

o-hydroxyphenyl-1-hexene-2, which was synthesized for purposes of comparison. The physical properties of these compounds were determined.

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

THE USE OF NICKEL AS A CATALYST FOR HYDROGENATION. II

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A study of the preparation of nickel catalysts¹ indicated that in general sodium bicarbonate was to be preferred to sodium carbonate or potassium hydroxide as a precipitant in the preparation of nickel catalysts. This was true because the resulting catalysts were somewhat more active and less sensitive to variations in the procedure of preparation. More recently it has become evident that ammonium carbonate is in general the most satisfactory precipitant.

Procedure Recommended for the Preparation of a Nickel Catalyst.—Fifty-eight grams of Baker and Adamson or Mallinckrodt c. p. nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), dissolved in 80 ml. of distilled water, was ground for thirty to sixty minutes in a mortar with 50 g. of acid washed kieselguhr (*ex* Johns-Manville "Filter-Cel") until the mixture was apparently homogeneous and flowed as freely as a heavy lubricating oil. It was then slowly added to a solution prepared from 34 g. of Mallinckrodt c. p. ammonium carbonate, monohydrate ($(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$) and 200 ml. of distilled water. The resulting mixture was filtered with suction, washed with 100 ml. of water in two portions, and dried overnight at 110°. The yield was 66 g. Just before use, 2 to 6 g. of the product so obtained was reduced for one hour at 450° in a stream of hydrogen which passed over the catalyst at a rate of 10 to 15 ml. per minute. The catalyst was then cooled to room temperature and transferred in a stream of hydrogen to the reaction vessel, which had been filled with carbon dioxide.

Time of Reduction, Nickel Content and Activity of Catalysts.—Some years ago the time and temperature for the reduction of nickel on a kieselguhr support in this Laboratory was rather arbitrarily set as one hour at 450°, since this gave a catalyst of good activity. Diwoky in this Laboratory observed that for certain rather inactive preparations the catalyst was more active if a higher temperature or a longer time was used in the reduction of the nickel oxide. On the basis of this observation it seemed desirable to ascertain the optimum conditions for the reduction of various types of nickel catalysts. Armstrong and Hilditch² showed that the activity of

¹ Adkins and Covert, *J. Phys. Chem.*, 35, 1684–1691 (1931).

² Armstrong and Hilditch, *Proc. Roy. Soc. (London)*, 99A, 490–495 (1921).

nickel catalysts increased with the content of metallic nickel, so that analyses for nickel in combination with other elements were made upon the catalyst before reduction and analyses for metallic nickel after reduction. There is recorded in Table I a summary of significant data on the relationship of temperature and time of reduction, content of nickel and catalytic activity as measured against acetone.

TABLE I
EFFECT OF TIME AND TEMPERATURE UPON EXTENT OF REDUCTION AND ACTIVITY OF
NICKEL ON KIESELGUHR

Catalyst	Reduction		Metallic nickel, % ^b	Time for reduction of acetone ^c	
	Temp., °C.	Time, minutes		"Middle 60%"	100%
No. 8. Kieselguhr nickel nitrate added to soln. of Na ₂ CO ₃ (12.6% Ni)	450	30	..	26	52
	525	30	..	22	55
	525	45	..	17	35
	450	60	5.14	23	39
	500	60 ^a	7.66	10	16
	550	60	..	16	26
	450	90	..	17	25
No. 15. Soln. of Na ₂ CO ₃ added to kieselguhr nickel nitrate (12.5% Ni)	450	30	..	20	40
	525	30	..	21	59
	525	45	..	17	35
	450	60	5.14	21	47
	500	60 ^a	7.38	18	30
	550	60	..	21	85
	450	90	..	29	40
No. 16. Soln. of NaHCO ₃ added to kieselguhr nickel nitrate (13.6% Ni)	450	30	..	86	150
	525	30	..	24	45
	525	45	..	44	74
	450	60	9.88	11	30
	500	60 ^a	10.2	21	60
	550	60	..	103	160
	450	90	..	10	25
No. 24. Kieselguhr nickel ni- trate added to soln. of (NH ₄) ₂ CO ₃ (14.9% Ni)	450	60	10.4	10	23
	500	60	10.3	25	55
No. 23. Soln. of (NH ₄) ₂ CO ₃ added to kieselguhr nickel ni- trate (13.6% Ni)	450	60	7.85	10	20
	500	60	7.95	19	45

^a The content of metallic nickel was not materially increased by longer times for reduction even up to five hours.

^b Metallic nickel was determined by a standard method (Treadwell and Hall, "Quantitative Analysis," John Wiley and Sons, New York City, Vol. II, 1928, p. 520) except that ferric sulfate was substituted for ferric chloride. The dimethylglyoxime method was used for the determination of total nickel.

