

POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.

12.* C–Fur BOND CLEAVAGE IN THE SERIES OF POLYFURYL(ARYL)ALKANES

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Reactions taking place with cleavage of the C–Fur bond are examined. It was established that disproportionation in two directions, leading to the formation of tris(5-methyl-2-furyl)methane, takes place when 3,4-dimethoxyphenylbis(5-methyl-2-furyl)methane is boiled in an acidic medium. The acid-catalyzed reaction of 5-methylfurfural with ethylene glycol leads to the formation of either 2-(5-methyl-2-furyl)-1,3-dioxolane or tris(5-methyl-2-furyl)methane, depending on the catalyst. The treatment of 2-(5-methyl-2-furyl)-1,3-dioxolane or gem-tris(5-methyl-2-furyl)ethane with trityl perchlorate leads to tris(5-methyl-2-furyl)carbenium or bis(5-methyl-2-furyl)methylcarbenium perchlorates respectively.

The lability of the C–Ar bonds in *gem*-polyarylalkanes has been known for a long time. As a rule, their cleavage takes place in superacidic media (as observed by NMR spectroscopy [2]), in concentrated sulfuric acid (according to the data from electronic spectroscopy [3]), and under the conditions of experiments with equimolar amounts of Friedel–Crafts catalysts [4]. It should be noted that the cleavage takes place more readily the higher the π -basicity of the aromatic ring and the more stable the leaving particle (the carbocation or its transformation product).

Some reactions in which the C–Ar bond is cleaved are of practical interest. For example, the condensation of anisole and propionaldehyde followed by disproportionation of the obtained 1,1-bis(4-methoxyphenyl)propane gave 1-(4-methoxyphenyl)propene (anethole) [5, 6], which was isolated earlier from anise oil.

Such reactions must be expected to take place more readily in the series of furan derivatives, since the furan ring has a greater π excess than the benzene ring [7]. In spite of the familiar acidophobic nature of alkylfurans, with the choice of suitable conditions the cleavage of C–Fur bonds can be used for preparative purposes. Thus, the synthesis of aryl-substituted salicylic acids [8, 9] and benzofuro[2,3-h]-1-oxazulenium derivatives [10], produced as a result of the elimination of 2-methylfuran from the initial compound, has been reported.

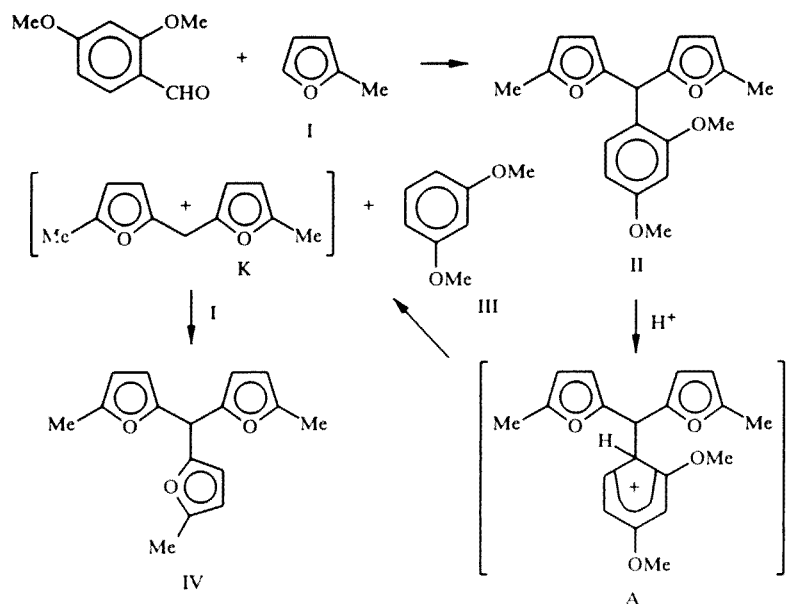
In the present work we describe a series of reactions taking place with cleavage of C–Fur bonds with the participation of polyfuryl(aryl)alkanes or leading to the formation of such structures.

