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Andrzej Zwierzak & Krystyna Osowska-Pacewicka
[a] Institute of Organic Chemistry, Technical University (Politechnika) , Żwirki 36, 90-924 Lodz, Poland
[b] Institute of Organic Chemistry, Technical University (Politechnika) , Żwirki 36, 90-924 Lodz, Poland

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NOVEL ORGANOPHOSPHORUS REAGENTS FOR THE SYNTHESIS OF AMINES

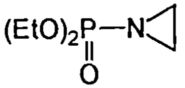
ANDRZEJ ZWIERZAK and KRYSTYNA OSOWSKA-PACEWICKA
Institute of Organic Chemistry, Technical University (Politechnika),
Żwirki 36, 90-924 Lodz, Poland

Abstract: New organophosphorus equivalents of a^2 type N-protected amine synthons are presented.

Key Words: Aminoethylation of Grignard reagents, deprotection of P-N bond, homocuprates, allylamines.

INTRODUCTION

Considerable effort is still being expended toward the development of new effective procedures for the synthesis of amines. In the course of our studies on the use of diethoxyphosphoroyl group for protection of an amino function we have discovered two convenient equivalents **1** and **2** of acceptor type amine synthons **1'** and **2'** :



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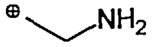

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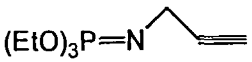

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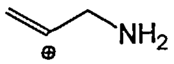
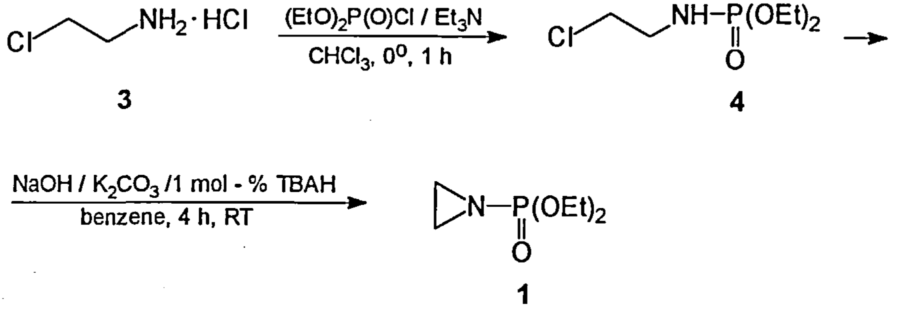


2'

AMINOETHYLATION OF GRIGNARD REAGENTS:

It was found that N-(diethoxyphosphoroyl)-ethyleneimine **1** can be conveniently applied for aminoethylation of Grignard reagents. Compound **1** was first prepared by phosphorylation of strongly toxic ethyleneimine with diethyl phosphorochloridate [1]. We were able to overcome the use of ethyleneimine and to synthesize **1** according to the following sequence starting from commercially available 2-chloroethylamine hydrochloride **3**:



Diethyl N-(2-chloroethyl)phosphoroamidate **4** was cyclized in crude state according to the previously described procedure [2] but in the presence of only 1 mol-% of tetrabutylammonium hydrogen sulfate as catalyst to give **1** (purified by distillation in vacuo) in 65% overall yield. Nucleophilic ring opening of **1** by means of 2-3 equivalents of organomagnesium bromides occurs smoothly and cleanly in the presence of 5 mol-% of CuI at 0° to give N-alkylphosphoramidate **5**. This compound can be easily deprotected [3] by refluxing with p-toluenesulfonic acid monohydrate in ethanol to afford the corresponding amine tosylate **6** (Table I):

