hr. at 0°, the aqueous layer was washed twice with 10-ml. portions of benzene, then discarded. The organic layer, kept cold during the interim, was combined with the benzene washes, dried with magnesium sulfate, filtered, then heated under reflux for 0.5 hr., until the evolution of nitrogen was complete. Decomposition of the acyl azide began at about 60°. Only enough heat was applied to maintain a modestly brick evolution of gas. A few drops of the resulting, sharp-smelling isocyanate solution was used for the preparation of a phenylurea derivative (below). The remaining solution was cooled and 20 ml. of concentrated hydrochloric acid was added. The mixture was stirred, slowly at first and then more rapidly until the vigor of evolution of carbon dioxide was much diminished (15 min.). The mixture was heated under reflux with vigorous stirring for just 5 min., when a droplet of saturated barium hydroxide solution no longer became turbid when suspended in the effluent gas stream. The mixture was evaporated to dryness, the residue agitated with 10 ml. of absolute ethanol, then evaporated to dryness again to remove the last of the water and hydrogen chloride. The resulting solid was agitated with acetone, collected by filtration, and washed with acetone to yield 3.77 g. (82%) of hygroscopic needles, m.p. 219–221°. Recrystallization from absolute ethanol did not raise the melting point.

Anal. Calcd. for $C_5H_{10}NCl$: C, 50.21; H, 8.43; N, 11.71. Found: C, 49.87; H, 8.52; N, 12.18.

In a similar experiment where the isocyanate solution and concentrated hydrochloric acid were refluxed for a longer period (1 hr.)[15] the product was obtained in only 51% yield, m.p. 217–219°. The acetone washes were found to contain a considerable amount of another crude hydrochloride.

***N*-(3-Cyclopenten-1-yl)-*N'*-phenylurea (XIII).**—A little of the solution of 3-cyclopenten-1-yl isocyanate (XV) from the above experiment was combined with aniline. The resulting solid was washed with benzene. It crystallized from ethanol as needles, m.p. 218°.

Anal. Calcd. for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 70.98; H, 7.12; N, 14.03.

Acknowledgment.—The authors wish to thank Mr. Louis Brancone and his group for the elemental analyses and Mr. William Fulmor and his coworkers for the spectral data.

Hydrogenation-Hydrogenolysis Studies of Symmetrically Substituted 1,4-Acetylenic Glycols

ROBERT J. TEDESCHI

The Central Research Laboratories of the Air Reduction Company, Inc., Murray Hill, N. J.

Received January 24, 1962

The formerly difficult hydrogenation of 1,4-acetylenic glycols to the corresponding olefinic and saturated glycols at low pressures with palladium catalysts has been accomplished in high yield and purity. Hydrogenolysis side reactions at the tertiary hydroxyl groups, previously responsible for poor yields and quality of product have been eliminated by the novel use of very small amounts of base during the hydrogenation. The route through which hydrogenolysis takes place has been established.

The hydrogenation of 1,4-acetylenic glycols at low pressures to the corresponding olefinic and saturated diols was studied extensively by Zal'kind[1–4] and Du Pont[5,6] using both palladium and platinum catalysts. Both investigators found that on complete hydrogenation of acetylenic diols to the saturated derivatives extensive hydrogenolysis at the tertiary hydroxyl groups was encountered yielding a mixture of saturated carbinol, saturated hydrocarbon, and a minor amount of the desired 1,4-saturated glycol. Zal'kind believed hydrogenolysis to originate from further hydrogenation of the saturated diol but no experimental proof was offered to support this view.

Raney nickel has been recommended[7,8] as a selective catalyst for the preparation of olefinic glycols. Its use with small amounts of base as promoter was claimed by Vaughn[9] to result in a selective hydrogenation which halted exactly at the olefinic stage. Experiments in this laboratory[10] have shown that at low to moderate pressures Raney nickel, while resulting in less hydrogenolysis than palladium catalyst, does not completely hydrogenate the acetylenic diols to the corresponding saturated diols and is not selective for semihydrogenation with base promoters.

