*Chemistry of Heterocyclic Compounds, Vol. 45, No. 5, 2009*

# SYNTHESIS AND SOME TRANSFORMATIONS OF 5-(N-TOSYLAMINOMETHYL)FURFURYL ALCOHOLS

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*Preparative methods were developed for the synthesis of 5-(N-tosylaminomethyl)furfuryl alcohols, and their behavior during the action of acidic catalysts was studied. It was established that the furan ring of these compounds is stable in the presence of orthophosphoric acid in glacial acetic acid and that their hydroxyl and N-tosylaminomethyl groups are involved in the transformations.*

**Keywords:** N-tosylaminomethylfuran, furylmethanols, furfurylamine, acylation, acid catalysis, formylation.

Among the various furan derivatives furan alcohols (furylmethanols), which are widely used in fine organic synthesis, are of great interest. There are two main transformation paths for these compounds, i.e., with retention of and with opening of the furan ring.

One transformation of the first type often encountered in the literature is the self-condensation of furylmethanols, leading to the formation of symmetrical difurylmethane structures [1-4].

The reactions of furan alcohols taking place with opening of the heterocycle have found considerably wider application. Numerous papers have been devoted to intramolecular Diels–Alder reactions in which the furan acts as 1,3-diene [5, 6]. Such approaches have been used actively for the construction of the carbocyclic frameworks of natural compounds and their synthetic analogs [7, 8] and also for the formation of condensed heterocyclic systems [9].

The oxidative opening of the furan ring in 2-furylmethanols (the Akhmatovich reaction) has been used successfully in the synthesis of heterocycles [10-13]. The reaction products are derivatives of pyranone – convenient precursors for the production of sugars [14] and various biologically active compounds [15-19].

Examples of the protolytic opening of the furan ring are not so numerous, and this is probably explained by the well-known acidophobic nature of furan compounds and also by the possibility of self-condensation of furfuryl alcohols and the formation of difurylmethane structures [1, 3, 5]. With the fortuitous choice of conditions, however, the transformation provides a convenient method for the synthesis of heterocyclic systems [20].

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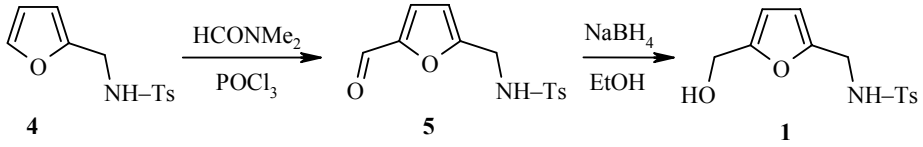
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 671-679, May, 2009. Original article submitted June 24, 2007. Revision submitted February 23, 2008.

In the present work we present the results from a study of the transformations of 5-(N-tosylaminomethyl)furfuryl alcohols **1-3** in acetic acid in the presence of orthophosphoric acid. Since furfurylamines, like furylmethanols, are widely used for the production of various nitrogen-containing heterocycles [21-24], it was of undoubted interest to investigate the mutual effect and possible competition of two nucleophilic substituents present in one furan ring.

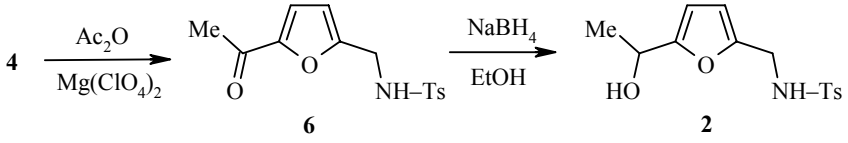
The alcohols **1-3** were synthesized on the basis of N-tosylaminomethylfuran **4**, which was obtained by the tosylation of furfurylamine.

The formylation of compound **4** and reduction of the obtained aldehyde **5** with $NaBH_4$ led to the alcohol **1**.