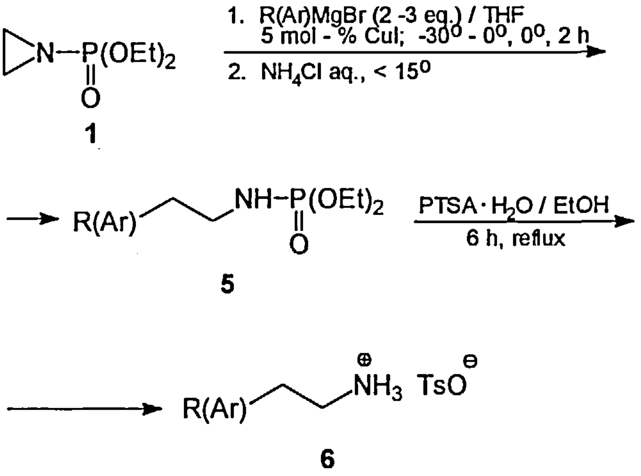


TABLE I Amine tosylates **6**

R (Ar)MgBr[a]	Yield (%)[b]	M.p.
Et (2)	90	118-120°
Bu (1.75)	70	125-127°
t-Bu-CH_2- (3)	52[d]	-
Me_2CH-CH_2-CH_2 (2)	69	107-109°
Ph-CH_2-CH_2 (1.75)	56	141-142°
CH_2=CH- (2)	70	103-104°
i-Pr (3)	75	99-101°
3-pentyl (3)	78[d]	-
cyclopentyl (2)	72	127-129°
Ph (2.5)	83	176-178°
1-naphthyl (3)[c]	81	185-187°
p-CH_3O-C_6H_4- (3)	83	148-150°
t-Bu (5)[e]	77	257-260°
CH_2=CH-CH_2-CH_2 (3)	73	111-113°

[a] Necessary equivalents of Grignard reagent securing full conversion of **1** are given in parentheses.

[b] Overall yield of pure amine tosylate **6**.

[c] 15 mol-% of CuI was necessary to complete opening of **1**.

[d] Isolated as free amine.

[e] 10 mol-% of CuI was used.

SYNTHESIS OF 2-ALKYLALLYLAMINES

N-Propargyltriethoxyiminophosphorane **2**, easily obtained by azidation of propargyl bromide followed by Staudinger reaction with triethyl phosphite [4], was found to be a useful reagent for the preparation of 2-alkylallylamines. Homocuprates prepared by the action of 2 moles of alkylmagnesium bromides on 1 mole of CuBr at -60° readily undergo nucleophilic addition to the triple bond of **2**. Protic work-up of the adducts (NH_4Cl aq.) followed by dephosphorylation of **7** (PTSA.H_2O in refluxing ethanol [3]) affords 2-alkylallylamines **8** in moderate yields (Table II):

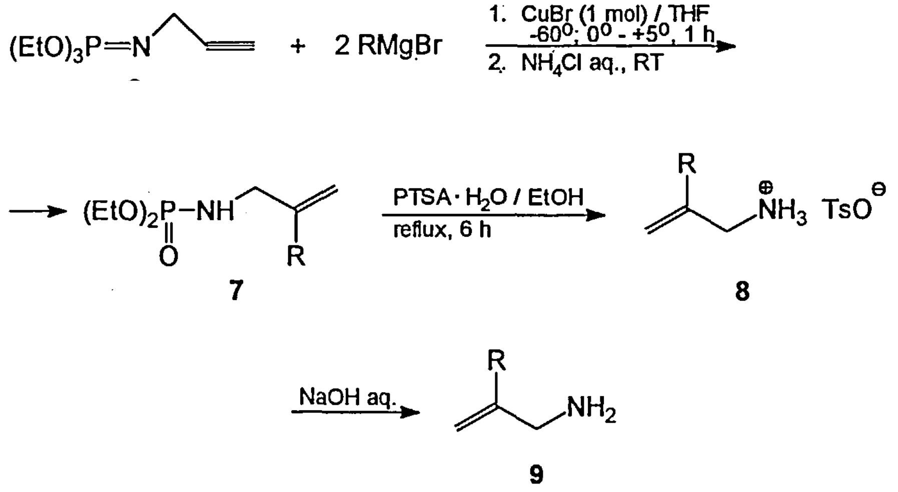


TABLE II 2-Alkylallylamines

R	Yield of **7** (%)	Yield of **7**→ **8** or **9** (%)	M.p. of **8** or b.p. of **9**
Et	46	90 (8)	101-102°
Bu	48	50[a]	166-168°
i-Bu	50	88 (9)	126-128°
i-Pr	50	70 (9)	115-116°
s-Bu	51	73 (9)	123-125°
c-C_6H_{11}	50	90 (8)	92-94°

[a] Yield and m.p. of amine hydrochloride.

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