ing the position of the ring double bond has been shown to lead to inconclusive results. These esters were shown to be genuine α-β isomers by ozonolysis experiments.

The α- and β-ionylidene-propyl and -isopropyl ketones were prepared and their absorption spectra measured. The spectral anomaly exhibited by the previously reported α- and β-ionylidene-acetones was found to persist in these homologs.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Investigations on the Stereoisomerism of Unsaturated Compounds. VIII. The Catalytic Hydrogenation of Butadiene[1]

BY WILLIAM G. YOUNG, RICHARD L. MEIER, JEROME VINOGRAD, HOWARD BOLLINGER, LOUIS KAPLAN AND SEYMOUR L. LINDEN

The catalytic hydrogenation of butadiene derivatives by Paal[2] led to the belief that in the presence of highly dispersed platinum or palladium, only completely hydrogenated products were formed even though the reaction was interrupted when only one mole of hydrogen had been absorbed per mole of diene. Lebedev and Yakubchik[3] studied the reduction of several conjugated systems using platinum as a catalyst and obtained evidence for the formation of all possible dihydro-addition products. Since their conclusions were based entirely on the interpretation of the curves for the variation of the rate of absorption of hydrogen with time without verification by chemical analysis, the validity of the work was questioned by other workers.[4,5,6] Ingold and Sha[5] were unable to establish the presence of any dihydro-addition products after 50% hydrogenation of ethyl muconate, and sorbic and vinylacrylic acids. On the basis of this work Ingold and Sha[5] concluded that formation of dihydro products during the hydrogenation of conjugated systems was not the general case. On the other hand, many other workers,[4,7] have reported that the partial catalytic hydrogenation of several butadiene derivatives gave rise to the formation of intermediate dihydro addition products.

The present investigation was undertaken in an attempt to clarify the situation by presenting additional evidence that the formation of intermediate dihydro-addition products is indeed the general case. It is our contention that most of the common low pressure hydrogenation catalysts exhibit a considerable degree of selectivity permitting in certain cases the isolation of dihydro products in excellent yields from partial hydrogenation of conjugated carbon–carbon double bonds. Butadiene was chosen for study because the reaction products readily lend themselves to analysis by several methods.

The hydrogenation of butadiene was studied in the presence of four catalysts, platinum (from platinum oxide), palladium (from palladium oxide), palladium on barium sulfate and Raney nickel. The hydrogenations were carried out at one to two atmospheres pressure in 95% ethanol. In preliminary experiments butadiene was hydrogenated to various degrees and the reaction products analyzed for butane, butene and butadiene by the micro methods of Blacet and Leighton.[8] The analyses were calculated from equations (1) and (2) as follows

$$H = 2N + N_1 \qquad (1)$$

$$N + N_1 + N_2 = 1 \qquad (2)$$

H is moles of hydrogen absorbed and N, N_1 and N_2 are the mole fractions of butane, butene and butadiene, respectively. Equation (1) represents the fact that at any given time the moles of hydrogen absorbed are equivalent to the sum of the moles of butene plus twice the moles of butane formed. N, the mole fraction of butane, is estimated by combustion of the butane after the unsaturated hydrocarbons have been removed. Since the amount of hydrogen absorbed at any given time is accurately known, the values of N_1 and N_2 can be calculated from the simultaneous solution of equations (1) and (2).

Figures 1 and 2 are typical of graphs obtained when per cent. composition is plotted against per cent. hydrogenation. The concentrations of butadiene, butane and butene were found to vary linearly with increase in degree of hydrogenation

TABLE I

COMPOSITION AT THE CRITICAL POINT OF THE HYDROCARBON MIXTURE FROM HYDROGENATION OF BUTADIENE IN 95% ETHANOL

Catalyst	Temp., °C.	% Hydrogenation	% C_4H_6	% C_4H_8	% C_4H_{10}
Pt	−12	70	0	61	39
Pd	−12	54	0	94	6
Pd–$BaSO_4$	− 8	80	0	40	60
Ni	− 8	83	0	34	66

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(1) A portion of this paper was presented before the Division of Organic Chemistry at Cincinnati, April, 1940.

(2) Paal, *Ber.*, **45**, 2221 (1912).