The need for a low pressure, efficient, selective process[11] for hydrogenating 1,4-acetylenic glycols to the corresponding olefinic and saturated diols in high yield and purity arose in this laboratory. Consequently, both the mechanism and route by which hydrogenolysis takes place and its inhibition were studied. Zal'kind's original contention that hydrogenolysis arose from the saturated diols was found erroneous since both the saturated diols and their analogous carbinols were found completely stable to hydrogenolysis showing no pressure drop

[1] Y. S. Zal'kind, *J. Russ. Phys. Chem. Soc.*, **45**, 1875, 1896 (1913); *Chem. Abstr.*, **8**, 1419 (1914).

[2] Y. S. Zal'kind and I. G. Bezsonova, *J. Russ. Phys. Chem. Soc.*, **53**, 279 (1921); *Chem. Abstr.*, **18**, 2327 (1924).

[3] Y. S. Zal'kind, *et al.*, *J. Russ. Phys. Chem. Soc.*, **47**, 680 (1915); *Chem. Abstr.*, **9**, 2510 (1915).

[4] A. W. Johnson, "Acetylenic Compounds, Vol. I, the Acetylenic Alcohols," Edw. Arnold Co., London, 1946, pp. 188, 195, 207.

[5] G. DuPont, *Ann. Chim.*, **30**, 485 (1913).

[6] G. DuPont, *Compt. rend.*, **156**, 1623 (1913); *Chem. Abstr.*, **7**, 3112 (1913).

[7] G. DuPont, *Bull. soc. chim.* (5), **3**, 1030 (1936).

[8] N. Lozac'h, Ecole Normale Superieure, Publications des Laboratoires Chemie, Vol. III, p. 30 (1945).

[9] T. H. Vaughn, U.S. Patent **2,157,365**, May 9, 1939.

[10] J. Casey, unpublished work. Air Reduction Co., Murray Hill, N. J.

[11] R. J. Tedeschi; U.S. Patent 2,992,278, July 11, 1961.

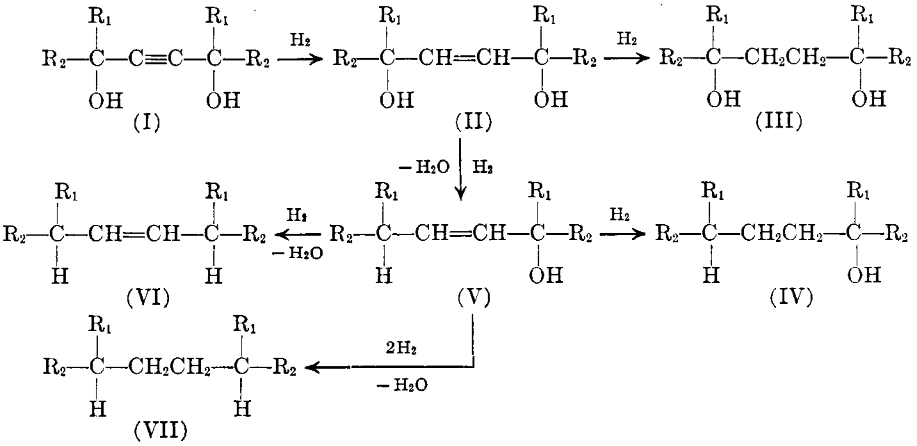
on hydrogenation or detectable water of hydrogenolysis.

Results and Discussion

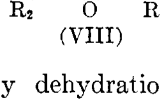
In the present work finely divided palladium (5%) on charcoal catalyst[12] was employed. Hydrogenolysis was found to originate mainly from the intermediate olefinic diol (II) with a minor amount possible from the acetylenic starting material (I). Complete hydrogenation always yielded a mixture of products such as saturated carbinol (IV), hydrocarbon (VII), and diol (III). If the hydrogenation was interrupted before complete hydrogen absorption, unsaturated compounds such as (V) or (VI) could be readily detected. The relative order of hydrogenolysis of the diol (I) under identical conditions based on the group R_2, (R_1 = CH_3) and total water formed from 0.50 mole acetylenic glycol during the hydrogenation was:

R_2	CH_3>	C_6H_5>	C_4H_9(iso)>	C_2H_5,	>C_6H_{10}(cyclohexyl)>	n-C_3H_7
g. H_2O	10.2	9.2	9.0	7.5	7.4	6.9

