Note

Cathodic Crossed Hydrocoupling of Acetone with Cyanourea*

Tsutomu NONAKA**, Norio YUI**
and Keiji ODO**

In the previous work¹⁾, it was found that 2,4-diimino-5,5-dimethyloxazolidine (DDMO) forms in electrolytic reduction of a mixture of acetone and dicyandiamide, and two possible mechanisms for this crossed hydrocoupling reaction were proposed. They are as follows (X=NH in the case of dicyandiamide, X=O in the case of cyanourea):

In the present work, the crossed hydrocoupling of acetone with cyanourea, which is a hydrolysis product of dicyandiamide, was attempted by the similar means to the case of dicyandiamide. The crossed hydrocoupling product was 2-keto-4-imino-5,5-dimethyloxazolidine (KIDO) which is a new compound.

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** Department of Electrochemistry, Faculty of Engineering, Tokyo Institute of Technology (Ookayama, Meguro-ku, Tokyo)

In this case, the mechanism A is undoubtedly supported, because in the mechanism A KIDO forms but in the mechanism B its isomer, which is 2-imino-4-keto-5,5-dimethyloxazolidine (IKDO), will be produced. Dicyandiamide and cyanourea are alike in molecular structure and several chemical properties. Accordingly, it is analogized that the reaction with dicyandiamide proceeds in the mechanism A.

The crossed hydrocoupling reactions of acetone with other cyanamino compounds (*N*-cyanoformamide, cyanoguanylurea, and cyanobiguanide) were further attempted by the similar means to the case of cyanourea, but no crossed hydrocoupling product was isolated.

Experimental: Cyanourea was prepared from potassium cyanate and cyanamide, which was previously desulfurized with cyanamide silver salt²⁾, by Fallwach's method³⁾.

The electrolysis cell used was the same as described earlier¹⁾: cathode, mercury pool (area, 12.0 cm²); anode, platinum disk (diameter, 2 cm). Catholyte was a mixture of 1.70 g of cyanourea, 35 g of acetone, and 35 g of 20% sulfuric acid. Anolyte was adequate amount of 20% sulfuric acid. Electrolysis was carried out by passing the constant current, 0.36 amp (cathodic current density, 3.0 amp/dm²), and the amount of electricity supplied for 16 hours was 5.8 amp·hour (11 Fr/mole of cyanourea). Temperature of the catholyte was maintained below 5°C to preserve cyanourea and KIDO from hydrolysis with acid.

After the electrolysis, the catholyte was neutralized with an aqueous solution of sodium hydroxide, and the resulting sodium sulfate and very small amount of the other suspended particles were removed by filtration. When an aqueous solution of silver nitrate was added to the filtrate, no precipitate of cyanourea silver salt was observed. The filtrate was thoroughly extracted with ether, and then the aqueous layer, from which no picrate of IKDO precipitated by addition of an aqueous solution of ammonium picrate, was evaporated to dryness under reduced pressure. The resulting residue was extracted with absolute alcohol. When the alcoholic solution was evaporated to dryness, 1.56 g of crude KIDO remained. The yield based on the starting cyanourea and the current

efficiency were 61% and 11% respectively.

KIDO recrystallized from absolute alcohol was a white prismatic crystal: melting point, 255~258°C; elemental analysis, Found: C, 46.21; H, 6.50; N, 21.62 %. Calcd. for C₅H₈N₂O₂: C, 46.78; H, 6.29; N, 21.86%. The principal absorption bands in IR spectrum were appeared at 3280, 1716, 1260, and 793 cm⁻¹. The σ valued in NMR spectrum (60 MHz) were 1.41(s, 6H), 2.49 (s, 1H), and 3.58 (s, 1H) in dimethylsulfoxide-*d*₆ at room temperature. The melting point and the spectra of KIDO were considerably different from those of the isomer (IKDO) prepared authentically¹⁾.

Identity was further confirmed by converting KIDO to 2,4-diketo-5,5-dimethyloxazolidine (DKDO) which is a known compound¹⁾. 0.25 g of KIDO was heated in a mixture of 1 ml of alcohol and 0.5 ml of concentrated hydrochloric acid at 90°C for 3 hours. The reaction mixture was evaporated to dryness under reduced pressure and the residue was extracted with ether. The extract was concentrated and cooled strongly, 0.065 g (yield, 44%) of DKDO was obtained as white needles. DKDO recrystallized from water melted at 72~74°C (lit.¹⁾, 73~74°C) and a mixed melting point with the authentic sample¹⁾ showed no depression.

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