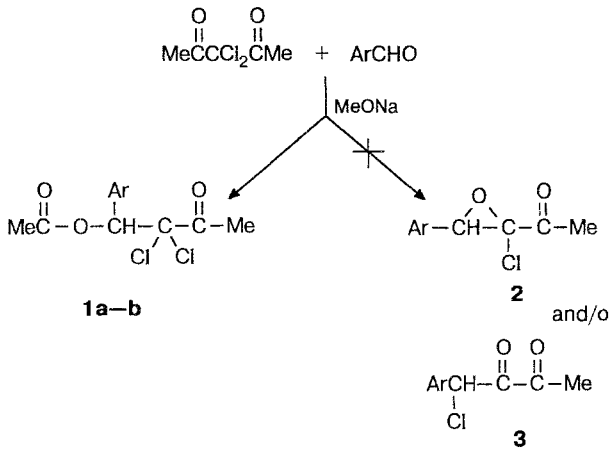
Scheme 1



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

MeONa powder (0.1 mol) was added at −15÷−10 °C to a solution of 3,3-dichloropentanedione (0.1 mol) and benzaldehyde (0.1 mol) in absolute ether (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; C, 25.85. $C_{12}H_{12}Cl_2O_3$. 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. ^{1}H NMR (CCl_4), δ: 7.60—7.00 (m, 5 H, C_6H_6); 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 ($\underline{C}H_3COO$); 21.3 ($\underline{C}H_3CO$); by similar procedure from *p*-MeO—C_6H_4CHO and *p*-O_2N—C_6H_4—CHO **1b** (53 %) and **1c** (11 %) were obtained.

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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 recently[2] are stable due to the presence of a developed conjugation chain in their molecules. We have studied the interaction of $Cu(OAc)_2$ 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*-butylmethylene-quinonyl-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 data[4] for copper(II) acetylacetonate. The correlation of the *g*-factors observed for compound **2a** points to tetragonal or distorted tetrahedral geometry. The increased $g_{\|}$ and degreased $a_{\|}$ 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

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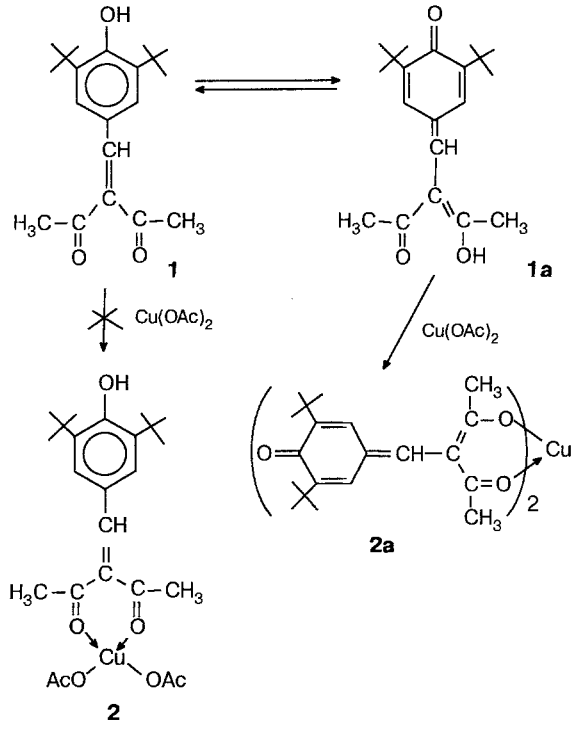

reaction, the formation of the anionic acetylacetonate structure proved to be preferable than coordination of the metal atom with β-diketone by a neutral type.

It is important to point out that the application of the ESR method ascertained the absence of any interactions between the free radicals generated by single-electron oxidation of the phenol fragment of ligand **1**, and the copper(II) ions (both independent paramagnetic species can be registered by ESR spectra). This indicates that the formation of the enolized form of β-diketone **1a** does not include oxidation and complex **2a** does arise from the tautomeric conversion of the ligand.

Table 1. Parameters of anisotropic EPR spectra of compound **2a** and copper acetylacetonate (EtOH, 77 K)

Compound	$g_{\parallel}$	$g_{\perp}$	$a_{\parallel}$/G	$a_{\perp}$/G
Complex **2a**	2.281	2.063	167	22
Copper acetylacetonate	2.253	2.057	183	23

UV spectrum of compound **2a** (DMFA), λ_{max}/nm: 259.6; 331.8; 640. IR spectrum of compound **2a** (suspension in vaselin): multiplet, ν 1590—1640 cm^{-1}.

The characteristics of compound **2a**: b.p. 128—129 °C. Found (%): C, 69.41; H, 8.03; Cu, 9.08. $C_{40}H_{54}O_6Cu$. Calculated (%): C, 69.21; H, 7.79; Cu, 9.16.

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