SYNTHESIS AND PROPERTIES OF 1-ARYLSULFONYL AMINOPROPYL SILATRANES

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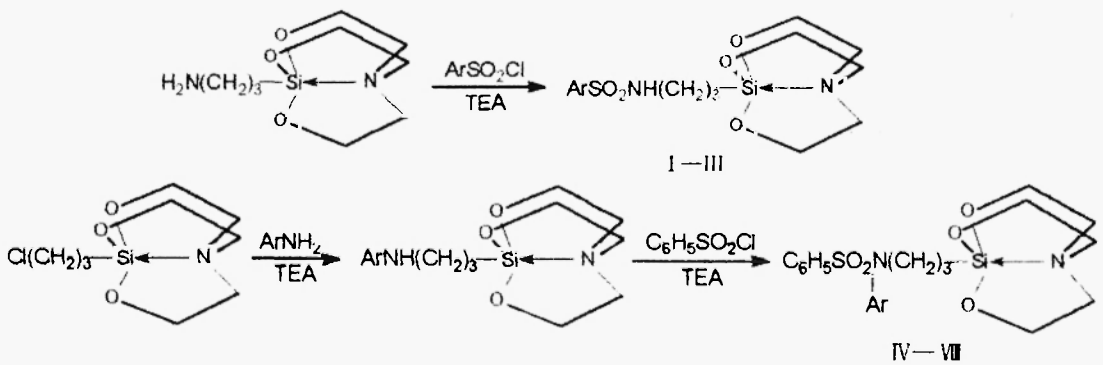
Abstract: 1-N-arylsulfonyl aminopropyl silatranes (Ⅰ-Ⅷ) were synthesized by the reaction of 1-aminopropylsilatrane and/or 1-N-phenylaminopropylsilatrane with aryl sulfonyl chlorides in the presence of triethylamine. IR, 1HNMR, MS and elemental analysis identified their structures. The antibacterial activities of these compounds were carried out and the result showed they were activities against staphyloccus aureus.

Key words: silatranes, arylsulfonamides, antibacterial activity

INTRUDUCTION

Silatranes, 1-substituted-5-aza-2, 8, 9-trioxa-1-silabicyclo [3, 3, 3]-undecanes, are cyclic nitrogen-containing organosilicon compounds which have specific structures and marvelous properties, the most important characteristic is they have obvious physiological activity and their activities greatly related to the substituted groups on silicon atom[1]. It was known sulphonic acid amides were compounds with outstanding biological activities and widely used as medicine and agricultural chemicals[2]. According to the depending of the activity on structures, eight arylsulfonyl aminopropyl silatranes (Ⅰ-Ⅷ) were synthesized by the functional group exchange on silicon atom, their structures were characterized by elemental analysis, IR, ^{1}HNMR and MS measurements. The antibacterial activity of the target compounds was determined and the result showed they were efficient against staphylococcus aureus.



Ⅰ—Ⅲ

Ⅳ—Ⅷ

Ⅰ: Ar=C_6H_5; Ⅱ: Ar=4-MeC_6H_4; Ⅲ: Ar=4-$NO_2C_6H_4$; Ⅳ: Ar=C_6H_5,
Ⅴ: Ar=4-ClC_6H_4, Ⅵ: Ar=4-MeC_6H_4; Ⅶ: Ar=4-$MeOC_6H_4$; Ⅷ: Ar=4-$EtOC_6H_4$

RESULTS AND DISCUSSIONS

The synthesis was carried out in two different ways, one is the reaction of aminopropyl silatrane with arylsulfonyl chlorides (for Ⅰ-Ⅲ), another is the reaction of chlorpropyl silatrane and arylamine to

form N-aryl aminopropyl silatrane which then react with substituted aryl sulfonyl chlorides (for Ⅳ-Ⅷ). It was found the reaction hard to take place when electron-withdrawing substituents on the aromatic rings, because the electron density on nitrogen atom was reduced and the nucleophility of aromatic amine was weakened, the fact was consist with the theoretical expections[3]. The reaction results and some experimental data were shown in Table 1.

