[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Specificity of Nickel Catalysts. Effect of Organic Additives upon the Reductive Dehydroxymethylation and Dehydroxylation of Primary Alcohols

BY HERMAN PINES, MUTHU SHAMAIENGAR AND W. S. POSTL

RECEIVED APRIL 20, 1955

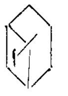
It was reported previously that nickel–kieselguhr, Raney nickel or precipitated nickel catalyzed the reductive dehydroxymethylation of saturated primary alcohols. The reaction proceeded according to the equation: $RCH_2OH + 2H_2 \rightarrow RH + CH_4 + H_2O$. It was found subsequently that another reaction occurred, mainly reductive dehydroxylation, when small amounts of sulfur-containing compounds, such as thiophene, dimethyl disulfide, dibenzyl sulfoxide, etc., were added to the alcohol. The reaction proceeded as: $RCH_2OH + H_2 \rightarrow RCH_3 + H_2O$. The hydrogenolysis of 2-cyclohexylethanol and 3-cyclohexylpropanol in the prescence of thiophene produced methyl- and ethylcyclohexane, respectively. In the case of 3,3-dimethylbutanol (I) and 1-methyl-1-hydroxymethylcyclohexane (II) the reductive dehydroxylation was accompanied by a skeletal isomerization. Alcohol I formed 2,2- and 2,3-dimethylbutane, while alcohol II yielded ethylcyclohexane, methylcycloheptane and 1,2-dimethylcyclohexane. The presence of chloroform also caused the reductive dehydroxylation to occur. It is suggested that a nickel catalyst possesses inherent acid properties and that the sulfur compounds, through their ability to poison the active contact sites of a nickel catalyst, accentuate the acid properties of the catalyst. In conformity with the above views it was found that in the presence of pyridine and thiophene both reductive dehydroxymethylation and dehydroxylation reactions are inhibited.

Introduction

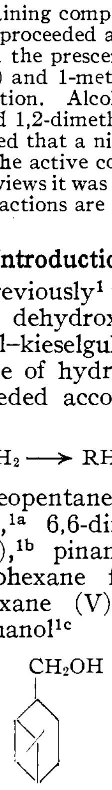
It was reported previously[1] that primary alcohols undergo reductive dehydroxymethylation when treated with nickel–kieselguhr catalyst at 150–250° in the presence of hydrogen under pressure. The reaction proceeded according to the general formula

$$RCH_2OH + 2H_2 \longrightarrow RH + CH_4 + H_2O$$

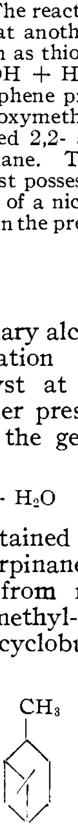
Good yields of neopentane were obtained from 3,3-dimethylbutanol,[1a] 6,6-dimethylnorpinane (I) from myrtanol (II),[1b] pinane (III) from nopol (IV),[1c] methylcyclohexane from 1-methyl-1-hydroxymethylcyclohexane (V)[1d] and cyclobutane from cyclobutylmethanol[1c]



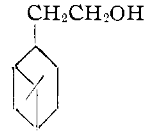
I



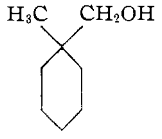
II



III



IV

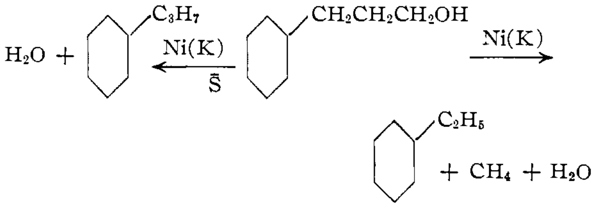


V

The reductive dehydroxymethylation was proved to be not only a valuable tool for the synthesis of hydrocarbons, but it also was applied as an indirect method for the degradation of acids when the latter were reduced to the corresponding alcohols.[2]

