with dilute acetic acid. The pyrazolone separated as a sticky solid, crystallizing on standing; yield 18.2 g. (85.5%); recrystallized from alcohol, m. p. 173–173.5° (cor.).

Anal. Calcd. for $C_{10}H_8ON_2Cl_2$: N, 11.52. Found: N, 11.8.

If the Johnson[2] procedure is used for reaction of diketene and 2,5-dichlorophenylhydrazine, only little of the 5-pyrazolone is obtained, the main reaction product being the 2,5-dichlorophenylhydrazone of acetoacetic 2,5-dichlorophenylhydrazide. A solution of 4.2 g. (0.05 mole) of diketene in 25 cc. of benzene was dropped into a boiling solution of 8.8 g. (0.05 mole) of the hydrazine in 100 cc. of benzene; 60 cc. of benzene was distilled off. On cooling, 7.3 g. (69.4%) of the hydrazide crystallized (m. p. 188–189°) and the mother liquor gave on evaporation 1.5 g. (14.2% only) of impure 1-(2′,5′-dichlorophenyl)-3-methyl-5-pyrazolone (m. p. 161–163°).

Coupling Reactions of 1-Phenyl-5-methyl-3-pyrazolone (V).—In parallel experiments diazotized 2,5-diethoxy-4-benzoylamino-aniline was coupled on V and also on the isomeric 1-phenyl-3-methyl-5-pyrazolone (II) which is a very popular coupling component for azo dyestuffs. The pyrazolones were dissolved in dilute aqueous soda ash solution, V requiring more (3.5 mole) sodium carbonate than II (2.5 moles). The diazo solution was added at 5° and the alkalinity was adjusted to a faint test on Brilliant Yellow paper by adding sodium carbonate solution. II coupled very rapidly, precipitating bright, red crystals, m. p. 254.5–255.0° (cor.); yield 94%.

Anal. Calcd. for $C_{27}H_{27}O_4N_5$: C, 66.79; H, 5.61; N, 14.43. Found: C, 67.1; H, 5.70; N, 14.6.

The 3-pyrazolone (V) coupled much more slowly than did II and after thirty minutes a strong positive test for unreacted diazo was obtained with alkaline R Salt. Further addition of sodium carbonate to give a strong, alkaline test on Brilliant Yellow paper resulted in a more rapid disappearance of the R Salt test. This was negative after fifteen minutes, indicating complete reaction. The precipitated dye was filtered and dried; yield 4.0 g. (87.5%); recrystallized from alcohol as light brown crystals, m. p. 236.0–236.8° (cor.).

Anal. Calcd. for $C_{27}H_{27}O_4N_5$: C, 66.79; H, 5.61; N, 14.43. Found: C, 66.5; H, 5.60; N, 14.5.

A few other diazo components of commercial interest were diazotized and coupled on V; in all cases V coupled considerably slower than II.

Summary

1. At low temperature diketene and arylhydrazines give arylhydrazones of acetoacetic arylhydrazides in good yield. These seem to undergo a reversible thermal dissociation into aryl hydrazine and diketene-arylhydrazone which forms a 1-aryl-3-methyl-5-pyrazolone by internal ring closure. The latter reaction is enhanced if the arylhydrazine is removed from the equilibrium by the aid of diketene or by an undissociated acid.
2. If, on the other hand, the arylhydrazones of acetoacetic arylhydrazides are heated with strong, aqueous mineral acids, the hydrazone linkage is apparently hydrolyzed and the resulting acetoacetic arylhydrazide forms readily a 1-aryl-5-methyl-3-pyrazolone by internal ring closure. Heating with concentrated hydrochloric acid constitutes an excellent method for preparing these pyrazolones. The phenyl, the 2′,5′-dichlorophenyl, the 4′-nitrophenyl, and the 1′-naphthyl derivatives are dealt with.
3. The 1-aryl-5-methyl-3-pyrazolones couple with diazo compounds, but slower than the isomeric 1-aryl-3-methyl-5-pyrazolones.
4. A tautomeric diketene formula is briefly discussed.