^c 1.0 mole of acetone, 2 g. of catalyst, 125°, 125 atmospheres pressure.

In brief it may be said that for one of the sodium carbonate catalysts (8), sixty minutes at 500° were the optimum conditions, while ninety

minutes at 450° or sixty minutes at 550° gave identical and inferior catalysts. For the bicarbonate catalyst (16), sixty to ninety minutes at 450° were the best conditions, while a shorter time at 450° or a higher temperature are definitely deleterious in their effect upon the activity of the catalyst. For catalyst 15 (sodium carbonate type B), the relative merits of the different conditions for the reduction of the catalyst were dependent upon whether the basis of comparison for activity is the time for the "middle 60%" reduction of acetone or the time for complete reduction. On the former basis quite similar activity was found for five sets of conditions for the reduction of the catalyst. On the basis of a comparison of the time required for the complete hydrogenation of acetone, temperatures above 500° and times over sixty minutes are definitely injurious. There appears to be no reason why longer than sixty minutes or temperatures higher than 450° should be used for the reduction of the ammonium carbonate type of catalysts (23 and 24).

A correlation of the data on the content of metallic nickel with the activity of the catalysts makes it clear why higher temperatures and longer times were required for the reduction of the sodium carbonate (8 and 15) than for the bicarbonate (16) or ammonium carbonate catalysts (23 and 24) and in part why the latter were more active. Although it is evident that the activity was not strictly proportional to the content of reduced nickel, yet it is significant that the sodium carbonate catalysts had a less content of nickel originally, and the nickel compound was reduced to metallic nickel more slowly at 450° than was true for the bicarbonate or ammonium carbonate catalysts. Moreover, for all the catalysts there was a considerable proportion of the nickel which was not reduced even after several hours, but this proportion was greater for the sodium carbonate catalysts. The deleterious effect of longer times and higher temperatures than the optimum is, of course, due to the well-known slow deactivation of metallic catalysts at temperatures above perhaps 400°.

Promotion of Nickel Catalysts for Hydrogenation.—There are numerous claims in the literature, especially in patents, with regard to the promotion of the activity of nickel catalysts through the inclusion of another element. A group of catalysts was therefore made up by the bicarbonate method which contained in addition to nickel either copper, zinc, chromium, molybdenum, barium, manganese, cerium, iron, cobalt, boron, silver, magnesium, tungsten, tin or silicon (other than in the kieseluhr). These catalysts were tested in the hydrogenation of acetone, the diethyl acetal of furfural, and to a limited extent on toluene. A summary of the data is given in Table II. The activity of the catalyst may be compared on the basis; (1) of the observed "inflection temperature," *i. e.*, the temperature at which the pressure in the bomb reached its maximum,

or (2) on the basis of the percentage of the compound reduced below 125° for acetone and 175° for the acetal, or (3) on the basis of the time required for complete hydrogenation. The first two of these bases give an indication of the initial activity of the catalyst at lower temperatures, while the third is the most significant from a practical standpoint.

In the case of acetone, activity was promoted by molybdenum, tin, chromium, cobalt and boron, while tungsten reduced the activity of the

TABLE II
EFFECT OF VARIOUS ELEMENTS UPON THE CATALYSIS BY NICKEL OF THE HYDROGENATION OF ACETONE^a AND THE ETHYL ACETAL OF FURFURAL^b

Catalysts ^c	Inflection temp.		% Hydrogenated		Minutes for 100 %	
	Acetone	Acetal	Below 125° Acetone	Below 175° Acetal	Acetone	Acetal ^h
Ni	100	118	18	83	13	12
+Cu	105	108	30	85	25	10
+Cu ^d	105	120	28	88	16	12
+Zn	125	110	16	40	15	160 ^e
+Cr	95	105	38	96	16	11
+Mo	80	105	47	100	10	0
+Ba	100	100	33	96	24	1
+Mn	100	138	20	100	24	0
+Ce	100	115	28	100	20	0 ^g
+Fe	112	130	17	100	16	0 ^g
+Co	100	125	35	88	10	8 ^g
+B	100	108	30	88	10	16 ^g
+Ag	100	105	24	63	15	11 ^g
+Mg	95	108	27	98	12	8
+W	120	130	12	92	140	17 ^g
+Sn	80	105	46	63	16	71 ^g
+Si	100	110	28	100	16	0 ^g
+Ce	115 ^f		40 ^f		4 ^f	
+Cu	115 ^f		24 ^f		15 ^f	
+Ba	110 ^f		30 ^f		24 ^f	

^a 1.0 mole of acetone, 2 g. of catalyst, 125° and 125 atm. pressure.

^b 0.25 mole of acetal, 2 g. of catalyst, 175° and 125 atm. pressure.

