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Unexpected alkoxyl migration in the reaction of silyl ketene acetals with *p*-toluenesulfonyl azide

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Abstract—The reaction of *p*-toluenesulfonyl azides with several silyl ketene acetals has been investigated. 1-Trimethylsilyloxy-ethylene reacted with TsN_3 to give a good yield of *N*-*p*-toluenesulfonyl substituted glycinates exclusively. However, during the reaction of 1-trimethylsilyloxy-propene with TsN_3, an unexpected alkoxyl migration occurred to give *N*-acylsulfonyl amides; other products, *N*-*p*-toluenesulfonyl substituted aziridines were also obtained. In the case of dialkyl substituted silyl ketene acetals, three products were formed, i.e. aziridines, α-amino esters, and *N*-acylsulfonyl amides. The mechanism for the alkoxyl migration was discussed. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The use of enolsilanes such as silyl enol ethers and silyl ketene acetals as enolates towards electrophiles has often been exploited in organic synthesis.[1] For instance, the Mukaiyama aldol reaction is one of the most powerful tools for the construction of new C–C bonds.[2] The development of efficient approaches to the synthesis of non-proteinogenic amino acids remains a topic of considerable interest.[3] In this field, some methods to effect the direct electrophilic amination of silyl ketene acetals were introduced by many research groups.[4] These frequently used electrophilic amination agents such as imines,[4a] azodicarboxylates[4a,4b] and *N*-heterocyclic compounds.[4d] Recently, Tardella et al. studied the amination of silyl ketene acetals by thermolysis (110°C) or photolysis with ethyl azidoformate, which provided a variety of *N*-ethoxylcarbonyl α-amino esters.[5] Here we wish to report the reaction of silyl ketene acetals with *p*-toluenesulfonyl azides in which an unexpected alkoxyl migration occurred.

2. Results and discussion

The silyl ketene acetals **1a** and **1b** (1-trimethylsilyloxy-ethylene) reacted with *p*-toluenesulfonyl azide **2** easily in anhydrous acetonitrile at 0°C and nitrogen evolved immediately. After stirring for 4 hours, TLC analysis indicated that the reaction had finished. The reaction afforded only one product **3**, which was readily identified by analytical and spectral data as the *N*-substituted α-amino esters (glycinates). Purification of the product was easily achieved by column chromatography or simply recrystallization (Scheme 1, Table 1).

Extension of the reaction to the dialkyl substituted silyl ketene acetal **1e** provided a mixture of three products after 72 hours stirring at room temperature. These products could be separated by column chromatography. The first component, a colorless liquid, was easily identified as highly substituted aziridine **5e**. Two other compounds **3e** and **4e** were crystalline compounds. They afforded ^{1}H NMR spectra that showed slightly but nonetheless significant differences in chemical shift, except they had very different N–H shift in **3e** (5.41 ppm) and **4e** (9.10 ppm). A disparity was also evident in the absorption of the carbonyl group in the IR spectra, **3e** had 1714 cm^{-1} and **4e** had 1731 cm^{-1}. Finally, elemental analysis and mass spectra established that **3e** and **4e** were, indeed, isomeric. Fortunately, the spectra of compound **3e** matched with ethyl 2-methyl-*N*-*p*-tolylsulfonyl alaninates exactly.[6] It was evident that **3e** was an *N*-tosyl amino ester, and **4e** was a positional isomer of **3e** (Scheme 2).

The same result was observed in the reaction of disubstituted silyl ketene acetals **1f** and **1g**. The spectra, analytical and chemical data derived with **4f**,**g** were indicative of corresponding positional isomers of amino ester **3**. The structure of compound **4f** was investigated by X-ray analysis, which confirmed that compound **4f** was the ethoxy migration product, an *N*-acylsulfonamide (Fig. 1).

In this connection, it has been reported that alkoxyl migration can occur.[7] Apparently, the reaction of a silyl ketene acetal with *p*-toluenesulfonyl azide has the characteristic of

Keywords: amino esters; aziridines; migration; silyl ketene acetals; sulfonyl azides.

