modify the relative rates of competitive hydrogenations such as are encountered in the preparation of phenylethyl alcohol from ethyl phenylacetate so that larger yields of the alcohols were obtained. The procedure for the preparation of the most active catalysts containing barium is that described for the catalyst labeled 37 KAF, while the most active catalyst yet prepared is that containing calcium and is labeled 39 KAF.

Copper–chromium oxide catalysts have also been prepared by the decomposition of oxalates, by the mechanical mixture of copper and chromium oxides, by the decomposition of their nitrates, by the combination of copper and chromic oxide and by the decomposition of the precipitated copper, chromium, ammonium carbonates. All the products which contained divalent copper catalyzed hydrogenation. The most active catalysts (30 RAC) from this group were prepared by the decomposition of coprecipitated copper, chromium, barium, ammonium carbonates. Such a catalyst was similar in activity to the better catalysts obtained by the decomposition of the corresponding chromates.

MADISON, WISCONSIN

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

THE CATALYTIC HYDROGENATION OF ESTERS TO ALCOHOLS. II

BY KARL FOLKERS AND HOMER ADKINS

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The catalytic hydrogenation over copper–chromium oxide of the carbethoxy to the carbinol group in 80–98% yields for seven esters was recently described.[1] Because of the utility of this process for the reduction of an ester to the corresponding alcohol, several of the variables involved have been studied further, and the method has been extended to other types of esters, over modified and improved copper–chromium oxide catalysts. This paper, then, is a summary of the significant results of all these experiments. The apparatus and procedure were the same as those previously described.[2]

In Table I there is recorded a summary of the data obtained on the hydrogenation of various esters at 250° and under a pressure of 200 to 300 atmospheres. Table II contains the data on the rates of hydrogenation of

[1] Adkins and Folkers, THIS JOURNAL, **53**, 1095 (1931). Since the publication of this paper and the completion of most of the experimental work described herewith, there have appeared three publications describing the hydrogenation of a few acids and esters of high molecular weight to alcohols. Schrauth, Schenck and Steckdorn, *Ber.*, **64**, 1314 (1931); Norman, *Z. angew. Chem.*, **44**, 714 (1931); Otto Schmidt, *Ber.*, **64**, 2051 (1931).

[2] Adkins and Cramer, THIS JOURNAL, **52**, 4349 (1930).

eight caproic esters as determined at 225° and under a pressure of 177 ± 13 atmospheres of hydrogen, using 2 g. of copper–barium–chromium oxide These conditions were selected so that differences in the rates of hydrogena-

TABLE I

HYDROGENATION OF ESTERS (250°) (200–300 ATMOSPHERES)

