Activation energies were calculated from the Arrhenius equation for the interval 30.00–39.95°. The log *PZ* factors for each ester were calculated using the activation energy and the corresponding rate constant at 39.95°. These values are given in Table IV.

Discussion

Inspection of the rates of methanolysis of the *l*-menthyl substituted benzoates reveals (see Table IV) that there is very little difference in rate from the slowest, *p*-methyl, to the fastest, *m-t*-butyl. All react more slowly than *l*-menthyl benzoate. The order for the para series, $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$, is that to be expected if the hyperconjugative effect of the alkyl groups is of more importance than the direct inductive effect. It is assumed that electron release to the carbonyl group retards the rate of methanolysis. This assumption is supported by the results previously obtained in a study of alkaline methanolysis.[2]

Since hyperconjugation involving a *meta* group is not thought to be of importance, the results for the *meta* series are unexpected. Here the same order, $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$, is observed as for the *para* series. To account for the facts we suggest that a steric effect is operative. Examination of accurate scale models reveals that when the carboxyl function is held so that the two oxygens are coplanar with the ring a *t*-butyl group in the *meta* position interferes with the *l*-menthyl group when the two are on the same side. Since this interference is absent in the methyl ester methanolysis should be accompanied by a release of strain. Since the release of strain should be greatest for the *m-t*-butyl and least for the *m*-methyl groups the observed order of reactivity can be explained by the assumptions that the release of strain is more important than the inductive effect and that the hyperconjugative effect is negligible.

The steric effect above outlined is different from that used to account for the rates of alkaline hydrolysis of a few *m*- and *p*-alkyl substituted ethyl benzoates in aqueous acetone[17] and also different from that used to account for the low base strength of 2,6-di-*t*-butylpyridine.[18]

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[17] C. C. Price and D. C. Lincoln, This Journal, **73**, 5836 (1951).

[18] H. C. Brown and B. Kanner, *ibid.*, **75**, 3865 (1953).

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[Contribution No. 359 from the Chemical Department and Polychemicals Department, Experimental Station, E. I. du Pont de Nemours & Co., Inc]

Ruthenium-catalyzed Hydrogenation of Acids to Alcohols

By J. E. Carnahan, T. A. Ford, W. F. Gresham, W. E. Grigsby and G. F. Hager

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Carboxylic acids have been hydrogenated smoothly to the corresponding alcohols in the presence of a ruthenium catalyst.

Catalytic hydrogenation of carboxylic acids to the corresponding alcohols has been accomplished heretofore with copper catalysts[1] at temperatures above 300°, with promoted copper catalysts[2] at temperatures above 240°, or with cobalt catalysts[3] at temperatures above 220°. However, direct hydrogenation of carboxyl groups has not been used widely in synthetic work because better yields could generally be obtained through hydrogenation of the corresponding esters.

The present work[4] shows that ruthenium catalysts can be used for the direct hydrogenation of carboxylic acids to the corresponding alcohols in good yields at temperatures in the neighborhood of 150°. The reaction has been applied to monocarboxylic acids, dicarboxylic acids and a hydroxy acid (Table I). Either ruthenium dioxide or ruthenium-on-carbon catalyst was effective. Platinum and palladium were ineffective under similar conditions or under even more severe conditions (experiments 10, 11 and 12).

The specific conditions required for the ruthenium-catalyzed hydrogenation varied somewhat depending upon the acid being hydrogenated. In general, the optimum temperature appeared to be about 150°. In one series of experiments (experiments 13, 14, 15 and 16) using the same reactants and pressures, better yield was obtained at 149–155° for 1 hour than was obtained at 250–255° or at 97–111° or at 144–145° for only 0.18 hour. In another series (experiments 17, 18 and 19) with a different catalyst, better yield was obtained at 146–151° for 0.16 hour than at 129–136° for 0.33 hour. In the same series, experiment 19 shows that hydroxyacetic acid can be hydrogenated in reasonable yields at pressures below 100 atmospheres; however, isolated carboxyl groups are less reactive and pressures in excess of 500 atmospheres have been required for best results. In experiment 9, about the same yield was obtained with twice as much catalyst. On the other hand, the difference in yields between experiments 8 and 14 can be attributed to the different quantities of catalyst used. Water (experiment 5) and carbon dioxide (experiment 3) were satisfactory as diluents.

