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COMMUNICATION

PREPARATION OF TRANSITION METAL COMPLEXES OF CHIRAL DERIVATIVES OF ACETOACETIC ACID. TETRAALKYLAMMONIUM TETRACHLOROMETALLATES AS AN ORGANIC SOURCE OF METALS

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Abstract—Bis(benzyltrimethylammonium) tetrachlorocuprate, tetrachlorocobaltate and hexachlorodiferrate react in organic solvents with alkaline salts of $CH_3COCH_2CO\text{-}X_c$ [X_c-H = (*d*)-menthol, (4*S*)-4-benzyl-2-oxazolidinone and (2*R*)-bornane-10,2-sultam] to give homochiral β-dicarbonyl metal complexes.

Enantioselective synthesis induced by transition metal homochiral complexes is a research field of high interest.[1] However, the preparation and catalytic use of complexes of homochiral β-dicarbonyl compounds is scarcely represented in the chemical literature.[1] This is probably due to the difficulty of preparing transition metal complexes of β-dicarbonyl compounds other than simple diketones or ketoesters. In part, this difficulty comes from the fact that ligands are normally soluble in organic phase whereas the metals are introduced as water soluble ionic inorganic salts. The use of trimethylsilyl ethers and of lithium and caesium enolates of β-dicarbonyl compounds has been recommended for the synthesis of certain complexes which are difficult to prepare, including the cobalt(II) complex of (*l*)-menthyl acetoacetate (enantiomer of **8**).[2]

We have developed methods to alkylate β-diketones and β-ketoesters with unusual alkyl halides by means of the cobalt(II) and copper(II) complexes.[3] When in continuation of our research we required metal complexes of homochiral acetoacetic acid derivatives, we were confronted with the above mentioned problem. We want to present in this communication a preparation of difficultly accessible metal complexes of β-dicarbonyl compounds that is based on previous work by Everett and Holm who used bis(tetraalkylammonium) tetrahalogenometallates as metal sources for the preparation of the metal complexes of several α,β-unsaturated β-ketoenamines.[4]

(*d*)-Menthyl acetoacetate, **1**, (4*S*)-*N*-acetoacetyl-4-benzyloxazolidin-2-one, **2**, and *N*-acetoacetyl-(2*R*)-bornane-10,2-sultam, **3**, were prepared by reaction of 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (diketene acetone adduct) with (*d*)-menthol, (4*S*)-benzyloxazolidin-2-one or (2*R*)-bornane-10,2-sultam (Oppolzer sultam).[5] This method is superior to the use of diketene that has been used before to prepare similar products.[6,7]

Bis(benzyltrimethylammonium) tetrachlorocuprate, **4**, tetrachlorocobaltate, **5**, and hexachlorodiferrate monohydrate, **6**, were chosen as metal sources due to their reasonable solubility in organic solvents and because after some experimentation we noticed that benzyltrimethylammonium was superior to other quaternary ammonium cations. Salts **4**–**6** are easily prepared by mixing benzyltrimethylammonium chloride with hydrated copper(II), cobalt(II) or iron(II) chloride in ethanol and filtration.

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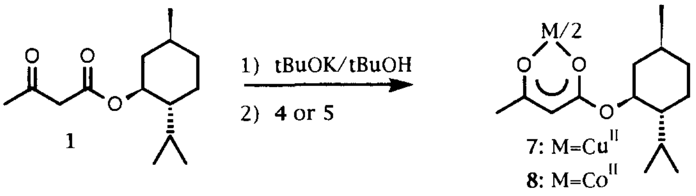
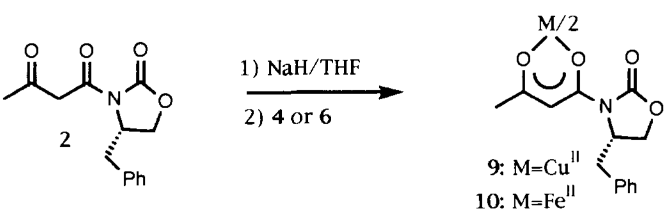
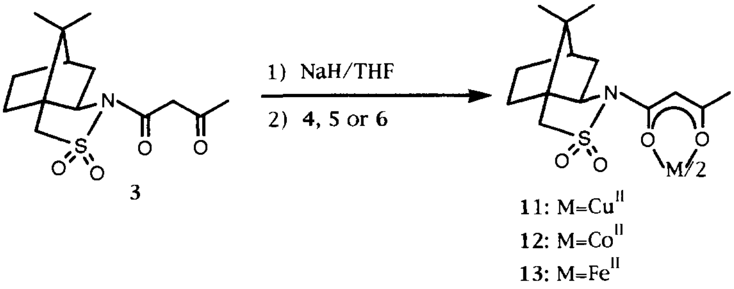
$$CuCl_2 + 2Cl^- \ PhCH_2N^+Me_3 \longrightarrow \underset{\mathbf{4}}{[Cl_4Cu]^{-2}[PhCH_2NMe_3]_2^{+1}}$$

$$CoCl_2 + 2Cl^- \ PhCH_2N^+Me_3 \longrightarrow \underset{\mathbf{5}}{[Cl_4Co]^{-2}[PhCH_2NMe_3]_2^{+1}}$$

$$2FeCl_2 + 2Cl^- \ PhCH_2N^+Me_3 \longrightarrow \underset{\mathbf{6}}{[Cl_6Fe_2]^{-2}[PhCH_2NMe_3]_2^{+1} \ H_2O}$$







Generation of the potassium enolate of **1** with potassium tert-butoxide in tert-butanol followed by addition of either **4** or **5** afforded complexes **7** and **8**. Complexes **9** and **10** were better prepared by generation of the sodium enolate of **2** with sodium hydride in THF followed by addition of either **4** or **6**. The same method was used to prepare complexes **11–13** from **3**.

