

It has been established that attempted cyclization of β -(2-methoxy-5-bromophenyl)-propionic acid produces 6-bromo-3,4-dihydrocoumarin as the main product.

The structure of a minor product (β -(2-methoxy-5-bromophenyl)-ethyl 2'-methoxy-5'-bromo-

phenyl ketone) of the cyclization has been proved. This substance must have been formed by the elimination of a propionic side chain in the presence of aluminum chloride.

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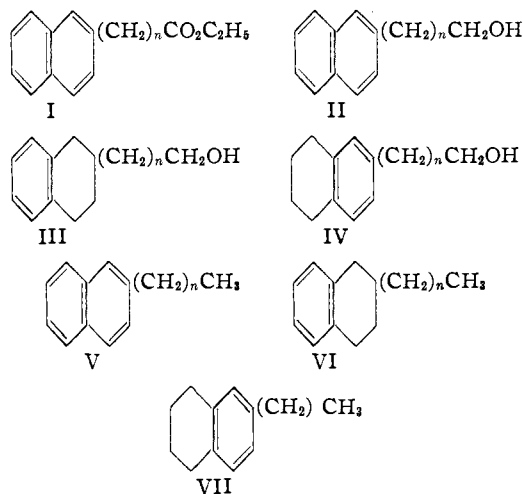
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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Selective Hydrogenation of Esters Containing a Naphthalene Nucleus

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The selective hydrogenation of a carbethoxy to a carbinol group, in an ester containing a naphthalene nucleus, has not seemed a feasible process. This was true because the naphthalene nucleus is rather rapidly and quantitatively hydrogenated to a tetralin over the copper chromium oxide catalyst at 150–190°. A further complication arises from the fact that the unsaturation of the rings labilizes an attached carbinol group toward hydrogenolysis. Thus the hydrogenation of esters of the type shown in I may give one or all of the three types of alcohols II, III and IV, and the hydrocarbons V, VI and VII resulting from hydrogenolysis.



Ethyl and methyl esters where "n" has a value of 0, 1, 2 and 3, and the chain is in the 1- or the 2-position of the nucleus, have been subjected to hydrogenation over a copper chromium oxide catalyst.² A summary of the numerical results

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(2) The catalyst was prepared as described by Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, 1937, p. 13, except the decomposition step was carried out by a procedure recommended by Dr. Ralph Mozingo. This consisted of decomposing 2 g. of copper ammonium chromate, stirring in another 2 g. and carefully decomposing, then adding 4 g., etc., each time doubling the amount added and carrying out the decomposition at the minimum temperature with constant stirring until a total of 60–100 g. of material was used.

of several of the more significant hydrogenations is given in Table I. The extent of hydrogenation is indicated in the fourth column of the table by stating the percentage to which the carbethoxy group reacted, as well as the moles of hydrogen absorbed during the period of reaction. A hydrogenation of ethyl benzoate to benzyl alcohol is also listed in the table. The result at 125° was similar to that reported at 165° by Mozingo and Folkers, who were the first to hydrogenate a carbethoxy group on a benzenoid nucleus to a carbinol group.³

The experimental conditions, as well as the structure of the ester, make important differences in the rates and relative rates of the various types of hydrogenation and hydrogenolysis. The compounds, where n equals 1, 2 or 3 in formula I, underwent hydrogenation to alcohols smoothly at 190–200°. The yield of alcohols when n equals 1 was lower (77%) than where n equals 2 or 3 (90%). There was no significant difference in behavior between the esters containing the 1- as compared with the 2-naphthyl group. However, in all the four esters just mentioned, four moles of hydrogen per mole of ester were absorbed so that the alcohol produced contained a tetrahydronaphthyl, rather than a naphthyl, group. That is to say, the naphthalene nucleus is sufficiently labile toward hydrogenation in the presence of the copper oxide–chromite catalyst so that hydrogenation of the ring took place under the same conditions required for the hydrogenation of the carbethoxy to a carbinol group. The relative distribution of hydrogen between the substituted and unsubstituted rings during catalytic hydrogenation, will be considered in more detail below, but it will suffice for the present to state that the tetrahydronaphthyl alcohols of structure IV predominate with lesser amounts of alcohols of type III.

