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SOLID-PHASE REARRANGEMENT OF AMINALS OF 5-HALOFURFURALS TO 5-N,N-DIALKYLAMINOFURFURLYIDENE-N,N-DIALKYLIMMONIUM SALTS

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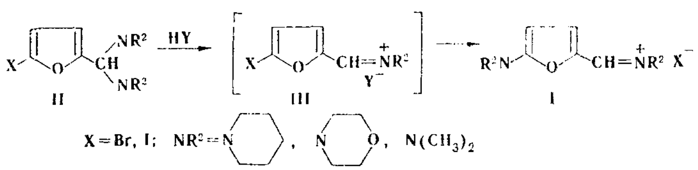
Aminals of 5-halofurfurals (products of the reaction of 5-halofurfurals with 2 moles of secondary amines) in the solid phase undergo rearrangement to 5-N,N-dialkylaminofurfurylidene-N,N-dialkylimmonium salts. The kinetics of the reaction were studied. A mechanism for the reaction is proposed.

It is known that 5-halo- and 4,5-dihalofurfurals [1-3], 5-halofurylacroleins [4], and 5-halofurfurylideneanilines [5] react with secondary amines to give 5-N,N-dialkylaminofurfurylidene-N,N-dialkylimmonium salts (I). Some of these salts have been obtained in crystalline form [1, 5]. The mechanism of this transformation was studied in [6-8]; in particular, it was established [8] that the reaction can be stopped at the step involving the formation of relatively stable aminals II. In [8] it was also noted that II are isolated from alcohol solutions in the form of white crystals; however, these crystals turn yellow rapidly during storage. It was found that the resulting salts I can be isolated in high yields with a high degree of purity. This reaction is of undoubted interest as a rare example of solid-phase nucleophilic substitution of halogen in the furan ring:



The kinetics of the rearrangement of aminals II are presented in Fig. 1. All of the kinetic curves are broken down into two sections: in the first section the reaction proceeds with acceleration, whereas in the second section it proceeds at a constant rate. The composition of the atmosphere in which the process takes place, particularly in the case of moisture, carbon dioxide, and traces of volatile mineral acids as impurities, has a pronounced effect on the rate. Most of the experiments were therefore carried out in a dry nitrogen atmosphere; the gaseous medium was varied intentionally only in a few cases. Thus II reacts in air approximately twice as fast as in dry nitrogen, whereas in a carbon dioxide atmosphere the reaction is accelerated to an even greater extent. However, varying the atmos-

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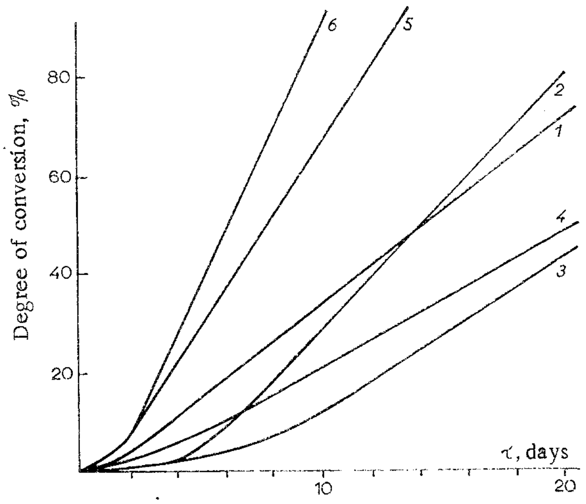

Fig. 1. Kinetics of the solid-phase rearrangement of aminals II, 1) X = I, NR$_2$ = piperidyl, in a nitrogen atmosphere; 5) the same in air; 6) the same in a carbon dioxide atmosphere; 2) X = I, NR$_2$ = morpholyl, in a nitrogen atmosphere; 3) X = Br, NR$_2$ = piperidyl, in a nitrogen atmosphere; 4) X = Br, NR$_2$ = morpholyl, in a nitrogen atmosphere.

phere has no effect on the length of the induction period, and its magnitude depends only on the nature of the amine and the character of the haolgen atom in the ring.

The peculiarity of the mechanism via which the solid-phase reactions proceed, the special role in them of intermolecular interaction in the crystal lattice, the effect of impurities, and the diffusion factor all hinder the interpretation of the kinetic data. Nevertheless, we assume that this reaction proceeds via a mechanism similar to the SN_2Ar mechanism, i.e., the substitution is nucleophilic and activated. Aminals II themselves do not contain activating groups and are only potentially capable of substitution reactions. A peculiarity of the structure of their molecules is the presence of two fragments, viz., a highly basic amine fragment that is connected to its relatively electrophilic antipode, which is capable of accepting the electron pair from the nucleophile (when there is an activating substituent in the 2 position) with the subsequent elimination of halogen. This peculiarity is also the driving force in disproportionation.

