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Acyclic and cyclic aminophosphonic acids: asymmetric syntheses mediated by chiral sulfinyl auxiliary

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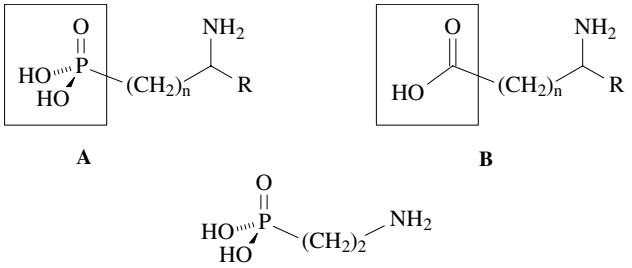
Abstract

Aminophosphonic acids have become increasingly important in different fields of chemistry, medicine and agriculture. This account outlines the results obtained in the author's laboratory on the asymmetric synthesis of acyclic and cyclic aminophosphonic acids mediated by chiral sulfinyl auxiliary. A key reaction in the synthesis of enantiopure α- and β-aminoalkanephosphonic acids involving a highly diastereoselective addition of phosphite anions or α-phosphonate carbanions to enantiopure sulfinimines is discussed. The asymmetric cyclopropanation of enantiopure α-phosphorylvinyl sulfoxides with sulfur ylides is presented as a platform for developing a new approach to optically active β-aminocyclopropanephosphonic acids. It is exemplified by the total synthesis of enantiopure β-amino-γ-phenylcyclopropanephosphonic acid – a constrained analogue of the $GABA_B$ antagonist phaclofen.

Keywords: Aminoalkanephosphonic acids; Aminocyclopropanephosphonic acids; Asymmetric synthesis; Sulfinimines; α-Phosphorylvinyl sulfoxides

1. Introduction

Aminophosphonic acids of general structure **A** are phosphorus analogues of amino acids **B** in which the carboxylic group is replaced by a phosphonic acid moiety [1]. α-Aminophosphonic acids (**A**, $n = 0$) are direct analogues of natural α-amino acids (**B**, $n = 0$) and occupy a special position among the diverse structures of aminophosphonic acids. However, the first aminophosphonic acid isolated from natural sources was ciliatine (**1**) – a member of the β-aminophosphonic acids family.



Because of the tetrahedral configuration at phosphorus, aminophosphonic acids serve as stable analogues of the unstable tetrahedral carbon intermediates formed in enzymatic processes and, therefore, act as enzyme inhibitors. In addition to naturally occurring aminophosphonic acids, a large number of phosphonic acid analogues of protein or nonprotein amino acids have been synthesized and investigated. This resulted in a

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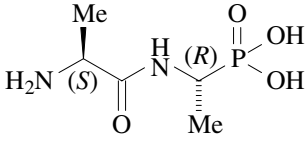
discovery of a wide spectrum of biological activity exhibited by these compounds [1,2]. For example, some of aminophosphonic acids have been reported to exhibit antibacterial, anticancer and antiviral properties as well as pesticidal, insecticidal and herbicidal activity. As such, a few of them have found commercial applications in agriculture and medicine.

As in the case of other classes of chiral bioactive compounds, the biological activity of aminophosphonic acids depends on the absolute configuration of the stereogenic carbon atom bearing the amino group. Thus, for example the (*R,S*)-diastereomer of alafosfalin (**2**) shows significant activity against Gram-positive microorganisms, whereas the other diastereomers are less potent. Similarly, the (*S*)-enantiomer of 2-amino-4-phosphonobutanoic acid (**3**) is ca. 20 times more active than the (*R*)-form in the suppression of glutamate mediated neurotransmission. The activity of 2-amino-5-phosphonopentanoic (**4**) acid as the *N*-methyl-D-aspartate antagonist has been attributed mainly to its (*R*)-enantiomer.



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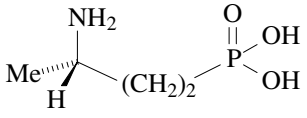

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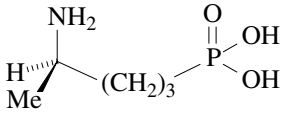

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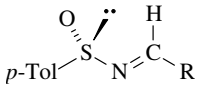
For these reasons, the synthesis of chiral, nonracemic aminophosphonic acids is a challenging task. During the past two decades a great number of syntheses of optically active aminophosphonic acids have been devised [1,3]. Among them, the asymmetric addition of dialkyl or trialkyl phosphites to chiral imine derivatives was found to be very useful approach. However, in contrast to the widely investigated α-aminophosphonic acids, the synthetic approaches to chiral racemic and enantiomeric β-aminophosphonic acids are few in number and of limited applicability. This prompted us to search in the first place for a simple, general and efficient method for the synthesis of optically active β-aminophosphonic acids. We turned our attention to enantiopure sulfinimines **5** as chiral auxiliaries [4]. They contain an arylsulfinyl moiety as a powerful stereodirecting group inducing high diastereoselectivity and an activated carbon–nitrogen double bond prone to attack by nucleophilic reagents. Moreover, they are easily to synthesize and recently commercially available [5].



