Most noteworthy, however, is the fact that the results here recorded appear to bear little or no relationship to the results of the sulfuric acid polymerization experiments of Norris and Joubert.

A theory has been developed to explain the results herein recorded, and will be published at a later date. From the present data, however, it may be concluded that the *average* internal double bond is much more prone to autoxidation than is the *average* end double bond. It would, therefore, follow that in diolefins the internal double bond would be the first to be attacked. As a matter of record, the authors have previously reported[7] acrolein as being an important constituent among the products resulting from the autoxidation of cracked gasoline, an observation which is in accord with experiments reported herein.

The present paper is intended by the authors as a report of general work on autoxidation now in progress. It is hoped that further details will be ready for publication in the near future.

D. Summary

1. The autoxidation of the amylenes has been investigated.

2. Results indicate that, in general, internal double bonds are more readily oxidized by molecular oxygen than end double bonds.

3. Kirrmann's method of preparation of pentene-1 has been confirmed. A new hydrocarbon obtained as a by-product of this reaction is mentioned.

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THE USE OF NICKEL AS A CATALYST FOR HYDROGENATION

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The hundreds of papers and patents published on the use of nickel as a catalyst for the hydrogenation of organic compounds might well be considered to render unnecessary any extended research in this field. In spite of this profusion of publications and in a sense because of it, a beginning has been made in what is intended to be a systematic investigation of the use of nickel as a catalyst for the hydrogenation and condensation of organic compounds especially with regard to selective reaction, *i. e.*, the modification of the proportion of simultaneous reactions through control of the temperature, pressure, reaction medium and character of the catalyst. For a number of reasons it does not seem that here or now is a suitable place or time for a comprehensive review of the extensive literature on the use of nickel as a catalyst. It must suffice for the present to refer to some of the more prominent investigators such as Sabatier, Senderens, Mailhe, Ipatiev, Schrotter, Brochet, von Braun, Zelinsky, Armstrong and Hilditch, and to the American and German translations of Sabatier's "La Catalyse en Chimie Organique."[1] The German edition contains a valuable review of the literature, prepared by Dr. Hans Hauber for the period 1920 to 1926.

The use of pressures in the range of 50 to 300 atmospheres is usually referred to as the method of Ipatiev and is the one used in the present investigation.[2] It should be pointed out however that Ipatiev, in general, used temperatures of from 200–400°. These high temperatures with their accompaniment of serious side reactions, were necessary, we believe, because he used rather inactive catalysts. Ipatiev believed that the oxide rather than the metal was the real catalyst for hydrogenations. While this is questioned by Sabatier and many others, there can be no doubt that nickel oxide at the temperatures used by Ipatiev is active in promoting reactions other than hydrogenation.

In this paper are described the preparation of a satisfactory catalyst and experimental conditions under which some forty-five representative organic compounds have been hydrogenated to give good yields of various compounds.

The Apparatus.—The material to be reduced was placed in copper or glass bottles or "liners" having an internal volume of from 100 to 600 ml. Each liner bore a pin-hole in the side half-way between its top and bottom. The effective capacity, *i. e.*, the volume below the pin-hole was thus 50 to 300 ml. The glass liners were closed by a ground-glass joint and the copper ones by a cap screwing down against a lead gasket. The caps of both types of bottle were designed with a tube extending downward to accommodate the thermocouple well projecting from the head of the bomb. The bombs were made of chrome vanadium steel by the American Instrument Company of Washington, D. C., using the type of bomb closure described by Ernst.[3] One of the bombs had outside dimensions of 26.7 cm. long by 14 cm. diameter, and the other 42 cm. by 11.4 cm. The inside diameter was 6 cm. for both bombs, one having a depth of 16.5 cm. and the other of 31.5 cm. Each bomb bore in the head a thermocouple so well designed that the end of a thermocouple could be extended beyond the center of the reaction chamber. The thermocouples were of No. 20 iron–constantan wire encased in 2-holed insulation tubes 4 mm. in outside diameter.

Lead gaskets were used in most instances for the bomb closure. Copper gaskets made of copper wire 3 mm. in diameter were used for pressures above 200 atmospheres. The bomb was placed in a horizontal position in a shaker similar in principle to the one described by Peters and Stanger.[4] The bombs were electrically heated using 110-volt a. c. current and nichrome wire 0.1 mm. in diameter. Two heating units for each bomb

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[1] "Catalysis in Organic Chemistry," by Sabatier and Reid, D. Van Nostrand Company, New York, 1922; "Die Katalyse in der Organischen Chemie," by Sabatier and Finkelstein, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1927.