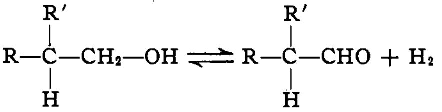
Received June 28, 1944

[Contribution from the Frick Chemical Laboratory of Princeton University]

Mechanism of Catalytic Hydrogenation and Dehydrogenation of Aldehydes and Alcohols

By Elmer J. Badin[1] and Eugene Pacsu

Previous mechanisms for catalytic hydrogenation of carbonyl groups and catalytic dehydrogenation of alcohols. have usually pictured the carbonyl group itself and the hydrogens on the functional group as being involved. Since it appears to be a general phenomenon that the methylene group in a position *alpha* to a functional group contains reactive hydrogens, it seemed quite probable that carbon atom 2 should figure in the reaction. In order to determine whether the second carbon or an "enol" mechanism were involved, an optically active alcohol and the corresponding optically active aldehyde with asymmetry on carbon atom 2 were prepared and the reaction studied in the liquid phase and in the vapor phase



$$R-\overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-OH \rightleftharpoons R-\overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{C}}-CHO + H_2$$

using nickel catalysts. Optically active compounds were selected as tracer compounds because any mechanism involving an activated state which would destroy the tetrahedral configuration would necessarily result in racemization and, further, exchange reactions such as are present in the deuterium hydrogenation–dehydrogenation equilibrium would not have to be considered.[1a]

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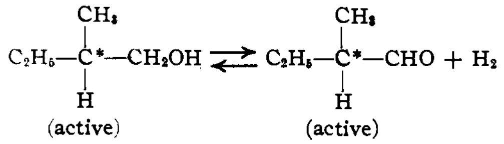
(1) This paper is based upon a thesis submitted by Elmer J. Badin to the Faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(1a) An initial investigation regarding the mechanism was carried out by preparing a deutero alcohol in which the hydroxyl hydrogen was replaced by deuterium. This alcohol was prepared by shaking decanol-1 in a shaking mechanism with D_2O and the uptake of deuterium determined mass spectrographically. The deutero alcohol, after drying and distillation, was dehydrogenated in the liquid phase

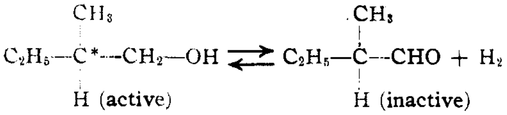
On the basis of his experiments on catalytic dehydrogenation of a series of alcohols on a copper surface, Constable[2] arrived at the conclusion that the alcohol molecules are so oriented on the catalyst surface that the polar end of the molecule is adsorbed at an active center on the surface leaving the hydrocarbon chain perpendicular to the surface. This conclusion, however, does not preclude an enol-type mechanism. By studying the reactions of acetone and isopropyl alcohol with deuterium–hydrogen, Farkas and Farkas[3] have concluded that the keto-enol equilibrium does not appear to be involved in the mechanism of propane formation from acetone at temperatures below −10°. Above 0° considerable exchange of deuterium was observed to take place on the alpha carbon. These results are interpreted by them as three separate reactions: hydrogenation of acetone to propane, hydrogenation of acetone to isopropyl alcohol, and exchange of the hydrogens of the methyl group of acetone. Some direct evidence for the mechanism of hydrogenation of carbonyl compounds was obtained by Anderson and MacNaughton[4] from the catalytic reduction of certain aldehydes and ketones with a hydrogen–deuterium mixture and comparison of the Raman spectra of the reduced products and of the oxidized products. They found that at low temperatures reduction occurred through addition of hydrogen to the carbonyl group while at higher temperatures reduction occurred through addition of hydrogen to the carbon–carbon double bond of the enol form. Deuterium exchange also took place in these reactions.

The compounds chosen for the present investigation were (−)2-methylbutanol-1 and the aldehyde, (+)2-methylbutanal-1, obtained by oxidation of this alcohol. Two obvious possibilities for the dehydrogenation of the alcohol exist. (1) An optically active product indicating retention of configuration.



$$C_2H_5-\underset{\underset{(\text{active})}{H}}{\overset{CH_3}{C^*}}-CH_2OH \rightleftarrows C_2H_5-\underset{\underset{(\text{active})}{H}}{\overset{CH_3}{C^*}}-CHO + H_2$$

(2) An optically inactive product indicating racemization.



$$C_2H_5-\underset{\underset{H\ (\text{active})}{\vdots}}{\overset{CH_3}{C^*}}-CH_2-OH \rightleftarrows C_2H_5-\underset{\underset{H\ (\text{inactive})}{|}}{\overset{CH_3}{C}}-CHO + H_2$$

Hydrogenation could be postulated by analogous reactions. In the first case retention of the configuration would imply that an enol-type molecule is not an intermediate since it is generally accepted that asymmetry is destroyed only when the asymmetric carbon is doubly bound to another element. In the second case racemization would be produced as a result of participation of the second carbon in the reaction. Experimentally, it was found that under mild temperature conditions an active product was obtained and with increasing temperature and in the vapor phase an increasingly racemized product was formed. Furthermore, by hydrogenating the active aldehyde, consistent results were obtained. It was concluded that at low temperatures carbon atom 2 was not necessarily involved but that at higher temperatures carbon atom 2 was involved. These results have led to the formulation of (1) an ionic mechanism similar to acid catalysis in solution, (2) an ionic mechanism similar to base catalysis, and (3) the conventional atomic mechanism for the reaction. This will be discussed in some detail later.

