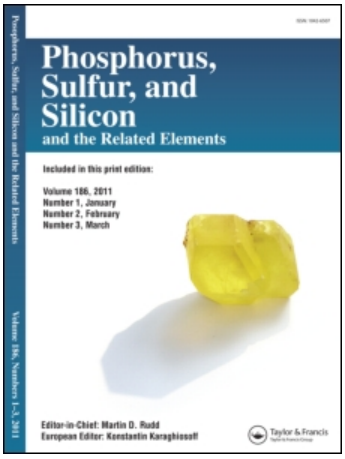

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Synthesis and Stereochemistry of α-Aryl-β-Nitroalkylphosphinate

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SYNTHESIS AND STEREOCHEMISTRY OF α-ARYL-β-NITROALKYLPHOSPHINATE

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Abstract Twenty-three new α-aryl-β-nitroalkylphosphinates **3**$_{a-y}$ were synthesized in high yields under very mild conditions. Compounds **3** consist of two pairs of diastereomeric isomers (A) and (B)

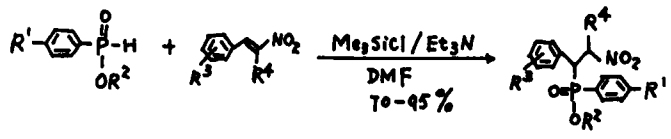
INTRODUCTION

β-Nitroalkylphosphinates can be considered as analogues of β-aminoethylphosphonic acid [$(HO)_2P(O)CH_2CH_2NH_2$] which is the important metabolite in organism, and their sythesis has attracted attention for a long time[1-2]. In general, β-nitroalkylphosphinates were synthesized by the addition reaction of phosphites or phosphonites with derivatives of β-nitrostyrenes. However, the normal adducts (β-nitroalkylphophinates) have hardly been obtained except a patent[3], because the reaction is affected by many factors[4]. In the present paper, we report a very convenient method for the preparation of the title compounds **3** and their stereochemistry rarely studied before.

RESULTS AND DISCUSSION

Chemical Reactions

The one-pot reaction of O-alkyl arylphosphonites **1** with α-aryl-β-nitroalkenes **2** in DMF under excess Me_3SiCl/Et_3N gives twenty-three new compounds **3**$_{x-y}$ in high yields (70-90%),



1 2 3a-y

R^1, R^4: H, Me

R^2: Alkyl

R^3: H, P-MeO, P-OH, m-C_6H_5O, P-Me_2N, 3,4 

This One-pot reaction is very convenient and there is nearly no side reaction to take place. The reaction conditions have been studied in detail.

Stereochemistry of Products 3

The reaction takes place as Michael-Arbuzov mechanism shown as follows (Figure 1):

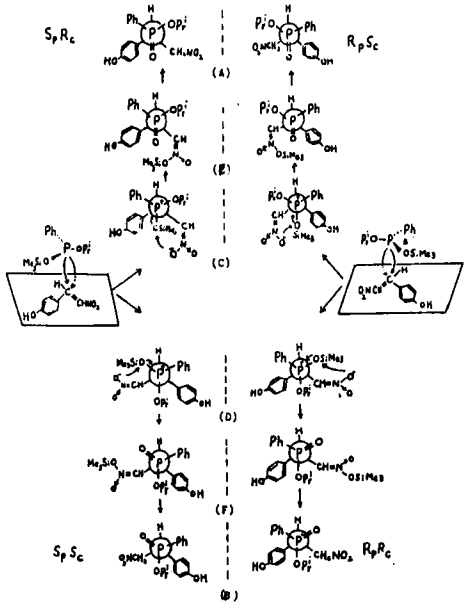


FIGURE 1 Possible mechanism for producing two pairs of diastereomeric isomers (A) and (B)

Crystal Structure of Compound (A) 3k

It is found that the compounds 3 consist of the two racemic pairs (A) and (B)

The amount of (A) is much more than that of (B). The pair (A) 3k was separated by recrystallization and its structure was determined by X-ray diffraction on single crystal (Figure 2). Thus, the Newman's projective torsion angles of (A) 3k(R_P S_C) have been calculated and in which the angle of O(1)-P(1)-C(21) is the smallest one.

The conformation of molecule can be considered as syn-clinal. and a pair of racemic (A) (R_PS_C, S_PR_C) becomes the stable preferential conformation.

