# SYNTHESIS OF 1-SUBSTITUTED BENZOYL AMINOPROPYL SILATRANES AND THEIR BIOLOGICAL ACTIVITIES

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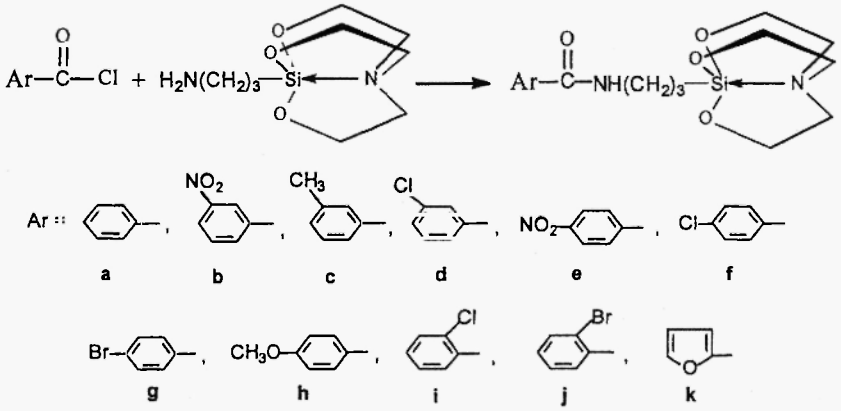
**Abstract:** Silatranes are organosilicon compounds with outstanding biological activities. Eleven substituted benzoyl aminopropyl silatranes(**a-k**) have been synthesized by the reaction of aminopropyl silatrane with various substituted benzoyl chlorides. IR, $^1$HNMR, MS and elemental analysis confirmed their structures. The antibacterial test showed that they were efficient against Fusarium and Rhizataonia.
**Key words:** silatrane, organosilicon compounds, biological activity

## Introduction

It is known that silatranes, 1-organyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,0$^{1,5}$] undecanes, have many special characteristics, but the most important property may be their outstanding biological activity and their biological activity greatly related to the substituents on silicon atom [1,2,3]. 1-Arylsilatranes, for example, are highly toxic and even used as raticide, while 1-alkyl and 1-alkoxysilatranes are nonpoisonous, some of them are of great interest in biology, physiology, pharmacology, medicine and agriculture [4,5].

In order to study the biological activities of different silatrane derivatives, we prepared eleven substituted benzoyl aminopropyl silatranes (**a-k**) by the reaction of aminopropyl silatrane and various substituted benzoyl chlorides with yield of 56 to 85%, their structures were confirmed by IR, $^1$HNMR, MS and elemental analysis. The antibacterial activity of the compounds was determined and the result showed they were efficient against Fusarium oxysporium and Rhizatonia solani.




## Results and Discussions

The reaction of substituted benzoyl chlorides and aminopropyl silatrane is nucleophilic substitution, which does not precede by the familiar SN1 and SN2 mechanisms favored by saturated systems, but by a two-step addition-elimination pathway with the first step rate determining [6]. An acyl group greatly increases the reactivity to substitution of a chloride over that of the corresponding alkyl or aryl derivative. Different substituents and their position on the benzene ring have a quite effect on the reactivity. The presence of electron withdrawing groups at ortho or para position of benzoyl chloride reduces the electron density on carbonyl carbon that is favorable for nucleophilic attack and enhances the rate of displacement of the chloride, electron-donating groups inactivate the

reaction. The reaction of p-nitrobenzoyl chloride with aminopropyl silatrane, for example, completed smoothly nearly in tens minutes, but p-methylbenzoyl chloride even need a few hours.

Silatranes were relatively more stable to hydrolyze than the corresponding derivations of triethoysilane $RSi(OC_2H_5)_3$. The presence of an Si←N transannular interaction which decrease the effective positive charge on the silicon atom and hinders nucleophilic attack by water or $OH^-$ ion. But acidic medium could cause the silatrane ring cleavage and that would lead further to some polymer formation [7]. In order to avoid the side reactions, an alkaline substance such as tertiary amine or pyramiding should be added to remove the zcidic by-product generated in the reaction and the temperature should be controlled refluxing smoothly to ensure completion of the reaction, in this way the result is satisfactory. Table 1, table 2 give the experimental results, elemental analysis, IR and $^1$HNMR data of the compounds **a-k** respectively.

