

Pure 1,2,3,4-tetrahydro-2-naphthol has  $n_D^{20}$  of 1.5630  $\pm$  2 and a m. p. 22.9°.<sup>5</sup>

The alcohol was oxidized by transfer of hydrogen to ethylene, over a copper-zinc-nickel-barium-chromium oxide catalyst, by a method previously described.<sup>6</sup>

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<sup>6</sup> 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  $\beta$ -tetralone,  $n_D^{20}$  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%.  $\beta$ -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.

(6) Reeve and Adkins, *This Journal*, **62**, 2874 (1940).

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RECEIVED AUGUST 5, 1948

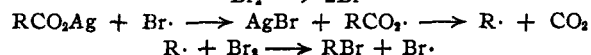
## Reactions of Silver Salts of Carboxylic Acids with Halogen

BY RICHARD T. ARNOLD AND PERRY MORGAN

Simonini<sup>1</sup> 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<sup>2</sup> 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<sup>3</sup> has proposed a free radical mechanism for this transformation as follows.



(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.

In the event that the  $\alpha$ -carbon atom of  $\text{RCO}_2\text{Ag}$  is asymmetric, one might expect an optically inactive alkyl bromide to result from the optically active silver salt since the tetrahedral configuration (at the  $\alpha$ -carbon atom) is lost in the formation of  $\text{R}\cdot$ .

Experimentally we have verified this fact. Both the *d*- and *l*-forms of  $\alpha$ -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  $\text{R}\cdot$  occurred was shown by converting the 3-bromoheptane into *dl*- $\alpha$ -ethylcaproic acid.

### Experimental

*d*- and *l*- $\alpha$ -Ethylcaproic Acids.—The resolution was carried out as described by Kenyon and Platt.<sup>4</sup>

*dl*-3-Bromoheptane.—The dextro form of  $\alpha$ -ethylcaproic acid (24 g.,  $[\alpha]_D^{20} +1.68^\circ$ ) 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 ( $-$ ) $\alpha$ -ethylcaproic acid (21.0 g. having a rotation of  $-3.39^\circ$  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*- $\alpha$ -ethylcaproic acid. The amide of this compound melts at 101°.<sup>5</sup>

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  $\text{C}_{18}\text{H}_{22}\text{ON}$ : C, 80.24; H, 8.61. Found: C, 80.13; H, 8.73.

This interesting derivative was formed from the starting *dl*- $\alpha$ -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.

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

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

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RECEIVED JULY 26, 1948

## The Acyloin Condensation of 2-Thiophenealdehyde

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Grishkewitsch-Trochimowsky and I. Matschur-evitsch<sup>1</sup> 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.<sup>2</sup> In view of the stability of the thiophene ring toward other reagents there ap-

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

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

peared to be no reason to expect it to be unstable to potassium cyanide. This was verified by heating thiophene with potassium cyanide in aqueous alcohol. The thiophene was recovered unchanged.

The acyloin condensation of 2-thiophenealdehyde to thenoin was effected by boiling the aldehyde with a solution of potassium cyanide in aqueous alcohol and neutralizing the reaction mixture. Thenoin was oxidized to thenil by the action of copper sulfate in dilute pyridine solution and thenil was converted to thenilic acid by the action of alcoholic potassium hydroxide.

#### Experimental

**2-Thiophenealdehyde.**—This aldehyde was prepared from 2-chloromethylthiophene by the method of Dunn, Waugh and Dittmer.<sup>3</sup> The 2-chloromethylthiophene was prepared by the chloromethylation of thiophene by the method of Blicke and Burckhalter.<sup>4</sup> In this preparation it was found that concentrated hydrochloric acid at a temperature of 20–25° could be used, instead of gaseous hydrogen chloride at 0–5°, without lowering the yield.

**2,2'-Thenoin.**—A solution of 3 g. of potassium cyanide in 20 cc. of water was added to a solution of 25 g. of thiophenealdehyde in 40 cc. of alcohol. The mixture darkened immediately. It was boiled for a half hour, allowed to cool, and acidified with 5 cc. of concentrated hydrochloric acid. The dark green solution turned light yellow in color and on standing deposited brown crystals. These were filtered off and recrystallized from alcohol using decolorizing charcoal. Eight grams, a yield of 32%, of white crystals, m. p. 107–108°, was obtained.

*Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>S<sub>2</sub>: S, 28.54. Found: S, 28.43.

Thenoin rapidly reduces Fehling solution and Tollens reagent. Like benzoin, an alcohol solution is colored deep green upon adding a drop of dilute alkali and the color disappears temporarily upon shaking. The oxime, prepared by the action of hydroxylamine in pyridine, is a white crystalline solid, m. p. 142–143°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>S<sub>2</sub>N: S, 26.78. Found: S, 26.86.