[2] Ipatiev, *Ber.*, **37**, 2961 (1904); *J. Russ. Phys.-Chem. Soc.*, **36**, 786 (1904); **42**, 1557 (1910); Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Company, New York City, 1922, p. 206.

[3] Ernst, *Ind. Eng. Chem.*, **18**, 664 (1926).

[4] Peters and Stanger, *ibid.*, **20**, 74 (1928).

were used, each having a resistance of about 27 ohms. The temperature was controlled by a Leeds and Northrup potentiometer controller and recorder.

The valves and connections used were similar in design to those described by Ernst and were supplied by the American Instrument Company. The tubing was $^1/_4$-inch O. D. by $^1/_{16}$-inch I. D. of molybdenum steel. The gages were of the ordinary commercial type having ranges from 0 to 5000 or 0 to 10.000 pounds per square inch and were purchased from the United States Gauge Company, New York.

The Catalyst.—The procedure finally adopted for the preparation of a nickel catalyst was a development from that recommended by Reid and Rather.[5] According to their procedure 100 g. of infusorial earth was treated with a solution of 50 g. of nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] in about 150 ml. of water, and the resulting moist mass added to a strong water solution of 60 g. of sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, to precipitate the nickel as carbonate. The product was well washed, dried, reduced with hydrogen just below red heat and cooled in carbon dioxide. This method was modified in the following particulars: (1) the infusorial earth was digested with nitric acid before use because otherwise inactive catalysts were obtained; (2) the ratio of nickel to infusorial earth was doubled; (3) the precipitation of nickel carbonate was made at 70–80° in order to avoid loss of nickel salts during washing; (4) the reduction was carried out at 450° for one hour; (5) the catalyst was cooled and transferred in an atmosphere of hydrogen.

The procedure for the preparation of the catalyst was as follows: one-half kilo of infusorial earth, obtained from the Meyer Drug Company, St. Louis, was digested on the steam-bath for sixteen hours with enough nitric acid (*d* 1.4) to give a suspension of porridge-like consistency. This material, after dilution with an equal volume of water, was filtered on a Büchner funnel and washed repeatedly with distilled water until the wash water gave only a faint acid test. After being thoroughly dried at 110–120° it was pulverized and stored in glass-stoppered bottles.

One hundred grams of acid-washed infusorial earth was treated with a filtered solution of 100 g. of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, in 150-175 ml. of water, and the whole thoroughly mixed. The resulting paste, warmed to 70–80°, was poured into a filtered solution of 120 g. of sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) in 100 ml. of water, which had also been warmed to 70–80°. After thorough mixing with a large stirring rod, the material was filtered on a Büchner funnel and washed, first with 300 ml. of water in 75-ml. portions, taken from the filter, dispersed in 300-400 ml. of water and again sucked dry on a filter and washed with 300 ml. of water. The mixture was dried at 110–120° and stored in dry glass-stoppered bottles. The yield from such a preparation was 134 g. Considering that no nickel was lost in the preparation, this material contained by calculation 16% nickel. The product was reduced in a stream of dry hydrogen at 450°. The hydrogen was ordinary electrolytic hydrogen with no purification other than drying by passing through a calcium chloride tube. The reduction was carried out in a pyrex tube, 15 mm. by 40 cm. in length, heated in a small electric tube furnace. The hydrogen was passed through the catalyst at the rate of 10 to 15 ml. per minute. The temperature of the furnace was maintained at 450 ± 3°.

The tube containing the catalyst was removed from the furnace after reduction had proceeded for one hour, and allowed to cool to room temperature under a pressure of 1.004 atmospheres of hydrogen. The catalyst was then poured from the tube (through which a stream of hydrogen was rapidly passing) into the liner containing the material to be reduced. The air in the liner had been previously displaced with carbon dioxide. The liner was then closed, placed in the bomb, the latter closed and placed in the shaker, the system evacuated to 15 or 20 mm. and hydrogen introduced to the desired pressure. The shaker was then started at a rate of about 40 cycles per minute. There was a drop

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[5] Reid and Rather, THIS JOURNAL, **37**, 2116 (1915).

in pressure during the first few minutes but if the connections were all tight the pressure remained constant after ten minutes of shaking. The bomb was then heated to the desired temperature. About an hour was required for reaching 100° and about two hours for 200°. After the reduction was complete the bomb was allowed to cool to room temperature (eight to twelve hours), the liner removed and the catalyst filtered off under suction on a Jena sintered glass filter.

