

INTERACTION OF *N*-ALKOXY-*N'*-ARYLUREAS WITH PHENYLGLYOXAL, 2-THIENYLGLYOXAL AND NINHYDRIN

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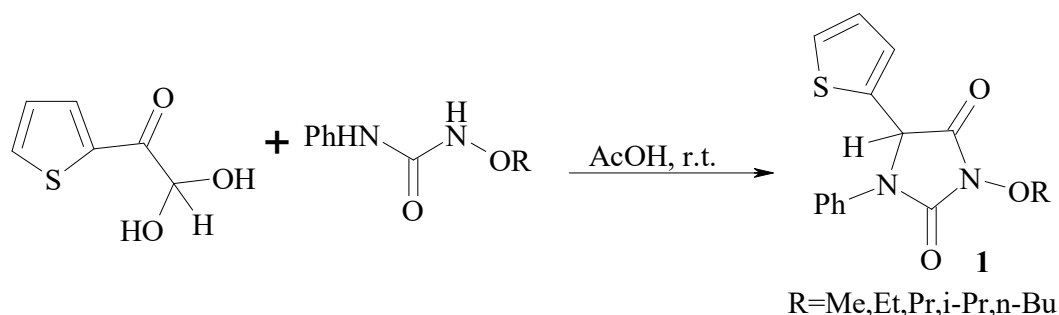
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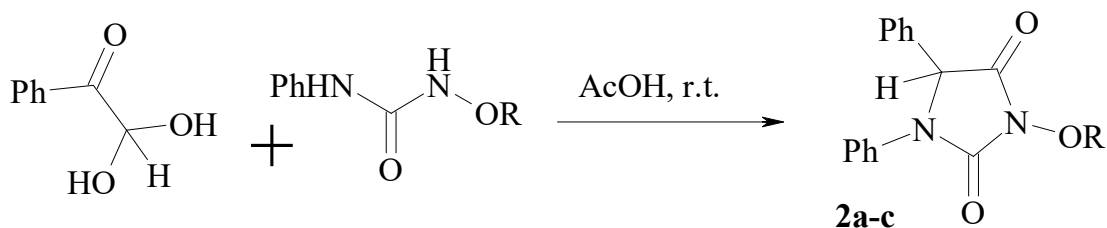
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The relevance of the products which can be obtained by the *N*-alkoxy-*N'*-arylureas interaction with the arylglyoxals and ninhydrin is significant because of the importance of imidazolidin-2-ones and hydantoin among pharmaceutical materials. Aryl glyoxals and ninhydrin are widely used in synthesis of these biologically active nitrogen-containing heterocycles. It is therefore important to create the reaction strategies that give access to such new biological relevant scaffolds.

We had found that 2-thienylglyoxal selectively reacted with *N*-alkoxy-*N'*-phenylureas in acetic acid at room temperature yielding only the unknown 3-alkoxy-1-phenyl-5-(2-thienyl)hydantoin **1**.

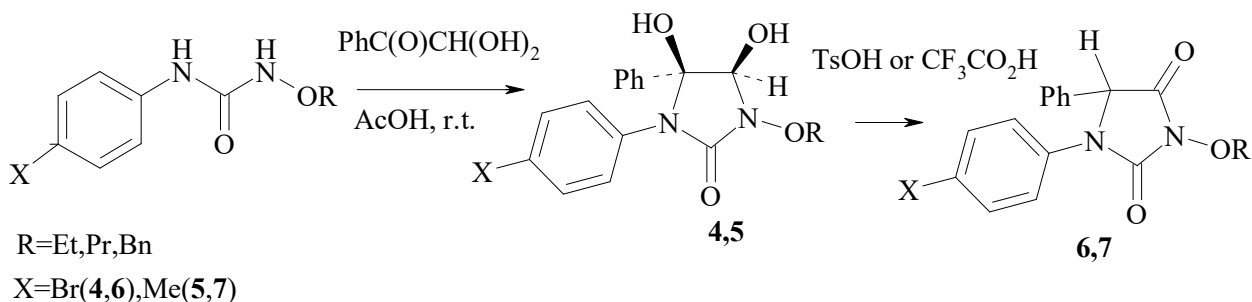
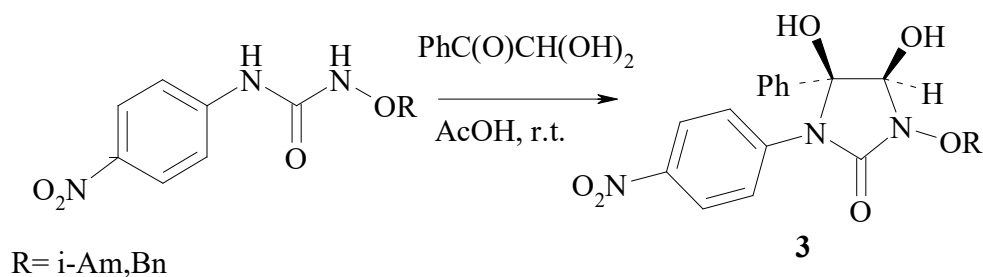


Phenylglyoxal reacts with *N*-alkoxy-*N'*-phenylureas in acetic acid at room temperature in most cases giving only 3-alkoxy-1,5-bis(phenyl)hydantoin **2**.

