REACTIONS OF AROMATIC AND HETEROAROMATIC COMPOUNDS BEARING ELECTRON-ACCEPTOR SUBSTITUENTS

X.* ALKYLATION AND ACYLATION OF FURFURAL

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A mixture of products of mono- and polyalkylation is formed in the isopropylation of furfural in chloroform in the presence of excess aluminum chloride. The acetylation of furfural under such conditions gives only 5-acetylfurfural, the formation of which probably proceeds through the intermediate addition of acetyl chloride to the carbonyl group of furfural.

A specific peculiarity of heteroaromatic compounds that is due to their very structure is a sharply expressed nonuniformity of the distribution of the electron density and consequently, nonequivalence of the various positions of the molecule with respect to the attacking agent. In particular, substitution reactions of various types in thiophene and furan molecules proceed several orders of magnitude more rapidly in the α position than in the β position [2, 3]. The characteristic difficulty in obtaining β-substituted derivatives that is observed for these systems is associated with this. For example, electrophilic substitution reactions, even for compounds in which one of the α positions is occupied by orienting groups of the II type, are usually directed predominantly to the free α' position rather than to the 4 position, which corresponds to the meta position in the benzene series.

It has been shown in our laboratory that complexing with aluminum chloride [3-5] or protonation [6, 7] of α-carbonyl compounds of the thiophene series substantially increases the electron-acceptor capacity of the substituent, and because of conjugation, the electron density in the 3 and 5 positions is reduced to a maximum degree, while the 4 position is deactivated to a much lesser extent. The products of electrophilic substitution reactions of such compounds under the indicated conditions are therefore predominantly or exclusively 4 substituted derivatives. The effect of complexing on the direction of electrophilic substitution is not displayed quite so distinctly in the furan series as in the thiophene series. Up until recently, it could be assumed as a rule that the 5 position of the heteroring retains the greatest activity, even in those cases in which complexes of Lewis acids with carbonyl compounds of the furan series participate in the reaction. As far as we know, only one fact that contradicts this "rule" has been described – 4-isopropylfurfural is formed, although in low yield (~10%), in the isopropylation of furfural in the presence of excess $AlCl_3$ [8]. The exceptional character of this result is emphasized by the fact that 5-tert-butylfurfural is formed in the tert-butylation of furfural under similar conditions [9].

The number of facts that do not agree with the indicated "rule" have recently begun to increase. In particular, the application of modern methods of anlysis, particularly gas-liquid chromatography (GLC) and PMR spectroscopy, in a number of cases has made it possible to detect the formation of 2,4-substituted isomers along with the 2,5-substituted derivatives. Thus the action of caproic anhydride on methyl furan-2-carboxylate in the presence of tin chloride gives the 4- and 5-substituted derivatives in a ratio of ~2:3 [10]. Isopropylation of the same ester in the presence of aluminum chloride gives a mixture of the 4- and

*See [1] for communication IX.

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5-mono- and 4,5-disubstituted compounds; the formation of a considerable amount of the latter does not make it possible to judge the relative rates of substitution in the 4 and 5 positions [11]. We will examine this problem in greater detail in a subsequent paper [12] in the case of bromination of the complex of furfural with aluminum chloride.

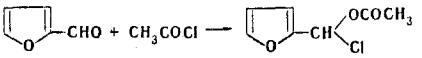
In addition to the above, in studying the direction of electrophilic substitution in the furan series, it is necessary to take into account the fact that the process may be complicated as a consequence of the acidophobic character, diene properties, and capacity for ring opening that are peculiar to furan compounds and are also retained in compounds bearing electron-acceptor substituents [7]. For example, it is known that some reactions that lead to products involving the replacement of the hydrogen in the free α position, particularly nitration, proceed through 2,5-addition [13].

The data presented made it possible to assume that the compounds described in [8, 9] are by no means the only reaction products, and their isolation consequently cannot serve as a basis for judgment regarding specificity of the alkylation of the complex of furfural with aluminum chloride. We isopropylated furfural in chloroform in the presence of excess $AlCl_3$ and studied the composition of the products by means of GLC and PMR spectroscopy. In doing this, it was found to be convenient to oxidize the resulting mixture of aldehydes and analyze it, after treatment with diazomethane, as the methyl esters, which are quite stable compounds, and in addition, have been studied by PMR spectroscopy and GLC [11]. We found that the monoisopropylfurfural formed is actually a mixture of 4- and 5-isomers in a ratio of ~7 : 1. 4,5-Diisopropylfurfural, triisopropylfurfural, and undistillable resinification products are obtained along with them. The latter are probably formed to a considerable extent from the products of the alkylation of furfural, since ~40% of the starting furfural is recovered unchanged. In order for one to be able to form a judgment regarding the predominant direction of the alkylation process from these data, one should carry out the competitive isopropylation of mixtures of 4- and 5-isopropylfurfural and study the possibility of the isomerization and stability of these compounds under the reaction conditions. Considering the difficulty involved in the preparation and isolation and the low stability of 4- and 5-isopropylfurfurals, we decided to clarify the problem of the specificity of electrophilic substitution for the complex of furfural with $AlCl_3$ by a different path by using a reaction that stops at the monosubstitution stage.