Standardization of the Apparatus.—The course of the reductions was followed by means of the drop in pressure of hydrogen in the system. The volume of hydrogen equivalent to a given drop in pressure on the gage was a function of the volume of the reaction mixture, of the liner and of the temperature of the gas in the bomb. In order to ascertain the amount of hydrogen equivalent to a given drop in pressure on the gage it was necessary to determine the drop in pressure which occurred when a known quantity of material was reduced. Such compounds as acetone, toluene and dimethylacetoacetic ester reduce quantitatively with no side reactions, so that they were used for the purpose of standardization. By means of various fillers. liners and volumes of reactants the drop in pressure per mole of hydrogen absorbed could be varied from 625 to 3000 pounds per square inch measured at 20°. The gages could be read with an accuracy of ten pounds or less. The loss of hydrogen due to diffusion and leaks was less than thirty pounds in the great majority of the experiments. That is to say, if the original pressure was 2000 pounds at 20° and the bomb was then heated to 200°, kept there for perhaps six hours and cooled to 20°, the pressure would be at least 1970 pounds, and in many cases would be 1990 or higher. It is safe to say then that in a successful experiment the drop in pressure of hydrogen was accurate to within considerably less than fifty pounds.

The temperature to be used for the reduction of a compound was usually decided upon as a result of observation of the increase in pressure in the system as the temperature of the bomb increased. If no reduction had occurred at a given temperature, the pressure would be within twenty or thirty pounds of that predicted by the gas laws. The beginning of reduction would be evidenced by an increasing divergence between the actual pressure and the calculated pressure for that temperature. There is no doubt that the pressures used are in numerous cases considerably above those necessary for satisfactory results. The relationship of pressure to the rate of reduction varies materially with different types of compounds and this matter will be considered in subsequent papers.

Solvents.—Solvents have been used by workers in this Laboratory to a greater extent than has been done by others using nickel catalysts. It therefore seems worth while to point out the merits of a few of the common solvents. Ether may be used up to 197° if the pressure is above forty atmospheres and methanol to 240° if the pressure is above eighty atmospheres. The other common solvents may be used to even higher temperatures with similar pressures, so that in so far as the boiling point of the solvent is concerned, there is no limitation on the practical use of any of the common solvents up to approximately 200°. The use of a solvent greatly facilitates the handling of the reaction mixture both during the introduction of the catalyst and in filtering it off after the reduction is complete.

The amount of hydrogen absorbed may be readily and accurately calculated from the drop in pressure in the system if the volume of reaction mixture is constant in a series of experiments. This may be most satisfactorily done by using a solvent for making the various mixtures up to constant volume. A solvent is sometimes advantageous for maintaining the homogeneity of the reaction mixture. For example, the reduction of diphenyl carbinol practically stopped with the formation of diphenylmethane because the water formed in the reduction of the alcohol formed an immiscible layer holding the catalyst out of contact with the diphenyl methane. In the presence of alcohol the reduction proceeded smoothly to dicyclohexylmethane. Conversely, it may be desirable to use as a solvent a compound which will give a non-homogeneous mixture with the reaction products and thus prevent its further reduction.

Alcohol was the solvent most commonly used in this investigation, but it apparently cannot be used with amines above perhaps 165° because it reacts with them to form secondary or tertiary amines. Methylcyclohexane has proved itself to be an excellent solvent. It is inert and has a good boiling point (100°) for easy separation from the reaction products. Ether proved itself of value in that butyl cyanide reduced more rapidly and gave a higher ratio of primary amines to secondary amine when ether was used than in the absence of a solvent. This was even more marked in the case of isonitrosopropiophenone, which reduced faster at 85° in an ether solution than at 125° in methylcyclohexane. The formation of condensation products was much less in ether, but it is not certain whether this was due to the specific influence of ether or to the lower temperature at which it was possible to carry out the reduction. The effect of alcohol in increasing the yield of β-hydroxyethyl butyrate from acetoacetic ester by 50% will be considered in another paper. Water has not been extensively used as a solvent in this work but it did not materially reduce the rate of reduction when it was used with acetone.