Ester		Catalyst				Time,	Yields,	
Name	Mole	Oxides			g.	No.	hours	%	Products
Methyl caproate[a]	0.20	Cu	Ba	Cr	5	19	2.25	92.2	*n*-Hexanol (152–153°)
n-Butyl caproate[a]	.20	Cu	Ba	Cr	5	19	0.58	95.5	*n*-Hexanol (152–153°)
Ethyl caprylate	.20	Cu	Ba	Cr	5	19	2.0	93.6	*n*-Octanol (189–190°)
Methyl salicylate	.25	Cu	Cr		6	18	6.0	19.2	*o*-Cresol (182–185°)
								61.3	2-Methyl cyclohexanol (161–162°)
Ethyl hexahydrobenzoate	.25	Cu	Ba	Cr	5	25	0.87	97.5	Cyclohexylcarbinol (180–181°)
Ethyl hexahydrobenzoate	1.78	Cu	Ba	Cr	10	20	3.5	97.5	Cyclohexylcarbinol
Diethyl malonate	0.20	Cu	Ba	Cr	6	20	7.5	...	Ethyl propionate, *n*-propanol
Diethyl ethylmalonate	.20	Cu	Ba	Cr	5	25	2.0	77.9	2-Methylbutanol-1 (ester free) (120–124°)
Diethyl ethylmalonate	.27	Cu	Ba	Cr	6	25	0.5	71.9	2-Methylbutanol-1 (120–124°)
								19.3	Ethyl 2-methylbutyrate
								8.8	Diethyl ethylmalonate
Dimethyl α-phenylsuccinate Methanol	.23 .87	Cu	Ba	Cr	8	24	1.5	100	Dimethyl α-phenylsuccinate
Dimethyl α-phenylsuccinate[b]	.23	Cu	Ba	Cr	6	24	6.0	67.3	3-Phenylbutanol-1 (92–94°)
								12.6	2-Phenylbutanediol-1,4
								1.2	Dimethyl α-phenylsuccinate
Ethyl β-phenylpropionate[m]	.17	Cu	Ba	Cr	4	20	1.0	93.0	3 - Phenylpropanol - 1 122–125° (19 mm.)
Di-*n*-butyl glutarate	.20	Cu	Ba	Cr	7	24	1.83	92.2	Pentanediol-1,5 (108–110, 2.5 mm.)
Diethyl sebacate	.12	Cu	Ba	Cr	5	20	1.66	94.0	Decanediol-1. 10 (150–151, 3 mm.) (m. p. 70.8–71.8°)
Ethyl lactate[b]	.26	Cu	Ba	Cr	5	25	4.42	83.5	Propanediol-1,2 (186.5–187) (ester free)
Ethyl lactate[b]	.26	Cu	Ba	Cr	5	25	3.5	90.5	Propanediol-1,2 (186.5–187)
								0.5	Ethyl lactate
Ethyl β-hydroxybutyrate	.30	Cu	Ba	Cr	6	19	5.0	55.5	Pri. and *sec.*-butanols
Ethyl β-acetyloxybutyrate	.19	Cu	Ba	Cr	5	24	4.0	...	Ethyl, pri. and *sec.*-butanols and their acetic and butyric esters
γ-Valerolactone	.28	Cu	Ba	Cr	5	24	0.0	78.5	Pentanediol-1,4 (114–115, 8 mm.)
								8.1	*n*-Pentanol
Caproic acid *n*-Butanol[c]	.26 1.16	Cu	Ba	Cr	6	20	3.25	14.7	*n*-Hexanol (152–153°); recovered acid (95.5% as ester, 4.5% as free acid)
Caproic acid Ethanol[c]	0.26 1.16	Cu	Ba	Cr	6	20	3.0	10.0	*n*-Hexanol (152–153)°; recovered acid (93.8% as ester, 6.2% as free acid)
Stearic acid *n*-Butyl stearate *n*-Butanol	0.056 .144 .54	Cu	Ba	Cr	8	24	11.0	77.1	Octadecanol
Spermaceti[m]	.15	Cu	Ba	Cr	5	25	2.0	97	Cetyl alcohol (ester free)

TABLE I (*Concluded*)

