curate within 4%, since the relationship of one-third reaction life to compositions is linear within this error.

2. A greater accuracy may be attained by use of shorter reaction life periods, and this is possible with the higher dilution of mercury which can be titrated with the dithizone reagent.

3. A mixture of methoxy chloromercurials is evidently produced owing to the weak directive influence of the centralized double bond in oleates and elaidinates.

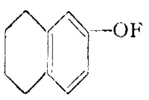
TORONTO, CANADA RECEIVED JULY 13, 1945

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

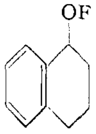
The Catalytic Dehydrogenation of 1-Substituted 1,2,3,4-Tetrahydronaphthalene Derivatives

BY MELVIN S. NEWMAN AND FR. TIMOTHY J. O'LEARY[1]

The work herein reported is a continuation of studies designed to obtain more information about the fate of oxygenated functions in hydroaromatic compounds when submitted to liquid phase catalytic dehydrogenation. In a previous report[2] the dehydrogenation over palladium-on-charcoal of a series of 2-substituted-5,6,7,8-tetrahydronaphthalenes, A, was described. In this paper similar studies on 1-substituted 1,2,3,4-tetrahydronaphthalenes, B, are discussed. Thus not only is the position of the oxygenated functions (OF) on the nucleus changed but also the relative positions of the hydrogen to be removed and the oxygenated functions are different.



A



B

Throughout the discussions Ar will be used to designate the 5,6,7,8-tetrahydro-2-naphthyl radical, R, the 1,2,3,4-tetrahydro-1-naphthyl radical, and R′, the 1-naphthyl radical.

The results obtained with two methyl esters, $RCOOCH_3$, I, and RCH_2COOCH_3, II, three ketones, $RCOCH_3$, III, RCH_2COCH_3, IV, and $RCH_2CH_2COCH_3$, V, and two alcohols and their acetates, RCH_2OH, VI, RCH_2CH_2OH, VII, RCH_2OCOCH_3, VIII, and $RCH_2CH_2OCOCH_3$, IX, are summarized in Table I.

TABLE I

No.	Compound R =	Flask	Temp., °C.	Time, hr.	% H_2[a]	Products R =	% Yield[b]
I	$RCOOCH_3$	A	306–315	8.0	82.8	$R'COOH$	74.7
II	RCH_2COOCH_3	A	260–310	5.2	99.4	$R'CH_2COOH$	90.9
III	$RCOCH_3$	B	288–310	7.0	19.0	$R'COCH_3$	14.7[c]
						$RCOCH_3$	70.0[c]
IV	RCH_2COCH_3	B	290–315	10.0	85.8	$R'CH_2COCH_3$	84.2
V	$RCH_2CH_2COCH_3$	B	325–327	7.5	47.3	$R'CH_2CH_2COCH_3$	16.0[d]
						$RCH_2CH_2COCH_3$	57.0[d]
						$R'CH_3$	14.0
VI	RCH_2OH	B	275–300	13.0	53.6[2]	$R'CH_3$	4.0
						$R'H$	95.6
VII	RCH_2CH_2OH	B	280–303	8.6	75.9[e]	$R'CH_3$	76.7
						$R'CH_2CH_2OH$	12.0
VIII	RCH_2OCOCH_3	B	290–295	5.0	25.8	$R'CH_2OH$	26.0
						$R'CH_3$	10.0
						RCH_3	14.0
IX	$RCH_2CH_2OCOCH_3$	B	290–302	5.7	76.0	$R'CH_2CH_2OH$	62.5
						$R'CH_2CH_3$	28.3

[a] The theoretical amount of hydrogen in each case is calculated as two moles per mole of hydroaromatic compound. [b] The yields represent purified material except as noted. [c] Yields estimated from index of refraction measurements. [d] Yields estimated from distillation data. [e] The theoretical amount of gas is four moles ($3H_2 + 1CO$) per mole.