5

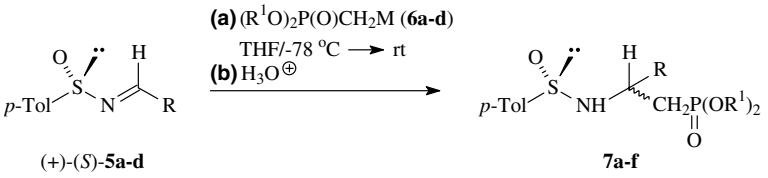
It was found that the addition of phosphite anions or α-phosphonate carbanions to enantiopure sulfinimines **5** is a key reaction in a new asymmetric synthesis of α- and β-aminophosphonic acids. The first part of this contribution compiles the results obtained in the author's laboratory in this area. The second part deals with the recently developed asymmetric synthesis of β-aminocyclopropanephosphonic acids which are conformationally constrained analogues of acyclic aminophosphonic acids.

2. Asymmetric synthesis of β-aminophosphonic acids

As it was mentioned above, the first aim of our study was to develop a new synthesis of optically active β-aminophosphonic acids. Therefore, a series of (+)-(*S*)-sulfinimines **5a–d**, prepared according to the procedure described by Davis et al. [5], was treated with 1.5 equivalent of the lithium or sodium salt of dialkyl methanephosphonates **6a–d** at low temperature. After typical work-up, the diastereomeric adducts **7a–f** formed were isolated in 75–80% yield. The diastereomeric ratio of the adducts **7** was determined by ^{31}P NMR spectroscopy. Analysis of the results collected in Scheme 1 shows that the addition occurred in a highly diastereoselective way, the highest dr ratio was 10:1. The major diastereomers of **7** were isolated by flash chromatography and converted into enantiopure β-aminophosphonic acids [6] (see Scheme 2).

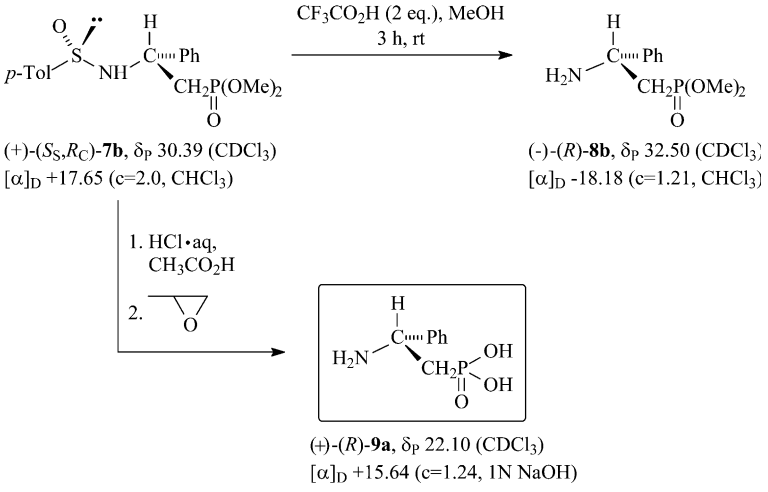
In a typical example, the major diastereomer of (+)-**7b** was converted to β-aminophosphonate (−)-**8b** by trifluoroacetic acid catalyzed methanolysis [7] which allowed to deprotect selectively the amino function. The direct conversion of (+)-**7b** into the corresponding β-aminophosphonic acid (+)-**9a** was found to occur under more forced conditions (heating under reflux for 7 h in a mixture of glacial acetic and hydrochloric acid [8]). The absolute configuration of the acid (+)-**9a** was determined as (*R*) by a single crystal X-ray analysis.