Table 1 Some experimental data of the compounds

Compd.	Yield	m.p.	Elemental anal. (%, cald.)		
	%	℃	C	H	N
Ⅰ	51	146-147	48.50 (49.39)	6.16 (6.45)	7.65 (7.53)
Ⅱ	53	140-141	49.18 (49.74)	7.34 (6.74)	7.15 (7.25)
Ⅲ	23	138-140	42.96 (43.16)	5.65 (5.52)	9.85 (9.67)
Ⅳ	47	166-168	57.34 (57.14)	6.35 (6.49)	7.14 (7.25)
Ⅴ	48	190-193	52.95 (53.17)	5.91 (5.84)	6.44 (6.87)
Ⅵ	49	184-186	57.78 (57.98)	6.58 (6.72)	6.03 (5.88)
Ⅶ	30	180-182	57.65 (57.38)	6.63 (6.45)	5.56 (5.38)
Ⅷ	51	184-187	55.95 (56.10)	6.72 (6.50)	5.37(5.69)

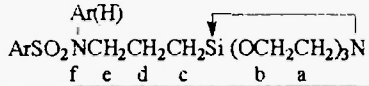
The spectra of the substituted silatrane molecules can be discussed in two parts[4]. To the first part, common to all molecules, belongs the main cyclic silatrane skeleton with an approximate symmetry of C3v. In the second, the variable part is the substituted groups bound to the silicon atom. A number of publications have appeared dealing with vibration spectra of organic silicon compound containing the Si-O-C groups[5], It is known the IR absorption spectra of compounds with Si-O-C grouping, a very intense band is present at 1100cm^{-1} and bands of variable intensity in the interval of 620-840cm^{-1}. The frequency near 1100cm^{-1} is assigned to the unsymmetric stretching vibration of Si-O-C with the stretched C-O bond prevailing, frequency of 800-840cm^{-1} are attributed to symmetric stretching vibration of Si-O bond.

A distinguishing characteristic of the silatrane was the participation of the unshared nitrogen electron pair with the silicon atom achieved through its vacant 3d-orbital to form a trans-annular dipole coordinate Si←N feedback bond. This peculiar electronic trait of the silatrane molecules could be easily observed in their IR and NMR spectra.

The stretching vibrations of the normal Si-N bond emerged in the region of 920-980cm^{-1} (in silazenes) and 790-830cm^{-1} (in aminosilanes) [6], it appears from these data that the Si-N frequency is situated lower than the C-N bond. The frequency of the coordinate bond Si←N should correspondingly be even lower than that of the ordinary Si—N bond . Therefore the frequency of Si←N bond at about 585cm^{-1} in silatranes is reasonable.

The ^{1}HNMR data of the compounds are shown in Table 2. The NMR spectrum of the OCH_2CH_2N fragment in the silatrane molecules reflects the A_2X_2 system expressed in small constant values of the spin-spin interaction between OCH_2 and CH_2N protons as compared with their chemical shifts. A certain asymmetry of the two triplets is due to the fact that A_2X_2 system is not clearly expressed and tends toward A_2B_2 [7]. A comparison of the OCH_2 and $SiCH_2$ proton chemical shift in silatranes with those in triethanolamine and triethoxysilane revealed that the Si←N bond formation led to screening of the silicon atom but the nitrogen atom became unscreened .The chemical shift is consistent with the trigonal bipyramidal model that would certainly appear to involve increased electron supply at the silicon atom.