Earlier [11] we found that during the condensation of 2,4-dimethoxybenzaldehyde and sylvane (I) in benzene in the presence of catalytic amounts of perchloric acid resorcinol dimethyl ether (III) and trifurylmethane (IV) are also produced during the reaction in addition to the aryldifurylmethane (II) (Scheme 1). While explaining this fact, we assumed that the formation of the products (III) and (IV) became possible on account of the protonation of compound (II) at position 1 of the aromatic ring, followed by decomposition of the obtained Wheland complex (A) into the difurylmethyl cation (K) and compound (III). In turn, the reaction of the cation K with sylvane present in excess led to the product (IV).

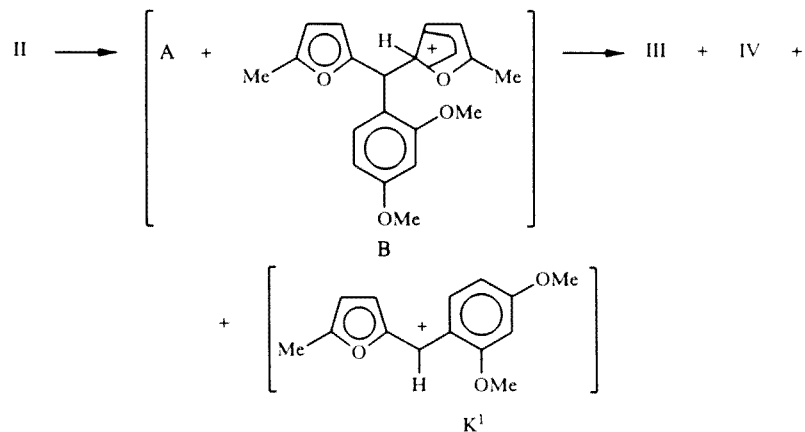
The π -excessive furans undergo electrophilic attack considerably more readily than activated benzenoid compounds. In this connection we assumed that disproportionation of aryldifurylmethane (II) with the elimination of the alkylfuran molecule was possible. To confirm this hypothesis, the previously purified compound (II) was kept in benzene in the presence of catalytic

*For Communication 11, see [1].

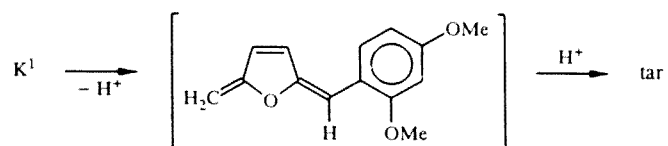
Scheme 1



amounts of perchloric acid. After a certain time, compounds (III) and (IV) were found in the reaction mixture by GLC in addition to the initial aryldifurylmethane (II). Such a result can probably be achieved only in the case of the disproportionation of the initial (II) in two directions (through the σ complexes A and B).



The absence of any other products in the reaction mixture gave us reason to consider oligomerization of the cation K¹ through a dihydrofuran derivative, which explains the appearance of tar on the walls of the flask.



