to the final ground state if the C–N stretching frequency is to be as high as 1540 cm.$^{-1}$. This should at the same time lower the carbonyl frequency markedly, since it acquires a large amount of single bond character. This frequency is indeed lower in amides than in aldehydes and unconjugated ketones, but by nowhere nearly the amount expected. Secondly one wonders why the 1540 cm.$^{-1}$ band is found only in monosubstituted amides, whereas with the vinylogs the 1500–1560 band appears regardless of whether the amine group is unsubstituted, monosubstituted, or disubstituted. We are therefore inclined to feel that the origin of the 1540 band is fundamentally different in the amides and in their vinylogs. Conversely if the origin is actually different, several of our unsaturated ketones might be expected to exhibit *two* bands between 1500 and 1600 cm.$^{-1}$ (in addition to any phenyl bands) ... namely the characteristic band at 1500–1560 cm.$^{-1}$ due to the resonance effect already described, and a second band due to the N–H bending in a secondary amine. Two bands are found in compounds I, VII and VIII, although there is only one in II and IX.

Compounds XI–XV.—Compounds XI and XII have been indicated to be the *trans* and *cis* modifications, respectively, of 1-benzyl-2-phenyl-3-*p*-toluylethyleneimine,[6,8,9] and it is of interest that while the *trans* form (XI) exhibits a carbonyl band in the normal region for α,β-unsaturated carbonyls (including aromatic unsaturation), the *cis* form (XII) has a band about 25 cm.$^{-1}$ below this region. These spectra help settle the rela-

tionship of the configuration of structure XIII to that of XI, inasmuch as its band in the α,β-unsaturated carbonyl region, 1680–1700 cm.$^{-1}$, resembles that of XI rather than XII.

Compound XV is the structure shown for the reaction product of phenylhydrazine with the ethyleneimine XII,[9] but the possibility was considered that the correct structure might instead be represented by XVI. A comparison of its infrared spectrum with that of the other four compounds (XI–XIV) confirms the previous conclusion that it has the pyrazoline structure (XV) rather than the ethyleneimine form (XVI). Thus for example it has the moderately strong bands at 1138 and 1394 cm.$^{-1}$ which have counterparts in XIV but not in XI, XII, nor XIII. Moreover it does not exhibit the strong bands at 1020–1060, 1175–1185, 1220–1240 and 1325–1360 cm.$^{-1}$ shown by each of XI, XII and XIII.

Summary

1. Certain β-amino α,β-unsaturated ketones have been shown to behave chemically more like amides, of which they are vinylogs, than like ketones or vinyl amines.

2. Infrared spectra of fifteen unsaturated amino ketones or derivatives thereof have been studied and their peculiarities discussed. The presence of an amino group (either substituted or unsubstituted) on the beta carbon atom of an α,β-unsaturated ketone lowers the carbonyl band by 20–80 cm.$^{-1}$.

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# The Catalytic Dehydrogenation of 2-Substituted Tetrahydronaphthalene Derivatives

BY MELVIN S. NEWMAN AND J. ROGER MANGHAM[1]

The following report describes a continuation of studies designed to obtain more information about the liquid phase dehydrogenation over palladium-on-charcoal of oxygenated hydroaromatic compounds. The previous reports,[2,3] respectively, dealt with 6-substituted 1,2,3,4-tetrahydronaphthalenes, A, and 1-substituted 1,2,3,4-tetrahydronaphthalenes, B, where OF indicates the oxygenated function. Since the oxygenated functions of A and B differed both in their positions with respect to the point of ring fusion and in their relative positions with respect to the hydrogen to be removed, it is necessary to study compounds of type C and D before a complete

discussion can be attempted. In this paper we describe the behavior of 2-substituted-1,2,3,4-tetrahydronaphthalenes, C, under the above conditions.
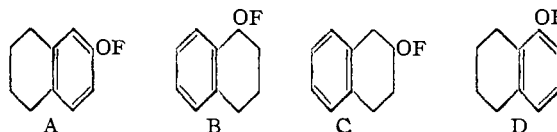
In the discussion R will be used to designate the 1,2,3,4-tetrahydro-2-naphthyl radical and R', the 2-naphthyl radical. In Table I are summarized the results with the following compounds: RCOOCH₃, I; RCH₂OH, II; RCH₂OCOCH₃,
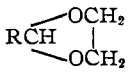
III; RCHO, IV; RCHOCH₂CH₂O, V; RCOCH₃, VI; RCH₂COCH₃, VII; and RCH₂CH₂COCH₃, VIII.

(1) This work was taken from the dissertation submitted by J. R. Mangham to The Ohio State University in partial fulfilment of the requirements for the Ph.D. degree. December, 1948.

(2) Newman and Zahm, THIS JOURNAL. **65**, 1097 (1943).

(3) Newman and O'Leary, *ibid.*, **68**, 258 (1946).

