# SYNTHESIS OF METHYL[N-ALKYL(ARYL)AMINOMETHYL]DIFURFURYLOXY-SILANES AND METHYL[N-ALKYL(ARYL)AMINOMETHYL]DITETRAHYDRO-FURFURYLOXYSILANES

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Transesterification of methyl[N-alky(aryl)aminomethyl]-diethoxy-silanes with furfuryl and tetrahydrofurfuryl alcohols gives four new substituted furfuryloxysilanes and three new substituted tetrahydrofurfuryloxysilanes, with a secondary or tertiary amino group in the organic group. Some of the physical properties, as well as the IR spectra of the compounds, are given.

The information in the literature regarding furfuryloxysilanes is quite sparse. Patents [1, 2] describe the preparation of tetrafurfuryloxysilane by transesterification of tetraethoxysilane with furfuryl alcohol. A patent [3] deals with preparation of tetrafurfuryloxysilane by reacting furfuryl alcohol with $SiS_2$.

Mixed orthosilicic esters derived from ethanol and furfuryl alcohol are prepared by esterifying ethoxyhalogenosilanes with dry furfuryl alcohol [4].

A number of papers [5–10] describe substituted furfuryloxysilanes prepared by reacting alkyl(aryl)-chlorosilanes with furfuryl alcohol in the presence of pyridine, and by transesterification of ethoxysilanes with furfuryl alcohol, as well as by dehydrocondensing hydrosilanes with furfuryl alcohol in the presence of sodium or $H_2PtCl_6$.

Hitherto substituted furfuryloxysilanes containing an amino group have been unknown. The present paper describes the preparation of some methyl[N-alkyl(aryl)aminomethyl]difurfuryloxysilanes and methyl[N-alkyl(aryl)aminomethyl]ditetrahydrofurfuryloxysilanes by transesterifying the corresponding methyl[N-alkyl(aryl)aminomethyl] diethoxysilanes with furfuryl and terahydrofurfuryl alcohols, the equation being

$$CH_3(RR'NCH_2)Si(OC_2H_5)_2 + 2R''OH \rightarrow$$

$$\rightarrow CH_3(RR'NCH_2)Si(OR'')_2 + 2C_2H_5OH$$

$R = C_2H_5$, $C_6H_5$; $R' = H$, $C_2H_5$; $R'' =$  $CH_2$,  $CH_2$

Transesterification by a stoichiometric quantity of R"OH was effected at 115°–145°, 70% of the theoretical amount of ethanol being distilled off. The rest of the ethanol was removed under slight vacuum (total yield of EtOH 85–90% theory). The yields of the nitrogen-containing furfuryloxysilanes, isolated by vacuum-distillation, amounted to 50–83% theoretical.

By transesterifying methyl(N-phenylaminomethyl)-diethoxysilane (VIII), methyl(N-ethyl-N-phenylaminomethyl)diethoxysilane, and methyl(N-diethylaminomethyl)diethoxysilane, the following have been synthesized for the first time: methyl(N-phenylaminomethyl)difurfuryloxysilane (I); methyl(N-phenylaminomethyl)ditetrahydrofurfuryloxysilane (III); methyl(N-ethyl-N-phenylaminomethyl)difurfuryloxysilane (IV); methyl(N-ethyl-N-phenylaminomethyl)ditetrahydrofurfuryloxysilane (V); methyl(N-diethylaminomethyl)-difurfuryloxysilane (VI); and methyl(N-diethylaminomethyl)ditetrahydrofurfuryloxysilane (VII).

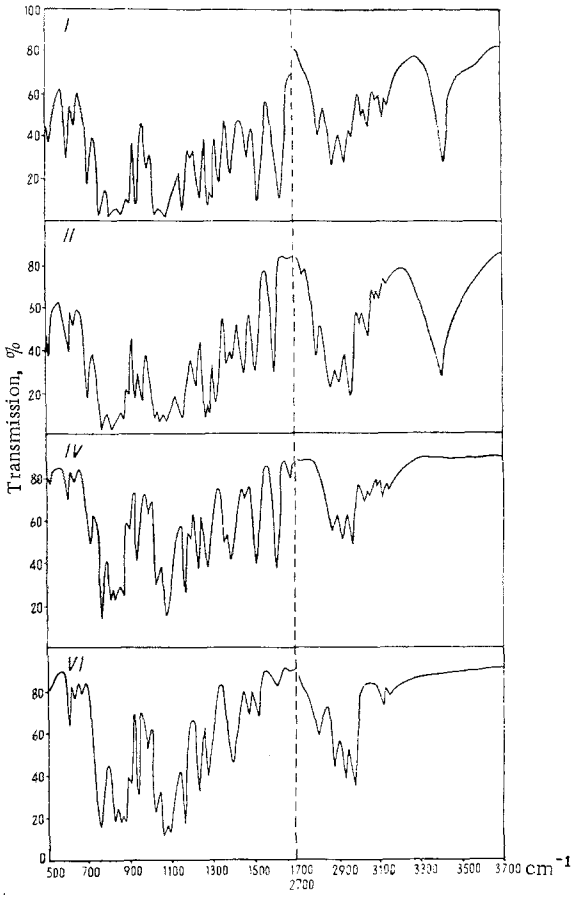



Fig. 1. IR spectra of I, II, IV, and VI.