^c Unless otherwise noted catalysts referred to in this table were prepared by the addition of a solution of sodium bicarbonate to nickel nitrate on kieselguhr. One part of copper, zinc, chromium, barium or manganese as nitrates was incorporated into the kieselguhr along with ten parts of nickel nitrate. One part of molybdenum as ammonium molybdate, boron as borax, tungsten as sodium tungstate, or silicon as sodium silicate was added to the nickel nitrate (10 parts) kieselguhr mixture just before the addition of the precipitant.

^d The precipitant was sodium carbonate.

^e Two applications of catalyst were necessary.

^f These figures are for the hydrogenation of toluene at 175°.

^g The rate of hydrogenation was so rapid as to make it necessary to stop the rocking of the bomb in order to avoid an excessive rise in temperature.

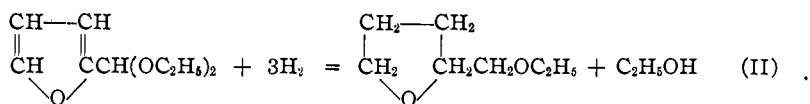
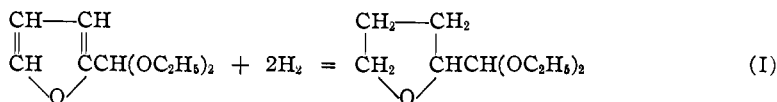
^h The yield of saturated acetal in only one of these hydrogenations was more than a few per cent., and in most of them it was zero. The bicarbonate catalyst containing copper gave a 30% yield of the saturated acetal.

nickel. Against the acetal, molybdenum, barium, manganese, cerium, iron and silicon exerted a promoting effect, while zinc was as deleterious in this hydrogenation as was tungsten for acetone. Cerium distinctly promoted the hydrogenation of toluene.

It is apparent that these so-called promoters are so specific in their action that an element that promotes the hydrogenation of one compound may inhibit that of another. It is further apparent that none of the promoters tested greatly increased the activity of the nickel catalyst.

Competitive Hydrogenations.—The most interesting hydrogenations are those in which there are simultaneous reactions resulting in two or more products both of which are resistant to further hydrogenation under the given conditions. It was previously shown¹ that the ratio of cyclohexylcarbinol to toluene produced by the hydrogenation of benzyl alcohol varied from 1 : 2 to 1 : 9, and the ratio of cyclohexanediol to cyclohexanol produced from resorcinol varied from a ratio of 9 : 1 to 1 : 3, with changes in the method of preparation of the nickel catalyst.

Previous investigators have found that the hydrogenation of acetals over nickel resulted in the cleavage of one oxygen to carbon linkage with the formation of ethers.³ However, it has been found possible to avoid this reaction in considerable part during the hydrogenation of the diethyl acetal of furfural. The ratio of products is, however, dependent upon the purity of the acetal and of the character of the catalyst. The competitive reactions involved are illustrated in equations I and II.



There is also produced resinous material of unknown composition.

There is recorded in Table III a summary of more significant data obtained during the course of an extensive study of the hydrogenation of diethyl furfural acetal. The variations in the proportion of the products for a sodium carbonate catalyst (15), a bicarbonate catalyst (44) and for an ammonium carbonate catalyst (24) are given at the top of the tabulation. It was suspected that the reason that catalyst 15 produced the hydrogenated acetal in a yield of 43% while catalysts 24 gave only 11% was because of the (probable) alkali content of the former. Therefore 0.5 g. of sodium carbonate was added to a sample of the latter catalyst and the mixture tested in the hydrogenation of the acetal. The hydrogenation

³ Sigmund and Marchart, *Monatsh.*, **48**, 267 (1927); Sigmund and Uchann, *ibid.*, **51**, 234 (1929); and Cabanac, *Compt. rend.*, **188**, 1257 (1929).

was very much slower but the yield of saturated acetal was raised to 44%, a yield which is practically identical with the best previous yield with catalyst