(3) Lebedev and Yakubchik, *J. Chem. Soc.*, 823, 2190 (1928); 220 (1929).

(4) Farmer, *et al.*, *ibid.*, 688 (1933); 304, 1929 (1934).

(5) Ingold and Sha, *ibid.*, 885 (1933).

(6) Campbell and Campbell, *Chem. Rev.*, **31**, 77 (1942).

(7) Muskat and Knapp, *Ber.*, **64**, 779 (1931); Dupont and Pacquot, *Compt. rend.*, **205**, 805 (1937); Issacs and Wilson, *J. Chem. Soc.*, 202, 574, 810 (1936).

(8) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).

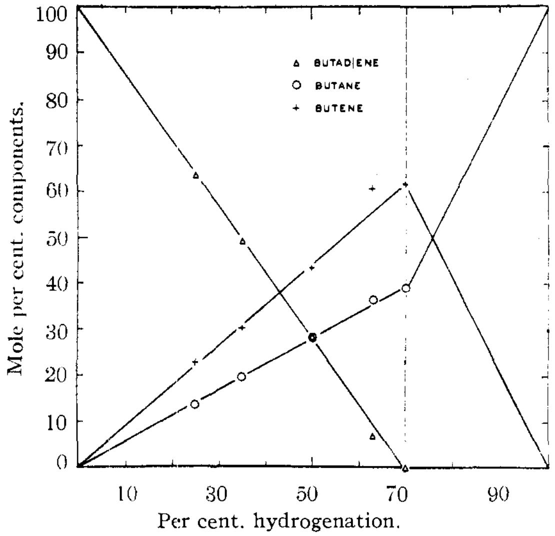

Fig. 1.—Composition of reaction mixture during hydrogenation of butadiene with platinum at −12°.

and the point of disappearance of butadiene (also the point of maximum concentration of butene) readily can be obtained. The per cent. hydrogenation at which the concentration of butadiene becomes zero is the "critical point" of the hydrogenation. Table I lists the composition at the critical point with the catalysts studied.

The linear relationship between butadiene and per cent. hydrogenation is of considerable theoretical interest. Three reactions are possible during the hydrogenations

$$C_4H_6 + H_2 \longrightarrow C_4H_8 \qquad (3)$$

$$C_4H_6 + 2H_2 \longrightarrow C_4H_{10} \qquad (4)$$

$$C_4H_8 + H_2 \longrightarrow C_4H_{10} \qquad (5)$$

One reasonable explanation[9] of the aforementioned linear relationship is the slow rate of reaction (5) in the presence of butadiene (assuming that reaction (3) and (4) proceed with the same order with respect to butadiene). The slow rate of reactions (5) can arise by either a slow specific rate of reaction or by a low concentration of butene on the catalyst due to selective adsorption of butadiene. Since the rate of hydrogenation of butene in the absence of butadiene is comparable to that of butadiene, the observed linear relationship indicates selective adsorption of butadiene preventing the adsorption of appreciable quantities of butene. This will effectively prevent reaction (5) from taking place as long as butadiene is present.

If the proposed explanation be true, the butane formed must arise from the addition of two moles of hydrogen to the butadiene in one step (reaction 4). The hydrogenation of butadiene may thus proceed as two simultaneous reactions, (*a*) the addition of one mole of hydrogen followed by desorption of the butene and (*b*) the addition of two moles of hydrogen producing the butane.

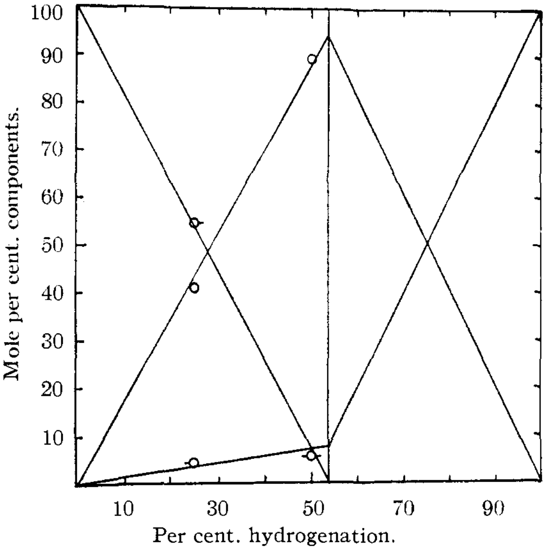

Fig. 2.—Composition of reaction mixture during hydrogenation of butadiene with palladium at −12°: O, butene; O-, butadiene; -O, butane.