Ester: Name	Mole	Catalyst: Oxides	g.	No.	Time, hours	Yields, %	Products
Ethyl β-piperidino-propionate	.29	Cu Ba Cr	8	24	10.75	...	Piperidine; N-ethyl and propylpiperidines; ethyl propionate γ-piperidino-propanol; residue
Ethyl nicotinate	.22	0.6 g. reduced Ni on kiselguhr (165°)	3.4		3.25	72.6	Ethyl nipecotate (78.7–79.5, 5 mm.); 3-Methyl piperidone-2[j] (102–102.5, 3 mm.) m. p. 54.5–56.5)
Ethanol	1.08					27.0	
N-capropylpiperidine	.12	Cu Ba Cr	2	25	5.0	92.3	N - *n* - hexylpiperidine (212–213°)
Ethyl nicotinate	.175	0.75 g. reduced Ni on kieselguhr (200°)			7.0	68.0	Ethyl N-ethyl nipecotate (80.5–82 (4 mm.))
Ethanol	.874						
Ethyl N-ethylnipecotate	.13	Cu Ba Cr	3	37	2.2	99.0	N - ethyl - β - pipecoline (142–144°)
Ethyl nicotinate	.22	Cu Ba Cr	6	25	7.0	...	Alkyl piperidines, ethyl nipecotate, cleavage and condensation products
Ethyl α-phenylbutyrate[d,k] (81–83° (4 mm.))	.25	Cu Cr	6	18	7.0	0.0	Ethyl α-phenylbutyrate
						48.0	Hydrocarbons [l]
						47.5	β-Ethylphenethyl alcohol (234–236°)
Ethyl α-phenylbutyrate[d]	.25	Cu Cr	6	18	0.58	3.2	Ethyl α-phenylbutyrate
						14.6	Hydrocarbons [l]
						78.1	β-Ethylphenethyl alcohol
Ethyl α-phenylbutyrate[d]	.25	Cu Cr	6	18	0.05	24.0	Ethyl α-phenylbutyrate
						9.3	Hydrocarbons [l]
						63.5	β-Ethylphenethyl alcohol
Ethyl α-phenylbutyrate[d]	.25	Cu Ca Cr	6	39	0.08	1.3	Ethyl α-phenylbutyrate
						19.4	Hydrocarbons [l]
						79.2	β-Ethylphenethyl alcohol
Ethyl phenylacetate[e]	.25	Cu Ba Cr	6	25	0.85	1.3	Ethyl phenylacetate
						52.5	Ethylbenzene
						39.7	Phenylethyl alcohol
Cyclohexyl phenylacetate[e] (129–130.5° (3.5 mm.))	.25	Cu Ba Cr	6	25	0.53	5.9	Ethyl phenylacetate
						35.4	Ethylbenzene
						58.7	Phenylethyl alcohol
Cyclohexyl phenylacetate[e]	.25	Cu Ca Cr	6	39	0.53	10.2	Cyclohexyl phenylacetate
						26.4	Ethylbenzene
						63.3	Phenylethyl alcohol
Ethyl phenylacetate[f]	.28	Cu Ba Cr	2.5	25	5.0	0.0	Ethyl phenylacetate
						69.7	Ethylbenzene
						20.3	Phenylethyl alcohol
Ethyl phenylacetate[f]	.28	Cu Mg Cr	2.5	38	1.78	7.5	Ethyl phenylacetate
						30.6	Ethylbenzene
						58.3	Phenylethyl alcohol
Ethyl phenylacetate[f]	.28	Cu Ca Cr	2.5	39	0.42	37.8	Ethyl phenylacetate
						8.4	Ethylbenzene
						50.7	Phenylethyl alcohol
Ethyl phenylacetate[f]	.28	Cu Sr Cr	2.5	40	1.6	90.1	Ethyl phenylacetate
						...	Ethylbenzene
						2.9	Phenylethyl alcohol
Ethyl phenylacetate[g]	.20	Cu Cr	5	18	1.0	0.0	Ethyl phenylacetate
						88.7	Ethylbenzene
						4.5	Phenylethyl alcohol
Ethyl phenylacetate[g]	.20	Cu Ba Cr	5	29	1.0	0.0	Ethyl phenylacetate
						66.0	Ethylbenzene
						29.9	Ethyl phenyl alcohol

[a, b, c, d, e, f, g, h]. Experiments bearing the same letter were carried out under identical conditions with the same sample of ester, etc.

[i] This ester was supplied by Dr. C. F. H. Allen of McGill University, Montreal.

[j] M. p. 53.5–55° [Aschan, *Ber.*, **24**, 2445 (1891)]; m. p. 55–56° [Lipp and Widnmann, *Ann.*, **409**, 144 (1915)].

[k] This ester was supplied by Dr. V. H. Wallingford of the Mallinckrodt Chemical Works, St. Louis.

[l] Apparently a certain amount of cleavage had occurred as the mixture of hydrocarbons distilled from 135 to 170°, and appeared to be a mixture of ethyl and secondary butylbenzenes boiling chiefly at 138–140 and 169–170°, respectively.

[m] These esters were hydrogenated by Mr. Ralph Connor.

TABLE II

RATE OF HYDROGENATION OF CAPROIC ESTERS (225°) (177 ± 13 ATMOSPHERES)

Ester (0.12 mole)	Hydrogenation after 1.5 hrs., %	Total time, hrs.	Products: *n*-Hexanol	Products: Ester
Ethyl caproate	44.7	7.5	62.4	37.6
n-Butyl caproate	57.7	6.25	85.0	15.0
n-Butyl caproate, methanol	42.1	7.5	89.4	10.6
Sec.-butyl caproate	58.6	8.0	82.8	17.2
β-Ethoxyethyl caproate, 74–76° (2 mm.)	60.1	6.84	90.9	9.1
n-Hexyl caproate, 84–86° (3 mm.)	65.2	7.64	96.3	3.7
Cyclohexyl caproate, 116–117° (11 mm.)	91.6	3.0	100.0	0.0
Hexahydrobenzyl caproate, 100–102° (2 mm.)	68.2	10.41	94.7	5.3
Lauryl caproate, 148–149° (2 mm.)	43.8	8.66	68.9	31.1

tion of the esters would be more marked than they are at higher temperatures. The hydrogenation of any of these caproates could have been easily made 100% by a slight increase of temperature, pressure or ratio of catalyst to ester. The yields of the major products given are those actually obtained by fractional distillation through Widmer columns, while the minor products were determined by titration, saponification, etc., of small samples. The preparation of the catalysts is described in the accompanying paper.[3]

