

tereomeric β -phenylthio- α,β -disilylalkoxides **7A** and **7B** generated from the reactions of acylsilanes **2** with phenylthio(trimethylsilyl)methylithium (**3**) (Scheme 2). It is well established that α -silyl alkoxides having a β -leaving group undergoes rearrangement of silicon from carbon to oxygen (Brook rearrangement), and occurs simultaneously anti elimination of the leaving group.^{3c,d} Thus, the C to O silyl migration in the erythro intermediate **7A**, the trimethylsilyl group must some point be eclipsed with a hydrogen at the second carbon. Meanwhile the threo intermediate **7B'**, conformer of **7B** properly arranged to be anti between the trimethylsilyl and phenylthio groups, the silyl migration must be eclipsed with the much bulkier trimethylsilyl group. As previously reported,^{3d} the erythro intermediates **7A** is expected to occur Brook rearrangement-elimination much faster than **7B** to give silyl enol ethers **E-5**. In the reactions of *p*-methoxybenzoyltrimethylsilane (**4e**) and aliphatic acylsilanes **4h** and **4i** the Brook rearrangement would be somewhat retard, which caused the decrease of silyl enol ethers. Unfortunately, silyl enol ethers could not be isolated and spontaneously hydrolyzed to methyl ketones *via* α -silyl ketones during work up.⁸

It is well known base-induced elimination reactions of β -hydroxy silanes take place in highly stereospecific syn manner.⁹ Thus, **Z-4** is expected from the erythro **7A'** and **E-4** from the threo **7B'**. The threo intermediate **7B** undergoes the silyl migration and elimination process much slower than the erythro **7A**, so that threo **7B** take place Peterson reaction *via* its conformer **7B'** to afford *E*-vinylsilanes **4**. For this reason, the preferential formation of *E*-vinyl silanes over *Z* isomers was resulted.

Experimental

All reactions were carried out under the argon atmosphere. ¹H NMR spectra were recorded on a Varian EM-360A (60 MHz) or a JEOL JSX 270 (270 MHz) spectrometer using tetramethylsilane as an internal standard. ¹³C NMR spectra were obtained on a JEOL JSX 270 (58 MHz) spectrometer with CDCl₃ as solvent and internal standard. GC-MS analyses were performed with a Hewlett-Packard 5971 A spectrometer using an HP-1 column (0.2 mm ID, 15 m). Acylsilanes were prepared in good yields by the reaction of acid chlorides with LiAl(SiMe₃)₄ or LiMeAl(SiMe₃)₃ in the presence of a catalytic amount of CuCN.¹⁰

General procedure for the reaction of acylsilane with phenylthio(trimethylsilyl)methylithium. The reaction of **2a** with **3** is representative. *n*-Butyllithium (0.8 mL of a 1.5 M solution in hexane, 1.2 mmol) was added to the THF (2 mL) solution of phenylthio(trimethylsilyl)methane (235 mg, 1.20 mmol) at 0°C, and after being stirred for 1 hr, benzoyltrimethylsilane (**2a**) (206 mg, 1.15 mmol) in THF (2 mL) was added. The reaction mixture, after 20 min, was poured into 10 mL of saturated aqueous NH₄Cl, and extracted three times with 10 mL portions of ether. The combined organic extract was washed with water, dried over Na₂SO₄, concentrated. The residue was chromatographed on silica gel (hexane : ether = 3 : 1) to give **E-4a** (158 mg, 49%) and acetophenone (56 mg, 40%).

