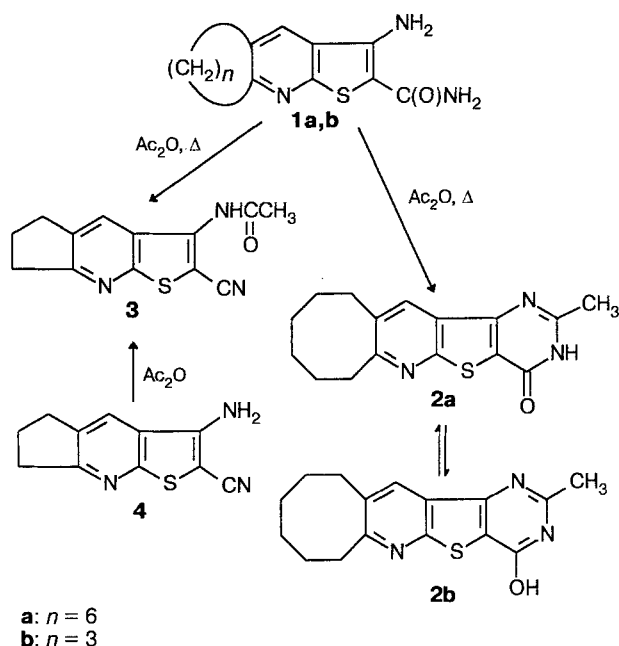


Scheme 1



IR spectra of the compounds were recorded on UR-20 and Perkin Elmer-457 spectrophotometers in KBr pellets. ^1H NMR spectra were obtained on a Bruker WM-250 spectrometer (250 MHz, DMSO- d_6 , TMS as the internal standard). The purity of the compounds obtained was monitored by TLC on Silufol-254 plates in

the acetone—heptane system (3:5). The chromatograms were visualized by iodine vapors.

A mixture of substituted pyridine **1a** (0.28 g, 0.001 mol) and acetic anhydride (10 mL) was refluxed for 1 h and cooled, then water (5 mL) was added. The residue was filtered off and washed with water, ethanol, and hexane to give 0.08 g (28 %) of compound **2**, m.p. > 300 °C. Found (%): C, 64.9; H, 5.2; N, 13.8; S, 10.7. $\text{C}_{16}\text{H}_{17}\text{N}_3\text{OS}$. Calculated (%): C, 64.5; H, 5.7; N, 14.0; S, 10.5. IR (KBr), ν/cm^{-1} : 1670 (δNH); 1720 (CO); 3268 (NH). ^1H NMR (DMSO- d_6), δ : 1.33 (m, 4 H, C(7) H_2 , C(8) H_2); 1.74 (m, 4 H, C(6) H_2 , C(9) H_2); 2.50 (s, 3 H, CH_3 in tautomer **b**); 2.54 (s, 3 H, CH_3 in tautomer **a**); 2.96 (m, 2 H, C(5) H_2); 3.07 (m, 2 H, C(10) H_2); 8.05 (s, H, C(4)H in tautomer **a**); 8.28 (s, H, C(4)H in tautomer **b**); 10.62 (s, H, OH); 12.76 (s, H, NH).

Similarly, product **3** was obtained from compounds **1b** or **4** in 57 or 78 % yield, respectively, m.p. 272–274 °C. Found (%): C, 60.9; H, 4.5; N, 15.9; S, 12.7. $\text{C}_{13}\text{H}_{11}\text{N}_3\text{OS}$. Calculated (%): C, 60.7; H, 4.2; N, 16.3; S, 12.4. IR (KBr), ν/cm^{-1} : 1678 (δCONH); 2216 (CN); 3236 (CONH); 3432 (br, NH). ^1H NMR (DMSO- d_6), δ : 2.15 (m, 2 H, C(6) H_2); 2.21 (s, 3 H, CH_3); 3.03 (q, 4 H, C(5) H_2 , C(7) H_2); 8.13 (s, H, C(4)H); 10.68 (s, H, NH).

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Unusual insertion of product the reaction of 3,3-dichloropentanedione with aromatic aldehydes

V. A. Mamedov,^{a*} E. A. Berdnikov,^b I. A. Litvinov,^a and F. G. Sibgatullina^a

^aA. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.

