Hydrogenolyses with Chloroaluminum Hydrides. III. Allylic Alcohols

JAMES H. BREWSTER AND HORST O. BAYER[1]

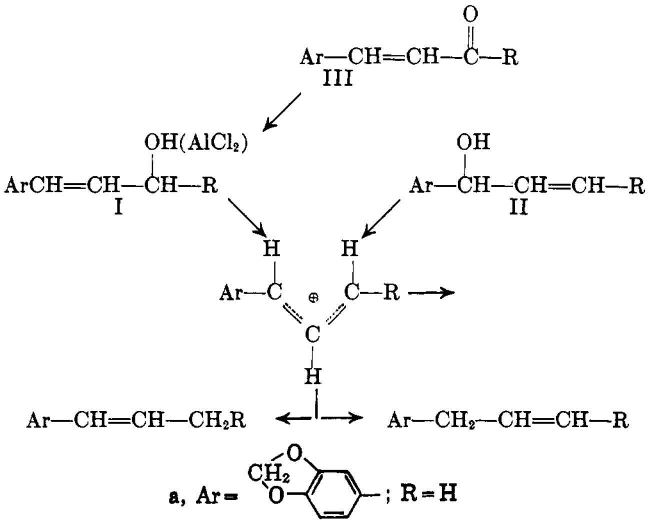
Department of Chemistry, Purdue University, Lafayette, Indiana

Received June 7, 1963

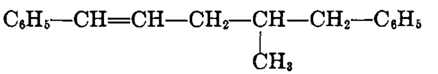
Hydrogenolysis of an allylic alcohol with a 3:1 mixture of aluminum chloride and lithium aluminum hydride gives the products to be expected from reduction of the allylic carbonium ion, often accompanied by dehydration products. In several cases the corresponding α,β-unsaturated carbonyl compounds were found to give the same mixtures of products, indicating that they are hydrogenolyzed *via* the alcohols. Several allylic isomers were shown to give identical distributions of *reduction* products, but tertiary alcohols gave larger amounts of dehydration products. The products of hydrogenolysis of cinnamyl alcohol, 1-phenylallyl alcohol, benzalacetone, carvone, 1,5-dimethylcyclohexen-3-one (and 3-ol), 1-vinylcyclohexanol, cyclohexylideneethanol, 1-acetylcyclohexene, pulegone, linalool, nerol (and neral), and geraniol were determined. The products derived from nerol were largely cyclic, those from geraniol largely acyclic.

Our studies of the hydrogenolysis of the diphenylallyl alcohols[2] and of benzylic alcohols[3] with mixtures of aluminum chloride and lithium aluminum hydride indicated that this reaction was potentially of value in synthesis since in some cases single products were formed in such large amounts that isolation and purification was easy. In other cases more complex mixtures were obtained but these were often rich in the less stable products and so could serve as sources from which small amounts of these substances might be isolated by v.p.c. A preference for retention of the geometry of the original allylic double bond was observed, suggesting that this reaction also might be useful in stereochemical correlations. It seemed desirable, therefore, to establish the characteristics of this method of hydrogenolysis by determining the products formed from a variety of allylic alcohols.