**2,2'-Thenil.**—Thenil was obtained by the oxidation of thenoin by the method used by Hartman and Dickey<sup>5</sup> for the preparation of furil from furolin. Fifteen grams of copper sulfate was dissolved in a mixture of 21 g. of pyridine and 10 g. of water on a steam-bath. Six grams of thenoin was added and the mixture heated on a steam-bath, with stirring, for two hours. The mixture was poured into water and the thenil precipitated as a black solid. It was filtered, washed free of copper salts, and was recrystallized from methyl alcohol using charcoal. Two grams of yellow needles, a 33% yield, melting at 83–84° was obtained.

*Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>S<sub>2</sub>: S, 28.83. Found: S, 28.73.

**2,2'-Thenilic Acid.**—Three grams of thenil was added to a solution of 3 g. of potassium hydroxide in 50 cc. of 50% alcohol. The mixture was allowed to stand overnight at room temperature and was then poured into 100 cc. of water. The solution was carefully neutralized with hydrochloric acid and a tarry precipitate settled out and was filtered off. The filtrate was extracted with ether, the ether extract was evaporated to a small volume, and then shaken with 100 cc. of water. One and one half grams, a yield of 45%, of grayish white crystals separated out and were dried in a desiccator. The thenilic acid darkened rapidly on standing and decomposed, without melting, at about 80°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>O<sub>3</sub>S<sub>2</sub>: S, 26.7; neut. equiv., 240. Found: S, 26.8; neut. equiv., 241.

(3) Dunn, Waugh and Dittmer, *THIS JOURNAL*, **68**, 2118 (1946).

(4) Blicke and Burckhalter, *ibid.*, **64**, 477 (1942).

(5) Hartman and Dickey, *ibid.* **55**, 1228 (1933).

An attempt to prepare thenilic acid from thenoin by the method of Ballard and Dehn<sup>6</sup> for the preparation of benzoic acid from benzoin, gave only 2,2'-dithienyl ketone, m. p. 88°.

(6) Ballard and Dehn, "Organic Syntheses," Collective Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 89.

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RECEIVED JULY 2, 1948

### The Identity of "x-Benzylphenanthrene"

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In 1881 Goldschmiedt<sup>1</sup> prepared a hydrocarbon, C<sub>21</sub>H<sub>16</sub>, m. p. 155–156°, by heating a mixture of phenanthrene, benzyl chloride and zinc dust. He offered no proof of structure for this product, and referred to it merely as benzylphenanthrene. In Beilstein's "Handbuch" it is listed as "x-benzylphenanthrene," and heretofore no one has attempted to locate the position of the benzyl group in Goldschmiedt's product. In connection with another problem we became interested in the structure of this substance.

In 1934 Bachmann<sup>2</sup> gave an unequivocal synthesis of 9-benzylphenanthrene, m. p. 153–154°, by the action of benzyl chloride on 9-phenanthrylmagnesium bromide. A substance believed to be 9-benzylphenanthrene, m. p. 91–92°, had been previously prepared by Willgerodt and Albert<sup>3</sup> by reduction of the supposed 9-benzoylphenanthrene resulting from the Friedel-Crafts acylation of phenanthrene with benzoyl chloride. In an extensive synthetic study Bachmann later showed<sup>4</sup> that the structures of Willgerodt's products were in error, but the possible identity of authentic 9-benzylphenanthrene with Goldschmiedt's "x-benzylphenanthrene" was apparently not considered.

We have repeated the reactions of Goldschmiedt and Bachmann with essentially their results. The products from these two reactions had identical melting point and showed no mixed melting point depression. Their identity was further established by measurement of their absorption spectra which, as seen in Fig. 1, proved remarkably similar.

#### Experimental

**9-Benzylphenanthrene.**—This was prepared in 52% crude yield by refluxing benzyl chloride with a benzene and ether solution of 9-phenanthrylmagnesium bromide after the method of Bachmann.<sup>2</sup> After extensive recrystallization from benzene the pure product was obtained, m. p. 155–156°.

**"x-Benzylphenanthrene."**—In the preparation of this product the essential reaction conditions of Goldschmiedt<sup>1</sup> were employed, but the method of isolating the product was varied slightly. Phenanthrene (32 g., 0.179 mole, m. p. 99–100.5°), benzyl chloride (44 g., 0.346 mole) and zinc dust (10 g., 0.153 mole) were mixed and heated on the steam-bath for one and one-half hours. The

(1) Goldschmiedt, *Monatsh.*, **2**, 444 (1881).

(2) Bachmann, *THIS JOURNAL*, **56**, 1363 (1934).

(3) Willgerodt and Albert, *J. prakt. Chem.*, [2] **84**, 383 (1911).

(4) Bachmann, *THIS JOURNAL*, **57**, 555 (1935).