Acknowledgment.—The authors are grateful to Professor A. B. Burg of the University of Southern California for his helpful suggestions, and to Dr. L. A. Burkardt for preparing the X-ray photographs.

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RECEIVED JULY 16, 1951

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

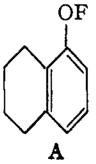
The Catalytic Dehydrogenation of 5-Substituted 1,2,3,4-Tetrahydronaphthalene Derivatives

BY MELVIN S. NEWMAN AND THEODORE S. BYE[1]

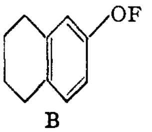
The syntheses of $RCOOCH_3$, RCH_2OH, RCH_2OCOCH_3, $RCOCH_3$, RCH_2COCH_3 and $RCH_2CH_2COCH_3$, where R is the 1,2,3,4-tetrahydro-5-naphthyl radical, are described. The products arising from liquid phase catalytic dehydrogenation of these compounds over palladium-on-charcoal are described and the results compared with those previously obtained with 1,2,3,4-tetrahydro-6-naphthyl, 1,2,3,4-tetrahydro-1-naphthyl and 1,2,3,4-tetrahydro-2-naphthyl derivatives.

The work reported herein is a continuation of studies designed to obtain more information concerning the fate of oxygenated functions in hydroaromatic compounds when submitted to liquid phase dehydrogenation over palladium-on-charcoal. The previous reports dealt with 6-substituted 1,2,3,4-tetrahydronaphthalenes,[2] B, 1-substituted 1,2,3,4-tetrahydronaphthalenes,[3] C, and 2-substituted 1,2,3,4-tetrahydronaphthalenes,[4] D.

Since the oxygenated functions, OF, of B, C and D differed both in their positions with respect to the point of fusion and in their relative positions with respect to the hydrogen to be removed, it was necessary to study compounds of type A before a complete discussion could be attempted. In this paper, we describe the dehydrogenation of 5-substituted-1,2,3,4-tetrahydronaphthalenes, A, under the above conditions. The results are summarized in Table I.



A



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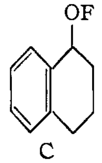

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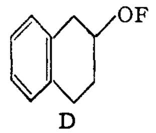

D

Experimental[5]

1,2,3,4-Tetrahydro-5-naphthoic Acid. A. Hydrogenation of Ethyl α-Naphthoate.[6]—The ester to be hydrogenated was heated for two hours with Raney nickel at 150°. After cooling, the catalyst was filtered and the ester rectified through a column with a one-foot packed section containing glass helices. There was obtained 1920 g. of pure ester. The hydrogenation was carried out as a 20% ethanol solution, using a Raney nickel catalyst, a temperature of 130–150° and a pressure of 50 atmospheres. After removal of the solvent, the mixture of hydrogenated esters was rectified to yield 1532 g. (79.8%) of hydrogenated ester.

B. Preparation of 1,2,3,4-Tetrahydro-5-naphthoic Acid.—This acid was obtained pure from the above mixture of esters in two ways. The last two fractions of ester, 365.7 g., were combined and saponified with alcoholic potassium hydroxide. The acid, after recrystallization from 50% alcohol, weighed 283 g., m.p. 150.7–151.9°. The other fractions were saponified individually to mixtures of 1,2,3,4-tetrahydro-5-naphthoic acid and 1,2,3,4-tetrahydro-1-naphthoic acid. Separation was accomplished by fractional acidification from alkaline solution. Batches of two or three fractions of the mixture of acids were saponified and fractionally acidified according to the principles outlined previously.[7] By this method, there was obtained 261 g. of pure 1,2,3,4-tetrahydro-5-naphthoic acid, m.p. 150.0–151.5°. The total yield of pure acid was 544 g. (32.2% based on the ethyl α-naphthoate).

Methyl 1,2,3,4-Tetrahydro-5-naphthoate (I).—The methyl ester prepared from the above acid in 90% yield formed a colorless liquid, b.p. 93.5–96.5° at 0.5–1.0 mm., $n^{25}D$ 1.5431.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.4, 75.3; H, 7.3, 7.5.