TABLE I

DEHYDROGENATION EXPERIMENTS

No.	Compound	Time, hr.	Temp., °C.	H_2,[a] %	Products	Yield.[b] %
I	RCOOCH$_3$	3.5	290–320	100	R'COOCH$_3$	92
II	RCH$_2$OH	17.5	260–300	49[c]	R'H	28
					R'CH$_3$	60
III	RCH$_2$OCOCH$_3$	6.0	270–290	49	R'CH$_2$OCOCH$_3$	3[d]
					R'CH$_3$	83[e]
IV	RCHO	10.0	275–305	82[f]	R'H	97
V	RCH$\begin{smallmatrix}\diagup OCH_2\\[2pt]\diagdown OCH_2\end{smallmatrix}$	4.0	295–305	28	R'CH$_3$	16[g]
VI	RCOCH$_3$	7.5	310	62	R'COCH$_3$	55
					R'CH$_2$CH$_3$	39
VII	RCH$_2$COCH$_3$	23.0	320	90	R'CH$_2$COCH$_3$	55
					R'CH$_3$	16[h]
VIII	RCH$_2$CH$_2$COCH$_3$	15.0	330	88	R'CH$_2$CH$_2$COCH$_3$	63
					R'CH$_2$CH$_3$	16[h]

[a] The yields of hydrogen are based on the assumption that each mole of tetralin derivative will evolve two moles of hydrogen during dehydrogenation. [b] Yields represent purified naphthalene derivatives, except as noted. [c] The theoretical amount of gas is four moles ($3H_2$ + 1 CO) per mole. [d] Yield based on index of refraction measurements. Recovered 9.0% of original acetate. [e] A portion of the yield was derived from a saponification equivalent determination. [f] The theoretical amount of gas is three moles ($2H_2$ + 1 CO) per mole. [g] Probably contaminated with 2-methyltetralin. Recovered 50.5% of the original acetal. [h] Yield based on slightly impure material.

Experimental[4]

Methyl 1,2,3,4-Tetrahydro-2-naphthoate, I.—A large scale synthesis of 1,2,3,4-tetrahydro-2-naphthoic acid, involving a modification of Baeyer's synthesis,[5] was carried out in 12 gallon Pyrex solution bottles. A solution of potassium hypochlorite was prepared from 8.11 kg. of commercial calcium hypochlorite (H. T. H., Mathieson Alkali Co.), 5.66 kg. of potassium carbonate, 1.62 kg. of potassium hydroxide and 43 l. of water. Since the 2.50 kg. (14.2 moles) of methyl 2-naphthyl ketone to be oxidized was much greater than that previously used,[6] it was added portionwise, during two hours, to the vigorously stirred oxidizing solution,[7] held between 60 and 70° by external cooling. After an additional one and one-half hours of stirring at this temperature, a solution of 1.40 kg. of sodium bisulfite in 3.5 l. of water was added. The 2-naphthoic acid was precipitated by the addition of 7.4 l. of concentrated hydrochloric acid and the liquid was removed by suction filtration with fritted filter sticks. The damp acid was dissolved in 18 l. of solution containing 825 g. of potassium hydroxide. With carbon dioxide bubbling in to control the basicity of the reducing medium,[5,8] 37.8 kg. of 3% sodium amalgam was added during eight hours. At this point reduction to the dihydro acids[9] was complete as indicated by an oxidation test[5] with cold dilute potassium permanganate. This solution was filtered free of insoluble material and combined with 9.2 l. of 18 N sulfuric acid. After removal of the liquid, the damp mixture of dihydro acids was dissolved in 28 l. of solution containing 4.83 kg. of sodium hydroxide. To this solution was added 4.46 kg. of Raney nickel–aluminum alloy[10] in portions during thirty hours. After removal of the nickel catalyst by filtration, the alkaline solution was divided into two equal amounts, each of which was

(4) All melting points corrected. Microanalyses marked ° by Oakwold Laboratories, Fairfax, Virginia; [k] by Mrs. E. K. Klotz; ° by Clark Microanalytical Laboratory, Urbana, Illinois.

(5) Baeyer and Besemfelder, Ann., 266, 198 (1891).

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

(7) A glass centrifugal stirrer was used in concentrated hypochlorite solutions.

(8) Sowinski, Ber., 24, 2361 (1891).

(9) Derick and Kamm, THIS JOURNAL, 38, 400 (1916).

(10) A method of reduction described in papers by Papa, Schwenk and Whitman, J. Org. Chem., 7, 587 (1942), and Schwenk, Papa and Ginsberg, Ind. Eng. Chem., Anal. Ed., 16, 576 (1943).

allowed to siphon slowly into 19 l. of vigorously stirred concentrated hydrochloric acid. After the batches of precipitated acid had been freed of filtrate, dissolved in a total of 30 l. of water containing 650 g. of potassium hydroxide and combined, the solution was cooled to about 10° by the addition of ice. Potassium permanganate was added until no further decolorization occurred (500 ml. of saturated solution). After clarification with saturated sodium bisulfite solution, the solution was siphoned slowly into 4.5 l. of vigorously stirred concentrated hydrochloric acid. The solid was washed with water until free of aluminum salts.

