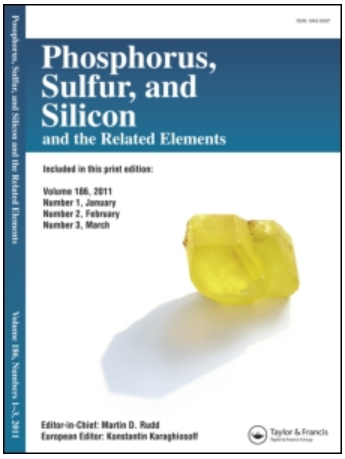

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Zhonghua Li[a]; Demei Tian[a]; Chuanfang Zhu[a]
[a] Department of Chemistry, Central China Normal University, Wuhan, China

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SYNTHESIS OF 1-ARYLAMINOPROPYL SILATRANES

ZHONGHUA LI*, DEMEI TIAN and CHUANFANG ZHU

Department of Chemistry, Central China Normal University, Wuhan 430079 China

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Ten 1-substituted arylaminopropyl silatranes (I – X) were synthesized by the reaction of aromatic amines with chloropropyl silatrane and aryl chloride with aminopropyl silatrane respectively. Their structures were identified by elemental analysis, IR, ^{1}HNMR, and MS measurement. An antimicrobial test was done and the result showed that some of them had obvious antibacterial activity.

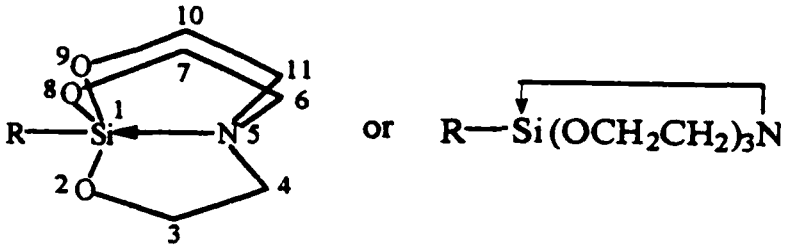
Keywords: silatranes; organosilicon compounds; biological activity

INTRODUCTION

Silatranes, 1-substituted-5-aza-2, 8, 9-trioxa-1-silabicyclo[3, 3, 3]-undecanes, are cyclic nitrogen-containing organosilicon compounds which were first patented by A.B. Finestone in 1960.[1] The next year, Frye et al[2] reported the melting points for a number of new 1-substituted silatranes and some data which supported the intramolecular transannular Si←N bond existed in silatranes. From then on, silatranes have received much attentions by numerous researchers in virtue of their special structures and properties.

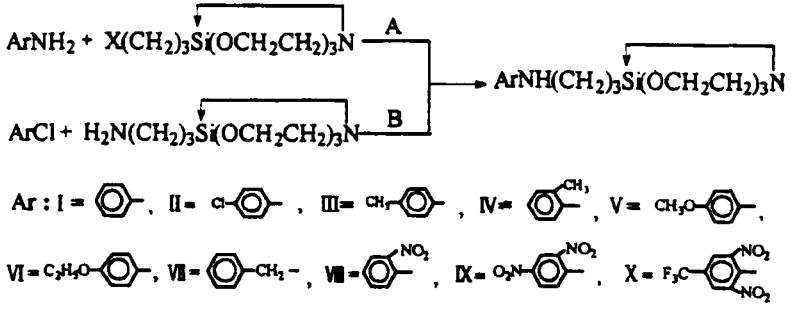
Silatranes have many specific characteristics, but the most important property may be their physiological activity and their biological activity that is greatly related to the substituents on silicon atom. 1-arylsilatranes, for example, are highly toxic while 1-alkyl and 1-alkoxysilatranes are physiologically inactive.[3] Some of the silatranes are of great interest in biology, physiology, pharmacology, medicine and agriculture.[4] In the

* Corresponding Author.



Silatrane

present paper, ten of new 1-substituted silatranes are synthesized by the reaction of aromatic amines with chloropropyl silatrane (method A) and of aryl chloride with aminopropyl silatrane (method B) respectively, and their structures are deduced from elemental analysis, IR, ^{1}HNMR and MS measurements. Bioassay results show that some of them exhibit good biological activity but some do not.