Experimental

Materials.—The optically active alcohol was prepared by systematic fractionation of refined fusel oil ([α]D −1.40°) through a twelve theoretical plate column. After eight fractionations, an alcohol having b. p. 128–129°, [α]D −5.42°, d^{25}_4 0.8186 was obtained. Based on an optical rotation [α]D −6.0° for pure (−)2-methylbutanol-1,[5,6] the alcohol used contained 90.3% (−)2-methylbutanol-1 and 9.7% 3-methylbutanol-1. This small percentage of inactive alcohol present could not conceivably affect the conclusions drawn from the experiment.

The optically active aldehyde, (+)2-methylbutanal-1, with b. p. 90–92°, [α]D +28.50°, d^{25}_4 0.8055 was prepared by oxidation of the above alcohol ([α]D −5.42°) with sodium dichromate.[7] In addition to these two materials, an aldehyde having [α]D +17.73°, d^{20}_4 0.8060 corresponding approximately to 59.2% (−)2-methylbutanal-1 and 40.8% 3-methylbutanal-1 was used in the hydrogenation experiments.

Aldehyde Determination.—The amount of aldehyde formed was determined by precipitating it quantitatively as the 2,4-dinitrophenylhydrazone from aqueous 3 *M* hydrochloric acid solution containing 0.5% of 2,4-dinitrophenylhydrazine. It was not feasible to isolate the pure aldehyde and, since small quantities were used, the optical rotation of the 2,4-dinitrophenylhydrazone in acetone solution was measured and the rotation of the aldehyde calculated by direct proportion from the deter-

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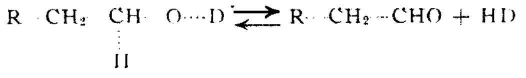
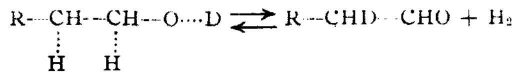
with Raney nickel. Samples of the gas evolved were taken at intervals and analyzed for their deuterium content. A different curve of HD evolution *versus* time was expected depending on which mechanism had been involved.

(1) Carbonyl mechanism.



$$R-CH_2-\underset{\underset{H}{\vdots}}{CH}-O\cdots D \rightleftarrows R-CH_2-CHO + HD$$

(2) Enol mechanism.



$$R-\underset{\underset{H}{\vdots}}{CH}-\underset{\underset{H}{\vdots}}{CH}-O\cdots D \rightleftarrows R-CHD-CHO + H_2$$

Actually a curve was obtained which, on extrapolation to zero time, yielded zero deuterium evolution indicating that mechanism (2) would apply. However, the results were inconclusive since they were liable to the objection that there was a considerable amount of hydrogen originally present on the catalyst surface which could conceivably account for the initially large amount of hydrogen evolution. The ready exchange of deuterium with hydrogen was also considered to be a complicating factor.

(2) Constable, *Proc. Roy. Soc.* (London), **108**, 355–377 (1925).

(3) Farkas and Farkas, THIS JOURNAL, **61**, 1336–1341 (1939).

(4) Anderson and MacNaughton, *ibid.*, **64**, 1456–1459 (1942).

(5) Ehrlich, *Ber.*, **40**, 2556 (1907).

(6) Whitmore and Olewine, THIS JOURNAL, **60**, 2569–2570 (1938).

(7) Details of this preparation will appear in a later publication.

mined rotation, $[\alpha]_D$ +29.5° (acetone solution), of the 2,4-dinitrophenylhydrazone of the aldehyde. The specific rotations of the aldehyde determined by this indirect method were concluded to be within ±0.60° although on a homogeneous sample the rotations were within ±0.02°.