Experimental[3]

Methyl 1,2,3,4-Tetrahydro-1-naphthoate, I.—In a typical experiment 101 g. of ethyl 3,4-dihydro-1-naphthoate,[4] 70 cc. of ethyl alcohol and 15 g. of powdered nickel-on-kieselguhr catalyst were charged into a bomb under 1000 lb. pressure of hydrogen. At 140° reduction was complete after two hours to yield 96.5 g. (94.6%) of ethyl 1,2,3,4-tetrahydro-1-naphthoate, b. p. 115° (0.5–1.0 mm.). On hydrolysis, the free acid, m. p. 80–81°, was obtained.[5] This acid was also obtained in 94% yield by reduction of

---

[1] This work was taken from the thesis submitted by Fr. T. J. O'Leary to The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, June, 1945.

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

[3] All melting points corrected. Microanalyses marked [a] by J. A. Curtiss, [b] by S. R. Olsen, [c] and by the Arlington Laboratories, Fairfax, Virginia.

[4] Fieser and Holmes, THIS JOURNAL, **58**, 2319 (1936).

[5] Baeyer and Schroder, *Ann.*, **266**, 184 (1891).

an aqueous solution of the sodium salt of the dihydro acid by 2% sodium amalgam. On esterification with methanol, the methyl ester, I, was secured as a colorless oil, b. p. 106–107° (1 mm.).

Anal.[b] Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.5, 75.8; H, 7.5, 7.3.

Methyl 1-(1,2,3,4-Tetrahydro)-naphthylacetate, II.—The mixture of unsaturated acids obtained in 69% yield from the Reformatsky reaction of ethyl bromoacetate and α-tetralone was converted into ethyl 3,4-dihydro-1-naphthylacetate by esterification using hydrogen chloride.[6] The ethyl ester was reduced to the tetrahydro ester, b. p. 116.5–117° (1 mm.), in 96% yield using high pressure at 120° as above. The methyl ester, II, b. p. 118–119.5° (1 mm.), $n^{25}\mathrm{D}$ 1.5275, was obtained from the ethyl ester by hydrolysis and reësterification using methanol.

Anal.[b] Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 76.8, 76.6; H, 7.9, 7.7.

The free acid was characterized by means of its amide,[7] m. p. 120.4–121.2°.

Anal.[c] Calcd. for $C_{12}H_{15}ON$: C, 76.2; H, 8.2; N, 7.4. Found: C, 76.4, 76.4; H, 8.1, 8.2; N, 7.5, 7.3.

Methyl 1-(1,2,3,4-Tetrahydronaphthyl Ketone, III.—A solution of the acid chloride, prepared from 40.3 g. (0.24 mole) of tetrahydronaphthoic acid, in 50 cc. of ether was added slowly to a mixture made from an ethereal solution of 0.48 mole of methylmagnesium bromide and 46 g. of anhydrous cadmium chloride.[8] After refluxing for one hour the mixture was treated with dilute hydrochloric acid and the neutral portion was distilled to yield 27 g. (65%) of desired ketone, III, as a colorless oil, b. p. 92–94° (1 mm.). A redistilled portion, $n^{25}\mathrm{D}$ 1.5221, was analyzed. The analyses were low in carbon but since the semicarbazone gave good analytical values, the preparation was not repeated for additional analyses. The semicarbazone was prepared in 70% yield and melted at 170.2–170.5° with decomposition.

Anal.[a] Calcd. for $C_{12}H_{14}O$: C, 82.7; H, 8.1. Found: C, 81.2, 81.2; H, 7.8, 7.9. Calcd. for $C_{13}H_{17}ON_3$: C, 67.5; H, 7.4; N, 18.2. Found: C, 67.6, 67.4; H, 7.4, 7.3; N, 18.1, 18.0.

1-(1,2,3,4-Tetrahydro)-naphthyl-2-propanone, IV.—By a process similar to the above,[8] the ketone, IV, was obtained in 69% yield, from 1-(1,2,3,4-tetrahydro)-naphthylacetyl chloride and dimethylcadmium, as a colorless oil, b. p. 127–129° (1 mm.), $n^{25}\mathrm{D}$ 1.5377. The semicarbazone melted at 178.6–179°.

