

1,3-Dipolar Cycloaddition of Diazoalkanes to Racemic and Optically Active α -(Diethoxyphosphoryl)vinyl p-Tolyl Sulfoxides: A New Synthesis of 3-Phosphorylpyrazoles and Asymmetric Synthesis of Cyclopropanes

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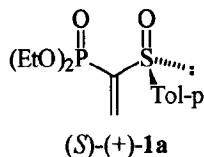
Abstract

Cycloaddition of diazomethane and ethyl diazoacetate to α -(diethoxyphosphoryl)vinyl p-tolyl sulfoxide **1a** and its β -substituted analogues (Me, Ph) results in the formation of 3-phosphorylpyrazoles in high yield. The reaction of chiral (*S*)-(+)-**1a** with diphenyldiazomethane proceeds fully diastereoselectively to give the corresponding cyclopropane (+)-**6a** with the (*S*_C, *S*_S) configuration determined by X-ray diffraction analysis. Diazopropane reacts with (*S*)-(+)-**1a** to give only one diastereoisomer of the pyrazoline cycloadduct (+)-**2e** which undergoes decomposition to the cyclopropane (+)-**6b** with preservation of configurational integrity. © 1999 Elsevier Science Ltd.

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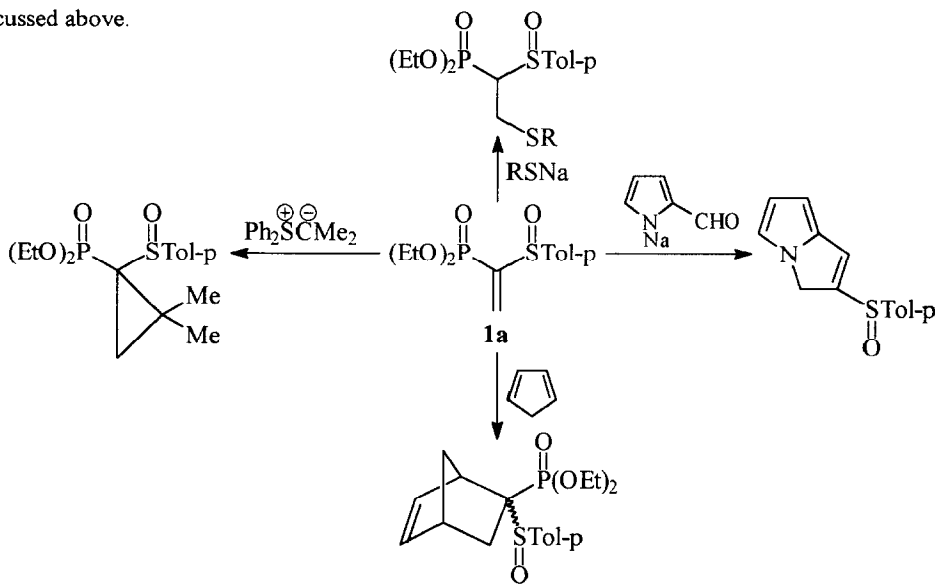
INTRODUCTION

α,β -Unsaturated sulfoxides are valuable intermediates in a variety of synthetic transformations and useful building blocks in the synthesis of biologically active compounds.¹ Especially important are chiral, enantiomerically pure vinyl sulfoxides which have recently found a wide application in numerous asymmetric syntheses.^{2,3} Since simple vinyl sulfoxides having no additional electron-withdrawing substituents on the double bond exhibit low reactivity, we recently designed a new type of activated racemic and optically active vinyl sulfoxide, namely α -(diethoxyphosphoryl)vinyl p-tolyl sulfoxide **1a** and its β -substituted analogues (Me, Ph, Buⁿ).⁴



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The presence of the phosphoryl group not only increases the reactivity of these sulfoxides but also allows them to perform further reactions such as *e.g.*, the Horner-Wittig reaction. The chiral sulfoxides **1** were found to undergo asymmetric Michael reaction, Diels-Alder cycloaddition and cyclopropanation, the latter being fully diastereoselective.⁵ They are also key reagents for the construction of carbo- and heterocycles *via* tandem Michael addition/intramolecular Horner-Wittig reaction. The selected reactions shown in Scheme 1 illustrate the reactivity of **1** discussed above.