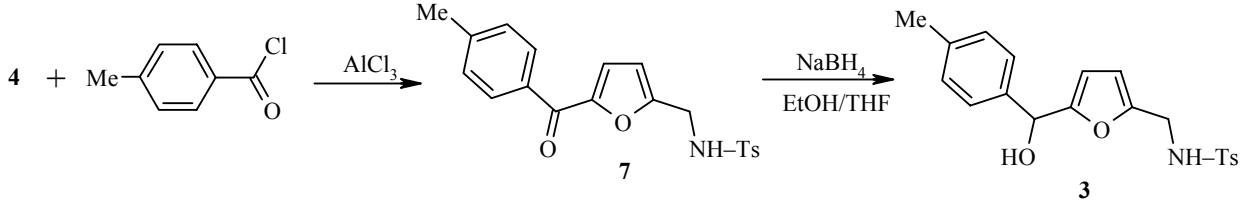

**4** **5** **1**

The secondary alcohol **2** was synthesized by the acylation of compound **4** with acetic anhydride followed by reduction of the acetyl derivative **6** with $NaBH_4$.




**6** **2**

The secondary alcohol **3** was obtained from the corresponding aryl furyl ketone **7**, which was synthesized by acylation of the tosylate **4** with *p*-toluoyl chloride in the presence of aluminium chloride (yield 57%).




**7** **3**

The composition and structure of compounds **1-3** and **5-7** agree with the results from elemental analysis and $^1H$ NMR spectra (Tables 1 and 2).

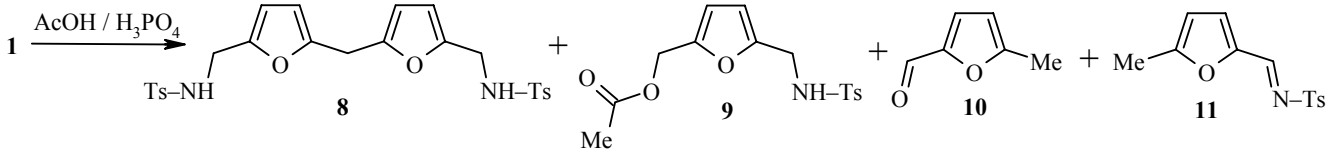
Preliminary investigation of the behavior of the alcohols **1-3** in various solvent–catalyst systems ($AcOH–H_3PO_4$, AcOH–HCl, dioxane–$HClO_4$) showed that each of the compounds **1-3** under various conditions gave a mixture of identical products and that appreciable resinification of the reaction mixture was always observed. For subsequent investigations we chose the $AcOH–H_3PO_4$ system, in which resin formation was lowest.

The treatment of furfuryl alcohol **1** with phosphoric acid in glacial acetic acid gave a mixture of products, from which compounds **8-11** were isolated by column chromatography (Tables 1 and 2).

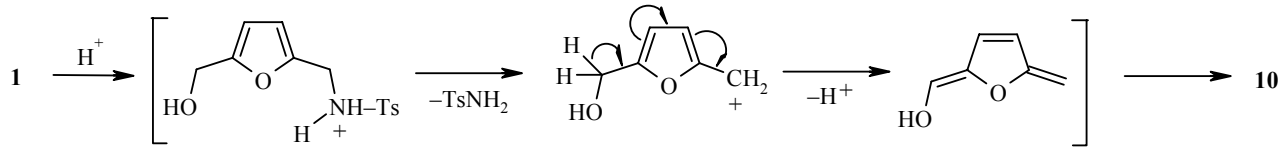
The main products of this transformation were difurylmethane **8** and the ester **9**. The formation of the difurylmethane **8** (yield 33%) is explained by the already mentioned tendency of furfuryl alcohols to undergo self-condensation during the action of a mineral acid. The fairly high yield of the ester **9** (25%) demonstrates the ease of esterification of the primary alcohol under the selected conditions.