1,2,3,4-Tetrahydro-5-naphthylcarbinol (II).—During two hours, a solution of 110 g. (0.58 mole) of I in 800 ml. of anhydrous ether was dropped into an ethereal solution of 13.5 g. of lithium aluminum hydride.[8] After the reaction mixture had been decomposed with water and dilute sulfuric acid, distillation yielded 91.5 g. (97.7%) of the desired carbinol, II, as a colorless viscous oil, b.p. 105–107° at 0.5–1.0 mm., $n^{20}D$ 1.5682. Its 1-naphthylurethan melted at 136.7–137.7°.

Anal. Calcd. for $C_{11}H_{14}O$: 81.5; H, 8.6. Found[c]: C, 81.7; H, 8.6. Calcd. for $C_{22}H_{21}O_2N$: C, 79.8; H, 6.3; N, 4.2. Founds: C, 80.5, 80.3; H, 6.0, 6.40 N, 4.3.

The corresponding acetate, III, was formed in 88% 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. 102° at 0.4–0.8 mm., $n^{25}D$ 1.5325.

Anal.[c] Calcd. for $C_{13}H_{16}O_2$: C, 76.5; H, 7.9. Found: C, 76.3; H, 8.0.

Methyl 1,2,3,4-Tetrahydro-5-naphthyl Ketone (IV).—Into a solution made from 12.2 g. (1.75 moles) of metallic lithium, 114 g. (0.8 mole) of methyl iodide and 500 ml. of anhydrous ether[9] was slowly added a solution of 20 g. (0.114 mole) of RCOOH in 800 ml. of ether. The mixture was treated with water and the neutral portion distilled to yield 19.5 g. (99%) of the desired ketone, IV, as a colorless oil, b.p. 95.5–99.0° at 0.5–1.0 mm., $n^{20}D$ 1.5550. The semicarbazone melted at 221.5–223.5° with decomposition.

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[1] This work was taken from the dissertation submitted by T. S. Bye to The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, March, 1951.

[2] M. S. Newman and H. V. Zahm, THIS JOURNAL, 65, 1097 (1943).

[3] M. S. Newman and Fr. T. J. O'Leary, *ibid.*, 68, 258 (1946).

[4] M. S. Newman and J. R. Mangham, *ibid.*, 71, 3342 (1949).

[5] All melting points are corrected. Microanalyses marked [b] by Mrs. E. K. Klotz; [c] by Clarke Microanalytical Laboratory, Urbana, Illinois.

[6] S. I. Sergievskaya and E. G. Nikhamkina, *J. Gen. Chem.* (*U. S. S. R.*), 15, 988 (1945). We wish to thank the Hooker Electrochemical Company, Niagara Falls, New York, for carrying out the large scale hydrogenation. The following sentences are quoted from a letter: "The hydrogenation was carried out as a 20% ethanol solution and it was found that three separate autoclave runs were required to process the solution. Our Operations Department advises us furthermore, that absorption was rapid and complete after the first hour but that the runs were continued for a total of 5 hours as advised in the reference."

[7] M. S. Newman, R. B. Taylor, T. Hodgson and A. B. Garrett, THIS JOURNAL, 69, 1784 (1947).

[8] R. F. Nystrom and W. G. Brown, *ibid.*, 69, 1197 (1947).

[9] D. A. Van Dorp and J. F. Arens, *Rec. trav. chim.*, 65, 338 (1946).

TABLE I

DEHYDROGENATION EXPERIMENTS

No.	Compound[a]	Time, hr.	Temp., °C.	H_2 %	Products	Yield,[b] %
I	$RCOOCH_3$	3.5	279–322	102	$R'COOCH_3$	89.3
II	RCH_2OH	10.0	265–276	51.8[c]	$R'H$	47.6
					$R'CH_3$	45.5
III	RCH_2OCOCH_3	8.0	275–304	18.2	$R'CH_3$	23.1[d]
					RCH_3	12.2[d]
IV	$RCOCH_3$	10.25	295–314	67.2	$R'COCH_3$	51.1
					$R'CH_2CH_3$	29.2
V	RCH_2COCH_3	27.0	320–345	89.4	$R'CH_2COCH_3$	30.8
					$R'CH_3$	16.3
VI	$RCH_2CH_2COCH_3$	4.0	297–312	94.4	$R'CH_2CH_2COCH_3$	90.2
VII	β-$RCH_2CH_2COCH_3$[a]	6.0	324–336	91.8	β-$R'CH_2CH_2COCH_3$	68.0