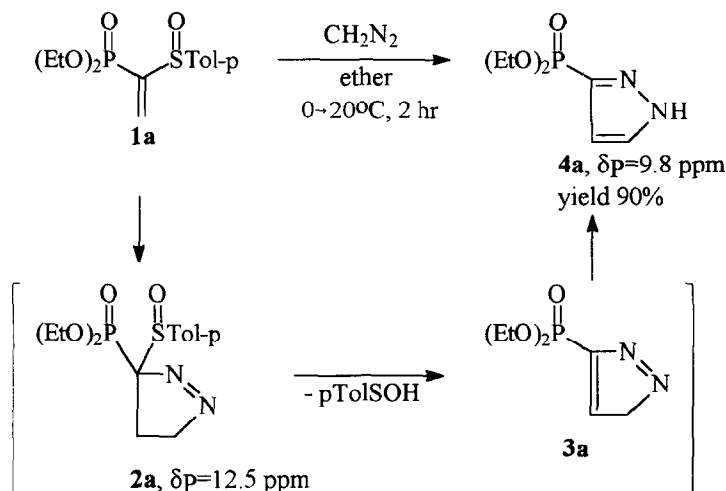
Scheme 1

Continuing our studies on the reactivity and potential synthetic applications of the vinyl sulfoxides **1** we decided to investigate their behaviour towards diazoalkanes which are known to act in cycloaddition reactions as 1,3-dipoles with either retention or loss of the nitrogen moiety. Surprisingly, the use of vinyl sulfoxides as dipolarophiles in such cycloaddition reactions has not been widely investigated⁶⁻⁸ and only recently the first asymmetric cycloaddition of diazomethane to chiral 5-ethoxy-p-tolylsulfinylfuran-2(5H)-ones has been described by Garcia Ruano and his co-workers.⁹ In this paper we wish to disclose the results of our studies on the title reaction and its diverse course, depending on the structure of the diazo compound used.

RESULTS AND DISCUSSION

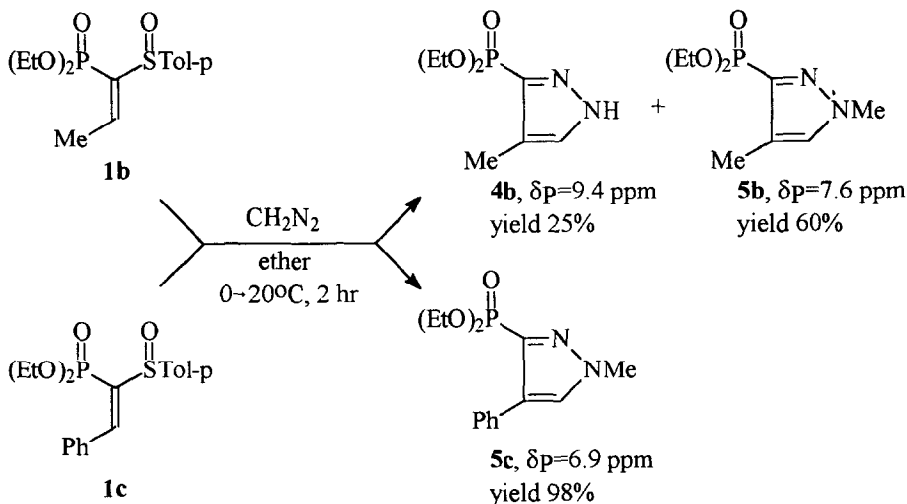
In the first place the reaction of *diazomethane* with the vinyl sulfoxides **1** was investigated because this reagent is one of the simplest and best known 1,3-dipoles. Thus, treatment of **1a** with diazomethane resulted in the formation of the two products as indicated by the ³¹P-NMR spectra (two signals at δ_p =12.5 and 9.8 ppm) of the crude reaction mixture. Purification of this mixture by flash chromatography afforded a single product (δ_p =9.8 ppm) in 90% yield which was identified as 3-diethoxyphosphorylpyrazole **4a**. It is reasonable to assume that the pyrazoline cycloadduct **2a** primarily formed, which was recognized by ³¹P-NMR spectroscopy (δ_p =12.5 ppm), is unstable and eliminates p-toluenesulfenic acid to give the isopyrazole **3a**. The latter undergoes rapid tautomerization

to the final product **4a** (Scheme 2).



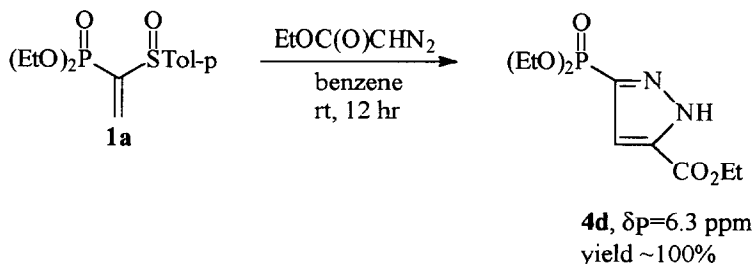
Scheme 2

Cycloaddition of diazomethane (used in excess) to β -substituted vinyl sulfoxides **1b** and **1c** was carried out under similar reaction conditions. In the case of **1b**, the ^{31}P -NMR spectrum of the crude reaction mixture revealed two signals at 7.6 and 10.8 ppm in a 2:1 ratio. The first of them was assigned to 1-methyl-3-diethoxyphosphoryl-4-methylpyrazole **5b**.¹⁰ It was isolated from the reaction mixture in 60% yield by flash chromatography. The second signal corresponds most probably to the primary pyrazoline cycloadduct which upon purification by flash chromatography, was converted to the pyrazole **4b**¹⁰ isolated in 25% yield. With the vinyl sulfoxide **1c** the only cycloaddition product was the N-methyl pyrazole **5c** obtained in 98% yield.