There is recorded in the table a summary of the experimental conditions and results obtained in the reduction of a group of representative organic compounds. The fifty experiments whose results are reported have been selected as representative out of a group of approximately 200 experiments devoted to the study of the reduction of these forty-five compounds. There is given in order the number of the experiment according to our laboratory record, the name of the compound reduced, the amount of material (expressed in moles) placed in the reaction vessel, the moles of hydrogen absorbed, the weight and number of the catalyst according to our laboratory records, the volume and kind of solvent, if any, the temperature at which the reaction was carried out, the range of pressure in atmospheres during the reduction, the approximate time required for the absorption of the hydrogen, the name and yield of product(s) expressed in percentages of the theoretical and the observed physical constants as compared with those given in the literature. The yields were calculated in three ways and the method of calculation used in any particular case is indicated by prefixing the letters A, B or C to the figure giving the percentage yield. "A" shows the yield of the compound actually obtained, "B" gives the percentage of the theoretical yield obtained after making an allowance for the mechanical losses. In calculating "C" allowance was made for mechanical losses and also for that part (if any) of the original compound in the reaction mixture which had not been reduced. In almost every case it would be easy materially to increase the "A" yields by using larger quantities of materials and refinements in working up the products. In our opinion the value for the moles of hydrogen absorbed is a better index, in the great majority of cases, of the quantitativeness of the reduction than is the yield given under "A."

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS

			H_2 abs.,	Catalyst		Solvent		Temp.,	Press. range,	Time,	Products			Boiling point		Literature Boiling points	
Expt.	Compound	Moles	moles	g.	No.		ml.	°C.	atm.	hours	Yield, %		Compound	°C.	mm.	°C.	mm.
187	Acetone	1.0	1.0	2	12	....	...	125	165–15	1.5	A88	B100	Propanol-2	......	...	......	...
10	Pinacolone	0.40	0.38	2	1	....	...	100	127–13	8	A85	C100	Methyl *tert.*-butyl carbinol	115–118	740	117–121^{a}	...
175	Acetylbenzoylmethane	.06	.20	2	11	EtOH	50	100	165–15	0.5	A95	...	1-Phenylbutanediol-1,3	167–169	13	162–164^{b}	13
162	Acetophenone	.20	..	2	11	EtOH	50	175	160–10	8	...	C60	Methyl phenyl carbinol	202–203	742	203.6^{c}	740
231	Ethyl phenyl ketone	.19	..	2	12	EtOH	50	125	170–20	1–2	A85	B100	Phenyl ethyl carbinol	213–215	740	212^{d}	...
170	Diacetone alcohol	1.0	1.0	3	11	....	...	150	175–25	2	A93	B100	2-Methylpentanediol-2,4	110–112 195–196	22 740	190–194^{e}	740
154	Salicylaldehyde	0.46	0.48	2	9	....	...	100	160–10	1–2	A41	...	o-Hydroxybenzyl alcohol	84 (m. p.)		86 (m. p.)^{f}	...
103	Cyclopentanone	.50	.49	2	7	....	...	100	130–30	6	A91	B100	Cyclopentanol	137–137.5	...	139^{g}	...
45	Cinnamic aldehyde	.40	.76	2	6	....	...	100	92–22	...	A63	...	3-Phenylpropanol-1	118–124	12	120^{h}	12
46	Cinnamic aldehyde	.40	.46	2	6	....	...	100	105–15	1	A53	...	3-Phenylpropanal-1	102–106	12	100–105^{i}	12
44	Benzaldehyde	.50	.45	2	6	....	...	100	110–10	0.4	A70	...	Benzyl alcohol	......	...	......	...
204	Benzophenone	.10	.11	1	12	EtOH	35	125	160–10	1	A87	...	Diphenyl carbinol	65 (m. p.)	...	65.5–68^{j} (m. p.)	...
84	Benzoin	.25	.40	2	6	EtOH	50	125	162–13	1	A90	...	1,2-Diphenyl-ethanediol-1,2	136–136.5 (m. p.)	...	138^{k} 134 ^{l} (m. p.)	...
80	Benzil	.10	.30	2	6	EtOH	65	125	160–10	1	A90	...	1,2-Diphenyl-ethanediol-1,2	......	...	......	...
70	Diphenyl carbinol	.17	.20	2	6	....	...	200	180–30	3	A80	B92	Diphenylmethane	......	...	......	...
41	Benzyl alcohol	.48	.52	2	6	....	...	175	75–25	0.5	A75	B95	Toluene	......	...	......	...
180	Benzyl alcohol	.50	.87	2	11	....	...	125	150–25	2	A64	...	Toluene	......	...	......	...
											A23	...	Cyclohexyl carbinol	179–180	740	181^{m}	755
63	Benzyl acetate	.33	.36	2	6	....	...	125	175–25	6	...	C100	Toluene	......	...	......	...
131	Trimethylene cyanide	.25	1.05	2	9	Methylcyclohexane	50	150	100–10	3	A33	...	Piperidine	105–106	...	......	...
213	Butyl cyanide	.50	0.98	2	12	....	...	110	100–20	3	A45	B50	*n*-Pentylamine	102–104	740	103–104^{n}	...
											A35	B40	Di-*n*-pentylamine	202–203	...	187°; 95–97°	12
217	Butyl cyanide	.50	1.02	2	12	Ether	35	105	175–15	...	A45	B61	*n*-Pentylamine	......	...	......	...
											A30	...	Di-*n*-pentylamine	......	...	......	...
200	o-Tolyl cyanide	.35	0.68	2	12	C_7H_{14}	40	125	160–10	1.5	A69	...	o-Methylbenzylamine	203–204; 102–105	740 20	199.5^{p}	...
256	Phthalimide	.25	.52	2	12	C_7H_{14}	60	200	200–50	4–5	A76	B80	Phthalimidine	151–151.5 (m. p.)	...	150^{q} (m. p.)	...
													Phthalimidine picrate	148 (m. p.)	...	140^{q} (m. p.)	...
													Nitrosophthalimidine	159 (m. p.)	...	156^{q} (m. p.)	...
235	Isonitrosopropiophenone	.025	.08	1	12	Ether	45	85	100–10	1.5	A55	...	1-Phenyl-2-aminopropanol-1	101 (m. p.)	...	103^{r} (m. p.)	...
													1-Phenyl-2-aminopropanol-1·HCl	189–191 (m. p.)	...	191^{r} (m. p.)	...
152	Benzene	.66	..	2	9	....	...	135	160–10	0.1	A85	B100	Cyclohexane	......	...	......	...
145	Toluene	3.0	..	2	9	....	...	175	175–25	0.3	A96	B100	Methylcyclohexane	99–100	740	100.1^{s}	...
164	Ethylbenzene	0.60	1.83	2	11	....	...	175	180–30	1	A93	B100	Ethylcyclohexane	131	740	130^{s}	...
166	Butylbenzene	.10	..	2	11	....	...	150	155–15	0.1	...	B100	Butylcyclohexane	178	740	176–177^{t}	760