Further purification was accomplished by fractional precipitation from alkaline solution.[9] After six fractions of impure acid had been obtained by addition of successive portions of 50 ml. of concentrated hydrochloric acid, the remainder of the product was precipitated, dried, and recrystallized from petroleum ether (b. p. 65–69°). The yield of 1,2,3,4-tetrahydro-2-naphthoic acid (RCOOH) from the last fraction was 1200 g., m. p. 96.0–96.6°. Fractions 1–6 were fractionally precipitated individually by a similar procedure and yielded an additional 179 g. of pure acid. The total yield was 1379 g. (53.2%). The methyl ester, I, boiled at 102–105° (1 mm.), n^{20}D 1.5314.

Anal.° Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.6, 75.6; H, 7.7, 7.6.

The acid chloride boiled at 122–126° at 2 mm. The amide melted at 138.0–138.8°.

Anal.° Calcd. for $C_{11}H_{13}ON$: N, 8.2. Found: N, 8.0.

Methyl 1,2,3,4-Tetrahydro-2-naphthyl Ketone, VI.—Into a solution made from 16.5 g. of metallic lithium, 200 g. of methyl iodide, and 900 ml. of ether[11] was slowly added a solution of 35.0 g. (0.2 mole) of RCOOH in 1.4 l. of ether. The mixture was treated with water and the neutral portion was distilled to yield 21.4 g. (61.7%) of the desired ketone, VI, as a colorless oil, b. p. 135–138° (4 mm.), n^{20}D 1.5426. The semicarbazone melted at 192.0–193.2° with dec.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.7; H, 8.1. Found°: C, 82.7, 82.9; H, 8.1, 8.3. Calcd. for $C_{13}H_{17}ON_3$: N, 18.2. Found°: N, 18.2.

1,2,3,4-Tetrahydro-2-naphthaldehyde, IV.—This aldehyde was prepared in 67% yield by the Rosenmund

(11) van Dorp and Arens, Rec. trav. chim., 65, 338 (1946).

method,[12] the reaction requiring two hours for evolution of 84% of the theoretical amount of hydrogen chloride gas. Upon vacuum distillation the aldehyde[13] was obtained as a colorless oil, b. p. 90–92° (0.5 mm.), which solidified rapidly at room temperature. This solid product was probably the trimer since it broke down readily at elevated temperatures to yield the oily aldehyde. The semi-carbazone melted at 194.8–196.8° with dec.

Anal.° Calcd. for $C_{12}H_{16}ON_3$: C, 66.3; H, 7.0; N, 19.3. Found: C, 66.2, 66.3; H, 7.1, 7.1; N, 19.3, 18.9.

2-(1,2,3,4-Tetrahydro-2-naphthyl)-1,3-dioxolane, V.— A mixture of 54.5 g. (0.34 mole) of aldehyde IV, 40 ml. of ethylene glycol, 500 ml. of benzene and a trace of *p*-toluenesulfonic acid was refluxed for three days under a fractionating column with a special take-off head for removing the bottom layer of distillate.[14] After the acid catalyst had been removed by washing with sodium bicarbonate solution, 54.5 g. (78.5%) of the acetal, V, was obtained as a colorless oil, b. p. 126–128° (1 mm.), n^{20}D 1.5423.

Anal.° Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 75.9, 76.0; H, 7.8, 7.9.

1,2,3,4-Tetrahydro-2-naphthylcarbinol, II.—During one hour a solution of 194 g. (0.95 mole) of ethyl 1,2,3,4-tetrahydro-2-naphthoate, prepared by esterification of RCOOH with ethanol, in 1 l. of ether was dropped into an ethereal solution of 20 g. (0.52 mole) of lithium aluminum hydride.[15] After the reaction mixture had been decomposed with water and dilute sulfuric acid, 147.2 g. (95.5%) of the desired carbinol, II, was obtained as a colorless oil, b. p. 114–116° (1 mm.), n^{20}D 1.5559. Its 1-naphthylurethan melted at 108.6–109.2°.

Anal.[k] Calcd. for $C_{11}H_{14}O$: C, 81.4; H, 8.7. Found: C, 81.4, 81.4; H, 8.8, 9.2. Calcd. for $C_{22}H_{21}O_2N$: C, 79.7: H, 6.4; N, 4.3. Found: C, 79.9, 79.9; H. 6.1. 6.0; N, 4.4, 4.3.

The corresponding acetate, III, was formed in 94% yield by heating the carbinol, II, in benzene with acetic anhydride and a trace of *p*-toluenesulfonic acid. It formed a colorless oil, b. p. 124–126° (1.5 mm.), n^{20}D 1.5238.

Anal.[k] Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 76.8, 76.7; H, 8.2, 8.5.