It seemed to us that acylation, which we previously studied in the case of 2-acetothienone [4], could serve as this sort of reaction. Considering the greater activity of the furan ring in electrophilic substitution reactions, we assumed that the acylation of furfural may be realized under milder conditions than the acylation of acetothienone (by the action of acetyl chloride without a solvent in the presence of excess $AlCl_3$ at ~100°C). The experiments that we set up confirmed, as it were, these assumptions. Furfural is acetylated to give a product in ~45% yield when the reaction is carried out in chloroform (at no higher than 50°). In this case, the only reaction product was 5-acetylfurfural, the structure of which was proved by oxidation to the known 5-acetylfuran-2-carboxylic acid.

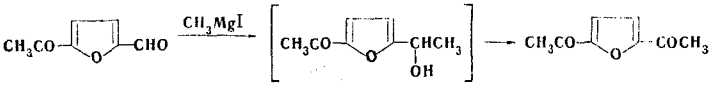
However, a more detailed study of the problem demonstrated that the production of 5-acetylfurfural can hardly constitute evidence that the complexes of α-carbonyl compounds of the furan series with aluminum chloride are in themselves acylated in the 5 position. Thus our attempts to exhaustively acetylate 2-acetylfuran were unsuccessful. Even under conditions more severe than those used for the acetylation of 2-acetothienone (temperatures up to 115°), we could not detect the formation of diacetylfuran. In this case, the greater portion of the starting 2-acetylfuran was recovered unchanged; in addition to it, we were also able to isolate small amounts of two reaction products with the $C_{11}H_{12}O_4$ composition, which are 2,6-dimethyl-3,5-diacetyl-4-pyrone and 2,4-diacetylorcinol, which are probably not products of transformation of 2-acetylfuran but are formed by autocondensation of acetyl chloride, which possibly proceeds through a step involving dehydroacetic acid (see [14-16]). 2-Methyl-5-acetylfuran, which is more active than 2-acetylfuran, is not acetylated under the conditions that were found for furfural. Its acetylation product – 2-methyl-3,5-diacetylfuran – is formed in yields of ~20% based on the amount of monoketone taken for the reaction, 45% based on the amount of ketone entering into the reaction, only as a result of reaction at 80° of excess complex of aluminum chloride with acetyl chloride. In this connection, we note that 2-methyl-3,5-diacetylthiophene is obtained in 57% yield (based on the amount of 2-methyl-5-acetylthiophene [17] taken for the reaction) under milder conditions (at room temperature). These results lead to an unexpected conclusion, the net result of which is that carbonyl compounds of the furan series in complexes with aluminum chloride are less active with respect to an electrophilic particle than the complexes of their thiophene analogs with $AlCl_3$. In the light of this conclusion it is, however, necessary to give an explanation of the ease with which furfural is converted to 5-acetylfurfural. From all appearances, this can be reduced to the following.

Furfural can form a chloroacetate with acetyl chloride.



This sort of compound has been described for aromatic aldehydes, including furfural [18]. Some of them, mainly those that are formed from acid bromides of aromatic acids, are solids under ordinary conditions and can be isolated in the pure state, but the haloacylals are generally extremely unstable and, particularly on reaction with silver salts of organic acids, are converted to the corresponding acylals [18]. The substituent in the chloroacetate and diacetate of furfural is not an orienting group of the II type, so that substitution should naturally be directed to the 5 position. We were unable to isolate furfural chloroacetate in the pure state because of its instability, but its formation was confirmed by indirect data (see the Experimental section). It seems to us that the presence of excess aluminum chloride is responsible for the fact that the chloroacetate is formed gradually from the furfural that is formed due to dissociation of its complex with $AlCl_3$ and is immediately acetylated. When we introduced the previously prepared chloroacetate or diacetate of furfural into the reaction, we obtained 5-acetylfurfural in very low yields because of pronounced resinification.