Discussion of Experimental Results

It is unnecessary to make any extended comment upon the hydrogenation of ethyl hexahydrobenzoate, caproate, caprylate, β-phenyl propionate, stearate, palmitate, glutarate and sebacate for these esters, like those of valeric, trimethylacetic, myristic and lauric acids reported in the earlier paper, were hydrogenated smoothly and almost quantitatively to the corresponding alcohols. However, the hydrogenation of esters is somewhat modified if there are certain groups or linkages in the vicinity of the carbethoxy group. Among these active substituents are the phenyl, hydroxyl, carbethoxy and amino groups. The hydrogenation is also modified by a number of other factors which are discussed below.

Phenyl Group.—Benzyl alcohol, phenylmethylcarbinol and diphenylcarbinol were readily hydrogenated over copper–chromium oxide catalysts

[3] Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

to the corresponding hydrocarbons at temperatures 50 to 100° lower than are necessary for the hydrogenation of esters.[4] It thus appeared hopeless to attempt to hydrogenate, to the corresponding phenylcarbinols, esters having a carbethoxy group attached to a benzenoid ring. This expectation was borne out by the absence of *o*-hydroxybenzyl alcohol in the products from the hydrogenation of methyl salicylate.

A similar hydrogenation to a hydrocarbon (ethylbenzene) was encountered in the earlier experiments on the hydrogenation of ethyl α-phenylacetate. However, it was found that if the hydrogenation was stopped before the absorption of hydrogen was complete, a 39.7% yield of β-phenylethyl alcohol could be obtained. The yield of ethylbenzene in this case was 52.5% of the theoretical amount. It thus appears that if the phenyl group is one carbon removed from the carbethoxy (or the resulting carbinol group), it is far less effective in labilizing the oxygen than it is when it is directly attached to the carbethoxy or carbinol group. This is further evidenced by the results of the hydrogenation of α-phenylbutyric ester. Under favorable conditions this compound was hydrogenated to give a 78% yield of 2-phenylbutanol-1 (β-ethylphenethyl alcohol), with only a 14.6% yield of hydrocarbons. The better yield of alcohol from α-phenylbutyric ester as compared with the yield from α-phenylacetic ester is apparently dependent upon the more rapid hydrogenation of the former ester. The more rapid hydrogenation of the ester makes it unnecessary to expose the alcohol so long to the conditions which convert it to a hydrocarbon.

The yield of phenylethyl alcohol from the esters of phenylacetic acid may be materially increased over the figure given (39.7%) above as the maximum so far obtained from the ethyl ester over a copper–barium–chromium oxide catalyst. For example, the actual yield of phenylethyl alcohol from the cyclohexyl ester was 58.7% over a barium containing catalyst and 63.3% over a catalyst containing calcium. These yields were 62 and 70%, respectively, based upon the amount of ester undergoing hydrogenation. In another experiment with a calcium-containing catalyst the yield of the alcohol, based upon the amount of ester hydrogenated, was approximately 80%.

The removal of the phenyl group one position further from the carbethoxy (or carbinol) group, as in β-phenylpropionic ester, almost eliminates its effect in labilizing the hydroxyl group for hydrogenation. This is shown by the fact that β-phenylpropionic ester (or cinnamic ester) was hydrogenated in a high yield to 3-phenylpropanol-1.

Carbethoxy and Carbinol Groups.—The effects of the carbethoxy and carbinol groups upon the hydrogenation of esters are considered together, because in this work it is impractical to distinguish the labilizing effect of

[4] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

the former from that of the carbinol group which is produced from it by hydrogenation.