In compounds where n equals zero in I, hydrocarbons are almost the only products resulting when the esters are hydrogenated at 190–200°. Fortunately, the esters where n equals 0 or 1, can be hydrogenated under milder conditions than when n equals 2 or 3. The naphthoates and naphthylacetates may be hydrogenated at tempera-

(3) Mozingo and Folkers, *THIS JOURNAL*, **70**, 280 (1948).

TABLE I

HYDROGENATION OF ESTERS AT 300 ATMOSPHERES				
0.1 mole in 100 ml. of methanol				
Temp., °C.	Time, hr.	Catalyst, g.	% Hyd./Moles H ₂	Yield of product, %
Ethyl γ -(1-naphthyl)-butyrate ^a				
200	7	5	100/0.4	92 4-(Tetrahydro-1-naphthyl)-butanol-1
Ethyl γ -(2-naphthyl)-butyrate ^b				
200	7	5	100/0.4	92 4-(Tetrahydro-2-naphthyl)-butanol-1
Methyl β -(1-naphthyl)-propionate ^c				
200	3.5	10	10/0.4	89 3-(Tetrahydro-1-naphthyl)-propanol-1
Ethyl 1-naphthylacetate ^d				
190	3	5	100/0.4	77 2-(Tetrahydro-1-naphthyl)-ethanol
				17 1-Ethyltetrahydronaphthalene
Methyl 1-naphthylacetate ^e				
120	0.67	20	41/0.19	40 2-(1-Naphthyl)-ethanol
108	2	20	37/0.23	28 2(1-Naphthyl)-ethanol
Ethyl 1-naphthoate ^f				
88	3.5	10	40/0.22	5 1-Naphthylcarbinol
				35 1-Methylnaphthalene
80	7	10	66/0.22	51 1-Methylnaphthalene
Methyl 2-naphthoate ^g				
108	1.5	10	65/0.24	35 2-Naphthylcarbinol
				5 2-Methylnaphthalene
166	7	10	100/0.48	70 2-Methyltetrahydronaphthalene
Ethyl benzoate				
125	5	10	79/0.37	65 Benzyl alcohol

^a 7,9 b. p. 139-140° (0.5 mm.), n_D^{25} 1.5652. ^b 7,9 b. p. 145-146 (1.5 mm.), n_D^{25} 1.5650. ^c 8 b. p. 145-147° (2 mm.), m. p. 34-5°, n_D^{25} 1.5832. ^d 8 b. p. 112-117° (0.5 mm.), n_D^{25} 1.5795. ^e 4,5,6 b. p. 122-122.5° (1 mm.), n_D^{25} 1.5952. ^f 10 b. p. 110° (0.05 mm.), n_D^{25} 1.5931, Z 33.5. ^g 11,12 m. p. 75-77°.

tures as low as 80° with an activated catalyst. At temperatures in the range 90-110°, with a high ratio of catalyst to ester, alcohols containing the unhydrogenated naphthalene nucleus were obtained. The best yields, so far obtained, are 35-40% for 2-(1-naphthyl)-ethanol and 2-naphthylcarbinol and only 6% for 1-naphthylcarbinol although the percentage yield of the naphthyl-ethanol would be increased to almost 100% and

the others by 50%, if allowance were made for the amount of ester not reacting.

In order to obtain the best yields it is necessary to carefully control the extent of hydrogenation and to stop the reaction after about 70% of the ester has been hydrogenated. If the reaction is allowed to proceed, then the carbinol is destroyed more rapidly than it is produced. Hydrogenolysis of the carbinols and hydrogenation of the naphthalene nucleus do take place over the catalyst even at temperatures below 100°. In fact, if too low a temperature is used in attempting to convert esters to alcohols, the reaction proceeds so slowly that hydrocarbons are produced just as they are at too high a temperature.

Since the hydrogenation of esters of formula I, when n was 3 or 4, gave only alcohols of formulas III and IV rather than of II, it became of interest to attempt to prepare the latter from III and IV through dehydrogenation. Two general methods were used with a palladium on activated carbon catalyst. In one method the dehydrogenation was carried out under pressure of ethylene in a steel reaction vessel at 200-225° for 8-13 hours, with benzene or cymene as the medium.¹³ In the other the compound to be dehydrogenated was heated with a palladium catalyst under reflux at 180-185° for 18-29 hours in cymene. The extents of dehydrogenation obtained in both methods seemed to be about 65-80%. However, the yields of naphthyl alcohols were quite poor, both with respect to amount and quality of product. In every case hydrocarbons were produced, even when the dehydrogenations were far from complete. These results are similar to those reported by Newman and Zahn¹⁴ and by others.

