138°. It did not give a depression of the melting point when mixed with authentic material.[3]

Anal. Calcd. for $C_{20}H_{22}O_2Br_2$: Br, 35.2. Found: Br, 35.5.

Dinitrometanethole.—About 10 mg. of the sponge product was dissolved in 2 ml. of hot glacial acetic acid, and the solution cooled rapidly to obtain a fine suspension of crystals. Addition of a few drops of concentrated nitric acid brought about a gradual disappearance of the suspended material, and upon cooling crystallization of the nitroderivative took place. It was collected, washed with acetic acid and recrystallized from ethanol; m.p. 190°. It did not give a depression of the melting point when mixed with authentic material.[3]

Anal. Calcd. for $C_{22}H_{22}O_6N_2$: N, 7.25. Found: N, 7.41.

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The Succinoylation of the Naphthols[1]

BY ERNST BERLINER, SHIRLEY B. DANIELS AND ALINA SURMACKA[2]

Although various phenols have been converted into the corresponding substituted β-benzoylpropionic acids with succinic anhydride and aluminum chloride,[3] the only reference to the succinoylation of the naphthols is an unsuccessful attempt with α-naphthol using either aluminum chloride or zinc chloride in tetrachloroethane or nitrobenzene solution.[4] Actually, both naphthols can be succinoylated, although the yields of keto acids are very small.

β-Naphthol, which was studied in greater detail, forms predominantly β-(2-hydroxy-1-naphthoyl)-propionic acid in refluxing benzene as well as in tetrachloroethane on the steam-bath. The acid was identified by converting it into the known methyl ether.[5] Between 60 and 70° in benzene solution there is obtained, in addition to the 1-acid, β-(6-hydroxy-2-naphthoyl)-propionic acid, and in tetrachloroethane at the same temperature β-(7-hydroxy-1-naphthoyl)-propionic acid. In carbon disulfide the yield of the 1-acid is very small, and an unidentified compound, melting at 146.5–147.5° is also formed. The formation of the 1-, 6- and 8-acid is anticipated in electrophilic substitution of β-naphthol. It was not ascertained whether the isomeric acids were obtained by direct substitution, or by a Fries rearrangement, as has been suggested for the succinoylation of phenols.[6] When the reaction in benzene was carried out in the presence of three equivalents of aluminum chloride, instead of the usual two, the only product isolated was β-benzoylpropionic acid. The complex between β-naphthol and aluminum chloride is therefore less susceptible to electrophilic attack than benzene.[7]

In boiling benzene or in tetrachloroethane at 100° α-naphthol is converted into β-(1-hydroxy-4-naphthoyl)-propionic acid, which forms the known β-(1-methoxy-4-naphthoyl)-propionic acid on methylation.[8] At 80° in tetrachloroethane an isomeric acid is obtained which gives a blue coloration with ferric chloride.[9]

Experimental

Succinoylation of β-Naphthol.—A mixture of 18 g. (0.12 mole) of β-naphthol, 10 g. (0.1 mole) of succinic anhydride and 26 g. (0.2 mole) of aluminum chloride was refluxed in 80 ml. of dry, thiophene-free benzene for one hour. The reaction mixture was worked up as usual,[3] and the oil (6.2 g.), which separated after acidifying the carbonate solution, was allowed to solidify. It was extracted with hot benzene and material melting between 200 and 230° was left behind. On addition of ligroin the benzene extract deposited 3.2 g. (13%) of β-(2-hydroxy-1-naphthoyl)-propionic acid which, after several recrystallizations from benzene–ligroin, formed almost colorless plates melting at 112.8–113.5°.[10] Crystallized from 50% methanol the acid melts at 118.3–118.8°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.94; H, 5.13.

The acid was converted into the methyl ether (m.p. 136.7–138.2°) which gave no depression of the melting point when mixed with an authentic sample.[5] The above run was repeated with the same amounts of reagents, but the temperature was kept between 60 and 70°. The 1-acid was extracted with benzene, and the remainder was recrystallized from 50% methanol. The acid thus obtained melted at 230.1–230.7°. The values reported for β-(6-hydroxy-2-naphthoyl)-propionic acid are 229–231°[11] and 235°.[12] When the run was repeated with three equivalents of aluminum chloride the only acid isolated was β-benzoylpropionic acid (m.p. and mixed m.p.).

A mixture of 0.06 mole of β-naphthol, 0.1 mole of succinic anhydride and 0.3 mole of aluminum chloride was heated on the steam-bath in tetrachloroethane (100 ml.) solution. After two hours the reaction mixture was worked up as usual. The 1-acid was formed in an 11% yield.