5-Acetylfurufural was converted to 2,5-diacetylfuran by the action of a Grignard reagent and subsequent oxidation.



The same ketone and 2,5-diacetylthiophene are formed in the homolytic acetylation of the corresponding monoketones; we carried out this acetylation under the conditions described for the acylation of deactivated nitrogen heterocycles [19].

EXPERIMENTAL

The chromatographic analyses were carried out with an LKhM-8M chromatograph (from the Mosneftekip Plant) with a flame ionization detector. The carrier gas was nitrogen, and the 4×2000 mm stainless steel column was packed with 15% polyethylene glycol adipate on Chromosorb W. The column temperature was 175°, and the gas flow rate was 55 ml/min. The PMR spectra were recorded with an RS-60 spectrometer (Special Design Office of the Institute of Organic Chemistry, Academy of Sciences of the USSR) with hexamethyldisiloxane as the internal standard. The chemical shifts are given on the δ scale relative to tetramethylsilane (TMS).

Isopropylation of Furfural. A solution of 24 g (0.25 mole) of furfural in 50 ml of chloroform was added to 40 g (0.3 mole) of $AlCl_3$ at 0° with stirring, after which 19.7 g (0.25 mole) of isopropyl chloride was added without cooling. The mixture was then allowed to stand at 20° for 24 h. The mass was poured over ice, and the organic layer was separated, washed twice with sodium acetate solution, and steam distilled. The distillate was extracted thoroughly with chloroform, and the extract was washed with water, dried with $MgSO_4$, and vacuum distilled to give 9.5 g of unchanged furfural (40% recovery) and 6.5 g (~20%) of a mixture of isopropylation products with bp 91-130° (12 mm). A 3.6 g sample of this mixture was oxidized with silver oxide to a mixture of acids (3.6 g) with mp 53-75°.* A mixture (2.45 g) of methyl esters with bp 103-110° (12 mm) was obtained from 2.8 g of the latter mixture by the action of diazomethane; judging from the results of GLC and PMR spectroscopy, the mixture of methyl esters contained the methyl esters of 4-isopropyl-, 5-isopropyl-, and 4,5-diisopropylfuran-2-carboxylic acids in a ratio of ~7:1:1, as well as traces of a substance, which is probably methyl 4,5-diisopropylfuran-2-carboxylate. The same substance is also formed as an impurity in methyl 4,5-diisopropylfuran-2-carboxylate, which we obtained by isopropylation of 2-methylfuroate by the method in [11]; the ratio of di- and triisopropyl-substituted compounds in the sample that we obtained was 85:15, according to PMR spectroscopy and GLC. The ratio of substituted esters of furan-2-carboxylic acid was determined by PMR spectroscopy from the areas of the signals of the nuclear protons (in CCl_4; the assignment of the signals was made from the data in [11]): 7.28 ppm, 5-H of the ester of 4-isopropylfuran-2-carboxylic acid; 7.00 and 6.94 ppm, 3-H of all three esters (partially superimposed); 6.05 ppm, 4-H of methyl 5-isopropylfuran-2-carboxylate. The conclusion regarding the formation of the triisopropyl-substituted compounds was made on the basis of the magnitude of

*Recrystallization of 0.1 g of the mixture of acids gave 4-isopropylfuran-2-carboxylic acid with mp 76-77° (from hexane), in agreement with the reported melting point [20].

the retention volume (the relative retention volume as compared with methyl 4,5-diisopropylfuran-2-carboxylate was 1.25) and the absence of signals of nuclear protons differing from the 3-H signal of the 4,5-diisopropyl-substituted compound in the PMR spectrum of the mixture. The ratio of the tri- and diisopropyl-substituted compounds was determined from the areas of the CH_3O signal (3.76 ppm), common to both compounds, and the 3-H signal of methyl 4,5-diisopropylfuran-2-carboxylate (6.94 ppm).