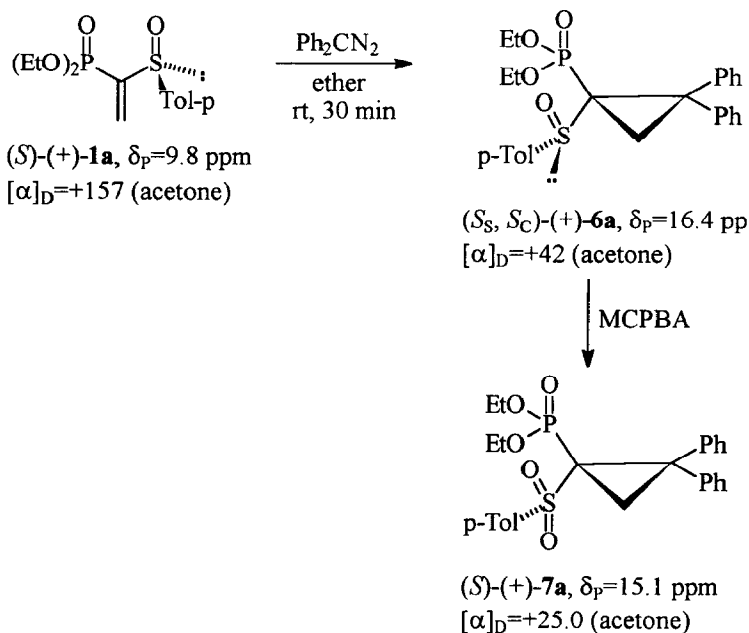


Scheme 3

When **1a** was treated with *ethyl diazoacetate*, 3-diethoxyphosphoryl-5-ethoxycarbonyl-pyrazole **4d**¹¹ was obtained in quantitative yield. However, *ethyl diazomalonate* was found to be unreactive towards **1a**, most probably for steric reasons.



In contrast to the 1,3-cycloaddition reactions of the vinyl sulfoxides **1** with diazoalkanes described above, the reaction of **1a** with *diphenyldiazomethane* occurred with elimination of nitrogen leading exclusively to the corresponding cyclopropane **6a**.¹² Moreover, it was found that when (*S*)-(+)-**1a** was reacted with diphenyldiazomethane, a single diastereoisomer of **6a** was formed as indicated by the ^1H and ^{31}P -NMR spectra of the crude product. Flash chromatography afforded the analytically pure cyclopropane (+)-**6a** in 86% yield, mp 89–91°C.



Scheme 4

In order to confirm the full diastereoisomeric purity of the cyclopropane (+)-**6a** obtained as above, it was oxidized to the optically active sulfone (+)-**7a** in which the only stereogenic atom was the newly formed quaternary α -carbon atom. The ^1H -NMR spectra of (+)-**7a** recorded in the absence and in the presence of (*R*)-(+)-*tert*-butylphenylphosphinothioic acid as a chiral solvating agent¹³ showed a single set of the cyclopropyl methylene proton signals (two doublets of doublets) while in the spectrum of the racemic sulfone (\pm)-**7a** all the signals of the same protons were doubled (see Fig. 1). This provided an unequivocal proof of the full enantiomeric purity of (+)-**7a** and consequently of the full diastereoisomeric purity of (+)-**6a**.

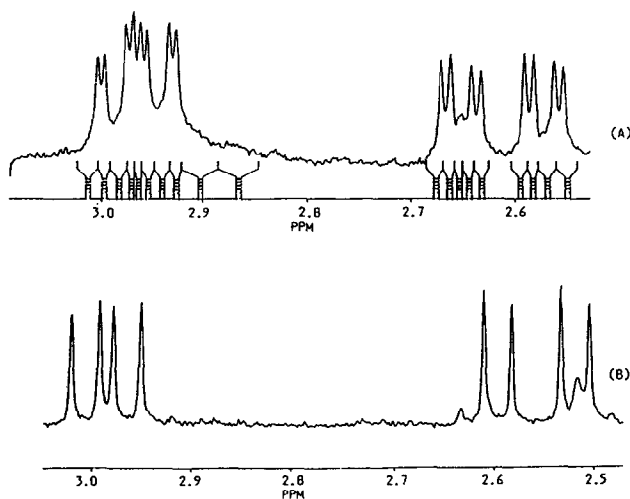
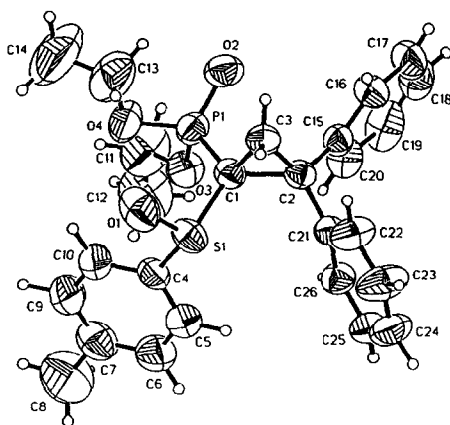


Fig. 1. ^1H NMR spectra of racemic (A) and optically active (B) sulfone **7a** with chiral solvating agent.