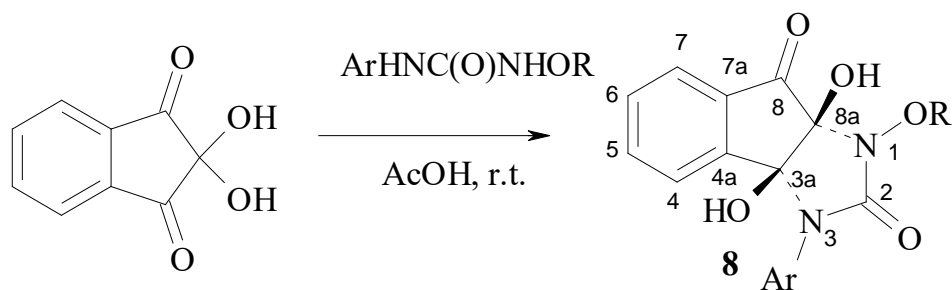


R=Et (a), n-Bu (b), n-C₈H₁₇ (c)

Phenylglyoxal interacts with *N*-alkoxy-*N'*-(4-nitrophenyl)ureas, *N*-alkoxy-*N'*-(4-bromophenyl)ureas, *N*-alkoxy-*N'*-(4-tolyl)ureas in the similar conditions yielding only 3-alkoxy-*cis*-4,5-dihydroxy-1-(4-nitrophenyl)-5-phenylimidazolidin-2-ones **3**, 3-alkoxy-*cis*-4,5-dihydroxy-1-(4-bromophenyl)-5-phenylimidazolidin-2-ones **4** and 3-alkoxy-*cis*-4,5-dihydroxy-1-(4-tolyl)-5-phenylimidazolidin-2-ones **5**, respectively. Compounds **4,5** give hydantoin **6,7** by the TsOH or CF₃COOH action.



We had found that ninhydrin reacted with *N*-alkoxy-*N'*-arylureas in acetic acid at room temperature selectively forming the 1-alkoxy-3-aryl-3a,8a-dihydroxy-1,3,3a,8a-tetrahydroindeno[1,2-*d*]imidazole-2,8-diones **8** [1]. The XRD study of the synthesized compounds **8** has revealed that there is the mutual *cis*-orientation of the C(3a)–OH and C(8a)–OH hydroxyl groups towards to each other. It has also found that the C(3a)–C(8a) and C(8)–C(8a) bonds are some elongated.



$\text{Ar} = \text{C}_6\text{H}_4\text{Me-p}$, $\text{R} = \text{Bu, Me}$
 $\text{Ar} = \text{C}_6\text{H}_4\text{Br-p}$, $\text{R} = \text{Pr, Bu, Bn}$
 $\text{Ar} = \text{Ph}$, $\text{R} = \text{Bn}$

1. Shtamburg V. G.; Shtamburg V. V.; Anishchenko A. A.; Mazepa A.V.; Rusanov E.B. Interaction of Ninhydrin with *N*-alkoxy-*N'*-arylureas and *N*-alkoxy-*N'*-alkylureas. 1-Alkoxy-3-aryl(alkyl)-3a,8a-dihydroxy-1,3,3a,8a-tetrahydroindeno [1,2-*d*]imidazole-2,8-diones: Synthesis and Structure.// J. Mol. Structure. – 2022. – 1248.

LOW BASIC OXIME-FUNCTIONALIZED IMIDAZOLIUM SURFACTANTS: DESIGN, SYNTHESIS AND REACTIVITY IN ORGANOPHOSPHATES DECOMPOSITION

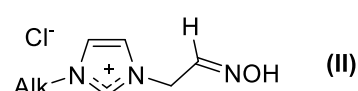
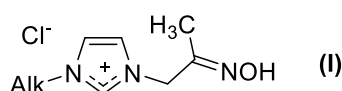
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Oxime-functionalized imidazolium salts (I) and (II) are very efficient reagents for organophosphates decomposition, but disadvantage of these compounds is high basicity of oxime moiety.

Based on analysis of compounds (I, II) structure we have proposed two way of core structure modification: insertion of additional electron acceptor (III) and oxime group relocation (IV). These changes have to help decrease basicity of oxime group.