1-(1,2,3,4-Tetrahydro-2-naphthyl)-2-propanone, VII.— To a cooled solution of 224.0 g. (1.38 moles) of carbinol, II, 109.0 g. (1.38 moles) of dry pyridine and 250 ml. of dry toluene was added slowly 164 g. (1.38 moles) of purified thionyl chloride. After heating the reaction mixture on the steam-bath overnight, the yield of chloride, RCH₂Cl, b. p. 114–118° (1.5 mm.), was 233.8 g. (93.8%). As a structure proof of the product, a portion was refluxed for thirty-six days with potassium acetate and a trace of sodium iodide in anhydrous ethanol. The acetate, thus formed, was readily hydrolyzed by aqueous alkali and the product (68% from the chloride) was shown to be identical with authentic 1,2,3,4-tetrahydro-2-naphthyl-carbinol, II, by comparison of the 1-naphthylurethans, m. p. 108.2–108.6 and mixed m. p. 108.5–109.2°.

The Grignard reagent prepared from 54.2 g. (0.3 mole) of the chloride, RCH₂Cl, was added over a period of two hours to a solution of 57.0 g. (0.56 mole) of acetic anhydride in 57 ml. of ether cooled by an external Dry Ice–acetone-bath at −78°.[16] After the reaction mixture has been treated with ammonium chloride solution, 44.3 g. (78.6%) of the ketone, VII, was obtained as a colorless oil, b. p. 114–117° (1 mm.), n^{20}D 1.5362. The semicarbazone melted at 199.8–201.6° with dec.

Anal.° Calcd. for $C_{13}H_{16}O$: C, 82.9; H, 8.6. Found:

C, 82.4, 82.5; H, 8.5, 8.7. Calcd. for $C_{14}H_{12}ON_3$; N, 17.1. Found: N, 16.9.

1-(1,2,3,4-Tetrahydro-2-naphthyl)-3-butanone, VIII.— The preparation of VIII from RCH₂Cl by way of the aceto-acetic ester synthesis failed. The low boiling material obtained probably resulted from dehydrohalogenation of the starting alkyl chloride. Alternately, gaseous form-aldehyde was passed into the Grignard reagent[17] made from 161.9 g. (0.895 mole) of RCH₂Cl until the color test[18] for the Grignard reagent was negative (about thirty minutes). After decomposition of the reaction mixture with dilute sulfuric acid, there was obtained 96.4 g. (61%) of 2-(1,2,3,4-tetrahydro-2-naphthyl)-ethanol as a colorless oil, b. p. 123–127° (1 mm.), n^{20}D 1.5490.

Anal.° Calcd. for $C_{12}H_{16}O$: C, 81.7; H, 9.2. Found: C, 81.8; H, 9.4.

By a process similar to one above, the alcohol was treated with thionyl chloride to yield the corresponding chloride (93.1%) as a colorless oil, b. p. 104–109° (0.5 mm.). In a reaction similar to one above involving the Grignard reagent from 42.5 g. (0.22 mole) of the chloride, RCH₂CH₂Cl, and 42.4 g. (0.415 mole) of acetic anhydride there was obtained 27.4 g. (62%) of the desired butanone, VIII, as a colorless oil, b. p. 124–126° (1 mm.) n^{20}D 1.5320. The semicarbazone melted at 171.4–173.4° with dec.

Anal.° Calcd. for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 82.1, 82.4; H, 9.2, 9.0. Calcd. for $C_{15}H_{21}ON_3$: N, 16.3. Found: N, 16.4.

Dehydrogenation Experiments

Palladium-on-Charcoal Catalyst.—The catalyst used in this work was similar to that of the previous investigations.[2,3] A check on the activity of the catalyst was made by dehydrogenation of methyl 1,2,3,4-tetrahydro-6-naphthoate as before.[2] About the same amount of hydrogen was evolved in about the same amount of time.

General Description of Dehydrogenations.—The apparatus made for the dehydrogenations was designed to improve on the two-flask technique in the previous investigations.[2,3] It consisted of a 50-ml. Claisen flask with a condenser and receiver sealed onto its horizontal side arm. In the verticle side-arm was sealed a coil-type condenser through which water was circulated during those dehydrogenations in which water was not liberated. In the dehydrogenation experiments where water was evolved, acetic acid vapor was refluxed through the sealed-in coil. The heated coil served to allow the water to distill from the reaction mixture and prevent excessive splattering and to condense the organic vapors. The remainder of the dehydrogenation procedure was essentially the same as before.

Three duplicate runs were made on each compound, the first served as a pilot run. In the second and third the products were isolated as nearly quantitatively as possible and served as checks on the reproducibility of the results obtained. Since the results of the last two were in substantial agreement, a description is given only for the third run. In each case 0.07 mole ± 0.01 g. of the compound was dehydrogenated. Table I summarizes the experimental details recorded. In working up the products of the reactions, the material was always vacuum distilled from the catalyst prior to further treatment.

RCOOCH₃, I.—The distilled dehydrogenated ester was saponified and the acid was recrystallized from ethanol. It melted, alone and mixed with authentic 2-naphthoic acid, at 183.4–185.0°.