Taking advantage of the fact that the cyclopropane (+)-**6a** is crystalline, we determined its crystal and molecular structure by X-ray diffraction (Fig. 2).¹⁴



Analysis of the X-ray data revealed that the absolute configuration of the newly formed chiral centre at the α -carbon atom is *S*. Moreover, both polar sulfinyl and phosphoryl groups in **6a** were found to adopt an *anti*-like orientation with the torsional angle S(1)–O(1)–P(1)–O(2) equal to $93.3 (\pm 0.1)^\circ$. Therefore, it is reasonable to assume that (*S*)-(+)-**1a** adopts also a similar conformation and the approach of diphenyldiazomethane to the carbon-carbon double bond in **1a** takes place exclusively from the less hindered diastereotopic face occupied by the lone electron pair at sulfur, as schematically depicted in Fig. 3.

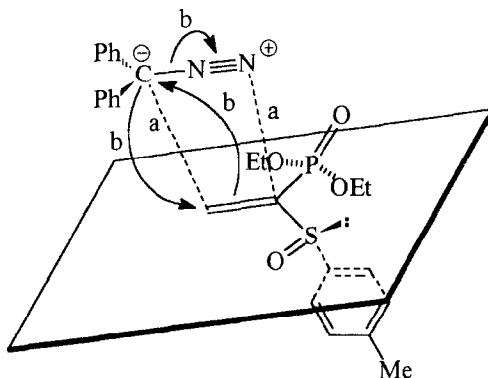


Fig. 3. The proposed steric course of the reaction of Ph_2CN_2 with the sulfoxide (*S*)-(+)-**1a**

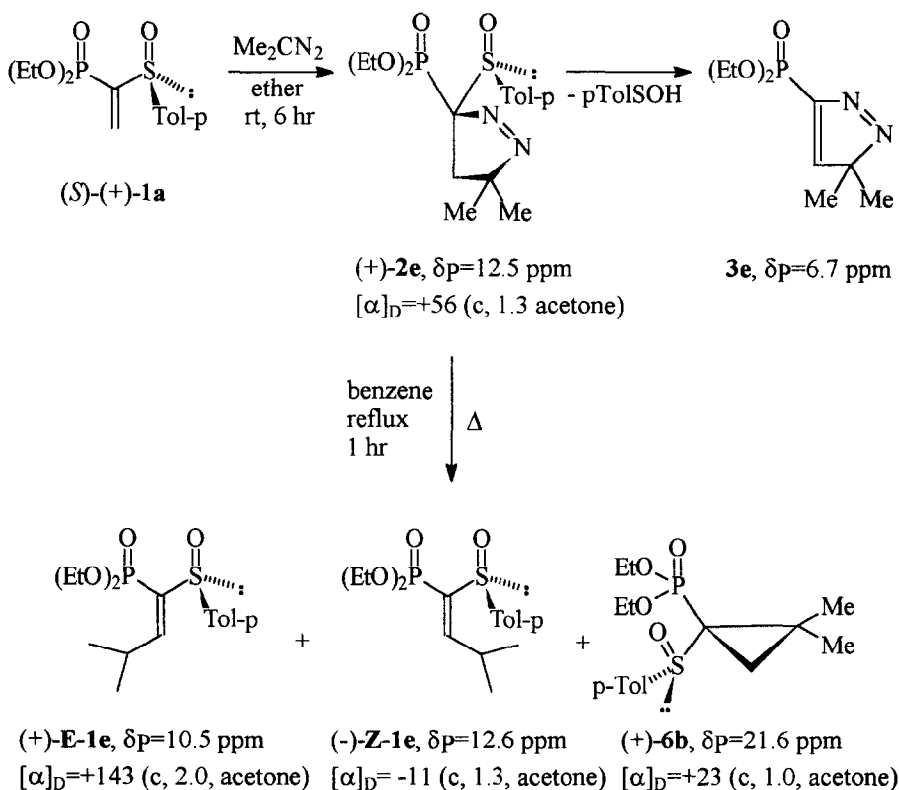
Although it is not clear at present whether the cyclopropane (+)-**6a** is formed *via* the pyrazoline cycloadduct and subsequent nitrogen extrusion (pathway a) or by nucleophilic addition of diphenyldiazomethane to the vinyl β -carbon atom of (+)-**1a** followed by the closure of the three-membered ring (pathway b), this transition state model explains the complete regio- and diastereoselectivity of the reaction under discussion.

Finally, the reaction of *diazopropane* with the sulfoxide (*S*)-(+)-**1a** was investigated. To our satisfaction we were able to isolate from the reaction mixture the primary cycloadduct (+)-**2e** which was formed in quantitative yield. It can be stored in a refrigerator for a few days provided that it was purified by flash chromatography. Any traces of bases as well as aqueous work-up cause immediate elimination of *p*-toluenesulfenic acid and formation of the pyrazoline **3e**. An inspection of the spectral data (^1H and ^{31}P -NMR) of (+)-**2e** revealed the formation of this compound as a single diastereoisomer thus confirming the complete stereoselectivity of this cycloaddition.

