NOTES

Reactions of Coordinated Organic Ligands with Cupric Bromide

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Metal halides, such as cupric bromide, are known to act as halogenating agents for ketones and reactive aromatics. We have now been able to extend these reactions to include the halogenation of some coordinated organic nuclei.

The treatment of the copper(II) chelate of 8-hydroxyquinoline with cupric bromide in absolute alcohol produces a mixture of products. Hydrolysis with hydrochloric acid yields 5, 7-dibromo-8-hydroxyquinoline,[1] plus some monobrominated material.

The copper(II) chelate of salicylaldehyde is brominated in a similar fashion to yield 5-bromosalicylaldehyde upon acid hydrolysis.

Several metal acetylacetonates also undergo this type of reaction. The treatment of bis(2, 4-pentanedionato)copper(II) with cupric bromide produced bis(3-bromo-2, 4-pentanedionato)copper(II) very rapidly. The cobalt(III) and chromium(III) chelates of acetylacetone were brominated in the same manner as the copper(II) complex, except that the reaction proceeded somewhat more slowly. Substitution occurred only on the number 3 carbon of the ligands. No detectable amounts of bis(3-bromo-2, 4-pentanedionato)copper(II) were found to result from these reactions which might be formed through ligand exchange in a solution.[2] We have found that the copper(II) complexes readily form from the free ligand and cupric bromide under the conditions of the bromination, whereas the cobalt(III) and chromium(III) complexes do not. In agreement with a variety of such brominations reported by Collman et al.,[3] the bromination of these trivalent metal chelates may involve direct electrophilic substitution on the chelate ring.

Experimental

The Bromination of Bis(8-hydroxyquinolinato)-copper(II) and Bis(salicylaldehydato)copper(II).—A mixture of one of the metal chelates (0.01 mol.) of 8-hydroxyquinoline (A) or salicylaldehyde (B) and cupric bromide (0.02 mol.) in 100 ml. of absolute ethanol was stirred for 1 hr. at 50—60°C. (A): The reaction mixture was collected on a filter and dissolved in 6 N hydrochloric acid by being warmed. The resulting solution was saturated with hydrogen sulfide to precipitate cupric sulfide and then filtered. The free base of 5, 7-dibromo-8-hydroxyquinoline was recovered from the aqueous filtrate and recrystallized from *N*, *N*-dimethylformamide. It was identified by comparing its infrared spectrum with that of standard spectra shown in the Sadtler catalog (No. 7168); yield, 30%. (B): The reaction mixture was collected on a filter. The evaporation of the filtrate left some residue. These materials were put together and dissolved in 6 N hydrochloric acid to give a precipitate. An alcoholic extract of the precipitate gave needles of 5-bromosalicylaldehyde (yield, 35%), identified by a comparison of its m. p. (105°C) (Beilstein's Handbook) and infrared spectrum (Sadtler No. 5769) with those of a standard sample.

The Bromination of the Metal Acetylacetonates.—A mixture of one of the complexes (0.0075 mol.) and well-dried cupric bromide (0.018 mol.) in 100 ml. of absolute ethanol was stirred for 30 min. at room temperature. After filtration to remove the cuprous bromide formed during the reaction, the filtrate was evaporated to dryness under reduced pressure. Recrystallization from chloroform and heptane produced the pure product in the copper(II) series (yield, ca. 20%), but cobalt(III) and chromium(III) products required further purification by chromatography on alumina in order to remove small amounts of mono- and dibrominated materials from them. Each compound was identified by a comparison of its melting point and infrared spectra with those in the literature[3]; yields after chromatography: 10% for the chromium(III) complex and 17% for the cobalt(III) complex.

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[2] R. W. Kluiber, ibid., **82**, 4839 (1960).

[3] J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, ibid., **83**, 531 (1961); J. P. Collman, *Angew. Chem., Intern. Ed.*, **4**, 132 (1965) and the references quoted therein.