The data of Table I indicate beyond doubt the fallacy of the conclusions reached by Ingold and Sha[5] regarding the absence of dihydro-addition products during the catalytic hydrogenation of conjugated systems. The selective nature of the catalysis is exemplified by the results with palladium (from oxide) which permits the isolation of dihydro products (butenes) in 94% yield. These results are in accordance with those of Farmer and co-workers,[4] who obtained the highest yield of dihydrosorbic acid with palladium.

It was of interest to determine whether there would be any change in the composition of the butenes if the hydrogenation were carried past the critical point. A sample of butene made up of 55% 1-butene and 45% 2-butene was hydrogenated to 50% of the theoretical value over palladium (from oxide). The residual butene was found to contain only 5% 1-butene indicating preferential hydrogenation of 1-butene or perhaps more probably a rearrangement of the butenes to an equilibrium mixture during the hydrogenation (see below). These results are in accordance with those of other workers[6,10] obtained from competitive hydrogenations of olefins with different degrees of substitution. A similar experiment using palladium as a catalyst for the hydrogenation of a mixture of *cis*- and *trans*-2-butene indicated that these isomers are reduced simultaneously but that the rate of reduction of the *cis* isomer is somewhat greater than that of the *trans*. These results indicated that during the hydrogenation experiments on butadiene designed to study the com-

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[9] It is also possible to explain this linearity by assuming that the hydrogenation proceeds with zero order with respect to butadiene and butene. Preliminary experiments, however, indicate that this may not be the case.

[10] Davis, Thompson and Crandall, THIS JOURNAL, **54**, 2340 (1932).

position of the hydrogenation products it was undesirable to carry the hydrogenation beyond the critical point.

As had been anticipated, the dihydro-addition product was found to consist of a mixture of 1-butene and *cis*- and *trans*-2-butene. The butene fractions analyzed were those obtained from experiments in which the hydrogenation had been stopped at or before the critical point. The gaseous hydrogenation products were converted to the bromides (to remove butane) and then distilled to remove butadiene tetrabromide if present. The butenes were recovered from the dibromobutanes by treatment with zinc in boiling ethanol. It has previously been shown[11] that conversion to the dibromides and regeneration with zinc causes no appreciable change in the configuration of the butenes. The butene mixtures were analyzed by isothermal distillation according to the method of Frey and Hepp.[12] Analysis of the dibromobutanes by the method of Dillon, Young and Lucas[13] gave results which were within experimental error of those obtained by the fractional distillation method.

The results of the butene analyses, listed in Table II, clearly indicate the marked dependence of the proportions of 1-butene and *cis*- and *trans*-2-butene in the butene mixture upon the catalyst employed. It must be borne in mind that the yields of 1- and 2-butene do not necessarily represent corresponding amounts of 1,2- and 1,4-addition (in the sense that the hydrogen atoms from the same molecule add on the first and second or first and fourth atoms of butadiene respectively). During the reaction of hydrogen and olefin on the catalyst, whether by an associative[14] or dissociative[15] mechanism, there is a possibility of rearrangement of the butene produced to an equilibrium mixture before desorption.

TABLE II

COMPOSITION OF BUTENES OBTAINED FROM PARTIAL HYDROGENATION OF BUTADIENE IN 95% ETHANOL

Catalyst	Temp., °C.	% Hydrogenation	% 1-Butene	% *trans*-2-Butene	% *cis*-2-Butene
Pt	−12	68	72.1	18.4	9.5
Pd	−12	50	48.5	40.1	11.4
Pd–$BaSO_4$	28	55–75	5.0	67.5	25.7
Pd–$BaSO_4$	− 8	78	6.0	75.0	19.0
Ni	28	55–75	21.5	61.0	17.5