As in the case of the reaction of diphenyldiazomethane with (*S*)-(+)-**1a**, it is reasonable to assume that the approach of diazopropane takes place from the face of the dipolarophile occupied by the lone electron pair on sulfur. Therefore, the pyrazoline cycloadduct (+)-**2e** so formed should have the S_C -configuration at the α -carbon atom.

Heating the pyrazoline (+)-**2e** in refluxing benzene for 1 hr resulted in extrusion of nitrogen and formation of three products: *E*- and *Z*-vinyl sulfoxides **1e** and cyclopropane (+)-**6b** in a 2:1:1 ratio (^{31}P -NMR assay),

respectively. Formation of the vinyl sulfoxides **1e** was not unexpected because olefination is known as a side reaction occurring on pyrolysis of pyrazolines.¹⁵ However, in our case it was a main reaction pathway in comparison with cyclopropanation. It is also worth noting that the cyclopropane (+)-**6b** isolated in 25% yield from the thermolysis of (+)-**2e** was a single diastereoisomer the stereostructure of which was identical with that obtained in the cyclopropanation reaction of (*S*)-(+)-**1a** with diphenylsulfonium isopropylide.⁵



Scheme 5

Attempts to increase the yield of the cyclopropane (+)-**6b** by photolysis of the pyrazoline (+)-**2e** failed completely. However, it was found that addition of lithium chloride promoted the decomposition of (+)-**2e**, and occasionally improved the yield of cyclopropane. Unfortunately, the reaction is very sensitive to experimental conditions. We found that the solvent had a very important effect on the lithium chloride promoted decomposition of the pyrazoline **2e**. Thus, when **2e** was stirred in a tetrahydrofuran-methanol solution in the presence of lithium chloride, the *E*, *Z*-sulfoxides **1e** were formed as the only decomposition products.

CONCLUSIONS

In conclusion, a new and efficient method for the synthesis of 3-phosphorylpyrazoles has been developed which is based on the reaction of α -(phosphoryl)vinyl sulfoxides **1** with diazomethane and its analogues. It has been demonstrated that the reaction involves the initial formation of a pyrazoline cycloadduct which eliminates sulfenic acid to give isopyrazole. The latter tautomerizes rapidly to 3-phosphorylpyrazole as the final product. Such a reaction course has been confirmed by ^{31}P -NMR spectroscopic studies and isolation of the primary pyrazoline cycloadduct in the reaction of the sulfoxide **1a** with diazopropane. The reaction of (*S*)-(+)- α -(diethoxyphosphoryl)-vinyl *p*-tolyl sulfoxide **1a** with diphenyldiazomethane has been found to occur with nitrogen elimination affording the corresponding (*S*_C, *S*_S)-(+)-cyclopropane **6a** as the only diastereoisomer. The complete regio- and diastereoselectivity of this reaction has been rationalized in terms of steric approach control of diphenyldiazomethane from the less hindered face of the chiral sulfinyl group occupied by the lone electron pair. Similarly, the cycloaddition reaction of (*S*)-(+)-**1a** with diazopropane has occurred with a full stereoselectivity and gave only one diastereoisomeric pyrazoline cycloadduct (+)-**2e** to which the absolute configuration (*S*_C, *S*_S) has been tentatively assigned. Its decomposition gave also the corresponding cyclopropane (+)-**6b** as a pure diastereoisomer.

EXPERIMENTAL

General

Flash column chromatography was conducted on silica gel Merck 60 (70–230 mesh). NMR spectra were recorded on Bruker MSL 300 and Bruker AC 200 spectrometers in CDCl_3 solution (unless otherwise stated). The optical rotations were measured on a Perkin-Elmer 241 MC photopolarimeter in acetone solution.

3-Diethoxyphosphorylpyrazole (**4a**).

A solution of diazomethane (3–5 mmol) in 25 ml of ether was added dropwise to an ethereal solution (10 ml) of sulfoxide **1a** (0.3 g, 1 mmol) at 0°C. The temperature was then allowed to reach 20°C. The mixture was stirred for 2 hours. The solvent was evaporated under vacuum affording the crude product (δ_{P} 12.5 and 9.8 ppm). After purification by flash chromatography the pure pyrazole **4a** was obtained as a pale solid (0.18 g, 90% yield); m.p. 63–64°C (hexane); ^{31}P NMR: 9.8 ppm; ^1H NMR: (200 MHz, CDCl_3): 1.31 (3 H, dt, $J=7.0$; 0.4 Hz, $\text{CH}_3\text{CH}_2\text{O}$); 4.15 (4 H, m, $\text{CH}_3\text{CH}_2\text{O}$); 6.73 (1 H, m, $J=2.0$ Hz, $\text{CH}=\text{}$); 7.74 (1 H, m, $J=2.0$ Hz, $\text{CH}=\text{}$); HRMS (EI): M^+ , found 204.0652. $\text{C}_7\text{H}_{13}\text{O}_3\text{PN}_2$ requires 204.0663.