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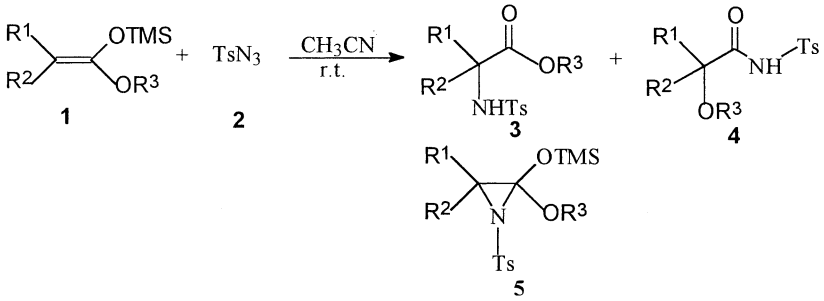


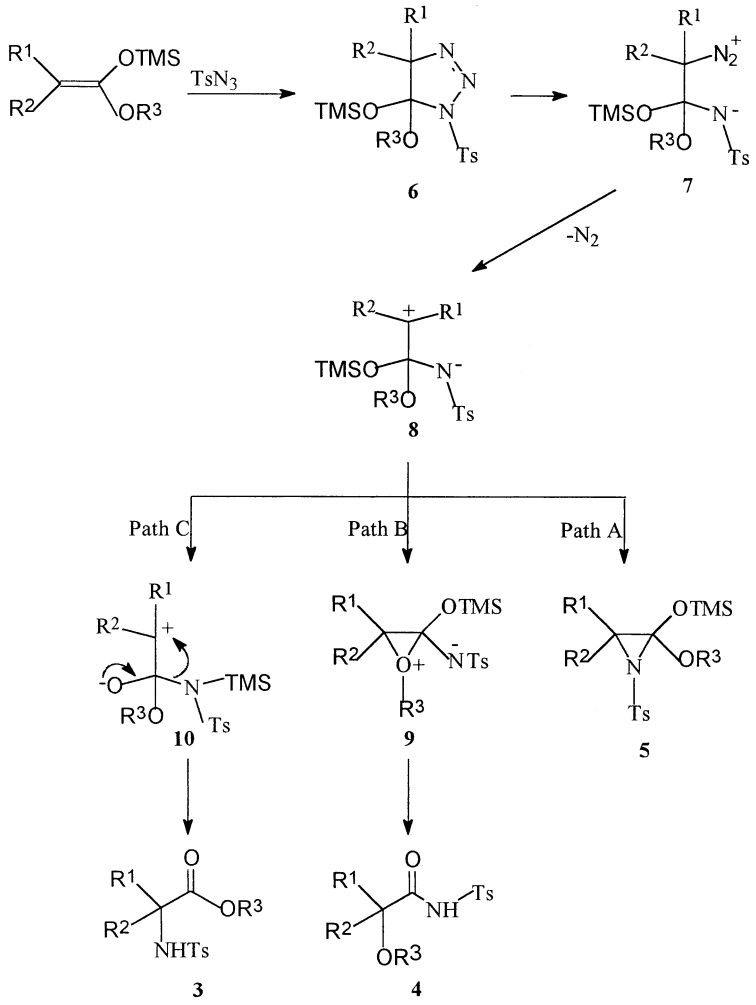
R^1, R^2=H, R^3=CH_3. (a); R^1, R^2=H, R^3=C_2H_5. (b); R^1, R^3=CH_3, R^2=H. (c);
R^1=CH_3, R^2=H, R^3=C_2H_5. (d); R^1, R^2, R^3=CH_3. (e);
R^1, R^2=CH_3, R^3=C_2H_5. (f); R^1, R^2=$(CH_2)_5$, R^3=CH_3. (g).

Scheme 1.

