[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Catalytic Dehydrogenation of 2-Substituted-5,6,7,8-tetrahydronaphthalene Derivatives[1]

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The dehydrogenation of hydroaromatic to aromatic compounds is an operation of considerable importance in synthetic organic chemistry. It may be accomplished by chemical methods, in which the substance to be dehydrogenated is heated with an oxidizing agent, and by catalytic methods.[3] In general, the dehydrogenation of hydrocarbons may be accomplished easily by a variety of chemical and catalytic processes. We have found frequently that chemical dehydrogenation of oxygen-containing molecules is unsatisfactory both in regard to yield and purity of product. Consequently we decided to investigate the catalytic procedure, especially with regard to finding out whether the hydrogen would be liberated in molecular form or would attack the oxygenated functions.

We chose 2-substituted-5,6,7,8-tetrahydronaphthalene derivatives for study not only because they could be prepared easily from tetralin but also because their successful dehydrogenation might facilitate the synthesis of certain 2-substituted naphthalene derivatives. In this paper we report the results obtained with the following 2-substituted tetralin derivatives (Ar represents the 2-(5,6,7,8-tetrahydronaphthyl) radical throughout this paper): $ArCOOCH_3$, I; $ArCH_2COOCH_3$, II; $ArCH_2CH_2COOCH_3$, III; $ArCH_2CH_2CH_2COOCH_3$, IV; $ArCH{=}CHCOOCH_3$, V; $ArCOCH_2CH_2COOCH_3$, VI; $Ar\overline{CHCH_2CH_2COO}$, VII; $ArCOCH_3$, VIII; $ArCHO$, IX; $ArCH_2OH$, X; $ArCHOHCH_3$, XI; and $ArCOCl$, XII. These compounds were prepared by well-known methods from tetralin. Esters II to VII, the acids corresponding to II, III, and V, carbinol XI, and the semicarbazide of VIII are new. The dehydrogenations were carried out over a 20% palladium-on-charcoal catalyst[4] as described under the experimental part. As a result of these experiments it appears justifiable to make three generalizations.

1. The Carbomethoxy Group Is Not Affected by the Hydrogen under the Conditions of These Experiments.—Evidence for this lies in the fact that compounds I, II, III, and IV were converted in high yields to the corresponding 2-naphthyl derivatives according to the following equation

$$C_{10}H_{11}(CH_2)_nCOOCH_3 \longrightarrow C_{10}H_7(CH_2)_nCOOCH_3 + 2H_2$$
$$\text{where } n = 0, 1, 2, \text{ and } 3$$

2. The Ketonic Carbonyl Group Adjacent to the Aromatic Nucleus Is Reduced to a Methylene Group.—Evidence for this lies in the fact that VIII yielded 63% of 2-ethylnaphthalene[5] and VI yielded 70% of γ-2-naphthylbutyric acid (after hydrolysis) according to the equations

$$\text{(VIII)}\quad C_{10}H_{11}COCH_3 \longrightarrow C_{10}H_7CH_2CH_3 + H_2O$$
$$\text{(VI)}\quad C_{10}H_{11}COCH_2CH_2COOCH_3 \longrightarrow C_{10}H_7CH_2CH_2CH_2COOCH_3 + H_2O$$

3. A Carbon–Oxygen Single Bond Adjacent to the Aromatic Nucleus Is Hydrogenolyzed.—Evidence for this lies in the fact that VII was converted into γ-2-naphthylbutyric acid and X into 2-methylnaphthalene in fair yields according to the equations

$$\text{(VII)}\quad C_{10}H_{11}\overline{CHCH_2CH_2COO} \longrightarrow C_{10}H_7CH_2CH_2CH_2COOH + H_2$$
$$\text{(X)}\quad C_{10}H_{11}CH_2OH \longrightarrow C_{10}H_7CH_3 + H_2O + H_2$$

Results of interest were also obtained with compounds V, IX, XI, and XII. The unsaturated ester V reacted almost quantitatively according to the equation

$$C_{10}H_{11}CH{=}CHCOOCH_3 \longrightarrow C_{10}H_7CH_2CH_2COOCH_3 + H_2$$

The aldehyde IX lost carbon monoxide readily to yield tetralin which was then slowly dehydrogenated to naphthalene. While not a new reaction, the loss of carbon monoxide on pyrolysis of aldehydes is a reaction about which little is known.[6]

The secondary alcohol XI readily lost water on heating but only a small yield of 2-ethylnaphtha-

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[2] The material herein presented represents part of the Thesis presented by H. V. Zahm to the Ohio State University in partial fulfillment of the requirements for the Ph.D. degree.