Birch and Slaytor[4] found that 3,4-methylenedioxycinnamyl alcohol (Ia) was reduced to a mixture of the 1- and 3-arylpropenes by a 2:1 mixture of aluminum chloride and lithium aluminum hydride in ether, but stated that cinnamyl alcohol (Ib) was not reduced under their conditions. These observations are consistent with the carbonium ion mechanism[4] shown subsequently. On the other hand, it has been reported that benzalacetone (IIIc), which should be reduced easily to the alcohol (Ic), gave a mixture of 1-phenyl-1-butene (isolated) and *n*-butylbenzene (detected by v.p.c. analysis)[5] when reduced with a similar reagent system. We have found that cinnamyl alcohol (Ib) can be reduced in a few hours at room temperature with excess 3:1 reagent[6] ("dichloroaluminum hydride") to a hydrocarbon mixture, the monomer fraction of which consisted of 71% *trans*-1-phenylpropene, 29% of allylbenzene, and *ca.* 0.5% of *n*-propylbenzene. Each of these products was isolated by preparative v.p.c. and identified by refractive index and infrared spectrum; the identification and v.p.c. analysis were checked by use of authentic samples. The same mixture (63% yield) was obtained from a reaction run at reflux temperature for one day, indicating again[2] that simple olefins are neither reduced nor isomerized by the reagent. As expected from the carbonium ion mechanism for cleavage of the carbon–oxygen bond,[4] the same monomer mixture also was received (64%) from 1-phenylallyl alcohol (IIb) under these conditions. In this case the still-pot residue was examined; from this residue was obtained about 16% of a product which appears, from its boiling point, composition, infrared, ultraviolet and n.m.r. spectra to be *trans*-1,5-diphenyl-4-methyl-1-pentene (IV). This by-product is that to be expected from alkylation of 1-phenylpropene by the carbonium ion, followed by reduction. Benzalacetone (IIIc) was similarly reduced with excess 3:1 reagent, giving 69% of a monomer fraction consisting of 76% of *trans*-1-phenyl-1-butene and 33% of *trans*-1-phenyl-2-butene (both isolated by v.p.c.). No *n*-butylbenzene was found; even trace amounts could have been detected in our v.p.c. analyses.



b, Ar = C_6H_5; R = H
c, Ar = C_6H_5; R = CH_3



C_6H_5—CH=CH—CH_2—CH(CH_3)—CH_2—C_6H_5

IV

The reduction of (+)-carvone (V, v.p.c. purified, 96% optically pure) with excess 3:1 reagent gave nearly *racemic* dipentene (2% excess (−) isomer, v.p.c. purified) suggesting that most of the product was formed from the symmetrical carbonium ion. Assuming that the slight optical activity is not due to trace impurities, this result indicates that another pathway of reaction,

---

[1] The authors gratefully acknowledge the financial support of this research by the National Science Foundation (NSF-G 10051).

[2] J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105 (1964).

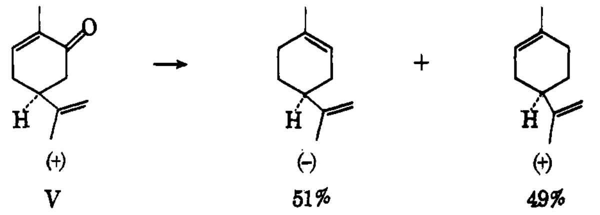
[3] J. H. Brewster, H. O. Bayer, and S. F. Osman, *ibid.*, **29**, 110 (1964).

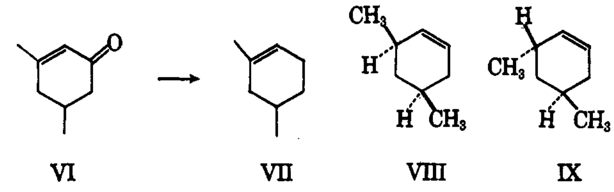
[4] A. J. Birch and M. Slaytor, *Chem. Ind.* (London), 1524 (1956).

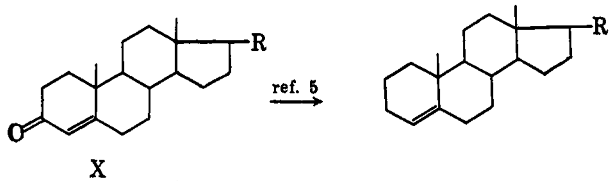
[5] J. Broome, B. R. Brown, A. Roberts, and A. M. S. White, *J. Chem. Soc.*, 1406 (1960).