TABLE I (*Concluded*)

			H_2	Catalyst		Solvent		Temp.,	Press.	Time,	Products			Boiling point		Literature Boiling points	
Expt.	Compound	Moles	abs., moles	g.	No.		ml.	°C.	range, atm.	hours	Yield, %		Compound	°C.	mm.	°C.	mm.
227	Diphenyl	0.17	..	2	12	EtOH	60	200	200–40	..	A95	...	Dicyclohexyl	118–120	20	234–236[u]	745
																240–241[v]	...
220	Diphenyl ether	.17	1.20	2	12	....	...	150	160–50	3–4	A42	...	Dicyclohexyl ether	238–239	740	239–240[w]	...
140	Phenol	.50	1.51	2	9	....	...	150	200–50	...	A88	B100	Cyclohexanol[x]	......	...	......	...
122	Hydroquinone	.33	1.10	2	7	EtOH	50	150	170–30	4–6	A88	...	*Cis*-cyclohexanediol-1,4	101–102 (m. p.)	...	102[y] (m. p.)	...
68	2-Phenylethanol	.32	1.09	2	6	....	...	200	155–45	5–6	A66	B75	2-Cyclohexylethanol-1	205–206	740	206–207[z]	740
167	Benzophenone	.20	1.70	2	11	EtOH	100	175	210–60	6	A90	B100	Dicyclohexylmethane	250–251	740	251.5[aa]	760
72	Diphenylmethane	.09	0.58	2	6	EtOH	50	150	175–25	6–7	A83	B91	Dicyclohexylmethane	......	...	......	...
40	Ethyl benzoate	.35	.73	2	6	....	...	150	80–20	7–8	A52	C100	Ethyl hexahydrobenzoate	97–100	22	196.6[bb]	...
														198–200	745	......	...
147	Aniline	1.00	3.07	5	9	C_7H_{14}	100	175	205–55	9	A71	C90	Cyclohexylamine	133.5	740	134[cc]	...
88	Aniline	0.25	0.71	2	7	EtOH	50	200	250–90	...	A91	C95	Ethylcyclohexylamine	162–165	745	164[dd]	...
118	Acetanilide	.25	..	2	7	EtOH	50	175	180–30	6–7	A75	C100	Acetylcyclohexylamine	106–107 (m. p.)	...	107[ee] (m. p.)	...
238	β-Naphthylamine	.14	.20	2	12	C_7H_{14}	35	140	180–20	5	A71	...	*Aci*-tetrahydro-β-naphthylamine	143–147	15	......	...
														158–162	36	162[ff]	36
75	Pyrrole	.75	1.18	2	6	....	...	200	190–40	5–6	A37	C52	Pyrrolidine	88–89	740	87.5–88.5[gg]	...
82	Pyrrole	.50	0.93	2	6	EtOH	50	200	190–40	6–8	A43	...	Pyrrolidine	......	...	......	...
203	Diphenylamine	.17	1.02	2	12	C_7H_{14}	60	175	200–20	3	A73	B95	Dicyclohexylamine	144–145	30	145[cc]	30
														250–252	740	250[cc]	750
205	Quinoline	.20	1.03	2	12	....	...	175	175–15	6–8	A95	...	*Cis-trans*-decahydroquinoline	204–206	...	......	...
98	Quinoline	.40	0.72	2	7	....	...	150	160–10	1–4	A88	C96	Tetrahydroquinoline	122–124	10	244–246[hh]	725
														244–245	745	250–255[ii]	...
74	Pyridine	.50	1.45	2	6	....	...	200	175–25	9–11	A80	...	Piperidine	105–106	...	......	...
58	α-Methylpyridine	.50	1.41	2	6	....	...	175	190–30	8–10	A82	B100	α-Methylpiperidine	116–118	...	118–119[jj]	...
144	β-Methylpyridine	.33	..	2	9	C_7H_{14}	25	175	190–40	9–11	A88	...	β-Methylpiperidine	123–127	...	124–126[kk]	...