TABLE 1. The Physicochemical Characteristics of the Synthesized Compounds

| Compound | Empirical formula | Found, % / Calculated, % | | | mp, °C | Yield, % |
|---|---|---|---|---|---|---|
| | | C | H | N | | |
| **1** | $C_{13}H_{15}NO_4S$ | 55.47 / 55.50 | 5.40 / 5.37 | 5.00 / 4.98 | 100-102 | 83 |
| **2** | $C_{14}H_{17}NO_4S$ | 56.89 / 56.93 | 5.76 / 5.80 | 4.78 / 4.74 | 113-114 | 84 |
| **3** | $C_{20}H_{21}NO_4S$ | 64.64 / 64.67 | 5.76 / 5.70 | 3.75 / 3.77 | 159-161 | 74 |
| **5** | $C_{13}H_{13}NO_4S$ | 55.92 / 55.90 | 4.71 / 4.69 | 4.97 / 5.01 | 84-86 | 84 |
| **6** | $C_{14}H_{15}NO_4S$ | 57.31 / 57.32 | 5.17 / 5.15 | 4.73 / 4.77 | 91-92 | 81 |
| **7** | $C_{20}H_{19}NO_4S$ | 65.05 / 65.02 | 5.17 / 5.18 | 3.81 / 3.79 | 137-138 | 57 |
| **8** | $C_{25}H_{26}N_2O_6S_2$ | 58.42 / 58.35 | 5.02 / 5.09 | 5.46 / 5.44 | 96-98 | 33 |
| **9** | $C_{15}H_{17}NO_5S$ | 55.67 / 55.72 | 5.32 / 5.30 | 4.29 / 4.33 | 115-116 | 25 |
| **11** | $C_{13}H_{13}NO_3S$ | 59.33 / 59.30 | 5.00 / 4.98 | 5.28 / 5.32 | 120-122 | 22 |
| **12** | $C_{14}H_{15}NO_3S$ | 60.65 / 60.63 | 5.40 / 5.45 | 5.10 / 5.05 | 148-149 | 39 |
| **15** | $C_{20}H_{19}NO_3S$ | 68.02 / 67.97 | 5.55 / 5.42 | 3.93 / 3.96 | 193-195 | 42 |




The formation of 5-methylfurfural (**10**) is obviously due to protonation at the nitrogen atom of the amide group and removal of the tosylamide molecule. Redistribution of electron density in the obtained cation leads to the ejection of a proton and rearrangement of the produced enol with restoration of the furan aromatic system. Evidence for such a mechanism is provided by the discovery of tosylamide in the reaction mixture (TLC, in comparison with an authentic sample).




Analogous transformations probably provide the basis for the formation of the imine **11**. In this case the reaction begins with protonation of the hydroxyl group of the alcohol **1**.