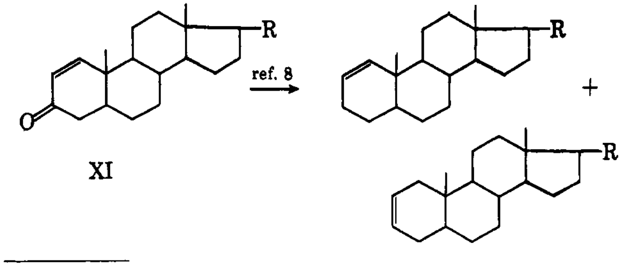
[6] This reagent is prepared by mixing 3 moles of aluminum chloride with one of lithium aluminum hydride in ether to give solutions about 1 *M* in active hydride. This reagent can be stored for several months at −4° if it is freed of the sediment which forms within an hour of mixing. In most of our work we have used amounts of reagent solution containing 4 moles of active hydride per mole of alcohol or ketone.

possibly involving reduction of the olefinic double bond followed by dehydration, may be available[7]; this pathway does not seem to be of great importance with 3:1 reagent. Hydrogenolysis of 1,5-dimethylcyclohexen-3-one (VI) gave, after two hours at room temperature, 65% of a hydrocarbon containing (v.p.c. analysis) six components. One of these, forming 70% of the mixture, was isolated by v.p.c.; its n.m.r. spectrum was that to be expected of 1,5-dimethylcyclohexene (VII). Two other components (15% and 3%) had retention times on oxyadiponitrile suggesting that they also were monoolefins. They were collected and hydrogenated to give a mixture of two saturated hydrocarbons; the principal component of this mixture (80%) was isolated (v.p.c.) and identified (infrared spectrum) as *cis*-1,3-dimethylcyclohexane, indicating the second most abundant monoolefin product to be *cis*-3,5-dimethylcyclohexene (VIII). The third monoolefin might, thus, be the *trans* isomer (IX), these being the three expected reduction products. The retention times of the remaining components (totaling 12%) suggest that they are dienes, formed by dehydration of the allylic alcohol. A sample of the alcohol formed as major product on reduction of the ketone with aluminum isopropoxide gave the same mixture of mono- and diolefins as the ketone. These results, taken with those obtained in the steroid series, where cholest-4-en-3-one (X) gave cholest-4-ene[5] and where cholest-1-en-3-one (XI) gave (in low yield) a 2:1 mixture of cholest-1-ene and cholest-2-ene (among other products),[8] suggest that a cyclohexenyl carbonium ion will tend to add hydride at its less sterically hindered end. This often will give the more stable olefin but the stability of the olefins cannot be crucial since cholest-1-ene is less stable than cholest-2-ene,[9] yet is formed in greater amounts.[8]

