



**STUDY OF THE REACTION OF N-2,2-DICYANOETHINYLSULFONAMIDES
WITH 1,3-DIOXY COMPOUNDS. SYNTHESIS OF 2-
AMINOPYRANOSULFONAMIDES**

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ABSTRACT

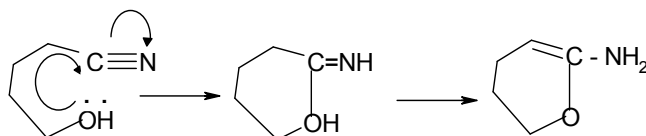
The influence of sulfamide group on the heterocyclization reaction of N-2,2-dicyanoethinylsulfonamide with dimedone, acetylacetone and resorcin was investigated. It was established that as a result of the reaction with high yield 2-aminopyranosulfonamides, which are potential biologically active substances, are formed.

KEYWORDS: *aminopyranosulfonamides, N-2,2-dicyanoethinylsulfonamide, dimedone, acetylacetone, resorcin*

INTRODUCTION

Amino-pyranes take significance importance in organic chemistry, since they are of particular interest for producing new medicinal preparations, pesticides, analogues of natural products and dyestuffs. They can be easily modified to organic compounds of different classes (arenes, azines), which are hardly synthesized by other methods. General questions on conversions of pyranes and pyrylium salts were widely highlighted in the reviews [I – III], but the data on 2-aminopyranosulfonamides were presented with examples.

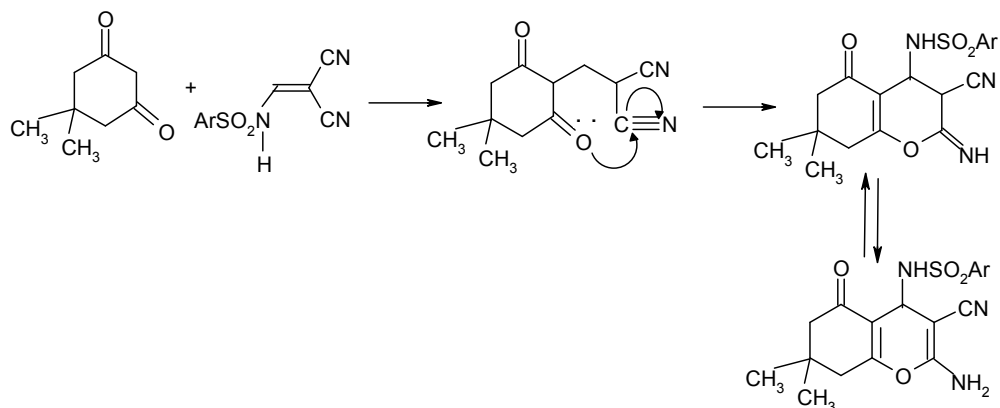
The main methods of producing 2-aminopyranes are based on intramolecular cyclization of δ -oxy- or δ -oxonitriles of type:



As a result of interaction of nucleophilic center (oxygen atom) with electrophilic center of nitrile group the formation of pyranes occurs. Interaction of dimedone [IV, VI] and active phenols should be related to the considered type of reactions: resorcin [VII], aminophenols [VIII] and others.

2-Formyldimedone reacts with malononitrile forming the mixture of 2-aminopyrane and 2 (H) pyridone with yields of 79 % and 20 % correspondingly [IX].

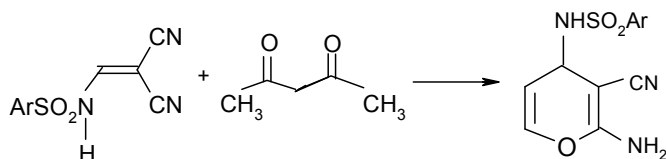
The effect on the reaction of sulfamide group of compounds with dimedone and resorcin has not been studied yet. We studied the reaction of N-2,2-dicyanoethynylsulfonamide with dimedone in the presence of morpholinium:



1a – v

Ar = C₆H₅ (**1a**), 4-CH₃C₆H₄ (**1b**), 4-CH₃OC₆H₄ (**1v**)