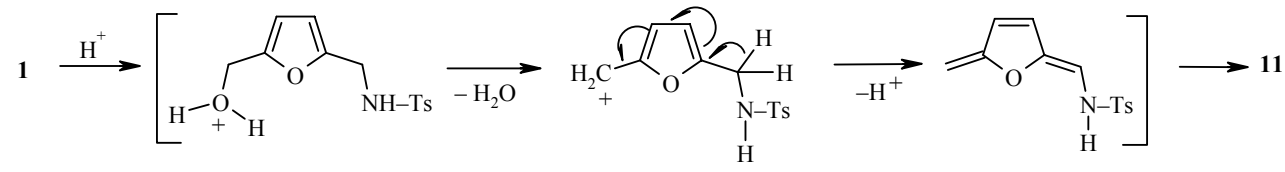


TABLE 2. The $^1$H NMR Spectra of the Synthesized Compounds

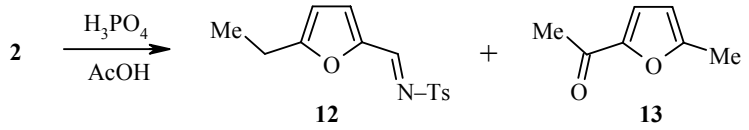
| Compound | Chemical, δ, ppm (*J*, Hz) |
|---|---|
| **1** | 2.43 (3H, s, $CH_3$*); 4.16 (2H, d, *J* = 5.5; $CH_2N$); 4.56 (2H, s, $CH_2O$); 4.92 (2H, br. s, NH, OH); 6.06 (1H, d, *J* = 3.2, H Het); 6.11 (1H, d, *J* = 3.2, H Het); 7.29 (2H, d, *J* = 7.8, H Ts); 7.73 (2H, d, *J* = 7.8, H Ts) |
| **2** | 2.22 (3H, d, *J* = 6.2, $CH_3$); 2.43 (3H, s, $CH_3$*); 4.30 (1H, br. s, CHO); 4.55 (2H, s, $CH_2N$); 4.86 (2H, br. s, NH, OH); 6.32 (1H, d, *J* = 3.2, H Het); 6.44 (1H, d, *J* = 3.2, H Het); 7.24 (2H, d, *J* = 7.8, H Ts); 7.60 (2H, d, *J* = 7.8, H Ts) |
| **3** | 2.42 (3H, s, $CH_3$*); 2.47 (3H, s, $CH_3$); 4.26 (1H, br. s, CHO); 4.53 (2H, s, $CH_2N$); 4.92 (2H, br. s, NH, OH); 6.22 (1H, d, *J* = 3.2, H Het); 6.41 (1H, d, *J* = 3.2, H Het); 7.17 (4H, m, H Tol); 7.26 (2H, d, *J* = 7.8, H Ts); 7.63 (2H, d, *J* = 7.8, H Ts) |
| **5** | 2.40 (3H, s, $CH_3$*); 4.46 (2H, s, $CH_2N$); 4.92 (1H, br. s, NH); 6.16 (1H, d, *J* = 3.2, H Het); 6.25 (1H, d, *J* = 3.2, H Het); 7.26 (2H, d, *J* = 7.8, H Ts); 7.66 (2H, d, *J* = 7.8, H Ts); 9.24 (1H, s, CH=O) |
| **6** | 2.41 (3H, s, $CH_3$*); 2.49 (3H, s, $CH_3$); 4.47 (2H, s, $CH_2N$); 4.96 (1H, br. s, NH); 6.13 (1H, d, *J* = 3.2, H Het); 6.29 (1H, d, *J* = 3.2, H Het); 7.26 (2H, d, *J* = 7.8, H Ts); 7.63 (2H, d, *J* = 7.8, H Ts) |
| **7** | 2.40 (3H, s, $CH_3$*); 2.53 (3H, s, $CH_3$); 4.51 (2H, s, $CH_2N$); 4.96 (1H, br. s, NH); 6.12 (1H, d, *J* = 3.2, H Het); 6.38 (1H, d, *J* = 3.2, H Het); 7.26–7.57 (8H, m, H Ar) |
| **8** | 2.42 (6H, s, $CH_3$*); 3.71 (2H, s, $CH_2$); 4.12 (4H, d, *J* = 5.7; $CH_2N$); 4.82 (2H, br. s, NH); 5.86 (2H, d, *J* = 3.2, H Het); 6.23 (2H, d, *J* = 3.2, H Het); 7.26 (4H, d, *J* = 7.8, H Ts); 7.71 (4H, d, *J* = 7.8, H Ts) |
| **9** | 2.07 (3H, s, $CH_3$); 2.43 (3H, s, $CH_3$*); 4.18 (2H, d, *J* = 6.0, $CH_2N$); 4.79 (1H, br. s, NH); 4.90 (2H, s, $CH_2O$); 6.08 (1H, d, *J* = 3.2, H Het); 6.23 (1H, d, *J* = 3.2, H Het); 7.28 (2H, d, *J* = 7.8, H Ts); 7.73 (2H, d, *J* = 7.8, H Ts) |
| **11** | 2.43 (6H, s, $CH_3$, $CH_3$*); 6.29 (1H, d, *J* = 3.2, H Het); 7.24 (1H, d, *J* = 3.2, H Het); 7.32 (2H, d, *J* = 8.0, H Ts); 7.87 (2H, d, *J* = 8.0, H Ts); 8.71 (1H, s, CH=N) |
| **12** | 2.18 (3H, t, *J* = 7.6, $CH_3$); 2.43 (3H, s, $CH_3$*); 2.51 (2H, q, *J* = 7.6, $CH_3C\underline{H}_2$); 6.39 (1H, d, *J* = 3.2, H Het); 6.95 (1H, d, *J* = 3.2, H Het); 7.33 (2H, d, *J* = 8.0, H Ts); 7.67 (2H, d, *J* = 8.0, H Ts); 8.79 (1H, s, CH=N) |
| **15** | 2.20 (3H, s, $CH_3$); 2.42 (3H, s, $CH_3$*); 3.60 (2H, s, $CH_2$); 6.49 (1H, d, *J* = 3.2, H Het); 6.90 (1H, d, *J* = 3.2, H Het); 7.08 (2H, d, *J* = 8.1, H Tol); 7.21 (2H, d, *J* = 8.1, H Tol); 7.33 (2H, d, *J* = 8.0, H Ts); 7.67 (2H, d, *J* = 8.0, H Ts); 8.93 (1H, s, CH=N) |