TABLE III
HYDROGENATION OF THE ETHYL ACETAL OF FURFURAL

Catalyst G.	No.	Moles acetal	Added material, g.		Moles H ₂	Hrs. at 175°	Ethyl tetrahydrofurfuryl ether ^g	Ethyl tetrahydrofurfural acetal ^h	Residue
4	15 ^a	0.74 ^e	1.84	7.5	18	45	16
4	44 ^b	.3	0.75	0.2	60	5	13
2	24 ^c	.3 ^e93	0.0	61	11	10
2	24 ^c	.3	0.5	Na ₂ CO ₃	.90	4.0	12	44	14
2	24 ^c	.3	.2	Furoic acid	.87	1.5	31	30	14
4	24 ^{c,d}	.3	.1	NaOH	.81	4.0	13	59	13
4	24 ^{c,d}	.7	.2	NaOH	2.28	8.0	6	71	12
2	24 ^c	.3	.01	NaOC ₂ H ₅	0.82	0.05	17	41	9
4	24 ^c	.65	.5	Piperidine	1.95	2.8	5	51	17
3	24 ^c	.3	.5	Cyclohexylamine	0.80	1.8	21	48	14
3	24 ^c	.3	.5	Di- <i>n</i> -amylamine	.76	0.33	14	63	9
3	24 ^c	.3	.5	<i>n</i> -Amylamine	.76	.16	6	74	9
3	24 ^c	.3	.5	α -Methylpiperidine	.79	.25	10	62	9
3	24 ^c	.3	.5	<i>n</i> -Butylamine	.83	.20	5	75	9
3	24 ^c	.3	.5	N-Cyclohexylpiperidine	.76	.15	5	75	9
3	24 ^c	.3	1.0	<i>n</i> -Amylamine	.82	.13	5	75	10
3	24 ^c	.3	0.5	β -Phenylethylamine	.77	.30	4	75	13
3	15 ^a	.3	.5	<i>n</i> -Amylamine	.83	.66	9	63	11
2	44 + Cu ^f	.3	.5	<i>n</i> -Amylamine	.67	.6	4	76	9
2	44 + Ce ^f	.3	.5	<i>n</i> -Amylamine	.67	.1	33	28	9
2	44 + Fe ^f	.3	.5	<i>n</i> -Amylamine	.75	.25	15	58	11

^a Sodium carbonate was added as a precipitant to the nickel nitrate on kieselguhr.

^b Sodium bicarbonate was added as a precipitant to the nickel nitrate on kieselguhr.

^c The nickel nitrate on kieselguhr was added to ammonium carbonate solution as a precipitant.

^d Two applications of catalysts were necessary.

^e These samples of acetal were not of the same lot as used in testing catalysts 24 and 44.

^f These catalysts were prepared as was No. 44, *i. e.*, by the use of NaHCO₃ as a precipitant as in *b* above, and in addition contained the indicated element in the ratio of 1 part of it to approximately 9 parts of nickel.

^g This fraction was taken 47 to 55° (11 mm.). Ethyl tetrahydrofurfuryl ether was reported by Kirner [THIS JOURNAL, 52, 3251 (1930)] to have a boiling point 152–154° (726 mm.).

^h This fraction was taken 76 to 80° (11 mm.). The diethyl acetal of tetrahydrofurfural was reported by Scheibler, Sotscheck and Friese [Ber., 57, 1443 (1924)] to have a boiling range of 187–190°. Bolander and Minne in this Laboratory have found the boiling point of the pure compound to be 194.5°.

15. Sodium hydroxide (0.2 g.) was even more effective in increasing the yield of the acetal, although the rate of hydrogenation was so decreased that it was necessary to open the bomb and add a second sample of catalyst in order to complete the hydrogenation. Unfortunately for the hypothesis that the increased yield of acetal was due to the alkali, it was found that the addition of furoic acid to the reaction mixture had a similar but not so great beneficial effect as the bases.

The most effective reagents for increasing the yield of acetal are the amines. A number of them were tried as indicated in Table III, the most effective being *n*-amyl, *n*-butyl and β -phenylethylamines, and *N*-cyclohexylpiperidine. The addition of 0.5 g. of *n*-amylamine to 50 g. of the acetal made it possible to obtain 75% of the theoretical yield of the saturated acetal. This is to be contrasted with the yield of 11% in the absence of the amine, or of 43% with the sodium carbonate catalyst.

Mr. Nels Minné in this Laboratory has had occasion during recent months to use this process for the preparation of considerable quantities of diethyl tetrahydrofurfural acetal. He has consistently obtained approximately 220 g. of the saturated acetal by hydrogenating 280 g. (1.65 moles) of diethyl furfural acetal, containing 1.0 g. of *n*-amylamine, with 8 g. of an ammonium carbonate type of nickel catalyst in five hours at 200 atmospheres. This represents an actual yield of 76% of the theoretical or 80% if allowance is made for the mechanical losses.

The amines are also effective as shown in the table in increasing the yield of acetal for the sodium carbonate and sodium bicarbonate catalysts and for bicarbonate catalysts containing copper, cerium and iron although in the case of the latter two the yield of acetal was considerably lower than for the other catalysts. It is significant that the amines which are so effective in modifying the ratio of the products accomplish this without any considerable decrease in the *rate* of hydrogenation. As has been repeatedly emphasized in publications from this Laboratory, there is no necessary relationship between the activity of a catalyst and the proportion of the competitive reactions produced over it.