RCH₂OH, II.—The product from 11.36 g. of II was fractionated under reduced pressure. The first fraction, 2.47 g. (27.6%), naphthalene, was obtained by careful sublimation into a chilled receiver. A portion, after recrystallization from ethanol, melted at 78.6–80.2°,

(12) Hershberg and Cason. "Organic Syntheses," Vol. XXI. John Wiley and Sons, Inc., New York, N. Y., 1941, p. 84.

(13) Weil and Ostermeier. *Ber.*, **54.** 3218 (1921).

(14) Fieser. Fields and Lieberman. *J. Biol. Chem.*, **156.** 191 (1934).

(15) Nystrom and Brown. THIS JOURNAL. **69.** 1197 (1947).

(17) Newman and Booth. *ibid.*, **67,** 154 (1945).

(17) Gilman and Catlin. "Organic Syntheses." Coll. Vol. I. 2nd ed.. John Wiley and Sons. Inc.. New York, N. Y.. 1941. p. 188.

(18) Gilman and Schulze. THIS JOURNAL. **47.** 2002 (1925); Gilman and Heck, *ibid.*, **52.** 4949 (1930).

mixed m. p. 79.0–80.4°. The second fraction, 5.96 g. (59.8%), b. p. 69–74° (1 mm.), formed a picrate, m. p. 115.8–116.4°, mixed m. p. not depressed with picrate of 2-methylnaphthalene.

A gas analysis[19] showed that the gas evolved was a mixture of carbon monoxide and hydrogen. The amounts of carbon monoxide and naphthalene obtained corresponded rather closely, but a quantitative balance was not undertaken.

RCH_2OCOCH_3, III.—The product obtained from 12.41 g. of III was separated into three fractions by vacuum distillation. Fraction 1, 7.26 g. (73.0%), b. p. 126–131° at 23 mm., formed 2-methylnaphthalene picrate, m. p. and mixed m. p. 116.4–117.4°. Fraction 2, 1.58 g., b. p. 131–177° at 23 mm., was shown by a saponification equivalent determination (assuming the molecular weight of III) to consist of about 40% of ester and 60% of 2-methylnaphthalene. The picrate of 2-methylnaphthalene was isolated and identified. Fraction 3, b. p. 177–180° at 23 mm., weighed 1.06 g. After a portion had been saponified, the carbinol product boiled at 120–125° at 2 mm. The 1-naphthylurethan which was prepared melted at 102–106°, which indicated a mixture of the two 1-naphthylurethans, that of 1,2,3,4-tetrahydro-2-naphthylcarbinol (m. p. 108.6–109.2°) and that of 2-naphthylcarbinol (m. p. 141.2–142.8°). The latter was prepared from 2-naphthylcarbinol,[20] m. p. 81.2–82.0°, obtained by reduction of 2-naphthoic acid with lithium aluminum hydride.[21] Authentic 2-naphthylmethyl acetate,[22] m. p. 57.2–57.8°, was prepared by refluxing 2-naphthylcarbinol with acetic anhydride and a trace of p-toluenesulfonic acid in benzene. Mixtures of III and 2-naphthyl acetate were made and their refractive indices determined.

% 2-naphthylmethyl acetate	$n^{20}D$
20	1.5344
40	1.5479
50	1.5530

Since the refractive index of Fraction 3 was $n^{20}D$ 1.5473, it contained about 40% 2-naphthylmethyl acetate and 60% unchanged III. Thus, in all, there was obtained 3.0% of 2-naphthylmethyl acetate, 82.5% of 2-methylnaphthalene and 9.0% of III based on the starting 14.21 g. of III.

RCHO, IV.—Pure naphthalene was obtained by direct sublimation from the catalyst. By analysis[19] the gas collected was shown to contain carbon monoxide, hydrogen and methane. The amounts of carbon monoxide and methane obtained account reasonably well for the amount of naphthalene obtained in the experiment; however, a quantitative balance was not established.

$\overline{RCHOCH_2CH_2O}$, V.—The product from 14.30 g. of V was separated into two main fractions by vacuum distillation. Fraction 1, 1.58 g. (15.9%), b. p. 104–109° at 6 mm., yielded 2-methylnaphthalene picrate. Since the yield of picrate was somewhat lower (54%) than that from authentic 2-methylnaphthalene prepared in a similar manner (68%), we conclude that Fraction 1 probably contained a small amount of 2-methyltetralin. Fraction 2, b. p. 157–160° at 6 mm., weighed 7.21 g. A portion was hydrolyzed by boiling with dilute aqueous alcoholic hydrochloric acid and the product converted to its semicarbazone in 72% over-all yield. The semicarbazone melted alone and mixed with the semicarbazone of 1,2,3,4-tetrahydro-2-naphthaldehyde at 191–194° with dec. Fraction 2, then, was essentially unchanged V and represents a 50.5% recovery of the starting material. In addition to the two fractions, there remained 3.3 g. of residue.

(19) Gas analysis through the courtesy of D. J. Demorest, The Ohio State University, Department of Metallurgy.