Table 1. The reaction results of silyl ketene acetal **1** with TsN_3

Entry	Silyl ketene acetal	Reaction time (h)	Product (%)		
			3	**4**	**5**
1	**1a**	4	76	–	–
2	**1b**	4	92	–	–
3	**1c**	4	–	55	29
4	**1d**	8	–	25	38
5	**1e**	72	48	32	17
6	**1f**	72	45	28	20
7	**1g**	72	51	27	11

a carbenium ion reaction. These considerations raised the possibility that methoxy or ethoxy migration had occurred. The formation of **4e**, **f**, **g** could be achieved, in principle, through the generation of an alkoxonium ion which subsequently underwent alkoxyl migration from C_1 to C_2. Structure assignment that derived from a mechanistic hypothesis, which consider the carboncationic characteristic of intermediates, and more importantly, which was consistent with the chemical and spectral evidence, involves neighboring alkoxyl participation during the decompose of



Scheme 2.

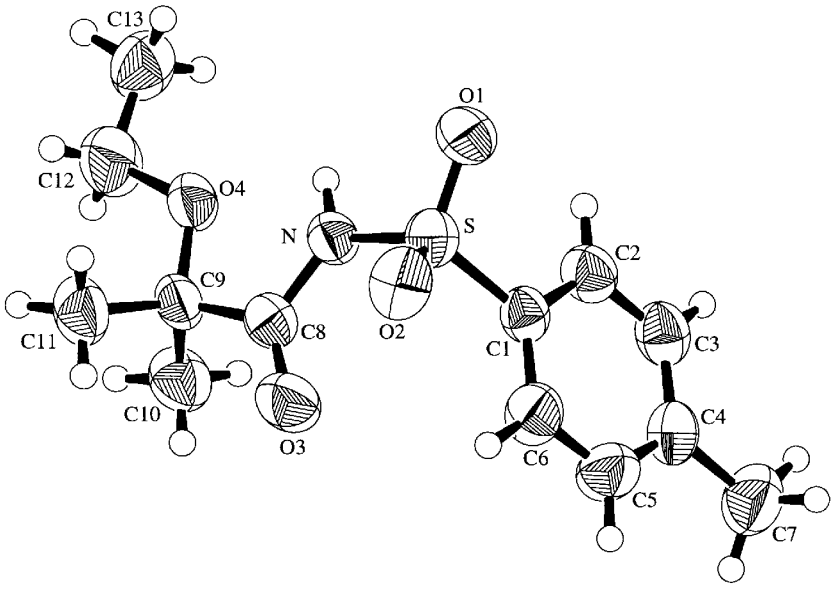


Figure 1. The molecular structure of compound **4f**

the triazoline intermediate. Migration of the alkoxyl group from C_1 to C_2 via the cyclic oxonium ion and synchronous or subsequent fromation of amides **4**, which were tentatively assigned to the formation of product **4**.

The ready occurrence of alkoxyl migration, under relatively mild conditions, was further indicated in the reaction of monoalkyl substituted silyl ketene acetal **1c**,**d** with TsN_3. However, two products were obtained in these reactions. One was identified as aziridines **5**, retaining the trimethylsilyl group. The other was readily assigned as alkoxyl migration product **4** *N*-acylsulfonamides, not the expected α-amino esters. Moreover, *N*-acylsulfonamides **4d** were one kind of herbicidal antidote.[8]

The attempted hydrolysis of aziridines **5c** and **5d** with catalytic concentrated hydrochloric acid in THF at room temperature led to the isolation of *p*-toluenesulfonyl amide $TsNH_2$ in good yields, 87% and 92%, respectively. However, the hydrolysis of aziridines **5** using SiO_2 as catalyst in moist acetonitrile at room temperature for 7 days failed. As a result, the aziridines was recovered quantitatively. From this observation, it could be concluded that the formation of product **3**, does not proceed through the decomposition of aziridine **5**. The result of the present study lend credence to the suggestion that the reaction of *p*-toluenesulfonyl azide with silyl ketene acetals in acetonitrile involves carbocation intermediates. Clearly, the cyclic oxonium ion was a reasonable precursor of *N*-acylsulfonamide product **4**.

In conclusion, during the study on the reaction of silyl ketene acetals with *p*-toluenesulfonyl azide, we have found a novel and facile method for the synthesis of *N*-acylsulfonyl amides **4** through alkoxyl migration.