[a] R = 1,2,3,4-tetrahydro-5-naphthyl-; R′ = 1-naphthyl; β-R = 1,2,3,4-tetrahydro-6-naphthyl; β-R′ = 2-naphthyl-. [b] Represents yields of purified materials. [c] Calculated for four moles of gas. Carbon monoxide was also evolved. [d] 53.6% of the original acetate was recovered. Yields of $R'CH_3$ and RCH_3 based on index of refraction measurements.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.8; H, 8.1. Found[c]: C, 82.9; H, 8.2. Calcd. for $C_{13}H_{17}ON_3$: N, 18.2. Found[k]: N, 18.2, 18.3.

1-(1,2,3,4-Tetrahydro-5-naphthyl)-2-propanone (V).—To a cooled solution of 31.5 g. (0.194 mole) of 1,2,3,4-tetrahydro-5-naphthylcarbinol (II), 15.3 g. (0.194 mole) of dry pyridine and 35 ml. of anhydrous toluene was added slowly 23.0 g. (0.194 mole) of purified thionyl chloride. After heating the reaction mixture on the steam-bath for 12 hours, the chloride was obtained in 80% yield as a colorless oil, b.p. 88–92° at 0.5–1.0 mm., which solidified. A portion after recrystallization from absolute alcohol melted at 50.0–50.5°.

Anal. Calcd. for $C_{11}H_{13}Cl$: C, 73.1; H, 7.2. Found[k]: C, 73.5, 73.7; H, 7.5, 7.3.

The Grignard reagent prepared from 30.0 g. (0.172 mole) of the chloride, RCH_2Cl, was added over a period of 75 minutes to a solution of 36.0 g. (0.35 mole) of acetic anhydride in 100 ml. of dry ether cooled by an external Dry Ice-acetone-bath at -78°.[10] After the reaction mixture had been treated with ammonium chloride solution, 20.4 g. (63.2%) of the ketone, V, b.p. 115–119° at 0.5–0.7 mm., $n^{25}D$ 1.5498, was obtained. The semicarbazone melted at 214.8–217.0° with decomposition.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.9; H, 8.6. Found[c]: C, 82.7; H, 8.3. Calcd. for $C_{14}H_{19}ON_3$: N, 17.1. Found[k]: N, 17.3, 17.3.

1-(1,2,3,4-Tetrahydro-5-naphthyl)-3-butanone (VI).—After 3.23 g. (0.14 mole) of sodium metal had been dissolved in 70 ml. of absolute alcohol, 36.5 g. (0.28 mole) of ethyl acetoacetate was added rapidly to this solution. There was added rapidly a warm solution containing 25.3 g. (0.14 mole) of 1,2,3,4-tetrahydro-5-naphthylmethyl chloride in 90 ml. of absolute alcohol. After stirring and heating for one hour, a drop or two of glacial acetic acid was added to neutrality, and the precipitated sodium chloride filtered. As preliminary experiments showed that the product was essentially the theoretical amount of substituted acetoacetic ester, the next step was carried out directly on the undistilled product. After distilling the alcohol, the residue was stirred overnight with 280 ml. of 10% sodium hydroxide at room temperature and then for three hours at 35–40°. There was obtained 25.4 g. (89.9%) of the desired ketone, VI, b.p. 108.5–110.5° at 0.3 mm., $n^{25}D$ 1.5388. The semicarbazone melted at 138.5–139.5°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.1; H, 8.9. Found: C, 82.8; H, 8.9. Calcd. for $C_{15}H_{21}ON_3$: N, 16.2. Found: N, 16.4.