Since in the conversions (+)-**7b** → (−)-**8b** and (+)-**7b** → (+)-**9a** the bonds around the stereogenic β-carbon atom are not broken, it was possible to assign the (S_S,R_C) and (*R*) configuration to (+)-**7b** and (−)-**8b**, respectively. From the point of view of configurational assignments to the adducts **7**, it is very interesting to emphasize that the ^{31}P NMR chemical shifts of all major diastereomeric adducts **7** were found to be at lower field with respect to the minor ones (see Table 1). Therefore,



5		6			Solvent	7		
No	R	No	R^1	M		No	R^1	Dr
a	Ph	**a**	Et	Li	THF	**a**	Et	7.8:1
a	Ph	**b**	Et	Na	Et_2O	**a**	Et	4.7:1
a	Ph	**b**	Et	Na	THF	**a**	Et	4.8:1
a	Ph	**c**	Me	Li	THF	**b**	Me	10.3:1
a	Ph	**d**	i-Pr	Li	THF	**c**	i-Pr	6.6:1
b	PhCH=CH	**a**	Et	Li	THF	**d**	Et	4.9:1
c	α-furyl	**a**	Et	Li	THF	**e**	Et	6.6:1
d	α-furyl	**a**	Et	Li	THF	**f**	Et	9.2:1

Scheme 1. Asymmetric addition of the salts of phosphonates **6** to enantiopure sulfinimines **5**.



Scheme 2. Conversion of the major diastereomeric adduct (+)-**7b** into phosphonate (−)-**8b** and β-aminophosphonic acid (+)-**9a**.

this clear relationship was taken as an indication that the newly generated stereogenic β-carbon atom in all major diastereomeric adducts **7** has the absolute configuration (*R*).

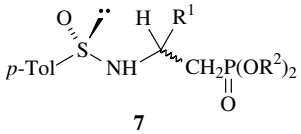
Such a stereochemical course of the addition of α-phosphonate carbanions to enantiopure sulfinimines (+)-(*S*)-**5** was rationalized in terms of the transition state in which the nucleophilic attack on the *s-cis* conformation of the sulfinimine **5** takes place from the less hindered π-face as depicted in Fig. 1.

Finally, it is worthy of notice that our methodology for asymmetric synthesis of β-aminophosphonic acids has recently been applied for the synthesis of optically pure α,α-difluoro-β-aminophosphonic acids [9].

3. Asymmetric synthesis of α-aminophosphonic acids

In extension of our study on asymmetric synthesis of β-aminophosphonic acids we found that the use of dialkyl or diamido phosphite **10** anions instead of α-phosphonate carbanions in the reaction with enantiopure sulfinimines **5** results in the formation of the corresponding adducts **11** which may be converted into enantiomerically pure α-aminophosphonic acids **12** [10]. Thus, the lithium or sodium salts of dialkyl phosphites **10a–c** and diamido phosphites **10d–e** were added at −78 °C to a THF solution of the (+)-(*S*)-sulfinimine **5a**. After quenching the reaction mixture at this temperature and usual work-up the diastereomeric adducts **11a–e** were obtained in 70–90% yield. However, it should be pointed out that the room temperature addition is not efficient, most probably due to reversibility of the reaction at this temperature. Moreover, chemical yield of the adducts **11** and their diastereomeric ratio depend on the reaction conditions (solvent, concentration of reagents, nature of cation). Generally, the use of lithium phosphites **10** and more diluted solutions enhance the diastereoselectivity of the addition. The highest diastereomeric ratio (ca. 94:6) was observed in the addition

Table 1
^{31}P NMR chemical shifts of the diastereomeric addition products **7**



7

	Major, δ_P (ppm)	Minor, δ_P (ppm)
7a, R^1 = Ph, R^2 = Et	27.87	27.43
7b, R^1 = Ph, R^2 = Me	30.39	29.91
7c, R^1 = Ph, R^2 = Pr^i	26.29	25.56
7d, R^1 = E-PhCH=CH, R^2 = Et	28.78	28.03
7e, R^1=  , R^2=Et	27.87	27.31
7f, R^1=  , R^2=Et	27.91	27.34
7g, R^1 = p-F-Ph, R^2 = Et	30.29	29.81

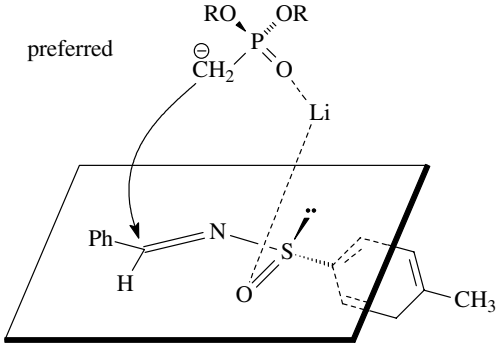
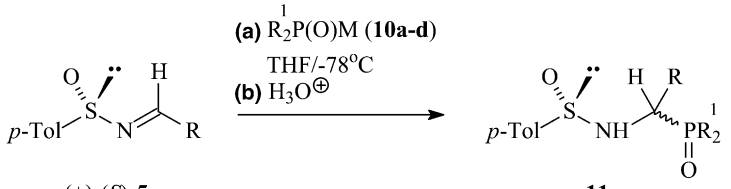


Fig. 1. The proposed transition state model for the α-phosphonate carbanion addition to (+)-(*S*)-**5**.

of lithium dimethyl phosphite **10a** to the sulfinimine (+)-(*S*)-**5a** as well as to (+)-(*S*)-**5c** and (+)-(*S*)-**5d**. In Scheme 3 are collected some selected results of this series of experiments.