One of the carbethoxy groups (or the resulting carbinol group) labilizes the hydrogenation of the carbinol group from the second carbethoxy group of malonic ester so that it is completely hydrogenated, there being no glycol produced but only ethyl propionate and its hydrogenation product, propyl alcohol. Similarly the monoethyl derivative of malonic ester is converted in a 78% yield to 2-methylbutanol-1. When this hydrogenation was interrupted before completion there was no evidence in the products that there was any glycol or hydroxy ester present. In a similar way neither β-hydroxybutyric ester nor its acetyl derivative hydrogenated to give a glycol. Moreover, the labilizing action of one oxygen-containing substituent not only manifests itself in labilizing the hydrogenation of the other, but in addition a carbon to carbon linkage is labilized so that the molecule is cleaved between the 2 and 3 carbon atoms as shown in the case of 2,2-dimethylacetoacetic ester.

If the carbethoxy groups are separated by two carbon atoms as in succinic ester, the effect of one upon the hydrogenation of the other is greatly minimized and tetramethylene glycol was produced in over 80% yield. In a similar way the oxygen containing groups in valerolactone exerted relatively little effect on each other so that pentanediol-1,4 was obtained in 78.5% yield, with only 8.1% *n*-pentanol. When the carbethoxy groups were still further apart as in glutaric and sebacic esters, the groups exerted no appreciable effect upon the hydrogenation of each other.

The hydrogenation of the methyl ester of α-phenylsuccinic acid to the glycol was not successful as a yield of only 12.6% was obtained, the main product (67.3%) being 3-phenylbutanol-1. It appears that the combined labilizing influence of the carbmethoxy and phenyl groups was too great to permit the preparation of the glycol in a satisfactory yield.

The experimental results referred to above are harmonious, indicating that phenyl, carbethoxy and carbinol groups labilize the hydrogenation of carbethoxy, carbonyl and carbinol groups when they are relatively near to these latter groups in the chain. However, in the case of ethyl lactate this generalization is invalid, for this ester yielded on reduction propanediol-1,2 in more than 90% yield.

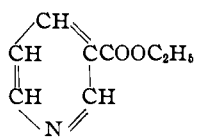
Carbethoxy and Carbinol Groups and the Stability of Carbon to Nitrogen Linkages.—The carbon to nitrogen linkages as in N-butylpiperidine are apparently quite stable under the experimental conditions used for the catalytic hydrogenation of esters since the amine was recovered unchanged after several hours at 250° and 260 atmospheres of hydrogen in the presence of an active copper–chromium–barium oxide catalyst. However, the oxygen-containing groups labilize the carbon to nitrogen linkage so that in certain compounds it is rather readily cleaved. In the

hydrogenation of ethyl β-piperidinopropionate the yield of the corresponding alcohol, 3-piperidinopropanol-1, was negligible, the chief products being piperidine, ethyl propionate, and N-ethyl and propylpiperidines. These products were, no doubt, formed as the result of the reactions noted below

$$C_5H_{10}NCH_2CH_2CO_2C_2H_5 + H_2 \longrightarrow C_5H_{10}NH + CH_3CH_2CO_2C_2H_5 \quad (I)$$
$$CH_3CH_2CO_2C_2H_5 + H_2 \longrightarrow C_3H_7OH + C_2H_5OH \quad (II)$$
$$C_5H_{10}NH + C_3H_7OH \longrightarrow C_5H_{10}NC_3H_7 + H_2O \quad (III)$$
$$C_5H_{10}NH + C_2H_5OH \longrightarrow C_5H_{10}NC_2H_5 + H_2O \quad (IV)$$

The presence of piperidine and ethyl propionate can hardly be accounted for except on the basis of equation I. Equation II represents the usual hydrogenation of an ester. The validity of equations III and IV is upheld by the finding that under the experimental conditions used for the hydrogenation of the ester, an 88% yield of N-hexylpiperidine was obtained from the reaction of piperidine and *n*-hexanol. The use of nickel as a catalyst for this type of reaction has recently been described.[5]

When ethyl nicotinate (I) was subjected to hydrogenation over a nickel or a copper–barium–chromium oxide catalyst, a cleavage occurred similar to that indicated in reaction 1. A mixture of bases was obtained but the chief product over nickel was 3-methyl-2-piperidone (III).



