of each of these compounds is compared with that actually obtained on analysis. The dithizone obtained by the above procedure was purified by the method of Clifford and Wichman,[7] the other three by the procedure listed above.

The transmittancy curves for chloroform solutions of five of the carbazones produced are illustrated in Fig. 1. Our studies of these compounds with various metallic ions are not completed, but Fig. 2 gives transmittancy curves for the mercury complexes in chloroform. The mercury dithizonate (not shown) has maximum absorption at 490 mμ while the curves in Fig. 2 in all cases show shifts toward longer wave lengths. Similar shifts were obtained for bismuth and lead[2] and zinc[3] complexes of di-β-naphthylthiocarbazone.

A point of interest in the synthesis described above was that the diphenylthiocarbazide could be isolated as a fairly stable dry compound, whereas the di-β-naphthylthiocarbazide was relatively unstable. When diphenylthiocarbazide was used to produce the carbazone, heat was necessary, whereas with the latter compound the oxidation to carbazone had to be accomplished immediately and without heat.

Summary

The marked superiority of di-β-naphthylthiocarbazone over diphenylthiocarbazone (dithizone) as a microanalytical reagent in the quantitative determination of certain trace metals in biological material, such as mercury and zinc, has brought about the immediate need for a good method for its synthesis.

A new method of synthesis is here reported. It is similar to Bamberger's method for the synthesis of dithizone and was found to be superior to other methods such as that of Suprunovich and an adaptation of it previously reported by one of us.

CINCINNATI, OHIO RECEIVED JULY 9, 1943

---

[7] *Assoc. Official Agr. Chem.*, Official and Tentative Methods, 5th ed., p. 396 (1940).

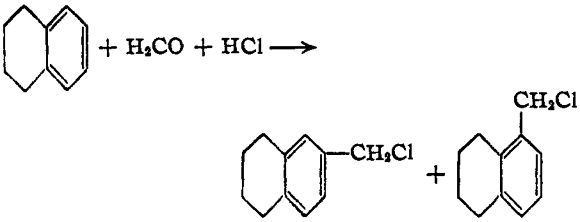
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Chloromethylation of Tetralin. A Synthesis of β-5-Tetralylpropionic Acid

BY RICHARD T. ARNOLD AND RODERICK BARNES

The chloromethylation of tetralin has been effected in several laboratories. Although it is implied in the patent literature[1] that the chloromethyl group is introduced into the 6-position only, most investigators[2,3,4] have claimed the formation of a mixture of isomers. A semiquantitative analysis of this mixture by Vavon and coworkers[4] indicates the presence of 5- and 6-chloromethyltetralins to the extent of 9 and 91%, respectively.

As a result of many experiments we have discovered that the chloromethylation of tetralin can be carried out in such a manner to give a mixture containing more than thirty per cent. of 5-chloromethyltetralin. Although it has not been definitely established we believe that the composition of this mixture depends markedly on the experimental conditions employed.



When used in a malonic ester synthesis, the chloromethylation product from tetralin gave a crude propionic acid (m. p. 75–90°) which after several recrystallizations yielded pure β-5-tetralylpropionic acid (m. p. 136–137°). Dehydrogenation of this acid resulted in the formation of β-1-naphthylpropionic acid. Additional confirmation of the structure assigned to β-5-tetralylpropionic acid was obtained by an independent preparation of β-6-tetralylpropionic acid from 6-propionyltetralin by means of the Willgerodt synthesis.[5]

Cyclization of β-5-tetralylpropionic acid gave 6,7,8,9-tetrahydrobenz[e]indanone-3 which on reduction by Clemmensen's method followed by dehydrogenation gave benz[e]indane.

Upon numerous occasions in this Laboratory we have introduced methyl groups into aromatic nuclei by the catalytic reduction of chloromethyl derivatives. It has been observed frequently that satisfactory results are obtained only when the reduction is attempted shortly after fractionation of the chloromethyl compound. When reduced within a few hours after its preparation, the chloromethylation product from tetralin was hydrogenated quantitatively within twenty minutes to give a mixture of 5- and 6-methyltetralins. If twenty-four hours elapsed between the distillation of the chloromethyltetralin and the reduction experiment, the absorption of hydrogen was sluggish

---

[1] Lange (I. G. Farbenindustrie), German Patent 533,132.

[2] Darzens and Levy, *Compt. rend.*, **201**, 902 (1935).

[3] Martin, *J. Chem. Soc.*, 679 (1941).

[4] Vavon, Bolle and Calin, *Bull. soc. chim.*, [5] **6**, 1025 (1939).