The chief side reaction appeared to be hydrogen-

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[1] W. Schrauth, O. Schenck and K. Stickdorn, *Ber.*, **64**, 1314 (1931); W. Normann, *Z. angew. Chem.*, **44**, 714 (1931); W. Normann and H. Prückner, German Patent 594,481 (1934); W. Normann, German Patent 648,510 (1937).

[2] W. A. Lazier, U. S. Patent 1,839,974 (1932); U. S. Patent 2,066,533 (1937); U. S. Patent 2,094,127 (1937); U. S. Patent 2,094-611 (1937); G. Schiller, U. S. Patent 2,121,367 (1938); G. Von Schuckman, U. S. Patent 2,332,834 (1943); E. A. Duintjer, "Über die katalytische Reduktion der Carboxylgruppe ungesättigter Fettsäuren," dissertation, Eidgenössischen Technischen Hochschule in Zürich, 1941; A. Guyer, A. Bieler and K. Jaberg, *Helv. Chim. Acta*, **30**, 39 (1947).

[3] I. G. Farbenindustrie, British Patent 356,731 (1930); H. R. Arnold and W. A. Lazier, U. S. Patent 2,116,552 (1938); G. Schiller, U. S. Patent 2,121,367 (1938).

[4] T. A. Ford, U. S. Patent 2,607,807 (1952); W. F. Gresham, U. S. Patent 2,607,805 (1952).

TABLE I

HYDROGENATION OF ACIDS TO ALCOHOLS

Expt. no.	Substrate, g.	Temp.,[b] °C.	Time, hr.	Pressure,[b] atm.	Diluent, g.	Catalyst, g.	Alcohol	Yield, %
1	Acetic acid, 120	147–170	10	700–950		RuO_2, 1.8	Ethanol	88
2	Acetic acid, 120	200	4.5	200		RuO_2, 1.8 KOH, 5.6	Ethanol Ethyl acetate	41 17
3	Acetic acid, 100	250	10	600–800	CO_2, 100	RuO_2, 3	Ethanol Ethyl acetate	44 16
4	Oxalic acid (dihydrate), 252	94–170	10.5	630–990		RuO_2, 3.8	Ethylene glycol Ethanol	47
5	Adipic acid, 20	150–175	0.5	520–700	H_2O, 100	RuO_2, 5	Hexamethylene glycol	48
6	Succinic acid, 118	152–192	4–5	720–950		RuO_2, 1.8	Tetramethylene glycol Propanol Butanol	59
7	Hydroxyacetic acid, 20	145–149	0.16	700–775	H_2O, 80	Water-washed RuO_2, 5	Ethylene glycol	83
8	Hydroxyacetic acid, 20	145–150	1	650–710	H_2O, 80	10% Ru-on-carbon, 10	Ethylene glycol	80
9	Hydroxyacetic acid, 20	139–140	0.5	55–78	H_2O, 80	RuO_2, 10	Ethylene glycol	40
10	Hydroxyacetic acid, 20	149–157	1	675–690	H_2O, 80	10% Pd-on-carbon, 3	None (7.5 g. non-distillables)	
11	Hydroxyacetic acid, 20	149–157	1 1	675–690	H_2O, 80	10% Pt-on-carbon, 3	None (12.7 g. non-distillables)	
12	Hydroxyacetic acid, 20	249–255	1	675–690	H_2O, 80	10% Pt-on-carbon, 3	None	
13	Hydroxyacetic acid, 20	250–255	0.25	540–700	H_2O, 80	10% Ru-on-carbon, 3	Ethylene glycol Hydrocarbons[a]	32
14	Hydroxyacetic acid, 20	149–155	1	660–700	H_2O, 80	10% Ru-on-carbon, 3	Ethylene glycol	68
15	Hydroxyacetic acid, 20	144–145	0.18	660–690	H_2O, 80	10% Ru-on-carbon, 3	Ethylene glycol	4
16	Hydroxyacetic acid, 20	97–111	1	660–705	H_2O, 80	10% Ru-on-carbon, 3	None	
17	Hydroxyacetic acid, 20	129–136	0.33	630–700	H_2O, 80	RuO_2, 5	Ethylene glycol	58
18	Hydroxyacetic acid, 20	146–151	0.16	700	H_2O, 80	RuO_2, 5	Ethylene glycol	80
19	Hydroxyacetic acid, 20	141–147	0.5	65–85	H_2O, 80	RuO_2, 5	Ethylene glycol	39