Acetylation of Furfural. A solution of 4.8 g (0.05 mole) of furfural in 15 ml of $CHCl_3$ was added to 16.6 g (0.125 mole) of anhydrous $AlCl_3$ in 10 ml of dry chloroform at such a rate that the temperature did not rise above 40°. A 7.9 g (0.1 mole) sample of acetyl chloride was added to the resulting solution, and the mixture was held at 50° for 1 h, after which it was cooled and poured over ice. The acetylation product was extracted thoroughly with chloroform, and the solvent was removed by distillation. The residue was steam distilled, and the distillate was extracted with chloroform. The chloroform extract was washed with water and dried with $MgSO_4$, and the solvent was removed by distillation to give 3.1 g (45%) of a pure (according to GLC), crystalline substance with mp 94-94.6° (from heptane). Found: C 60.9; 61.1; H 4.3; 4.4%; mol. wt. (by mass spectrometry) 138. $C_7H_6O_3$. Calculated: C 60.9; H 4.4%; mol. wt. 138. PMR spectrum (in CCl_4): CH_3, singlet, 2.48 ppm; singlet corresponding to two nuclear protons, 7.08 ppm; singlet of the formyl group, 9.65 ppm. The 5-acetylfurfural structure of the reaction product was proved by its oxidation with 0.8 N chromic acid solution (Jones reagent [21]) to 5-acetylfuran-2-carboxylic acid with mp 208.5-210° (vacuum sublimation). Found: C 54.5; 54.4; H 3.9; 3.7%. $C_7H_6O_4$. Calculated: C 54.6; H 3.9%. The acid did not depress the melting point of a sample obtained by A. P. Yakubov from 2-acetylfuran diethyl ketal by the action of n-butyllithium and subsequent treatment with CO_2. The methyl ester (obtained by the action of diazomethane) melted at 100.5-101.5° (sublimed). According to [22], 5-acetylfuran-2-carboxylic acid melts at 206-207°, and its methyl ester has mp 101-102°.

Acetylation of 2-Methyl-5-acetylfuran. A 4 g (0.032 mole) sample of 2-methyl-5-acetylfuran [23] was added dropwise to 8.6 g (0.065 mole) of $AlCl_3$ at such a rate that the temperature of the mixture did not rise above 35°, and 5.3 g (0.065 mole) of acetyl chloride was then added. The mixture was heated at 80-85° for 3 h, after which it was worked up as in the acetylation of furfural. Distillation yielded 2.15 g of unchanged 2-methyl-5-acetylfuran with bp 68-80° (7 mm). Crystallization of the residue in the flask gave 1.1 g of 2-methyl-3,5-diacetylfuran with mp 94-95°. The yield was 21% based on the amount of 2-methyl-5-acetylfuran taken for the reaction and 45% based on the amount consumed in the reaction. A sample for analysis, obtained by crystallization from aqueous alcohol and heptane, had mp 94.5-95.5°. Found: C 64.9; 64.9; H 6.1; 6.1%. $C_9H_{10}O_3$. Calculated: C 65.0; H 6.1%.

Attempts to Acetylate 2-Acetylfuran. A 5.5 g (0.05 mole) sample of 2-acetylfuran was added with stirring to 16.6 g (0.125 mole) of $AlCl_3$, during which a temperature rise from 20 to 45° and the formation of a dark-brown liquid mass were observed. A 7.9 g (0.1 mole) sample of acetyl chloride was added dropwise to the resulting complex in the course of 3 h at 100 ± 3° (in the flask), and the mixture was allowed to stand at the same temperature with stirring for another 3 h. After this, the contents of the flask were poured over ice and worked up in the usual manner (see above). Distillation yielded 3.8 g (69%) of unchanged acetylfuran with bp 56-57° (9 mm). Crystallization of the residue from heptane gave 0.2 g of a substance with mp 105-120°, which melted at 123.5-124° after recrystallization from heptane. Found: C 63.5; 63.2; H 5.8; 5.7%; mol. wt. (by mass spectrometry) 208. $C_{11}H_{12}O_4$. Calculated: C 63.5; H 5.8%; mol. wt. 208. PMR spectrum (in $CDCl_3$): CH_3 groups, singlets at 2.34 and 2.52 ppm. According to [24], 2,6-dimethyl-3,5-diacetylpyrone has mp 123-124°. Gas-liquid chromatography established the formation of the same reaction product when acetyl chloride was heated with $AlCl_3$ for 3 h (molar ratio 4:5, 90-100°).

When the reaction was carried out with a threefold excess of acetyl chloride at 115°, 0.1 g of an aqueous NaOH-soluble product with mp 94-94.5° (from heptane) was isolated in addition to 3.4 g (62%) of acetylfuran and 0.1 g of 2,6-dimethyl-3,5-diacetylpyrone. Found: C 63.7; 63.5; H 5.8; 5.9%; mol. wt. (by mass spectromety) 208. $C_{11}H_{12}O_4$. Calculated: C 63.5; H 5.8%; mol. wt. 208. The PMR spectrum (in CCl_4) contains three CH_3 singlets at 2.50, 2.55, and 2.62 ppm, the singlet of a ring proton at 5.77 ppm, and two OH singlets at 15.75 and 16.53 ppm. The substance did not depress the melting point of a sample of 2,4-diacetylorcinol obtained from O,O-diacetylorcinol [25] via the method in [26]. The recovery of unchanged 2-acetylfuran was 90% when the reaction was carried out under milder conditions (at ~60°).