In a similar way the addition of 0.2 g. of *n*-amylamine doubled the yield of cyclohexylcarbinol (see Table IV) formed in the reduction of 25 g. of benzyl alcohol over an ammonium carbonate catalyst. However, no catalyst has been prepared which was more effective in producing cyclohexylcarbinol than are those prepared by the original sodium carbonate method. This is also true for the production of methylphenylcarbinol from acetophenone (Table IV), for which the carbonate type of catalyst was the most effective. Another interesting observation in this connection is that catalyst 8 gave only one-third as much of the carbinol when the catalyst had been reduced at 575° as when it was reduced at 450°.

TABLE IV
HYDROGENATION OF VARIOUS COMPOUNDS

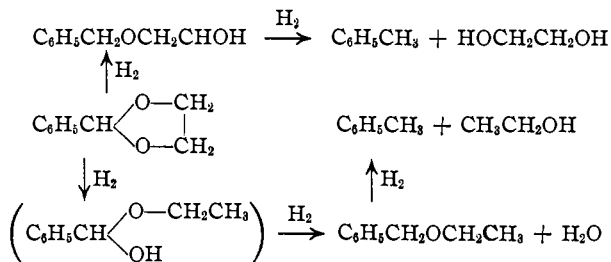
Name	Compound	H ₂ Mole moles,	Time, hrs.	Temp., °C.	Pressure, atm.	Cata- lyst ^a G. No.	Solvent, ml.	%	Products and yields
Benzilidene ether of ethylene glycol (118-20° (22 mm.))		0.29	0.9	6.5	125	2 9	31	Toluene, ethanol and loss ^d
								21	Ethylene glycol and benzyl ethyl ether (96-106°) (24 mm.) ^e
Benzyl ether of ethylene glycol		.1	..	2.0	175	125 2 9	35 Ether	48	Monobenzyl ether of ethylene glycol (132-144°) (22 mm.) ^f
								53	Methylcyclohexane and loss ^d
								25	Ethylene glycol
Benzyl ethyl ether ^f		.31	..	0.5	175	120 3 16	22	Hexahydrobenzyl ether of ethylene glycol (123.5-125.5°) (25 mm.) ^g
								37	Cleavage of the ether to toluene and ethanol. Complete cleavage on reapplication of catalyst
Benzilidene ether of ethylene glycol ^g		.33	..	4.5	175	120 3 24	53	Ethylene glycol
								41	Toluene and methylcyclohexane ^h
								12	Benzyl ethyl ether ^h
								21	β -Hydroxyethyl benzyl ether ^h
Benzilidene ether ethylene glycol		.33	0.84	2.0	175	120 6 ^a 24	86	Glycol
								80	Hydrocarbons ^h
Benzilidene ether of trimethylene glycol ⁱ (137-138) (22 mm.)		.31	1.3	4.5	175	120 3 24	87	Trimethylene glycol
								67	Hydrocarbons ^h
Benzilidene ether of trimethylene glycol and 0.5 g. of <i>n</i> -amylamine		.31	1.3	8.0	175	120 6 ^a 24	10	Ethers ^h
								54	Trimethylene glycol
								56	Hydrocarbons ^h
								34	Ethers ^h
1,2-Benzilidene ether of glycerol		.25	0.70	4.0	175	120 6 ^a 24	80	Glycerol, 70% hydrocarbons ^h , 14% of other products
Dimethylaniline		.83	2.46	5	185	102 3 1	95	Dimethylcyclohexylamine, (50.8-51.5° (15 mm.)), 3.5 g. (53-71° (15 mm.)) 1.5 g. residue
{ Benzyl acetate { Dimethylcyclohexylamine		.33	0.33	5	135	123 3 1	100	Cleavage to toluene and acetic acid
								.37	
Benzalacetone ⁱ		.50	.59	0.03	45-87	122 3 5	57 EtOH	96	Benzyl acetone (130-133 (15 mm.))
Mesityl oxide		.33	.33	1	125	120 2 15	95-100	Methyl isobutyl ketone (114-116° (740 mm.))
Methyl isobutyl ketone (contained the carbinol)		.39	..	3	150	120 2 15	95-100	Methylisobutylcarbinol (130-131° (740 mm.))
Catechol		.22	.68	4	175	120 4 15	30 EtOH	95-100	<i>Cis</i> and <i>trans</i> cyclohexanediol 1,2 (119-122 (10 mm.)) (cryst. from ether, m. p. 71-72°)
Ethyl levulinate ⁱ		.21	..	1.4	100	120 4 15	85	Ethyl γ -hydroxyvalerate (84-85° (3 mm.))
Nitrobenzene		.50	..	1.1	100	120 4 16	50 EtOH	95-100	Aniline (182-186° (740 mm.))
<i>m</i> -Dinitrobenzene		.25	..	1.12	100-110	120 2 15	50 Ether	95-100	<i>m</i> -Diaminobenzene (153-154° (10 mm.))
<i>N</i> -methyl α -pyridone ⁱ		1.24	2.48	1.33	100	120 2 15	95-100	1-Methyl-2-piperidone (97-98° (11 mm.))