3. Experimental

Mps were measured in a melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian-360L or Bruker AM-300 instruments with Me_4Si as internal standard. NMR spectra were recorded in chloroform-d unless otherwise stated. IR spectra were obtained with an Perkin–Elmer 983G spectrophotometer using KBr disks of the compounds. Low mass spectra was obtained with HP 5989a instrument. Elemental analyses were performed by this Institute. All reactions as well as column chromatography were monitored routinely with the aid of TLC. Acetonitrile was distilled from CaH_2. Reagents were purified before use. Silyl ketene acetals were prepared by the method of Ainsworth.[9] *p*-Toluenesulfonyl azides were prepared as described.[10]

3.1. General method for the reaction of silyl ketene acetal 1 with azides 2

To a solution of *p*-toluenesulfonyl azide **2** (0.271 g, 1.376 mmol, in 5 mL acetonitrile), was added **1f** (0.310 g, 1.651 mmol, 1.2 equiv) dropwise with magnetic stirring under a nitrogen atmosphere at ambient temperature. The resulting mixture was stirred until the starting reagents had disappeared (monitored by TLC). After removal of the excess solvent, the residue was chromatographed on a silica gel column, elution with light petroleum ether–ethyl acetate (10:1) gave aziridine **5f** (0.096 g, 0.269 mmol, 20%), and elution with light petroleum ether (bp 60–90°C)– ethyl acetate (5:1) gave *N*-acylsulfonyl amides **4f** (0.113 g, 0.396 mmol, 29%) and α-amino esters **3f** (0.175 g, 0.614 mmol, 45%).

3.2. General procedure for the hydrolysis of aziridine 5

To a solution of **5e** (45 mg, 0.134 mmol) in moist THF (3 mL) was added concentrated hydrochloric acid (0.05 mL) at room temperature. After the reaction completed, water (5 mL) was added. The mixture was extracted with ether (10 mL×3). The organic layer was combined and washed with brine, dried over Na_2SO_4, and

concentrated to give a residue which was subject to silica gel chromatography.

3.2.1. Methyl *N*-*p*-toluenesulfonyl glycinate (3a). Colorless crystals, mp 92–3°C, lit.[11] 92–3°C. Structural data agree with those of lit.

3.2.2. Ethyl *N*-*p*-toluenesulfonyl glycinate (3b). Colorless crystals, mp 62–4°C, lit.[6] 64–5°C. Structural data agree with those of lit.

3.2.3. 2-Methoxyl-*N*-*p*-toluenesulfonyl propanamide (4c). Colorless crystals, mp 62–4°C. ν_{max} (KBr)/cm^{-1} 3167vs, 2985m,1716s, 1429s, 1375s, 858m. $\delta_H(CDCl_3)$: 9.00 (1H, s), 7.97 (2H, d, *J*=8.5), 7.34 (2H, d, *J*=8.5), 3.72 (1H, q, *J*=6.8), 3.36 (3H, s), 2.44 (3H, s), 1.30 (3H, d, *J*=6.8). *m/z* 227 (M^++1-OCH_3, 1.84), 198 (M^+-C_3H_7O, 2.87), 155 (Ts^+, 6.29), 91 ($C_7H_7^+$, 20.77), 59 ($C_3H_7O^+$, 100.00). (Found: C, 51.17; H, 5.98; N, 5.25%. Calcd. For $C_{11}H_{15}NO_4S$ C, 51.36; H, 5.84; N, 5.45%.)

3.2.4. 1-*p*-Toluenesulfonyl-2-methoxyl-2-trimethylsilyloxy-3-methyl-aziridine (5c). Colorless liquid. ν_{max} (KBr)/cm^{-1} 2952m, 1607vs, 1315s, 1157s, 850m. $\delta_H(CDCl_3)$: 7.68 (2H, d, *J*=8.2), 7.15 (2H, d, *J*=8.2), 5.33 (1H, t, q 6.5), 3.60 (3H, s), 2.27 (3H, s), 1.34 (3H, d, *J*=6.5), 0.01 (9H, s). *m/z* (ESI): 331 (M^++2, 20.0), 330 (M^++1, 100.0). (Found: C, 51.17; H, 7.00; N, 4.17%. Calcd. For $C_{14}H_{23}NO_4S$ C, 51.06; H, 6.99; N, 4.26%.)