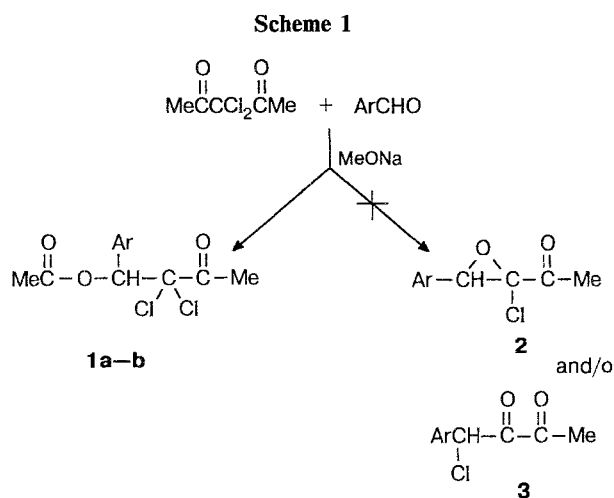
Fax: +7 (843) 275 2253

^bV. I. Ulyanov-Lenin Kazan' State University, 420008 Kazan', Russian Federation.

Fax: +7 (843) 238 0122

In the reaction of 3,3-dichloropentanedione with aromatic aldehydes under the conditions of alkali catalysis 4-acetoxy-4-aryl-3,3-dichloro-2-butanones (**1**)

which are the products of the insertion of aromatic aldehydes into 3,3-dichloropentanedione at C₂—C₃, are formed, and not the expected α -chloroepoxides (**2**)



(100 mL) with stirring in an argon atmosphere. The temperature of the reaction mixture was increased to 20 °C and then the mixture was refluxed for 1 h. 4-Acetoxy-3,3-dichloro-4-phenyl-2-butanone (**1a**) was isolated. Yield 33 %, b.p. 122–130 °C (0.06 Torr), m.p. 38–40 °C. Found (%): C, 52.79; H, 4.44; Cl, 25.85. $\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{O}_3$. Calculated (%): C, 52.39; H, 4.40; Cl, 25.77; IR (vaseline oil), ν/cm^{-1} : 800, 945, 1030, 1050, 1230, 1370, 1460, 1500, 1730, 1760, 3045, 3065. ^1H NMR (CCl_4), δ : 7.60–7.00 (m, 5 H, C_6H_5); 6.25 (s, 1 H, CH); 2.40 (s, 3 H, CH_3CO); 1.96 (s, 3 H, CH_3COO). ^{13}C NMR (CCl_4 , external standard C_6D_6 + HMDS), δ : 194.7 (CO); 168.3 (COO); 134.9 (C_i); 130.3 (C_o); 128.7 (C_m); 130.0 (C_p); 89.3 (CCl_2); 77.34 (CH); 25.2 (CH_3COO); 21.3 (CH_3CO); by similar procedure from *p*-MeO- $\text{C}_6\text{H}_4\text{CHO}$ and *p*-O $_2\text{N}$ - $\text{C}_6\text{H}_4\text{CHO}$ **1b** (53 %) and **1c** (11 %) were obtained.

and(or) α -chloroketones (**3**)¹ (Scheme 1).

MeONa powder (0.1 mol) was added at $-15 \div -10$ °C to a solution of 3,3-dichloropentan-2-one (0.1 mol) and benzaldehyde (0.1 mol) in absolute ether

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Formation of a complex with the anionic quinoid structure in the interaction of 3-(3',5'-di-*tert*-butyl-4'-hydroxybenzylidene)-pentanedione-2,4 with copper(II) acetate

I. A. Zav'yalov, E. R. Milaeva,* and A. I. Prokof'ev

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

It is known that β -diketones in the non-enolized form are capable of forming complexes with various metal ions.¹ Cu, Co, and Zn complexes of 3-(benzylidene)acetylacetone described recently² are stable due to the presence of a developed conjugation chain in their molecules. We have studied the interaction of $\text{Cu}(\text{OAc})_2$ in EtOH with 3-(3',5'-di-*tert*-butyl-4'-hydroxybenzylidene)pentanedione-2,4 (**1**),³ which exists as two tautomeric forms in solution (Scheme 1).

It might be thought that the reaction would go in two main directions to yield compounds **2** and **2a**, but the only product was 3-(3',5'-di-*tert*-butylmethylenequinonyl-4') copper acetylacetonate **2a**.

In the IR spectrum of compound **2a** there are absorption bands corresponding to valent vibrations of the C=O bond of the quinoid group and of the enolized form of β -diketone.

The parameters of the anisotropic ESR spectrum of compound **2a** are also in good agreement with the literature data⁴ for copper(II) acetylacetonate. The correlation of the g -factors observed for compound **2a** points to tetragonal or distorted tetrahedral geometry. The increased g_{\parallel} and degreased a_{\parallel} relative to copper acetylacetonate indicate pseudo-tetrahedral distortions in the structure of complex **2a** (Table 1).

Thus, of the two possible routes of the complexation