# SYNTHESIS OF β-DIKETONES OF THE FURAN AND THIOPHENE SERIES

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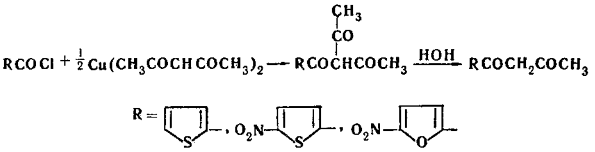
UDC 547.733+547.724

A method for obtaining β-diketones of the furan and thiophene series by acylation of cupric acetylacetonate with 5-nitro-2-furoyl, 2-thenoyl, and 5-nitro-2-thenoyl chlorides was developed.

The literature contains little information regarding methods for obtaining β-diketo compounds of the furan and thiophene series. The existing methods are rather difficult to carry out, involve many steps, and do not lead to high yields. Thus, for example, the yields of 2-furoylacetone do not exceed 45% [1, 2], and those of 2-thenoylacetone are also low [3, 4].

β-Diketo compounds of the 5-nitrofuran and 5-nitrothiophene series are even less accessible. Attempts to obtain them by the Claisen method do not give positive results because of resinification of the reaction products in alkaline media. (5-Nitro-2-furoyl)acetone was obtained by acylation of 5-nitro-2-acetylfuran with acetic anhydride in the presence of $BF_3$ complexes [5], while (5-nitro-2-thenoyl)acetone has not been previously obtained.

In this paper we propose a new method for obtaining β-diketones of the furan and thiophene series and of their 5-nitro derivatives. Copper chelates have recently begun to be used not only to isolate and purify diketones but also in organic synthesis [6]. Our investigations have indicated that cupric acetylacetonate is satisfactorily acylated by acyl chlorides of the furan and thiophene series. The reaction for obtaining the β-diketones proceeds through the formation of triketones which, without isolation from the reaction mixture, are deacetylated on heating in the presence of acidic or alkaline agents to form the corresponding diketones.



$$RCOCl + \tfrac{1}{2}Cu(CH_3COCHCOCH_3)_2 \longrightarrow RCO\underset{}{\overset{\overset{CH_3}{|}\,CO}{\overset{|}{C}}}HCOCH_3 \xrightarrow{HOH} RCOCH_2COCH_3$$

The yields of the diketones reach 62-85% when this method is used.

The β-diketones obtained were converted to the corresponding 5-(3-thienyl)- and 5-(3-furyl)pyrazoles and their nitro derivatives by condensation with hydrazine.

## EXPERIMENTAL

2-Thenoylacetone (I). 2-Thiophenecarboxylic acid chloride (5 g) in 45 ml of dry chloroform was added to 9 g of cupric acetylacetonate (obtained via the method in [7]), dissolved in 80 ml of dry chloroform, and the mixture was stirred at room temperature for 14-16 h. The resulting cupric chloride was filtered, the chloroform was removed, and 3-N ammonium hydroxide was added to the residue until a neutral reaction was obtained. Dilute (~0.2-N) sulfuric acid (10 ml) was added, and the mixture was heated for 1.5-2 h

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N. G. Chernyshevskii Saratov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1452-1453, November, 1970. Original article submitted July 18, 1969.

at 75-80°C. The diketone was extracted with ether, and the extract was dried with $Na_2SO_4$. The ether was removed, and the residue was distilled in vacuo at 125-128° (4 mm) to give 4.2 g (74%) of I. Literature data: bp 129-131° (8 mm), 57% yield [3], 21.4% yield [4].

(5-Nitro-2-thenoyl)acetone (II). This was obtained by the method described for the preparation of I; 13% aqueous sodium acetate (77 ml) was used for the deacetylation. The reaction mixture was heated for 1 h at 80° and then allowed to stand at room temperature for several hours, during which the crystalline diketone precipitated. Cupric acetylacetonate (6.2 g) and 5 g of 5-nitrothenoyl chloride yielded 3.4 g (62%) of II in the form of dark-brown crystals with mp 122-123.5° (from ethanol). The crystals were soluble in benzene, dimethylformamide, and methanol. Found %: C 45.42; H 3.51; N 6.50. $C_8H_7NO_4S$. Calculated %: C 45.09; H 3.31; N 6.56.

(5-Nitro-2-furoyl)acetone (III). This compound [4.3 g (85%)] was obtained, in the same way as II, from 7.6 g of cupric acetylacetonate and 5 g of 5-nitrofuroyl chloride in the form of brown crystals with mp 112-114°. According to [5], III was obtained in 73% yield and had mp 112-113.5°.

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