1-Methyl-3-diethoxyphosphoryl-4-methylpyrazole (**5b**).

Diazomethane (10–15 mmol) in 30 ml of ether was added dropwise to an ethereal solution (10 ml) of sulfoxide **1b** (0.3 g, 1 mmol) at 0°C. The mixture was warmed up to room temperature and stirred for 3 hours. Evaporation of solvent gave the crude product showing two signals in ^{31}P -NMR spectrum at 10.8 and 7.6 ppm. After purification

by flash chromatography **5b** was obtained (0.14 g, 60% yield); oil; ^{31}P NMR: 7.6 ppm; ^1H NMR (CDCl_3): 1.32 (6 H, t, $J=7.0$ Hz, $\text{CH}_3\text{CH}_2\text{O}$); 2.23 (3 H, d, $J=1.4$ Hz, $\text{CH}_3\text{C}=\text{C}$); 4.04 (3 H, s, CH_3N); 4.15 (4 H, m, $\text{CH}_3\text{CH}_2\text{O}$); 7.33 (1 H, d, $J=2.0$ Hz, $\text{CH}=\text{C}$). HRMS (EI): M^+ , found 231.9986. $\text{C}_9\text{H}_{17}\text{O}_3\text{PN}_2$ requires 231.9998.

3-Diethoxyphosphoryl-4-methylpyrazole (**4b**).

Purification by flash chromatography of the mixture of products obtained in the reaction of diazomethane with sulfoxide **1b** afforded 0.056 g (25%) of **4b** as a white solid; m.p. 76–77°C (hexane); ^{31}P NMR: 9.2 ppm; ^1H NMR (CDCl_3): 1.32 (6 H, t, $J=7.0$ Hz, $\text{CH}_3\text{CH}_2\text{O}$); 2.31 (3 H, d, $J=1.6$ Hz, $\text{CH}_3\text{C}=\text{C}$); 4.15 (4 H, m, $\text{CH}_3\text{CH}_2\text{O}$); 7.59 (1 H, d, $J=2.0$ Hz, $\text{CH}=\text{C}$); HRMS (EI): M^+ , found 218.08187. $\text{C}_8\text{H}_{15}\text{O}_3\text{PN}_2$ requires 218.0802.

1-Methyl-3-diethoxyphosphoryl-4-phenylpyrazole (**5c**).

Diazomethane (10–15 mmol) in 30 ml of ether was added dropwise to an ethereal solution (10 ml) of sulfoxide **1c** (0.38 g, 1 mmol) at 0°. The mixture was warmed up to room temperature and stirred for 3 hours. Evaporation of solvent gave the crude product which was purified on silica gel affording **5c** (0.26 g, 98% yield) as an oil; IR (Nujol): 2983, 1253, 1020 cm^{-1} ; ^{31}P NMR: 6.9 ppm; ^1H NMR (CDCl_3): 1.12 (6 H, dt, $J=7.1, 0.7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$); 3.86–4.13 (4 H, m, $\text{CH}_3\text{CH}_2\text{O}$); 4.21 (3 H, d, $J=0.8$ Hz, CH_3N); 7.32–7.42 (5 H, m, Ph); 7.54 (1 H, d, $J=2.0$ Hz, $\text{CH}=\text{C}$); ^{13}C NMR (CDCl_3): 15.8 (d, $J=5$ Hz); 40.2 (s, N-Me); 62.5 (d, $J=6.5$ Hz); 127.4; 127.9; 129.5; 132.2; 135.2; 135.5; 138.3. HRMS (CI): M^+ , found 295.1211. $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_3\text{P}$ requires 295.1223.

3-Diethoxyphosphoryl-5-carboethoxypyrazole (**4d**).

Ethyl diazoacetate (0.17 g, 1.2 mmol) was added to vinyl sulfoxide **1a** (0.3 g, 1 mmol) in 10 ml of benzene. The mixture was stirred overnight at room temperature. The solvent was evaporated under vacuum affording 0.27 g of **4d** in 100% yield; oil; IR (Nujol): 2984, 1729, 1233, 1024 cm^{-1} ; ^{31}P NMR: 6.3 ppm; ^1H NMR (200 MHz); (CDCl_3): 1.35 (9 H, t, $J=7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$); 4.1–4.4 (6 H, m, $\text{CH}_3\text{CH}_2\text{O}$); 7.20 (1 H, d, $J=1.8$ Hz, $\text{CH}=\text{C}$). HR-MS (CI): M^+ , found 277.0949. $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_5\text{P}$ requires 277.0953.

(S_C, S_S)-(+)-1-Diethoxyphosphoryl-1-p-tolylsulfinyl-2,2-diphenylcyclopropane (**6a**).