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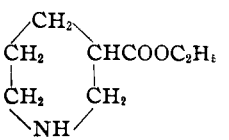
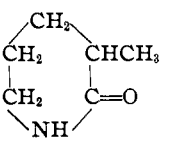


II



III

The carbethoxy group in nicotinic or nipecotic (II) ester is in the 3 position with respect to the nitrogen, just as it is in ethyl β-piperidinopropionate so that a similar cleavage of a nitrogen to carbon bond is not unexpected. Nicotinic ester would first be hydrogenated to nipecotic ester, this then must have undergone cleavage to the open-chain ester ($NH_2CH_2CH_2$-$CH_2CH(CH_3)COOC_2H_5$), ethyl α-methyl-δ-aminovalerate. The interaction of the amino and carbethoxy groups of this ester would result in the formation of 3-methyl-2-piperidone.

As noted above, a carbethoxy group on a benzenoid ring was completely reduced to a methyl group, while ethyl hexahydrobenzoate was converted almost quantitatively to cyclohexylcarbinol. It therefore seemed possible that if the pyridinoid ring of nicotinic ester was saturated before attempting to reduce the carbethoxy group, it might be possible to prepare a 3-piperidinocarbinol from nicotinic ester. Nipecotic ester was therefore prepared by hydrogenating nicotinic ester over nickel at 165°. It was then alkylated with ethanol over a nickel catalyst according to the method

[5] Winans and Adkins, THIS JOURNAL, **54**, 306 (1932)

recently described.[5] The resulting ethyl N-ethylnipecotate ester was subjected to hydrogenation over a copper–barium chromium catalyst but the only product was N-ethyl-3-methylpiperidine, which was obtained in a 99% yield. This does not show, however, that it was formed as was *o*-cresol from methyl salicylate, that is, by the hydrogenation of the corresponding carbinol. It is more probable that it was formed through the cleavage of the ring and the formation of the piperidone as described above, followed by the hydrogenation of that cyclic amide. This hypothesis is borne out by the fact that an amide, N-caproylpiperidine was smoothly hydrogenated over the copper–barium–chromium oxide catalyst to N-*n*-hexylpiperidine in a 92% yield.

Acids.—The presence of free acid in the reaction mixture retards the hydrogenation as shown by the following experiment: five grams of copper–barium–chromium oxide catalyzed the reduction of 0.2 mole of *n*-butyl caproate to the extent of 75% in two minutes, and 100% in thirty-five minutes, whereas under exactly the same conditions 0.19 mole of *n*-butyl caproate and 0.01 mole of caproic acid was hydrogenated to the extent of 75% in thirty-eight minutes and 100% in 110 minutes. Furthermore, mixtures of caproic acid and *n*-butanol, or caproic acid and ethanol, could be hydrogenated only slightly, although the extent of esterification was 90–95%. However, the presence of a considerable amount of stearic acid in *n*-butyl stearate did not retard the hydrogenation to so great an extent.

Alkyl Groups and Methanol.—Methyl esters have been found to be unsatisfactory when a fast hydrogenation was desired. From Table I it is seen that methyl caproate hydrogenated 25% as rapidly as *n*-butyl caproate. Methanol cannot advantageously be used as a solvent, for dimethyl α-phenylsuccinate could not be hydrogenated in methanol, while in the pure state it was slowly hydrogenated. However, in the hydrogenation of butyl caproate, the presence of methanol merely retarded the rate (Table II). Possibly, methanol acts in the same inhibiting capacity as an acid. Brönsted has pointed out that methanol is 0.4 and ethanol only 0.06 as strong an acid as is water.[6] Although these figures are subject to numerical uncertainty, their great difference in magnitude suggests that methanol would be much more detrimental to the catalyst than ethanol.

The rates of hydrogenation of the nine caproic esters are perhaps best compared by considering the amount of hydrogen adsorbed after one and one-half hours (Table II). Although *sec.*-butyl caproate had a higher initial rate than *n*-butyl caproate, its final rate was less. Ethyl and lauryl caproates hydrogenated about 77% as rapidly as *n*-butyl caproate. Cyclohexyl caproate had by far the highest rate and it may also be seen from the data in Table I that the cyclohexyl ester of phenylacetic acid hydrogenated faster than did the ethyl ester. Since there was so little difference in the

[6] Brönsted, *Chem. Reviews*, **5**, 311 (1928).

rates of the *n*- and *sec.*-butyl esters, and such a large difference in the rates of the *n*-hexyl and cyclohexyl esters, the high rate of the cyclohexyl ester can hardly be attributed to the difference between primary and secondary alcohols, but rather to a specific effect of the cyclohexyl ring. Apparently, this effect is not entirely lost in the caproate of cyclohexylcarbinol, for this ester is next to cyclohexyl caproate in rate of hydrogenation.