1-(1,2,3,4-Tetrahydro-6-naphthyl)-2-butanone (VII).—This compound was prepared in 85% yield from 1,2,3,4-tetra-6-naphthylmethyl chloride essentially as in the synthesis of ketone, VI. The halide was obtained in 81.5% yield from 1,2,3,4-tetrahydro-6-naphthylcarbinol as above described. The carbinol was obtained in 70% yield by lithium aluminum hydride reduction of methyl 1,2,3,4-tetrahydro-6-naphthoate.[2] The desired ketone, VII, formed an almost colorless oil, b.p. 105.5–110.5° at 0.2–0.3 mm., $n^{25}D$ 1.5348. The semicarbazone melted 174.0–175.0°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.1; H, 8.9. Found[c]: C, 82.8; H, 8.9. Calcd. for $C_{15}H_{21}ON_3$: N, 16.2. Found[k]: N, 16.2; 16.3.

Dehydrogenation Experiments. Palladium-on-charcoal Catalyst.—The catalyst used in this work was similar to that of the previous investigations.[2,3,4] A check on the activity of the catalyst was made by dehydrogenation of methyl 1,2,3,4-tetrahydro-2-naphthoate as before.[5] About the same amount of hydrogen was evolved in about the same amount of time.

General Description of Dehydrogenations.—The apparatus used was the same as that previously described.[4] Two duplicate runs were made on each compound. In each run, the products were isolated as nearly quantitatively as possible and served as checks on the reproducibility of the results obtained. Since the results of these runs were in substantial agreement, a description is given only for the second run. In each case, 0.07 mole ±0.01 g. of the compound was dehydrogenated. In Table I, the experimental details are recorded. In working up the products of the reactions, the material was always vacuum distilled from the catalyst prior to further treatment.

$RCOOCH_3$ (I).—The distilled dehydrogenated ester was saponified and the acid was recrystallized from dilute acetic acid. It melted alone and mixed with authentic α-naphthoic acid, at 161.4–162.4°.

RCH_2OH (II).—The product was fractionated under reduced pressure. The first fraction, 3.88 g. (47.6%), naphthalene, was obtained by careful sublimation into a chilled receiver. A portion, after recrystallization from ethanol, melted 79.0–80.0°, mixed m.p. 79.0–80.2°. The second fraction, 4.54 g. (45.5%), b.p. 63.0–67.0° at 0.5–1.0 mm., formed a picrate, m.p. 140.5–142.0°, mixed m.p. not depressed with the picrate of 1-methylnaphthalene.[11]

A gas analysis[12] showed that the gas evolved was a mixture of carbon monoxide and hydrogen.

RCH_2OCOCH_3 (III).—The product obtained from 14.20 g. of III was separated into two fractions by vacuum distillation. Fraction 1; b.p. 61.5–67.0° at 0.5–1.0 mm. gave a picrate, m.p. 141.2–142.0° and did not depress the melting point of the picrate from an authentic sample of 1-methylnaphthalene.[11] The index of refraction of this fraction, $n^{20}D$ 1.5915 lay between that of 1-methylnaphthalene (1.6175) and that of 1,2,3,4-tetrahydro-5-methylnaphthalene (1.5439). By assuming a straight line relationship between the refractive index and percentage composition of these very similar compounds, the value 1.5915 indicates that fraction 1 is a mixture of 65.0% 1-methylnaphthalene and 35.0% 1,2,3,4-tetrahydro-5-methylnaphthalene. Fraction 1 weighed 3.55 g. (35.5%). Fraction 2, b.p. 105.0–110.0° at 0.5–1.0 mm., was shown to be recovered III by saponification of a portion to an alcohol which formed an α-naphthylurethan, m.p. 137.0–139.0°, which gave no depression when mixed with an authentic sample of 1,2,3,4-tetrahydro-5-naphthylcarbinol-α-

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[10] M. S. Newman and W. T. Booth, THIS JOURNAL, **67**, 154 (1945).

[11] G. Darzens and A. Levy, *Compt. rend.*, **199**, 1132 (1934).

[12] Gas analysis through the courtesy of D. J. Demorest, The Ohio State University, Department of Metallurgy.

naphthylurethan. Thus, the total yield of products obtained was: 23.1% of 1-methylnaphthalene, 12.2% of 1,2,3,4-tetrahydro-5-methylnaphthalene, and 53.6% of III.