Vapor Phase Apparatus.—A nickel catalyst on kieselguhr prepared from nickel nitrate, sodium carbonate and kieselguhr by the method of Fischer and Meyer[8] was used. After drying at 110° and screening (8–10 mesh), 25 g. was placed in a down flow apparatus consisting of a 25 mm. o. d. Pyrex tube 65 cm. long. The catalyst was placed in the lower portion of the tube, the top portion serving as a preheater for the alcohol vapor. A thermocouple in the center of the catalyst bed recorded the temperature and a buret at the top of the apparatus was used to introduce the charge at a rate timed by a stop watch. The tube was electrically heated and asbestos jacketed. Immediately preceding a run the catalyst was reduced with hydrogen for two hours at a rate of 10 liters of hydrogen per hour and at a temperature of 425°. The temperature was then lowered to the temperature of the run. A water condenser, ice-cooled receiver, and carbon dioxide–acetone trap were used to collect the products. This apparatus and type of catalyst were used for the vapor phase experiments.

Hydrogenation.—An experiment was carried out by hydrogenating 7.0 g. of (+)2-methylbutanal-1 ($[\alpha]_D$ +17.73°) in an Aminco superpressure apparatus using 70 ml. of 95% ethanol as solvent and 4 g. of Raney nickel as catalyst. An initial hydrogen pressure of 1475 pounds was used and the reaction mixture was gradually heated over a period of two and one-half hours to 145–150°, where the temperature was maintained for one hour. Complete reduction resulted and 5.5 g. of alcohol having b. p. 128–129° and $[\alpha]_D$ −3.12° was obtained by fractionation of the product through a five-plate semi-micro column. Since the aldehyde was prepared from alcohol having $[\alpha]_D$ −3.55°, the amount of racemic alcohol present was calculated to be 12%.

Further experiments were carried out in the vapor phase using the same aldehyde. The aldehyde (9.66 g.) was passed over freshly reduced nickel kieselguhr catalyst at 155° with a hydrogen rate of 200 ml. per minute, the addition rate of the aldehyde being 0.37 g. per minute. The catalyzate weighing 8.0 g. had $[\alpha]_D$ −2.29°. Fractionation yielded 5.5 g. of alcohol with b. p. 128–129° and $[\alpha]_D$ −2.53°. Calculation gave the percentage of racemic alcohol present as 28.8%. Hydrogenation at 200° using identical quantities and rates yielded alcohol having $[\alpha]_D$ −0.56° corresponding to 84.2% racemic alcohol while hydrogenation at 250° yielded an alcohol with $[\alpha]_D$ 0.0° corresponding to 100% racemization. At the higher temperatures considerable loss of aldehyde occurred due to deformylation of the aldehyde. The results of these experiments are presented in Fig. 1.

Liquid Phase Dehydrogenation.—Twenty grams of (−)2-methylbutanol-1 ($[\alpha]_D$ −5.42°) was dehydrogenated by refluxing with 2.0 g. of Raney nickel for two and one-half hours at 128°. After removal of the catalyst by filtration, the liquid had $[\alpha]_D$ −4.98°. A 13.10-g. sample reacted with 2,4-dinitrophenylhydrazine in 3 *N* hydrochloric acid solution. The dried 2,4-dinitrophenylhydrazone weighed 0.290 g., corresponding to an aldehyde content of 0.8%. The optical rotation of this hydrazone was $[\alpha]_D$ +30.2° (acetone, *C* 4.07, 1-dm. tube) corresponding to an aldehyde with $[\alpha]_D$ +28.2°. *Anal.* Calcd. for $C_{11}H_{14}N_4O_4$: N, 21.03. Found: N, 20.84.

Vapor Phase Dehydrogenation.—Four grams of (−)2-methylbutanol-1 ($[\alpha]_D$ −5.42°) was dehydrogenated by passing over 25 g. of freshly reduced catalyst as in the hydrogenation runs except that no hydrogen but that present on the catalyst was used. The rate of alcohol addition was 1.23 g. per minute and the temperature was 190°. The rotation of the catalyzate was $[\alpha]_D$ −1.22°. A 0.3365-g. sample yielded 0.1057 g. of the 2,4-dinitrophenylhydrazone, indicating a yield of 10.2% aldehyde. The unrecrystallized dried 2,4-dinitrophenylhydrazone had $[\alpha]_D$ +3.4° (acetone, *C* 4.63, 1-dm. tube) corresponding to an aldehyde of $[\alpha]_D$ +3.3°.

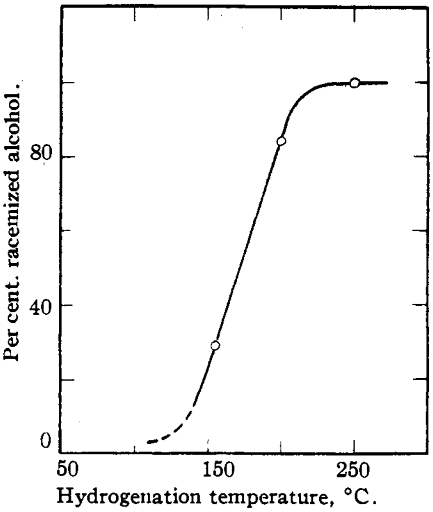


Fig. 1.—Hydrogenation of (+)2-methylbutanal-1, vapor phase.