[3] See Linstead, *J. Chem. Soc.*, Ann. Reports, **33**, 312 (1936).

[4] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[5] For an example of a similar reaction see Fieser and Joshel, THIS JOURNAL, **61**, 2958 (1939).

[6] Hurd, "The Pyrolysis of Carbon Compounds," American Chemical Society Monograph No. 50, Chemical Catalog Co., New York, N. Y., 1929, pp. 236–242. The use of metallic catalysts for such decarbonylations is mentioned but palladium-on-charcoal does not seem to have been used previously.

lene was obtained, presumably because the 2-naphthylethylene first formed underwent rapid polymerization, for most of the reaction product consisted of a resin. The dehydrogenation of the acid chloride XII yielded a mixture from which no pure product was isolated.

In working up the reaction mixture from the dehydrogenation of the keto ester VI it was found that part of the product was free γ-2-naphthylbutyric acid and part methyl γ-2-naphthylbutyrate. It is suggested that reduction of the ketonic ester proceeds by two mechanisms, both involving primary reduction of the ketone group to a secondary alcohol. One mechanism then proceeds by dehydration to yield an unsaturated ester which is further reduced to methyl γ-2-naphthylbutyrate. The other mechanism involves lactone formation by splitting out methanol followed by further reduction to γ-2-naphthylbutyric acid. The ready reduction of the lactone VII to γ-2-naphthylbutyric acid under similar conditions shows that the lactone mechanism is a possible one.

In all of the work herein reported one fact seems to be particularly important, namely, that when a functional group is attacked by hydrogen activated by the catalyst, the hydrogen is very efficiently used. This suggests that the reduction takes place within the molecule as a sort of internal oxidation–reduction process.

From the point of view of synthetic organic chemistry the work we have done should serve to emphasize the desirability of using partly hydrogenated aromatic hydrocarbons as starting materials in order to circumvent unfavorable orientation effects in the fully aromatic counterparts. For example, from our experience in the preparation of pure γ-2-naphthylbutyric acid it is simpler to condense tetralin with succinic anhydride, esterify the keto-acid formed, and dehydrogenate over palladium-on-charcoal than to condense naphthalene with succinic anhydride, separate the isomers, and reduce the β-2-naphthoylpropionic acid by the Clemmensen method.

Experimental(7)

$ArCOCH_3$, VIII.—To a well-stirred and cooled solution of 396 g. of purified tetralin and 240 g. of pure acetyl chloride in 1.8 l. of dry sulfur-free benzene was added one pound of anhydrous aluminum chloride in small portions over a period of ninety minutes, the temperature in the mixture being held below 10°. Stirring was continued until the hydrogen chloride evolution had practically ceased (six hours). The mixture was poured on ice and hydrochloric acid and the ketone isolated by vacuum distillation. The fraction, b. p. 132.5–134.5° at 3.5–4 mm., weighed 468 g. (90%).(8)

$ArCOOCH_3$, I, and ArCOCl, XII.—A solution of sodium hypochlorite was prepared from 500 g. of commercial calcium hypochlorite (H. T. H., Matheson Alkali Co.), 270 g. of sodium carbonate, 76 g. of sodium hydroxide, and 2.9 liters of water. The above ketone (174 g.) and 80 cc. of dioxane were added and the oxidation carried out near 100° as in similar cases.(9,10) There was obtained 148 g. (84%) of pure ArCOOH, m. p. 154–155°, after crystallization from benzene–ligroin. The methyl ester, I, boiled at 149–150° at 4–4.5 mm. The acid chloride, XII, boiled at 121–122° at 2 mm.