TABLE IV (Concluded)

Name	Compound	H ₂ Mole moles.		Time, hrs.	Temp., °C.	Pressure, atm.	Catalyst [†] G. No.		Solvent, ml.	%	Products and yields
<i>o</i> -Hydroxybenzaldehyde		0.20	0.31	1.00	75	120	2	15	57	<i>o</i> -Hydroxybenzyl alcohol (m. p. 85-86° from benzene)
										26	<i>o</i> -Cresol
Ethyl formyl phenoxy acetate [‡]		.04	..	0.1	110	100	2	13	40 EtOH		Ethyl α -phenoxyhydrocrylate (168-170° (10 mm.))
Glucose		.11	..	2.5	150	170	2	17	35 H ₂ O (or ether)	97	Sorbitol
Fructose		.11	..	2.5	150	170	2	17	25 H ₂ O	97	Mannitol (m. p. 127-132°)
Glucose		.11	..	4.0	160	170	1	Cu-Cr	60 95% EtOH	97	Sorbitol
Benzalacetophenone		.36	..	0.1	65	125	3	13	80 EtOH	90-95	Phenyl β -phenylethyl ketone
Ethyl benzoate [‡]		2.09	..	1.0	190-250	200	8	4	95-100	Ethyl hexahydrobenzoate (84-86° (16 mm.))
Acetophenone		0.40	0.77	0.33	175	120	2	16	10	Methylphenylcarbinol
										84	Ethylcyclohexane
Acetophenone		.40	.84	.16	175	120	2	15	30	Methylphenylcarbinol
										65	Ethylcyclohexane
Acetophenone		.40	.86	.40	175	120	2 ^b	8	25	Methylphenylcarbinol
										70	Ethylcyclohexane
Acetophenone		.40	.83	.10	175	120	2 ^c	8	8	Methylphenylcarbinol
										88	Ethylcyclohexane
Benzyl alcohol		.23	.30	.16	125	120	2	24	8	Cyclohexylcarbinol
										88	Toluene
Benzyl alcohol		.23	.30	.40	125	120	2	24	16	Cyclohexylcarbinol
0.2 g. <i>n</i> -Amylamine										78	Toluene
Hydrofurfuramide [‡]											

^a Two applications of 3 g. each of catalyst were necessary for the hydrogenation. ^b The catalyst was reduced 0.75 hr. at 450°. ^c The catalyst was reduced 1.0 hr. at 575°. ^d The loss of the more volatile components was high because of the difficulty of filtering off the catalyst and therefore the yields are not given as percentage of the theoretical yield, but represent the distribution of the weights of the various products. ^e These two compounds were separated on the basis of their solubility in water. A dibenzoate of the glycol was made of m. p. 68-70°, and the ether characterized by its boiling point and its inertness toward the ordinary alcoholic reagents. ^f The benzyl ether of ethylene glycol was characterized by its boiling point (138° (15 mm.)) [Bennett, *J. Chem. Soc.*, 127, 1277 (1925)], and by its urethan from α -naphthyl isocyanate, m. p. 89-90°. ^g The hexahydrobenzyl ether of ethylene glycol gave a urethan with α -naphthol isocyanate, m. p. 57-58.5°. The compound was analyzed by Mr. E. F. Struss. Calcd. for C₉H₁₈O₂: H, 11.39; C, 68.37. Found: H, 11.40; C, 68.40. ^h The benzenoid rings were no doubt partially hydrogenated. ⁱ The losses in these experiments were nominal (5%), as the water-soluble layer was separated from the hydrocarbon layer before filtering. Alcohol was then added to the glycol layer so that the filtration could be expedited and losses minimized. ^j These compounds were hydrogenated in collaboration with Messrs. E. A. Prill, Ralph Thomas, E. F. Struss, C. F. Koelsch, George Pfeiffer or Karl A. Folkers. ^k Ammonium carbonate was used as the precipitant in the preparation of catalysts 23, 24 and 37, sodium bicarbonate was used for catalysts 4, 5, 9, 16, 17 and 44, while the sodium carbonate A method was used for catalysts 1, 8, and 13 and the B method for 15 (see reference 1 for details of these preparations). ^l Hydrofurfuramide upon hydrogenation over nickel behaves similarly to hydrobenzamide in that at 80° it was converted in more than 90% yield to an easily separated equimolecular mixture of mono- and di-tetrahydrofurfuryl amines.