Hydrogenolysis can be represented as proceeding *via* the following route:



The following results support the above as the principal route for hydrogenolysis: (a) Hydrogenation of the acetylenic diol (I) to the olefinic diol (II) using one mole of hydrogen per mole of (I) yields considerably less water of hydrogenolysis than is obtained on complete hydrogenation. 2,5-Dimethyl-3-hexyne-2,5-diol and 3,6-dimethyl-4-octyne-3,6-diol yielded only 17.2% and 11.0%, respectively, of the total water expected from the first stage (—C≡C— → —CH=CH—) of the hydrogenation. These figures are maximum values for hydrogenolysis at the acetylenic stage since the olefinic diol formed during the hydrogenation probably undergoes competitive hydrogenolysis, particularly near the end of the first stage. (b) The formation of the saturated carbinols (IV), 2,5-dimethylhexane-2-ol and 3,6-dimethyloctane-3-ol, in respective yields of 57% and 58% from the olefinic diols (II), 2,5-dimethyl-3-hexene-2,5-diol and 3,6-dimethyl-4-octene-3,6-diol, takes place in essentially the same yield as that obtained from the corresponding acetylenic diols. (c) By stopping the hydrogenation of 3,6-dimethyl-4-octyne-3,6-diol after the absorption of two moles hydrogen per mole of diol, a 49% conversion to a mixture of (V), 3,6-dimethyl-4-octene-3-ol (79%), and (IV), 3,6-dimethyloctane-3-ol (21%), results. Both products exhibit identical boiling points under reduced pressure and hence are not readily separable. (d) No hydrogenolysis occurs from either the saturated diols (III) or the saturated carbinols (IV). Exhaustive hydrogenation of pure samples of 2,5-dimethylhexane-2,5-diol, 3,6-dimethyloctane-3,6-diol, 2,5-dimethylhexane-2-ol, and 3,6-dimethyloctane-3-ol gave no evidence of pressure drop or water of hydrogenolysis. (e) The saturated hydrocarbon (VII) is isolated in varying amount as a low-boiling fraction depending on the degree of hydrogenolysis. (f) Formation of water by an acid-catalyzed dehydration mechanism is very unlikely since dehydration of the 1,4-ethylenic or saturated diols always results in a significant amount of the corresponding tetrahydrofuran derivative. Hydrogenation with palladium catalyst in these experiments yields no detectable amounts of furan. However, the use of catalytic amounts (0.10 g./mole acetylenic diol) of either phosphoric or *p*-toluenesulfonic acid in the hydrogenation results in mixtures containing large amounts of the corresponding tetrahydrofuran (VIII) and hydrocarbon



(VIII)

(VII), formed by dehydration. No detectable acidic impurities were found either in the catalysts, starting materials, or solvents used. Hence, it is

---

[12] Standard catalyst available from the American Platinum Works, Newark, N. J.

concluded that hydrogenolysis is not caused by traces of acid in the catalyst or carrier.

Very small amounts of base, 0.05–0.1 g. per mole diol, such as potassium hydroxide or sodium hydroxide dissolved in the acetylenic diol–solvent mixture before hydrogenation reduced hydrogenolysis side reactions to a negligible point resulting in high yields (85–94% of distilled product) of either the olefinic or saturated diols. The same hydrogenation in the absence of potassium hydroxide gave low yields (7–33%) of the saturated diols and a predominance of the saturated carbinol and hydrocarbon arising from hydrogenolysis.

Hydrogenations carried out in the presence of base showed a significant decrease in reaction rate at a point corresponding closely to the completion of the first stage of the hydrogenation ($—C\equiv C— \rightarrow —CH=CH—$). This decreased rate was readily discernable as a break in the hydrogenation curve of pressure drop versus time. In the absence of base no discernible break was noted as claimed by Zal'kind.[1] The first stage of the hydrogenation either in the presence or absence of base is rapid and exothermic at 55–85°. Below 55° the rate is very slow. The rate of the second stage ($—CH=CH— \rightarrow —CH_2CH_2—$) is greatly decreased by very small amounts (0.05–0.1 g. base per mole of diol) of base and inhibited by 0.10–0.30 g. to the extent that incomplete hydrogenation to the saturated diol results. Sodium hydroxide was found to inhibit the second stage of the reduction considerably more than potassium hydroxide. The latter base is consequently preferred for preparing saturated diols although sodium hydroxide in smaller amounts than 0.050 g. per 0.50 mole acetylenic diol might be useful.