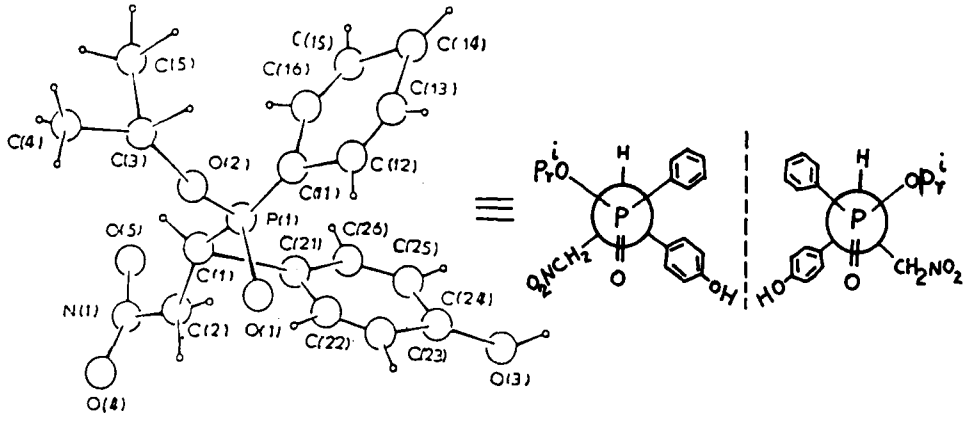


FIGURE 2 Perspective view of the molecule structure of (A)3k with numbering

Spectral Data

In ^1H, ^{13}C and ^{31}P NMR spectra of compounds 3 the two peaks with different intensity appear obviously. The further investigation shows that the form, position and intensity of the signals of ^1H NMR of compound 3n keep constant at various temperatures which indicates that the two peaks are not caused by the conformation of molecule but by the formation of the two pairs of racemic isomers (A) and (B), as shown in Figure 3.

In the IR spectra all products 3 show two characteristic bands for nitroaliphatic compounds, occurring in the region 1540-1560 cm^{-1}(s) and 1370-1380 cm^{-1}(m). In MS spectra it is observed that most of compounds 3 exhibit normal molecular ion peaks and have a fragment ion $PhP(O)OH^{+}$ m/z 141 or as a base peak of compounds with or without substituent at aromatic ring respectively.

The torsion angles of Newman's projective (Fig.4) of (A)3k(RpSc) have been calculated from X-ray crystal diffraction analysis, the conformation of (A)3k can be considered as syn-clinal.

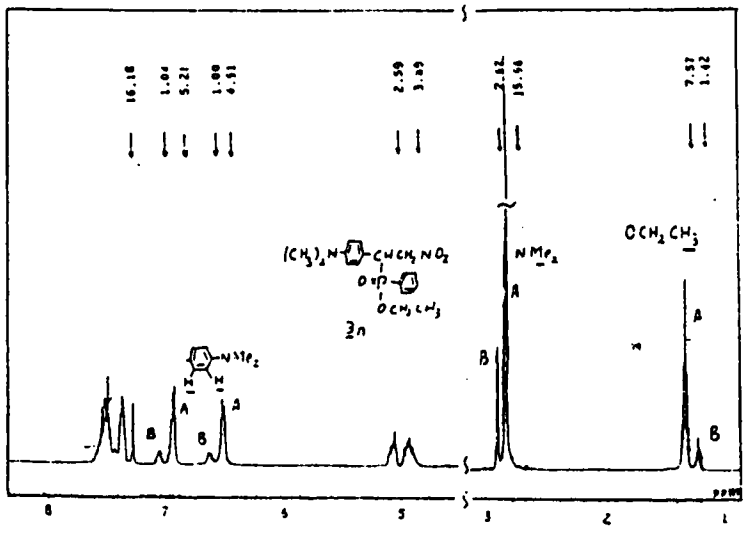


FIGURE 3 Higher resolution ^1H NMR(400 Hz) of 3n

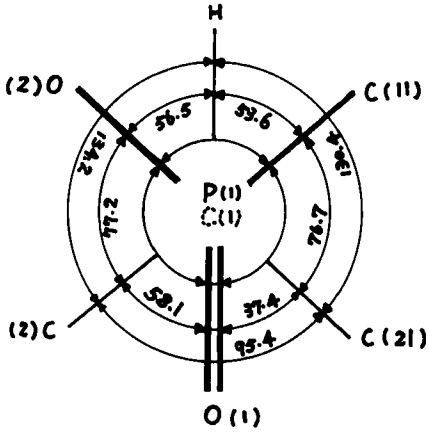


Figure 4 Newman's projective formula of (A)3k

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