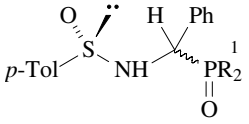
An inspection of the ^{31}P NMR chemical shifts of the adducts **11** (see Table 2) revealed that the signals of the major diastereomers of the adducts **11a–c** appear in the spectra at higher field and those of minor diastereomers at lower field. The opposite relationship was found for the diastereomeric adducts **11d–e** obtained from diamido phosphites. In this case the signals of major diastereomers lie at lower field. This observation strongly suggested that the stereochemical outcome of



5		**10**			**11**		
No	R	No	R^1	M	No	R^1	Dr
a	Ph	**a**	MeO	Na	**a**	MeO	88.12
a	Ph	**a**	MeO	Li	**a**	MeO	94:6
a	Ph	**b**	EtO	Li	**b**	EtO	90:10
a	Ph	**c**	Pr^iO	Li	**c**	Pr^iO	74:26
a	Ph	**d**	Me_2N	Li	**d**	Me_2N	63:37
a	Ph	**e**	Et_2N	Na	**e**	Et_2N	69:31
a	Ph	**e**	Et_2N	Li	**e**	Et_2N	90:10
c	α-furyl	**f**	MeO	Li	**f**	MeO	94:6
d	α-thienyl	**g**	MeO	Li	**g**	MeO	95:5

Scheme 3. Asymmetric addition of the salts of phosphites **10** to enantiopure sulfinimines **5**.

Table 2
^{31}P NMR chemical shifts of the diastereomeric addition products **11**



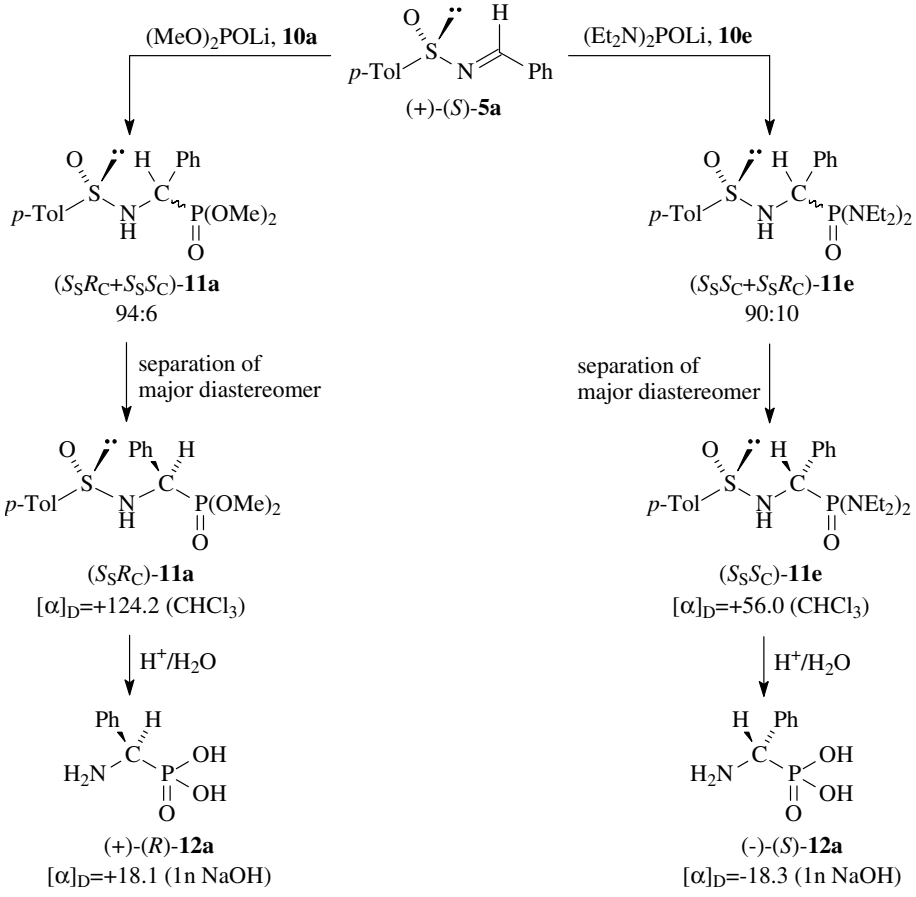
11

	Major, δ_P (ppm)	Minor, δ_P (ppm)
11a, R^1 = MeO	23.6	24.5
11b, R^1 = EtO	21.3	22.0
11c, R^1 = Pr^{i}O	19.6	20.4
11d, R^1 = Me_2N	33.1	32.3
11e, R^1 = Et_2N	32.4	31.4