[5] This acid (m. p. 81.5–82.5°) was identical with a sample kindly furnished to us by Professor M. S. Newman. See Newman and Zahm, THIS JOURNAL, **65**, 1097 (1943).

and incomplete. After standing at room temperature for four days, the chloromethylation product could not be reduced with hydrogen and Pd–$BaSO_4$ catalyst. We believe that the polymers which form when most benzyl halides are allowed to stand at room temperature poison the catalyst by being preferentially adsorbed.

By means of sulfur dehydrogenation, the mixture of methyltetralins was converted into α- and β-methylnaphthalene from which 2-methyl-1,4-naphthoquinone could easily be obtained by oxidation.

This is the first instance in which pure crystalline substances have been obtained from each of the two components present in the chloromethylation product from tetralin.

Experimental Part

Chloromethylation of Tetralin.—An efficiently stirred mixture of tetralin (237 g., 1.8 moles), aqueous formaldehyde solution (225 ml., 40%), and hydrochloric acid (382 ml.) was heated at 60–65°, while concentrated sulfuric acid (250 ml.) was slowly (five to six hours) added. After twenty-two hours of heating and stirring, the reaction mixture was poured into cold water (2000 ml.) and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and the ether was removed by distillation. There was obtained 231 g. (71.5%) of chloromethyltetralin which boiled at 110–114° (3 mm.).

Mixture of 5-(and 6)-Methyltetralin.—The mixture of isomeric chloromethyltetralins (25 g.) was dissolved in ethanol (75 ml., 95%) and shaken with hydrogen (45 lb. pressure) in the presence of palladium on barium sulfate catalyst (1.2 g.). When the reduction was complete (twenty minutes), the catalyst was removed by filtration and the solution fractionated. There was obtained 19.3 g. (96%) of methyltetralin which boiled at 115–117° (15 mm.).

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 89.99; H, 9.59.

Mixture of 1-(and 2)-Methylnaphthalene.—The mixture of isomeric methyltetralins (20 g.) was refluxed with sulfur (8.5 g.) for four hours. The product was distilled directly from the reaction mixture. There was obtained 6.7 g. (34%) of product which boiled at 117–120° (23 mm.).

2-Methyl-1,4-naphthoquinone.—The mixture of isomeric methylnaphthalenes was oxidized by the usual procedure[6] with chromic acid. Upon steam distillation of the reaction mixture there was obtained 1 g. of the quinone, which melted at 104–105°. Fieser[6] reports 105–106°. Reductive acetylation gave an acetate melting at 111–112°.[7]

Mixture of 5-(and 6)-Tetralylpropionic Acids.—Sodium (37 g., 1.61 moles) was gradually added, with stirring, to absolute alcohol (1000 ml.). Upon complete solution of the sodium, diethyl malonate (320 g., 2 moles) was added. This was followed by the slow (four hours) addition of the mixture of chloromethyltetralins (300 g., 1.61 moles). The mixture was stirred at room temperature for four hours and finally refluxed for two hours. The excess alcohol was removed by distillation and the residue was poured into water (1000 ml.). The product was extracted with ether (400 ml.); the ether extract was dried over sodium sulfate, and the ether was removed by distillation. Fractionation of the residue, yielded 320 g. (65%) of substituted malonic ester which boiled at 150–155° (2 mm.). This product (290 g.) was refluxed with a solution of potassium hydroxide (120 g.) in methanol (500 ml.) and water (50 ml.) for two hours. Most of the alcohol was removed by distillation. The residue was dissolved in water (1000 ml.), and acidified (congo red) with concentrated hydrochloric acid. The liquid malonic acid was extracted with ether (600 ml.), and the ether was removed by distillation. The residual malonic acid was decarboxylated by heating in a metal bath, gradually raising the temperature to 180°. The solid acid obtained on cooling was dissolved in sodium carbonate solution (750 ml., 10%). The acid was precipitated by acidifying (congo red) this solution with concentrated hydrochloric acid. There was obtained 173 g. (90%) of acid which melted about 75–90°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.47; H, 7.96.