Calculations based on the data of Thacker, Folkins and Miller[16] indicate that the thermodynamic equilibrium between 1-butene and *cis*- and *trans*-2-butene at −10° is: 1.3–2.0% 1-butene, 14–22% *cis*-2-butene and 76–84% *trans*-2-butene.[17] A consideration of the data of Table II indicates the marked similarity between the calculated thermodynamic equilibrium composition and the composition of the butenes obtained with palladium on barium sulfate. Experiments were carried out in an effort to determine whether or not this similarity was due to a rearrangement to a true equilibrium during the hydrogenation. The results of the experiments described below indicate that the rearrangement does occur. Such a rearrangement of the butenes to an equilibrium over nickel has been reported by Twigg.[18]

. A sample of 1-butene was hydrogenated to 20% of the theoretical value at −8° and one atmosphere pressure in 95% ethanol over palladium on barium sulfate. Analysis of the residual butenes showed the presence of 8% 1-butene and 92% 2-butene. Hydrogenation of 2-butene to 50% of the theoretical at room temperature and two atmospheres pressure using the same solvent and catalyst yielded a butene fraction containing 8.5% 1-butene, 20.5% *cis*- and 71.0% *trans*-2-butene. The composition of the butenes from both of the above described experiments were within experimental error of the calculated equilibrium value indicating that the supported palladium catalyst causes rearrangement of both 1- and 2-butene to an equilibrium mixture.

The catalyst itself (palladium on barium sulfate) in the absence of hydrogen does not cause the rearrangement to take place. 1-Butene remained unchanged when shaken for twenty-four hours with this catalyst in ethanol. This result was to be expected in view of the proposed mechanisms for such a reaction[14,15] and the experiments with nickel by Twigg.[18] A sample of this same catalyst was shaken with hydrogen in ethanol and then the excess hydrogen removed under moderate vacuum. This treated catalyst, containing presumably a layer of adsorbed hydrogen, also failed to catalyze rearrangement of 1-butene. Apparently the adsorbed hydrogen (whose presence is necessary for rearrangement[18]) was removed by formation of butane too quickly for any appreciable amount of rearrangement to occur.

Experimental

Purification of Butadiene,[19] Preparation of Tetrabromide.—Fifty-gram portions of crude butadiene were passed into an all-glass wash bottle containing slightly more than the calculated quantity of bromine in two parts of carbon tetrachloride, maintained at a temperature of −10°. Near the end of the reaction the solid tetrabromide began to crystallize. The reaction mixture was

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[11] Young and Winstein, THIS JOURNAL, **58**, 102 (1936).

[12] Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933); Goldsby, Doctorate Dissertation, Northwestern University.

[13] Dillon, Young and Lucas, THIS JOURNAL, **52**, 1953 (1930).

[14] Twigg, *Trans. Faraday Soc.*, **35**, 934 (1939); Rideal, *Chemistry & Industry*, 335 (1943).

[15] Farkas, *Trans. Faraday Soc.*, **35**, 906 (1939).

[16] Thacker, Folkins and Miller, *Ind. Eng. Chem.*, **33**, 584 (1941).

[17] Calculation of the equilibrium composition from the standard free energies at −10° from the equations of Thacker, *et al.*,[15] yield the following composition: 1.5% 1-butene, 17.8% *cis*- and 80.7% *trans*-2-butene. The limits of the calculated composition reported above in the text are obtained by calculation assuming, at best, a minimum error of 100 cal. in the free energies.

[18] Twigg, *Proc. Roy. Soc.* (*London*), **A178**, 106 (1941).

[19] Purchased from Ohio Chemical Co., Cleveland. Butadiene for some of the early experiments was kindly furnished by the Shell Development Co., Emeryville, Calif., through the courtesy of Dr. E. C. Williams.

allowed to warm to room temperature before being poured into a beaker where it was washed successively with dilute aqueous sodium bisulfite, sodium bicarbonate and water. The aqueous phase was removed each time by decantation. The solid tetrabromide was finally filtered by suction and dried. It was then recrystallized several times from 95% ethanol; m. p. 117°. No attempt was made to purify the liquid tetrabromide as such. Instead, the carbon tetrachloride was removed and the crude liquid tetrabromide treated with zinc and alcohol. The resulting butadiene was passed into the bromination apparatus and more solid tetrabromide prepared.