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References

1. T. Sato, T. Abe, and I. Kuwajima, *Tetrahedron Lett.*, 259 (1978).
2. I. Kuwajima and K. Matsumoto, *Tetrahedron Lett.*, 4095 (1979).
3. (a) H. J. Reich, J. J. Rusek, and R. E. Olson, *J. Am. Chem. Soc.*, **101**, 2225 (1979); (b) H. J. Reich, M. J. Kelly, T. E. Olson, and R. C. Holtan, *Tetrahedron*, **39**, 949 (1983); (c) P. F. Hudrlik, A. M. Hudrlik, and A. K. Kulkarni, *J. Am. Chem. Soc.*, **107**, 4260 (1985); (d) H. J. Reich, R. C. Holtan, and C. Bolm, *ibid.*, **112**, 5609 (1990) and references therein.
4. A. G. Brook and S. A. Fieldhouse, *J. Organomet. Chem.*, **10**, 235 (1967); A. G. Brook, *Acc. Chem. Res.*, **7**, 77 (1974); J. A. Soderquist and C. L. Anderson, *Tetrahedron Lett.*, **29**, 2425 (1988).
5. D. J. Ager, *J. Chem. Soc. Perkin Trans. 1*, 1131 (1983).
6. K.-T. Kang, C. Y. Park, and J. S. Kim, *Bull. Korean Chem. Soc.*, **13**, 48 (1992).
7. P. Magnus and D. Quagliato, *J. Org. Chem.*, **50**, 1621 (1985).
8. A silyl group in the α -position of a ketone, ester or nitrile is very susceptible to displacement. V. Chvalovsky, *Organometallic Reactions*, **3**, 191 (1972).
9. For a review, see: D. J. Ager, *Synthesis*, 384 (1984).
10. J. Kang, J. H. Lee, K. S. Kim, J. U. Jeong, and C. Pyun, *Tetrahedron Lett.*, **28**, 3261 (1987).

NMR Spectra of 4,4'-Bipyridyl, Pyrazine, and Ethylenediamine Coordinated to Undecatungstocobalto(III)silicate and -borate Anions. Identification of 1 : 1 and Dumbbell-Shaped 1 : 2 Complexes

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Some heteropolyanions contain more than two transition metal ions having replaceable water molecules.¹⁻³ We have been trying to prepare extended systems by connecting these heteropolyanions with bidentate ligands such as 4,4'-bipyridyl, pyrazine, and ethylenediamine. However, it has not been easy to characterize the reaction products. So we have turned to simpler systems containing heteropolyanions with one transition metal ion having a replaceable water molecule. For these systems one can expect to obtain 1 : 1 and dumbbell-shaped 1 : 2 complexes by replacing the water molecule with a bidentate ligand.

Recently our NMR study has shown that 4,4'-bipyridyl

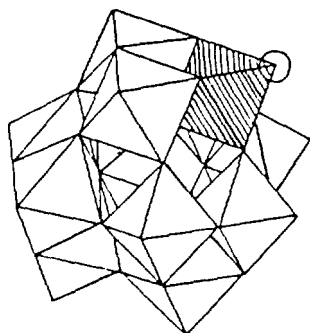


Figure 1. Polyhedral representation of the heteropolyanion $[XW_{11}Co(H_2O)O_{39}]^{n-}$ ($X = Si, B$). The circle represents the position of a water molecule which can be replaced by other ligands.

forms both 1 : 1 and 1 : 2 complexes with paramagnetic $[SiW_{11}O_{39}Co^{II}]^{6-}$ or $[SiW_{11}O_{39}Ni^{II}]^{6-}$ anions.⁴ However, kinetically inert complexes cannot be obtained for these anions, because the ligand substitution is fast for Co^{2+} and Ni^{2+} ions. In order to get stable, kinetically inert complexes, we have chosen two heteropolyanions containing a Co^{3+} ion, namely $[SiW_{11}O_{39}Co^{III}(H_2O)]^{5-}$ and $[BW_{11}O_{39}Co^{III}(H_2O)]^{6-}$ (denoted as $SiW_{11}Co$ and $BW_{11}Co$, respectively). In these heteropolyanions the Co^{3+} ion carries a water molecule which can be replaced by other ligands; see Figure 1. 4,4'-Bipyridyl, pyrazine, and ethylenediamine (denoted as bipy, pz, and en, respectively) were used to replace the water molecule and to connect two heteropolyanions as intermolecular bidentate ligands.

The UV-visible spectrum of an aqueous solution containing $BW_{11}Co$ and bipy was examined before, and it was suggested that a stable 1 : 1 complex was formed at high $[bipy] : [Co]$ ratio, and a less stable 1 : 2 complex was formed at lower ratios.⁵ Baker and Figgis stated that pyrazine formed 1 : 1 and 1 : 2 complexes with $SiW_{11}Co$.⁷ We have used NMR spectroscopy to identify 1 : 1 and 1 : 2 complexes.