RESULTS AND DISCUSSION

The synthetic reaction consists of two relative methods. One is the reaction of aromatic amines with chloro propyl silatrane (method A), it is favorable when the electron-donating substituents are incorporated on the benzene ring. Another is the reaction of aryl chlorides with aminopropyl silatrane (method B), in this case, the electron- withdrawing groups on aromatic rings facilitate the reaction.

The reaction is often accompanied by silatrane ring cleavage and that leads further to some polymer formation.[5] In order to avoid the side reactions, the control of reaction conditions is rather important. An alkaline substance should be added to remove the acidic by-product and the temperature should be controlled to reflux smoothly, ensuring completion of the reaction. In this way the yield of 1-arylaminopropyl silatranes is acceptable. Table I and table II give the experimental results, elemental analysis and ^{1}HNMR data respectively.

TABLE I Some experimental data of the compounds

Compd.	*Yield %*	*m.p. °C*	*Elemental anal.(%, cald.)* –		
			C	*H*	*N*
I	49	141–142	58.74 (58.44)	7.44 (7.79)	9.31 (9.09)
II	50	142–144	52.34 (52.63)	6.86 (6.72)	8.32 (8.18)
III	63	130–131	60.03 (59.62)	8.06 (8.07)	8.82 (8.70)
IV	45	132–134	59.89 (59.62)	8.31 (8.07)	8.69 (8.70)
V	70	136–138	56.51 (56.80)	7.68 (7.69)	8.22 (8.26)
VI	62	146–147	57.65 (57.93)	8.13 (7.95)	7.96 (7.93)
VII	80	138–140	59.88 (59.62)	8.25 (8.07)	8.59 (8.70)
VIII	43	142–143	50.76 (50.99)	6.44 (6.52)	11.41(11.90)
IX	73	168–170	45.29 (45.23)	5.43 (5.53)	14.33(14.41)
X	82	152–154	41.13 (41.20)	4.35 (4.51)	11.96(12.02)

Silatranes are a unique class of heterocyclic pentacoordinate silicon compounds, in which transannular electron donor-acceptor interactions exist between the silicon and nitrogen atoms, the interaction is associated with a partial transfer of an unshared electron pair of the nitrogen to the vacant 3d-orbital of the silicon atom forming a Si←N bond. The hybridization of the silicon in the trigonal bipyramidal molecule is probably of the sp3d type, wherein the oxygens are coplanar with the silicon aid situated at the three equatorial positions($\angle$OsiO = 120°), while the nitrogen and R group occupy the axial positions[5]. All these features influence their spectroscopic and other physic or chemical properties. The peculiar nature of silatranes is probably in a great extent due to the specificity of their stereo-structure and their electron-density distribution.

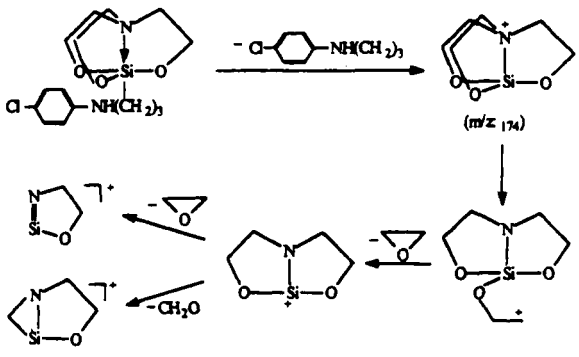
TABLE II Data of ^{1}HNMR(δ) for Ar NHCH$_2$CH$_2$CH$_2$Si (OCH$_2$CH$_2$)$_3$N (g f e d c b a)

Compd	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*Others*
I	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.72(m,2H)	3.1(t,2H)	2.9(1H)	6.5–7.3(m,5H)	
II	2.8(t,6H)	3.8(t,6H)	0.51(t,2H)	1.72(m,2H)	3.1(t,2H)	2.9(1H)	6.4–7.2(m,4H)	
III	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.8(m,2H)	3.1(t,2H)	3.5(1H)	6.4–7.3(m,4H)	2.28(s,3H)
IV	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.8(m,2H)	3.1(t,2H)	3.5(1H)	6.4–7.2(m,4H)	2.6(s,3H)
V	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.8(m,2H)	3.2(t,2H)	3.5(1H)	6.5–7.2(m,4H)	3.76(s,3H)
VI	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.8(m,2H)	3.2(t,2H)	3.5(1H)	6.5–7.3(m,4H)	3.9(q.2H), 1.2(t.3H)
VII	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.8(m,2H)	3.1(t,2H)	2.6(1H)	6.4–7.4(m,4H)	3.1(s,2H)
VIII	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.8(m,2H)	3.3(t,2H)	6.5(1H)	6.5–8.2(m,4H)	
IX	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.8(m,2H)	3.3(t,2H)	8.7(1H)	7.0–9.1(m,3H)	
×	2.8(t,6H)	3.8(t,6H)	0.48(t,2H)	1.8(m,2H)	3.5(t,2H)	8.65(1H)	6.4–8.3(m,2H)	