Repetition of the experiment with a rate of 0.55 g. per minute gave a catalyzate having $[\alpha]_D$ −0.98° and 8.6% aldehyde the 2,4-dinitrophenylhydrazone of which had $[\alpha]_D$ +2.0° (acetone, *C* 4.99, 1-dm. tube); with a rate of 0.28 g. per minute the catalyzate obtained had $[\alpha]_D$ −0.85° and 7.0% aldehyde with the corresponding 2,4-dinitrophenylhydrazone having $[\alpha]_D$ +1.4° (acetone, *C* 5.05, 1-dm. tube). The decrease of aldehyde with increase of contact time was due to deformylation or decomposition of some of the aldehyde formed. These results are presented in Fig. 2.

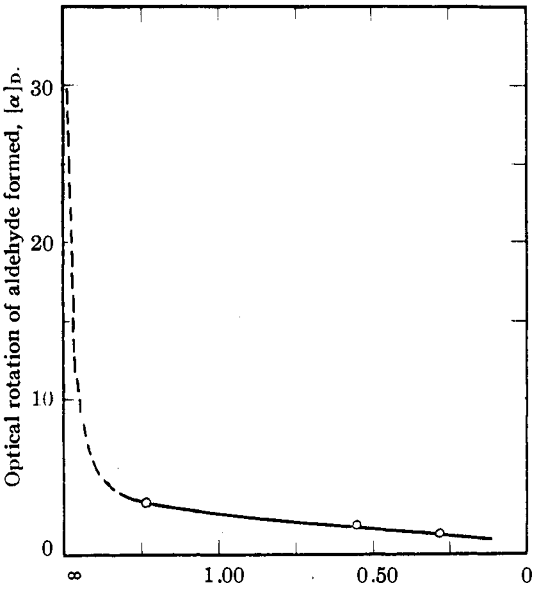


Fig. 2.—Dehydrogenation of (−)2-methylbutanol-1 at 190°.

Racemization of Aldehyde on the Catalyst Surface.—To determine the extent of racemization of the pure aldehyde, (+)2-methylbutanal-1 with $[\alpha]_D$ +28.50° was passed over a freshly reduced catalyst surface at different rates using no external hydrogen source. At 190° with

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(8) Fischer and Meyer, *Brennstoff Chem.*, **12**, 226 (1931).

a rate of 0.48 g. per minute, 3.63 g. of the aldehyde was passed over the catalyst. The catalyzate had $[\alpha]_D$ +0.41° corresponding to an over-all drop in rotation of 28.09°. It analyzed for 51.2% aldehyde.

The 2,4-dinitrophenylhydrazone (acetone, *C* 5.00, 1 dm. tube) had no detectable rotation which would indicate that the aldehyde possessed a specific rotation less than $[\alpha]_D$ +0.60°, this being the upper limit of the error previously mentioned. The 48.8% alcohol formed was, therefore, almost completely racemic.

Experiments were carried out to determine whether racemization of the alcohol or of the aldehyde could be caused by heat alone. One and one-half milliliters of alcohol having $[\alpha]_D$ −5.42° was placed in a glass tube which was sealed off and heated for two and one-half hours at 250°. The alcohol removed from the tube had $[\alpha]_D$ −5.40°. A similar experiment with an active aldehyde with $[\alpha]_D$ +4.40° was carried out and indicated that, when the aldehyde was passed through the catalyst tube packed with glass beads instead of the catalyst, no racemization occurred when the rate was 1.07 g. per minute and the temperature 240°. The rotation of the recovered aldehyde was $[\alpha]_D$ +4.37°. The effect of temperature alone on the rate of racemization of the alcohol and of the aldehyde under the conditions of the experiments was concluded to be negligible.

Discussion and Results

From the experimental data it is apparent that in the hydrogenation–dehydrogenation equilibrium at temperatures above 128° not only was a racemized alcohol formed but also a racemized aldehyde. In addition, the pure aldehyde, when passed over the catalyst in the absence of any hydrogen except that present on the catalyst surface, racemized at such a fast rate that even at 190° at a rate of 1.10 g. per minute over the nickel surface almost complete racemization resulted. Experiments had shown that the pure alcohol was extremely stable to heat alone and resisted racemization at all temperatures employed.