Experimental

Syntheses of Compounds. $Cs_5[SiW_{11}O_{39}Co(H_2O)] \cdot nH_2O$ and $K_6[BW_{11}O_{39}Co(H_2O)] \cdot nH_2O$ were prepared according to the literature methods.^{5,6}

Bipyridyl- $[SiW_{11}O_{39}Co]^{5-}$ Complexes. 4,4'-Bipyridyl and $Cs_5[SiW_{11}O_{39}Co(H_2O)]$ in 1 : 2 mole ratio were dissolved in water, and the solution was stirred for one hour at 60°C. A precipitate was obtained by adding KCl to the solution. The 1H NMR spectrum of the precipitate dissolved in D_2O showed four doublets of equal intensity, indicating that the precipitate contained the 1 : 1 complex. Elemental analysis revealed that this precipitate also contained some heteropolyanions carrying no 4,4'-bipyridyl. This precipitate was used to measure the pH dependence of the chemical shifts for the 1 : 1 complex. The pH of solutions was adjusted by stirring in small amounts of D_2O solutions of H_2SO_4 or NaOD. The pH values of D_2O solutions are given as uncorrected pH meter readings.

Another precipitate was obtained by adding CsCl to the filtrate. The 1H NMR spectrum of the precipitate in D_2O showed two strong doublets of equal intensity, indicating that the precipitate contained the 1 : 2 complex. However, it also

showed weak signals originating from the 1 : 1 complex.

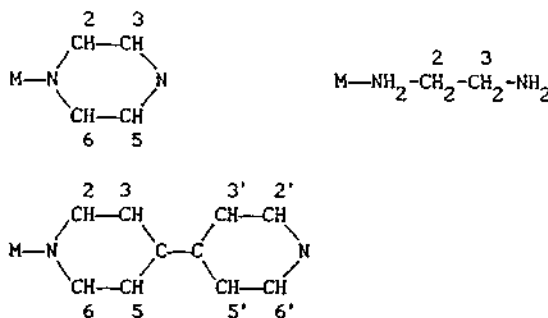
1 : 2 Bipyridyl- $[BW_{11}O_{39}Co]^{6-}$ Complex. 4,4'-Bipyridyl and $K_6[BW_{11}O_{39}Co(H_2O)] \cdot nH_2O$ in 1 : 2 mole ratio were dissolved in water, and the solution was stirred for one hour. A precipitate was obtained by saturating the solution with ether. The 1H NMR spectrum of the precipitate dissolved in D_2O showed two doublets of equal intensity, indicating that the product was a 1 : 2 complex. Anal. Calcd for $K_{12}[(BW_{11}O_{39}Co)_2(C_{10}H_8N_2)] \cdot 15H_2O$: C, 1.89; H, 0.36; N, 0.44. Found: C, 1.92; H, 0.38; N, 0.40.

Pyrazine and Ethylenediamine Complexes. Complexes of pyrazine and ethylenediamine coordinated to $SiW_{11}Co$ or $BW_{11}Co$ were prepared using procedures similar to those described above for the 4,4'-bipyridyl complexes.

Measurements. 1H NMR spectra were obtained in the Fourier-transform mode with Varian spectrometers (Gemini-300 and -200) equipped with broad band, narrow-bore probes. NMR measurements were made at ambient temperature (22–25°C). The line-broadening factor used in exponential apodization was 0.1 Hz. Typical 90° pulse lengths were 10 μs , the acquisition time was 2 s, and the delay time between pulses was 3 s. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid was used as an internal reference.

Results and Discussion

The following numbering system is used to designate protons of the ligands coordinated to a metal ion, M.



4,4'-Bipyridyl Complexes. The 1H NMR spectra of free 4,4'-bipyridyl, 1 : 1, and 1 : 2 bipy- $SiW_{11}Co$ complexes are shown in Figure 2. The two "doublets" at 8.86 and 8.17 ppm for the free ligand are assigned to 2-H and 3-H, respectively.⁴ Each "doublet" has some additional lines, as is expected from an AA'XX' system of the pyridyl ring. (Therefore, these are not true doublets.) The two doublets at 8.42 and 8.16 ppm for the 1 : 2 complex are assigned to 2-H and 3-H, respectively. It is noted that the 2-H lines are shifted upfield, while the 3-H lines remain unshifted on coordination of bipy to two Co^{3+} ions.

