Copper Complexes of Heptan-2, 4, 6-triones*

Fumio SAGARA, Hiroshi KOBAYASHI and Keihei UENO

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka

(Received October 14, 1967)

Heptan-2, 4, 6-trione [H_2A] (I),[1] which was for the first characterized by Feist,[2] behaves as a bidentate or a terdentate ligand, depending upon the degree of enolization, to give a mononuclear 1 : 2 (metal : ligand) complex as well as a dinuclear 2 : 2 complex with a metal ion forming a square planer coordination. The degree of enolization of I seems to increase at a higher temperature in a less polar solvent.

Here we present some interesting behaviors of I upon complex formation with cupric ion. A blue mononuclear copper complex [$Cu(HA)_2 \cdot 2H_2O$] (II) precipitates when an aqueous cupric acetate is added into a methanolic solution of I at about 0°C. Found: C, 43.75; H, 6.09; Cu, 16.4%. Calcd: C, 43.80; H, 5.81; Cu, 16.6%. When the preparation is carried out at about 30°C, a green dinuclear complex [Cu_2A_2] (III) is obtained. Found: C, 41.41; H, 3.89; Cu, 31.0%; mol wt (Vapor Pressure Osmometer), 411.7. Calcd: C, 41.27; H, 3.96; Cu, 31.2%; mol wt, 407.4.

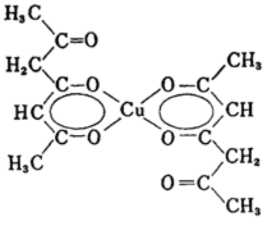
The complex III shows a multiplet absorption between 1500 and 1600 cm^{-1} ascribable to ethylenic bonds and coordinated carbonyl groups. In addition to those, in the case of II, a free carbonyl band at 1715 cm^{-1}, an enolic hydroxy band at 3530 cm^{-1} and a sharp absorption at 795 cm^{-1} of coordinated water are observed together with a broad band extending from 3200 to 3500 cm^{-1}.

The complex II dissolves in methanol, acetone and chloroform to some extent as long as the solution being kept at low temperature, while III dissolves only in pyridine, affording a pyridine adduct; two pyridine molecules bound to III [$Cu_2A_2 \cdot 2Py$].

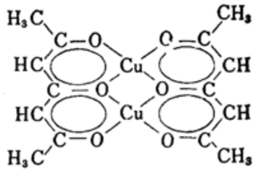
The solid complex II transforms into III at about 80°C under reduced pressure, liberating an excess of the ligand. The same is observed when the methanolic solution of II is heated at its boiling point. On the other hand, the complex III in pyridine changes into II in the presence of a large excess of the ligand, when the solvent is removed at 0°C under reduced pressure. The observed transformations seem to indicate that III is stable at an elevated temperature, while II prefers a lowered temperature, and that the conversion from one to the other is reversible.

Alkylation of 3- and 5-carbon atoms of I affords the ligands which have the similar chelating tendencies for copper ion. Alkylation are carried out by treating a disodium salt of I with a little more than two moles of alkyl iodide in ethanol, to give a monomethyl- (IV) and a dimethyl triketone (V), mp 82.5—83.5°C (Found: C, 63.23; H, 8.54%. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29%), with methyl iodide, and with *n*-propyl iodide only a mono-*n*-propyl derivative (VI). The triketones IV and VI were characterized as copper complexes, which are best fractionated by column chromatography on silica gel. The copper complexes of the alkylated triketones are again 2 : 2 dinuclear as well as 1 : 2 mononuclear, and the latter structure seems to be enough stable even at room temperature; it gives usually a mononuclear complex alone at room temperature and, in order to obtain a dinuclear complex of V, the mononuclear complex once formed has to be heated at 60°C for a long time.

It is interesting to note that the mononuclear complexes of the alkylated ligands do not carry any coordinated water and that the uncoordinated carbonyl group takes a keto form and not an enol at all.



II



III

---

* Contribution No. 124. from the Department of Organic Synthesis, Kyushu University.

[1] J. R. Bethell and P. Maitland, *J. Chem. Soc.*, **1962**, 3755.

[2] F. Feist, *Ann.*, **257**, 276 (1890).