Anal.[a] Calcd. for $C_{13}H_{16}O$: C, 82.9; H, 8.6. Found: C, 82.2, 82.1; H, 8.4, 8.4. Calcd. for $C_{14}H_{19}ON_3$: C, 68.5; H, 7.8; N, 17.1. Found: C, 68.2, 68.1; H, 7.5, 7.5; N, 16.9, 16.9.

1-(1,2,3,4-Tetrahydro-1-naphthyl)-3-butanone, V.—To a cooled solution of 141 g. (0.8 mole) of β-(1,2,3,4-tetrahydro-1-naphthyl)ethyl alcohol (see below) and 62.3 g. (0.8 mole) of dry pyridine was added slowly 95.1 g. (0.8 mole) of purified thionyl chloride. After heating the reaction mixture on the steam-bath for three hours, the yield of β-(1,2,3,4-tetrahydro-1-naphthyl)-ethyl chloride, b. p. 117–118° (1 mm.), was 141.4 g. (90.8%). The Grignard reagent prepared from the above chloride was added over a period of two and one-half hours to a solution of 150 g. of acetic anhydride in 150 cc. of ether cooled by an external Dry Ice–acetone-bath at −78°.[9] After the reaction mixture had been decomposed with ammonium chloride solution, the ketone, V, was obtained in 61% yield as a twice distilled colorless oil, b. p. 130° (1 mm.), $n^{25}\mathrm{D}$ 1.5336. The semicarbazone melted at 126.8–127.2°.

Anal.[a] Calcd. for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 82.8, 82.2; H, 9.0, 8.8. Calcd. for $C_{15}N_{21}ON_3$: C, 69.5; H, 8.2; N, 16.3. Found: C, 69.3, 69.1; H, 8.0, 8.1; N, 16.2, 16.1.

1,2,3,4-Tetrahydro-1-naphthylcarbinol, VI.—Thirty grams (1.3 mole) of sodium cut into 2.5-cm. cubes was added all at once to a solution of 47.5 g. (0.23 mole) of ethyl 1,2,3,4-tetrahydro-1-naphthoate in 400 cc. of dry butanol[10] at 60°. The temperature soon rose to 125° and after the reaction had subsided a bit the mixture was heated to 135–140° until the sodium was consumed. After cooling to 95°, 26 cc. of water was added cautiously and the mixture refluxed one hour. After cooling, there was added 200 cc. of water and the butanol layer was separated. The desired carbinol, VI, was obtained in 79% yield as a colorless oil, b. p. 106–109° (1 mm.), $n^{25}\mathrm{D}$ 1.5408. Its α-naphthylurethan melted at 125.4–126.2°.

Anal.[c] Calcd. for $C_{11}H_{14}O$: C, 81.4; H, 8.7. Found: C, 81.1, 80.8; H, 9.0, 9.1. Calcd. for $C_{22}H_{21}O_2N$: C, 79.7; H, 6.4; N, 4.3. Found: C, 79.9, 80.2; H, 6.5, 6.6; N, 4.5, 4.6.

The corresponding acetate, VIII, was formed in 87% yield by heating the carbinol, VI, with acetic anhydride and a trace of *p*-toluenesulfonic acid. It formed a colorless oil, b. p. 98–99° (1 mm.), $n^{25}\mathrm{D}$ 1.4970.

Anal.[c] Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 75.9, 76.0; H, 8.6, 8.8.

β-(1,2,3,4-Tetrahydro-1-naphthyl)-ethanol, VII.—In a reaction similar to the above[10] involving 141 g. (0.64 mole) of ethyl 1,2,3,4-tetrahydro-1-naphthylacetate, 1200 cc. of butanol and 76 g. (3.3 moles) of sodium there was obtained 86 g. (89.6%) of the desired alcohol,[11] VII, as a colorless oil, b. p. 128° (1 mm.), $n^{25}\mathrm{D}$ 1.5507. The α-naphthyl urethan melted at 80.0–81.4°.