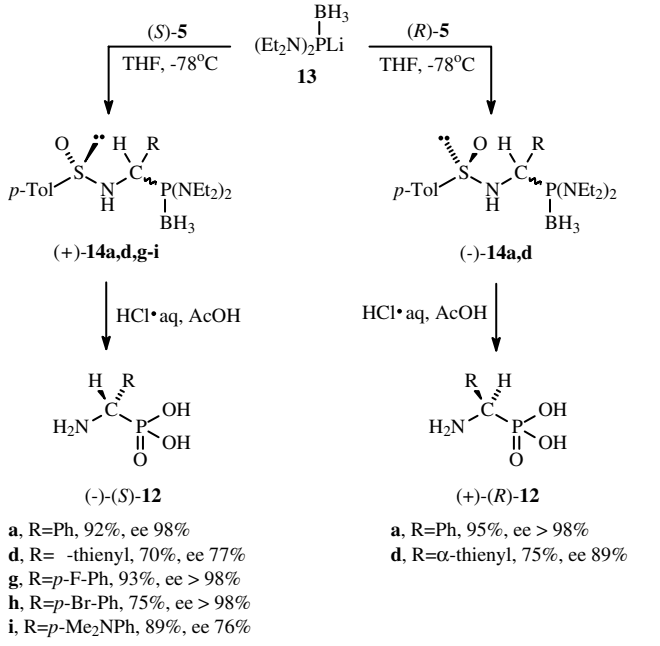
the addition of dialkyl phosphites **10a–c** and diamido phosphites **10d–e** to (+)-(*S*)-sulfinimine **5a** is opposite. The experiments shown in Scheme 4 demonstrate that this is the case. The formation of (+)-(*R*)- and (−)-(*S*)-α-aminobenzylphosphonic acid **12a** [11] unequivocally proves that the major diastereomers formed in the reaction of (+)-(*S*)-**5a** with lithium dimethyl phosphite **10a** and lithium bis-diethylamido phosphite **10e** have opposite configurations at the newly generated stereogenic α-carbon atom i.e., (R_C)- and (S_C)-configuration, respectively. The reasons for the different stereochemical courses of the additions discussed above are still obscure.

In searching of improvement of our procedure for the asymmetric synthesis of α-aminophosphonic acids **12** we turned our attention to the lithiated diaminophosphine borane complex **13** as a powerful phosphorus nucleophile [12]. In fact, it was found to add very efficiently to (*S*)- and (*R*)-sulfinimines **5** in THF at −78 °C affording the corresponding addition products **14** in very high yields (70–100%). These adducts were converted into the corresponding free α-aminophosphonic acids **12** by heating for 4 h in a refluxing mixture of glacial acetic acid and hydrochloric acid [13]. The yields and enantiomeric purities of **12** prepared in this way are collected in Scheme 5.

It is interesting to point out that the steric course of the above additions is analogous to that of the additions of lithium diamido phosphites to sulfinimines **5**. The formation of the major diastereomers with the (S_C)-configuration in the addition of **13** to (*S*)-**5** may reasonably be explained in terms of the transition state model shown in Fig. 2, where steric approach control is a decisive factor and lithium of **13** is coordinated to the nitrogen atom lone pair, facilitating the delivery of the phosphorus atom to



Scheme 4. Synthesis of both enantiomers of α-aminobenzylphosphonic acid **12a** from (+)-(*S*)-sulfinimine **5a**.



Scheme 5. Asymmetric addition of the aminophosphine borane complex **13** to (*S*)- and (*R*)-sulfinimines **5** and hydrolysis of the adducts **14** to α-aminophosphonic acids **12**.

the prochiral trigonal carbon centre from the less hindered face occupied by the lone pair of electrons on sulfur.