3-Phenyl- and 3-Cyclohexylpropanol. Effect of Thiophene.—The original purpose of the present investigation was to extend the reductive dehydroxymethylation method to primary aromatic alcohols. 3-Phenylpropanol was used as a model compound, since the phenyl group in the γ-position in respect to the hydroxyl group is not supposed to have an influence upon the latter.[3] Nickel–kieselguhr as such could not be employed for this reaction, since under the experimental conditions used for the dehydroxymethylation, the hydrogenation of the aromatic ring occurs. In order to prevent the reduction of the aromatic ring, small amounts of thiophene were added to 3-phenylpropanol in order to deactivate partially the nickel catalyst. The hydrogenation was carried out in the usual manner, which consisted of treating the alcohol in a rotating autoclave at about 250–300° in the presence of nickel–kieselguhr catalyst and 100 atmospheres of initial hydrogen pressure. The product obtained from the hydrogenolysis was not the expected ethylbenzene, but *n*-propylbenzene, which was produced by the reductive dehydroxylation of 3-phenylpropanol.

In order to determine whether the reductive dehydroxylation reaction was specific to aromatic hydrocarbons or whether the thiophene added to the carbinol was responsible for this reaction, experiments were made using 3-cyclohexylpropanol as the starting material. It was found that in the absence of thiophene, nickel–kieselguhr catalyzed the dehydroxymethylation of 3-cyclohexylpropanol which resulted in the formation of ethylcyclohexane. When small amounts of thiophene were added to the carbinol, reductive dehydroxylation occurred and the product consisted of *n*-propylcyclohexane.



The reductive dehydroxylation takes place at a higher temperature than reductive dehydroxymethylation.

The reductive dehydroxylation occurred also when 3-cyclohexylethanol was hydrogenolyzed in the presence of thiophene; ethylcyclohexane was

---

(1) (a) V. N. Ipatieff, W. W. Thompson and H. Pines, THIS JOURNAL, **73**, 553 (1951); (b) V. N. Ipatieff, G. Czajkowski and H. Pines, *ibid.*, **73**, 4098 (1951); (c) H. Pines, H. G. Rodenberg and V. N. Ipatieff, *ibid.*, **75**, 6065 (1953); (d) H. Pines, H. G. Rodenberg and V. N. Ipatieff, *ibid.*, **76**, 771 (1954).

(2) (a) V. N. Ipatieff, J. E. Germain, W. W. Thompson and H. Pines, *J. Org. Chem.*, **17**, 272 (1952); (b) V. N. Ipatieff, W. D. Huntsman and H. Pines, THIS JOURNAL, **75**, 6222 (1953).

(3) K. Folkers and H. Adkins, *ibid.*, **54**, 1145 (1932).

TABLE I

REDUCTIVE DEHYDROXYLATION AND DEHYDROXYMETHYLATION OF 2-CYCLOHEXYLETHANOL AND 3-CYCLOHEXYLPROPANOL

The experiments were made in a rotating autoclave of a 450-ml. capacity. About 32 ± 2 g. of carbinol and 3.2 ± 0.2 g. of catalyst were used in each experiment. About 0.8 g. of thiophene, when used, was added to the carbinol. The initial pressure of hydrogen was 100 atmospheres, and the duration of the experiments was 3 hours.

Experiment	1	2	3	4	5	6	7	8	9	10
Alcohol	2-Cyclohexylethanol ←		→ 3-Cyclohexylpropanol							
Thiophene, used	No	Yes	No	No	Yes	Yes	No	Yes	No	Yes
Catalyst[a]	← Ni (K) →						Ni	Ni	Ni (R)	Ni (R)
Temp., °C.	330	330	225	250	250	300	250	300	267	300
Conversion, %	93	100	12	100	10	95	32	78	100	67
Compn. of reacn. prod., wt. %										
Methylcyclohexane	100									
Ethylcyclohexane		100	100	100			100		100	
Propylcyclohexane					100	100		100		100

[a] Ni (K), nickel–kieselguhr; Ni, precipitated nickel; Ni (R), Raney nickel.

produced. In the absence of thiophene methylcyclohexane was formed.

Precipitated nickel or Raney nickel yielded results similar to that of nickel–kieselguhr catalyst (Table I).