The NMR spectrum of the 1 : 1 complex exhibits four doublets of similar intensity. The spin decoupling technique was used to identify the pair of doublets originating from the same pyridyl ring. The chemical shifts of the four doublets depend on the pH of the solution, as shown in Figure 3. It is noted that one pair (denoted by 2' and 3' in Figure 3) is much more sensitive to pH than the other. The largest change in chemical shifts for this pair occurs near pH=5, which agrees with $pK_2=4.82$ of 4,4'-bipyridyl, indicating that the chemical shifts are affected by the extent of protonation

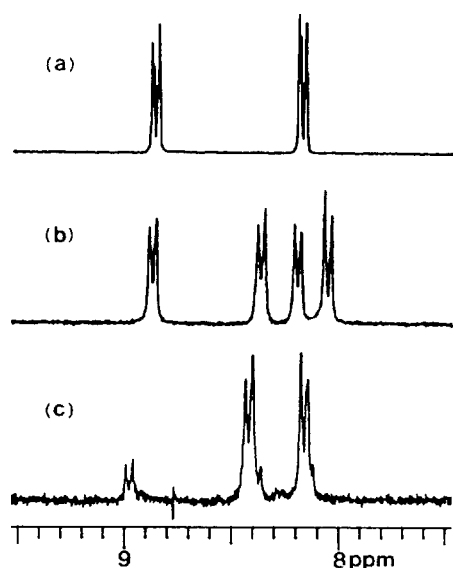


Figure 2. ^1H NMR spectra of (a) 4,4'-bipyridyl (bipy) at pH=3.8, (b) 1:1 bipy-SiW₁₁Co complex at pH=4.7, and (c) 1:2 bipy-SiW₁₁Co complex at pH=3.9 in D₂O solutions. The weak signals in (c) originate from the 1:1 complex. Chemical shifts in ppm from TMS.

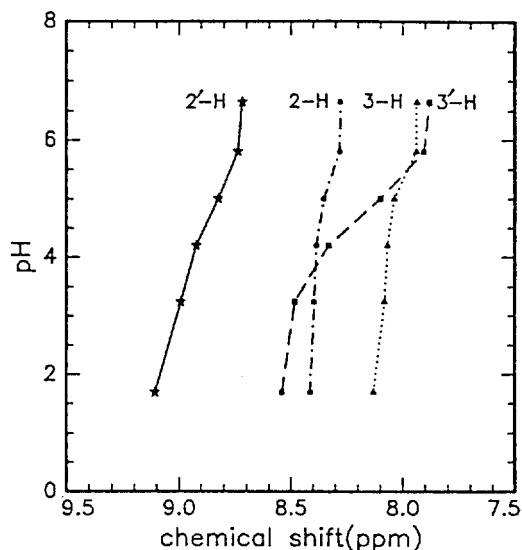


Figure 3. The pH dependence of the NMR spectrum of 1:1 bipy-SiW₁₁Co complex. Chemical shifts in ppm from TMS.

on the nitrogen atom. Therefore, the sensitive pair is assigned to the protons on the uncoordinated ring. And the low-field doublet in each pair is assigned to 2-H or 2'-H. Then the chemical shifts of the protons on the uncoordinated ring at pH=6.7 and 1.7 are similar to those of the protons on pyridine (2-H, 8.60; 3-H, 7.25 ppm) and the pyridinium ion (2-H, 9.23; 3-H, 8.50 ppm), respectively.⁸ The NMR data are listed in Table 1.

NMR spectra of the bipy-BW₁₁Co system show that formation of the 1:2 complex is more favorable than the 1:1 complex. When bipy and BW₁₁Co were reacted in 1:1 mole ratio, the amount of the 1:2 complex formed was twice as large as that of the 1:1 complex. For bipy and SiW₁₁Co

Table 1. Chemical Shifts^a of 4,4'-Bipyridyl, Pyrazine, and Ethylenediamine Coordinated to [SiW₁₁Co^{III}O₃₉]⁵⁻ or [BW₁₁Co^{III}O₃₉]⁶⁻