ArCHO, IX.—After an unsuccessful attempt to prepare IX from tetralin and *n*-methylformanilide,(11) this aldehyde was prepared in 65–70% yield by the Rosenmund method(12) using cymene instead of xylene as solvent. Five hours were needed for 90% reduction, at which point the reaction should be stopped. The catalyst was collected by filtration and could be used over again four times. The same batch of catalyst could then be reactivated by heating in a casserole for one hour over a strong flame. The aldehyde boiled at 116–119° at 3 mm., and its semicarbazone melted at 223–224° with decomp.

Anal. Calcd. for $C_{12}H_{15}ON_3$: C, 66.3; H, 7.0; N, 19.3. Found: C, 66.7; H, 6.9; N, 19.3.

A CH_2OH, X.—The aldehyde IX was converted into the alcohol X, b. p. 133–134° at 4 mm., in 75% yield by catalytic hydrogenation in alcohol using Adams platinum oxide catalyst and a trace of ferrous chloride.(13)

$ArCH_2COOCH_3$, II.—During seventy minutes there was added a solution of 47.4 g. of the alcohol X in 175 cc. of dry benzene to 24 cc. of pure thionyl chloride. After refluxing for six hours the solvent was removed under reduced pressure and the residue was refluxed for six hours with a solution of 20 g. of sodium cyanide in 26 cc. of water and 125 cc. of methanol. The organic product was then isolated by vacuum distillation. This crude nitrile (34 g., b. p. 133–142° at 3 mm.) was washed with warm 50% sulfuric acid and then hydrolyzed to the corresponding acid by vigorous stirring of a mixture of the nitrile with 75 g. of concentrated sulfuric acid, 27 cc. of water, and 50 cc. of acetic acid in a three-necked flask heated by a glycerol-bath at 122–130°. The crude acid was esterified with methanol to yield the pure ester, II, b. p. 141–143° at 4 mm., in 31% yield (based on X).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 76.4; H, 7.8.

The free acid obtained on hydrolysis of the above ester melted at 97.0–97.5°.

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(7) All melting points corrected. Semimicro analyses by J. E. Varner.

(8) Compare Scharwin, *Ber.*, **35**, 2511 (1902).

(9) Newman and Holmes, "Organic Syntheses," **17**, 66 (1937).

(10) See also G. Schroeter, *Ber.*, **57**, 2003 (1924).

(11) Fieser, *et al.*, *ibid.*, **20**, 11 (1940).

(12) Hershberg and Cason, *ibid.*, **21**, 84 (1941); compare V. Braun, *Ber.*, **55**, 1700 (1922).

(13) Carothers and Adams, THIS JOURNAL, **45**, 1071 (1923); see v. Braun, ref. 12.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.7; H, 7.4.

ArCH=CHCOOCH$_3$, V.—A mixture of 32 g. of aldehyde, IX, 28 g. of malonic acid, and 10 cc. of pyridine was heated on a steam-bath for six hours, cooled, and treated with hot concentrated ammonium hydroxide. After filtration the clear filtrate was acidified and the acid which precipitated was collected and recrystallized from acetic acid. There was obtained 30.0 g. (76%) of pure acid, m. p. 170.8–171.8°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.2; H, 6.9. Found: C, 76.8; H, 7.3.

The ester, prepared from methanol and hydrogen chloride, boiled at 157–158° at 2.5–3 mm. The melting point was 40°.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.8; H, 7.5. Found: C, 77.6; H, 7.5.

ArCH$_2$CH$_2$COOCH$_3$, III.—After unsuccessful attempts at catalytic hydrogenation using Adams platinum catalyst, the above acid was reduced by sodium amalgam. Fifty grams of β-(2-tetralyl)-acrylic acid was dissolved in an excess of sodium hydroxide and the solution was neutralized with hydrochloric acid. A pinch of nickel powder[14] was added and then 400 g. of 4% sodium amalgam in several portions over a period of two hours. After each amalgam addition the mixture was shaken vigorously and the mixture was frequently brought back to neutrality by additions of hydrochloric acid. After all the amalgam had been added, the reaction mixture was heated on the steam-bath for several hours. The alkaline solution was then acidified and the colorless acid collected and crystallized from dilute acetic acid. This product melted for the most part near 80° but some parts did not melt until 180°. For further purification the product was esterified with methanol and the fraction, b. p. 136–137° at 2.5–3 mm., weighed 24.8 g. (71%). A portion was redistilled for analysis.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 76.9; H, 8.4.