Effect of Additives.—The effect of additives used in the hydrogenolysis reactions of 3-cyclohexylpropanol is summarized in Table II. The concentration of the sulfur compounds added to the carbinol amounted to 0.3–1%, based on the weight of the sulfur content. It was found that in the presence of dimethyl disulfide, dibenzyl sulfoxide, thiophene and camphorsulfonic acid only reductive dehydroxylation took place. In the presence, however, of dibutyl sulfone the reaction product consisted of 48% ethyl- and 52% *n*-propylcyclohexane.

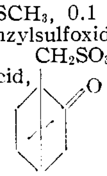
TABLE II

EFFECT OF ADDITIVES UPON THE HYDROGENOLYSIS OF 3-CYCLOHEXYLPROPANOL

The experiments were made in a 450 ml. capacity rotating autoclave at 300° for 3 hours and at an initial hydrogen pressure of 100 atmospheres. In each experiment 31–34 g. of 3-cyclohexylpropanol and 3–4 g. of nickel-kieselguhr were used.

Experiment	11	12	13	14	15	16	17	18
Additive, kind	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
Concentration[i]	0.3	0.9	0.9	1.0	1.5[j]			
Conversion, %	89	95		98	91	100	2	<2
Compn. of reacn. prod., mole %								
Ethylcyclohexane	0	52	0	1	0	100	..	..
Propylcyclohexane	100	48	100	99	100	0	..	..

[a] Dimethyldisulfide, CH_3SSCH_3, 0.1 g. [b] Butylsulfone, $(n\text{-}C_4H_9)_2SO_2$, 1.6 g. [c] Benzylsulfoxide, $(C_6H_5CH_2)_2SO$, 2.2 g. [d] Camphorsulfonic acid, CH_2SO_3H,



2.3 g. [e] Chloroform, 0.5 g. [f] Pyridine, 1 g. [g] Pyridine, 1 g., and thiophene, 0.8 g. [h] Aniline, 1 g., and thiophene, 0.8 g. [i] Calculated on the basis of weight per cent. of sulfur added to the carbinol. [j] Weight per cent. of chloroform based on cyclohexylpropanol used.

Chloroform seems to exert an effect similar to that of thiophene; in its presence reductive dehydroxylation of 3-cyclohexylpropanol occurred.

Pyridine does not seem to affect the reductive dehydroxymethylation reaction. If, however, pyridine and thiophene are added to 3-cyclohexylpropanol, the hydrogenolysis reaction is inhibited and almost all the carbinol is recovered unchanged (expt. 16 and 17). Aniline and thiophene likewise inhibit the hydrogenolysis of the carbinol (expt. 18).

It was found that as little as 0.6% of thiophene based on the weight of 3-cyclohexylpropanol used was sufficient to cause a complete reductive dehydroxylation of the carbinol. In the presence of 0.3% of thiophene both reactions occurred, the dehydroxylation was, however, the main reaction (Table III).

TABLE III

EFFECT OF THE CONCENTRATION OF THIOPHENE UPON THE HYDROGENOLYSIS OF 3-CYCLOHEXYLPROPANOL

The experimental conditions and the amounts of reagents used were the same as those described in Table II.

Experiment	19	20	21	22[a]
Thiophene, wt. %	1.2	0.6	0.3	..
Conversion, %	89	93	95	97
Compn. of reacn. prod., mole %				
Ethylcyclohexane	0	0	18	72
n-Propylcyclohexane	100	100	82	28

[a] The experiment was made immediately preceding experiment 18. The autoclave was used previously for experiments in which sulfur-containing additives were present.

In the study of the effect of additives upon the dehydroxylation reaction it is important that the autoclave be free of any sulfur contamination. It was found that the hydrogenolysis of 3-cyclohexylpropanol in the absence of thiophene, but made in an autoclave previously used for reactions in which sulfur-containing compounds were present, yielded a mixture of hydrocarbons consisting of 75% ethyl- and 25% *n*-propylcyclohexane.

The hydrogenolysis of alcohols can be used as a sensitive method for determining the chemical state of an autoclave.