(20) Sah. *Rec. trav. chim.*, **59**, 461 (1940).

(21) Nystrom and Brown, THIS JOURNAL. **69**, 2548 (1947).

(22) Tarbell, Fukushima and Dam. *ibid.*, **67**, 197 (1945).

$RCOCH_3$, VI.—The addition of 0.10 g. of fresh catalyst, after an hour's heating, caused a considerable increase in the pace of the dehydrogenation reaction. The distilled material from 12.20 g. of VI was separated into two main fractions by vacuum distillation. The first fraction, 4.24 g. (38.7%), b. p. 70–77° (0.5 mm.), formed a picrate which melted at 76–78° alone and mixed with the picrate of authentic 2-ethylnaphthalene. The second fraction, 6.58 g. (55.2%), b. p. 95–99° (0.5 mm.), after recrystallization from an alcohol–water mixture, melted alone and mixed with authentic methyl 2-naphthyl ketone at 53–54°. The semicarbazone of the second fraction melted alone and mixed with the semicarbazone of authentic methyl 2-naphthyl ketone at 222.0–223.4°.

RCH_2COCH_3, VII.—The slow rate of evolution of hydrogen from 13.18 g. of VII was not increased by the addition of a fresh portion of catalyst at the end of two hours of heating. After removal of the product from the catalyst by vacuum distillation, there remained 3.4 g. of high boiling residue. The product was separated into two fractions by distillation at reduced pressure. Fraction 1, 1.55 g. (15.6%), b. p. 66–129° (1 mm.), consisted mainly of 2-methylnaphthalene as judged by the ready formation of the picrate. Fraction 2, 7.02 g. (54.5%), b. p. 129–131° (1 mm.), was shown to be 2-naphthyl-2-propanone by comparison with an authentic sample. A portion of Fraction 2, after recrystallization from petroleum ether (b. p. 30–60°), melted alone and mixed at 36.0–37.2°. Its semicarbazone melted at 182.8–184.4° with dec.; a mixed melting point showed no depression.

The previously unknown 2-naphthyl-2-propanone was synthesized in 42% yield from 2-naphthylacetic acid[23] and methyl lithium by a procedure similar to that described in the experimental discussion above. It boiled at 131.5–132.5° at 1.5 mm. and after recrystallization from petroleum ether (b. p. 30–60°) melted at 36.0–37.2°. The semicarbazone melted at 183.0–184.6° with dec.

Anal.[c] Calcd. for $C_{13}H_{12}O$: C, 84.7; H, 6.6. Found: C, 84.9; H, 6.5. Calcd. for $C_{14}H_{15}ON_3$: N, 17.4. Found: N, 17.3.

$RCH_2CH_2COCH_3$, VIII.—With the catalyst remained 2.8 g. of resinous material. The product from 14.16 g. of VIII was fractionated. Fraction 1, 1.71 g. (15.6%), b. p. 76–80° (1 mm.), was shown to be 2-ethylnaphthalene by formation of its picrate which, after one recrystallization from ethanol, melted at 75.2–76.8° alone and mixed with an authentic sample. Fraction 2, 8.73 g. (62.8%), b. p. 139–142° (1 mm.) was shown to be 1-(2-naphthyl)-3-butanone by its melting point, after recrystallization from petroleum ether (b. p. 30–60°), of 48.4–49.0° (lit.[24] 50°), of its semicarbazone, 171.2–172.8° (lit.[24] 173°) and of its oxime, 119.4–120.8° (lit.[24] 115–116°).

Discussion of Results

A number of the compounds in this dehydrogenation study contained the same oxygenated substituents as those of the previous studies.[2,3] The carbomethoxy group (-$COOCH_3$) was unharmed in all three cases by the hydrogen which was eliminated from the ring. It is, therefore, concluded that a carboxyl group in a hydroaromatic compound may be protected easily during dehydrogenation[*] over palladium-on-charcoal by conversion to its methyl ester.

In the cases of the compounds containing the carbinol group (-CH_2OH) the results of the three studies show graded differences. The primary alcohol group on the beta position of the benzenoid ring[2] was hydrogenolyzed to the methyl group, whereas this same group on the alpha position of the saturated ring[3] lost both hydrogen and carbon

(23) Newman. *J. Org. Chem.*, **9**, 518 (1944).

(24) Mayer and Sieglitz. *Ber.*, **55**, 1854 (1922).

monoxide to yield naphthalene almost quantitatively. Hydrogenolysis of the alcohol group to 1-methylnaphthalene occurred only to the extent of 4%. The compound containing the carbinol group on the beta position of the hydrogenated ring lost water in part and carbon monoxide in part, giving 2-methylnaphthalene and naphthalene in the approximate ratio of 2:1. The last results show some similarity to those of each of the others. It seems, therefore, that the fate of the primary alcohol function is dependent both on its position with respect to the point of ring fusion and on the type of ring to which it is bound.