The pure aldehyde, when passed through the apparatus packed with glass beads at 250° in the absence of catalyst, also resisted racemization. It was, therefore, concluded that a metal catalyst containing hydrogen possesses a remarkable ability to catalyze enolization in a manner analogous to acid-base catalysis in keto-enol tautomerism.

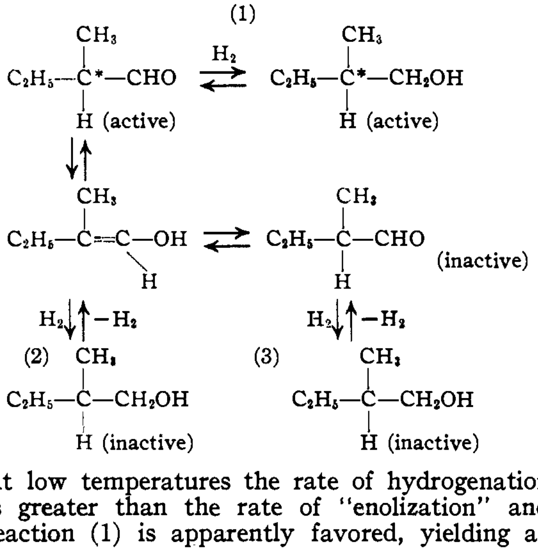
When the alcohol was dehydrogenated by simply heating at 128° with Raney nickel, the 2,4-dinitrophenylhydrazone of the aldehyde, produced in 0.8% yield, had $[\alpha]_D$ +30.2° corresponding to an aldehyde with complete retention. Increasing the temperature to 200° using the same catalyst in a glass-lined steel bomb led to an aldehyde having $[\alpha]_D$ +16.8° based on the rotation of the 2,4-dinitrophenylhydrazone which was $[\alpha]_D$ + 17.0°. This corresponded to 57.6% retention of activity. The latter result might be explained by saying that the primary step was dehydrogenation yielding an active aldehyde followed by partial racemization of the aldehyde. This explanation is not tenable, however, since the reverse reaction of hydrogenation also occurred yielding a partly inactive alcohol all the reactions being in equilibrium. Production of inactive alcohol has been shown to occur in the hydrogenation itself (Fig. 1) and may also be illustrated by calculation from the data of dehydrogenation. When (−)2-methylbutanol-1 having $[\alpha]_D$ −5.42° was dehydrogenated at 190° with a rate of 1.23 g. per minute, the catalyzate containing 10.2% aldehyde with $[\alpha]_D$ +3.3° had a rotation of $[\alpha]_D$ −1.22°. Since it had been shown previously by fractionation that the only two components present in similar reaction mixtures were aldehyde and alcohol, the rotation the mixture would have if no racemic alcohol were present was calculated to equal (0.102)(+3.3) + (0.898)(−5.42), or $[\alpha]_D$ −4.53°. Further calculation showed that the rotation of the alcohol actually present was $[\alpha]_D$ −1.74°, indicating that racemization of the alcohol to the extent of 68% had occurred *during the dehydrogenation*. This result together with data for other rates is given in Table I.

TABLE I

VAPOR PHASE DEHYDROGENATION OF (−)2-METHYLBUTANOL-1

Feed rate of alcohol, g./min.	Aldehyde yield, %	Aldehyde racemized, %	Alcohol racemized, %
1.23	10.2	89	68
0.55	8.6	93	79
0.28	7.0	95	81

Formation of inactive and active alcohol can be postulated as taking place by alternative paths. The enol form has been written as such but as will be shown later it does not necessarily exist.



At low temperatures the rate of hydrogenation is greater than the rate of "enolization" and reaction (1) is apparently favored, yielding an active alcohol. This is shown by Fig. 1. The actual formation of inactive alcohol coupled with other results[3,4] which show that hydrogen or deuterium will attach itself to the alpha carbon at higher temperatures indicate that (2) should be the preferred reaction over (3). If reaction (3) applied, no exchange on carbon atom 2 could occur. As a matter of interest, Ives and Wilks[9] have shown that the rate of deuterium exchange

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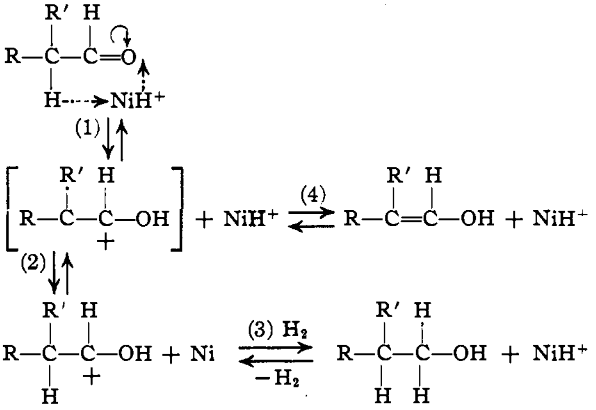
(9) Ives and Wilks, *J. Chem. Soc.*, 1455 (1938).

on the alpha carbon equals the rate of racemization for phenyl *p*-tolyl acetic acid in solution.