β-5-Tetralylpropionic Acid.—The mixture of isomeric acids (150 g.) was dissolved in benzene (500 ml.). Benzene was distilled from this solution until the distillate was no longer cloudy (in order to remove a small quantity of water). Petroleum ether (200 ml., b. p. 60–68°) was added and the warm solution was allowed to cool slowly. The crystals thus obtained, when recrystallized once more from benzene and petroleum ether, melted at 136–137°. The combined filtrates were concentrated to about 300 ml. and a second crop of crystals was obtained by addition of petroleum ether (150–200 ml.) followed by cooling. Repetition of this procedure gave a third crop. These latter crops were recrystallized again from benzene and petroleum ether; there was obtained finally, 38 g. of acid, m. p. 136–137°, and 11 g. of acid, m. p. 127–130°. (The remainder of the material is largely a eutectic mixture of β-5(and 6)-tetralylpropionic acid, m. p. 72°.)

6,7,8,9-Tetrahydrobenz[e]indanone-3.—Pure β-5-tetralylpropionic acid (10 g.) was dissolved in cold benzene (50 ml.) and thionyl chloride (20 ml.), and pyridine (10 drops) were added. The mixture was allowed to stand overnight. The excess thionyl chloride was removed under vacuum; benzene (10 ml.) was added and removed again under vacuum. The residue was dissolved in nitrobenzene (75 ml.) and this solution was slowly (thirty minutes) added to a cooled (ice-bath), stirred solution of stannic chloride (15 ml.) in nitrobenzene (100 ml.). The reaction mixture was stirred in the ice-bath for another half hour, then, at 30–35° for two hours. After treatment of the reaction mixture with ice and hydrochloric acid, the organic layer was separated and washed with dilute hydrochloric acid several times and finally steam distilled until the odor of nitrobenzene had disappeared from the distillate. The non-volatile residue was extracted with ether, the ether was removed by distillation to give a crystalline solid (7.5 g., 81%). On recrystallization from ethanol and water the ketone melted at 63–64.5°.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.59. Found: C, 83.45; H, 7.45.

6,7,8,9-Tetrahydrobenz[e]indane.—A mixture of amalgamated zinc (150 g.), water (75 ml.), concentrated hydrochloric acid (150 ml.), acetic acid (36 ml.), toluene (75 ml.), and the ketone, (12.1 g.) was refluxed for twenty-seven hours with intermittent addition of concentrated hydrochloric acid (*ca.* 100 ml.). After cooling, the toluene layer was separated, washed with dilute hydrochloric acid, sodium bicarbonate solution, and water, and the toluene was removed by distillation. Fractionation of the residue gave 9.2 g. (83%) of product boiling at 143–147° (15 mm.). A mixture of the hydrocarbon (0.5 ml.) dissolved in a minimum of ethanol, and a saturated solution of picric acid in ethanol (3 ml.), was warmed on the steam-bath for five minutes. On cooling, golden-orange needles separated, which melted at 107.5–108.5°.[8]

β-1-Napthylpropionic Acid.—Sulfur (3 g.) and β-5-tetralylpropionic acid (10 g.) were heated for two hours at 225–250°. Upon cooling the product was thoroughly extracted with sodium carbonate solution (60 ml., 10%). The sodium carbonate solution was treated with Norite, filtered and acidified. There was obtained 4.6 g. (47%) of crude acid. Recrystallization from ethanol and water gave white plates which melted at 151–152°.[9] The anilide

---

[6] Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Company, Boston, Mass., 1941, p. 233.

[7] Anderson and Newman, *J. Biol. Chem.*, **103**, 405 (1935), give the m. p. as 114°.

[8] Denisenko, *J. Gen. Chem.* (U. S. S. R.), **8**, 410 (1939); *Chem. Abs.*, **33**, 7889 (1939), reports the m. p. as 109–110°.

[9] Mayer and Sieglitz, *Ber.*, **55**, 1855 (1922), report the m. p. as 151°.

(m. p. 139–140°) was shown to be identical with an authentic sample.

β-6-Tetralylpropionic Acid and Methyl Ester.—A mixture of 6-propionyltetralin (20 g.), dioxane (80 ml.), sulfur (10 g.), and concentrated ammonia solution saturated with hydrogen sulfide (100 ml.) was heated in a closed steel tube at 165° for twenty-four hours. The solvents were removed by evaporation on the steam-bath and the residue was hydrolyzed by heating with potassium hydroxide solution (150 ml., 25%) until the odor of ammonia was no longer apparent. The alkaline solution was treated with Norite, filtered and acidified. The crude acid was esterified by refluxing for four hours with methanol (200 ml.), and sulfuric acid (3 ml.). The reaction mixture was poured into water (800 ml.) and extracted with ether; the ether extract was washed with sodium bicarbonate solution, and water, and the ether was removed by distillation. Distillation of the residue gave 15.5 g. (71.5%) of the methyl ester, which boiled at 165–168° (12 mm.). The aforementioned crude acid after recrystallization melted at 81.5–82.5°.[5]