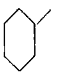
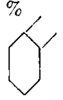
3,3-Dimethylbutanol and 1-Methyl-1-hydroxymethylcyclohexane.—In order to determine whether the reductive dehydroxylation reaction proceeds by a direct hydrogenolysis of the hydroxy group or whether it involves an ionic intermediate 3,3-dimethylbutanol and 1-methyl-1-hydroxymethylcyclohexane were chosen as model compounds (Table IV).

It was found that the hydrogenolysis of 3,3-dimethylbutanol containing small amounts of thiophene involved reductive dehydroxylation.

TABLE IV

REDUCTIVE DEHYDROXYMETHYLATION OF 1-METHYL-1-HYDROXYMETHYLCYCLOHEXANE AND OF 3,3-DIMETHYLBUTANOL

The experiments were made under conditions similar to those described in Table II. In each experiment 32 ± 2 g. of carbinol, 3.2 g. of catalyst and 0.6 g. of thiophene were used.

				Compn. of reacn. prod., wt. %			
Expt.	Catalyst	Alcohol	Conversion, %				
23	Ni (K)	[a]	88		61	16	23
24	Ni	[a]	84		68	13	9
25	Ni (R)	[a]	84	5	44	5	46
26	Ni (K)	[b]	97[c]				

[a] 1-Methyl-1-hydroxymethylcyclohexane. [b] 3,3-Dimethylbutanol. [c] Composition of the hydrocarbons: 2,3-dimethylbutane, 40%; 2,2-dimethylbutane, 55%.

The product of the reaction was composed of 55% 2,2- and 40% 2,3-dimethylbutane. The formation of the latter compound indicates that at least part of the reductive dehydroxylation reaction must proceed through an ionic intermediate. In the absence of thiophene, neopentane was the only product formed.[1a]

1-Methyl-1-hydroxymethylcyclohexane containing small amounts of thiophene underwent reductive dehydroxylation in the presence of nickel catalysts. The hydrogenolysis was accompanied by skeletal isomerization and the product obtained was composed of ethylcyclohexane, methylcycloheptane and 1,3-dimethylcyclohexane. 1,1-Dimethylcyclohexane was not detected among the products of reaction, which indicates that a direct hydrogenolysis of the hydroxy group does not occur. In the absence of thiophene only methylcyclohexane was formed.[1e]

The results which are summarized in Table IV indicate that the reductive hydrogenolysis is an ionic reaction, and that the products are those expected on the basis of carbonium ion mechanism. It is believed that the formation of 1,2-dimethyl- and ethylcyclohexane proceeds through a ring contraction of methylcycloheptylcarbonium ion. It is, however, not excluded that ethylcyclohexane also may be formed through a migration of a methyl group in the originally produced (1-methylcyclohexyl)-methylcarbonium ion.

Interpretation of the Results.—It was shown above that the behavior of a nickel catalyst toward the hydrogenolysis of primary alcohols can be changed drastically when small amounts of sulfur-containing compounds are present. In the absence of the latter reductive dehydroxymethylation occurs and in the presence of sulfur compounds reductive dehydroxylation takes place. It was further shown that the reductive dehydroxylation reaction proceeds *via* an acid-type mechanism and it is very probable that a dehydration of the alcohol is the intermediate step in this reaction. When the dehydration cannot occur directly as in the case of 1-methyl-1-hydroxymethylcyclohexane, a skeletal rearrangement accompanies the hydrogenolysis reaction. All of the above facts indicate that the sulfur-containing compounds contribute to or accentuate the acid character of the nickel catalyst.

It was observed previously[4,5] that nickel–kieselguhr, Raney nickel or even precipitated nickel have an acid character, which under favorable experimental conditions, or by the use of hydrocarbons sensitive to the action of acids, may cause skeletal isomerization to occur. It was found that the hydrogenolysis of pinane was accompanied by a skeletal isomerization.[4] The reaction product contained a large amount of alkylcyclopentanes admixed with some bicyclic dihydroterpenes. It likewise was found that cyclohexene, 4-methylcyclohexene and *p*-menthene at hydrogen pressures of 2–10 atmospheres underwent a similar type of hydroisomerization, in which alkylcyclopentanes were produced.