*$CH_3$ in Ts.

A similar mechanism was considered earlier to explain the formation of methylfurfural during the treatment of 2,5-dihydroxymethylfuran with an alcohol solution of HCl under the conditions of the Marckwald reaction [25].

Two products, i.e., the imine **12** and acetylsilvan **13**, were obtained with yields of 39 and 46% respectively as a result of treatment of the alcohol **2** with $H_3PO_4$ in acetic acid.

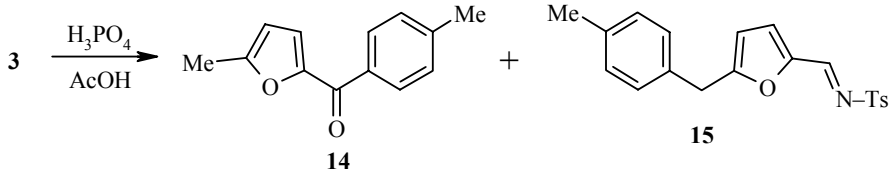
It is clear that the mechanisms of formation of compounds **12** and **13** are similar to those examined above for compounds **10** and **11**.




**12** **13**

The presence of trace quantities of a product with a difurylmethane structure in the reaction mixture was also detected by TLC (a characteristic color with bromine vapor), but it was not possible to isolate it by column chromatography.

We supposed that the reaction of the alcohol **3** with orthophosphoric acid would not lead to a derivative of difurylmethane since it had previously been established [26] that arylfurylmethanols do not form difurylmethane structures under acidic conditions. Actually, two products were obtained as a result of the reaction of the alcohol with an acidic catalyst – the ketone **14** and the imine **5** – with yields of 41 and 42% respectively. The structure of the ketone was confirmed by an alternative synthesis by the acylation of toluene with 5-methylpyromucic chloride in the presence of aluminium chloride.




The composition and structure of the products from the transformations of compounds **1**-**3** agree with the results from elemental analysis and the $^1$H NMR spectra (Table 2).

Thus, our results from study of the behavior of 5-(N-tosylaminomethyl)furfuryl alcohols indicate that the furan ring does not undergo any transformations under the selected conditions while all the transformations of the alcohols take place with the participation of the hydroxymethyl and N-tosylaminomethyl groups.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded on a Brucker AMX-400 instrument (400 MHz) in $CDCl_3$ with TMS as internal standard. Thin-layer chromatography was performed on Silufol UV-254 plates and Sorbfil (OOO "Sorbpolimer") with iodine and bromine vapor and 2,4-dinitrophenylhydrazine as developer. For column chromatography we used silica gel KSK ("Sorbpolimer") (50-100 μ).

