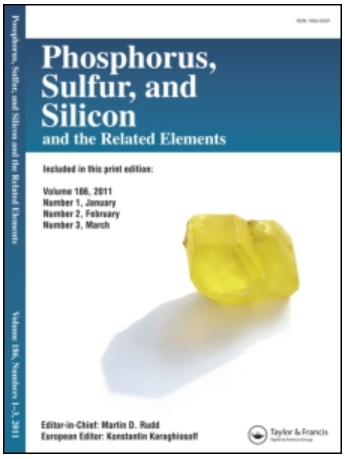

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REACTION OF CYCLIC AMINO PHOSPHONIUM SALTS WITH α-CHLOROVINYL SULFONE

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A cyclic aza-ylide that was generated from 5- or 6-membered cyclic amino phosphonium salts **1a,b** was reacted with α-chlorovinyl sulfone **3** in the presence of sodium hydride to give adducts **4a,b** via the Michael addition followed by dehydrochlorination. The structure and formation pathways are discussed.

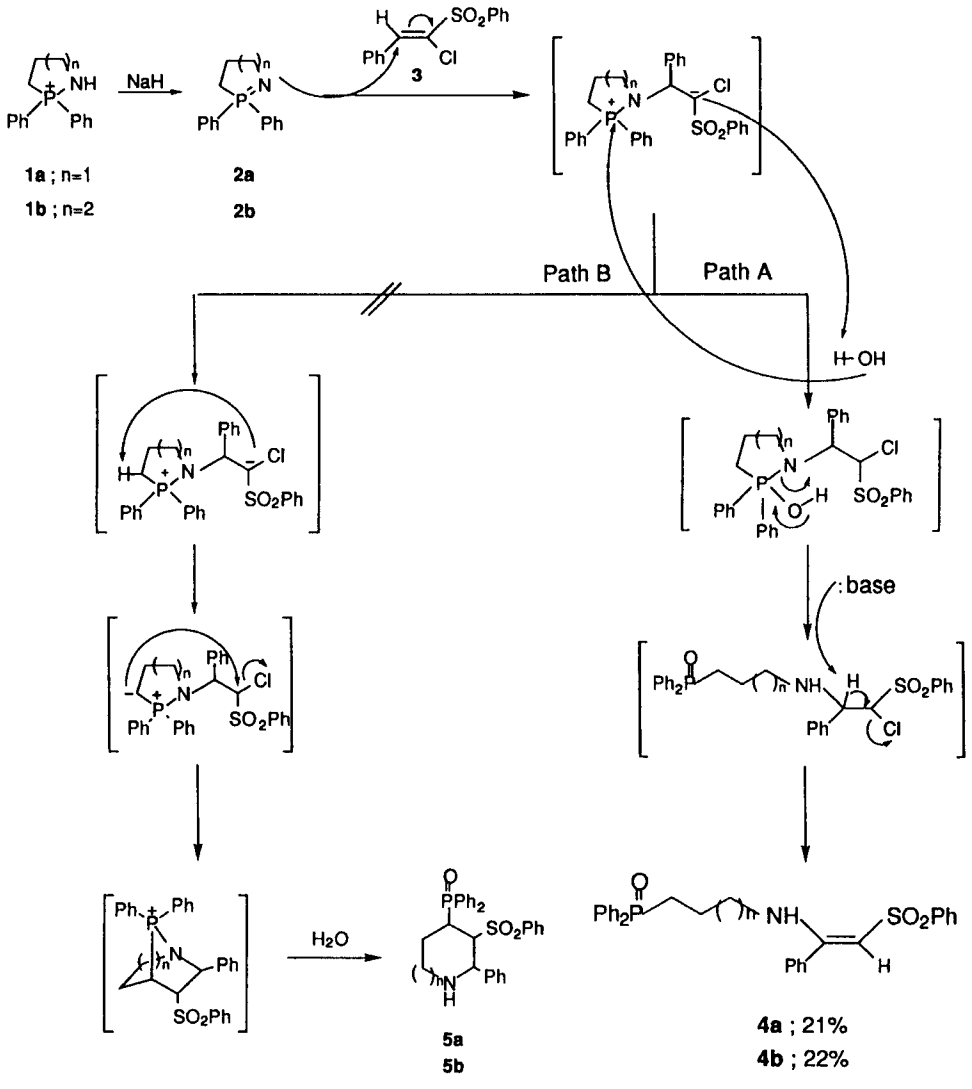
Key words: Cyclic aza-ylide; vinylsulfone; Michael addition.