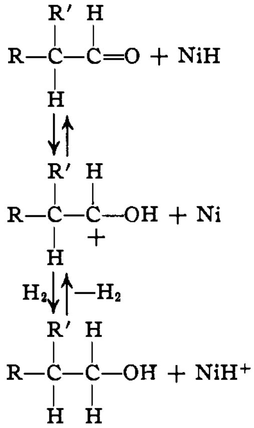
1. Since electrical conductivity measurements of metal surfaces containing hydrogen have indicated that hydrogen is present partly in ionized form as protons,[10] it seems logical to formulate the mechanism on a metallic surface as involving ions. An ionic mechanism has been postulated by Eyring, Hulburt and Harmon[11] for various metal-oxide catalyzed reactions. These authors have stated that an activated complex with ionic binding may be formed even if the reactant and product are essentially covalent. Further credence is lent to the ionic mechanism when it is realized that an aldehyde can racemize on a surface analogously to the manner in which it can racemize by acid catalysis in solution. The protons present in the "cracks" of any freshly reduced metal surface serve as the active centers for reaction. That it is necessary for hydrogen to be present is apparent from the observation that metal surfaces containing no hydrogen are considerably less active than those containing hydrogen. Complete removal of the hydrogen from the surface of Raney nickel, for example, results in complete sintering or inactivation of the catalyst.

A complete formulation of the mechanism for hydrogenation-dehydrogenation equilibrium involving carbon atom 2 based on catalysis similar to a general acid catalysis can be postulated. The first step is the addition of a proton with the simultaneous elimination of a proton at another part of the molecule; the metal catalyst has been written as NiH^+ simply to show the proton function. The activated complex has been formulated so that the catalyst by virtue of geometric and atomic radii considerations can occupy such a position in relation to the reactant molecule that it acts as a proton donor to one part of the molecule and as a proton acceptor for the other part. This necessarily includes carbon atom 2 and involves a complex similar to the butene-1-butene-2- catalyst complex in the isomerization by electrophilic catalysts. This isomerization has been studied by R. K. Smith,[12] who has postulated this type of activated complex. A nickel catalyst satisfies the atomic model considerations for the following general mechanism in which the activated complex has been written as involving carbon atom 2. This mechanism would apply for both low temperatures and high temperatures.



Actual formation of true enol as shown by step (4) may or may not occur. It is not necessary for this mechanism that it actually be formed. Ingold and Wilson[13] and Ives[14] have shown that prototropy does not necessarily involve enolization but, as shown by Hsü, Ingold and Wilson,[15] it does involve ionization. The above formulation can account for formation of optically active products at low temperatures by assuming that the carbanion type intermediate produced by step (1) can *retain* its asymmetry at low temperatures but that high temperatures cause the tetrahedron to "flatten out" yielding racemized products. *A priori* no definite conclusion can be arrived at regarding this point although it has been shown by Wallis and Adams[16] that a carbanion intermediate might be capable of retaining asymmetry.

An alternative low temperature mechanism which would account for retention of configuration observed at low temperatures could be postulated analogously without the *alpha* carbon.



This mechanism, however, is not essential if the carbanion carbon postulated for the mechanism proceeding by steps (1), (2) and (3) can maintain its asymmetry at low temperatures by forming a catalyst-carbon bond without loss of asymmetry of the carbon atom. An increase of temperature would cause a loosening of this bond and would result in racemization as observed.

(10) Schmidt, *Chem. Rev.*, **12**, 393 (1933); D. P. Smith, *Z. Physik*, **69**, 253 (1931); Moore and D. P. Smith, *Trans. Electrochem. Soc.*, **71**, 19 (1937).

(11) Eyring, Hulburt and Harmon, *Ind. Eng. Chem.*, **35**, 511 (1943); *cf.* also Schmidt, *Chem. Rev.*, **12**, 363 (1933).

(12) R. K. Smith, Ph.D. Thesis submitted to the Department of Chemistry, Princeton University, 1944.