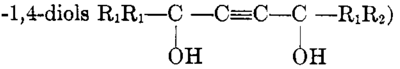
Other basic materials which were evaluated as inhibitors for hydrogenolysis were potassium, triethylamine, sodium methoxide, potassium carbonate and potassium bicarbonate. Potassium was observed to inhibit hydrogenation to such an extent that the hydrogenation halted selectively at the end of the first stage with only slight hydrogenolysis. Potassium carbonate was about one tenth as effective as potassium hydroxide in preventing hydrogenolysis while potassium bicarbonate was without effect. The inhibitory action of potassium carbonate may be due in part to its hydrolysis to potassium hydroxide resulting from minor hydrogenolysis. In Table II the effect of these basic materials is tabulated.

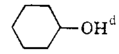
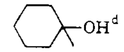
Olefinic diols in fairly high purity (94.5–99.7%) can be obtained by halting the hydrogenation manually at the end of the first stage. Amounts of potassium hydroxide as high as 0.30 g. were ineffective in selectively halting the hydrogenation, in contrast to the selectivity observed with potassium. The hydrogenation generally proceeded 5–10% beyond this point before halting. Attempts to halt the hydrogenation selectively at the olefinic stage using Lindlar catalyst[13] (palladium on calcium carbonate inactivated with lead acetate) or small amounts (0.20 g.) of palladium-on-charcoal catalyst were also unsuccessful.

The elimination of hydrogenolysis *via* bases, such as potassium, potassium hydroxide, and sodium hydroxide, suggests that base-diol interaction may be an important precursor to selective hydrogenation. The addition of powdered base to a solution of the acetylenic diol in a nonpolar solvent, such as hexane, prior to hydrogenation results in complete solution of the base. This effect is more indicative of complex formation rather than the less probable formation of an alkoxide from a tertiary diol.

TABLE I

HYDROGENATION IN THE PRESENCE AND ABSENCE OF POTASSIUM HYDROXIDE

Acetylenic-1,4-diols

$R_1R_1—\underset{OH}{C}—C\equiv C—\underset{OH}{C}—R_1R_2)$

		Per mole diol		Per cent yield		
R_1	R_2	G. KOH	G. H_2O formed	(C=C) diol	Saturated diol	Saturated[a] carbinol
CH_3	CH_3	0.050	<0.04	87.5[e]	84.7	0
CH_3	CH_3	0	20.4	...[b]	31.5	34.2
CH_3	C_2H_5	0.100	<0.04	94.3[e]	87.4	0
CH_3	C_2H_5	0	15.0	..[b]	15.0	58.2
CH_3	$C_3H_7(n)$	0.100	<0.04	97.3[e]	94.0	0
CH_3	$C_3H_7(n)$	0	12.0	..[b]	7.2	57.7
CH_3	$C_3H_7(n)$	0.100	<0.04	..[b]	98.0[c]	0
CH_3	$C_3H_7(n)$	0.100		..[b]	90.0	0
CH_3	$C_4H_9(i)$	0.100	<0.04	86.0[e]	89.5	0
CH_3	$C_4H_9(i)$	0	18.0	..[b]	33.0	42.3
CH_3	C_6H_5	0.100	<0.04	..[b]	94.8	0
CH_3	C_6H_5	0	10.4	..[b]	35.6	...
[d]		0.100	<0.04	..[b]	94.0	0
[d]		0	14.8	..[b]	8.9	59.0

[a] Saturated carbinol formed by the loss of one molecule of water. [b] The olefinic diol was not isolated. [c] Saturated diol contained 2.6% olefinic diol by bromination value. [d] Cyclohexanol group of the glycol, bis-1-(1-hydroxycyclohexyl)acetylene. [e] Separate runs to prepare and isolate the olefinic diol were carried out.