EXPERIMENTAL

Typical procedures

Copper complex of (d)-*menthyl acetoacetate*, **7**. To a solution of potasium tert-butoxide (1.027 g, 9.15 mmol) in anhydrous tert-butanol (25 cm^3) was added, at 60°C under argon and with vigorous stirring, a solution of (*d*)-menthyl acetoacetate, **1** (2.00 g, 8.32 mmol), in tert-butanol (5 cm^3). The mixture was kept under those conditions for 35 min and then the salt **4** (2.149 g, 4.25 mmol) was added at once. The mixture was stirred at 60°C for 2.5 h. After cooling at room temperature diethyl ether (20 cm^3) was added. Upon cooling a precipitate was formed and filtered off. The filtrate was evaporated and diethyl ether (50 cm^3) was added to the residue; the insoluble solid was filtered off and the filtrate was evaporated to dryness. The residue was taken in chloroform, the solution was dried with sodium sulfate and evaporated to give a foam that solidified *in vacuo* becoming a green solid (2.115 g, 93%) which was recrystallized from dichloromethane/hexanes: m.p. 114–115°C (dichloromethane/hexanes); IR(KBr): 1590, 1517, 1290 cm^{-1}; $[\alpha]_D = +76°$ (c, 1.00; $CHCl_3$). Found: C, 62.2; H, 8.6. Calc. for $C_{28}H_{46}CuO_6$: C, 62.2; H, 8.5%.

Copper complex of (4S)-N-*acetoacetyl*-4-*benzyloxazolidin*-2-*one*, **9**. To a stirred mixture of 60% sodium hydride in mineral oil (0.44 g, 9.19 mmol) and anhydrous THF (20 cm^3) was added dropwise at room temperature and under argon a solution of (4*S*)-*N*-acetoacetyl-4-benzyloxazolidin-2-one, **2**, (2.00 g, 7.65 mmol) in anhydrous THF (20 cm^3). After a few minutes the bubbling of hydrogen ceased and then the salt **4** (2.90 g, 5.74 mmol) was added at once. The mixture was stirred for 12 h and then filtered. The filtrate was evaporated to dryness and diethyl ether was added. The insoluble material was filtered off to afford product **9** (1.79 g, 80%): m.p. 230–232°C (washed with diethyl ether); IR (KBr): 1780, 1574, 1508, 1383, 1348, 1312, 1194 cm^{-1}; $[\alpha]_D = -109°$ (c, 1.00; $CHCl_3$). Found: C, 57.6; H, 4.8; N, 4.8. Calc. for $C_{28}H_{28}CuN_2O_8$: C, 57.6; H, 4.8; N, 4.8%.

Physical constants of products

1:[5] 94%, b.p. 101–102°C/0.1 mmHg, $[\alpha]_D = +140°$ (c, 1.055; $CHCl_3$); **2**:79% m.p. 97–98°C (hexanes), $[\alpha]_D = +64°$ (c, 1.00; $CHCl_3$), (C, H, N); **3**: 83%, m.p. 79–82°C (ethyl acetate/hexanes), (Lit.[8] m.p. 78–81°C), $[\alpha]_D = -77°$ (c, 1.06; $CHCl_3$); **4**: 84%, m.p. 169–170°C (tetrachloromethane), (C, H, Cl, N); **5**: 76%, m.p. 178–179°C (tetrachloromethane), (C, H, N); **6**: 45%, m.p. 136–137°C (methanol/diethyl ether), (C, H, N); **7**: 93%, m.p. 114–115°C (dichloromethane/hexanes), $[\alpha]_D = +76°$ (c, 1.00; $CHCl_3$), (C, H); **8**: 87%, m.p. 108–110°C (dichloromethane/hexanes), $[\alpha]_D = +97°$ (c, 1.00; $CHCl_3$), (C −1.18, H). A m.p. 87–89°C is reported in ref. 2 for the enantioisomer of **8** crystallized with two molecules of methanol; **9**: 80%, m.p. 230–232°C (washed with diethyl ether), $[\alpha]_D = -109°C$ (c, 1.00; $CHCl_3$), (C, H, N); **10**: 65%, m.p. 165–170°C (washed with diethyl ether), $[\alpha]_D = +85°$ (c, 1.00; $CHCl_3$), (C +1.05, H, N); **11**: 44%, m.p. 145–150°C (ethyl acetate/hexanes), $[\alpha]_D = +56°$ (c, 1.53; $CHCl_3$), (C, H, N); **12**: 34%, m.p. 188–190°C (washed with diethyl ether), $[\alpha]_D = -255°$ (c, 1.59; $CHCl_3$), (C, H, N as monohydrate); **13**: 47%, m.p. 222–223°C (dichloromethane/hexanes), $[\alpha]_D = -342°$ (c, 1.54; $CHCl_3$), (C, H, N).

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