(I) $pK_a = 10.67$; $k_2 = 0.008 \text{ M}^{-1}\cdot\text{s}^{-1}$ (Alk = CH₃; R = CH₃)

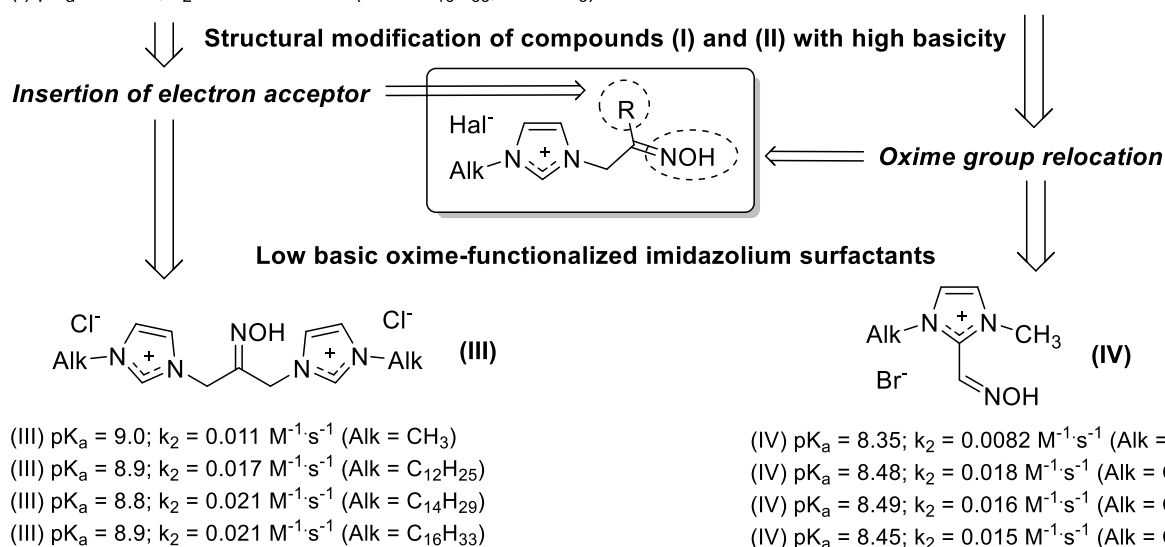
(I) $pK_a = 10.50$; $k_2 = 0.004 \text{ M}^{-1}\cdot\text{s}^{-1}$ (Alk = C₁₂H₂₅; R = CH₃)

(I) $pK_a = 10.60$; $k_2 = 0.006 \text{ M}^{-1}\cdot\text{s}^{-1}$ (Alk = C₁₄H₂₉; R = CH₃)

(I) $pK_a = 10.70$; $k_2 = 0.008 \text{ M}^{-1}\cdot\text{s}^{-1}$ (Alk = C₁₆H₃₃; R = CH₃)

(II) $pK_a = 10.10$; $k_2 = 0.019 \text{ M}^{-1}\cdot\text{s}^{-1}$ (Alk = CH₃; R = H)

(II) $pK_a = 9.94$; $k_2 = 0.025 \text{ M}^{-1}\cdot\text{s}^{-1}$ (Alk = C₁₆H₃₃; R = H)



Series of compounds (III) and (IV) were synthesized and investigated. Compared with initial structures (I, II) the basicity of novel compounds (III) and (IV) were on ca. 1.5 pK_a unit lower. In the same time nucleophilicity (k_2) in decomposition of 4-nitrophenyl diethyl phosphate (Paraoxon®) does not change significantly. These results have demonstrated that both way of structural modification was successful.

1. Zakharova L., Kashapov R., Pashirova T. Selfassembly strategy for the design of soft nanocontainers with controlled properties. *Mendeleev Commun.* 2016. 26 (6): 457. 6

2. Sadovsky Yu., Solomoichenko T., Turovskaya M., Kapitanov I., Piskunova J., Kostrikin M., Prokop'eva T., Popov A. Kapitanov I. Peroxyhydrolysis of 4-nitrophenylethyl-phosphate in micellar systems based on imidazolium dimeric surfactants. *Teoret. and Experim. Chem.* 2012. 48 (2): 112.

3. Shumeiko A., Kostrikin M., Kapitanov I., Serdyuk A., Burakov N., Popov A. Synthesis of surfactants functionalized with oxime groups based on imidazo-la, pyridine and alkylamines // *Ukr. chem. magazine* - 2019. - 85, No. 8. - S. 59-70.

4. Prokopyeva T., Kapitanov I., Belousova I., Shumeiko A., Kostrikin M., Turovskaya M., Razumova N., Popov A. Supernucleophilic systems based on functionalized surfactants in the cleavage of 4-nitrophenolic esters of phosphorus and sulfur acids. III. Reactivity of somicellar systems based on functionalized tetraalkylammonium and imidazolium surfactants. *Russ. J. Org. Chem.* 2015. 51 (8): 1105.