The development of synthetic methodology of heterocycles using an aza-ylide is now one of the important subjects in organic chemistry. Recently, we reported the synthesis and some aza-Wittig reactions of cyclic aza-ylides,[1] Furthermore, the reaction of cyclic phosphonium ylides with α,β-unsaturated ketones produces cycloalkenyl phosphine oxides via a tandem Michael-intramolecular Wittig reaction.[2,3] On the other hand, we studied the reactivities of α-chlorovinyl sulfones **3**[4,5] some years ago, i.e., the reactions of the sulfone **3** with the sodium salt of diethyl malonate and ethyl acetoacetate did not give a simple Michael adduct, but instead gave cyclopropane derivatives and 4,5-dihydrofuran-3-carboxylates in high yield, respectively. In this paper, we report the reactions of these cyclic aza-ylides with α-chlorovinyl sulfone.

RESULTS AND DISCUSSION

The cyclic aza-ylides **2a,b** were generated from 5- or 6-membered cyclic amino phosphonium salts **1a,b** treated with NaH in THF. The reactions of the aza-ylides **2a,b** with Z-(α-chloro-β-phenylvinyl)phenyl sulfone **3** in THF solution at room temperature produced the enamine type compounds **4a,b** in 21 and 22% yields, respectively. The products **4a,b** would come from Michael addition of cyclic aza-ylides **2a,b** to vinylsulfone **3** followed by hydrolysis and dehydrochlorination as shown in the Scheme I (path A). The reaction did not give the expected tetrahydropyridine **5a** or tetrahydroazepine derivatives **5b** (path B).[2,3,5]

The structure of **4a,b** was determined from spectral data. Especially, the structure of **4a** was determined by two dimensional NMR spectra, HH-COSY, HH-NOESY, HMQC and HMBC (Figure 1). It was observed that the values of the ^{13}C chemical shifts occurred at δ 23.32, 26.57, 45.02, 92.96, 132.24, 144.59, 160.06 and others for compound **4a**. It was determined that they corresponded to the C2, C1, C3, C5, C6, C12, C4 carbon and aromatic carbon peaks, respectively. Similarly, the values of the ^{1}H chemical shifts except for the aromatic protons were observed at δ 1.65–



SCHEME I

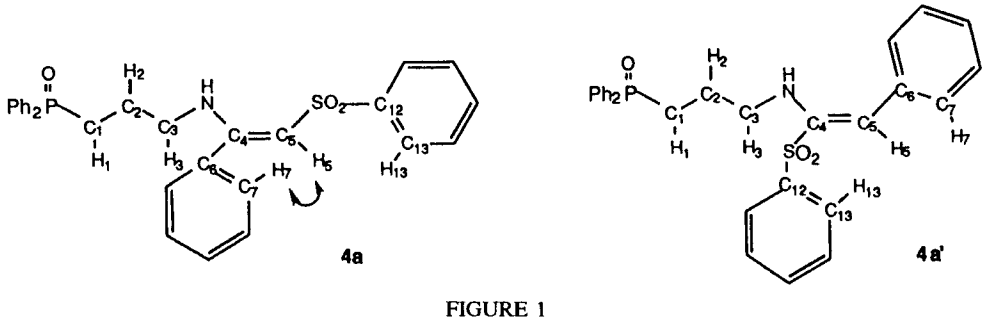


FIGURE 1

1.74, 1.95, 2.23–2.29, 3.10 and 5.28, and it was determined that they corresponded to the H2, NH, H1, H3 and H5 protons, respectively. The long range coupling peaks of H5—C6(^3J), H5—C12(^3J), H3—C4(^3J) and H7—C4(^3J) were observed from the HMBC spectrum. Also, the C5 carbon was only observed with a coupling peak to the H5 proton, not with other protons. Furthermore, it was observed NOE of H3—H7 and H5—H7 from the HH-NOESY spectrum. As a consequence, the structure of the enamine type compound can be assumed to be **4a**, not **4a'**. Because, if the structure of enamine type compound is **4a'**, the fact that the long range coupling of H5—C12(^3J) and H7—C4(^3J) are found and H7—C5(^3J) is not found can not be explained. In addition, it is considered that the large steric repulsion is between the phenyl group and phenylsulfonyl group. From the above results, it could be concluded that the structure of the enamine type compound is **4a**.