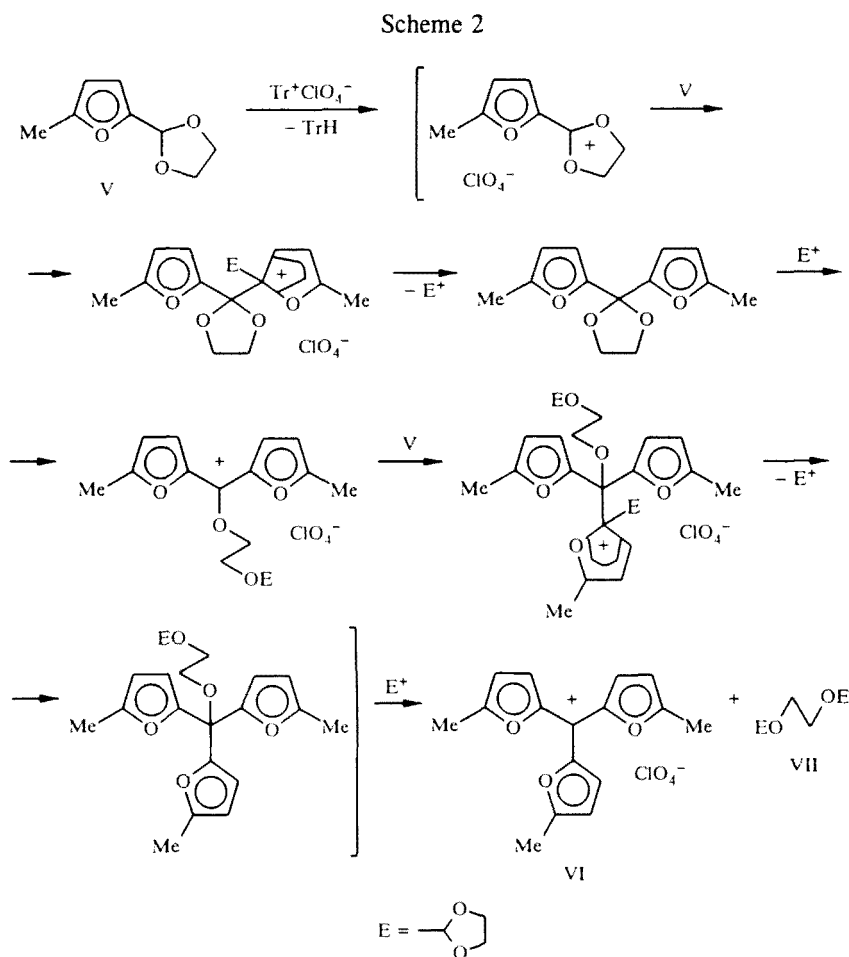
In the previous publication [12] we reported an unsuccessful attempt at the synthesis of a 2-furyldioxolanium salt by the familiar method for the production of its aromatic analogs [13]. As a result of the reaction of equimolar amounts of 2-(5-methyl-2-furyl)-1,3-dioxolane (V) and trityl perchlorate in methylene chloride or acetonitrile compound (VI) was obtained with a 90% yield (of the theoretical) instead of the expected dioxolane salt (V). In the present work we conducted the reaction with the reagent ratio V:Tr⁺ClO₄⁻ = 3:1 [as required by the stoichiometry of the transformation (V) → (VI)] and obtained a similar result.

TABLE 1. Dependence of the Ratio of the Products (IV):(V) from Acetalization of 5-Methylfurfural by Ethylene Glycol on the Catalyst

Catalyst	Ratio (IV):(V) (GLC)
KU-2 (10% of the weight of 5-methylfurfural)	V*
Amberlyst 15 (10% of the weight of 5-methylfurfural)	1 : 20
Amberlyst 15 (50% of the weight of 5-methylfurfural)	IV*
p-Toluenesulfonic acid	1 : 3
HClO ₄	5 : 1
Et ₂ O·BF ₃	IV*

*Contains traces of a second compound.

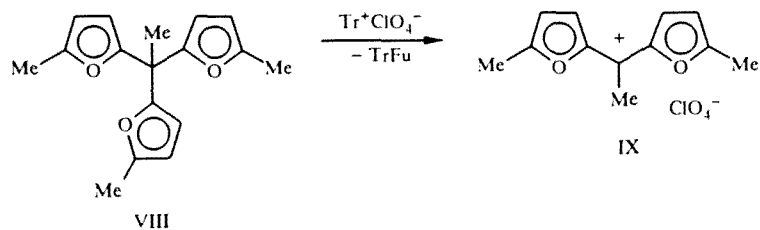
We suppose that the formation of the salt (VI) results from the mechanism shown in Scheme 2. It is favored by the presence of compound (VII) and its decomposition products [14], detected by GLC, in the reaction mixture. Trifurylmethane (IV), which may be be the product of the acid-catalyzed self-condensation of compound (V), was also found in the mixture. As we established, treatment of compound (V) in the presence of catalytic amounts of acids, including Tr⁺ClO₄⁻, led to the formation of compound (IV).



It is known that the synthesis of the acetal derivatives of pyrrole aldehydes involves certain difficulties. Thus, in the reaction of a derivative of formylpyrrole with ethylene glycol in the presence of p-toluenesulfonic acid [15], only tripyrrolyl-methane was isolated instead of the expected product. In view of the results presented above and the results that we obtained

in [15], we studied the effect of acidic catalysts on the selectivity and the direction of the reaction of 5-methylfurfural with ethylene glycol. As seen from the data presented in Table 1, obtained by GLC, the formation of the dioxolane (V) is preferred more, the less acidic the catalyst used in the reaction. [The yield of (V) when KU-2 catalyst is used amounts to 70-80% [16].] Vice versa, the use of stronger acids promotes the formation of trifurylmethane (IV). The most universal catalyst is Amberlyst 15. By varying its amount, it is possible to obtain either (V) or (IV).