Diphenyldiazomethane (0.39 g, 2 mmol) in 10 ml of ether was added dropwise to vinyl sulfoxide (S)-(+)-**1a** (0.3 g, 1 mmol) in 5 ml of ether. The solution was stirred for 30 minutes and then the mixture was quenched with aq NH_4Cl and extracted with CHCl_3 (3 x 25 ml). The extract was dried (MgSO_4), evaporated and the residue was purified by chromatography affording (S_S, S_C)-(+)-**6a** as a white solid (0.4 g, 86% yield); m.p. 89–91°C (ethanol), $[\alpha]_D^{25} = +42$ (c, 2.0, acetone). IR (KBr): 1319, 1026, 692 cm^{-1} ; ^{31}P NMR: 16.2 ppm; ^1H NMR (CDCl_3): 0.98 (3 H, dt, $J=0.6, 7.1$ Hz, $\text{CH}_3\text{CH}_2\text{OP}$); 1.07 (3 H, dt, $J=0.6, 7.0$ Hz); 2.42 (3 H, s, $\text{CH}_3\text{-Ph}$); 2.62 (1 H, dd, $J=6.2, 16.9$ Hz, -H-CH-); 2.89 (1 H, dd, $J=6.2, 8.5$, Hz H-CH); 3.34–3.65 (1 H, m, $\text{-CH}_2\text{OP}$); 3.68–3.82 (2 H, m, CH_2OP); 4.10–4.26 (1 H, m, $\text{-CH}_2\text{OP}$); 7.12–7.37 (8 H, m, arom.); 7.48–7.65 (6 H, m, arom.); ^{13}C NMR (50.3 Hz, CDCl_3): 1.0; 15.9; 21.5 (d, $J=2.1$ Hz); 29.6; 45.6; 62.4 (d, $J=6.3$ Hz); 125.9; 127.2; 127.5; 128.2; 128.7; 128.9; 129.4; 138.2;

139.5; 140.9; 141.2. HRMS (EI): M^+ , found 468.1481. $C_{26}H_{29}O_4PS$ requires 468.1524.

(+)-3-Diethoxyphosphoryl-3-p-tolylsulfinyl-5,5-dimethylpyrazoline (2e).

A solution of diazopropane (15 mmol) in 10 ml of ether was added dropwise to an ethereal solution of (*S*)-(+)-**1a** (0.3 g, 10 mmol) at room temperature. The mixture was stirred at this temperature overnight. After evaporation of solvent the residue was filtered through silica affording pyrazoline **2e** as an yellow oil (0.34 g, 90% yield), $[\alpha]_D^{25} +56$ (c, 1.3, acetone). ^{31}P NMR: 12.5 ppm; 1H NMR ($CDCl_3$): 1.14 (3 H, t, $J=7.0$ Hz, CH_3CH_2O); 1.19 (3 H, t, $J=7.0$ Hz, CH_3CH_2O); 1.34 (2 H, m, $C-CH_2-C$); 1.43 (3 H, s, CH_3C); 1.50 (3 H, s, CH_3C); 2.40 (3 H, s, CH_3Ph) 3.87-4.36 (4 H, m, CH_3CH_2O); 7.29 and 7.69 (A_2B_2 , aromat.).

3-Diethoxyphosphoryl-5,5-dimethylpyrazole (3e).

Pyrazoline **2e** (0.37 g, 1 mmol) was dissolved in 10 ml of acetone and Na_2CO_3 was added. The mixture was heated for 1 hour. Reaction was quenched with 15 ml of water and extracted with $CHCl_3$ (3 x 25 ml). The dried ($MgSO_4$) extract was evaporated affording, after flash chromatography 0.23 g of **3e**, in quantitative yield. IR (Nujol): 2983, 1243, 1031 cm^{-1} ; ^{31}P NMR: 6.7 ppm; 1H NMR ($CDCl_3$): 1.39 (6 H, t, $J=7.0$ Hz, CH_3CH_2O); 1.48 (6 H, s, $(CH_3)_2C$); 4.27 (4 H, m, CH_3CH_2O) 7.59 (1 H, d, $J=4.9$ Hz, $CH=$). HRMS (EI): M^+ , found 232.0963. $H_9H_{17}O_3PN_2$ requires 232.0976.

Thermal decomposition of pyrazoline (+)-2e.

Pyrazoline **2e** (0.19 g, 5 mmol) was heated under reflux in 10 ml benzene solution for 30 minutes. Evaporation of solvent afforded a mixture of cyclopropane **6b** and *E* and *Z* isomers of vinyl sulfoxide **1e** in a 1:2:1 ratio (^{31}P NMR assay), which were separated by chromatography (benzene/acetone 5:1).