The relative rates of hydrogenation of the substituted and unsubstituted rings in esters of the structure of I has apparently not been determined. The isomeric tetrahydro esters or the corresponding alcohols (III and IV), or hydrocarbons (VI and VII) are not readily separated nor the proportions of the isomers in a mixture estimated. Several esters have been hydrogenated over W-6 Raney nickel at room temperature and low pressures, *i.e.*, ethyl γ -(1-naphthyl)-butyrate, ethyl γ -(2-naphthyl)-butyrate, methyl β -(1-naphthyl)-propionate, ethyl 1-naphthoate, and methyl 2-naphthoate. The corresponding tetrahydronaphthyl esters were produced almost quantitatively, four moles of hydrogen per mole of ester being taken up within a few hours.

The saponification of the esters and the separation of the acids showed that the tetrahydro esters from ethyl γ -(1-naphthyl)-butyrate and ethyl γ -(2-naphthyl)-butyrate gave good yields of the 5,6,7,8-tetrahydro (III) acids. The isomeric 1,2,3,4-tetrahydro (IV) acids were not found. The tetrahydro ester from methyl β -(1-naphthyl)-propionate gave both acids, the

(4) Manske and Ledingham, *Can. J. Research*, **17B**, 14 (1939).
 (5) Arndt and Eistert, *Ber.*, **68**, 207 (1935).
 (6) Grummitt and Buck, "Organic Syntheses," **24**, 30 (1944), John Wiley and Sons, Inc., New York.
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 (10) Whitmore and Loder, "Org. Syntheses," Coll. Vol. II, 282 (1943), John Wiley and Sons, Inc., New York, N. Y.
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 (12) Vieth, *Ann.*, **180** 319 (1876).

(13) Adkins and Reid, *THIS JOURNAL*, **63**, 741 (1941).
 (14) Newman and Zahn, *ibid.*, **65**, 1097 (1943).

TABLE II
 PROPERTIES AND ANALYSES OF COMPOUNDS

Compounds	n_D^{25}	d_4^{25}	M_R		B. p. or m. p. °C.	Mol. form.	Carbon		Hydrogen	
			Calcd.	Found			Calcd.	Found	Calcd.	Found
4-(5,6,7,8-Tetrahydro-1-naphthyl)-butanol	1.5430	1.0247	62.6	62.8	131-133	$C_{14}H_{20}O$	82.30	81.85	9.83	9.73
Phenylurethan					M. 87.5-88	$C_{21}H_{23}O_2N$	77.98	78.02	7.79	7.97
3,5-Dinitrobenzoate					M. 88.5-89.5	$C_{21}H_{22}O_6N_2$	63.30	62.88	5.57	5.47
4-(5,6,7,8-Tetrahydro-2-naphthyl)-butanol	1.5385	1.0153	62.6	62.9	131-135	$C_{14}H_{20}O$	82.30	81.83	9.87	9.99
3,5-Dinitrobenzoate					M. 130-132	$C_{21}H_{22}O_6N_2$	63.30	63.28	5.57	5.71
4-(2-Naphthyl)-butanol 3,5-dinitrobenzoate					M. 139-140	$C_{21}H_{22}O_6N_2$	64.01	63.69	4.60	4.46
3-(5,6,7,8-Tetrahydro-1-naphthyl)-propanol	1.5507	1.0446	58.0	58.5	126-129	$C_{13}H_{18}O$	82.02	81.74	9.53	9.68
3,5-Dinitrobenzoate					M. 96-98	$C_{20}H_{20}O_6N_2$	62.48	62.12	5.24	4.95
3-(1-Naphthyl)-propanol 3,5-dinitrobenzoate					M. 153-153.5	$C_{20}H_{18}O_6N_2$	63.14	63.05	4.24	4.40
5,6,7,8-Tetrahydro-1-naphthylcarbinol phenylurethan					M. 102-103	$C_{18}H_{18}O_2N$	76.86	76.53	6.81	6.90
1-Naphthylcarbinol phenylurethan					M. 89-89.5	$C_{18}H_{18}O_2N$	77.96	77.50	5.45	5.43
Ethyl γ -(5,6,7,8-tetrahydro-1-naphthyl)-butyrate	1.5194	1.031	71.97	72.94	140-141	$C_{16}H_{22}O_2$				
Methyl β -(5,6,7,8-tetrahydro-1-naphthyl)-propionate	1.5308	1.096	62.73	61.6	105-113	$C_{14}H_{18}O_2$				
Methyl β -(1,2,3,4-tetrahydro-1-naphthyl)-propionate	1.5283	1.109	62.73	60.4	$C_{14}H_{18}O_2$				
Methyl 5,6,7,8-tetrahydro-1-naphthoate	1.5442	1.104	53.49	54.3	$C_{13}H_{14}O_2$				