It has been shown [8] that aminals II are extremely sensitive to acids. Traces of mineral acids evidently ensure "start" of solid-phase disproportionation to give immonium salt III. As in the case of liquid-phase reactions, halogen can undergo exchange via an SN_2Ar mechanism only with the development of an activating immonium group in the molecule. Aminal II rather than the free amine obviously acts as the nucleophile in this case. The participation in the reaction of its final products, viz., immonium salts I, as carriers of the amino group (as has also been proposed for liquid-phase reactions [8]) is also not excluded; the autocatalytic effect of salts I is probably the reason for inductive acceleration in its initial step. The reaction rate gradually reaches the "diffusion" limit, after which it is determined by the rate of disruption of the crystal lattice and diffusion in the crystal.

Data on the physical properties of salts I are presented in Table 1. A "change-transfer" band with a maximum at $\sim$400 nm, which does not depend on the nature of the gegenion and is only slightly dependent on the character of the NR$_2$ group, is observed in their electronic spectra. A qualitative comparison shows that the immonium group, with respect to its electron-acceptor properties, occupies an intermediate position between formyl and nitro groups [9, 10].

The order of the mutual orientation of the signals of the protons in the PMR spectra of salts I is not completely normal. Whereas the "aldehyde" proton is always observed at considerably weaker field for 5-N,N-dialkylaminofurfurals than for the proton in the 3 position [9], in the given case the signal of the "immonium" proton is shifted markedly to strong field and occupies an intermediate position between the signals of the protons in the 3 and 4 positions. The ability of the furan system to delocalize the positive charge that arises on the exocyclic atom in the α position of the ring is probably manifested here, and that is why the contribution of structure A to the electron density distribution in the cation becomes minimal, and the contribution of structure B increases markedly. Salt I is thus an example of furylium cation C, the charge in which is partially localized on the amino groups, and since in this case X = Z, the preferred drawing of the charge into the ring is due to its delocalization on the furan oxygen atom. The intermediate formation of C cations in many reactions has been frequently discussed [11-13]. Direct physical confirmation of the special

TABLE 1. Properties of Salts I

NR_2	X	mp, °C	λ_{max}, nm	lg ε	$\nu_{C=N}$	$\nu_{C=C}$	$\delta H_{CH=N}$, ppm	δ3H, ppm	δ4H, ppm	$J_{3,4}$, Hz
Piperidyl	Br	196[a]	403	4,89	1672	1612	7,65	7,83	6,20	4,7
The same	I	159—161[b]	403	4,82	1673	1610	7,58	7,80	6,17	4,7
Morpholyl	Br	246[c] (dec.)	403	4,79	1672	1588	—	—	—	—
The same	I	241[d] (dec.)	403	4,80	1670	1607	7,63	7,85	6,20	4,8
$N(CH_3)_2$	Br	191—192[c]	397	4,74	1685	1647	7,85	7,98	6,28	4,5
The same	I	198[c]	397	4,74	1683	1638	—	—	—	—

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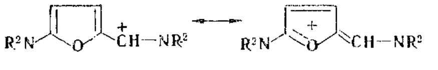
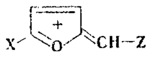
[a] From a mixture of benzene with hexane and PrOH. [b] From a mixture of benzene with hexane. [c] PrOH. [d] From a mixture of PrOH with water.

character of the distribution of the positive charge in the furylium cation has evidently been obtained for the first time.



A B



C

EXPERIMENTAL

The electronic spectra of solutions of the compounds in methanol were recorded with an SF-4A spectrophotometer. The IR spectra of mineral oil pastes were obtained with a UR-20 spectrometer. The PMR spectra of solutions in d_6-DMSO were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

Compounds II were obtained by the method in [8]. The kinetics of the solid-phase disproportionation of aminals II were measured by means of the following method. A sample of crystals of II was stored in a dry nitrogen atmosphere and analyzed for its I content at definite intervals of time. For this, a sample of the substance (~0.002 g) was withdrawn in a stream of nitrogen and dissolved in an amount of absolute propanol that was sufficient for the optical density in the region of extinction of I (~400 nm) to lie in the 0.1 to 1 range; after this, the $D_{\lambda max}$ value was measured, the I content was determined, and the percentage of the II → I transformation was calculated. It has been shown [8] that aminals II are stable in propanol solutions at room temperature for an unrestrictedly long time. Consequently, only salt I, obtained by the solid-phase reaction, is determined by this method.

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