[a] At the end of the experiment the gas in the pressure vessel was sampled for analysis by mass spectrometer. The results were: hydrogen, 78.3 mole %; methane, 1.8 mole %; ethane, 0.8 mole %; carbon dioxide, 0.04 mole %; oxygen, 0.8 mole %; argon, 0.09 mole %; nitrogen, 18.2 mole % (the last three constituents could have resulted from contamination of the sample with air and with nitrogen used to sweep the sampling lines). [b] In these experiments the measurement of reaction duration started when the intended temperature and pressure were reached or when a decrease in pressure indicated that reaction had begun, whichever occurred first. As a result the temperature and pressure ranges reported are rather broad in some experiments.

olysis of the alcohol. For example, in the hydrogenation of oxalic acid to ethylene glycol, a small amount of ethanol was formed as a by-product (experiment 4). No ethanol was detected in the product from hydroxyacetic acid, but when the hydrogenation was carried out at an excessively high temperature (250°), methane and ethane were formed (experiment 13). In a few experiments where the hydrogenation appeared to be sluggish (experiments 2 and 3), the ester derived from the alcohol and the acid was formed as a by-product.

Experimental

Catalysts.—Ruthenium dioxide and 10% ruthenium-on-carbon were purchased from Baker and Company, Newark, N. J. Since qualitative tests showed the ruthenium dioxide to contain water and nitrates, it was purified for experiment 7 by boiling in distilled water, filtering, boiling again in distilled water, and filtering. Spectroscopic analysis of the unwashed RuO_2 showed it to contain minor amounts of Si and trace amounts of Ca, Cu, Mg, Pb, Al, Mn and Ag.

Hydrogenation of Acetic Acid.—A 400-ml., silver-lined shaker tube, equipped with gas inlet, rupture disc and thermocouple well, was charged with the liquid and solid reactants and catalysts indicated in Table I. The air was removed by flushing with oxygen-free nitrogen, and the reactor was then closed and placed in a shaker mechanism. Hydrogen was added, and shaking and heating were begun. When the reaction temperature was reached, additional hydrogen was admitted as required to keep the pressure within the desired range. After hydrogen absorption ceased, the reactor was cooled and vented, and the contents were discharged and filtered to remove the catalyst.

The product was isolated by distillation. The fraction boiling at 76.5–78° was identified as 95% ethanol by its boiling point, refractive index and infrared spectrum. Titration of the crude reaction mixture indicated that less than 0.04% of the acetic acid survived hydrogenation in experiment 1, while in experiment 3 10% of the acetic acid was recovered in addition to the ethyl acetate and ethanol.

Hydrogenation of Oxalic Acid.—The equipment and reaction technique were the same as above. The product, isolated by distillation, was identified as ethylene glycol by its boiling point, 104° (20 mm.); melting point, −13°; and analysis.

Anal. Calcd. for $C_2H_6O_2$: C, 38.70; H, 9.75; –OH eq., 31.0. Found: C, 38.78; H, 9.95; –OH eq., 31.4.

The forerun contained a small amount of ethanol as indicated by boiling point.

Hydrogenation of Succinic Acid.—The apparatus and technique were the same as those for acetic acid. The product, isolated by distillation, was identified as tetramethylene glycol by its boiling point, 135° (20 mm.); melting point, 19.3°; and analytical data.

Anal. Calcd. for $C_4H_{10}O_2$: C, 53.20; H, 11.18; –OH eq., 45.1. Found: C, 53.27; H, 11.18; –OH eq., 46.3.