The remaining product consisted of a much higher boiling residue, presumably representing bimolecular reduction products. After alkaline saponification the free acid was crystallized from high boiling petroleum ether to yield pearly plates, m. p. 81–82°, in high yield.[15]

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 76.4; H, 7.9.

ArCOCH$_2$CH$_2$COOCH$_3$, VI, and ArCH$_2$CH$_2$CH$_2$COOCH$_3$, IV.—To a well-stirred mixture of 100 g. of pure tetralin, 50 g. of succinic anhydride, and 600 cc. of sulfur-free dry benzene was added 134 g. of anhydrous aluminum chloride during a period of ten minutes. The mixture was then heated and finally refluxed for three hours. The crude dry acid obtained in the usual manner from the reaction mixture was crystallized from benzene to yield 88 g. (76%) of β-2-(5,6,7,8-tetrahydronaphthoyl)-propionic acid, m. p. 114–116°. The methyl ester, VI, was prepared in 88% yield by the Fischer and Speier method and boiled at 170–172° at 1.5–2 mm. A time–temperature cooling curve of this ester showed it to be very pure as it gave a flat portion at 31.0° until it was too solid to stir.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.1; H, 7.4. Found: C, 73.2; H, 7.5.

By the Martin modification[16] of the Clemmensen method the keto acid was reduced to γ-2-tetralylbutyric acid, m. p. 47–49°, b. p. 195–200° at 4.5–5 mm., in 93% yield. Fischer and Speier esterification yielded the corresponding methyl ester IV, b. p. 181–184° at 3.5–4 mm., in 87% yield.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.5; H, 8.7. Found: C, 77.3; H, 8.7.

$\text{Ar}\overline{\text{CHCH}_2\text{CH}_2\text{COO}}$, VII.—This lactone was prepared by sodium amalgam reduction of the above keto acid.[17] From 50 g. of the keto acid there was obtained 27.5 g. (59%) of colorless lactone VII, b. p. 173–175° at 1 mm., which crystallized shortly. A time–temperature cooling curve on this material showed it to be quite pure as a long flat portion occurred at 33.2° until the material was too solid to stir.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.8; H, 7.5. Found: C, 77.6; H, 7.4.

ArCHOHCH$_3$, XI.—This alcohol was prepared in 85% yield by the aluminum isopropylate–isopropyl alcohol reduction[18] of the ketone VIII. In isolating the alcohol it is important to neutralize the aluminate solution in the cold with dilute mineral acid, for, if allowed to heat up, the product of the reaction is tetrahydronaphthylethylene, b. p. 96° at 2 mm., but no attempt at rigorous purification was made.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.1; H, 8.9. Found: C, 90.4; H, 8.8.

The desired alcohol, XI, boiled at 120–121° at 2 mm.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.2. Found: C, 81.6; H, 9.1.

Dehydrogenation Experiments

Palladium-on-charcoal Catalyst.[4]—The charcoal[19] used was warmed with dilute nitric acid (10 cc. of 12 *N* acid in 100 cc. of water) until fumes of nitric oxide were seen. After standing one hour the charcoal was collected, washed thoroughly with hot and then cold water, and dried at 100° for two days and at 200° under reduced pressure for two hours. Six grams of this charcoal was then stirred into a cold solution of 2 g. of palladium chloride in 12 cc. of water and 1.2 cc. of 12 *N* hydrochloric acid. A mechanical stirrer was introduced and 12 cc. of 40% formalin was added followed by a cold solution of 12 g. of potassium hydroxide in 12 cc. of water, the temperature being held

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[14] Suggested by Dr. J. S. Buck; see also Newman, THIS JOURNAL, **60**, 2947 (1938).