β-2-Naphthylpropionic Acid.—Sulfur (1 g.) and methyl β-6-tetralylpropionate (3.1 g.) were heated for two hours at 235–250°. The crude reaction mixture was saponified by refluxing for two hours with potassium hydroxide (5 g.) dissolved in methanol (25 ml.) and water (50 ml.). The solution was acidified (congo red) with hydrochloric acid. Recrystallization of the crude acid from benzene and petroleum ether (b. p. 60–68°) gave a product which melted at 134–135°.[9]

Summary

1. A study of the chloromethylation of tetralin has been made and it has been demonstrated that at least 30 per cent. of 5-chloromethyltetralin is present in the product.
2. A convenient synthesis of β-5-tetralylpropionic acid is described.

MINNEAPOLIS, MINNESOTA RECEIVED SEPTEMBER 7, 1943

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF KENTUCKY]

Polarographic Investigation of Hydrogen Bonding II. Some Nitrocresols[1]

BY MELVIN J. ASTLE AND WENDELL P. CROPPER[2]

In the first paper in this series[3] the polarographic technique was used to study hydrogen bonding in *o*- and *p*-nitrophenols. It was found that *o*-nitrophenol which contains an intramolecular hydrogen bond was only reduced to the hydroxylamine while the *p*-nitrophenol was reduced completely to the amine. The presence of the hydrogen bond in *o*-nitrophenol caused the nitro group to be more easily reduced than the nitro group in *p*-nitrophenol where no such bond is possible.

It was the purpose of this investigation to study the reduction of several nitrocresols at the dropping mercury cathode in order to determine the effect on the reduction of a nitro group of an OH group in positions which are ortho, meta and para to it when a methyl group is also present on the benzene ring.

Discussion of Results.—For convenience the nitro cresols investigated will be divided into three classes. Class I will consist of those compounds in which the OH group is para to the nitro group and includes 5-nitro-*o*-cresol and 6-nitro-*m*-cresol. Class II consists of those compounds in which the OH group is ortho to the nitro group and includes 3-nitro-*p*-cresol, 3-nitro-*o*-cresol and 4-nitro-*m*-cresol. Class III consists of those compounds in which the OH group is meta to the nitro group and includes 2-nitro-*p*-cresol and 4-nitro-*o*-cresol.

A typical compound of class I in which the nitro and hydroxyl groups are para to each other is illustrated with 6-nitro-*m*-cresol. Current–voltage curves for the reduction of this compound from carefully buffered solutions at 25° were obtained (Fig. 1). The waves were of approximately the same height over the entire *p*H range studied and averaged about 10 microamperes.

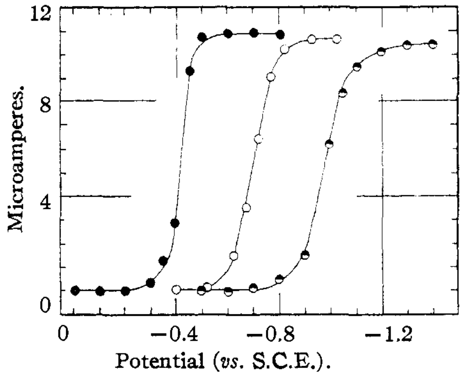


Fig. 1.—Current-voltage curves for 6-nitro-*m*-cresol (0.001 *M*): ●, *p*H 3.6; ○, *p*H 8.0; ◐, *p*H 10.0; $m^{2/3}t^{1/6} = 0.94$ mg.$^{2/3}$ sec.$^{-1/2}$.

The reduction of the nitro group might well be considered to go first to the nitroso group, then to the hydroxylamine and finally to the amine.

$$—NO_2 \xrightarrow{2e^-} —NO \xrightarrow{2e^-} —NHOH \xrightarrow{2e^-} —NH_2$$

Each step requires two electrons. The reduction of the normal nitro group has been postulated to go to completion with the formation of the amine. This should require six electrons. If we assume that this nitrocresol has about the same diffusion coefficient as a molecule of benzoic acid which is about the same size we get a value of 8.86×10^{-6}

---

[1] From the M.S. thesis of Wendell P. Cropper. Presented before the Organic Division of the American Chemical Society, Pittsburgh meeting, September 6 to 10, 1943.

[2] Present Address, Standard Oil Co. of Indiana, Whiting, Indiana.

[3] Astle and McConnell, THIS JOURNAL, **65**, 35 (1943).