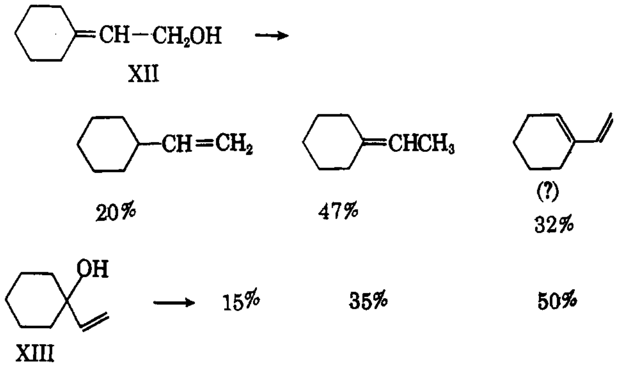


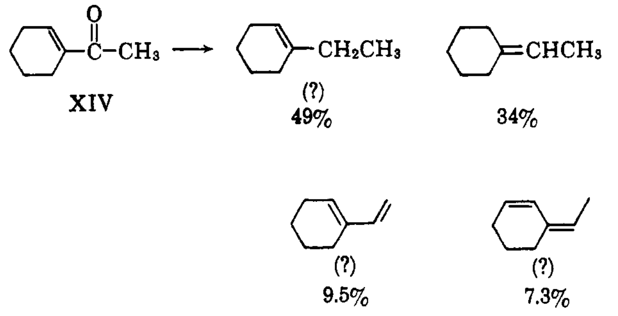


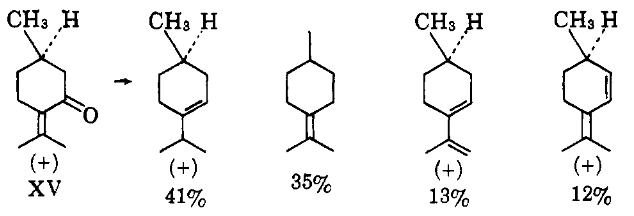




Cyclohexylideneethanol (XII) and 1-vinylcyclohexanol (XIII) can give the same carbonium ion and gave the same mixture of monoolefins (30% vinylcyclohexane and 70% ethylidenecyclohexane). Major amounts of a diene, believed to be 1-vinylcyclohexene, also were formed, XIII giving the larger amount, indicating that at least a part of the diene derived from the tertiary alcohol was formed by a pathway not involving the common carbonium ion. The hydrocarbon from 1-acetylcyclohexene (XIV, 71%) contained two major components (49% and 34%), the less abundant of which had the same retention time as ethylidenecyclohexane. These components could be separated from the others but not from one another on a preparative Carbowax column; the mixture showed all the infrared bands of ethylidenecyclohexane and of 1-ethylcyclohexene but no other bands; thus it is thought to be a mixture of the two. One of the minor components had the same retention time as the diene formed from XII and XIII, suggesting that it is 1-vinylcyclohexene. (+)-Pulegone (XV) gave four products, each of which was isolated. The two principal products were identified as (+)-3-menthene (41%) and 4-menthene (35%); the minor products (12% and 13%) were the dextrorotatory dienes, 2,4(8)-menthadiene and 3,8-menthadiene.







---

[7] The reduction of chalcones (III, R also aromatic) with 2:1 reagent systems is reported to occur with specific shifting of the double bond to the original carbonyl carbon atom: M. M. Bokadia, B. R. Brown, D. Cobern, A. Roberts, and G. A. Somerfield, *J. Chem. Soc.*, 1658 (1962).

[8] R. Albrecht and C. Tamm, *Helv. Chim. Acta*, **40**, 2216 (1957).

[9] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4122 (1957).