[15] Darzens, *Compt. rend.*, **201**, 902 (1935), gives 127° as the melting point of an acid supposed to be β-2-tetralylpropionic acid. From his method of preparation it is likely that he was dealing with the 1-isomer. The structure of our acid is certain because of its dehydrogenation to β-2-naphthylpropionic acid. Furthermore, in a private communication, Dr. R. T. Arnold of the University of Minnesota confirms our melting point of 81–82°.

[16] Martin, THIS JOURNAL, **58**, 1438 (1936).

[17] Fittig and Leoni, *Ann.*, **256**, 84 (1890). The authors are indebted to Mr. Rex Closson for the preparation of this lactone. Later work by Mr. Closson on another keto acid has shown that the recommended large excess of sodium amalgam is detrimental to the yield of lactone, for an 80% yield was obtained when only 6% excess amalgam was used.

[18] Lund, *Ber.*, **70**, 1520 (1937).

[19] Darco G-60, Darco Corp., New York, N. Y.

TABLE I

	Compound	Type of flask	Temperature, 0°C.	Time, hours	%H_2[a]	% Yield[b]
I	ArCOOCH_3	A	288–310	7	96	92
II	$\text{ArCH}_2\text{COOCH}_3$	A	275–307	4.25	96	73[d]
III	$\text{ArCH}_2\text{CH}_2\text{COOCH}_3$	A	280–300	6	97	87
IV	$\text{ArCH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3$	A	274–320	4.5	97	87
V	$\text{ArCH{=}CHCOOCH}_3$	A	235–305	3.75	50	89
VI	$\text{ArCOCH}_2\text{CH}_2\text{COOCH}_3$	B	245–290	7	12	70[e]
VII	$\text{Ar}\overline{\text{CHCH}_2\text{CH}_2\text{COO}}$	A	295–310	3.5	40	71
VIII	ArCOCH_3	B	270	13	19	63[f]
IX	ArCHO	A	275	6	65[c]	95[g]
X	ArCH_2OH	B	230–260	6.5	19	67[h]
XI	ArCHOHCH_3	B	210–290	21	38	28

[a] In all experiments the theoretical amount of hydrogen was considered as two moles of hydrogen per mole of tetralin derivative used. [b] Yields represent purified naphthalene derivatives. [c] Represents the carbon monoxide evolved during the first three hours only. [d] Minimum yield to be expected—early experiment. [e] Isolated 37% as acid, 33% as ester. [f] 2-Naphthyl methyl ketone isolated in 19% yield also. [g] A mixture of naphthalene and tetralin. [h] A mixture of 2-methylnaphthalene and 2-methyltetralin.

below 5°. After all the alkali had been added the temperature was raised to 60° for one-half hour. The catalyst was collected on a filter, washed thoroughly with dilute acetic acid and with hot water, and finally dried *in vacuo* at 100°. All dehydrogenations were carried out with portions of this catalyst.

General Description of Dehydrogenations.—Two flasks were used for carrying out the dehydrogenations. Flask A was a 50-cc. Claisen type carrying a small coil sealed in the take-off side. Water could be circulated through this coil so that no organic matter would distil out of the flask. Flask B was an ordinary 50-cc. distilling flask and was used when it was desired to remove the water formed during a reaction in order to prevent the sputtering that occurs when water droplets fall on a hot liquid. In both cases a rubber tube led from the side arm of the flask through a safety bottle to a gas collecting bottle where the hydrogen evolved was measured over water. Before introducing the catalyst (0.10 ± 0.01 g.) and substance to be dehydrogenated (0.07 ± 0.01 mole) the apparatus was swept out with nitrogen and after introduction of the charge nitrogen was passed through while the flask was being heated in a fused salt bath to 200°. The nitrogen was then stopped and a solid cork inserted in the neck of the flask. The temperature was raised fairly rapidly until evidence of reaction (usually evolution of gas or formation of water) was noticed, the temperature then being controlled at a slightly higher temperature so that the reaction would proceed at a moderate rate. From time to time the temperature would be raised as necessary to keep a fairly rapid reaction proceeding. The reaction was deemed to be essentially complete when no appreciable quantity of gas was evolved even on raising the temperature an additional 10°. Most of the findings are presented in Table I. The reaction mixtures were worked up as described below. In most cases the results were checked.