3.2.5. 2-Ethoxyl-*N*-*p*-toluenesulfonyl propanamide (4d). Colorless crystals, mp 90–1°C. ν_{max} (KBr)/cm^{-1} 3258vs, 2981m,1722s, 1438s, 1404vs, 822m. $\delta_H(CDCl_3)$: 8.99 (1H, br), 7.97 (2H, d, *J*=8.3), 7.31 (2H, d, 8.3), 3.59 (1H, m), 3.45 (1H, m), 2.44 (3H, s), 1.30 (3H, d–d, *J*=6.8, 0.7), 1.23 (3H, t, *J*=6.1). *m/z* 272 (M^++1, 31.16), 155 (Ts^+, 9.30), 91 ($C_7H_7^+$, 24.14), 73 (TMS^+, 100.00), 45 ($C_2H_5O^+$, 42.91). (Found: C, 53.25; H, 6.32; N, 5.11%. Calcd. For $C_{12}H_{17}NO_4S$ C, 53.14; H, 6.27; N, 5.17%.)

3.2.6. 1-*p*-Toluenesulfonyl-2-ethoxyl-2-trimethylsilyloxy-3-methyl-aziridine (5d). Colorless liquid. ν_{max} (KBr)/cm^{-1} 2958m, 1599vs, 1376m, 1071vs, 850m. $\delta_H(CDCl_3)$: 7.83 (2H, d, *J*=8.4), 7.31 (2H, d, *J*=8.4), 5.48 (1H, q, *J*=6.5), 4.19 (2H, q, *J*=7.1), 2.43 (3H, s), 1.50 (3H, d, *J*=6.5), 1.30 (3H, t, *J*=7.1), 0.16 (9H, s). *m/z* 343 (M^+, 0.26), 328 (M^+-CH_3, 10.30), 270 (M^+-TMS, 22.46), 188 (M^+-Ts, 100.00), 155 (Ts^+, 25.33), 91 ($C_7H_7^+$, 43.27), 73 (TMS^+, 71.73). (Found: C, 52.60; H, 7.43; N, 3.97%. Calcd. For $C_{15}H_{25}NO_4SSi$ C, 52.48; H, 7.29; N, 4.08%.)

3.2.7. Methyl 2-methyl-*N*-*p*-toluenesulfonyl alaninate (3e). Colorless crystals, mp 94–5°C ν_{max} (KBr)/cm^{-1} 3243vs, 2952m, 1734vs, 1431m, 1332s, 856,858m. $\delta_H(CDCl_3)$: 7.76 (2H, d, *J*=8.3), 7.27 (2H, d, *J*=8.3), 5.42 (1H, br), 3.66 (3H, s), 2.42 (3H, s), 1.47 (6H, s). *m/z* 272 (M^++1, 0.34), 256 (M^+-CH_3, 0.60), 212 (M^+-CO_2Me, 100.00), 155 (Ts^+, 54.13), 91 ($C_7H_7^+$, 81.33). (Found: C, 51.15; H, 6.27; N, 5.19%. Calcd. For $C_{12}H_{17}NO_4S$ C, 51.14; H, 6.27; N, 5.16%.)

3.2.8. 2-Methoxyl-2-methyl-*N*-*p*-toluenesulfonyl propanamide (4e). Colorless crystals, mp 107–8°C. ν_{max} (KBr)/cm^{-1} 3245vs, 2986m,1714vs, 1458m, 1413s, 859,821m. $\delta_H(CDCl_3)$: 9.14 (1H, br), 7.70 (2H, d, *J*=8.3), 7.34 (2H, d, *J*=8.3), 3.24 (3H, s), 2.44 (3H, s), 1.29 (6H, s). *m/z* 272 (M^++1, 6.05), 155 (Ts^+, 2.60), 91 ($C_7H_7^+$, 8.99), 73 (M^+-CONHTs, 100.00). (Found: C, 53.15; H, 6.27; N, 5.17%. Calcd. For $C_{12}H_{17}NO_4S$ C, 53.14; H, 6.27; N, 5.16%.)