Nucleus	δ_{ppm}	SiW ₁₁ Co		BW ₁₁ Co	
		$\delta_{1:1}$	$\delta_{1:2}$	$\delta_{1:1}$	$\delta_{1:2}$
4,4'-Bipyridyl					
		(pH 3.8)	(pH 4.7)	(pH 3.9)	(pH 3.9) (pH 4.9)
2-H	8.86	8.36	8.42	—	8.49
3-H	8.17	8.05	8.16	8.04	8.06
2'-H	8.86	8.87	8.42	8.92	8.49
3'-H	8.17	8.19	8.16	8.24	8.06
Ethylenediamine					
		(pH 8.0)		(pH 7.6)	(pH 7.6)
2-H	3.29	—	—	2.58	2.82
3-H	3.29	—	—	3.49	2.82
Pyrazine					
		(pH 6.9)	(pH 7.0)	(pH 6.9)	(pH 6.9)
2-H	8.66	8.41	—	8.53	8.63
3-H	8.66	8.70	—	8.69	8.63

^aIn ppm relative to TMS.

under the same condition, the dominant product was the 1:1 complex. The NMR spectra of the BW₁₁Co complexes are similar to those of the SiW₁₁Co complexes. The NMR data are listed in Table 1.

Ethylenediamine Complexes. When ethylenediamine is mixed with SiW₁₁Co in water, the solution turns red, indicating that Co(III) has been reduced to Co(II). In contrast, BW₁₁Co is not reduced by ethylenediamine. The relative insensitivity of BW₁₁Co to reduction has been noted previously.⁶

The ^1H NMR spectrum of a D₂O solution containing ethylenediamine and BW₁₁Co in 1:2 mole ratio (after stirring for one hour) is shown in Figure 4(a). The amine protons, which are completely exchanged with deuterium in D₂O solution, do not contribute to the spectrum. The two triplets ($J=6.0$ Hz) at 3.49 and 2.58 ppm are attributed to the 1:1 en-BW₁₁Co complex. The triplet at 2.58 ppm, which is shifted farther than the other one from the free ligand line, is assigned to 2-H. The intensity of the singlet at 2.82 ppm increases with an increase of the ratio [BW₁₁Co]/[en]. So this line is assigned to the 1:2 complex. When the ratio [BW₁₁Co]/[en] is reduced to 0.5, this line disappears and another singlet ascribable to the free ligand is observed at 3.29 ppm; see Figure 4(b).

Pyrazine Complexes. The ^1H NMR spectrum of a D₂O solution containing pyrazine and BW₁₁Co in 1:2 mole ratio is shown in Figure 5(a). The two doublets at 8.69 and 8.53 ppm are attributed to the 1:1 complex. The high-field doublet, which is shifted farther than the low-field one, is assigned to 2-H. The intensity of the singlet at 8.63 ppm increases with an increase of the ratio [BW₁₁Co]/[pz]. So this line is assigned to the 1:2 complex. When the ratio [BW₁₁Co]/[pz] is reduced to 0.25, this line disappears and another singlet ascribable to the free ligand is observed at 8.66 ppm; see Figure 5(b). Only the 1:1 complex was identified for the pyrazine-SiW₁₁Co system.

To summarize, NMR spectra show clearly that 4,4'-bipyridyl, ethylenediamine, and pyrazine form both 1:1 and 1:2 complexes with some heteropolyanions containing a Co³⁺ ion.

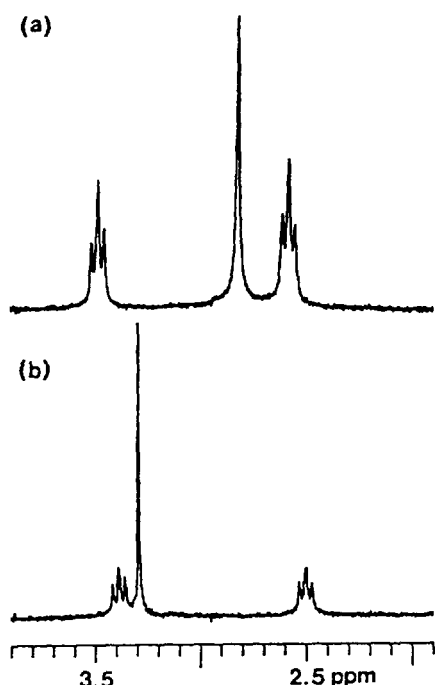


Figure 4. ^1H NMR spectra of D_2O solutions containing ethylenediamine and BW_{11}Co in (a) 1:2 mole ratio at $\text{pH}=7.6$, and (b) 2:1 mole ratio at $\text{pH}=8.0$. Chemical shifts in ppm from TMS. The singlet at 3.29 ppm is attributed to the free ligand.