Anal.[c] Calcd. for $C_{23}H_{23}O_2N$: C, 80.0; H, 6.7; N, 4.1. Found: C, 80.0, 80.1; H, 6.7, 6.8; N, 4.4, 4.4.

The corresponding acetate, IX, was prepared in 93% yield by heating the alcohol, VII, in benzene with acetic anhydride and a small amount of *p*-toluenesulfonic acid. It formed a colorless oil, b. p. 122.5–123.5° (1 mm.), $n^{25}\mathrm{D}$ 1.5220.

Anal.[c] Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 77.2, 77.6; H, 8.9, 8.5.

Dehydrogenation Experiments

Palladium-on-Charcoal Catalyst.—The catalyst used in this work was prepared exactly like that in the previous work.[2] As a check on its activity, Ar-$COOCH_3$ was dehydrogenated as before[2] and the same amount of hydrogen was evolved in about the same time.

General Description of Dehydrogenations.—The same flasks, A and B, previously described[2] were used for the dehydrogenations and the procedure was essentially the same as before.[2] Each experiment was run at least two times: the first time to make general observations as to the course of the reaction and the nature of the products; the second time to check as accurately as possible the quantities involved. The results recorded in Table I are those of the second run. In working up the products of the reactions, the material was always vacuum distilled from the catalyst prior to further treatment. In general the runs checked rather closely.

$RCOOCH_3$, I.—The distilled dehydrogenated ester was saponified and the acid was crystallized from dilute acetic acid. It melted, alone and mixed with authentic α-naphthoic acid, at 162.2–162.6°.

RCH_2COOCH_{31}, II.—The distilled dehydrogenated ester was saponified and the acid was crystallized from dilute alcohol. It melted, alone and mixed with authentic 1-naphthylacetic acid,[12] at 132.4–133.2°.

$RCOCH_3$, III.—After the incomplete evolution of gas, the product from 10.62 g. of $RCOCH_3$ was distilled to

---

(6) Schroeter, *Ber.*, **58**, 713 (1925).

(7) Braun, Gruber and Kirschbaum, *ibid.*, **55**, 3673 (1922), reported this amide but gave no melting point or analysis.

(8) Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936); De Benneville, *J. Org. Chem.*, **6**, 462 (1941).

(9) Newman and Booth, THIS JOURNAL, **67**, 154 (1945).

(10) Ziegler and Hechelhammer, *Ann.*, **528**, 134 (1937); also "Organic Syntheses," Coll. Vol. II, p. 468.

(11) Robinson and Walker, *J. Chem. Soc.*, 1530 (1935).

(12) Our sample was supplied by Mr. A. S. Hussey who prepared it from α-naphthoic acid by the Arndt–Eistert reaction.

yield 8.95 g. of oil b. p. 90–110° (1 mm.), n^{25}D 1.5397. The loss in weight was due mainly to undistilled residue. As preliminary experiments showed that fractionation or picrate formation methods would not separate the mixture of $RCOCH_3$ and $R'COCH_3$ well, the indices of refraction of these pure ketones was taken and the composition of the mixture determined by assuming a straight line plot of indices of refraction versus composition. Pure 1-naphthyl methyl ketone, n^{25}D 1.6266, was obtained from its pure picrate, which had been recrystallized several times. Pure $RCOCH_3$ has n^{25}D 1.5221. Thus the mixture was composed of 83% $RCOCH_3$ and 17% $R'COCH_3$, the yields of these ketones becoming 70 and 14.7%, respectively.

RCH_2COCH_3, IV.—The twice distilled product of this dehydrogenation formed a colorless oil, b. p. 132–134° (1 mm.), n^{25}D 1.5940. This proved to be practically pure 1-(1-naphthyl)-2-propanone as shown by analysis of the ketone and its semicarbazone, m. p. 190.5–191.5°.[13]

Anal.^c^ Calcd. for $C_{13}H_{12}O$: C, 84.7; H, 6.6. Found: C, 84.8, 84.6; H, 6.7, 6.9. Calcd. for $C_{14}H_{15}ON_3$: C, 69.7; H, 6.3; N, 17.4. Found: C, 69.6, 69.8; H, 6.2, 6.2; N, 17.8, 17.9.