2,5-Diacetylfuran. A. A solution of CH_3MgI (from 0.35 g of Mg and 2.07 g of CH_3I) in 30 ml of ether was added dropwise at 0° to 2 g (0.014 mole) of 5-acetylfurfural in 55 ml of tetrahydrofuran. The mixture was kept cool for 20 min and held at room temperature for 1.5 h. Ammonium chloride solution was added, and the mixture was extracted thoroughly with ether. The extract was washed with water and dried with

$MgSO_4$. Removal of the ether gave 1.85 g of an oil, which was converted to 0.6 g (28%) of 2,5-diacetylfuran with mp 137-139° (from heptane) by oxidation in 15 ml of acetone with 4.65 ml of the Jones reagent (see above).* Found: C 62.7; 62.8; H 5.2; 5.3%; mol. wt. (by mass spectrometry) 152. $C_8H_8O_3$. Calculated: C 63.1; H 5.3%; mol. wt. 152. PMR spectrum (in $CDCl_3$): CH_3 singlets at 2.57 ppm and ring proton at 7.46 ppm.

B. A 3.65 g (0.09 mole) sample of acetaldehyde in 37 ml of tert-butyl alcohol was added to a solution of 3.3 g (0.03 mole) of 2-acetylfuran in 22 ml of tert-butyl alcohol, and 8.4 g (0.09 mole) of tert-butyl hydroperoxide and a solution of 28 g (0.09 mole) of $FeSO_4 \cdot 7H_2O$ in 67 ml of water and 9 ml of concentrated H_2SO_4 were added simultaneously from two dropping funnels while maintaining the temperature of the mixture at +5°. The mixture was kept cool for 1.5 h and held at room temperature for 2 h. It was then poured into water, and the aqueous mixture was extracted with chloroform. The extract was washed with water, the chloroform was removed, and the residue was steam distilled. The distillate was extracted thoroughly with chloroform, and the extract was dried with $MgSO_4$. The residue from the removal of the chloroform was a liquid from which 2.2 g of unchanged 2-acetylfuran was distilled at 9 mm (up to 64°). Crystallization of the new residue from heptane gave 0.1 g of 2,5-diacetylfuran with mp 136-139°. The yield was 2% based on the amount of 2-acetylfuran used in the reaction and 6% based on the amount consumed in the reaction. The product did not depress the melting point of the sample of 2,5-diacetylfuran described above.

2,5-Diacetylthiophene. An 11.1 g (0.12 mole) sample of tert-butyl hydroperoxide and a solution of 33.5 g (0.12 mole) of $FeSO_4 \cdot 7H_2O$ in 90 ml of water and 12 ml of concentrated H_2SO_4 were added dropwise simultaneously at 8-10° in the course of 1 h to a solution of 5.04 g (0.04 mole) of 2-acetothienone and 4.85 g (0.12 mole) of acetaldehyde in 80 ml of tert-butyl alcohol and 60 ml of water. The mixture was worked up as in the previous experiment to give 2.9 g of unchanged 2-acetothienone and 0.26 g (4% based on the amount of 2-acetothienone used and 9% based on the amount consumed) of 2,5-diacetylthiophene with mp 170-172°. The product did not depress the melting point of a genuine sample of 2,5-diacetylthiophene [4].

Reaction of Furfural with Acetyl Chloride in the Absence of Aluminum Chloride. A dark liquid that was only slightly soluble in hexane and underwent considerable decomposition on distillation (see [18]) was formed when equimolar amounts of furfural and acetyl chloride were mixed; the distilled reaction product with bp 72-75° (2 mm) contained ~12% Cl (the figure should be 20.3% for furfural chloroacetate). Treatment of the undistilled product of the reaction of furfural with acetyl chloride with silver acetate via the method in [18] gave furfural diacetate with mp 51-52°, which was identical to a sample obtained by the reaction of furfural with acetic anhydride via the method in [28]. Pronounced resinification was observed when aluminum chloride reacted with a previously prepared mixture of furfural and acetyl chloride, and 5-acetylfurfural was formed in 1.5% yield. The acetylation of furfural diacetate was also accompanied by resinification, and the yield of 5-acetylfurfural was ~5%.

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*2,5-Diacetylfuran, obtained by the reaction of ketene with an organomercury compound (the specific compound is not indicated) was described in [27] as a compound with mp 94°, but no structural proof or even the results of elementary analysis were presented.

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