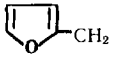
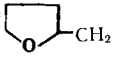
Transesterification of VIII with furfuryl alcohol led to the isolation of methyl(N-phenylaminomethyl)ethoxyfurfuryloxysilane II as a by-product. At the same time the latter was obtained in 55% yield by transesterifying VIII with furfuryl alcohol, using a 1:1 mole ratio.

The table gives the physical constants, yields, and analytical data for all the compounds synthesized. Their IR spectra are given in Figs. 1 and 2.

An attempt was made to ascribe some of the absorption bands in the spectra of the compounds syn-

Methyl[N-alkyl(aryl)aminomethyl]difurfuryloxysilanes and methyl[N-alkyl(arylaminomethyl]ditetrahydrofurfyloxysilanes

| Compound | Formula* | bp, °C (pressure mm) | $n_D^{20}$ | $d_4^{20}$ | $MR_D$ found | $MR_D$ calculated | Formula (empirical) | Found, % C | Found, % H | Found, % N | Found, % Si | Calculated, % C | Calculated, % H | Calculated, % N | Calculated, % Si | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | $CH_3(C_6H_5NHCH_2)Si(OR)_2$ | 186—188(1) | 1.5424 | 1.1619 | 93.01 | 92.50 | $C_{18}H_{21}NO_4Si$ | 62.53; 62.67 | 6.30; 6.56 | 4.10; 4.27 | 8.22; 8.27 | 62.90 | 6.12 | 4.08 | 8.16 | 50—52 |
| II | $CH_3(C_6H_5NHCH_2)Si(OR)OC_2H_5$ | 157—158(3) | 1.5248 | 1.1126 | 80.24 | 80.14 | $C_{15}H_{21}NO_3Si$ | 61.49; 61.57 | 7.22; 7.23 | 4.61; 4.79 | 9.81; 9.89 | 61.85 | 7.22 | 4.81 | 9.62 | 54—56 |
| III | $CH_3(C_6H_5NHCH_2)Si(OR')_2$ | 190—191(1) | 1.5189 | 1.1198 | 94.83 | 94.37 | $C_{18}H_{29}NO_4Si$ | 61.12; 61.18 | 8.34; 8.52 | 3.67; 3.85 | 8.27; 8.46 | 61.55 | 8.25 | 3.99 | 7.98 | 60—62 |
| IV | $CH_3[C_6H_5N(C_2H_5)CH_2]Si(OR)_2$ | 190—191(1) | 1.5439 | 1.1336 | 103.73 | 104.20 | $C_{20}H_{25}NO_4Si$ | 64.23; 64.32 | 7.01; 7.08 | 3.56; 3.63 | 7.26; 7.32 | 64.50 | 6.76 | 3.76 | 7.52 | 50—51 |
| V | $CH_3[C_6H_5N(C_2H_5)CH_2]Si(OR')_2$ | 201—202(1) | 1.5210 | 1.0895 | 106.09 | 106.50 | $C_{20}H_{33}NO_4Si$ | 62.89; 62.95 | 8.85; 8.91 | 3.78; 3.85 | 6.90; 7.06 | 63.20 | 8.76 | 3.69 | 7.39 | 60—62 |
| VI | $CH_3[(C_2H_5)_2NCH_2]Si(OR)_2$ | 125(1) | 1.4890 | 1.0980 | 84.96 | 84.59 | $C_{16}H_{25}NO_4Si$ | 59.12; 59.20 | 7.38; 7.56 | 4.10; 4.18 | 8.73; 8.76 | 59,50 | 7.75 | 4.34 | 8.68 | 78—80 |
| VII | $CH_3[(C_2H_5)_2NCH_2]Si(OR')_2$ | 132—133(1) | 1.4568 | 1.0241 | 88.07 | 87.73 | $C_{16}H_{33}NO_4Si$ | 57.69; 57.73 | 9.79; 9.87 | 3.95; 4.10 | 8.16; 8.23 | 57.90 | 9.96 | 4.22 | 8.45 | 81—83 |

* R=  ; R'=  .

thesized to particular groups and bonds, by comparing the IR spectra of I–VII and of model diethoxysilanes $RR'Si(OC_2H_5)_2$, as well as with literature data regarding spectra of furan and organosilicon compounds.