ARCOOCH_3, **I.**—The methyl 2-naphthoate distilled at 141–143° at 3–4 mm. That this ester was quite pure was shown by a time-temperature cooling curve which showed a flat at 73.2° until the material was too solid to stir. On hydrolysis pure 2-naphthoic acid, m. p. and mixed m. p. 184–185°, was obtained.

$\text{ARCH}_2\text{COOCH}_3$, **II.**—The reaction mixture was hydrolyzed with alcoholic alkali and pure 2-naphthylacetic acid, m. p. 141–142°, was obtained. This represents a minimum value for the yield for it was an early experiment.

$\text{ArCH}_2\text{CH}_2\text{COOCH}_3$, **III.**—The reaction mixture was hydrolyzed with alcoholic alkali and the recrystallized acid obtained was pure β-(2-naphthyl)-propionic acid, m. p. 134–135°.

$\text{ArCH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3$, **IV.**—The mixture was refluxed with alcoholic alkali and the alkaline solution was acidified. The crude but dry γ-(2-naphthyl)-butyric acid, m. p. 95–98°, was obtained in 97% yield.

$\text{ArCH{=}CHCOOCH}_3$, **V.**—The mixture was saponified with alcoholic alkali and the crude β-(2-naphthyl)-propionic acid, m. p. 134–136°, was obtained in 94% yield.

$\text{ArCOCH}_2\text{CH}_2\text{COOCH}_3$, **VI.**—When a mixture of 15.41 g. of VI and 0.10 g. of catalyst was heated in flask B evidence of reaction was seen at 245°. Hydrogen was slowly evolved and water was in evidence. The temperature was raised fairly rapidly to 275° and after seven hours of heating at 275–290° no further hydrogen was evolved. The reaction mixture was taken up in ether and benzene and the catalyst removed by filtration. A sodium carbonate extraction yielded on acidification an acid which was crystallized from benzene–ligroin to yield 4.96 g. (37%) of γ-(2-naphthyl)-butyric acid, m. p. and mixed m. p. 98–99°. The material remaining after the carbonate extraction was hydrolyzed with alcohol–alkali and the acid was crystallized from benzene–ligroin. There was obtained 4.38 g. (33%) of γ-(2-naphthyl)-butyric acid. An additional 1.46 g. (11%) of lower-melting acid was isolated from the mother liquors.

$\text{Ar}\overline{\text{CHCH}_2\text{CH}_2\text{COO}}$, **VII.**—Acidification of an alkaline extract of the reaction product from 12.94 g. of VII yielded 9.0 g. (71%) of pure γ-(2-naphthyl)-butyric acid, m. p. and mixed m. p. 98–99°. Vacuum distillation of the neutral reaction product yielded 0.96 g. of an unidentified liquid boiling at about 121–123° at 6 mm., and about 2 g. of a dark residue which did not distil at a bath temperature of 300° and a pressure of 6 mm.

$ArCOCH_3$, **VIII**.—In this experiment 15.54 g. of VIII was used and after the heating period considerable organic liquid had distilled into the trap. This material together with that remaining in the flask was separated by vacuum distillation at 3–4 mm. into three fractions: 1, 8.82 g., b. p. 95–100°; 2, 0.32 g., b. p. 100–140°; and 3, 2.04 g., b. p. 140–142°. About two grams of oily residue remained in the flask. A ferrox test[20] indicated that no oxygenated compounds were present in fraction 1. This fraction readily gave in high yield the picrate of 2-ethylnaphthalene as its melting point and mixed melting point was 76–78°. Since the yield of picrate from a weighed amount of fraction 1 did not quite equal the yield of picrate from pure 2-ethylnaphthalene, we conclude that fraction 1 probably contained a small amount of 2-ethyltetralin. The 8.82 g. of fraction 1 indicates approximately a 63% conversion of the ketonic group in VIII to a methylene group. Fraction 3 solidified on cooling and on recrystallization from aqueous alcohol melted at 49–50°. An authentic sample of 2-naphthyl methyl ketone melted at 53° (time–temperature cooling curve flat) and a mixed melting point was 52–53°. The 2.94 g. of fraction 3 represents a 19% yield if calculated as pure ketone. The semicarbazones from fraction 3 and from authentic 2-naphthyl methyl ketone were proved identical by the method of mixed melting points. The melting point was 222–223° with decomposition.