$RCOCH_3$ (IV).—The addition of 0.10 g. of fresh catalyst to 12.20 g. of IV, after an hours heating caused a considerable increase in the rate of the dehydrogenation. The product was separated into two main fractions by distillation through a special modified Claisen flask with a ten inch side arm insulated by an air jacket.

The first fraction, 3.19 g. (29.2%), b.p. 66.5–71.0° at 0.3–0.5 mm., gave no pure picrate or trinitrofluorenone derivative.[13] However, comparison of the infrared spectrum of fraction 1 with that of a pure sample of 1-ethylnaphthalene, obtained from a modified Wolff–Kishner reduction[14] of methyl 1-naphthyl ketone, showed fraction 1 to be slightly impure 1-ethylnaphthalene.

After fraction 1 had been collected, the residue was distilled from a modified Claisen flask to yield 6.07 g. (51.1%) of a liquid, b.p. 95.0–99.0° at 0.3–0.5 mm. whose semicarbazone, m.p. 222.5–224.0°, did not depress the melting point of the semicarbazone, m.p. 224.0–225.7° with decomposition, prepared from an authentic sample of methyl 1-naphthyl ketone.

RCH_2COCH_3 (V).—The slow rate of evolution of hydrogen from 12.20 g. of V was increased by addition of 0.10 g. of fresh catalyst after two hours. After vacuum distillation of the product from the catalyst, there remained about 5 g. of high boiling residue. The distillate was separated into two fractions by distillation under reduced pressure. Fraction 1, 1.50 g. (16.3%), b.p. 63.5–65.0° at 0.5–1.0 mm., formed a picrate, m.p. 139.0–141.5°, which did not depress the melting point of the picrate prepared from authentic 1-methylnaphthalene.[11] Fraction 2, 3.68 g. (30.8%), b.p. 128.0–132.0° (0.5–1.0 mm.) was shown to be 1-(1-naphthyl)-2-propanone, m.p. 91.5–92.5° alone and mixed with an authentic sample. Its semicarbazone melted at 222.8–223.2° with decomposition, alone and mixed with an authentic sample.

Anal.[e] Calcd. for $C_{13}H_{12}O$: C, 84.8; H, 6.5. Found: C, 84.7, 84.7; H, 6.4, 6.4. Calcd. for $C_{14}H_{15}ON_3$: N, 17.4. Found: N, 17.4.

Authentic 1-naphthyl-2-propanone, m.p. 91.5–92.5°, was prepared in 34% yield from the reaction of 1-naphthylmethylmagnesium chloride on acetic anhydride at −78°.[10] The semicarbazone of this ketone melted with decomposition at 223.0–224.2° and gave no depression when mixed with that of the ketone formed as described above. However, it did depress the melting point of the semicarbazone, m.p. 190.5–191.5°, previously reported[3] for this compound. Furthermore the ketone previously[3] supported to be 1-naphthyl-2-propanone was a liquid. We feel certain that 1-naphthyl-2-propanone has the properties described in this paper and further study will be necessary to discover the nature of the product previously reported.[3]

$RCH_2CH_2COCH_3$ (VI).—In a run using 14.16 g. of VI, there remained a residue of 1.5 g. after vacuum distillation from the catalyst. Redistillation yielded 12.49 g. (90.2%) of 4-(1-naphthyl)-2-butanone, b.p. 135–142° at 0.8–1.0 mm. The semicarbazone, prepared in high yield, melted alone and mixed with an authentic sample[3] at 177.2–178.2°.

β-$RCH_2CH_2COCH_3$ (VII).—In a run using 14.06 g. of 4-(1,2,3,4-tetrahydro-6-naphthyl)-2-butanone, there remained about 4 g. of residue with the catalyst. Rectification yielded 9.40 g. (68%) of 4-(2-naphthyl)-2-butanone, b.p. 124–129° at 0.3–0.5 mm., m.p. 48.9–49.6° alone and mixed with authentic ketone.[4,15] The m.p. of the oxime[15] was 119.4–121.0° and that of the semicarbazone was 171.8–173.0°, alone and mixed.