EXPERIMENTAL

1,1-[(Diphenylphosphino)propylaminophenyl]phenylsulfonylethylene (**4a**). A mixture of sodium hydride (60% dispersion in mineral oil, 90 mg, 2.25 mmol) and 1,1-diphenyl-2-azaphospholanium perchlorate **1a**[1] (680 mg, 2 mmol) in 10 ml of dry THF was stirred for 30 min at room temperature and 10 min at reflux temperature. After cooling to room temperature, Z-α-chloro-α-phenylsulfonyl-β-phenyl ethylene **3**[4] (560 mg, 2 mmol) in 8 ml of dry THF solution was added dropwise to the mixture at room temperature and stirred for 24 h at reflux temperature. The reaction mixture was then allowed to cool to room temperature. Water (20 ml) was added dropwise and dichloromethane (50 ml) was also added, then the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 50 ml). The combined organic extracts were washed with brine (3 × 50 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography on 100 g of silica gel using chloroform/ethanol (9:1) as the eluent to give pale yellow crystals which were recrystallized from ethanol. The crystals were filtered off and filtrate was concentrated under reduced pressure to give yellow crystals (210 mg 21%): mp 237–240°C; IR (neat) 3350, 3075, 2940, 1590, 1325, 1160, 1090, 755, 720, 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.26–3.21 (7H, m), 4.76 (1H, s), 7.18–8.05 (20H, m); ^{13}C-NMR ($CDCl_3$) δ 23.32 (d, $^2J_{PC}$ = 2.44 Hz), 26.57 (d, $^1J_{PC}$ = 73.24 Hz), 45.02 (d, $^2J_{PC}$ = 15.87 Hz), 92.96 (s), 160.06 (s), Ph: 125.74, 127.26, 127.69, 128.01, 128.23, 128.47, 128.77, 128.88, 128.99, 129.21, 129.83, 130.34, 130.91, 131.02, 131.73, 131.83, 132.24, 134.08, 134.98, 137.36, 144.59; MS m/z 502 (M^+ + 1); HRMS calcd for $C_{29}H_{28}O_3N_1P_1S_1$ (M^+ + 1) 502.1606, found 502.1638.

1,1-[Diphenylphosphino)butyraminophenyl]-2-phenylsulfonyl ethylene (**4b**). Prepared as above. Yellow syrup (230 mg, 22%): IR (neat) 3350, 3075, 2950, 1595, 1330, 1160, 1090, 760, 720, 685 cm^{-1}; ^{1}H-NMR ($CDCl_3$), d 1.19–3.10 (9H, m), 4.71 (1H, s), 7.17–8.06 (20H, m); ^{13}C-NMR ($CDCl_3$) d 18.77 (d, $^2J_{PC}$ = 3.60 Hz), 29.27 (d, $^1J_{PC}$ = 71.42 Hz), 32.10 (d, $^3J_{PC}$ = 13.43 Hz), 44.31 (s), 92.12 (s), 160.14 (s), Ph: 125.74, 127.72, 128.23, 128.39, 128.50, 128.75, 128.91, 129.18, 129.75, 130.34, 130.45, 130.89, 130.99, 131.18, 131.64, 131.75, 132.10, 134.05, 134.98, 137.39, 144.78; MS m/z 516 (M^+ + 1); HRMS calcd for $C_{30}H_{30}O_3N_1P_1S_1$ (M^+ + 1) 516.1763, found 516.1779.

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REFERENCES

1. T. Sakai, T. Kodama, T. Fujimoto, K. Ohta, I. Yamamoto and A. Kakehi, *J. Org. Chem.*, **59,** 7144 (1994); *J. Org. Chem.*, **60,** 1910 (1995).

2. T. Fujimoto, Y. Takeuchi, K. Kai, Y. Hotei, K. Ohta and I. Yamamoto, *J. Chem. Soc., Chem. Commun.* 1263 (1992).
3. T. Fujimoto, Y. Uchiyama, Y. Kodama, K. Ohta and I. Yamamoto. *J. Org. Chem.*, **58,** 7322 (1993).
4. I. Yamamoto, T. Sakai, S. Yamamoto, K. Ohta and K. Matsuzaki, *Synthesis*, 676 (1985).
5. I. Yamamoto, T. Sakai, S. Yamamoto, K. Ohta, K. Matsuzaki and K. Fukuyama, *J. Chem. Soc., Perkin Trans. I*, 2785 (1985).