TABLE I

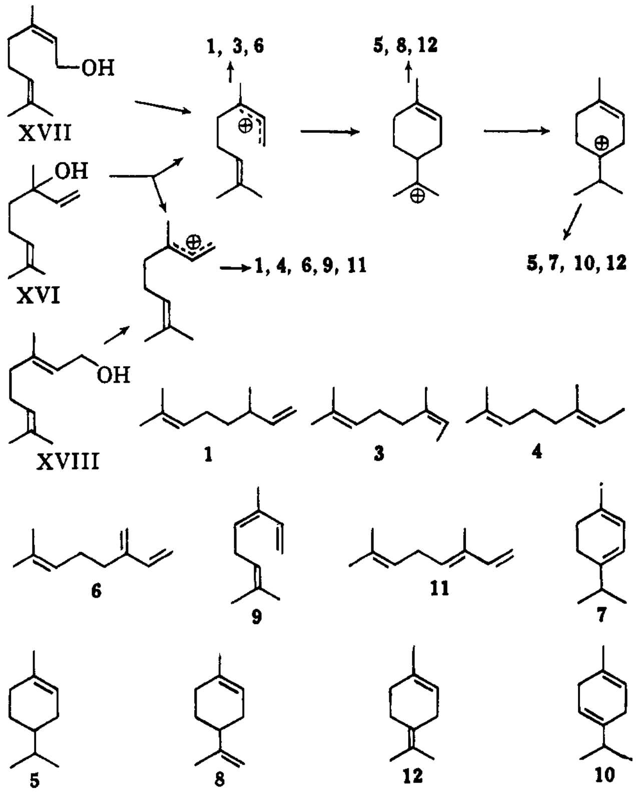
MIXED HYDRIDE REDUCTION OF ACYCLIC TERPENE ALCOHOLS

Product	Peak[a]	Relative retention time[b]	$n^{20}D$[c]	% in hydrocarbon from: Nerol	Geraniol	Linalool
3,7-Dimethyl-1,6-octadiene	**1**	0.33[d]	1.4376 (1.4370)[e,f]	1.7	14.0	13.0
Unknown	**2**	0.44	Not isolated	2.9	0.7	0.8
2,6-Dimethyl-*cis*-2,6-octadiene	**3**	0.48	1.4476	6.0	1.6	7.7
2,6-Dimethyl-*trans*-2,6-octadiene	**4**	0.53	1.4502 ($n^{17}D$ 1.4517)[g]	1.8	60.0	29.0
1-*p*-Menthene	**5**	0.68[d]	Not isolated	13.0	2.4	2.8
Myrcene	**6**	0.75[d]	1.4689 (1.4697)[e,h]	2.0	6.3	22.0
α-Terpinene	**7**	0.88[d]	Not isolated	3.8		1.0
Dipentene	**8**	1.00[d]	1.4728 (1.4720)[e,h]	51.0	3.9	7.0
Ocimene-A	**9**	1.18	1.4859 (1.4873)[h]		3.3	4.6
γ-Terpinene	**10**	1.30[d]	Not isolated	5.8		0.8
Ocimene B	**11**	1.35	1.4890 (1.4862)[i]		6.8	8.8
Terpinolene	**12**	1.60[d]	1.4888 (1.4888)[e,h]	13.0	1.5	1.7

[a] These numbers are used to identify the structures shown in the text. [b] On Carbowax 20 M at 70–85°, relative to dipentene as measured from an air peak. Ocimene B and γ-terpinene were not completely resolved on this column but were on oxyadiponitrile–silver nitrate. [c] Products from hydrogenolysis of linalool, trapped on emergence from v.p.c. on repetitive analyses. Reinjection showed each isolated substance to be at least 98% pure (sharp, smooth symmetrical v.p.c. peaks). Values in parentheses are literature values for samples from which published infrared spectra were obtained. [d] Retention time identical with that of an authentic sample (alone and in admixture). [e] Infrared spectrum identical with that of authentic sample (direct comparison). Authentic samples: **1**, International Flavors and Fragrances; **5**, Dr. K. Murray; **6**, Hercules Powder Co.; **8**, Eastman Kodak Co.; **7, 10, 12**, The Glidden Co. [f] See ref. 11. [g] See ref. 10. [h] See ref. 12. [i] See ref. 14.

The terpene alcohol, linalool (XVI), gave twelve products on reaction with four equivalents of 3:1 reagent for five hours at room temperature (Table I). Eight of these could be isolated by v.p.c. and were identified by their infrared spectra; three more were tentatively identified by comparisons of retention times with authentic samples. Most of the same products also were formed from the stereoisomeric primary alcohols, nerol (XVII) and geraniol (XVIII). About 87% of the product from nerol, but only 8% of that from geraniol, was cyclic. This result indicates that the stereoisomeric allylic carbonium ions are not interconverted to any great extent before further reactions intervene. The cyclized carbonium ion suffered loss of a proton to a greater extent than reduction while the reverse was true of the acyclic intermediate. Here again the tertiary alcohol of series XVI gave more direct dehydration (33%) than did the others.

Several of these products are of interest. The major product from geraniol (60%) and linalool (29%) has an infrared spectrum identical with that of the 2,6-dimethyl-2,6-octadiene formed on reduction of geraniol with sodium and alcohol[10]; it is, therefore, presumed to have the geranyl configuration about the double bond (**4**). A second substance, with a similar retention time and a very similar infrared spectrum, is the major *noncyclic* compound from nerol and is, therefore, probably the geometric isomer (**3**). All three of the terpene alcohols gave as the fastest moving product a substance having the same infrared spectrum as 3,7-dimethyl-1,6-octadiene (**1**), which has been prepared by pyrolysis of pinane at 450°[11]; this is the other product to be expected from reduction of either of the acyclic carbonium ions. Two ocimenes were obtained, as products of dehydration along with myrcene, from geraniol and linalool. The infrared spectrum of one ("Ocimene-A," **9**) is identical with that of a hydrocarbon prepared by cracking α-pinene[12,13] while the spectrum of the other ("Ocimene-B," **11**), though very similar, differs in just those respects in which that of the ocimene from oil of lavender differs from the first.[14] In this case the configurations cannot be deduced from those of the allylic alcohols; the formation of "Ocimene-A" from α-pinene[13] and the sensitivity of this isomer to thermal rearrangement[15] indicate that their configurations[16] are as shown.



---

(10) N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 1541 (1947); R. F. Naylor, *ibid.*, 1532 (1947).