Another example illustrating the lability of the C-Fur bond in polyfurylalkanes is our production of the salt (IX) from *gem*-trifurylethane (VIII) during treatment of the latter with trityl perchlorate.



The deciding role in this transformation was obviously played by the high stability of the salt (IX), which was previously isolated in the form of the perchlorate by hydride transfer from *gem*-difurylethane to $\text{Tr}^+\text{ClO}_4^-$ [17]. The "accepting" properties of trityl perchlorate toward 2,5-dialkylfurans have been described before [9, 10].

EXPERIMENTAL

Gas-liquid chromatography was conducted on a Chrom-5 instrument with a flame-ionization detector on a glass column (2500×3 mm) with 5% of PMFS-4 on Chromaton N-AW-DMCS (0.250-0.315 mm) (column temperature 140-210°C, detector temperature 150-230°C, evaporator temperature 200-320°C, carrier gas nitrogen, 30 ml/min). The purity and individuality of the products were monitored by TLC on Silufol UV-254 plates in the 3:1 hexane-chloroform system.

2,4-Dimethoxyphenylbis(5-methyl-2-furyl)methane (II), 2-(5-methyl-2-furyl)-1,3-dioxolane (V), and 1,1,1-tris(5-methyl-2-furyl)ethane were obtained by the respective methods described in [11, 16, 18].

Disproportionation of Compound (II). To a solution of 0.31 g (1 mmole) of compound (II) in 15 ml of benzene we added a drop of 70% perchloric acid. The mixture was boiled with a reflux condenser for 4 h. After cooling it was neutralized with sodium bicarbonate, washed with water, dried over sodium sulfate, evaporated to 2 ml, and analyzed by GLC.

General Procedure for the Reaction of 5-Methylfurfural with Ethylene Glycol. To a solution of 2.2 g (20 mmole) of 5-methylfurfural and 0.6 g (20 mmole) of ethylene glycol in 30 ml of benzene we added one of the following catalysts: 0.2 g of KU-2; 0.2 g of Amberlyst 15; 1 g of Amberlyst 15; 0.01 g of *p*-toluenesulfonic acid; three drops of 70% perchloric acid; three drops of boron trifluoride etherate. The mixture was boiled with azeotropic distillation of the water. After cooling the reaction mass was filtered (in the case of KU-2 or Amberlyst 15) or treated with a solution of sodium bicarbonate and with water, dried over sodium sulfate (in the case of *p*-toluenesulfonic acid, perchloric acid, or boron trifluoride etherate), evaporated to 3 ml, and analyzed by GLC.

Tris(5-methyl-2-furyl)carbenium Perchlorate (VI). To a solution of 0.46 g (3 mmole) of compound (V) in 10 ml of methylene chloride we gradually added 0.34 g (1 mmole) of $\text{Tr}^+\text{ClO}_4^-$. Five minutes after the catalyst had completely dissolved, the reaction mixture was diluted with 60-80 ml of ether and stirred. The precipitate was filtered off and washed with a small amount of ether. We obtained 0.31 g of the product (VI) as a red powder. The yield was 87%; decomp. 234-235°C. The decomposition point and the PMR and UV spectroscopic data of compound (VI) were identical with published data [17].

Bis(5-methyl-2-furyl)methylcarbenium Perchlorate (IX). To a solution of 0.27 g (1 mmole) of compound (VIII) in 3 ml of acetonitrile we gradually added 0.34 g (1 mmole) $\text{Tr}^+\text{ClO}_4^-$. After 10 min the reaction mass was diluted with ether, and the precipitate was filtered off and washed with ether and with hexane. We obtained 0.27 g of the product (IX) in the form of red crystals. The yield was 76%; decomp. 152-153°C. The decomposition point and the PMR and UV spectroscopic data were identical with published data [17].

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