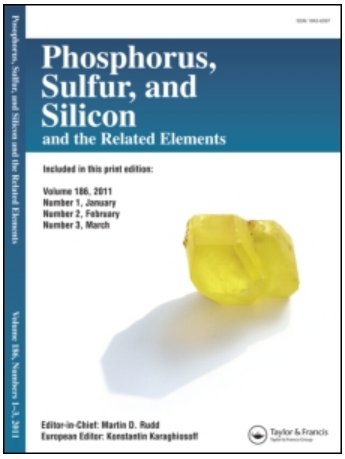

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1,3-Alkadienephosphonic Amidoesters and Their Cyclization with Electrophilic Reagents

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1,3-Alkadienephosphonic Amidoesters and Their Cyclization with Electrophilic Reagents

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The preparation of the titled compounds have been reported. The five-membered heterocyclization reaction of these compounds in the reaction with phosphorus-containing pseudohalogenes have been discussed.

Keywords 2-Chloro-1,3-alkadienephosphonates; amidoesters, electrophilic reagents

INTRODUCTION

The chemical behavior of the phosphorylated 1,3-dienes is well documented.[1–5] On the other hand, there are scant data for the synthesis of the amidoesters of the 2-chloro-1,3-alkadienephosphonates.

I wish to report my results in preparation investigation of the chemical behavior of the amidoesters of the 1,3-alkadienephosphonic acids.

RESULTS AND DISCUSSION

The 1,3-alkadienephosphonic amidoesters are obtained by the procedure described by us for the synthesis of the amidoesters of 1,2-alkadienephosphonic acids.[9]

After treatment of the dichlorides of the 1,2-alkadienephosphonic acids with chlorine in CH_2Cl_2, the dichlorides of 2-chloro-1,3-alkadienephosphonic acids were isolated.[6–8] These compounds smoothly react with aliphatic alcohols and secondary amines in the presence of triethylamine in nonpolar media (Scheme 1):

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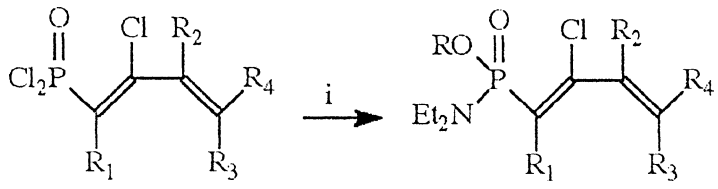


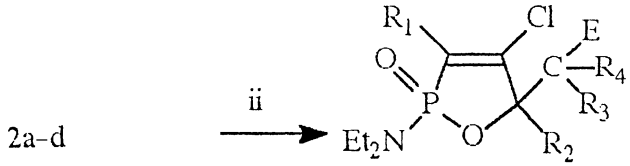
1 2 a–d

i = 1.ROH, Et_3N, ether
2.Et_2NH, Et_3N

SCHEME 1

The chromatography of purified amidoesters of 2-chloro-1,3-alkadienephosphonic acids 2a–d are investigated in the reaction with phosphorus-containing pseudohalogenes.[10] The reaction is carried out in CH_2Cl_2 and an inert atmosphere. As products of the reaction a five-membered heterocyclic compounds are isolated.

The reaction follows Scheme 2:



3a–d

ii = E, metilenechloride

E = $(RO)_2P(O)SCl$

SCHEME 2

The structure of the resulting heterocyclic compounds was determinated by means of IR and ^{1}H-NMR spectra. The formation of the five-membered heterocycles was judged on the basis of the signal for the ring methylene proton (R^1), which appears in a low field. The spin-spin coupling constant of this proton and phosphorus is in the range of (23.0–23.2 HZ), which is in agreement with the data reported for such a structure.[1] These results confirmed my suggestions that reaction the 1,3-alkadienephosphonate derivatives took part in an s-*trans*-reaction conformation when the reagent bore bulky substituents.

EXPERIMENTAL

Analytical Methods

^{1}H-NMR spectra were determined on a Tesla BS(80 MHz) at normal temperature as $CDCl_3$ solution with TMS as an internal standard. The IR spectra were recorded on an IR-72-spectrophotometer (Carl Zeiss Jena).

Starting Materials

The 2-chloro-1,3-butadienphosphonic dichloride was prepared by the procedure described earlier.[8] The phosphorus-containing pseudohalogenes were prepared following.[10]

Synthesis of N,N-dialkylamido-O-alkyl-2-chloro-1,3-butadienephosphonates 2a–d

General Procedure

To a solution of 0.05 M of dichloride of the 2-chloro-1,3-butadienephosphonic acid **1** in dry ether a solution of appropriate aliphatic alcohol and triethylamine in the same solvent at −20°C was stirred and inert atmosphere was added. After an hour, the solution of diethylamine and triethylamine in the same solvent at −10°C was added. The reaction mixture was stirred an additional hour at the same conditions, the precipitate was filtered off, the solvent was removed under reduced pressure, and the residue was distilled.

2a Yield 76%, b.p. 145–6°C/1 mm Hg, $C_7H_{12}O_2PNCl$, Found %: P, 14.80; Cl, 16.97; N, 6.69; Calcd. %; P, 14.84; Cl, 16.99; N, 6.71; ^{1}H-NMR, 5.98 d (1H $^2J_{HP}$ 13.6 Hz), 3.87 (MeO), 2.99, 1.00 (EtN), IR cm^{-1} 1602, 1652$\nu_{(C=C-C=C)}$, 1283 $\nu_{(P=O)}$, 1038 $\nu_{(P-O-C)}$.

2d Yield 75%, b.p. 152–3°C/1 mm Hg; $C_9H_{16}O_2PNCl$; Found %: P, 13.02; Cl, 14.95; N, 5.89; Calcd. %: P, 13.08; Cl, 14.98; N, 5.91; ^{1}H-NMR 5.82d(1H $^2J_{HP}$ 12.86 Hz), 2.99, 1.00(EtN), 4.60(i-PrO); IR cm^{-1} 1600, 1648$\nu_{(C=C-C=C)}$, 1277$\nu_{(P=O)}$, 1035 $\nu_{(P-O-C)}$.

Synthesis of N,N-dialkylamido-2,5-dihydro-1,2-oxaphosphole

General Procedure

To a solution of the appropriate amidoesters of 2-chloro-1,3-alkadienephosphonic acid in dry metilenechloride at 0–5°C a solution of the appropriate phosphor-containing pseudohalogene was added dropwise and was stirred for an hour. After removing of the solvent under

reduced presure, the crude products were purified by recristalization from heptane/benzene.

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