Anal. Calcd. for $C_{13}H_{13}ON_3$: C, 68.7; H, 5.8; N, 18.5. Found: C, 68.7; H, 5.8; N, 18.9.

$ArCHO$, **IX**.—When 11.64 g. of IX and 0.10 g. of catalyst were heated in flask A at 275° a mixture of hydrogen and carbon monoxide was evolved. After three hours about 65% of the theoretical amount of carbon monoxide had been evolved.[21] After a total of six hours the evolution of gas had slowed to about the normal rate of evolution of hydrogen from tetralin. Since this was quite slow the reaction mixture was worked up when the reaction was obviously still incomplete with regard to hydrogen evolution. On fractional vacuum distillation at 1.5–2 mm. there was obtained 9.14 g. of material boiling at 56–59° in two fractions. The lower boiling fraction was mainly tetralin, as shown by the fact on distillation at atmospheric pressure it boiled mainly at 204–206° and on treatment with acetyl chloride and aluminum chloride it yielded $ArCOCH_3$, **VIII**, in 75% yield. This ketone was further oxidized by sodium hypochlorite to give a high yield of pure ArCOOH, m. p. and mixed m. p. 154–155°. In addition to tetralin, the 9.14 g. of distillate contained naphthalene, isolated with the aid of picrate formation and identified by odor, melting point, and mixed melting point of 79–80°. About 2 of the 9.14 g. was isolated as naphthalene.

$ArCH_2OH$, **X**.—The organic matter which had distilled with the water was added to the main product and on vacuum distillation 6.64 g. of material, b. p. 68–70° at 2 mm., was obtained from 11.25 g. of X. By treating the distillate with picric acid, the picrate of 2-methylnaphthalene, m. p. and mixed m. p. 116–117°, was isolated. The distillate was presumably a mixture of 2-methylnaphthalene and 2-methyltetralin. There remained about 3 g. of resinous material in the distilling flask.

$ArCHOHCH_3$, **XI**.—On heating a mixture of 15.39 g. of XI and 0.12 g. of catalyst in flask B the formation of water was noticed at 210° and became rapid at 230°. After one hour practically all of the water had distilled. The temperature was raised slowly but the evolution of hydrogen was not appreciable until a temperature of 290° was reached. The organic material in the trap was combined with the rest and vacuum distilled to give 3.87 g. (28%) of a liquid, b. p. 96–100° at 3 mm. The material remaining in the flask was resinous. On treatment with picric acid a 75% yield of the picrate of 2-ethylnaphthalene, m. p. and mixed m. p. 76–77°, was obtained. This indicates that the liquid was largely 2-ethylnaphthalene.

Summary

The catalytic dehydrogenation of twelve 2-substituted-5,6,7,8-tetrahydronaphthalene derivatives over a palladium-on-charcoal catalyst is described.

The methyl esters, $C_{10}H_{11}(CH_2)_nCOOCH_3$, where $n = 0$, 1, 2, and 3, were converted in high yields into the corresponding naphthalene derivatives while the theoretical amount of hydrogen was evolved.

With other functional groups the hydrogen was used efficiently for reduction. The ketonic function in $C_{10}H_{11}COCH_2CH_2COOCH_3$ and $C_{10}H_{11}$-$COCH_3$ was reduced to a methylene group in 70 and 63% yields, respectively, and the carbon–oxygen single bond in $C_{10}H_{11}CH_2OH$ and $C_{10}H_{11}$-$CHCH_2CH_2COO$ was hydrogenolyzed.

In the case of $C_{10}H_{11}CH{=}CHCOOCH_3$, one mole of hydrogen was evolved as gas and one mole saturated the double bond.

The aldehyde $C_{10}H_{11}CHO$ readily lost carbon monoxide.

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(20) Davidson, *Ind. Eng. Chem., Anal. Ed.*, **12**, 40 (1940).

(21) The authors are indebted to Professor D. J. Demorest of the Department of Metallurgy, O. S. U., for the gas analyses.