The presence of small amounts of propanol and butanol was indicated by the boiling points of the foreruns.

Hydrogenation of Adipic Acid.—The liquid and solid reactants and catalysts were placed in a 325-ml. capacity, silver-lined tube equipped with a rupture disc, thermocouple well, and gas inlet. The tube was closed, pressured with hydrogen, heated and repressured, cooled and discharged. The product was filtered with "Filter-Aid"; water was used as a wash. The filtrate was distilled to give hexamethylene glycol which boiled at 120-125° (4 mm.) and melted at 39-43°.

Hydrogenation of Hydroxyacetic Acid.—The procedures for hydrogenation and product isolation were similar to those used for adipic acid. The product, ethylene glycol, had b.p. 76° (5.5 mm.), refractive index at 25° of 1.4300, and m.p. −13°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Quantitative Studies with Lithium Aluminum Hydride. The Reduction of Butenolides

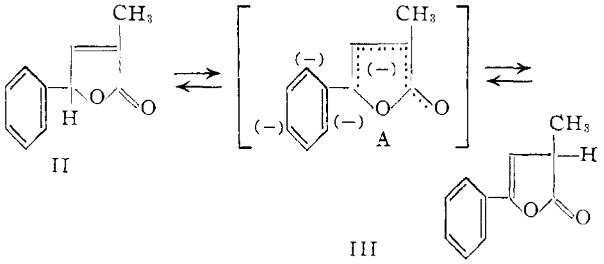
BY FAUSTO RAMIREZ AND MORDECAI B. RUBIN[1]

RECEIVED FEBRUARY 1, 1955

The lithium aluminum hydride reduction of the tautomeric unsaturated lactones α-methyl-γ-phenyl-$\Delta^{\alpha,\beta}$-butenolide (II) and α-methyl-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (III) has been examined quantitatively. The effect of varying the hydride–butenolide mole ratio and of varying the reduction time at several mole ratios, have been studied. The reduction of the α,β-unsaturated butenolide II yielded the keto alcohol IV, the unsaturated dialcohol VI, and the saturated dialcohol V. The β,γ-unsaturated butenolide III yielded the keto alcohol IV and small amounts of the saturated dialcohol V. The formation of the common reduction products, IV and V from both butenolides suggests that a common hybrid anion A is formed during the reductions. This study indicates that variations in the hydride–butenolide ratios result in the formation of different complexes which, however, yield the same products on hydrolysis.

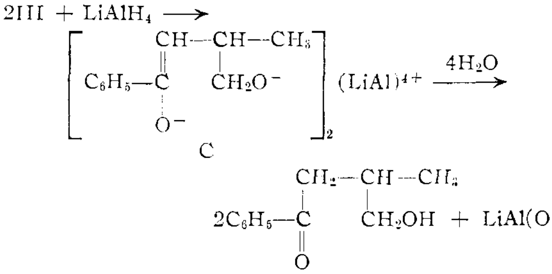
Examination of the literature on lithium aluminum hydride[2] discloses the reduction of one pair of tautomeric butenolides. Thus, Hochstein[3] reported a 65% yield of γ-acetylpropanol ($CH_3COCH_2CH_2CH_2OH$) from α-angelica lactone (γ-methyl-$\Delta^{\beta,\gamma}$-butenolide) and a 10% yield of 1,4-pentanediol ($CH_3CH(OH)CH_2CH_2CH_2OH$)[4] from β-angelica lactone (γ-methyl-$\Delta^{\alpha,\beta}$-butenolide.)

We have investigated the action of lithium aluminum hydride on two tautomeric crystalline butenolides, namely, α-methyl-γ-phenyl-$\Delta^{\alpha,\beta}$-butenolide (II) and α-methyl-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (III), interconvertible through a common hybrid anion A. The effect of varying the hydride–butenolide mole ratio and of varying the reduction time at several mole ratios, were studied. The composition of the reduction products was established by spectrophotometric methods in the infrared and ultraviolet and by chemical means.



