Pure 1,2,3,4-tetrahydro-2-naphthol has $n^{25}\text{D}$ of 1.5630 ± 2 and a m. p. 22.9°.[5]

The alcohol was oxidized by transfer of hydrogen to ethylene, over a copper–zinc–nickel–barium–chromium oxide catalyst, by a method previously described.[6]

Equimolecular amounts of 192 g. of 1,2,3,4-tetrahydro-2-naphthol and 36 g. of ethylene together with 12 g. of the copper–zinc–nickel–barium–chromium oxide catalyst[6] were placed in a 1300 ml. steel reaction vessel. The mixture was heated with rocking to 250° during one hundred minutes, the pressure rising from 400 to 675 p.s.i. The reaction mixture was kept at 250° for ninety minutes and then cooled to room temperature. The products were removed from the reaction vessel with the aid of 300 ml. of ether and the catalyst separated by centrifugation. The catalyst was extracted with 100 ml. of ether and separated again. The product and the ether washings were added to a 2-l. round-bottomed flask equipped with a mechanical stirrer and containing a solution of 506 g. (4.9 moles) of sodium bisulfite in 795 ml. of water. Precipitation of the addition compound began almost at once, and after fifteen to twenty hours another portion of 96 g. of sodium bisulfite was added. The bisulfite addition compound was filtered off, washed three times by suspension in 300-ml. portions of ether and returned to the 2-l. flask where it was treated with 500 ml. of water, 240 ml. of ether and a solution of 145 ml. of concentrated sulfuric acid in 290-ml. of water. When all of the solid material had disappeared after two and one-half hours, the ether layer was separated, and the water layer was extracted with two 200-ml. portions of ether. The combined ether layers were extracted with 150 ml. of water, ten to fifteen 200-ml. portions of saturated sodium bicarbonate solution, and finally with 200 ml. of water. All but the last four or five portions of bicarbonate solution caused the ether solution to effervesce. The ether layer was dried twenty hours over 150 g. of anhydrous sodium sulfate. After the distillation of the ether, the product was distilled rapidly at 121–132° (8 mm.). The yield of β-tetralone, $n^{25}\text{D}$ 1.5555, m. p. 17–18°, was 80 g. or over 40% of the theoretical. The preparation has been carried out, starting with 40 to 288 g. of 1,2,3,4-tetrahydro-2-naphthol, with yields of 35 to 42%. β-Tetralone was prepared by the process described, under contract OEMsr-304 with the Office of Scientific Research and Development, for the benefit of investigators of the Committee on Medical Research.

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(6) Reeve and Adkins, THIS JOURNAL, **62**, 2874 (1940).

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Reactions of Silver Salts of Carboxylic Acids with Halogen

BY RICHARD T. ARNOLD AND PERRY MORGAN

Simonini[1] has shown that silver salts of carboxylic acids react with iodine (in a molecular ratio of 2/1) to form esters and carbon dioxide.

More recently[2] it has been demonstrated that these silver salts and halogens (in a molecular ratio of 1/1) afford an alkyl halide and carbon dioxide.

Price[3] has proposed a free radical mechanism for this transformation as follows.

$$Br_2 \longrightarrow 2Br\cdot$$
$$RCO_2Ag + Br\cdot \longrightarrow AgBr + RCO_2\cdot \longrightarrow R\cdot + CO_2$$
$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot$$

In the event that the α-carbon atom of RCO_2Ag is asymmetric, one might expect an optically inactive alkyl bromide to result from the optically active silver salt since the tetrahedral configuration (at the α-carbon atom) is lost in the formation of R·.

Experimentally we have verified this fact. Both the *d*- and *l*- forms of α-ethylcaproic acid when converted into their silver salts and treated with bromine (in carbon tetrachloride) yield racemic 3-bromoheptane. That no rearrangement of the carbon skeleton in the supposed R· occurred was shown by converting the 3-bromoheptane into *dl*-α-ethylcaproic acid.

Experimental

***d*- and *l*-α-Ethylcaproic Acids.**—The resolution was carried out as described by Kenyon and Platt.[4]

***dl*-3-Bromoheptane.**—The dextro form of α-ethylcaproic acid (24 g., $[\alpha]^{22}\text{D}$ +1.68°) was treated with dry silver acetate (29 g.) and carbon tetrachloride (475 cc.), and the suspension was refluxed for ninety minutes then cooled to room temperature. A solution of bromine (9 cc.) in carbon tetrachloride (37.5 cc.) was added slowly at first (until the induction period was terminated) and then as rapidly as possible. The whole was then heated at the boiling point for seven hours. After cooling, the solution was filtered and shaken thoroughly with aqueous sodium bisulfite containing sodium hydroxide (15 cc., 20%). Distillation gave optically inactive 3-bromoheptane; yield 10.5 g.; b. p. 50.5° (12 mm.).

Using the same procedure (−)α-ethylcaproic acid (21.0 g. having a rotation of −3.39° in a 2-dm. tube at 33.8°) gave optically inactive 3-bromoheptane (7.7 g.).

The above *dl*-bromides were converted to their corresponding Grignard reagents and carbonated to give *dl*-α-ethylcaproic acid. The amide of this compound melts at 101°.[5]

It is of interest to point out that N-(1-naphthyl)-2-ethylcaproyl amide forms beautiful crystals which melt over a range from 100–127.5° and apparently forms liquid crystal structures.

Anal. Calcd. for $C_{18}H_{23}ON$: C, 80.24; H, 8.61. Found: C, 80.13; H, 8.73.

This interesting derivative was formed from the starting *dl*-α-ethylcaproic acid and from each of the acid samples resulting from the inactive 3-bromoheptanes. X-Ray diffraction patterns (kindly taken by Dr. William Lipscomb of This Laboratory) were identical.

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(1) Simonini, *Monatsh.*, **13**, 320 (1892).

(2) Hunsdiecker and Hunsdiecker, *Ber.*, **75**, 291 (1942).

(3) Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds." Interscience Publishers, New York, N. Y., 1946, p. 55.

(4) Kenyon and Platt, *J. Chem. Soc.*, 633 (1939).

(5) Weizmann, Bergmann and Haskelberg, *Chem. and Ind.*, **56**, 589 (1937).

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The Acyloin Condensation of 2-Thiophenealdehyde

BY SAMUEL Z. CARDON AND HERMAN P. LANKELMA

Grishkewitsch-Trochimowsky and I. Matschurevitsch[1] applied the acyloin condensation to 2-thiophenealdehyde with negative results. It is reported that this failure to obtain thenoin is due to the instability of the thiophene ring to potassium cyanide.[2] In view of the stability of the thiophene ring toward other reagents there ap-

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(1) Grishkewitsch-Trochimowsky and Matschurevitsch, *J. Russ. Phys. Chem. Soc.*, **44**, 570 (1912); *C. A.*, **6**, 2406 (1912).

(2) *British Chemical Abstracts*, **102**, i, 642 (1912).