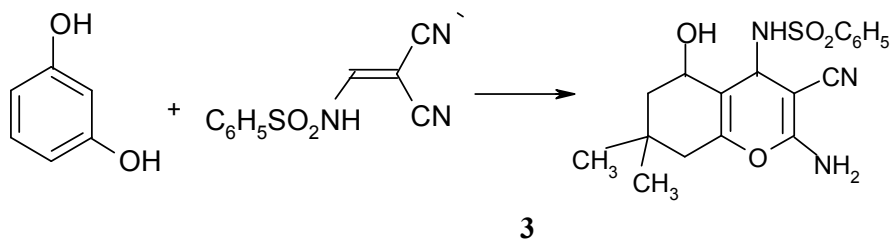
N-2,2-Dicyanoethynylarenesulfonamides with acetylacetone also form 2-aminopyranes:



2 a, b

Ar = C₆H₅ (**2a**), 4-CH₃C₆H₄ (**2b**)

2-Aminopyranes can be also synthesized by resorcin:



3

EXPERIMENTAL

Chemistry

2-Amino-4-arenesulfonamidepyranes (I – III). General method. 20 mol of dimedone (or acetylacetone, or resorcin) and 20 mol of N-2,2-dicyanoethynylarenesulfonamide were dissolved in 50 ml of absolute ethanol and 3 – 4 drops morpholinium was added. The mixture was boiled 2 hours; the precipitate was filtered and recrystallized from ethanol.

RESULTS AND DISCUSSION

In IR spectra of pyranes we observed a separate set of signals which confirm valence vibrations of functional groups (ν , cm^{-1}): 1380 – 1410 and 1140 – 1160 (SO_2N), 3420 – 3450 (NH_2), 2205 – 2210 (CN), 1700 – 1720 (C=O), 3520 (OH-phenol).

The compound (Ia). Yield 69.8%, melt.t. 314.5 – 315 °C. Found, %: C 58.29; H 5.13; N 11.64; S 8.93. $\text{C}_{18}\text{H}_{18}\text{N}_3\text{O}_4\text{S}$. Calculated, %: C 58.02; H 4.87; N 11.33; S 8.64.

The compound (Ib). Yield 71.2%, melt.t. 312 – 313 °C. NMR spectrum ^1H , δ , m.d.: 1.6 (2 CH_3), 2.1 (CH_3), 2.5 – 2.8 (2 CH_2), 6.39 d (NH_2), 7.6 c (CH). Found, %: N 11.25; S 8.42. $\text{C}_{19}\text{H}_{20}\text{N}_3\text{O}_4\text{S}$. Calculated, %: N 10.92; S 8.29.

The compound (Iv). Yield 61.2%, melt.t. 219 – 220 °C. Found, %: N 10.71; S 8.25. $\text{C}_{19}\text{H}_{20}\text{N}_3\text{O}_5\text{S}$. Calculated, %: N 10.48; S 7.96.

The compound (IIa). Yield 68.5%, melt.t. 332 – 333 °C. NMR spectrum ^1H , δ , m.d.: 2.1 – 2.5 (2 CH_3), 6.4 d (NH_2), 6.8 d (SO_2NH), 7.6 – 7.71 (5Hapom.). Found, %: N 14.82; S 11.13. $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_4\text{S}$. Calculated, %: N 14.34; S 10.90.

The compound (IIb). Yield 67.9%, melt.t. 285 – 286 °C. Found, %: N 13.26; S 10.14. $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_5\text{S}$. Calculated, %: N 13.04; S 9.91.

The compound (III). Yield 69.5%, melt.t. 312 – 313 °C. NMR spectrum ^1H , δ , m.d.: 6.4 d(2H, NH_2), 7.3 d (1H, NH), 7.7 c (OH), 7.8 – 8.4 (one- and trisubstituted aromatics). Found, %: N 12.59; S 9.63. $\text{C}_{16}\text{H}_{12}\text{N}_3\text{O}_4\text{S}$. Calculated, %: N 12.32; S 9.36.

IR-spectra of the compounds were registered on spectrometer NicoletIS-10.

NMR ^1H -spectra of the compounds were taken on spectrophotometer Tesla-467 with operating frequency of 90 MHz in solution CDCl_3 .

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