$RCH_2CH_2COCH_3$, V.—After distillation from the catalyst the product from 13.20 g. of V was fractionated. Fraction I, 1.27 g. (14%), b. p. 76–80° (1 mm.) was shown to be 1-methylnaphthalene by comparison of the picrates,[14] m. p. and mixed m. p. 139.8–141.4. Fraction II, 7.50 g. (57%), b. p. 115–117° (1 mm.), was shown to be essentially unchanged ketone, V, as judged by the ready formation of the semicarbazone which melted alone and mixed at 126–127°. Fraction III, 2.12 g. (16%), b. p. 124 (1 mm.), was shown to be essentially 4-(1-naphthyl)-2-butanone by the ready formation of a semicarbazone, m. p. 176–177.2° (literature[15] 176–177°), and an oxime, m. p. 91.6–93.2° (literature[15] 89–91°). In addition to the three fractions there remained about 2 to 3 g. of residue.

RCH_2OH, VI.—In the dehydrogenation of 9.69 g. (0.059 mole)of VI, 60% of the theoretical amount of gas (calculated as 4 moles per mole of VI) was obtained. The main product was naphthalene, of which 7.32 g. (95.6%) was obtained by sublimation. In addition a small amount, 0.34 g. (4%) of crude 1-methylnaphthalene, b. p. 239–240° at 746 mm., was left as a residue. It was identified as its picrate,[14] m. p. and mixed m. p. with an authentic sample, 140.4–141.4°.

An analysis of the gas evolved[16] showed that 0.095 mole of hydrogen and 0.033 mole of carbon monoxide were collected. In addition a small amount of methane, 0.002 mole, was present. The discrepancy between the amounts of hydrogen and carbon monoxide actually collected and the amounts which should have been formed as judged by the yield of naphthalene is probably accounted for by the formation of methanol which was lost in the water over which the gas was collected. At the time of the experiment the formation of water soluble products was not expected and the water was discarded. The methane formed probably came from a reaction of carbon monoxide and hydrogen on the catalyst.

RCH_2CH_2OH, VII.—In the dehydrogenation of 11.46 g. (0.065 mole) of VII, 83.6% of the theoretical amount of gas (calculated as 4 moles per mole of VII) was collected. By fractional distillation there was isolated 7.09 g. (76.7%) of 1-methylnaphthalene, b. p. 111–114° (13 mm.), 238° (744 mm.), n^{25}D 1.6110, picrate, m. p. 141.2–141.8°[14] and 1.34 g. (12%) of β-(1-naphthyl)-ethanol, b. p. 135–138° (1 mm.), phenyl urethan, m. p. 116.2–116.6°, mixed m. p. with authentic sample[17] not depressed.

At regular intervals during the dehydrogenation separate portions of the gas were collected and analyzed.[16] These results are summarized in Table II.

TABLE II

GAS SAMPLES

Gas	Sample, % 1	2	3	4	5	6
CO	7.8	9.6	13.0	18.2	25.6	32.3
H_2	84.5	85.1	80.3	75.9	66.8	63.0
CH_4	0.7	1.4	2.4	2.8	4.6	3.0
N_2	6.6	3.9	3.6	3.0	2.4	1.3
CO_2	0.0	0.1	0.1	0.1	0.1	0.1
O_2	0.4	0.0	0.5	0.1	0.4	0.2

In all, about 0.148 mole of hydrogen, 0.036 mole of carbon monoxide and 0.006 mole of methane were collected. These amounts agree quite well with those to be expected on the basis of the products isolated, assuming that the methane was formed from carbon monoxide and hydrogen. The nitrogen was present as the apparatus was swept out with nitrogen previous to the experiment.