The results of the dehydrogenation of the compounds containing the *ketonic group*, ($-COCH_3$) show graded differences. When the compound bearing this group attached to the beta position of the aromatic ring[2] was dehydrogenated, the carbonyl group was reduced to a methylene group; only a small amount of the corresponding naphthyl ketone being obtained. In contrast, the ketone function was not attacked by hydrogen when attached to the alpha position of the hydroaromatic ring.[3] In the latter case, the ring itself was resistant to dehydrogenation and only a small amount of the methyl 1-naphthyl ketone was obtained. The compound bearing the ketonic group at the beta position of the saturated ring, was partially converted to the 2-ethylnaphthalene and partially dehydrogenated to methyl 2-naphthyl ketone. The ratio of the amounts of 2-ethylnaphthalene and methyl 2-naphthyl ketone was approximately 2:3. The results in the last case cited are similar to some extent to those of both of the others. It may be concluded that the behavior of the ketonic group directly bound to the ring depends both upon the type of ring to which it is attached and upon its position relative to the point of ring fusion.

The *aldehyde function* ($-CHO$), when attached to the beta position of the aromatic ring[2] and when attached to the beta position of the hydroaromatic ring, lost carbon monoxide almost quantitatively. However, the decarbonylation reaction is undoubtedly catalyzed by the palladium and is not affected by the removal of hydrogen from the ring.

The two *acetates*, (having the group $-CH_2OCOCH_3$), differing in the position of the ester function on the hydrogenated ring, gave dehydrogenation products that differed in degree but not in kind. The oxygenated function was protected to the extent of 26% in the dehydrogenation of the alpha isomer[3] and only to the extent of 3% in the dehydrogenation of the beta isomer. The other products in each case resulted from hydrogenolysis of the acetate function. It thus appears that it is not feasible to attempt a catalytic dehydrogenation of a compound bearing an alcohol function either free or acetylated.

The two isomeric *propanones*, having the ketone group removed from the saturated ring

by a methylene group, yielded somewhat different products. The alpha substituted compound gave a high yield of the corresponding aromatic propanone,[3] whereas the beta substituted compound gave only a fair yield of the corresponding naphthalene derivative. The difference in yields is accounted for by the formation of 2-methylnaphthalene and resinous material in the latter case. Since the beta substituted isomer was heated about 30° higher and about twice as long as the alpha derivative before hydrogen evolution had ceased, the lower yields of aromatic ketone from the former may have been due to pyrolytic decomposition rather than to a dehydrogenation effect.

The differences between the dehydrogenation products of the two butanones, having the ketone group removed from the hydrogenated ring by two methylene groups, are quite a bit greater than those of the propanones described above. The alpha compound[3] in this case was resistant to dehydrogenation and yielded only a small amount (16%) of the corresponding naphthalene ketone, whereas the beta compound dehydrogenated slowly but steadily to give a fair yield (62.8%) of its corresponding naphthalene ketone. The hydrocarbons, isolated from the reaction products, represented the loss of a three carbon fragment (1-methylnaphthalene) from the alphabutanone and the loss of a two carbon fragment (2-ethylnaphthalene) from the beta-butanone. The hydrocarbon side reaction products presumably resulted from pyrolysis and do not therefore indicate a difference in hydrogenolysis effects resulting from the different relative positions of the parent functional groups on the hydrogenated ring.

Protection of the aldehyde function by formation of its cyclic acetal with ethylene glycol has been tried in only the present case. The only dehydrogenated product isolated, 2-methylnaphthalene, was in low yield. The remainder of the product consisted of high boiling material and unchanged starting material (50.5%). From these results it would appear that this method of protection of aldehydes from decarbonylation during catalytic dehydrogenation has little value.

Summary

The liquid phase catalytic dehydrogenation over a palladium-on-charcoal catalyst of eight oxygenated 2-substituted-1,2,3,4-tetrahydronaphthalenes is described.

The methyl ester, $C_{10}H_{11}COOCH_3$, was converted in high yield into the corresponding naphthalene derivative while the theoretical amount of hydrogen was evolved.

The primary alcohol, $C_{10}H_{11}CH_2OH$, was partially degraded to naphthalene by the loss of hydrogen and carbon monoxide and partially converted to 2-methylnaphthalene by loss of hydrogen and water.

Hydrogenolysis of the acetate function of $C_{11}H_{10}CH_2OCOCH_3$ occurred as the main reaction.

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

The cyclic acetal, $C_{10}H_{11}\overline{CHOCH_2CH_2O}$, did not dehydrogenate smoothly. The only dehydrogenated product isolated, 2-methylnaphthalene, resulted from hydrogenolysis of the acetal.

The ketones $C_{10}H_{11}COCH_3$, $C_{10}H_{11}CH_2COCH_3$ and $C_{10}H_{11}CH_2CH_2COCH_3$ gave fair yields of the corresponding aromatic ketones. The ketonic group of the first was reduced to a methylene group to a considerable extent. Small amounts of the last two were pyrolyzed to form hydrocarbons, with a resulting loss of a two-carbon fragment in each case.