**2-(N-Tosylaminomethyl)furan (4).** To a mixture of furfurylamine (9.7 g, 100 mmol) and pyridine (12 ml, 150 mmol) we added *p*-toluenesulfonyl chloride (28.5 g, 150 mmol). The reaction mass was kept at 30-35°C until the initial furfurylamine had disappeared (TLC, 1:2 acetone–petroleum ether) and was then poured into water. The precipitate was filtered off, dried in air, and recrystallized from 3:1 mixture of methylene chloride and hexane. We obtained 22.3 g (89%) of the product **4** in the form of colorless crystals melting at 111-112°C.

**5-(N-Tosylaminomethyl)furfural (5).** To a mixture of compound **4** (2.51 g, 10 mmol) and DMF (10 ml) with stirring and cooling in iced water we added dropwise over 30 min $POCl_3$ (2.8 ml, 30 mmol). The mixture was stirred at 40-45°C until the initial compound **4** had completely disappeared (TLC, 1:2 acetone–petroleum ether). The reaction mass was poured into iced water and neutralized carefully by the addition of dry sodium carbonate, after which it was extracted with ethyl acetate (3×20 ml). The extract was washed with sodium carbonate solution and with water and dried with sodium sulfate. Activated carbon was then added, and the suspension was filtered through a thin layer of silica gel. The filtrate was evaporated on a rotary evaporator to a quarter of its initial volume, and after crystallization (2.34 g) of the furfural **5** was obtained in the form of fine colorless needles.

**5-Acetyl-2-(N-tosylaminomethyl)furan (6).** A mixture of compound **4** (5 g, 20 mmol), acetic anhydride (15 ml), and $Mg(ClO_4)_2$ (anhydrone) (2.23 g, 10 mmol) was boiled with a reflux condenser until the initial compound **4** had disappeared. The cooled reaction mixture was then poured into iced water (200 ml) and neutralized with $NaHCO_3$. The crystalline precipitate was filtered off, washed with sodium carbonate solution and with water, dried in air, and recrystallized from a 3:1 mixture of methylene chloride and petroleum ether, and 2.37 g of the product **6** was obtained in the form of colorless crystals.

**5-(4-Methylbenzoyl)-2-(N-tosylaminomethyl)furan (7).** To a suspension of anhydrous aluminium chloride (2.0 g, 15 mmol) in dry methylene chloride (20 ml) with stirring and cooling with ice we slowly added dropwise 4-methylbenzoyl chloride (1.7 ml, 13 mmol). We then added in portions compound **4** (3.14 g, 12.5 mmol) at such a rate that the temperature of the reaction mixture did not exceed 25°C. The reaction mixture was stirred at room temperature for 4 h, after which it was carefully poured onto 50 g of crushed ice, 5-7 ml of concentrated hydrochloric acid was added, and the product was extracted with methylene chloride (5×20 ml). The extracts were washed with water, 2% sodium hydroxide solution, and again with water, and dried over sodium sulfate, and the solvent was distilled. The solid residue was dissolved in a 7:2 mixture of methylene chloride and petroleum ether, and the hot solution was passed through a layer of silica gel. The white crystals that separated after cooling were filtered off, and 2.36 g of the product **7** was obtained.

**Reduction of Compounds 5 and 6 (General Method).** To a solution of compound **5** or **6** (5 mmol) in ethanol (40 ml) we added in small portions finely divided $NaBH_4$ (0.1 g, 2.5 mmol). The reaction mass was heated to boiling. The heating was then stopped, and after 10 min 150 ml of water was added. The obtained mixture was carefully acidified to pH ~6-7 with dilute hydrochloric acid and extracted with methylene chloride (3×20 ml). The extract was dried over sodium sulfate, the solvent was evaporated on a rotary evaporator, the residue was crystallized from a 3:1 mixture of methylene chloride and petroleum ether, and **5-hydroxymethyl-2-(N-tosylaminomethyl)furan** (**1**) (1.16 g) or **5-(1-hydroxyethyl)-2-(N-tosylaminomethyl)furan** (**2**) (1.24 g) was obtained in the form of a fluffy white cotton.