RCH_2OCOCH_3, VIII.—The evolution of gas from 9.71 g. (0.048 mole) of VIII ceased after two hours when only 460 cc. of gas had been collected. The product was distilled and the distillate treated with a fresh portion of catalyst, but after an additional three hours of heating only 160 cc. more of gas was evolved. A distinct odor of acetic acid was present. The distilled mixture yielded 8.01 g. of a mixture which was treated as described. A saponification number indicated it to be about 21% unsaponifiable matter and 79% ester (assuming the molecular weight of VIII). The unsaponifiable matter, n^{25}D 1.5668, separated by steam distillation was shown to be a mixture of approximately 41% 1-methylnaphthalene, n^{25}D 1.6149 and 59% 1,2,3,4-tetrahydro-1-methylnaphthalene, n^{25}D 1.5332, by assuming an ideal index of refraction–composition relationship. In addition the picrate of 1-methylnaphthalene was isolated and identified.

The distilled ester, n^{25}D 1.5381, remaining after the steam distillation, was judged to contain about 37% of 1-naphthylmethyl acetate, n^{25}D 1.6075, and 63% of unchanged VIII, n^{25}D 1.4970, by the above method. Thus in all there was obtained about 10% of 1-methylnaphthalene, 14% of 1,2,3,4-tetrahydro-1-methylnaphthalene, 25% of 1-naphthylmethyl acetate and 41% of VIII based on the starting 9.71 g. of VIII.

$RCH_2CH_2OCOCH_3$, IX.—After the dehydrogenation of 14.61 g. (0.067 mole) of IX a strong odor of acetic acid was present. The distilled material was separated into two main fractions by vacuum distillation. Fraction I, 3.03 g. (28.3%), b. p. 81–86° (1–1.5 mm.), formed a picrate, m. p. 97–98.5°. A mixed m. p. with an authentic sample of pure 1-ethylnaphthalene picrate[18] gave no depression. Fraction II, 9.45 g. (62.5%), b. p. 133° (1 mm.), was saponified to an alcohol, b. p. 133° (1 mm.), which formed a phenylurethan, m. p. 115–116.8°, giving no depression when mixed with an authentic sample of β-(1-naphthyl)-ethanol phenyl urethan.[17]

Discussion of Results

The dehydrogenation of esters of the type $R(CH_2)_nCOOCH_3$ proceeded smoothly to give the aromatic counterparts in high yield. Coupled with the previous similar finding with esters of the $Ar(CH_2)_nCOOCH_3$ type,[2] this would indicate that in general hydroaromatic esters can be expected to be dehydrogenated smoothly to yield the corresponding aromatic esters.

With ketones no generalization may yet be drawn. $RCOCH_3$, III, and $RCH_2CH_2COCH_3$, V, were dehydrogenated only to a small extent whereas RCH_2COCH_3, IV, was smoothly dehydro-

---

[13] Tiffeneau and Daudel, *Compt. rend.*, **147**, 679 (1908), report the melting point of the semicarbazone as 205°. We were only able to secure this high melting point with extremely rapid heating.

[14] Darzens and Levy, *Compt. rend.*, **199**, 1131 (1934).

[15] Mayer and Stieglitz, *Ber.*, **55**, 1842 (1922).

[16] We are indebted to Prof. D. V. Demorest, Department of Metallurgy, for the gas analyses.

[17] Grignard, *Ann. Chim.*, **10**, 30 (1907).

[18] Levy, *Compt. rend.*, **193**, 174 (1931).

genated to $R'CH_2COCH_3$. In no case was there reduction of the carbonyl group. However, in the previous work,[2] the carbonyl groups in $ArCOCH_3$ and $ArCOCH_2CH_2COOCH_3$ were almost completely reduced to methylene groups.

With the primary alcohols RCH_2OH, VI, and RCH_2CH_2OH, VII, not only was the ring smoothly dehydrogenated but the primary alcohol function was degraded by loss of one mole of hydrogen and one of carbon monoxide according to the following equations:

$$C_{10}H_{11}CH_2OH \longrightarrow C_{10}H_8 + 3H_2 + CO$$
$$C_{10}H_{11}CH_2CH_2OH \longrightarrow C_{10}H_7CH_3 + 3H_2 + CO$$

Such degradation of primary alcohols to the next lower hydrocarbon is not new[19] and probably proceeds by dehydrogenation to an aldehyde[20] followed by decarbonylation to a hydrocarbon.[2,21] In these reactions we believe that the removal of the hydrogen from the ring precedes the degradative reaction, because gas analyses showed that the proportion of carbon monoxide increases with time. Furthermore the ease of dehydrogenation would indicate that the ring is being dehydrogenated while oxygen was still attached to the molecule, for we have noted repeatedly that tetralin hydrocarbons dehydrogenate very slowly in our experiments whereas oxygenated derivatives dehydrogenate easily if at all.