Table 2 ^{1}HNMR Data of the Compounds



Compd.	a	b	c	d	e	f	Ar-H	Others
I	2.78(t,6H)	3.75(t,6H)	0.33(t,2H)	1.58(m,2H)	2.92(t,2H)	5.65(1H)	7.5-7.6(m,5H)	
II	2.82(t,6H)	3.78(t,6H)	0.35(t,2H)	1.54(m,2H)	2.94(t,2H)	5.68(1H)	7.2-7.6(m,4H)	2.28(s,3H)
III	2.82(t,6H)	3.78(t,6H)	0.35(t,2H)	1.60(m,2H)	3.51(t,2H)	5.65(1H)	7.2-7.6(m,4H)	
IV	2.80(t,6H)	3.78(t,6H)	0.42(t,2H)	1.57(m,2H)	3.54(t,2H)		7.2-8.1(m,9H)	
V	2.80(t,6H)	3.78(t,6H)	0.42(t,2H)	1.60(m,2H)	3.52(t,2H)		6.9-7.6(m,8H)	
VI	2.82(t,6H)	3.78(t,6H)	0.40(t,2H)	1.62(m,2H)	3.50(t,2H)		7.3-7.9(m,8H)	2.6(s,3H)
VII	2.82(t,6H)	3.78(t,6H)	0.40(t,2H)	1.62(m,2H)	3.52(t,2H)		7.1-7.9(m,8H)	3.76(s,3H)
VIII	2.78(t,6H)	3.70(t,6H)	0.35(t,2H)	1.60(m,2H)	3.51(t,2H)		7.2-7.9(m,8H)	3.9(q,2H), 1.2(t,3H)

The mass spectroscopy of the compound V was made under electron impact condition and the relevant molecular ion peak appeared, the base peak with m/e=174 was related to a fragment removing the side substituent from silicon, which was nearly the base peak for all silatranes[8], it showed that the silatrane ring was very stable.

The minimal inhibition concentration (MIC) and minimal bactericide concentration (MBC) of the title compounds against pasakii and staphylococcus were determined. Their bactericidal action was found not efficient related to the corresponding arylaminopropyl analogues[9]. The MIC and MBC for compound V were 100μl/L and 200μl/L respectively, At the concentration of MBC, it could kill the fungi completely in ten minutes. The compounds with alkyl or alkoxyl phenyl substituted on nitrogen atom did not shown remarkable bactericidal activity.

EXPERIMENTAL

IR were recorded on a PE-983 spectrophotometer (KBr pellets), ^{1}HNMR were obtained in $CDCl_3$ using TMS as an internal standard on a Varian Associates EM-360 spectrometer, MS were made on a HP5988A mass spectrometer. Elemental analyses were performed on a PE-2400 automatic meter; Melting Points were determined with an X4-Meltler and uncorrected.

Chloropropyl silatrane and aminopropyl silatrane were prepared by the esterification of triethanolamine and triethoxysilanes[10]. Arylaminopropyl silatrane was synthesized by the method described in [9]

Synthesis of I -III (method A): 2.32g(10mmol) aminopropyl silatrane dissolved in 50ml benzene, 1.01g(10mmol) triethylamine was added, put the mixture in an ice bath and a solution of 1.77g(10mmol) arylsulfonyl chloride in 20ml benzene was added dropwise, then the mixture was stirred at room temperature for 1h, suspended matter was filtrated out and Crystalline occurred from the filtrate when cooling. Recrystallization from toluene afforded 1.90g (51%) of I, white needle crystal with m.p.146-147℃. II and III were got by the same way.

Synthesis of IV-VIII (method B): 1.1g (10mmol) of triethylamine was added into the solution of 3.8g(10mmol) phenylaminopropyl silatrane dissolved in 50ml benzene, a solution of 1.91g (10mmol) of tolylsulfonyl chloride and 20ml benzene was added dropwise with stirring when cooling, then the mixture reacted at room temperature for 1h. Separated out triethylaminium chloride and the product appeared from the residual when cooling, filtrated and recrystallized with 1:1 toluene-ethanol and afforded 2.18g (47%) white crystal of IV, with m.p.166-168℃. V-VIII obtained with the same method.

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