4. Asymmetric synthesis of β-aminocyclopropanephosphonic acids

The next stage of our study on the synthesis of optically active aminocyclopropanephosphonic acids was

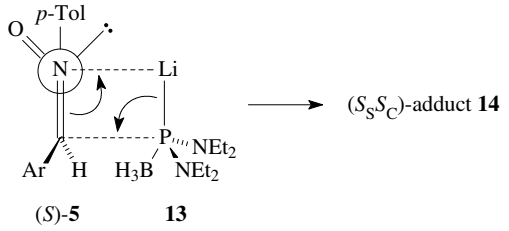
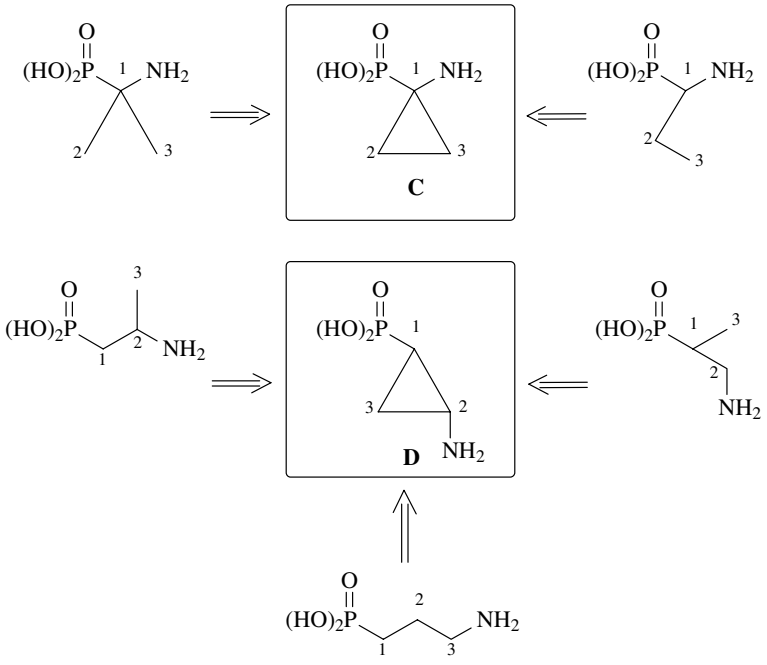


Fig. 2. The proposed transition state model for the addition of **13** to (*S*)-sulfinimine **5**.

stimulated by two facts. The first was that a wide variety of natural products and currently-used insecticides contain the chiral cyclopropane unit [14]. Secondly, aminocyclopropanephosphonic acids can be considered as conformationally constrained analogues of acyclic aminophosphonic acids. In this context, it should be emphasized that the design and synthesis of conformationally constrained peptidomimetics has recently been an important strategy in modern drug discovery processes [15].

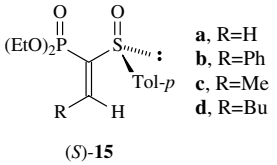
Thus, in accord with the concept of conformational constraints α-aminocyclopropanephosphonic acids **C** are conformationally constrained analogues of α-aminophosphonic acids while β-aminocyclopropanephosphonic acids **D** are this kind of analogues of β- and γ-aminophosphonic acids as schematically depicted in Scheme 6.

Before presenting our new asymmetric synthesis of β-aminocyclopropanephosphonic acids **D** it seems desirable to discuss briefly asymmetric cyclopropanation of optically active α-phosphorylvinyl sulfoxides because the basic studies on this reaction allowed the develop-



Scheme 6. α- and β-Aminocyclopropanephosphonic acids as conformationally constrained analogues of acyclic aminophosphonic acids.

ment of a new methodology for the synthesis of the enantiopure acids **D**.



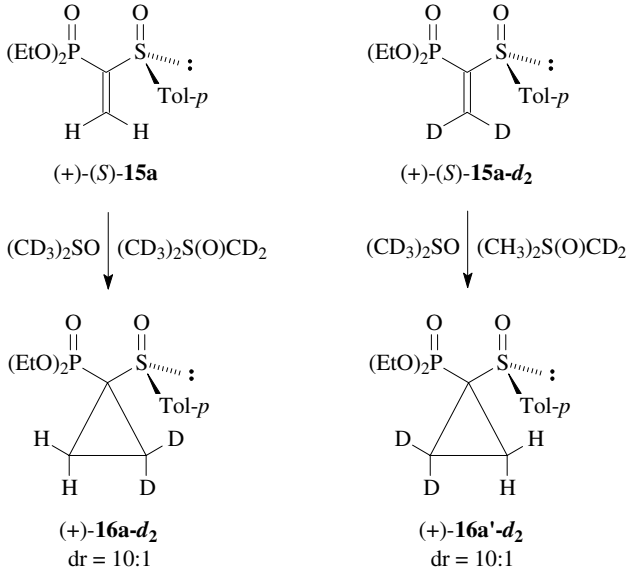
(*S*)-**15**

Recently, we designed a new type of enantiomerically pure vinyl sulfoxides, namely α-(diethoxyphosphoryl)vinyl *p*-tolyl sulfoxide (**15a**) and its β-substituted analogues [16].