TABLE II

HYDROGENATION IN THE PRESENCE OF OTHER BASIC INHIBITORS (1.0 M., 4,7-DIMETHYL-5-DECYN-4,7-DIOL)

Base	G. base/ mole diol	% yield	H_2O formed, g.
NaOH	0.10	94	<0.04
$NaOCH_3$	.10	96	<0.04
$N-(C_2H_5)_3$	.10	98	<0.04
K	.044	..[a]	<0.50
K_2CO_3	.08	..[a]	0.40
$KHCO_3$	.040	..[a]	8.8

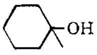
[a] No attempt to isolate product since yield is established and hydrogenolysis is negligible.

---

[13] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952); U.S. Patent 2,681,938, June 22, 1954.

TABLE III

PHYSICAL CONSTANTS AND ANALYTICAL DATA

Analog	R_1	R_2	Physical state[a]	M.p., °C.	Boiling point[b] °C.	Boiling point[b] Mm.	Per cent diol purity[c] C=C	Per cent diol purity[c] Sat.
CH=CH	CH_3	CH_3	Long needles	75.5–76	95	4	96.5	
CH_2CH_2	CH_3	CH_3	Small needles	88.8–89	95	4	(2.8)[d]	97.2
CH=CH	CH_3	C_2H_5	Viscous liquid	...	125–127	10	94.8	
CH_2CH_2	CH_3	C_2H_5	Viscous liquid	...	125–127	10	(0.1)[d]	99.9
CH=CH	CH_3	$C_3H_7(n)$	Viscous liquid	...	125–127	3	99.7	99.5
CH_2CH_2	CH_3	$C_3H_7(n)$	Viscous liquid	...	125–127	3	(0.4)[d]	99.6
CH=CH	CH_3	C_4H_9 (iso)	Viscous liquid	...	124–126	3	97.5	
CH_2CH_2	CH_3	C_4H_9 (iso)	Viscous liquid	...	124–126	3	(0.1)[d]	99.9
CH_2CH_2	CH_3	C_6H_5	Small needles	135–140–156	...	...	(0.1)[d]	99.9
CH_2CH_2	 		Needles	132–133	...	...	(0.1)[d]	99.9

[a] With the exception of demethylhexanediol and bis-1-(1-hydroxycyclohexyl)ethane, all other diols formed can exhibit either *cis-trans* or optical isomerism. Consequently, where a crystalline solid would normally be expected, a viscous oil often results. Also considerable range in melting point is sometimes noted due to the different modifications possibly present (for example, racemates or meso forms—*i.e.*, diphenylhexyndiol and derivatives). [b] The boiling point difference between the acetylenic, olefinic, and saturated diols at low pressures is insignificant and a close boiling fraction is always obtained. [c] The purity of the olefinic diols was determined by hydrogenation in the presence of potassium hydroxide to eliminate hydrogenolysis. No acetylenic diol impurity was present. Table V gives comparative values for an alternate bromination method. The purity of the saturated diols was determined by total pressure drop on hydrogenation, and bromination values for the olefinic diol impurity. [d] Olefinic diol impurity in the saturated diol was determined by bromination method, ref. 16.

Further, a quantitative reaction has been observed[14] repeatedly in the equimolar reaction of 2,5-dimethyl-3-hexyn-2,5-diol with powdered, essentially anhydrous potassium hydroxide in dry, inert solvents to yield a 1:1 mole complex. The resulting white, stable solid when employed as a substitute for potassium hydroxide in a concentration equivalent to the potassium hydroxide normally employed in a hydrogenation also completely inhibits hydrogenolysis, and allows complete hydrogenation to the saturated diol. 2,5-Dimethyl-3-hexene-2,5-diol forms a similar complex in 80–85% yield which gives identical results. The saturated diol does not form a complex.

Also at an equivalent concentration (0.05 g. potassium per mole diol) potassium metal readily dissolves as the tertiary alkoxide in the starting material–solvent mixture and inhibits the hydrogenation so strongly that hydrogenation proceeds only to the end of the first stage with no hydrogenolysis observed. This selective behavior of the alkoxide derivative for semihydrogenation is quite different from the unselective action of potassium hydroxide towards semihydrogenation. The preceding observations indicate that a base–diol complex, rather than free base, is the species which may function as a selective inhibitor at active sites on the surface of the catalyst responsible for hydrogenolysis.

