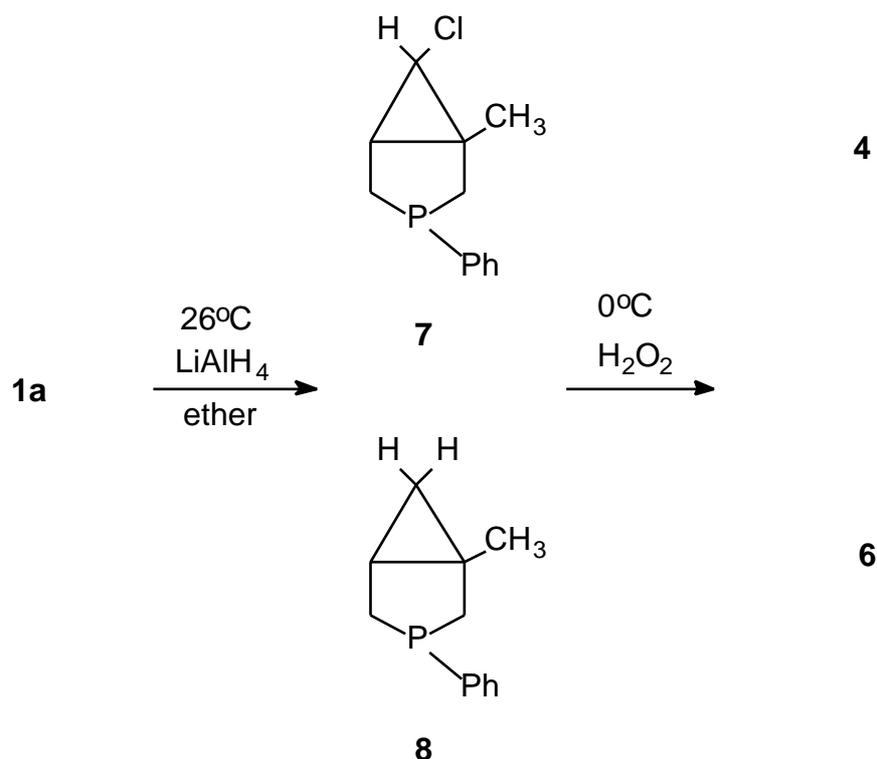
Scheme 1.

Y = Ph (a), n-Bu (b), MeO (c), EtO (d), i-PrOH (e)



Scheme 2.

Y = Ph (a), i-PrO (e)



Scheme 3.

Carrying out the hydrogenations in the presence of three equivalents of diethylamine, it was possible to stop the transformations at an intermediate stage. Such a mixture contained 40–64% of the two isomers (**isomer₁** and **isomer₂**) of the monochlorocyclopropanes (**4a** and **4e**) and 36–40% of the corresponding hexahydrophosphinine oxide (**3a** and **3e**) (Scheme 2). Isomers **4₁** and **4₂** could be distinguished on the basis of the different $^3J_{\text{HH}}$ values of the two $\text{H-C}_5\text{-C}_6\text{-H}$ moieties. In the case of the *P*-phenyl model, the fully dechlorinated derivative (**6**) could also be isolated in 20% yield.

Reduction of the dichlorocarbene adduct **1a** with LiAlH_4 resulted in the formation of partially and fully dehalogenated phosphines **7** and **8**, that gave phosphine oxides **4** and **6** after oxidation (Scheme 3).

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Sample Availability: Supporting sample **3a**, MDPI 4683, is available from MDPI.