It can be concluded, therefore, that nickel catalyst may act both as an acid and as a contact hydrogenation catalyst. As an acid catalyst it may either be able to dissociate a hydrogen molecule into a hydride and a proton or act toward the primary alcohols either as a Lowry–Brönsted[6] or a Lewis[7] acid. The ability of an acid catalyst to act as a hydrogenation catalyst has been demonstrated in the case of aluminum chloride catalyzed isomerization of saturated hydrocarbons.[8]

Sulfur-containing compounds through their ability to poison the active contact sites of a nickel catalyst seem to accentuate the acid properties of the nickel catalysts. For that probable reason the presence of small amounts of thiophene causes the nickel to act as a reductive dehydroxylation rather than a dehydroxymethylation catalyst.

It was reported that the toxicity of sulfur compounds toward nickel was due to the sulfur and that it was dependent on the presence in the valency shell of the sulfur of free electron pairs which are necessary for the formation of the link with the catalyst.[9] In agreement with the above it was observed that dibutyl sulfone was not as good an inhibitor for the dehydroxymethylation of 3-cyclohexylpropanol as were thiophene, dimethyl disulfide or dibenzyl sulfoxide.

Many of the catalytic reactions described in the literature where nickel "contaminated" with small amounts of sulfur compounds was used, can be explained also by the assumed acid character of the catalyst brought out by the interaction of the contacting sites of the nickel with sulfur. Thus the isomerization of unconjugated double bonds in linoleate to conjugated double bonds is favored by the presence of small amounts of sulfur on the nickel. Likewise, in the hydrogenation of fatty acids in the presence of a nickel catalyst containing

---

[4] V. N. Ipatieff, F. J. Pavlik and H. Pines, THIS JOURNAL, **75**, 3179 (1953).

[5] H. Pines, A. Rudin, G. M. Bô and V. N. Ipatieff, *ibid.*, **76**, 2740 (1954).

[6] T. M. Lowry, *Chemistry and Industry*, **42**, 43 (1923); J. N. Brönsted, *Rec. trav. chim.*, **42**, 718 (1923); *Chem. Revs.*, **5**, 231 (1928).

[7] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1923, p. 141; *J. Franklin Inst.*, **226**, 293 (1938).

[8] For references to the original literature see H. Pines, "Isomerization of Alkanes," Advances in Catalysis, Volume I, Academic Press, Inc., New York, 1948, pages 201–256.

[9] For general review of the literature see E. R. Maxted, "The Poisoning of Metallic Catalysts," in Advances in Catalysis, Volume III, Academic Press, Inc., New York, N. Y., 1951, pages 129–177.

only traces of nickel sulfide, an isomerization takes place and the product contains isoöleates (elaidates). In the absence of sulfur elaidinization does not take place.[10]

In conformity with the above hypothesis it was found that pyridine, which is a base, did not inhibit the reductive dehydroxymethylation of 3-cyclohexylpropanol using nickel–kieselguhr as a catalyst (expt. 16). If, however, thiophene and pyridine or thiophene and aniline are added together to 3-cyclohexylpropanol the nickel–kieselguhr catalyst becomes deactivated and the alcohol is recovered unchanged (expt. 17). This is not surprising since it was shown that thiophene deactivates the contact sites of the hydrogenation catalyst, and pyridine or aniline, being a strong base, deactivates the acid part of the catalyst. The combination of the two types of additives, therefore, deactivates the catalyst both for reductive dehydroxylation and dehydroxymethylation.

The effect of chloroform upon the hydrogenolysis of 3-cyclohexylpropanol can be interpreted also in the same manner as the effect of sulfur compounds. It had been reported that carbon tetrachloride or chloroform causes a partial deactivation of the hydrogenation properties of a nickel catalyst.[11,12]

Experimental

Materials. 2-Cyclohexylethanol and 3-cyclohexylpropropanol were prepared from the respective aromatic alcohols by catalytic hydrogenation in the presence of a nickel–kieselguhr catalyst at 150° and under 120 atmospheres of initial hydrogen pressure.