Due to the presence of two electron-withdrawing groups, phosphoryl and sulfinyl, these vinyl sulfoxides are very good Michael acceptors and reactive Diels–Alder dienophiles. The sulfoxides **15** are also key reagents for the construction of cyclic and heterocyclic compounds *via* tandem Michael addition/intramolecular Horner–Wittig reaction.

However, from the view-point of asymmetric synthesis the most interesting results were obtained in the reaction of **15** with sulfur ylides and diazoalkanes which affords cyclopropanes in a highly or fully diastereoselective way [17–19]. The most simple reaction of asymmetric cyclopropanation was realized when (+)-(*S*)-**15a** was treated with fully deuterated dimethyl(oxo)sulfonium methylide as the CD_2 transfer reagent. It resulted in the formation of the optically active cyclopropane **16a**-d_2 as the major diastereomer in which the newly formed quaternary α-carbon atom is chiral due to isotopic substitution (CH_2 vs CD_2). The diastereomer with opposite configuration at the α-carbon atom was prepared starting from 2,2-dideuterio substituted vinyl sulfoxide (+)-(*S*)-**15a-d$_2$** and undeuterated sulfur ylide (see Scheme 7). The diastereomeric ratio in both reactions was found to be ca. 10:1.

The reaction of (+)-(*S*)-**15a** with diphenylsulfonium isopropylide or diphenyldiazomethane yielded the corresponding cyclopropanes **16b** and **16c** as single diastereomers.



Scheme 7. Synthesis of diastereomeric cyclopropanes **16a**-d_2 chiral by isotopic substitution.

Based on X-ray structure analysis of crystalline (±)-α-(diphenylphosphinoyl)vinyl *p*-tolyl sulfoxide (**17**) and density functional calculations (B3LYP/6-31G*) on α-phosphorylvinyl sulfoxides, which revealed the origin of the observed diastereoselectivities, a transition state model for the cyclopropanation of chiral vinyl sulfoxides **15** was proposed (Fig. 3), where steric approach control is a decisive factor. Hence, the addition of sulfur ylide or diazoalkane to the vinyl β-carbon atom of **15** and subsequent ring closure occur preferentially or exclusively from the less hindered diastereotopic face occupied by the electron pair at sulfur (top-face attack). The bottom-face attack of a sulfur ylide is much less probable due to steric hindrance exerted by the *p*-tolyl group and substitutents at phosphorus. It is important to point out that in accord with the prediction of the above TS-model the X-ray structure of the cyclopropane (+)-**16c** confirmed the (*S*) absolute configuration of the newly formed stereogenic α-carbon atom [19].

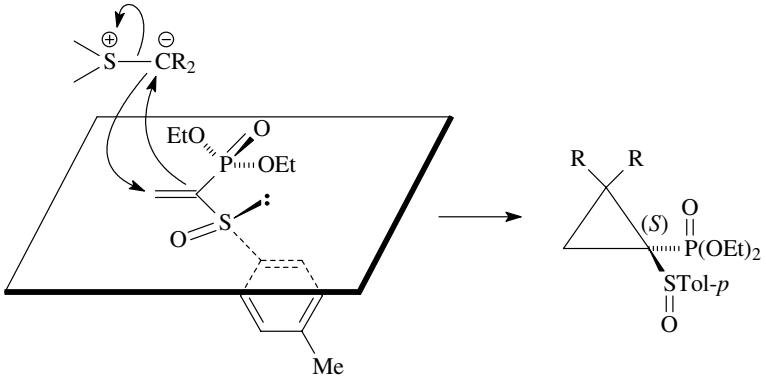
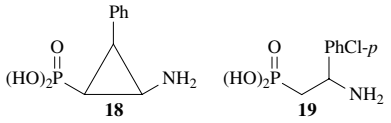
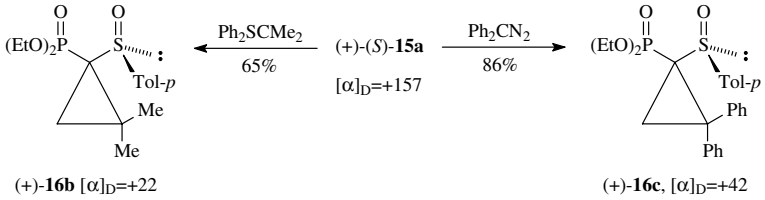


Fig. 3. The proposed transition state model of the reaction of (+)-(*S*)-sulfoxide **15a** with sulfur ylides.