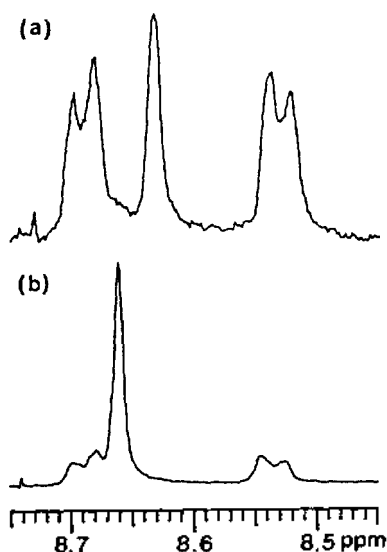


Figure 5. ^1H NMR spectrum of a D_2O solutions containing pyrazine and BW_{11}Co in (a) 1:2 and (b) 4:1 mole ratio at $\text{pH}=6.9$. Chemical shifts in ppm from TMS.

When these ligands are coordinated to the heteropolyanions, the 2-H lines are always shifted upfield. Heteropolyanions exhibit some difference in the ability to form dumbbell-shaped 1:2 ligand-heteropolyanion complexes: BW_{11}Co forms 1:2 complexes better than SiW_{11}Co does. These bidentate ligands may be useful in preparing extended systems from appropriate cobalt complexes.

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References

1. T. J. R. Weakley, H. T. Evans, Jr., J. S. Showell, G. F. Tourné, and C. M. Tourné, *J. Chem. Soc., Chem. Commun.*, 139 (1973).
2. R. G. Finke, M. Droege, J. R. Hutchinson, and O. Gansow, *J. Amer. Chem. Soc.*, **103**, 1587 (1981).
3. W. H. Knoch, P. J. Domaille, and R. L. Harlow, *Inorg. Chem.*, **25**, 1577 (1986).
4. M. Ko, G. I. Rhyu, and H. So, *Bull. Korean Chem. Soc.*, **14**, 519 (1993).
5. T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2935 (1967).
6. T. J. R. Weakley, *J. Chem. Soc., Dalton*, 341 (1973).
7. L. C. W. Baker and J. S. Figgis, *J. Amer. Chem. Soc.*, **92**, 3794 (1970).
8. E. Pretsch, J. Seibl, W. Simon, and T. Clerc, *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd Ed., Springer-Verlag, Berlin, 1989, p. H275.

A Convenient Synthesis of *N*-Alkyl-*N'*-(1-carboalkoxyalkyl)sulfamides

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3-Oxo-1,2,5-thiadiazolidine 1,1-dioxides(3) which can be easily obtained by the cyclization of *N*-(1-carboalkoxyalkyl)sulfamides 2 under the basic condition have been found to possess some pharmacological properties.¹ Three procedures have been reported for the preparation of 2; successive reactions of chlorosulfonyl isocyanate with formic acid or benzyl alcohol followed by α -amino acid alkyl esters,² treatment of α -amino acid alkyl esters with sulfamoyl chloride,³ and ethanolysis of 3-imino-1,2,5-thiadiazolidine 1,1-dioxides.⁴ These methods are, however, very tedious and complicated.

We now wish to report a new method to prepare the unsymmetrical sulfamides 2 from 2-hydroxyphenyl *N*-alkylsulfamates 1 which are easily obtainable from catechol sulfate and alkylamines by DuBois' procedure.⁵ Reaction of sulfamates 1 with various α -amino acid alkyl esters in the presence of *N,N*-dimethylaminopyridine (DMAP) in refluxing dioxane afforded the unsymmetrical sulfamides 2 in excellent to good yields. When DMAP was absent, the yield was quite low. This route thus represents a very convenient and general method to prepare unsymmetrical *N*-alkyl-*N'*-arylsulfamides which are valuable key intermediates for many heterocycles