yield of the 5,6,7,8-tetrahydro acid being three times as large as that of the 1,2,3,4-tetrahydro acid. Similarly ethyl 1-naphthoate gave the 5,6,7,8-tetrahydro acid and the 1,2,3,4-tetrahydro acid in a ratio of 5:3. Methyl 2-naphthoate gave the 5,6,7,8- and the 1,2,3,4-tetrahydro acids in a ratio of 15:1.

The distribution of hydrogen between the rings of an ester or alcohol over a copper chromium oxide catalyst under 300 atm. would not necessarily be the same as over a nickel catalyst at 2-3 atm. However, the evidence available is that the proportion of 1,2,3,4- and 5,6,7,8-tetrahydroalcohols is similar in the two cases. The 2-(1-tetrahydronaphthyl)-ethanol obtained (Table I) gave the 3,5-dinitrobenzoate of 2-(1-(5,6,7,8-tetrahydronaphthyl))-ethanol¹⁵ in good purity and yield.

Saponification of the residual ester in an incomplete hydrogenation of methyl β -(1-naphthyl)-propionate over copper chromium oxide gave 3-(1-tetrahydronaphthyl)-propanol-1 and after saponification of the residual esters, β -[1-(5,6,7,8-Tetrahydronaphthyl)]-propionic acid. This acid constituted at least 70% of the mixture of acids, a proportion in harmony with that obtained in the low pressure hydrogenation over W-6 Raney nickel. Thus the 5,6,7,8 isomers probably predominate in the tetrahydronaphthyl alcohols listed in Table I, although significant amounts of the 1,2,3,4 isomer are no doubt present.

Experimental Part

The esters used were distilled from Raney nickel before they were submitted to hydrogenation. They had the properties indicated in the footnotes to Table I. The ethyl γ -naphthylbutyrates were prepared from naphthalene (154 g.) through the reaction of succinic anhydride

with naphthalene^{7,9,16,17,18,19}; separation of the isomeric acids (m. p. 120-125° and m. p. 167-172°); their reduction to γ -(1-naphthyl)-butyric acid (m. p. 104-107°) and γ -(2-naphthyl)-butyric acid (m. p. 95-97°); and esterification of the acids. The over-all yield of the esters from naphthalene was approximately 50% of the theoretical, the two esters being obtained in a ratio of 4 parts of 1-naphthyl to 3 parts of the 2-naphthyl ester.

The catalyst was separated by centrifugation; solid potassium hydroxide (5 g.) added to the methanol solution; the solvent distilled off during a period of 3-4 hours; water added to the residue; the alcohols and hydrocarbons extracted with ether; the products dried and distilled; and the acids recovered from their salts. The products were crystallized where possible, or fractionated through a Vigreux column (12 mm. \times 15 cm.). The alcohol from ethyl 1-naphthylacetate was characterized as the 3,5-dinitrobenzoate, m. p. 126-127°, of 2-(1-(5,6,7,8-tetrahydronaphthyl))-ethanol.⁹ The 2-(1-naphthyl)-ethanol from the methyl 1-naphthylacetate (20 g.) was obtained in a yield of crude product of 6.9 g., b. p. 115-121° (0.12 mm.), n_D^{25} 1.6105-1.6180. Purification by distillation and crystallization from petroleum ether gave 3.8 g., m. p. 55-58° and recrystallization 3.3 g., m. p. 60.5-61.5°. The phenylurethan had a m. p. 116-116.5°.²⁰ 1-Naphthylacetic acid (11.0 g.) was recovered after saponification of the residual ester, indicating that the hydrogenation had not been more than 41% complete. Ethyl 1-naphthoate at 80° gave 1-methylnaphthalene (7.3 g., b. p. 97-99° (6.5 mm.), n_D^{25} 1.6140, Z 35.0. Ethyl 1-naphthoate at 88° gave products which after several recrystallizations gave 0.6 g. of 2-(1-naphthyl)-ethanol, m. p. 58-59°, and 0.3 g., m. p. 60-61°, with a phenylurethan m. p. 89-89.5°.^{21,22} There was also obtained in the usual way 1-naphthoic acid (9.5 g.) and 1-methylnaphthalene (4.9 g.) b. p. about 100° (7 mm.), n_D^{25} 1.6120-1.6132.