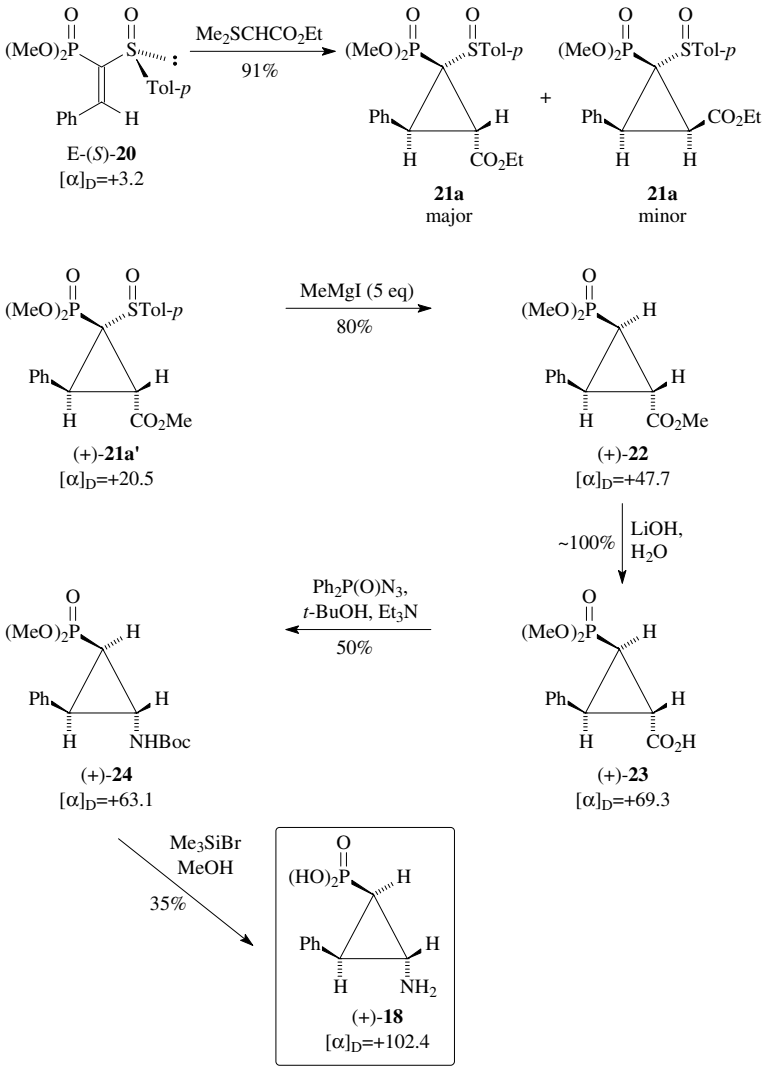
The asymmetric cyclopropanation of optically active α-phosphorylvinyl sulfoxides **15** presented above paved the way to β-aminocyclopropanephosphonic acids. The synthesis of enantiopure β-amino-γ-phenylcyclopropanephosphonic acid (**18**) – a constrained analogue of the $GABA_B$ antagonist phaclofen **19** – best exemplifies our new approach to the desired compounds [20] (see Scheme 8).



A key reaction in the total synthesis of **18** was asymmetric cyclopropanation of E-(*S*)-(1-dimethoxyphosphoryl-2-phenyl)vinyl *p*-tolyl sulfoxide (**20**) with ethyl



Scheme 8. Preparation of enantiopure cyclopropanes **16b** and **16c**.



Scheme 9. Asymmetric synthesis of (+)-(1*R*, 2*R*, 3*R*)-**18** – a constrained analogue of phaclofen.

(dimethylsulfuranylidene)acetate (EDSA). It was found that the cyclopropane **21** formed was a mixture of only two diastereomers in an 8:1 ratio. The major diastereomer **21a** isolated in a pure state was converted into the corresponding methyl ester **21a′**. Based on the transition state model and analysis of NMR spectra the absolute stereochemistry (1*S*, 2*R*, 2*R*) was assigned to the cyclopropane ring in **21a′**. In the next step, the chiral sulfinyl moiety was removed with retention of configuration at the α-carbon atom upon treatment of (+)-**21a′** with methylmagnesium iodide. Then, the ester group in the cyclopropane (+)-**22** was hydrolyzed to the corresponding carboxylic acid (+)-**23** which was, in turn, converted by the well-known procedure [21] into the N-Boc derivative (+)-**24**. Finally, deprotection of the amino and phosphonate functions afforded the enantiomerically pure (+)-(2*R*)-amino-(3*R*)-phenyl-(1*R*)-cyclopropanephosphonic acid (**18**). Our asymmetric synthesis of **18** shown in Scheme 9 afforded the dextrorotatory enantiomer and in this way is complementary to the asymmetric synthesis of the levorotatory enantiomer of **18** described by Hanessian and co-workers [22].

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