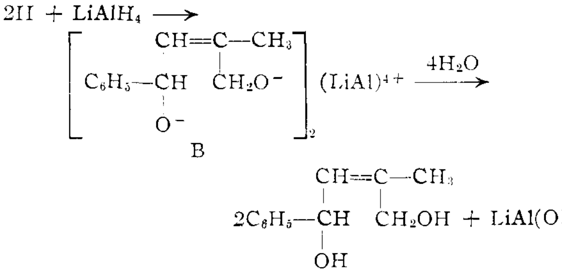
II A III

By analogy with the reduction of other lactones,[2] the stoichiometry of the reduction of butenolides II and III may be represented as



$$2\mathrm{III} + \mathrm{LiAlH_4} \longrightarrow \left[\mathrm{C_6H_5{-}\underset{O^-}{C}{=}CH{-}\underset{CH_2O^-}{CH}{-}CH_3}\right]_2(\mathrm{LiAl})^{4+} \xrightarrow{4\mathrm{H_2O}} 2\,\mathrm{C_6H_5{-}\underset{O}{\overset{}{\underset{\|}{C}}}{-}CH_2{-}\underset{CH_2OH}{CH}{-}CH_3} + \mathrm{LiAl(OH)_4}$$

C



$$2\mathrm{II} + \mathrm{LiAlH_4} \longrightarrow \left[\mathrm{C_6H_5{-}\underset{O^-}{CH}{-}CH{=}\underset{CH_2O^-}{C}{-}CH_3}\right]_2(\mathrm{LiAl})^{4+} \xrightarrow{4\mathrm{H_2O}} 2\,\mathrm{C_6H_5{-}\underset{OH}{CH}{-}CH{=}\underset{CH_2OH}{C}{-}CH_3} + \mathrm{LiAl(OH)_4}$$

B

It has been stated that simple enolate anions (such as C) generally resist reduction by $LiAlH_4$[5] although anions derived from β-dicarbonyl compounds are susceptible to reduction by the hydride.[5a,b] The behavior of anions such as A remains to be explored.[6]

Examples of *partial reductions* of saturated lactones to hydroxyaldehydes[7a] and of ortho esters[7b] to aldehydes have been reported. Such partial reductions, if possible with unsaturated lactones,

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(1) Union Carbide and Carbon Fellow, 1952–1953. From part of the Ph.D. Thesis of M. B. Rubin. Presented at the 126th National Meeting of the Amer. Chem. Soc., September, 1954.

(2) (a) W. G. Brown in "Organic Reactions," Vol. VI, R. Adams, Editor, John Wiley and Sons, Inc., New York, N. Y., 1951, Ch. 10; (b) U. Solms, *Chimia*, **5**, 25 (1951); (c) B. C. L. Weedon, *Ann. Rep.*, **49**, 139 (1952).

(3) F. A. Hochstein, THIS JOURNAL, **71**, 305 (1949).

(4) The original reference[3] gives "2,4-pentanediol" as the only product of the reduction of β-angelica lactone. This appears to be a misprint.

(5) (a) A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 939 (1953); (b) *ibid.*, **75**, 3723 (1953); (c) W. G. Dauben and J. F. Eastham, *ibid.*, **75**, 1718 (1953); (d) R. E. Lutz and J. S. Gillespie, *ibid.*, **72**, 2002 (1950); (e) R. L. Wears, *ibid.*, **73**, 2390 (1951).

(6) That the hydrogen in the type of butenolides here considered is significantly acidic and, therefore, capable of reacting with $LiAlH_4$ to generate anion A, is shown by the facile isomerization of III into II by triethylamine (*vide infra*). The action of $LiAlH_4$ on active hydrogens has been reviewed (H. E. Zaugg and B. W. Horrom, *Anal. Chem.*, **20**, 1026 (1948); F. A. Hochstein, THIS JOURNAL, **71**, 305 (1949); T. H. Higuchi in "Organic Analysis," Vol. II, Interscience Publishers, New York, N. Y, 1954.

(7) (a) G. A. Arth, THIS JOURNAL, **75**, 2413 (1953); (b) C. J. Claus and J. L. Morgenthau, *ibid.*, **73**, 5005 (1951).