Regeneration of the Butadiene.[20]—Purified butadiene was liberated from solid tetrabromide by the action of zinc in alcohol. The apparatus shown in Fig. 3 was devised to eliminate the difficulty of controlling the reaction. The flask (B) contains 80 g. of zinc suspended in boiling alcohol. The alcohol condensate from condenser (C) drops onto the tetrabromide in the Soxhlet extractor (A) and hence into flask (B) where butadiene is generated. The butadiene was purified by passing it through 23% perchloric acid (D), a drying train of calcium chloride and anhydrous calcium sulfate (E) into the receiver (F) maintained at −80°. The receiver was then sealed and held ready for use.

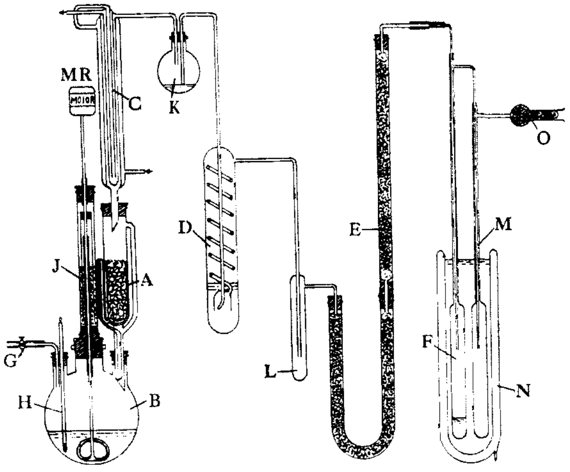

Fig. 3.

Preparation of the Catalysts.—The platinum oxide was prepared by the method of Adams, Voorhees and Shriner[21] and the palladium oxide was prepared by the method of Shriner and Adams.[22] The use of palladium nitrate in place of palladium chloride during the preparation of Schmidt's palladium on barium sulfate catalyst[23] yielded a catalyst of markedly lower activity unless the product was washed far more thoroughly than was required with catalyst prepared from palladium chloride. Use of excess formalin in the reduction of the palladium salts produced catalysts of almost no activity. The Raney nickel was prepared from aluminum-nickel alloy according to Covert and Adkins.[24]

The Hydrogenation Procedure.—The apparatus for the catalytic reduction is shown in Fig. 4. It consists of a reaction flask (B) which is mounted on a mechanical shaker (not shown in figure) and a buret (A) from which a known volume of hydrogen may be introduced. The pressure, measured by manometer (G) was kept as near to atmospheric as possible. The catalyst (or its oxide) was suspended in 50 ml. of 95% ethanol in the reaction flask (B). The flask was evacuated through the stopcock (J) by means of vacuum line (N) until the alcohol boiled. Hydrogen was then admitted through stopcock (J) from line (F) and the catalyst was reduced if necessary. The butadiene sample in ampule (C) was connected to the reaction flask with a short piece of heavy gum rubber tubing. The flask was again evacuated and a refrigerant was circulated through the glass jacket surrounding the flask (B) until the thermometer (E) recorded a constant temperature (usually −8 to −12°). The tip of the butadiene ampule was broken by bending the rubber connection and the butadiene was condensed in the flask which was then shaken for several minutes to ensure equilibrium conditions. Stopcocks leading to the hydrogen buret were then opened and the reduction of the butadiene was started. In the preliminary runs (see below) where small amounts of hydrogen were used a correction was applied for the volume of hydrogen needed to saturate the alcohol solution under the conditions of the experiment. The hydrogen used was commercial C. P. tank hydrogen.

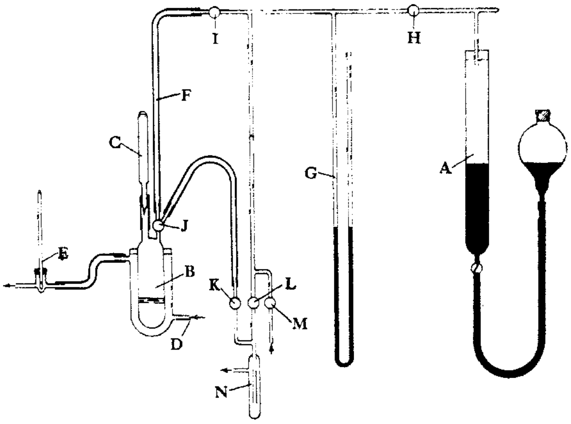

Fig. 4.