100	α-Pyridylphenylethylene	.11	0.40	2	7	EtOH	50	150	165–15	...	A82	...	α-(Phenylethyl)-piperidine[ll]	......	...	......	...
188	γ-Pyridylphenylethylene	.11	.47	2	11	EtOH	50	165	175–25	8	A92	...	γ-(Phenylethyl)-piperidine[ll]	......	...	......	...
241	α-Benzylpyridine	.31	1.03	2	12	EtOH	30	160	190–30	7	A85	...	α-Benzylpiperidine[ll]	......	...	......	...

[a] Delacre, *Bull. soc. chim.*, [4] **1**, 455 (1907). [b] Franke and Kohn, *Monatsh.*, **27**, 1115 (1906). [c] Klages and Allendorff, *Ber.*, **31**, 1003 (1898). [d] Wagner, *J. Russ. Phys.-Chem. Soc.*, **16**, 332 (1884). [e] Franke, *Monatsh.*, **27**, 1067 (1902). [f] Lederer, *J. prakt. Chem.*, [2] **50**, 225 (1894). [g] Wislicenus and Hentzschel, *Ann.*, **275**, 322 (1893). [h] Bouveault and Blanc, *Chem. Zentr.*, **II**, 1701 (1905). [i] Bouveault, *Bull. soc. chim.*, [3] **31**, 1332 (1904). [j] Linnemann, *Ann.*, **133**, 9 (1865). [k] Paal, *Ber.*, **16**, 637 (1883). [l] Wislicenus and Blank, *Ann.*, **248**, 5 (1888). [m] Sabatier and Mailhe, *Compt. rend.*, **139**, 343 (1904). [n] Hoffman, *Ber.*, **15**, 770 (1882). [o] Custer, *ibid.*, **12**, 1328 (1879); Rupe, Metzger and Vogler, *Helv. Chim. Acta*, **8**, 848 (1925). [p] Krober, *Ber.*, **23**, 1026 (1890). [q] Graebe, *ibid.*, **17**, 2598 (1884); *Ann.*, **247**, 29 (1888). [r] Hartung and Munch, THIS JOURNAL, **51**, 2262 (1929). [s] Sabatier and Senderens, *Compt. rend.*, **132**, 1255 (1901). [t] Faillebin, *Ann. chim.*, **4**, 421 (1925). [u] Sabatier and Murat, *Compt. rend.*, **154**, 1390 (1912); Borsche and Lange, *Ber.*, **38**, 2769 (1905). [v] Ipatiev, *ibid.*, **40**, 1287 (1907). [w] Schrouth and Wegc, *ibid.*, **57**, 858 (1924). [x] *Cf.* Brochet, *Bull. soc. chim.*, [4] **31**, 1270 (1922). [y] Willstätter, *Ber.*, **34**, 507 (1901). [z] Zelinsky, *ibid.*, **41**, 2628 (1908). [aa] Eijkman, *Chem. Weekblad*, **1**, 7 (1903). [bb] Lumsden, *J. Chem. Soc.*, **87**, 92 (1905). [cc] Sabatier and Senderens, *Compt. rend.*, **138**, 457(1904). [dd] Sabatier and Senderens, *ibid.*, **138**, 1257 (1904). [ee] Skita and co-workers, *Ber.*, **53**, 1242 (1920). [ff] Bamberger and Müller, *ibid.*, **21**, 850 (1888). [gg] Gabriel, *ibid.*, **24**, 3231 (1891). [hh] Hoffmann and Königs, *ibid.*, **16**, 728 (1883). [ii] Ipatiev, *ibid.*, **41**, 992 (1908). [jj] Ladenberg, *Ann.*, **247**, 62 (1888). [kk] Hesekiel and Ladenberg, *ibid.*, **247**, 67 (1888). [ll] Bailey and McElvain, THIS JOURNAL, **52**, 1633 (1930).