It is known that stretching vibrations of the normal Si-N bond are in the region of 920–980cm^{-1}(in silazenes) and 790–830cm^{-1}(in aminosilanes)[6]. It appears from these data as well as from the force constants 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 585cm^{-1} of Si←N bond in silatranes is fully acceptable.

Studies on the proton magnetic resonance spectra of 1-arylaminopropyl silatranes indicated that the protons of OCH_2 and NCH_2 showed two triplets at 3.8 and 2.8 ppm respectively, while the corresponding Protons in the starting material triethanolamine were 3.55 and 2.51 ppm [7]; the $SiCH_2$ protons resonanced at 0.48. A comparison of the OCH_2 and $SiCH_2$ proton chemical shift in silatraues with those in triethanolamine and triethoxysilane revealed that the N→Si bond formation led to screening of the silicon atom but the nitrogen atom became unscreened. The shift is consistent with the trigonal bipyramidal model which would certainly appear to involve increased electron supply at the silicon atom.

Most of the silatranes in mass spectroscopy gave their molecular ion-peaks, the stability of which was in a certain extent related to the properties of R groups [8]. The fragmentation of silatrane under electron impact in MS could take the following procedure: The first cleavage of Si-R bond to produce a highly stable ion(M-R)$^+$ with m/e =174, which in most cases was the base peak; then opening one of the ring followed by the lose of a neutral C_2H_4O to form a bicyclic fragment, which then decomposed by the lose of C_2H_4O or CH_2O •. The fragmentation sequence could be expressed as following:



An antimicrobial test was done for 1-arylaminopropyl silatranes both on standard strains of Gram-positive and Gram-negative germs clinically isolated from various infection sources. The test results showed that the compounds with chlorophenyl and nitrophenyl had significant activity. The minimal inhibition concentration (MIC), 80 μ l/L and minimal bactericide concentration (MBC), 90 μ l/L, were determined by the broth microdilution against staphylococcus aureus, the dilution range of antibacterial substance was of 10 μ l/L to 500 μ l/L, But the compounds with alkyl or alkoxyl phenyl did not have tangible antibacterial activity.

EXPERIMENTAL

IR were recorded on a PE-983 spectrophotometer, ^{1}HNMR were recorded on a Varian Associates XL-200 spectrometer, chemical shifts were reported in ppm on the δ scale relative to a tetramethylsilane internal standard, MS were recorded on a HP5988A mass spectrometer. Elemental analyses were performed on a PE-2400 automatic meter.

All reagents were redistilled. Chloropropyl silatrane and aminopropyl silatrane were prepared by the transesterization of triethanolamine and triethoxysilanes[9].

Synthesis of I-VI (method A): In a flask equipped with reflux condenser, mechanical stirrer, and addition funnel were placed 2.5g (10mmol) of chloropropyl silatrane, 1.4g (15mmol)of aniline and a little KI solid. The flask was heated to 80°C and 1.1g (10mmol) of triethylamine was added dropwise. The mixture was refluxed for 6 h, then 20ml methanol added and filtrered while the solution was hot. Crystalling product separated out from the filtrate with cooling. Recrystallization from toluene afforded 1.5g (49%) of I, white needles with m.p. 141–142°C (Lit[10] 141 ±0.2°C).

Synthesis of VII-X (method B): 1.1g (10mmol) of triethylamine was added into the solution of 2.32g (10mmol) of aminopropyl silatrane dissolved in 30ml benzene. Then a solution of 1.3g (10mmol) of benzyl chloride and 20ml of benzene was added dropwise with stirring, refluxing for 1h. Solid triethylaminium chloride was separated by filtration, The solvent was removed and the residual was added in 10 ml ethanol, filtrated and recrystallized with 1:1 toluene-ethanol and afforded 2.6g (80%) white crystal of VII, with m.p. 137–138°C.

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