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Pyrolysis of Butadiene[1]

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In the pyrolysis of unsaturated hydrocarbons in this Laboratory, it has been observed that the liquid products are frequently colored yellow. This was noted particularly in the pyrolyses of butadiene, isoprene,[3] and isobutylene,[4] where it appeared in the C_7-C_8 region of products. Similar observations were reported in 1932 by Frey and Hepp[5] in a study of the production of aromatic oils from the pyrolysis of simple paraffins. At 850° and atmospheric pressure, butane gave benzene, toluene, xylenes, and a number of olefins and diolefins, principally butadiene and cyclopentadiene. A few degrees above the boiling point of toluene a bright yellow hydrocarbon was obtained; another yellow hydrocarbon appeared in the xylene fraction. Neither of these was identified because they were present in such small amounts.

The first step in this investigation has been to pyrolyze large quantities of butadiene in order to isolate the yellow fraction in amounts large enough to analyze.

Experimental

The apparatus used for the pyrolysis was a quartz furnace 60 × 3 cm., connected to a series of traps, a manometer, a glycerol-filled vacuum pump and a gas meter. The traps were cooled to −78°. To prevent clogging, the first trap was cooled only to −10°. The furnace was heated by two external resistance heaters, and the temperature at the center was measured with a chromel-alumel thermocouple. The temperature was maintained within 10° during a given run. The pressure did not vary more than 2 mm.

The butadiene obtained from Shell Oil Company was of better than 98% purity; it was used without further purification. The hydrocarbon was introduced to the furnace from a pressure bottle kept in an ice-salt-bath, the input rate, usually a mole an hour, being regulated by a needle valve, and the amount put through determined by the loss

in weight of the bottle. The tar, largely naphthalene, collected in the first trap, while the lower aromatic fractions condensed mainly in the second and third traps. Nearly all of the unchanged butadiene condensed in the traps, but 2–5% of the total volume was detected in the effluent gases. The gaseous products (insoluble in glycerol, except acetylene to some extent) passed through the gas meter and escaped into the air. During the course of a run several samples were taken for analysis. At the end of each run the products collected were transferred to weighed bottles and stored at −15° until they were analyzed.

Five runs were made in all. In Table I are given the data for run 3. The analysis of the products was made as follows:

The gases were determined on a modified Hempel apparatus developed in this Laboratory.[6] The reagents for the absorption of the various gases were: acetylene, potassium mercuric iodide; isobutylene, 62.5% sulfuric acid; butenes, 71% sulfuric acid; propylene, 82.5% sulfuric acid; ethylene, fuming sulfuric acid. The different concentrations of acid were those recommended by Hurd and Spence[7] for the detection of the various hydrocarbons. Butadiene was determined by its reaction with maleic anhydride.[8] Since, according to Hurd and Spence, butadiene would be absorbed in both the propylene and isobutylene reagents, the values reported for the C_3 and C_4 hydrocarbons are affected by this amount. The saturated portion of the gas was analyzed for hydrogen by oxidation over copper oxide at 285°. The average value, 25%, checked analyses by combustion data which gave 25.8% for hydrogen and 12% for methane.

The tar in the first trap was collected over several runs and distilled. It was found to contain naphthalene and a small yellow fraction boiling above naphthalene, which we have not identified.

An approximate analysis from mass spectrometer data[9] for the liquid samples from the other traps showed, in agreement with Staudinger[10] that the liquids are almost exclusively aromatic. The relative abundance of the compounds was as follows: benzene, > 90%; toluene, ≦ 1%; indene, < 1%; dihydroindene, < 1%; tetralin, < 0.5%; styrene, < 1%; ethylbenzene, ≦ 1%. Other peaks not accounted for occurred at 83, 85, 117 and 119. It will be noticed that the benzene/toluene ratio of 90/1 found by the mass spectrometer differs widely from the ratios reported in Tables I and II (15.4/1.0 and 10.8/1.0, respectively), but no explanation for this deviation is apparent.

(1) Taken from the dissertation presented by Sister Ann Charles Duggan for the degree of Doctor of Philosophy at the Catholic University.

(2) (a) Sister Mary Thomas Murphy, S.S.J., College of Chestnut Hill, Philadelphia, Pa.; (b) Sister Ann Charles Duggan, O.P., Barry College, Miami, Florida.

(3) M. T. Murphy, Ph.D. dissertation, The Johns Hopkins University, 1938, pp. 38, 44.

(4) L. Wall, Ph.D. dissertation, Catholic University of America, 1945, p. 10.

(5) Frey and Hepp, *Ind. Eng. Chem.*, **24**, 282 (1932).

(6) Rev. Aquinas Sweeney, C.P., Master's thesis, Catholic University of America, 1945.

(7) Hurd and Spence, THIS JOURNAL, **51**, 3356 (1929).

(8) Tropsch and Mattox, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 104 (1934).

(9) We are indebted to Dr. Leo Wall of the National Bureau of Standards for this analysis.

(10) Staudinger, Endle and Herold, *Ber.*, **46**, 2466 (1913).