

naphthoyl)-propionic acid. It forms small, silvery-white crystals from toluene-methanol, or methanol alone, and melts at 232–232.5°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.72; H, 5.29.

The methyl ether, prepared from the acid with dimethyl sulfate, melted at 170–170.5° and gave no depression of the melting point when mixed with an authentic sample.⁸

The same acid was obtained in tetrachloroethane solution at 100–105° (5–10%). Above that temperature the yield was lower. Between 80–90° in tetrachloroethane, there was obtained, instead of the 4-acid, an isomeric acid which forms yellowish prisms from chloroform and a little methanol, and melts at 173.4–174°. It gives a blue color with ferric chloride and is perhaps β -(1-hydroxy-2-naphthoyl)-propionic acid.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.91; H, 5.18.

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The Reaction of Silver Acetate with 8-Quinolinol¹

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In connection with another problem we found it desirable to confirm the report by Nakatsuka that an aqueous solution of silver acetate will react with an alcoholic solution of 8-quinolinol at 60° to yield bis-(8-quinolinolo)-silver(II) and silver.³ Nakatsuka established the oxidation state of the silver by the interpretation of a bromine titration of the product in which seven equivalents of bromine reacted per atom of silver, rather than the eight equivalents expected for a silver(I) compound containing two 8-quinolinol molecules. The supposed silver(II) compound is green, while the corresponding silver(I) compound, also prepared by Nakatsuka, is yellow.

We were able to duplicate the physical description of the preparations as reported by Nakatsuka, but our analysis of the green solid indicates that it, too, is a silver(I) compound. Each of our preparations required 8 equivalents of bromine per atom of silver in the usual titrimetric determination of 8-quinolinol, and all were diamagnetic, as expected for silver(I) compounds. All other established silver(II) coordination compounds are paramagnetic, presumably because they contain one unpaired electron.⁴ Further, we found that the green solid is formed at 60° only if the silver acetate solution is not filtered before addition of the 8-quinolinol. If the traces of silver present in silver acetate are removed prior to the addition, the yellow silver(I) compound is formed at 60° also.

There are objections to expecting a silver(II) compound to be formed in the reaction mixture in question. First, of course, in the preparation of all other silver(II) compounds a powerful oxidizing agent is required to promote silver above the plus one level,⁵ and none is present here. Secondly,

potassium permanganate oxidizes 8-quinolinol to quinolinic acid,⁶ but silver(II) is an even more powerful oxidizing agent than the permanganate ion⁷ and would therefore be expected to cause the same oxidation. The conclusion that 8-quinolinol should be oxidized by silver(II) can be drawn also from the report that silver(II) oxidizes quinoline to quinolinic acid.⁸ Another objection to the hypothesis of the formation of silver(II) in the manner reported is that the ethyl alcohol present would almost certainly reduce any silver(II) as rapidly as it was formed.

The silver is probably formed by the reduction of some silver acetate by 8-quinolinol, rather than by a disproportionation. There is some precedent for such an explanation in that Freeman and Lions reported the reduction of silver acetate to silver by the action of 1-acridol,⁹ a homolog of 8-quinolinol. Hein and Regler have reported the conversion of the yellow silver(I) compound to an olive green silver(I) compound by recrystallization from concentrated ammonia.¹⁰ We were able to repeat this experiment. There are, then, two forms of 8-quinolinol-8-quinolinolo-silver(I), yellow and green; the yellow is the more readily formed, but it may be converted to the green by heating to 60° in water with a trace of silver, or by recrystallization from ammonia.

Experimental

Nakatsuka's Green Compound.³—The procedure reported by Nakatsuka³ was followed. A yellow solid was first precipitated, but almost immediately a dark green metallic-appearing mirror started to form. From 1 g. of 8-quinolinol and 1.2 g. of AgOAc, 1.1 g. of a yellow green solid mixed with a dark solid was obtained. *Anal.* Found: Ag, 27.9, 27.8; Br/mole, 8.04, 8.06. Calcd. for $Ag^+(C_8H_6NO)_2$: Ag, 27.2; Br/mole, 7.00. For $Ag^+(C_8H_6NO)(C_8H_7NO)$: Ag, 27.2; Br/mole, 8.00. The solid, in a modified Curie-Cheveneau balance, gave a deflection in the diamagnetic direction. Some of the solid was treated with pyridine, the mixture filtered, and the filtrate evaporated to give the compound reported to be $Ag^+(C_8H_6NO)_2 \cdot py$.³ *Anal.* Found: Br mole, 7.95. Calcd. for $Ag^+(C_8H_6NO)_2 \cdot py$: Br/mole, 7.00. For $Ag^+(C_8H_6NO)(C_8H_7NO) \cdot py$: Br/mole, 8.00. The substance gave a diamagnetic deflection.

Nakatsuka's Yellow Compound,³ Hein and Regler's Compounds.¹⁰—The experimental procedures in the literature were followed. The only difficulty encountered was in dissolving the yellow silver(I) compound in concentrated ammonia¹⁰; the compound was difficultly rather than readily soluble.

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A New Synthesis of Croweacin Aldehyde

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In a study associated with a previous investigation,¹ a simplified synthesis of croweacin aldehyde, 2-methoxy-3,4-methylenedioxybenzaldehyde (IV),

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(1) This investigation was begun under a grant from the Purdue Research Foundation and completed at the University of Illinois.

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