Discussion

With the experiments recorded herein, our work with the liquid phase catalytic dehydrogenation over palladium of oxygenated tetralin derivatives is completed. It was undertaken originally to define better what the fate of oxygenated functions on a tetrahydronaphthalene nucleus would be. It was hoped that the information thus obtained would be of value in guiding operations where synthetic programs based on purely aromatic nuclei would run into trouble because of unfavorable orientation. Since the orientation of partly hydrogenated aromatic nuclei is usually different from that of the corresponding aromatic nuclei, if suitable catalytic dehydrogenation could be later effected there would obviously be at hand improved sequences of reactions wherever the orientation of the hydroaromatic nuclei was that desired. For example, the succinoylation of naphthalene yields a difficulty separable mixture of α- and β-naphthoylpropionic acids from which the isolation of the β-isomer in fair yield is possible.[16] However, tetralin is succinoylated exclusively in the β-position.[17] Hence, if the desired product is γ-2-naphthylbutyric acid, it is easier to start from tetralin and eventually dehydrogenate than to start from naphthalene. The wisdom of this choice rests upon the ability of the carbomethoxy group to withstand catalytic dehydrogenation.[2]

As a result of the previous studies[2,3,4] and the present one a number of generalizations may be made. The sections below deal with the functional groups studied. For convenience the following notations will be used for the tetrahydronaphthalene derivatives studied: Ar^1 and Ar^2 mean that the functions are attached to the aromatic ring in the 1 and 2 positions, respectively; Al^1 and Al^2 mean that the functions are attached to the aliphatic ring in the 1 and 2 positions, respectively. The results are summarized in Table II.

(1) The $-COOCH_3$ Group: This group is quite stable in the temperature range 280–320°. All dehydrogenations involving compounds of types Ar^1, Ar^2, Al^1 and Al^2 went smoothly and the corresponding naphthalenic acids were obtained after saponification in 73–92% yields.

(2) The Primary Alcohol Function: (a) The $-CH_2OH$ group: This group may not be retained to any extent at all. Hydrogenolysis to a methyl group or decomposition to hydrogen and carbon monoxide or a combination of the two always occurs. (b) The $-CH_2CH_2OH$ group: In the one case studied[3] (Al^1) the chief reaction was loss of hydrogen and carbon monoxide to yield 1-methylnaphthalene. Here, however, protection can be given by acetylation, the corresponding acetylated alcohol undergoing dehydrogenation to 2-(1-naphthyl)-ethyl acetate in 62.5% yield.[3]

(3) The $-CH_2OCOCH_3$ Group: It is not practical to maintain the $-CH_2OH$ function by protection through acetylation since hydrogenolysis to a methyl group still occurs to a great extent. However, with $Al^1CH_2CH_2OCOCH_3$ a 62.5% yield of β-1-naphthylethyl acetate was obtained.[3]

(4) Ketones: (a) The $-COCH_3$ Group: It is not practical to maintain the $-COCH_3$ group as there is considerable reduction to an ethyl group. However, it is possible to obtain small to fair yields of naphthyl methyl ketones, the best cases being Ar^1 (51%) and Al^2 (55%). (b) The $-CH_2COCH_3$

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[13] M. Orchin and O. Woolfolk, This Journal, **68**, 1727 (1946).

[14] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

[15] F. Mayer and A. Sieglitz, *Ber.*, **55**, 1854 (1922), give the m.p. for the oxime as 115–116° whereas in ref. 4 m.p. of 119.4–120.8° is given for the oxime.

[16] M. S. Newman, R. B. Taylor, T. Hodgson and A. B. Garrett, This Journal, **69**, 1784 (1947).

[17] F. Krollpfeiffer and W. Schafer, *Ber.*, **56**, 628 (1923).