Isolation of Reduction Products. (A) Preliminary Runs.—These experiments were carried out with 1 g. (0.02 mole) samples of butadiene and thirty to fifty mg. of catalyst in the apparatus of Fig. 4 as described above. The hydrogenations were stopped at various degrees of hydrogenation and the gaseous reaction products were analyzed for butane, butene and residual butadiene. The time required to absorb the necessary quantity of hydrogen was usually fifteen minutes to one hour depending upon the experimental conditions and the catalyst.

After the calculated amount of hydrogen had been absorbed the stopcock (J) (Fig. 4) was closed and the refrigeration jacket surrounding the reaction flask was removed. A pinch-cock was placed on the heavy rubber tubing holding the ampule (C), the ampule removed and the reaction flask (B) was connected to condenser (P) of the apparatus shown in Fig. 5. The reaction flask (B) was then allowed to come to room temperature and finally was heated slowly to the boiling point of the alcohol by means of a water-bath. The hydrocarbon mixture of butadiene, butene and butane was freed of solvent by passing through the spiral gas washer (Q), containing 23% perchloric acid, and the calcium chloride tube (S) and then condensed at −80° in trap (Y). Stopcocks (3) and (4) were then closed and stopcock (2) was opened to the reservoir (U) which had previously been evacuated to a pressure of one mm. The Dewar flask was removed from (Y) and placed around reservoir (U). By warming (Y) the hydrocarbon mixture was transferred from trap (Y) to (U) by evaporation. Stopcock (2) was then closed and the Dewar flask removed from (U). The volume of the reservoir (U) had been adjusted so that 0.02 mole of gas would exert a pressure of about one and one-half

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(20) Thiele, *Ann.*, **308**, 339 (1899); Kistiakowsky, *et al.*, THIS JOURNAL, **58**, 146 (1936).

(21) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. I, p. 463.

(22) Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

(23) Schmidt, *Ber.*, **52**, 409 (1919).

(24) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

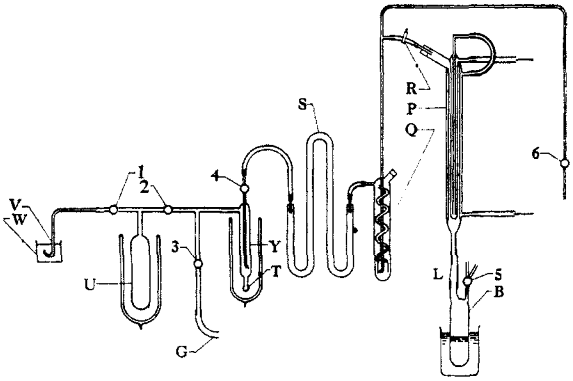

Fig. 5.

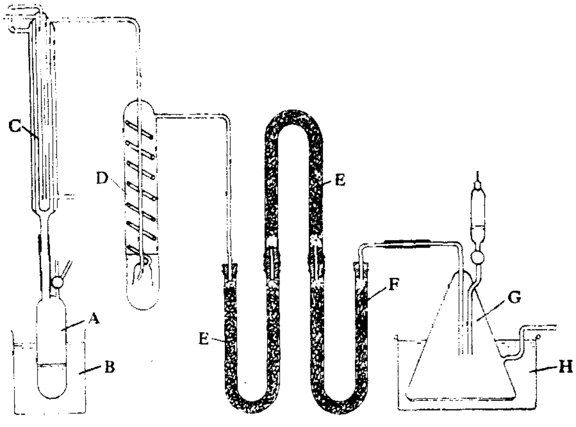

Fig. 6.