Cyclic Acetals.—In an attempt to protect the carbonyl group during hydrogenation of the benzene nucleus in the presence of nickel, cyclic acetals of benzaldehyde with ethylene glycol, trimethylene glycol and glycerol were prepared. A summary of experimental results obtained in the hydrogenation of these acetals is given in Table IV. In the hydrogenation, cleavage of oxygen to carbon linkages always occurred and no traces of the saturated cyclic acetal could be found. The ease of cleavage of an oxygen linkage on a carbon atom attached to a benzenoid ring has been noted by various investigators.⁴ The course of the hydrogenation of a cyclic acetal (benzilidene ether of ethylene glycol) may be represented as below



The scheme presupposes that the cleavage of oxygen to carbon linkages in the acetal occurs between the oxygen to methylene as well as between the oxygen to methine group. The above scheme accounts for the products obtained at 125°, *i. e.*, toluene, ethylene glycol, benzyl ethyl ether and the monobenzyl ether of ethylene glycol. At 175° these same products were obtained accompanied by the corresponding hexahydro compounds. Ethylene glycol and hydrocarbons were obtained at 175° from the benzyl ether of ethylene glycol. The hydrogenation of the benzilidene ether of trimethylene glycol and of the 1,2-benzilidene ether of glycerol yielded results similar to those obtained from the ether of ethylene glycol except that the hydrogenation proceeded more slowly.

It should be noted that there is a rather important difference between the hydrogenation of the cyclic acetals and that of furfural acetal or benzyl alcohol. In the case of these latter compounds the hydrogenation proceeded smoothly to a definite limit and the proportion of products was determined by the catalyst and not by the duration of the hydrogenation. In the case of the cyclic acetals the proportion of the products appears to be primarily determined by the duration of the hydrogenation and little, if any, by the presence of an amine or by the type of catalyst used for the hydrogenation. If the hydrogenation were allowed to go as long as hydrogen was absorbed, then ethanol, glycol and toluene were the only products. If the reaction were stopped at an earlier stage, then the ether alcohol, and the ether were found among the products.

⁴ Cf. Adkins and Cramer, *THIS JOURNAL*, **52**, 4349 (1930).

Other Hydrogenations.—There is recorded in Table IV a summary of the results obtained in the hydrogenation of a variety of organic compounds. The chief significance, for the present, of these results lies in the establishment of experimental conditions under which these compounds may be hydrogenated in good yield so that it is unnecessary to discuss them in detail. It will suffice to point out a few matters of importance.

In certain hydrogenations acids are produced which attack the nickel. It is desirable to have available a base that may be introduced into the hydrogenation mixture which will neutralize the acid and yet not poison the catalyst as would aniline or sodium hydroxide, for example. Dimethylcyclohexylamine has proven to be such a base. For example, the addition of the tertiary amine to benzyl acetate permitted the complete hydrogenation. Cramer⁴ found that in the absence of the amine the hydrogenation stopped due to the solution of the nickel in acetic acid.

The hydrogenation of benzal acetone, benzalacetophenone and mesityl oxide illustrates the feasibility of converting an unsaturated ketone into a saturated ketone by hydrogenation over nickel if the catalyst is sufficiently active to permit the hydrogenation to be carried out at a low temperature.

The rapid and almost quantitative hydrogenation of nitrobenzene and *m*-dinitrobenzene in alcohol to the corresponding amines indicates the practicability of this process. Without a solvent an immiscible layer was formed and the hydrogenation was unsuccessful. All attempts to produce *m*-nitroaniline from *m*-dinitrobenzene were unsuccessful. It should be noted that the hydrogenation of a nitro group is a very exothermic process so that the rate of hydrogenation must be carefully controlled in order to avoid so rapid a reaction that the temperature becomes excessively high. The rate of hydrogenation is determined by the ratio of catalyst to nitro compound, the temperature and pressure of hydrogen and especially by the rate of shaking of the bomb.⁵

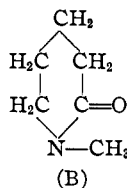
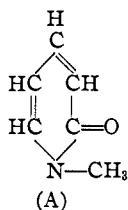
The smooth hydrogenation of the alkene linkage of ethyl formyl phenoxyacetate ($\text{HOCH}=\text{C}(\text{OC}_6\text{H}_5)\text{COOC}_2\text{H}_5$) to ethyl α -phenoxyhydracrylate ($\text{HOCH}_2\text{CH}(\text{OC}_2\text{H}_5)\text{COOC}_2\text{H}_5$) is significant in view of the fact that Koelsch found several other methods to result in failure due to cleavage of the molecule.⁶

The excellent results obtained in the hydrogenation of *N*-methyl- α -pyridone (A), to 1-methyl-2-piperidone (B) are worthy of note in view of the slowness of the hydrogenation of this compound over various platinum catalysts.⁷

⁵ Adkins, *THIS JOURNAL*, **53**, 2808 (1931).

⁶ Koelsch, *ibid.*, **52**, 2435 (1930).