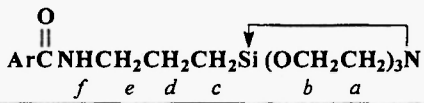
Table-1: Some physical data of the compounds (a-k)

| Compd | m.p. $^0$C | Yield % | Molecular formula (mol.wt.) | Elemental anal.(%, Calc.) C | H | N |
|---|---|---|---|---|---|---|
| **a** | 171~173 | 85 | $C_{16}H_{24}N_2O_4Si$(336) | 56.92 (57.14) | 7.30 (7.14) | 8.12 (8.33) |
| **b** | 152~153 | 83 | $C_{16}H_{23}N_3O_6Si$(381) | 50.58 (50.39) | 6.27 (6.04) | 10.80 (11.02) |
| **c** | 208~210 | 56 | $C_{17}H_{26}N_2O_4Si$(350) | 57.94 (58.29) | 7.15 (7.43) | 8.23 (8.00) |
| **d** | 211~213 | 78 | $C_{16}H_{23}ClN_2O_4Si$(370) | 51.30 (51.82) | 6.70 (6.21) | 7.93 (7.65) |
| **e** | 168~170 | 74 | $C_{16}H_{23}N_3O_6Si$(381) | 50.03 (50.39) | 6.52 (6.04) | 11.48 (11.02) |
| **f** | 200~203 | 58 | $C_{16}H_{23}ClN_2O_4Si$(370) | 51.98 (51.82) | 6.07 (6.21) | 7.89 (7.65) |
| **g** | 191~193 | 76 | $C_{16}H_{23}BrN_2O_4Si$(415) | 45.92 (46.27) | 5.08 (5.54) | 6.88 (6.75) |
| **h** | 176~178 | 62 | $C_{17}H_{26}N_2O_5Si$(366) | 55.40 (55.74) | 7.53 (7.10) | 7.88 (7.65) |
| **i** | 179~181 | 60 | $C_{16}H_{23}ClN_2O_4Si$(370) | 52.32 (51.82) | 5.84 (6.21) | 7.40 (7.65) |
| **j** | 177~178 | 70 | $C_{16}H_{23}BrN_2O_4Si$(415) | 46.01(46.27) | 5.12 (5.54) | 6.94 (6.75) |
| **k** | 173~174 | 66 | $C_{14}H_{22}N_2O_5Si$(326) | 51.79 (51.53) | 6.34 (6.75) | 8.73 (8.59) |

Formation of a trans-annular dipole coordinate Si←N feedback bond by the unshared nitrogen electron pair with vacant 3d orbitals on silicon atom was a distinguishing property of silatranes [8]. This peculiar electronic trait of the silatrane molecules could be easily observed in their IR and NMR spectra. The frequency of the coordinate bond Si←N (~585cm$^{-1}$) is lower than that of the ordinary Si—N bond in amines [9]. A comparison of the $SiCH_2$ and $OCH_2$ proton chemical shift in silatranes respectively with those in triethoxysilane and triethanolamine revealed that the Si←N bond formation led to screening of the silicon atom but the nitrogen atom became unscreened [10].The chemical shift is consistent with the trigonal bipyramidal model that would certainly appear to involve increased electron supply at the silicon atom.

A preliminary test of antibacterial activity was done for the compounds on Fusarium oxysporium, Rhizatonia solani, Gibberella zeae, Biopolaris mayalis, and Dochiorella gregaria, Table 3 gives the inhibition of the compounds to these fungi (the concentration is 50μl/L and compared with DMF as a standard). The results showed that the compounds **d, f, g, i, j, k** had remarkable activity for all the bacterial, especially for Fusarium oxysporium and Rhizatonia solani.