Methyl 2-naphthoate gave 2-naphthylcarbinol (5.7 g., m. p. 80-81°),²³ 2-methylnaphthalene (0.8 g., m. p.

(16) Adams and Thal, "Organic Syntheses," Coll. Vol. 1, 270 (1941), John Wiley & Sons, Inc., New York, N. Y.

(17) Haworth, *J. Chem. Soc.*, 1125 (1932).

(18) Fieser and Peters, *THIS JOURNAL*, **54**, 4354 (1932).

(19) Martin, "Organic Syntheses," Coll. Vol. II, 499 (1943), John Wiley and Sons, Inc., New York, N. Y.

(20) Shorugin and Shorugina, *J. Gen. Chem. (U. S. S. R.)*, **5**, 555 (1935), *C. A.*, **29**, 6886 (1935).

(21) Bamberger and Lotder, *Ber.*, **21**, 258 (1888).

(22) Rupe and Bretano, *Helv. Chim. Acta*, **19**, 581 (1936).

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

(15) Cook, Hewett, Mayneord and Roe, *J. Chem. Soc.*, 1736 (1934).

31–32°), and 2-naphthoic acid (5.8 g.) after saponification of the residual ester. The material not accounted for above was apparently a mixture of hydrocarbons which did not crystallize. When the hydrogenation was carried out at 166° the chief product was a hydrocarbon (10.2 g., b. p. 75–85° (6.5 mm.), n_D^{25} 1.5335, Z 23.2). The product was apparently predominantly 2-methyl-5,6,7,8-tetrahydronaphthalene.²⁴

Hydrogenation of Esters at 2–3 atm. Pressure.—The esters (0.05 mole) in 50–75 ml. of methanol or ethanol, depending upon whether a methyl or ethyl ester was used, were hydrogenated at room temperature, in a pyrex glass centrifuge bottle of 235 ml. capacity, with 5 g. of W-6 Raney nickel,²⁵ under a pressure of 45 to 30 p. s. i. The esters absorbed 2 moles of hydrogen per mole of ester during a period varying from 1.2 hours for ethyl 1-naphthoate to eight hours for ethyl γ -(2-naphthyl)-butyrate. The other esters ethyl γ -(1-naphthyl)-butyrate, methyl β -(1-naphthyl)-propionate and methyl 2-naphthoate required two to four hours for hydrogenation. The hydrogenations went quantitatively with the formation of the tetrahydro esters. The products were distilled and showed the properties and analyses given in Table II.

Samples of each of the six tetrahydro esters were saponified in the usual way and the acids isolated. The γ -[1-(5,6,7,8-tetrahydronaphthyl)]-butyric acid, 3.5 g., m. p. 96–97°,²⁶ was obtained by recrystallization from 5.2 g. of acid obtained from the saponification. None of the isomeric 1,2,3,4-tetrahydro acid could be found in the mother liquors. Similarly γ -[2-(5,6,7,8-tetrahydronaphthyl)]-butyric acid, 3.6 g., m. p. 46.5–47.5°,²⁷ was obtained in turn from 10.8 g. of the acid. The amide, m. p. 135–136°, was prepared.²⁸ None of the isomeric 1,2,3,4-tetrahydro acid could be found in the mother liquors from which the 5,6,7,8-tetrahydro acid had been obtained.