3,3-Dimethylbutanol and 1-methyl-1-hydroxymethylcyclohexane were prepared according to the methods described previously.[1a,d]

Catalysts.—The preparations of precipitated nickel, Raney nickel and the source of nickel–kieselguhr were reported previously.[4]

Analytical Procedure.—The liquid product obtained from the reaction was distilled in a Piros–Glover spinning band column,[13] and the various fractions were analyzed by means of infrared spectroscopy.

The infrared spectrogram of methylcycloheptane was furnished us by Dr. H. L. Dryden, Jr., the other spectra of the hydrocarbons are reported by the American Petroleum Institute Project 44.

The gaseous products from the reactions were analyzed in a few instances by means of mass spectroscopy by Dr. D. Mason, of the Chemical Engineering Department. Whenever reductive dehydroxylation occurred, the gas consisted of hydrogen only. When dehydroxymethylation took place both hydrogen and methane were found in the gaseous product.

EVANSTON, ILLINOIS

---

(10) For the survey of the literature see W. J. Kirkpatrick, "Nickel Sulfide Catalysts" in "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, pp. 329–339.

(11) R. Cornubert and J. Phélisse, *Bull. soc. chim.*, **19**, 403 (1952).

(12) R. Cornubert and M. Réal, *ibid.*, **19**, 407 (1952).

(13) Manufactured by H. S. Martin and Co., Evanston, Ill.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

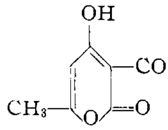
2-Pyrones. XV. Substituted 3-Cinnamoyl-4-hydroxy-6-methyl-2-pyrones from Dehydroacetic Acid

BY RICHARD H. WILEY, C. H. JARBOE AND H. G. ELLERT

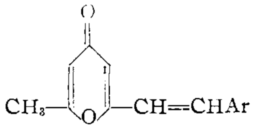
RECEIVED APRIL 13, 1955

The base-catalyzed condensation of dehydroacetic acid with fifteen aromatic aldehydes has been shown to give substituted 3-cinnamoyl-4-hydroxy-6-methyl-2-pyrones (I). The ultraviolet absorption characteristics of all of these products, some of which are unusually fluorescent, and the rearrangement of four of them to substituted 2-styryl-6-methyl-4-pyrones (II) are described. The available data are consistent with the 4-hydroxy-2-pyrone structure previously assigned to another product.

2-Pyrone structures resembling the chalcones have so far been unavailable for characterization and further study. One such chalcone-like structure is presented in the 3-cinnamoyl-4-hydroxy-2-pyrones (I) which are theoretically available by aldol condensations of aromatic aldehydes with the methyl ketone group of dehydroacetic acid. The possibility that such a reaction product could be obtained apparently was first recognized by Hale[1] who attempted the aqueous sodium hydroxide catalyzed condensation of benzaldehyde with dehydroacetic acid. He obtained a compound, m.p. 105°, to which he assigned the structure 3-cinnamoyl-4-hydroxy-2-pyrone (I, Ar = phenyl) on the basis of a satisfactory ultimate analysis. The product was said to decompose on heating to give dehydroacetic acid. This fact is difficult, if not impossible, to reconcile with the assigned structure. We wish to present data in this paper describing a different type of product, obtained from this reaction, whose structure has been established more adequately as that given in formula I.



I



II

The use of aqueous sodium hydroxide as a catalyst for the condensation of aromatic aldehydes with dehydroacetic acid does not appear to be promising. It is known that strong bases decompose dehydroacetic acid to acetone and carbon dioxide.[2] However, on the basis of Hale's prior reported successful condensation of benzaldehyde, several aldehydes—veratraldehyde, 3,4-diethoxybenzaldehyde, *p*-dimethylaminobenzaldehyde and 3,4-dichlorobenzaldehyde—were used in aqueous alkali-catalyzed condensations. The products obtained from

---

(1) N. J. Hale, THIS JOURNAL, **33**, 1119 (1911).

(2) W. H. Perkin and C. Bernhart, *Ber.*, **17**, 1522 (1884).