Experimental

All hydrogenations were carried out in a standard Parr apparatus using 5% palladium on charcoal as catalyst and solvents such as heptane, toluene, methanol, or isopropyl alcohol. Hydrocarbon solvents are preferable if the solubility of the starting material permits since water of hydrogenolysis can readily be determined by azeotropic distillation in the resulting two phase distillate. The average reaction temperature and pressure employed was 55–85° and 30–55 p.s.i.

Base Protected Hydrogenation. (Standard Parr Apparatus; 1.0 *M* Hydrogen Equivalent to 85 p.s.i. Drop).—The following standard reaction charge was employed: 0.50 mole of acetylenic-1,4-glycol, 100 cc. of *n*-heptane, 1.0 g. (5%) of palladium-on-charcoal catalyst, 0.025–0.05 g. of powdered potassium hydroxide, sodium hydroxide, or triethylamine. For relatively insoluble glycols, such as 2,5-dimethyl-3-hexyn-2,5-diol, 2,5-diphenyl-3-hexyn-2,5-diol, and bis-1-(1-hydroxycyclohexyl)acetylene, either methanol or isopropyl alcohol was preferred. Dimethylhexyndiol unlike the latter two glycols could be dissolved in toluene at 75–85° and a satisfactory hydrogenation carried out.

The resulting solution of the glycol at 60–65° was treated with powdered potassium hydroxide and stirred to solution. The catalyst was then added and the hydrogenation carried out without delay in the usual manner at 60–65° and 30–55 p.s.i.

Olefinic 1,4-Diols.—The hydrogenation was halted after the absorption of 0.50 mole hydrogen, filtered from catalyst, and subjected to azeotropic water analysis via a Dean-Stark tube. Insignificant amounts of hydrogenolysis water (less than 0.20 g.) were collected with potassium hydroxide protected runs. The hydrogenation was exothermic and rapid during the reduction of the acetylenic and air or water cooling was required occasionally. Reaction time was generally 15–20 min. for an 0.5-mole run.

Saturated 1,4-Diols.—The hydrogenation after reduction of the acetylenic diol was not significantly exothermic and heat had to be supplied to maintain the reaction temperature of 60–65°. The hydrogenation halted within several p.s.i. of the theoretical pressure drop for one mole of hydrogen if potassium hydroxide were used. Experiments not protected with base gave pressure drops as much as 30–40 p.s.i. over theory (85 p.s.i./mole) and a predominance of the saturated monoalcohol and hydrocarbon over the desired saturated diol. Azeotropic water analysis with potassium hydroxide protected runs gave insignificant hydrogenolysis (less than 0.20 g. of water) while unprotected runs averaged 6–10 g. of water.

Olefinic or saturated diols derived from dimethyloctyndiol, dimethyldecyndiol, and tetramethyldecyndiol were colorless, viscous liquids and best isolated by vacuum distillation

---

[14] R. J. Tedeschi and M. F. Wilson, Air Reduction Co.; the preparation of these complexes and evidence for their structures will be presented in a later paper.

through a 12–15-in. vacuum jacketed or heated Vigreux column after filtration from catalyst.

Diols derived from the higher melting acetylenic diols, such as dimethylhexyndiol, diphenylhexyndiol, and bis-1-(1-hydroxycyclohexyl)acetylene were readily isolated after alcohol solvent removal by recrystallization from toluene or xylene.

Unprotected Hydrogenation.—The experimental procedure was the same as above except that no base was employed. Distillation yielded three principal fractions: (1) saturated hydrocarbon (2) saturated carbinol, (3) saturated diol. The saturated hydrocarbon was not readily isolated pure due to azeotrope formation with the solvents used and the saturated carbinol. In fact, a fairly large intermediate distillation fraction of saturated hydrocarbon and carbinol was always obtained even with a Podbielniak Heli-Pak (20 plate) column. The final yield of distilled saturated diol was low (7–36%). Physical constants are summarized below for typical saturated carbinols isolated.