⁷ Ruzicka, *Helv. Chim. Acta*, **4**, 474 (1921); Ruzicka, Seidel and Leiff, *ibid.*, **7**, 1002 (1924); Graves, *THIS JOURNAL*, **46**, 1470 (1924); Prill and McElvain, unpublished work from this Laboratory with Adams' catalyst.



Glucose was successfully hydrogenated in the presence of a nickel or of copper-chromium oxide catalyst in ethanol, ether or water as a reaction media. Fructose could be hydrogenated by the use of nickel but copper-chromium oxide caused decomposition. The temperature of the reaction mixture should be kept below 160° in order to avoid decomposition. The completeness of hydrogenation of glucose to sorbitol was shown by the fact that the $(\alpha)_D^{25}$ for the product ranged from 0.0 to $+1.6$. The mannitol produced from fructose evidently contained a small percentage of sorbitol for the product although crystalline melted at $127-132^{\circ}$ instead of 166° .

Summary

A study of the preparation of nickel catalysts has shown that the amount of nickel held by the support and the proportion of the nickel compounds which are reducible to metallic nickel are a function of the precipitant and procedure of precipitation, as is also the optimum time and temperature for the reduction of the nickel oxides to the active catalyst. On the basis of this and previous investigations a procedure has been recommended which results in easily reproducible and very active nickel catalysts.

The incorporation of several different elements into the nickel catalyst promoted the hydrogenation of toluene, acetone and of the diethyl acetal or furfural. These so-called promoters are so specific in their action that an element that promotes the hydrogenation of one compound may inhibit that of another.

It has been found possible through the addition of various substances, especially of certain amines, to so control the hydrogenation of diethyl furfural acetal as to raise the yield of diethyl tetrahydrofurfural acetal from a few per cent. to 75-80% of the theoretical, there being a corresponding decrease in the yield of ethyl tetrahydrofurfuryl ether. The addition of *n*-amylamine had a similar but smaller effect in increasing the yield of cyclohexylcarbinol from benzyl alcohol.

Three cyclic acetals of benzaldehyde were subjected to hydrogenation under various conditions but in no case was there any evidence for the formation of hexahydrobenzaldehyde or its acetals. The products were hydrocarbons, ethers, hydroxy ethers and glycols.

Suitable experimental conditions have been established for the successful

hydrogenation of a variety of organic compounds as summarized in the paragraphs in "Other Hydrogenations" and in Table IV.

MADISON, WISCONSIN

[CONTRIBUTION FROM METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

ALIPHATIC GERMANIUM DERIVATIVES. II.
DIETHYLDIPHENYLGERMANE, DIETHYLGERMANIUM OXIDE
AND DIETHYLGERMANIUM DIBROMIDE

BY E. A. FLOOD

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I. Introduction

A study of the triphenyl,^{1,2} diphenyl^{1,3} and triethylgermanium⁴ compounds has revealed some interesting contrasts in the chemistries of these little known amphoteric groups. Continuing the study of this class of substances some diethylgermanium derivatives have been isolated and some of their properties determined. It has been found convenient in previous work to use the halide of the group under investigation as the source of subsequent derivatives. Accordingly, the first objective in this research was the preparation and study of diethylgermanium dibromide. The most satisfactory method of preparing this compound involved bromination of triethylgermanium fluoride,⁴ hydrolysis of the product and conversion of the resulting diethylgermanium oxide, after purification, into the corresponding bromide.

Diphenylgermanium dibromide can be prepared by the action of bromine on tetraphenylgermane⁵ and while it might be expected that diethylgermanium dibromide, $(C_2H_5)_2GeBr_2$, could be prepared by the analogous reaction of bromine on tetraethylgermane, this has not been found feasible. All attempts to substitute a second bromine atom for an ethyl group in triethylgermanium bromide by the direct action of bromine gave complex mixtures from which only very low yields of diethylgermanium dibromide could be obtained.

Some preliminary experiments indicated that diethylgermanium dibromide can be prepared by an indirect method starting with diphenylgermanium dibromide. The diphenylgermanium dihalide was treated with ethylmagnesium bromide and the resulting diphenyldiethylgermane on bromination gave impure diethylgermanium dibromide.

¹ Morgan and Drew, *J. Chem. Soc.*, 127, 1760 (1927).

² Kraus and Foster, *THIS JOURNAL*, 49, 457 (1927).

³ Kraus and Brown, *ibid.*, 52, 3690 (1930).

⁴ Kraus and Flood, *ibid.*, 54, 1635 (1932).

⁵ Kraus and Brown, *ibid.*, 52, 3690 (1930). $(C_6H_5)_2GeBr_2$ was obtained by Morgan and Drew¹ from the reaction of $GeBr_4$ with C_6H_5MgBr . Partial ethylation of $GeBr_4$ by C_2H_5MgBr yields $(C_2H_5)_3GeBr$ but little or no $(C_2H_5)_2GeBr_2$.⁴