A run with the same amounts of reagents was conducted at 60–70°. The mixture of acids was dissolved in hot benzene, and the benzene solution slowly deposited 0.4 g. (2.7%) of β-(7-hydroxy-1-naphthoyl)-propionic acid, which after two crystallizations from 50% methanol formed long, white needles melting at 179.2–179.4°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 69.00; H, 5.26.

The methyl ether of this acid, recrystallized from 50% methanol, melts at 145.6–146°. The value reported for β-(7-methoxy-1-naphthoyl)-propionic acid is 145–146°.[13] The benzene filtrate, after concentration and addition of ligroin, deposited 1.7 g. (11%) of the 1-acid.

In carbon disulfide only a small amount of the 1-acid was obtained in pure form. The remainder was a mixture which melted at first at 205–210°, but from which, after several crystallizations from 50% methanol, an apparently pure compound, melting at 146.5–147.5°, was isolated. The latter compound was not further investigated.

Succinoylation of α-Naphthol.—A run conducted on one-tenth of a mole of each α-naphthol and succinic anhydride and twice this amount of aluminum chloride in 100 ml. of boiling benzene afforded 1.5 g. (6.1%) of β-(1-hydroxy-4-

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(1) From the M.A. thesis of S. B. Daniels (1950) and the Senior Honors thesis of A. Surmacka, 1948.

(2) Mrs. Alina S. Szczesniak, Massachusetts Institute of Technology, Cambridge, Mass.

(3) E. Berliner in Adams "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1949, Vol. V, Chapter 5.

(4) R. D. Desai and V. H. Shroff, *J. Univ. Bombay*, **10**, Pt. 3, 97 1941) [*C. A.*, **36**, 3795 (1942)].

(5) W. F. Short, H. Stromberg and A. E. Wiles, *J. Chem. Soc.*, 319 1936).

(6) F. G. Baddar and L. S. El-Assal, *ibid.*, 3606 (1950).

(7) For a similar case see ref. 6.

(8) L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **58**, 2314 (1936).

(9) The syntheses of β-(1-hydroxy-4-naphthoyl)-propionic acid (m.p. 235°, dec.) and of β-(2-hydroxy-1-naphthoyl)-propionic acid (m.p. 116°) by demethylation of the corresponding methoxy acids have in the meantime been reported (R. B. Burtner and J. M. Brown, THIS JOURNAL, **73**, 897 (1951)). The authors also report the synthesis of β-(1-hydroxy-2-naphthoyl)-propionic acid (m.p. 106–108°), but no structure proof is given.

(10) All melting points are corrected.

(11) G. Swain, A. R. Todd and W. S. Waring, *J. Chem. Soc.*, 548 (1944).

(12) R. Robinson and J. M. C. Thompson, *ibid.*, 2009 (1938). This acid is probably identical with the acid m.p. 232° prepared by L. F. Fieser and M. Peters, THIS JOURNAL, **54**, 4347 (1932). See ref. 5.

(13) W. E. Bachmann and W. J. Horton, *ibid.*, **69**, 58 (1947).

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.[3]

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.

DEPARTMENT OF CHEMISTRY
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The Reaction of Silver Acetate with 8-Quinolinol[1]

BY B. P. BLOCK,[2a] JOHN C. BAILAR, JR., AND D. W. PEARCE[2b]

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) coördination 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 ion[7] 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 Nakatsuka[3] 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 $Ag''(C_9H_6NO)_2$: Ag, 27.2; Br/mole, 7.00. For $Ag'(C_9H_6NO)(C_9H_7NO)$: 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 $Ag''(C_9H_6NO)_2\cdot py$.[3] *Anal.* Found: Br mole, 7.95. Calcd. for $Ag''(C_9H_6NO)_2\cdot py$: Br/mole, 7.00. For $Ag'(C_9H_6NO)(C_9H_7NO)\cdot py$: 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 ammonia[10]; the compound was difficultly rather than readily soluble.

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[3] Y. Nakatsuka, *Bull. Chem. Soc. Jap.*, **11**, 45 (1936).

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[10] F. Hein and H. Regler, *Ber.*, **69B**, 1692 (1936).

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A New Synthesis of Croweacin Aldehyde

BY WM. B. BROWNELL AND ARTHUR W. WESTON

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] K. E. Hamlin and A. W. Weston, THIS JOURNAL, **73**, 2210 (1949).