Pressure of Hydrogen.—The effect of pressure of hydrogen on the rate of hydrogenation of ethyl laurate was shown by these experiments. Three grams of catalyst effected complete hydrogenation of 0.13 mole of ester at 250°, in seven hours at 106 ± 8 atm.; in one hour at 214 ± 9 atm.; and fifteen minutes at 333 ± 7 atm. Thus, from 100 atmospheres, a two-fold pressure increase caused a seven-fold increase in the rate, whereas a three-fold pressure increase caused a twenty-eight-fold increase in rate of hydrogenation.

Temperature.—The temperature required for hydrogenation of an ester over the copper–chromium oxide catalyst is within certain limits a function of the pressure of hydrogen, the activity of the catalyst, the ratio of the amount of ester to the amount of catalyst and of the nature and impurities present in the sample of ester under consideration. In general 250° has been found to be a suitable temperature for successfully carrying out the hydrogenation, although certain esters, such as cyclohexyl caproate, under the conditions chosen for test were rapidly and completely hydrogenated at 225°, while considerable hydrogen absorption occurred at 200° and lower. For example, ethyl laurate was hydrogenated for seven hours at 200° to determine the nature of the hydrogen absorption up to this temperature, and to see if aldehyde could be found in the product. The product contained 76.9% of the ethyl laurate used, and aldehyde tests with Tollens' and fuchsin reagents were negative. The amount of the hydrogen absorption indicated that 24% of the amount for complete reduction of the ester had been adsorbed. Therefore there is no evidence that even at 200° any stable intermediate reduction product is formed.

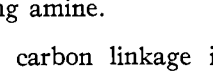
Catalyst.—The foregoing discussion has been based primarily upon the results obtained in the hydrogenation of esters over a copper–chromium oxide catalyst containing barium. The beneficial effect of barium in stabilizing the catalyst against reduction and consequent deactivation has been considered in the accompanying paper upon the preparation of catalysts. A comparison of the data in Table I on the hydrogenation of ethyl α-phenylbutyrate and ethyl phenylacetate indicates conclusively that magnesium and especially calcium are even more beneficial than is barium as a component of the catalyst. The rate of hydrogenation over these catalysts is much more rapid and in the case of ethyl phenylacetate the proportion of phenylethyl alcohol as compared with that of ethylbenzene is greatly increased.

Summary

A number of esters with one or two carbalkoxy groups in the molecule have been hydrogenated to the corresponding alcohols or glycols in yields of 90–98%. The rate of hydrogenation is retarded by free acid or methanol and is considerably modified by the nature of the alkyl group in the carbalkoxy group. Thus cyclohexyl caproate was hydrogenated very much more rapidly than was ethyl caproate, while the latter was hydrogenated several times as rapidly as the methyl ester.

The presence of a phenyl, carbethoxy or carbinol group in the vicinity of a carbethoxy or carbinol group (except with ethyl lactate) labilized the cleavage of the carbon to oxygen linkage, the carbethoxy or carbinol group being thus hydrogenated to a methyl or methylene group. This reaction occurred almost exclusively when a phenyl group was adjacent to the carbethoxy group, or a carbethoxy or carbinol group was in the 2-position with respect to the ester group. When the phenyl group was in the 2-position there was a strong tendency for a similar reaction; however, by proper choice of experimental conditions and especially by the incorporation of magnesium or calcium into the catalyst, it was possible to avoid this reaction in large part.

A substituted amide, N-caproylpiperidine, was smoothly hydrogenated to the corresponding amine.

The nitrogen to carbon linkage in the group  is apparently readily cleaved under the conditions used for hydrogenation of the ester. With ethyl nipecotate the cleavage occurred over nickel as low as 165° and resulted in the formation of 3-methylpiperidine-2 or its hydrogenation products.

The rate of hydrogenation of ethyl laurate at 100, 200 and 300 atmospheres' pressure has been found to show a 28-fold increase over this range. The hydrogenation of esters under the conditions chosen for test proceeded smoothly at temperatures from about 200° upward.

MADISON, WISCONSIN