3.2.9. 1-*p*-Toluenesulfonyl-2-methoxyl-2-trimethylsilyloxy-3,3-dimethyl-aziridine (5e). White solid, mp 84–5°C. ν_{max} (KBr)/cm^{-1} 2973m, 1627vs, 1313s, 1149vs, 843,823m. $\delta_H(CDCl_3)$: 7.86 (2H, d, *J*=8.1), 7.25 (2H, d, *J*=8.1), 3.68 (3H, s), 2.41 (3H, s), 1.64 (6H, s), 0.30 (9H, s). *m/z* 344 (M^++1, 2.13), 328 (M^+-CH_3, 25.73), 155 (Ts^+, 12.69), 131 ($C_5H_{11}O_2Si^+$, 100.00), 91 ($C_7H_7^+$, 45.44). (Found: C, 52.24; H, 7.34; N, 4.21%. Calcd. For $C_{15}H_{25}NO_4SSi$ C, 52.48; H, 7.29; N, 4.08%.)

3.2.10. Ethyl 2-methyl-*N*-*p*-toluenesulfonyl alaninate (3f). Colorless crystals, mp 100–1°C, lit.[6] 101°C. Structural data agree with those of lit.

3.2.11. 2-Ethoxyl-2-methyl-*N*-*p*-toluenesulfonyl propanamide (4f). Colorless crystals, mp 107–108°C. ν_{max} (KBr)/cm^{-1} 3275vs, 2983m,1714vs, 1465–1309vs, 1246s, 1178s. $\delta_H(CDCl_3)$: 9.10 (1H, s), 7.95 (2H, d, *J*=8.3), 7.33 (2H, d, *J*=8.3), 3.39 (2H, q, *J*=7.0), 2.43 (3H, s), 1.29 (6H, s), 1.22 (3H, t, *J*=7.0). *m/z* 286 (M^++1, 7.62), 240 (M^+-OEt, 1.86), 155 (Ts^+, 1.96), 91 ($C_7H_7^+$, 8.74), 87 ($C_5H_{11}O^+$, 100.00). (Found: C, 54.67; H, 6.76; N, 4.87%. Calcd. For $C_{13}H_{19}NO_4S$ C, 54.74; H, 6.67; N, 4.91%.)

X-Ray diffraction analysis were performed from transparent colorless crystals **4f**. The cell parameters were determined on the basis of 3162 reflections. The numbers of reflections were obtained with Mo-$K\alpha$ radiation and $2\theta_{max}$=55.0° (graphite monochromator). Measurements were made on a Rigaku AFC7R diffractometer. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. The programmes SHELXS 86 were employed. The structures were solved by direct methods and refined anisotropically by the full matrix least squares method. The weighting scheme for $R_w^2=\sum_w(|F_o|-|F_c|)^2/\sum_w F_o^2$. The positions of hydrogen atoms were calculated and included in the refinement with isotropic description. Crystal data: $C_{13}H_{19}NO_4S$, monoclinic, space group, $P2_1/n$(#14), a=8.512(1), b=10.967(4), c=15.946(4) Å, β=98.37(2)°, V=1473.9(6) $Å^3$, Z=4, Dc=1.290g. cm^{-3}, size of the crystal, 0.20×0.20×0.30 mm, reflection measured, 3162 independent intensities, 2064 observed ($F_o^2>3\sigma(F_o^2)$), R=0.041, Rw=0.055.

The atomic coordinates, equivalent isotropic distropic displacement parameters, lengths, bond angles, anisotropic displacement parameters, H-atom coordinates and isotropic displacement parameters of compound **4f** have been deposited at Cambridge Crystallographic Data Center as supplementary publication no. CCDC-149372.