The significance, for the present, of the results obtained in the reduction of the majority of the compounds dealt with in this paper lies in the establishment of experimental conditions under which these reductions may be carried out satisfactorily. For this reason and because of the need of economy in the use of space in THIS JOURNAL nothing will be added in most cases to the simple statement of experimental results given above. It should be pointed out, however, that the low yields in the case of the reduction of salicylaldehyde and isonitrosopropiophenone were due to mechanical losses, and in the case of acetophenone to the fact that it contained chlorine which necessitated a higher temperature for reduction with a resultant increase in side reactions. In the case of toluene and benzene the reduction was so rapid that the temperature of the mixture rose 100° above that at which the reduction was being carried out. Two hundred liters (N. T. P.) of hydrogen was absorbed by three moles of toluene within fifteen minutes, by far the larger part being taken up within five minutes.

Cinnamic aldehyde was reduced both to the corresponding saturated aldehyde and to 3-phenylpropanol at 100° by modifying the time of reaction. Von Braun and Kochendorfer, using an undescribed commercial nickel catalyst, obtained large yields of compounds resulting from the condensation of two moles of the aldehyde.[6]

Phthalimide was reduced in a good yield to phthalimidine, the hydrogen absorption being very close to the theoretical. The benzenoid ring was very resistant to reduction, as only small amounts of hexahydropthalimidine were obtained with the nickel catalyst although Willstätter and Jacquet[7] were able to reduce the ring using platinum as a catalyst. Succinimide and succinamide could not be reduced at 200°.

The hydroxyl group of alcohols is, in general, quite resistant to catalytic reduction but if the hydroxyl group is on a carbon atom to which is attached a benzenoid ring, its replacement by hydrogen takes place at 125° or lower. This is shown by the reduction of benzyl alcohol, diphenylcarbinol, triphenylcarbinol and *sym.*-diphenylethylene glycol to the corresponding hydrocarbons. If the hydroxyl group was in the beta position with respect to the ring, the rate of its reduction was retarded very greatly. This same ease of replacement of oxygen by hydrogen when the oxygen is alpha to an unsaturated ring is also met with in the ready reduction of benzyl acetate to toluene and acetic acid and in the rupture of the ether linkage in diphenyl ether when the latter is reduced at 150°. Benzyl alcohol is reduced almost exclusively to toluene at 175° but at 125° the hydrogen is distributed almost equally between alcohol and ring reduction. However, since three moles of hydrogen are required to reduce the ring and only one to reduce the alcohol, the yield of cyclohexylcarbinol is only about one-third that

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[6] Von Braun and Kochendorfer, *Ber.*, **56B**, 2172 (1923).