(13) Ingold and Wilson, *J. Chem. Soc.*, 93, 773 (1934).

(14) Ives, *ibid.*, 81 (1938).

(15) Hsü, Ingold and Wilson, *ibid.*, 28 (1938).

(16) Wallis and Adams, THIS JOURNAL, **55**, 3838 (1933).

2. In an ionic base catalyzed mechanism which might be formulated similarly to the acid catalyzed mechanism, the reaction complex would be essentially the same. Weichselfelder[17] has prepared a nickel hydride allegedly of the formula NiH_2, which might indicate that hydrogen associated with nickel would have a negative character. Since the negative nature of hydrogen in this hydride has been questioned by Schmidt,[17] this type of mechanism would probably not apply in this case.

3. The third type of mechanism involving atoms could again be postulated with the same activated complex and the same steps using, however, uncharged radicals and assuming completely covalent bonds in the reaction complex. Atomic mechanisms have been usually postulated for heterogeneous chemical reactions. However, differences in electronegativities of the atoms involved would favor a mechanism involving charged radicals or ions.

The authors are greatly indebted to Professor Hugh S. Taylor for his helpful suggestions and criticisms.

Summary

1. Catalytic dehydrogenation of optically active (−)2-methylbutanol-1 and catalytic hydrogenation of optically active (+)2-methylbutanal-1 using nickel catalysts in the temperature range 128–250° have led to optically active products at low temperatures and increasingly racemized products at increasingly higher temperatures.

2. Racemization or "enolization" of the optically active aldehyde on a metal surface containing adsorbed hydrogen has been shown to occur at a fast rate.

3. A generalized mechanism involving carbon atom 2 has been formulated. An alternative low temperature mechanism not involving the second carbon has also been postulated. The mechanisms have been formulated either ionically in a manner similar to acid-base catalysis or involving atoms.

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[17] Weichselfelder, *Ann.*, **447**, 64 (1926); however, *cf.* O. Schmidt, *Z. physik. Chem.*, **165**, 216 (1933).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MISSOURI]

The Preparation of Some Alicyclic Amines

BY DOROTHY NIGHTINGALE AND VIRGIL TWEEDIE[1,2]

The purpose of this investigation was to prepare a series of substituted unsaturated alicyclic amines and the corresponding saturated amines preliminary to a study of the action of nitrous acid on these compounds.

The six alicyclic amines selected for study were prepared from the 4-nitrocyclohexenes obtained by the addition of nitrostyrene to butadiene, (I); 2,3-dimethylbutadiene, (II); and 1,4-diphenylbutadiene (III), respectively.[3,4] No pure addition compounds were obtained with aliphatic nitroolefins and these dienes. The nitrocyclohexenes (I), (II) and (III) were reduced selectively with hydrogen and Raney nickel to form either unsaturated amines or saturated amines.

The nitro group reduced at a lower temperature than the olefinic double bond. The reaction temperatures differed sufficiently that the nitro group could first be reduced quantitatively at 200 atmospheres followed by reduction of the double bond at a higher temperature except in the case of (I). The reduction curve for (I) indicated a two step reaction, at 50 and 75° at 200 atmospheres, but the product was a mixture at 50° or the saturated amine at 75°. The pure 6-phenyl-3-cyclohexenylamine was obtained by the reduction of the nitro group under low pressure at room temperature. The presence of the two methyl groups on the double bonded carbons slowed the hydrogenation considerably. The double bond in (II) did not hydrogenate below 165°. Reduction of (III) took place in two steps, but more slowly than (I).

Factors that affected the selective reduction of the nitro group were the age of the catalyst and the purity of the compound. Freshly prepared Raney nickel was much more selective and caused more rapid reduction than catalyst which was four to six months old.

(I) can be reduced with stannous chloride in dilute alcohol solution to form 6-phenyl-3-cyclohexenylamine in 50% yield, but (II) yielded a complex mixture under the same conditions. Other reducing agents such as zinc and acetic acid, ferrous sulfate and ammonia were unsatisfactory.

The products of the reaction of nitrous acid and the six amines apparently were alicyclic alcohols. They were viscous oils which distilled over a narrow range and the saturated alcohols did not absorb bromine in carbon tetrachloride. Molecular refractions agreed closely with the calculated values. The possibilities for both position isomerism and stereoisomerism are numerous in these reaction products and they may be mixtures of

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[3] Allen and Bell, THIS JOURNAL, **61**, 521 (1939).

[4] Allen, Bell and Gates, *J. Org. Chem.*, **8**, 373 (1943).