**Table-2: Spectral data of the compounds**




| Compd | IR(KBr)ν(cm$^{-1}$) | $^1$HNMR($CDCl_3$)δ(ppm) |
|---|---|---|
| **a** | 3365(N-H),1656(C=O),1590,1540(C=C), 1032,762(Si-O-C),718(Si-C),588(Si←N) | 0.52(t,2H,*c*),1.73(m,2H,*d*),2.80(t,6H,a), .40(m,2H,e), 3.70(t,6H,b), 6.92(t,1H,f), 7.40□7.70(m,5H,Ar-H) |
| **b** | 3340(N-H),1660(C=O),1605,1560(C=C), 1016,752(Si-O-C),721(Si-C),590(Si←N) | 0.52(t,2H,c),1.74(m,2H,d),2.82(t,6H,a), .38(m,2H,e), 3.72(t,6H,b), 6.88(t,1H,f), 7.30□7.68(m,4H,Ar-H) |
| **c** | 3385(N-H),1654(C=O),1500,1565(C=C), 1017,758(Si-O-C),728(Si-C),585(Si←N) | 0.52(t,2H,c),1.74(m,2H,d),2.32(s,3H,$CH_3$),2.78 (t,6H,a), 3.40(m,2H,e),3.70(t,6H,b), 6.90(t,1H,f), 7.52□7.72(m, 5H, Ar-H) |
| **d** | 3312(N-H),1627(C=O),1555,1520(C=C), 1016,760(Si-O-C),716(Si-C),587(Si←N) | 0.54(t,2H,c),1.74(m,2H,d),2.82(t,6H,a), .40(m,2H,e), 3.75(t,6H,b), 7.08(t,1H,f), 7.34□7.70(m,4H,Ar-H) |
| **e** | 3342(N-H),1658(C=O),1505,1570(C=C), 1062,760(Si-O-C),727(Si-C),590(Si←N) | 0.52(t,2H,c),1.72(m,2H,d),2.78(t,6H,a),3.40 (m,2H,e), 3.72(t,6H,b), 6.84(t,1H,f), 7.40□7.70(m,4H,Ar-H) |
| **f** | 3318(N-H),1652(C=O),1650,1572(C=C), 1019,758(Si-O-C),725(Si-C),585(Si←N) | 0.50(t,2H,c),1.73(m,2H,d),2.82(t,6H,a),3.40 (m,2H,e), 3.70(t,6H,b), 6.92(t,1H,f), 7.42□7.68(m,4H,Ar-H) |
| **g** | 3356(N-H),1605(C=O),1590,1529(C=C), 1013,756(Si-O-C),724(Si-C),584(Si←N) | 0.52(t,2H,c),1.72(m,2H,d),2.80(t,6H,a), .40(m,2H,e), 3.73(t,6H,b), 6.84(t,1H,f), 7.46□7.62(m,4H,Ar-H) |
| **h** | 3335(N-H),1651(C=O),1601,1565(C=C), 1020,762(Si-O-C),723(Si-C),587(Si←N) | 0.54(t,2H,c),1.72(m,2H,d),2.80(t,6H,a),3.21(s,3H, $CH_3$),3.42(m,2H,e),3.74(t,6H,b),6.82(t,1H,f), 7.30□7.60(m, 4H, Ar-H) |
| **i** | 3384(N-H),1659(C=O),1600, 1553(C=C), 1018,755(Si-O-C),726(Si-C),585(Si←N) | 0.52(t,2H,c),1.74(m,2H,d),2.78(t,6H,a),3.40 (m,2H, e),3.74(t,6H,b),6.84(t,1H,f), 7.42□7.68(m,4H,Ar-H) |
| **j** | 3360(N-H),1658(C=O),1592,1530(C=C), 1022,763(Si-O-C),722(Si-C),586(Si←N) | 0.50(t,2H,c),1.73(m,2H,d),2.77(t,6H,a), .41(m,2H,e), 3.68(t,6H,b), 6.83(t,1H,f), 7.52□7.70(m,4H,Ar-H) |
| **k** | 3360(N-H),1662(C=O),1517,1450(C=C), 1022,761(Si-O-C),724(Si-C),585(Si←N) | 0.52(t,2H,c),1.72(m,2H,d),2.80(t,6H,a), .41(m,2H,e), 3.72(t,6H,b),6.88(t,1H,f), 7.20□7.70(m, 3H,furanyl) |

Table-3: Inhibition of the compounds (a-k) for bacterials (%)

| Compd. | Fusarium | Rhizatonia | Gibberella | Botrytis | Dochiorella |
|---|---|---|---|---|---|
| **a** | 30.2 | 45.8 | 29.0 | 30.8 | 56.7 |
| **b** | 51.7 | 47.9 | 38.2 | 40.5 | 30.0 |
| **c** | 28.5 | 30.4 | 23.8 | 34.3 | 25.4 |
| **d** | 64.5 | 86.1 | 70.0 | 52.4 | 80.0 |
| **e** | 37.4 | 47.0 | 32.3 | 38.5 | 30.9 |
| **f** | 62.4 | 78.5 | 50.6 | 47.8 | 56.3 |
| **g** | 63.6 | 80.6 | 75.0 | 65.2 | 66.7 |
| **h** | 34.7 | 42.1 | 32.0 | 26.7 | 23.2 |
| **i** | 67.1 | 66.7 | 52.4 | 48.6 | 55.2 |
| **j** | 61.2 | 54.3 | 48.8 | 36.7 | 40.0 |
| **k** | 72.7 | 77.8 | 60.0 | 56.3 | 80.0 |

**Experimental**

IR were recorded on a PE-983 spectrophotometer (KBr pellets), $^1$HNMR were obtained in CDCl3 using TMS as an internal standard on a Varian Associates EM-360 spectrometer, MS were given on a HP-5988A mass spectrometer. Elemental analyses were performed on a PE-2400 automatic meter; Melting Points were determined with an X4-Meltler and uncorrected.

Aminopropyl silatrane was prepared by the transesterificaction of triethanolamine and 3-aminopropyltriethoxysilane [11]. Substituted benzoyl chlorides were prepared by the chlorination of substituted benzoic and sulfonyl chloride as the method described in [12].

Synthesis of the target compounds: A solution of 1.77g(10mmol) benzoyl chloride in 5ml chloroform was added dropwise to a mixture of 2.32g(10mmol) aminopropyl silatrane, 1.06g (10mmol) triethylamine and 10ml chloroform in a cold water bath, then the mixture was refluxed for 2h, suspended matter was separated out from the mixture, solvent was evaporated and precipitate occurred from the remainder. Recrystallization from isopropanol afforded 2.5g (85%) of **a**, with m.p. 171-173□. **b~k** were prepared by the same way.

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