REACTION OF AZOMETHINES WITH ACYL ISOCYANATES IN PRESENCE OF SULFUR DIOXIDE

B. A. Arbuzov, N. N. Zobova, and N. R. Rubinova UDC 542.91:547.794.3:547.239.1

The reactions of the alkyl and aryl isocyanates with azomethines, amidines, and guanidines proceed by the 1,4-dipolar cycloaddition mechanism [1-5]; the reactions of acyl isocyanates with azomethines have not been studied.

Previously [6, 7] it was shown that acyl isocyanates react with azomethines to give cyclic isomers that are 1-acylamino-3,4-diaryl-2-oxo-1,3-diazetidine (II) and 4-oxo-2,3-dehydro-4H-1,3,5-oxazine (III) derivatives, in which connection the ratio of the cyclic isomers depends on the temperature, reaction time, electronic effects of the substituents, and nature of the solvent. The use of polar solvents leads to the formation of 1,3-diacetyl-5,6-diaryl-2,4-dioxohexahydro-1,3,5-triazine (IV) derivatives. On the basis of these data it may be assumed that the reactions of acyl isocyanates with azomethines belong to the class of 1,4-dipolar cycloaddition reactions and proceed by the following scheme



The role of a polar solvent evidently consists of the specific solvation of the 1,4-dipole (I), which increases its life span. Then follows attack by a second isocyanate molecule as a dipolarophile and (IV) is formed.

In order to establish the existence of the 1,4-dipole (I) we studied some three-component reactions in which various reagents fulfill the functions of electrophile and dipolarophile. As the dipolarophile we used SO_2 , while three types of azomethines served as the nucleophilic components of the 1,4-dipole: 1) those that form only (II) with acyl isocyanates, for example, p-diethylaminobenzal-p-methoxyaniline; 2) those that react to give a mixture of the (II) and (III) isomers, for example, p-dimethylaminobenzalaniline and p-diethylaminobenzalaniline; 3) those that are capable of giving only (III) with acyl isocyanates, for example, p-nitrobenzalaniline.

The reactions were run under identical conditions. As the solvent we used absolute diethyl ether, which is capable of solvating electrophilic centers. As a result, the nucleophilic center of the formed 1,4-dipole is suitable for electrophilic attack by SO_2 as the dipolarophile. An ether solution of an equimolar amount of the acyl isocyanate was added to an ether solution of the azomethine and SO_2 was passed in.

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The formation of 2-acyl-4,5-diaryl-3-oxo-1,2,4-thiadiazole 1,1-dioxides (V) and 3-acyl-5,6-diaryl-4-oxo-1,2,3,5-oxathiadiazine 2-oxides (VI) is possible as the result of three-component reactions. The choice between (V) and (VI) in favor of (V) was made on the basis of the IR spectra of the obtained compounds, in which are present the absorption bands of the stretching vibrations of SO₂ at 1135-1170 cm⁻¹ ($\nu_{\rm SSO_2}$) and 1290-1350 cm⁻¹ ($\nu_{\rm as SO_2}$) and of the C=O groups at 1660-1670 cm⁻¹ (cyclic CO) and 1690-1720 cm⁻¹ (acyl C=O). The presence of absorption bands in the 1290-1350 cm⁻¹ region, and the absence of very intense absorption bands in the 1030-1070 cm⁻¹ region, exclude structure (VI)



 $R = p - O_2 N C_6 H_4$, $R^1 = C_6 H_5$, $R^2 = C_6 H_5 (e)$

A polar solvent plays an important role in three-component reactions. Thus, the substituted 1,3-diazetidine [6] was obtained instead of the expected (V) when the reaction of p-nitrobenzal-p-methoxyaniline with trichloroacetyl isocyanate and SO₂ was run in CCl_4 .

EXPERIMENTAL METHOD

The IR spectra were taken as Nujol mulls on a UR-20 instrument.

 $\frac{2-\text{Trichloroacetyl-4-p-methoxyphenyl-5-p-diethylaminophenyl-3-oxo-1,2,4-thiadiazole 1,1-Dioxide}{(Va).}$ To a solution of 0.74 g of p-diethylaminobenzal-p-methoxyaniline in 25 ml of absolute ether was added a solution of 0.49 g of trichloroacetyl isocyanate in 10 ml of absolute ether, after which SO₂ was passed in until orange crystals were obtained, which were filtered, and repeatedly washed with CCl₄ and absolute ether. We obtained 0.86 g (66%) of (Va), mp 75-80° (decompn.). Found: C 47.71; H 4.00; N 8.22%. C₂₁H₂₂O₅N₃Cl₃S. Calculated: C 47.57; H 3.96; N 8.32%.

<u>2-Benzoyl-4-phenyl-5-dimethylaminophenyl-3-oxo-1,2,4-thiadiazole 1,1-Dioxide (Vb)</u>. To a solution of 0.07 g of p-dimethylaminobenzalaniline in 15 ml of absolute ether was added in drops a solution of 1.07 g of benzoyl isocyanate in 25 ml of ether, after which SO₂ was passed in until yellow-orange crystals were obtained, which were filtered and washed with CCl₄. We obtained 1.8 g (60%) of (Vb), mp 145-150° (decompn.). Found: C 63.32; H 4.84; N 9.60; S 6.84%. C₂₃H₂₁N₃O₄S. Calculated: C 63.44; H 4.83; N 9.60; S 7.15%.

 $\frac{2-\text{Benzoyl-4-phenyl-5-diethylaminophenyl-3-oxo-1,2,4-thiadiazole 1,1-Dioxide (Vd).}{\text{In a similar manner, from 1.17 g of p-diethylaminobenzalaniline, 0.72 g of benzoyl isocyanate, and SO₂ we obtained 1.36 g (72%) of (Vd), mp 65-70° (decompn.). Found: C 64.80; H 5.77; N 8.93%. C₂₅H₂₅N₃O₄S. Calculated: C 64.79; H 5.39; N 9.07%.$

CONCLUSIONS

The reactions of acyl isocyanates with azomethines belong to the class of 1,4-dipolar cycloaddition reactions. Substituted 3-oxo-1,2,4-thiadiazole 1,1-dioxides were obtained as the result of three-component reactions in the presence of SO_2 .

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