TABLE II

SUMMARY OF DEHYDROGENATION EXPERIMENTS

Compound	Temp., °C.	Time, hr.	Products		
$RCOOCH_3$[a]				$R'COOCH_3$[b] (% yield)	
Ar^1	279–322	3.5		89	
Ar^2	288–310	7.0		92	
Al^1	306–315	8.0		75	
Al^2	290–320	3.5		92	
RCH_2COOCH_3					
Ar^2	275–307	4.3		73	
Al^1	260–310	5.2		91	
$Ar^2(CH_2)_2COOCH_3$	280–300	6.0		87	
$Ar^2(CH_2)_3COOCH_3$	274–320	4.5		84	
RCH_2OH			$R'H$	$R'CH_3$	RCH_3
Ar^1	265–276	10.0	47.6	45.5	
Ar^2	230–260	6.5		(67)[c]	
Al^1	275–300	13.0	96.6	4	
Al^2	260–300	17.5	27.6	59.8	
RCH_2OCOCH_3			$R'CH_2OCOCH_3$	$R'CH_3$	RCH_3
Ar^1	275–304	8.0		23.1[d]	
Al^1	290–295	5.0	26	10	14[e]
Al^2	270–290	6.0	3	82.5[f]	
$RCOCH_3$			$R'COCH_3$	$R'CH_2CH_3$	
Ar^1	295–314	10.3	51.1	29.2	
Ar^2	270	13.0	19	63	
Al^1	288–310	7.0	14.7[g]		
Al^2	310	7.5	55.2	38.7	
RCH_2COCH_3			$R'CH_2COCH_3$	$R'CH_3$	
Ar^1	320–345	27.0	30.8	16.3	
Al^1	290–315	10.0	84.2[h]		
Al^2	320	23.0	54.5	15.6	
$RCH_2CH_2COCH_3$				$R'CH_2CH_2COCH_3$	
Ar^1	297–312	4.0		90.2	
Ar^2	324–336	6.0		68.0	
Al^1	326	7.5		16.0[i]	
Al^2	330	15.0		62.8[j]	
RCHO			$R'H + RH$		
Ar^2	275	6.0	(95.0)[k]		
Al^2	275–305	10.0	97.2		

[a] The symbols below general formulas for compounds represent: Ar^1 = 1,2,3,4-tetrahydro-5-naphthyl; Ar^2 = 1,2,3,4-tetrahydro-6-naphthyl; Al^1 = 1,2,3,4-tetrahydro-1-naphthyl; and Al^2 = 1,2,3,4-tetrahydro-2-naphthyl) radicals. [b] R^1 always indicates the naphthyl radical and the function thereto attached has the same position (1 or 2) as it had in the starting compound. Yields represent either purified materials or a value estimated by fairly accurate analysis. [c] The (67%) represents combined 2-methylnaphthalene and 2-methyltetralin which were not separated or analyzed. [d] 53.6% of unchanged $Ar^1CH_2OCOCH_3$ was recovered also. [e] 41.0% of unchanged $Al^1CH_2OCOCH_3$ was recovered also. [f] 9.0% of unchanged $Al^2CH_2OCOCH_3$ was recovered also. [g] 70.0% of unchanged Al^1COCH_3 was recovered also. [h] In the experiment reported[8] 1-naphthyl-2-propanone was reported as a liquid giving a semicarbazone of m.p. 190.5–191.5°. We have synthesized an authentic sample of this ketone and found it to be a solid, m.p. 91.5–92.5°, yielding a semicarbazone, m.p. 223.0–224.2°. Hence the structure of the ketone[8] is in doubt. [i] There was also obtained 57% of $Al^1CH_2CH_2COCH_3$ and 14% of 1-methylnaphthalene. [j] There was also obtained 15.6% of 1-ethylnaphthalene. [k] The proportions of R^1H and RH were not determined but other work indicated that all R^1H would result if sufficient time were allowed. Note Al^2 run.

Group: As above, small to fair yields of 1-naphthyl-2-propanones may be obtained but this function is not promising. In the one case where a good result was obtained, the structure of the product is in doubt and must be checked (see Table II, footnote *h*). It is noteworthy that in this series, the temperatures necessary for dehydrogenation are somewhat higher. (c) The $-CH_2CH_2COCH_3$ Group: The results here are somewhat encouraging with good (63–68%) to excellent (90%) yields being obtained with Al^2, Ar^2 and Ar^1, respectively.

(5) The –CHO Group: This function is not maintained at all as carbon monoxide is lost quantitatively. One attempt to maintain the aldehyde function by protection as a cyclic acetal (Al^2 series) failed, the main product being 2-methylnaphthalene[4] formed by hydrogenolysis.

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RECEIVED SEPTEMBER 20, 1951