The behavior of RCH_2OH stands in marked contrast to that of $ArCH_2OH$ in which the carbinol group was largely hydrogenolyzed to a methyl group.

When the hydroxyl groups in VI and VII were protected by acetylation, however, the carbon-oxygen bonds in VIII and IX were hydrogenolyzed only to the extent of 14 and 28%, respectively.[22] The main reaction with IX was dehydrogenation to the corresponding $R'CH_2CH_2OCOCH_3$, but with VIII, only 26% of ring dehydrogenation to $R'CH_2OCOCH_3$ occurred, VIII being recovered (51%) unchanged.

Thus it is apparent that the relative positions of the hydrogens to be removed and the oxygenated functions are quite important in determining the fate of the oxygenated function in catalytic dehydrogenation. Further experiments are necessary to ascertain how important is the position of the substituent on the aromatic nucleus.

Summary

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

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

The ketones $C_{10}H_{11}COCH_3$ and $C_{10}H_{11}CH_2CH_2COCH_3$ were largely recovered unchanged, but $C_{10}H_{11}CH_2COCH_3$ was smoothly dehydrogenated into $C_{10}H_7CH_2COCH_3$.

The alcohols $C_{10}H_{11}CH_2OH$ and $C_{10}H_{11}CH_2CH_2OH$ were smoothly degraded to the next lower hydrocarbon according to the type equation $RCH_2OH \rightarrow (R - 4H)H + 3H_2 + CO$.

Protection of the alcoholic hydroxyls by acetylation prevented the degradative reaction.

---

[19] Adkins and Wojcik, THIS JOURNAL, **55**, 1293 (1933); Paul, *Compt. rend.*, **208**, 1319 (1939); Badin, THIS JOURNAL, **65**, 1809 (1943).

[20] See, for example, Adkins and Reeves, *ibid.*, **62**, 2874 (1940).

[21] Hurd, "The Pyrolysis of Carbon Compounds," A. C. S. Monograph No. 50, Chemical Catalog Co., New York, N. Y., 1929, pp. 236–242.

[22] It is possible that the acetates were pyrolyzed into olefins and acetic acid and that the former were then dehydrogenated to the hydrocarbons observed. We prefer the hydrogenolysis mechanism.

COLUMBUS 10, OHIO RECEIVED OCTOBER 6, 1945

[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

The Catalytic Hydrogenolysis of Halogen Compounds[1]

BY RICHARD BALTZLY AND ARTHUR P. PHILLIPS

The removal of halogen during catalytic hydrogenations of organic compounds is a familiar phenomenon and has even been made—under special conditions—the basis of analytical methods. Largely as a result of this, and despite occasional instances to the contrary, most workers have considered loss of halogen inevitable in catalytic hydrogenations.

During a previous research,[2] one of the authors succeeded in isolating methyl-*p*-chlorobenzylamine hydrochloride after the reductive cleavage of methylbenzyl-*p*-chlorobenzylamine hydrochloride and this suggested that aromatic halogens might, on occasion, be fairly resistant to hydrogenolysis. From the practical side, it seemed desirable to study hydrogenolyses under the conditions usually employed for reductions with noble metal catalysts, namely, in acid or neutral solution. This was also indicated by the theoretical consideration that since the analytical procedures call for alkaline or alkaline-buffered media, experiments under conditions less favorable for dehalo-

---

[1] Presented in part before the Division of Organic Chemistry, A. C. S., Cleveland, Ohio, April, 1944.

[2] Baltzly and Buck, THIS JOURNAL, **65**, 1984 (1943).