**5-[Hydroxy-(4-methylphenyl)methyl]-2-(N-tosylaminomethyl)furan (3).** A mixture of compound **7** (1.85 g, 5 mmol), ethanol (5 ml), THF (20 ml), and finely divided $NaBH_4$ (0.3 g, 7.5 mmol) was boiled with a reflux condenser for 1 h and cooled, and 100 ml of water was added. The mixture was carefully acidified to pH ~6-7 with dilute hydrochloric acid and extracted with methylene chloride (3×25 ml). The extract was dried over sodium sulfate, the solvent was evaporated on a rotary evaporator, the residue was crystallized from a 4:1 mixture of methylene chloride and petroleum ether, and alcohol **3** (1.37 g) was obtained in the form of a white powder.

**Reaction of Compounds 1-3 with Orthophosphoric Acid in Glacial Acetic Acid.** A mixture of compound **1**, **2**, or **3** (0.5 g), glacial acetic acid (8 ml), and orthophosphoric acid (0.6 ml) was boiled with a reflux condenser until the initial alcohol had disappeared (TLC, 1.5:7:16 acetone–methylene chloride–petroleum ether). The cooled reaction mixture was poured into 100 ml of cold water, sodium bicarbonate was added to pH~7, and the product was extracted with methylene chloride (3×10 ml). The extract was dried with anhydrous sodium sulfate, and the solvent was evaporated to 3-4 ml on a rotary evaporator. The obtained solution was applied to a column of silica gel. Chromatographic separation of the reaction products from the transformation of the alcohol **1** (eluant 1.5:7:16 acetone–methylene chloride–petroleum ether) gave the following compounds: **2-(N-tosylaminomethyl)-5-[5-(N-tosylaminomethyl)-2-furylmethyl]furan** (**8**) (0.15 g). IR spectrum, ν, $cm^{-1}$: 3300 (NH–Ts). **5-(N-Tosylaminomethyl)-2-furylmethyl acetate** (**9**) (0.145 g). IR spectrum, ν, $cm^{-1}$: 1737 (C=O), 3296 (NH–Ts). **5-Methyl-2-(N-tosylaminomethyl)furan** (**11**) (0.104 g). IR spectrum, ν, $cm^{-1}$: 1646 (C=N–Ts). **5-Methylfurfural** (**10**) (0.027 g, 13%). Compound **10** was identified by comparison with an authentic sample (TLC, 1.5:7:16 acetone–methylene chloride–petroleum ether).

Chromatography of the products obtained from the alcohol **2** (4:7:30 acetone–methylene chloride–petroleum ether) gave the following compounds: **5-ethyl-2-(N-tosyliminomethyl)furan** (**12**) (0.184 g). IR spectrum, ν, $cm^{-1}$: 1643 (C=N–Ts). **2-Acetyl-5-methylfuran** (**13**) (0.100 g) identical with an authentic sample (TLC, 14:7:30 acetone–methylene chloride–petroleum ether).

Chromatography of the products from the transformations of compound **3** (2:5 ethyl acetate–petroleum ether) gave the following: **5-(4-methylbenzyl)-2-(N-tosyliminomethyl)furan** (**15**) (0.205 g). IR spectrum, ν, $cm^{-1}$: 1642 (C=N–Ts). **4-Methylphenyl-5-methylfuran-2-yl-methanone** (**14**) (0.103 g), identical (TLC, 2:5 ethyl acetate–petroleum ether) with a sample synthesized by the acylation of toluene (20 ml) with 5-methylpyromucic chloride (13 mmol) in the presence of aluminium chloride (15 mmol) at 20-25°C. The $^1H$ NMR spectrum of this sample was identical with that described in the literature for the ketone **14** [27].

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