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UNUSUAL MEERWEIN REACTION IN THE FURAN SERIES

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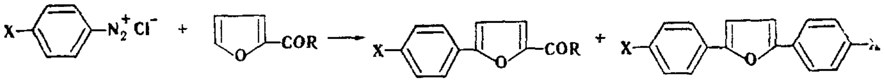
Aldehydes formed as side products in the Meerwein arylation of 2-acylfurans were detected by a polarographic method.

In previous papers [1,2] we showed that a series of side products are formed along with the major products — 5-aryl-2-acylfurans (I) — in the Meerwein arylation of acylfurans. Of these side products, the 2,5-diarylfurans (II) seemed of greatest interest.



I

II

$X = Cl, Br, NO_2$; $R = CH_3, C_2H_5, C_3H_7$

Up until now, the formation of compounds of the 2,5-diarylfuran type has never been noted in the Meerwein reaction either in the furan series or in the case of unsaturated compounds

Inasmuch as we have established* [1] that arylacetylfurans I are not intermediates in the formation of diarylfurans II, it might have been assumed that the 2,5-diarylfurans are formed directly during the arylation of 2-arylfurans.

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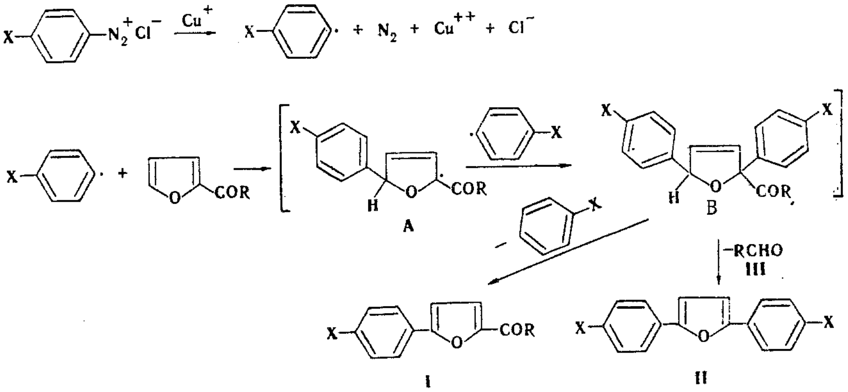
We propose the following scheme for the reaction under consideration, which leads to the formation of 2,5-diarylfurans as side products:



As seen from the above scheme, the first step in the reaction is assumed to be addition of an aryl radical, formed as a result of decomposition of the diazonium salt, to the acylfuran to give a new arylfuryl radical A.

The possibility of the formation of an intermediate radical similar to that depicted by structure A is confirmed by the results of polarography of substituted arylfurans.* The subsequent reaction of this newly formed radical A with an aryl radical gives a product of 2,5-addition to the furan ring — 2,5-diaryl-2,5-dihydrofuran (B).

One proof for the proposed scheme may be the direct detection in the reaction mixture of corresponding aldehyde III. In the present research we used a polarographic method for this purpose. Aliphatic aldehydes are reduced on a dropping-mercury electrode at rather negative potentials. In addition, in aqueous media the aldehydes exist to a considerable extent in a polarographically unactive hydrated form. It is therefore expedient to carry out the quantitative determination of aliphatic aldehydes in the presence of excess primary amine, with which the aldehydes react to form polarographically active Schiff bases, which are reduced substantially more easily than the starting aldehydes on a dropping-mercury electrode [4]. A buffer solution with pH 10.8 consisting of a mixture of a 0.1 M solution of hexamethylenediamine adipate and 0.1 M NaOH solution [5] was used for the analysis of the acetaldehyde and propionaldehyde. Under these conditions the half-wave potentials of the corresponding Schiff bases of acetaldehyde and propionaldehyde are identical (1.45 V), and the heights of the waves are proportional to the concentrations. However, prolonged passage of a stream of nitrogen through the solution undergoing polarography leads to a certain decrease in the height of the wave, inasmuch as the reaction involved in the formation of the Schiff bases is an equilibrium reaction, and the aldehydes themselves are readily flushed from the solution. In addition, the high volatility of acetaldehyde and propionaldehyde were used to isolate them from the reaction mixtures, the direct analysis of which was impossible because of the presence in them of other polarographically active substances (Cu^{2+}, azo compounds formed as side products, and the starting acylfurans). It is, of course, impossible to determine the precise amount of aldehyde formed in the reaction in this case, but we did not set out to do this, inasmuch as the reaction is accompanied by resinification. The Meerwein reaction was carried out in a test tube, and stirring was accomplished with a stream of nitrogen for 2-4 h. The liberated volatile substances were passed through a trap filled with a mixture of a solution of 0.1 M hexamethylenediamine adipate and a 0.1 M solution of NaOH. The aldehydes formed in the reaction (acetaldehyde and propionaldehyde) were absorbed by the solution and subsequently determined by polarography. The waves at −1.45 V, which coincided completely with the waves of the Schiff bases of the corresponding aldehydes artificially added to the test solution, were recorded on the polarograms of solutions selected from the trap.

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*The reduction of 5-(p-nitrophenyl)furfural in anhydrous dimethylformamide (DMF) with a tetrabutylammonium perchlorate base electrolyte gives, as result of reversible transfer of one electron, an anion radical, to the resonance hybrid of which a substantial contribution is made by a structure with localization of the negative charge on the nitro group and of the unpaired electron in the 2 position of the furan ring [3].

Thus in the present research we were able to detect the presence of the corresponding aldehydes in the reaction mixtures from the chlorophenylation of 2-acetyl- and 2-propionylfuran.

EXPERIMENTAL

The polarograms were recorded with a PO-4 Radiometer polarograph (Denmark). Polarography was carried out in a thermostated cell (25 ± 0.1 deg). The oxygen was removed from the solution with a stream of purified nitrogen. A capillary with a spatula for forced detachment of a drop with the following characteristics for $H = 45$ cm in a 0.1 M solution of potassium chloride was used: $m = 1.06$ mg, $t = 0.305$ sec, and $m^{2/3}t^{1/6} = 0.85$. An external saturated calomel electrode was used as the anode.

The Meerwein arylation of 2-acylfurans was carried out as previously described in [1,2] with p-chlorobenzenediazonium chloride; 0.5 g (4.5 mmole) of 2-acetylfuran and 0.554 g (4.46 mmole) of 2-propionylfuran were used for the reactions.

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NITRATION OF FURAN DERIVATIVES WITH ACETYL NITRATE. INVESTIGATION OF THE PRODUCTS OF NITRATION OF FURFURAL AND FURFURAL DIACETATE

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542.958

It was established that 5-nitro-2-acetoxy-2,5-dihydro-, 5-nitro-4-acetoxy-4,5-dihydro-, and 5-nitrofurfural diacetates and 5-nitrofurfural are formed in the nitration of furfural and furfural diacetate in acetic anhydride. 2,5-Diacetoxy-2,5-dihydro- and 4,5-diacetoxy-4,5-dihydrofurfural diacetate are present in small amounts in the nitration products. 5-Nitrofurfural and 5-nitrofurfural diacetate are formed as a result of direct electrophilic substitution of hydrogen by a nitro group.

A crystalline "intermediate" nitration product, which was found to be 5-nitro-2-acetoxy-2,5-dihydrofurfural diacetate (II) [2-5], was isolated [1] in the nitration of furfural diacetate (Ib). A molecule of acetic acid is split out by treatment of II with weakly alkaline reagents (pyridine, sodium acetate, etc.), and 5-nitrofurfural diacetate (III) is

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*Deceased.

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