[7] Willstätter and Jacquet, *ibid.*, **51**, 767 (1918).

of toluene under the optimum conditions so far discovered. The hydrogenation of the nucleus of aromatic alcohols without the elimination of the hydroxy group has not previously been accomplished.[8] Diphenyl ether reduced readily but the hydrogen absorption was high, due to rupture of the ether linkage, the ratio of straight reduction to reduction with splitting being approximately 2:3. The dicyclohexyl ether obtained boiled at 238–239° as reported by Schrauth and Wege[9] and not at 275–277° as given by Ipatiev.[10]

Aniline absorbed hydrogen more slowly than did the other benzenoid compounds studied. The absorption of hydrogen was almost, if not quite, the theoretical three-mole equivalents, but small amounts of aniline were always found in the reaction mixture. The rate of reduction was rather rapid at first but quickly decreased. Dicyclohexylamine was formed in the ratio of one part of the secondary amine to nine parts of the primary. The actual yield of cyclohexylamine was considerably lowered due to its being carried over with the methylcyclohexane used as a solvent. When alcohol was used as a solvent an excellent yield of ethylcyclohexylamine was obtained. Trimethylene cyanide and butyl cyanide took up the theoretical quantity of hydrogen but a secondary amine was formed to a considerable amount in each case. In fact piperidine was the only product isolated from the reduction of trimethylene cyanide.

The pyridinoid ring in quinoline was rapidly reduced at temperatures from about 125° upward. The tetrahydroquinoline was obtained in practically quantitative yields. The benzenoid ring requires a considerably higher temperature for its reduction but the absorption of hydrogen was that calculated for complete reduction. The product in all experiments had the correct boiling range of 204–206° but in the earlier experiments the product remained a liquid at 0° but on retreatment with nickel and hydrogen it would absorb no additional hydrogen. Bamberger and Lengfeld assign a melting point of 48.2–48.5° to decahydroquinoline while Skita and Meyer give 48° and Ipatiev 45.5°. Ipatiev gives a boiling point of 207–210° while the other authors report 204°. Bamberger and Lengfeld report a melting point of 275.5–276° for the hydrochloride. Later, 77 g. of quinoline was reduced and 71 g. of product obtained boiling at 204–206°. On cooling to 0°, 42 g. of crystals melting 48–49° was obtained. This is the *trans* isomer. The hydrochloride melted at 278–279°. The liquid has been identified by Mr. C. F. Bailey as the isomeric *cis* decahydroquinoline described by Hückel and Stepf,[11] who give an excellent bibliography on the isomeric decahydroquinolines.

[8] Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Company, New York, 1922, p. 168.

[9] Schrauth and Wege, *Ber.*, **57B**, 859 (1924).

[10] Ipatiev, *ibid.*, **41**, 100 (1908).

[11] Hückel and Stepf, *Ann.*, **453**, 167 (1927). Bailey and McElvain, THIS JOURNAL, **52**, 4015 (1930).

Nickel has been considered to be inferior to platinum as a catalyst for hydrogenation because, in general, nickel is not active as a catalyst at room temperature. This characteristic has its advantages, however, as it permits selective reduction between two reducible groups through control of temperature of hydrogenation. Such selective reduction was achieved at 125° with acetylbenzoylmethane, phenyl ethyl ketone, benzoin, benzil, benzophenone, isonitrosopropiophenone, benzyl cyanide and *o*-methyl phenyl cyanide when the carbonyl, oxime or cyanide group was reduced without affecting the benzenoid ring. At 175 to 200° complete reduction of these compounds occurred. By a similar temperature control it was found possible to reduce the pyridinoid ring in quinoline, α-pyridylphenylethylene, γ-pyridylphenylethylene and α-benzylpyridine without reducing the benzenoid ring.

Summary

The preparation of a reasonably active nickel catalyst has been described and experimental details are given for the satisfactory reduction of forty-five representative organic compounds. The results have been summarized and need not be repeated here. In general, it may be said that an apparatus and technique have been used which have made it possible to determine rather accurately the amount of hydrogen absorbed and the rate of the reduction. This has made it feasible readily to carry on selective reduction of one of two reducible structures through the control of the temperature or time interval of the reduction. The merits of methylcyclohexane, alcohol and ether as solvents during reduction have been discussed.

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[Contribution from the Laboratory of the University of Buffalo]

THE KETO-ENOL EQUILIBRIUM OF ETHYL ALPHA-PHENYL ACETOACETATE

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The keto-enol equilibrium of ethyl acetoacetate and its derivatives has already received considerable attention, most of the data published being concerned with the unsubstituted ester or its alkyl derivatives. The effect of substituents in the α-position, especially phenyl, has not been extensively investigated as far as the keto-enol equilibrium of the compounds is concerned. It was our purpose to prepare ethyl α-phenyl acetoacetate and to study its keto-enol equilibrium by means of bromine titration as well as its index of refraction.

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[1] Presented to the Committee on Graduate Study of the University of Buffalo by the second author in partial fulfilment of the requirements for the degree of Master of Arts.