TABLE IV

SATURATED CARBINOLS

Compound	°C.	Mm.	n^{20}_{D}
2,5-Dimethylhexane-2-ol	155	760	1.4261
3,6-Dimethyloctane-3-ol	195	760	1.4370
4,7-Dimethyldecane-4-ol	92–93	3	1.4445
			1.4419
2,4,7,9-Tetramethyldecane-4-ol	88–90	3	1.4354

Summary of Analytical Methods.[15]—The 1,4-olefinic diols were difficult to analyze with high accuracy due to the ease with which the tertiary hydroxyl groups underwent hydrogenolysis, dehydration, or substitution reactions. Two methods were used: (1) hydrogenation at 30–55 p.s.i. and 65–75° using small amounts of potassium hydroxide to inhibit hydrogenolysis and (2) bromination in methanol using excess sodium bromide and a catalytic amount of aqueous hydrochloric acid.[16]

The hydrogenation method gave pressure drops in the Parr apparatus within 1 p.s.i. of the theoretical value. Fairly good agreement between hydrogenation and bromination values were obtained except in the case of tetramethyldecene diol. The repeatedly high results obtained with this diol may be due to substitution reactions at the hydroxyl groups or the branched methyl groups.

TABLE V

OLEFINIC DIOLS. COMPARISON OF ANALYTICAL METHODS

Olefinic diol	% purity by bromination	% purity by hydrogenation
2,5-Dimethyl-3-hexene-2,5-diol	97.5	96.5
3,6-Dimethyl-4-octene-3,6-diol	98.8	94.8
4,7-Dimethyl-5-decene-4,7-diol	96.1	99.7
2,4,7,9-Tetramethyl-5-decene-4,7-diol	105.0	97.5

2,5-Dimethyl-3-hexene-2,5-diol on recrystallization from hexane gave a purity of 99.8% by bromination.

Purity by Hydrogenation.—An amount of distilled olefinic diol (0.15–0.25 mole) equivalent to a theoretical pressure drop of 12.8–21.3 p.s.i. was dissolved in 100 cc. of *n*-heptane, toluene, methanol, or isopropyl alcohol (heptane preferred if solubility of diol permits) at 65–75° and treated with 0.025 g. of powdered potassium hydroxide, stirred to solution, and hydrogenated to no further pressure drop at 65–75° and an average pressure of 30–55 p.s.i. The hydrogenations generally halted within 1 p.s.i. of the theoretical pressure drop. Azeotropic water analysis by the Dean-Stark method gave insignificant amounts of hydrogenolysis water.

Purity by Bromination.—This method was a modification of the method of Byrne and Johnson.[16] The acetylenic glycols did not react under the above conditions.

Acetylenic Diol Impurity.—Residual acetylenic diol impurity or essentially pure diol was determined by a modification[17] of the known base cleavage[4] of the acetylenic diols into the corresponding ketone and acetylene. The evolved acetylene was absorbed in silver nitrate solution and determined volumetrically.[18]

Water of Hydrogenolysis.—This was readily determined by azeotropic distillation via the Dean-Stark method using either heptane or toluene as hydrogenation solvent.

Saturated Diols.—The purity of the saturated diol was determined by (a) the total pressure drop during hydrogenation, (b) olefinic impurity (expressed as diol) by bromination, (c) water of hydrogenolysis, and (d) boiling range and yield. Both (b) and (c) are negligible while the pressure drop during the reaction was within 1–2 p.s.i. of the theoretical value of 85 p.s.i. per 0.5 mole acetylenic glycol.

---

[15] The services of L. J. Molinini and the Air Reduction Co., Analytical Department, are gratefully acknowledged.

[16] R. E. Byrne and J. B. Johnson, *Anal. Chem.*, **28**, 127 (1956).

[17] Private communication L. J. Molinini to R. J. Tedeschi. New analytical method to be published. Developed by L. J. Molinini (Air Reduction Co. Research Laboratories, Murray Hill, N. J.).

[18] L. Barnes, Jr., and L. J. Molinini, *Anal. Chem.*, **27**, 1025 (1955)