(+)-E-(α -Diethoxyphosphoryl- β -isopropyl)vinyl p-tolyl sulfoxide (1e)

$[\alpha]_D^{25} +143$ (c, 2.0, acetone); oil; IR (Nujol): 2957, 2926, 1680, 1259, 1046 cm^{-1} ; ^{31}P NMR: 10.5 ppm; 1H NMR ($CDCl_3$): 1.12 (6 H, t, $J=7.0$ Hz, CH_3CH_2O); 1.15 (3 H, d, $J=7.1$ Hz, CH_3CH); 1.19 (3 H, d, $J=7.1$ Hz, CH_3CH); 2.38 (3 H, s, CH_3Ph); 3.27 (1 H, m, $(CH_3)_2CH$); 3.52-4.19 (4 H, m, CH_3CH_2O); 7.12 (1 H, dd, $J=11.1, 41.2$ Hz, $CH=$); 7.25 and 7.57 (4 H, A_2B_2 , arom.); ^{13}C NMR (50. Hz, $CDCl_3$): 16.0 (d, $J=6.8$ Hz); 21.3; 21.81 (d, $J=9.1$ Hz); 29.7 (d, $J=6.5$ Hz); 30.8; 62.1; 129.5; 140.7; 156.1 (d, $J=8.0$ Hz); HRMS (CI): M^+ , found 232.0963. $C_{16}H_{26}O_4PS$ requires 345.1289.

(-)-Z-(α -Diethoxyphosphoryl- β -isopropyl)vinyl p-tolyl sulfoxide (1e)

$[\alpha]_D^{25} -11$ (c, 1.3, acetone); oil; IR (Nujol): 2965, 2928, 1251, 1046 cm^{-1} ; ^{31}P NMR: 12.6 ppm; 1H NMR ($CDCl_3$): 1.05 (3 H, t, $J=7.1$ Hz, CH_3CH_2OP); 1.07 (3 H, d, $J=6.5$ Hz, CH_3CH_2OP); 1.16 (3 H, d, $J=6.5$ Hz, CH_3CH); 1.35 (3 H, t, $J=7.0$ Hz, CH_3CH); 2.42 (3 H, s, CH_3Ph); 3.52 (1 H, m, Me_2CH); 3.54-4.24 (4 H, m, CH_3CH_2OP); 7.07 (1 H, dd, $J=10.6, 21.5$ Hz, $CH=$); ^{13}C NMR (50. Hz, $CDCl_3$): 15.8 (d, $J=6.8$ Hz); 18.4; 21.6 (d, $J=8.9$ Hz); 29.8

(d, $J=6.3$ Hz); 30.6; 62.1; 125.9; 126.9; 128.0; 144.4; 165.5 (d, $J=8.0$ Hz); HRMS (CI): M^+ , found 345.1284. $C_{16}H_{26}O_4PS$ requires 345.1289.

(+)-1-Diethoxyphosphoryl-1-p-tolylsulfinyl-2,2-dimethylcyclopropane (6b).

$[\alpha]_D^{+23}$ (c, 0.1, acetone); oil; IR (Nujol): 2981, 1251, 1023, 702 cm^{-1} ; ^{31}P NMR: 21.6 ppm; 1H NMR ($CDCl_3$): 0.84 (3 H, t, $J=7.0$ Hz, CH_3CH_2O); 1.34 (3 H, t, $J=7.0$ Hz); 1.48 (3 H, s, CH_3C); 1.63 (3 H, s, CH_3C); 1.77 (1 H, m, $-HCH-$); 1.99 (1 H, dd, $J=5.3, 16.5$ Hz, $-HCH-$); 2.42 (3 H, s, CH_3Ph); 3.45 (1 H, m, CH_3HCHO); 3.68 (1 H, m, CH_3HCHO); 4.15 (2 H, m, CH_3CH_2O); 7.28 and 7.47 (4 H, A_2B_2 , aromatic); 1H MNR (C_6H_6): 0.60 (3 H, t, $J=7.0$ Hz, CH_3CH_2O); 1.26 (3 H, s, CH_3C); 1.27 (3 H, t, $J=7.0$ Hz, CH_3CH_2O); 1.49 (3 H, s, CH_3C); 1.58 (1 H, dd, $J=5.3, 8.9$ Hz, HCH); 2.03 (3 H, s, CH_3Ph); 2.13 (1 H, dd, $J=5.3, 1.3$ Hz, HCH); 3.30 (1 H, m, CH_3CHHO); 3.57 (1 H, m, CH_3CHHO); 4.28 (1 H, m, CH_3CHHO); 4.52 (1 H, m, CH_3CHHO); 6.96 and 7.26 (4 H, A_2B_2 , aromatic); HRMS (CI): M^+ , found 345.1276. $C_{16}H_{26}O_4PS$ requires 345.12869.

Lithium chloride promoted decomposition of pyrazoline (2e) in methanol.

E,Z (α -Diethoxyphosphoryl- β -isopropyl)vinyl p-tolyl sulfoxides (1e).

Pyrazoline **2e** (0.37g, 1 mmol) was dissolved in 2 ml of THF and LiCl (~0.02 g) was added. After 15 min. 5 ml of methanol was added and the mixture was stirred for 1 hour. The reaction was then quenched with water and extracted with chloroform. Evaporation of solvent afforded *E* and *Z* sulfoxides **1e** in a 1:1.5 ratio (^{31}P NMR assay).

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