The following absorption bands are characteristic of the IR spectra of I–VII: 690–710 $cm^{-1}$ (asymmetric vibrations of the Si—C bond), 750–765, 780–830, 2875–2885 and 2930–2940 $cm^{-1}$ (valence vibrations of Me in the Si—Me group), 1200–1250 and 1270–1273 $cm^{-1}$ (deformation and respectively symmetric vibrations of the Me group in Si—Me), 1450–1470 and 1080–1110 $cm^{-1}$ (deformation vibrations of the $CH_2$ group and respectively, of Si—O—Si), and also 1280–1295 and 1310–1360 $cm^{-1}$ (C—N bond valence vibrations).

Unlike the IR spectra of model diethoxysilanes, the spectra of I–VII exhibit distinct absorption bands in the regions 875–885 and 940 $cm^{-1}$ corresponding to out-of-plane deformation vibrations of the heterocyclic ring C—H bonds, as well as in the region 985–1030 $cm^{-1}$ (symmetric vibrations of the heterocyclic ring's C—O—C group). The spectra of I–III have an absorption band in the region 3365–3415 $cm^{-1}$, corresponding to N—H valence vibrations, and absent from the IR spectra of IV–VII, containing a tertiary amino group. The IR spectra of I, II, IV, and VI have characteristic absorption bands at 605–610, 3120–3130 and 3145–3160 $cm^{-1}$, corresponding respectively to valence vibrations of the furan ring, valence vibrations of the C—H bond, and vibrations of the double bond in the —C—C—H group of the furan ring.

The IR spectra of all the alkoxysilanes containing a benzene ring, are characterized by intense absorption bonds in the regions 1510–1520 and 1600–1610 $cm^{-1}$, characteristic respectively of deformation and valence vibrations of the aromatic C=C bond. The absorption bands are lacking with VII, but appear distinctly in the IR spectrum of VI, and can be ascribed to furan ring valence vibrations, and to vibrations characteristic of the diene system of furan ring bonds. Hence the IR spectra of I, II, and IV exhibit superposition of absorption bands corresponding to deformation vibrations of benzene ring C=C bonds and furan ring valence vibrations, in the 1510–1520 $cm^{-1}$ region, while there is superposition of the absorption bands due to benzene ring C=C bond valence vibrations, and vibrations due to furan ring diene system bonds, in the region 1600–1610 $cm^{-1}$.

## EXPERIMENTAL

The starting methyl[N-alkyl(aryl)aminomethyl]-diethoxysilanes were synthesized as described in [11].

**Methyl[N-phenylaminomethyl]difurfuryloxysilane (I).** A 150 ml 3-necked flask was fitted with gas-tight stirrer, thermometer, condenser set for downward distillation, and receiver. 35.8 g (0.15 mole) VIII and 29.4 g (0.3 mole) furfuryl alcohol were added. The mixture was heated to 115°, and while the temperature was gradually raised to 145°, 9.65 g (70%) EtOH distilled off. After removing all available EtOH under a waterpump vacuum, the products were vacuum-distilled in a current of dry N. Yield of I, bp 186°–188° C (1 mm), 26.0 g (50.6%).

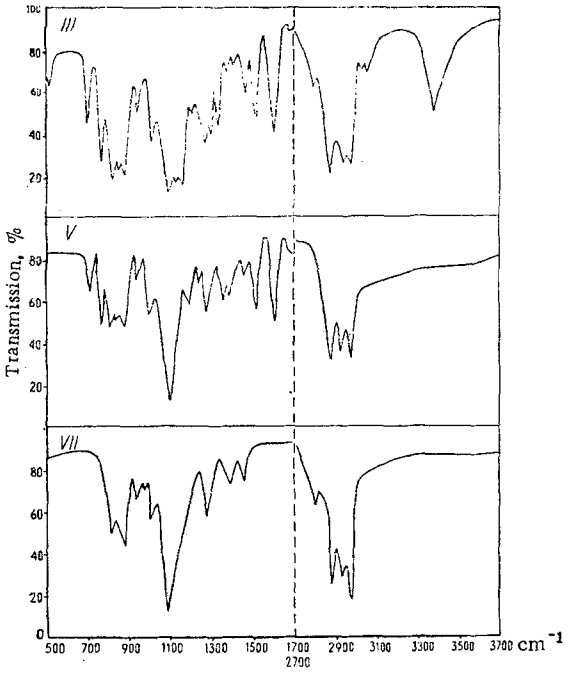



Fig. 2. IR spectra of III, I, and VII.

II, IV, and VI were prepared similarly.

**Methyl(N-phenylaminomethyl)ditetrahydrofurfuryloxysilane (III).** This was synthesized in the way described above, starting from 35.8 g (0.15 mole) VIII and 30.6 g (0.3 mole) tetrahydrofurfuryl alcohol. Yield 31.7 g (60.4%), bp 190°–191° (1 mm).

V and VII were prepared similarly.

The IR spectra of all the compounds were determined using a UR-10 2-beam spectrophotometer in the Dept. of Physical Chemistry of the Mendeleev Moscow Institute of Chemical Engineering.

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