atmospheres at room temperature. This procedure of converting the hydrocarbon mixture into the gaseous state assured the maintenance of a uniform sample for analysis. The recovery of the total hydrocarbon was usually 90–95%. After immersing the "goose neck" (V) in the beaker of mercury (W), stopcock (1) was cautiously opened and the air in (V) flushed out with the hydrocarbon mixture. A mercury filled gas cup was then placed over the "goose neck" and a 1-ml. sample of gas was collected by displacement of the mercury. This sample was analyzed by the micro methods of Blacet and Leighton.[8] The unsaturated hydrocarbons were removed with fuming sulfuric acid and the butane was determined by combustion. A new micro method[25] for the selective removal of butadiene was used in some cases. A small bead of maleic anhydride was introduced into a micro cup containing the hydrocarbon mixture suitably mixed with nitrogen. At the sintering point of the maleic anhydride (*ca.* 50°) butadiene was selectively absorbed, undergoing a Diels–Alder condensation. At higher temperatures small amounts of butenes were absorbed.

Isolation of the Hydrogenation Products. (B) Quantitative Analysis of the Butenes.—In these runs 0.1–0.4 mole of butadiene was partially hydrogenated (over 0.2–0.4 g. catalyst) in the apparatus of Fig. 4 so as to obtain a maximum yield of butene and a minimum of butadiene in the reaction mixture. The conditions used in these hydrogenations are listed in Table II. These hydrogenations usually required one to eight hours to attain the desired degree of hydrogenation. With Raney nickel the hydrogenation of the fairly large amounts of butadiene required in these runs proceeded too slowly at atmospheric pressure and −9° to be practicable. Therefore hydrogenations with this catalyst were run at 20–40 lb. pressure and at room temperature. The critical point under these conditions appeared to be at a lower (55–60%) degree of hydrogenation than at the lower pressure and temperature used in the preliminary runs. Some hydrogenation experiments at the higher pressure and temperature were also carried out with palladium on barium sulfate, see Table II.

The reaction flask containing the hydrocarbons was disconnected from the hydrogenation apparatus as has been described above and connected to condenser (C) of the apparatus pictured in Fig. 6. The hydrocarbon mixture was boiled out of the solvent and passed through 23% perchloric acid solution in gas washer (D), then through the calcium chloride tube (E) into the bromination flask (G) which contained a small amount of liquid bromine at a temperature of −12°. Bromine was added through the dropping funnel at such a rate that the reaction mixture contained only a slight excess of bromine at any time. At the conclusion of the experiment, dry nitrogen was passed through the flask to sweep out remaining traces of hydrocarbon. The crude dibromobutane mixture was washed with dilute sodium bisulfite solution, dilute sodium bicarbonate solution and water and was finally dried over calcium chloride. The dibromides were distilled at reduced pressure to ensure the absence of butadiene tetrabromide and dissolved butane. The comparatively large quantities of dibromobutanes rendered negligible the mechanical losses during the distillation. The dibromobutane mixture was then treated with zinc dust in hot alcohol to regenerate the butenes. The recovery of butenes from the dibromide was usually better than 90%. The butene gas was washed with 23% perchloric acid dried by passing over calcium chloride and calcium sulfate and condensed at −78° in a Pyrex bulb which was then sealed and kept until needed for analysis. The butenes were analyzed for 1-butene and *cis*- and *trans*-2-butene content by fractional distillation in a Frey–Hepp column.[12] The purified dibromobutanes were also analyzed by the method of Dillon, Young and Lucas.[13]

Comparison of the Distillation and Dibromide Method of Analysis.—The following are the results of analysis of a butene fraction by both the distillation method[12] and the dibromide method[13]: (the value obtained by the distillation method is listed first followed by the dibromide value in parentheses) 1-butene, 51.4% (49.5); *cis*-2-butene, 28.0% (30.6); *trans*-2-butene, 20.5% (20.0). Another butene sample yielded the following: *trans*-2-butene, 58.6% (58.4); *cis*-2-butene, 41.4% (41.6).

Summary

Butadiene has been hydrogenated in the presence of several common low pressure catalysts. These catalysts were found to exhibit a high degree of selectivity permitting the isolation in certain cases of high yields of dihydro-addition products. The dihydro products (butenes) have been analyzed for 1-butene and *cis*- and *trans*-2-butene content. Palladium on barium sulfate catalyst, in the presence of hydrogen, has been found to catalyze the rearrangement of 1-butene and 2-butene to an equilibrium mixture.

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[25] Blacet and Crose, unpublished work.