3.2.12. 1-*p*-Toluenesulfonyl-2-ethoxyl-2-trimethylsilyloxy-3,3-dimethyl-aziridine (5f). White solid, mp 107–8°C. ν_{max} (KBr)/cm^{-1} 2954m, 1623vs, 1465m, 1327s, 848s. $\delta_H(CDCl_3)$: 7.83 (2H, d, *J*=8.2), 7.25 (2H, d, *J*=8.2), 4.04

(2H, q, J=7.2), 2.40 (3H, s), 1.61 (6H, s), 1.22 (3H, t, J=7.2), 0.27 (9H, s). m/z 358 (M^++1, 7.42), 357 (M^+, 6.47), 155 (Ts^+, 7.92), 131 ($C_5H_{11}O_2Si^+$, 100.00), 91 ($C_7H_7^+$, 26.11), 73 (TMS^+, 46.87). (Found: C, 54.16; H, 7.75; N, 4.06%. Calcd. For $C_{16}H_{27}NO_4SSi$ C, 53.78; H, 7.56; N, 3.92%.)

3.2.13. Methyl 1-*N*-*p*-toluenesulfonyl-amino cyclohexanecarboxylate (3g). Colorless crystals, mp 143–4°C. ν_{max} (KBr)/cm^{-1} 3290vs, 3030w, 2946s, 1736s, 1450m, 1322s, 1279, 1241vs, 1170, 1125vs, 851m, 820s. $\delta_H(CDCl_3)$: 7.76 (2H, d, J=8.3), 7.27 (2H, d, J=8.3), 5.22 (1H, br), 3.51 (3H, s), 2.43 (3H, s), 1.83 (4H, m), 1.39 (6H, m). m/z 312 (M^++1, 0.23), 266 (M^++1-OCH_3-CH_3, 14.46), 252 (M^+-CO_2Me, 100.00), 155 (Ts^+, 23.76), 91 ($C_7H_7^+$, 35.65). (Found: C, 57.73; H, 6.95; N, 4.43%. Calcd. For $C_{15}H_{21}NO_4S$ C, 57.88; H, 6.75; N, 4.50%.)

3.2.14. 2-Methoyl-*N*-*p*-toluenesulfonyl-cyclohexanecarboamide (4g). Colorless crystals, mp 137–8°C. ν_{max} (KBr)/cm^{-1} 3274vs, 2942s,1718s, 1495m, 1379vs, 1179s, 876,852m. $\delta_H(CDCl_3)$: 8.94 (1H, br), 7.93 (2H, d, J=8.3), 7.33 (2H, d, 8.3), 3.15 (3H, s), 2.42 (3H, s), 1.73–1.41 (10H, m). m/z 312 (M^++1, 1.09), 280 (M^+-OMe, 3.51), 155 (Ts^+, 1.84), 113 ($C_6H_{13}O^+$, 100.00). (Found: C, 57.77; H, 6.96; N, 4.36%. Calcd. For $C_{15}H_{21}NO_4S$ C, 57.88; H, 6.75; N, 4.50%.)

3.2.15. 1-*p*-Toluenesulfonyl-2-methoxyl-2-trimethylsilyloxy-1-azaspiro[2,5]octane (5g). Colorless liquid. ν_{max} (KBr)/cm^{-1} 2934m, 1616s, 1449m, 1319m, 846m. $\delta_H(CDCl_3)$: 7.84 (2H, d, J=8.1), 7.28 (2H, d, J=8.1), 3.95 (3H, s), 2.42 (3H, s), 2.09 (2H, m), 1.84 (2H, m), 1.57–1.54 (6H, m). m/z 384 (M^++1, 0.98), 368 (M^+-CH_3, 8.84), 171 (M^+-Ts-C_4H_9, 100.00), 155 (Ts^+, 7.29), 91 ($C_7H_7^+$, 19.27), 73 (TMS^+, 28.18). (Found: C, 56.48; H, 7.49; N, 3.71%. Calcd. For $C_{18}H_{29}NO_4SSi$ C, 56.40; H, 7.57; N, 3.66%.)

Acknowledgements

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