The saponification of ethyl β -(1-tetrahydronaphthyl)-propionate gave a mixture of acids. From the mixture of acids (3.5 g.) there was obtained by recrystallizations from petroleum ether, β -[1-(5,6,7,8-tetrahydronaphthyl)]-propionic acid, 2.5 g., m. p. 136–137°.²⁹ The isomeric β -[1-(1,2,3,4-tetrahydronaphthyl)]-propionic acid, 0.5 g., m. p. 75–76°, was also obtained.³⁰ The ratio of the two isomeric acids was calculated to be about 3:1.

Two acids were obtained by the saponification of a sample of methyl 1-tetrahydronaphthoate. Through the usual procedures 1-(5,6,7,8-tetrahydro)-naphthoic acid, 1.7 g., m. p. 148–150°, was obtained from 2.2 g., m. p. 140–145°, which was in turn obtained from 4.7 g. of the mixture of acids from a saponification. The amide m. p. 185° was prepared.^{31,32} There was also obtained from the mixture of acids (4.7 g.) the 1-(1,2,3,4-tetrahydro)-naphthoic acid, 1.3 g., m. p. 74–80°. The amide m. p. 141–143° was prepared.³³

The chief component of the mixture of acids (8.6 g.)

from methyl 2-naphthoate was 5,6,7,8-tetrahydro-2-naphthoic acid, 6.8 g., m. p. 148–151°, 5.8 g., m. p. 152–153.5°. The amide m. p. 137–138° was prepared.^{34,35} There was also obtained 0.3 g. of somewhat impure 1,2,3,4-tetrahydro-2-naphthoic acid, m. p. 85–87°, and after recrystallization m. p. 86–88°.^{36,37}

Dehydrogenation of Tetrahydronaphthyl Alcohols.—A sample (10.2 g.) of 4-[2-(tetrahydronaphthyl)]-butanol-1 in 50 ml. of *p*-cymene was dehydrogenated with 2 g. of a 5% palladium on activated carbon catalyst,³⁸ by heating it in a bath held at 185–190°. The apparatus was equipped with ground glass connections and a mechanical stirrer. About 2.5 liters of hydrogen was evolved during a period of 28.5 hours. When the products of the reaction were worked up a hydrocarbon fraction 2.6 g., b. p. 83–116° (0.3 mm.), n_D^{25} 1.5718, Z 29.0, d_4^{25} 0.9647; and an alcohol fraction 4.2 g., b. p. 135–137° (0.3 mm.), n_D^{25} 1.5664, Z 25.6 were obtained. Upon the basis of the Z values, the mixture of alcohols was estimated to contain 60% of 4-(2-naphthyl)-butanol-1 mixed with 40% of the tetrahydro alcohol. A picrate m. p. 77–78° prepared from the hydrocarbon fraction indicated 2-(*n*-butyl)-naphthalene.³⁹ 3-[1-(Tetrahydronaphthyl)]-propanol-1 (9.5 g.) was dehydrogenated as described for the butanol above. Similar results were obtained, 2140 ml. of hydrogen was evolved and 5 g. crude γ -(1-naphthyl)-propanol-1, b. p. 131–133° (0.7 mm.), n_D^{25} 1.5917, Z 28.5, d_4^{25} 1.0719¹⁰ was obtained. Analysis for carbon and hydrogen as well as the Z values indicated that the product was not more than 80% pure. Hydrocarbons (2 g.) were also produced in the dehydrogenation.

Summary

Esters of formula I where n is 0, 1, 2 or 3, and the substituent is in the 1 or 2 position of the naphthalene nucleus, have been submitted to hydrogenation over the copper chromium oxide catalyst at temperatures from 80 to 200°. Through the use of a high ratio of catalyst to ester at 80–120° and by controlling the extent of hydrogenation, alcohols of formula II have been obtained where n is 0 or 1. Where n has a value of 2 or 3 the temperature required for the hydrogenation of the carbethoxy group was sufficiently high so that tetrahydronaphthyl alcohols of formula III and IV were obtained.

Esters of formula I have been quantitatively hydrogenated to the corresponding tetrahydronaphthyl esters, over W-6 Raney nickel at 2–3 atm. and room temperature. The unsubstituted ring is more susceptible to hydrogenation than the substituted ring in these esters.

MADISON, WISCONSIN

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