(11) H. Pines, N. E. Hoffman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **76**, 4412 (1954).

(12) R. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

(13) J. E. Hawkins and W. A. Burris, *J. Org. Chem.*, **24**, 1507 (1959).

(14) Y.-R. Naves and P. Tullen, *Helv. Chim. Acta*, **43**, 1619 (1960); **44**, 316 (1961).

(15) J. Wolinsky, B. Chollar, and M. D. Baird, *J. Am. Chem. Soc.*, **84**, 2775 (1962). These workers used samples of the two ocimenes isolated by v.p.c. from our product of reduction of linalool.

We conclude that this reaction cannot be counted on to give high yields of individual products; on the other hand, it does give mixtures from which small amounts of particular products can be isolated by v.p.c.[15] Even with purely aliphatic primary allylic alcohols where a direct displacement mechanism for cleavage of the carbon–oxygen bond would seem most likely, the products are those to be expected from an essentially free allylic carbonium ion. None of our results with 3:1 reagent require a significant amount of reaction *via* reduction of the double bond followed by elimination[7]; indeed the results reported in the following paper[16] indicate that the saturated alcohols which might be formed in such a process would not react further under the conditions used here. Dehydration of the allylic alcohol is, however, often a significant side reaction; our data suggest that this process cannot occur exclusively by way of a free allylic carbonium ion since it occurs to different extents with compounds which should give the same ion. Here, as before,[2] the geometric configuration of the original double bond is retained to a high degree, suggesting that this reaction may be useful in stereochemical correlations.

Experimental[17]

Hydrogenolysis of Cinnamyl Alcohol.—Cinnamyl alcohol (5.0 g., 37 mmoles) was added dropwise to a cooled solution prepared from 30 ml. of an ether solution containing 37 mmoles of lithium aluminum hydride and a solution of 13 g. (97 mmoles) of aluminum chloride in 60 ml. of ether. The solution was heated at reflux for 1 day and then cooled and treated cautiously with 33 ml. of water followed by 30 ml. of a 20% sodium potassium tartrate solution. The ether extract was extracted with brine, dried over magnesium sulfate, concentrated, and distilled to give 2.74 g. (63%) of hydrocarbons, $n^{22}\mathrm{D}$ 1.5379, collected at 88–92° (52 mm.). Analysis by v.p.c. (Carbowax 20 M, 110°) using authentic samples of allyl benzene (Columbia Organic Chemicals) and 1-phenylpropene (Sapon Laboratories) alone and in admixture for comparison indicated the presence of 70% of 1-phenylpropene and 30% of allylbenzene. Fractionation on a Carbowax preparative column gave 1-phenylpropene, $n^{22}\mathrm{D}$ 1.5489 (lit.[18] $n^{20}\mathrm{D}$ 1.5492), and allylbenzene, $n^{22}\mathrm{D}$ 1.5098 (lit.[19a] $n^{20}\mathrm{D}$ 1.5126, lit.[19b] $n^{25}\mathrm{D}$ 1.5042); the infrared spectra were identical with those of the authentic samples.

In a small scale run, 0.27 g. (2 mmoles) of cinnamyl alcohol was treated with 8 ml. (8 mmoles) of 1 *N* 3:1 reagent for 4 hr. at room temperature. Analysis of the hydrolyzed mixture by v.p.c. showed 71% 1-phenylpropene, 29% allylbenzene, and *ca.* 0.5% of *n*-propylbenzene.

1-Phenylallyl Alcohol.—The procedure of Goering and Dilgren,[20] involving addition of benzaldehyde to vinylmagnesium bromide, was followed to give 83% of crude product, b.p. 74–75° (2 mm.). V.p.c. on Carbowax 20 M at 155° showed the presence of two components; the major component (64%, longer retention time) was readily isolated by use of a preparative Carbowax column and was identified as 1-phenylallyl alcohol, $n^{23}\mathrm{D}$ 1.5392 (lit.[21] $n^{25}\mathrm{D}$ 1.5390). The other component had $n^{23}\mathrm{D}$ 1.5227 and an infrared spectrum indicating the presence of a phenyl group and a hydroxy group but it was not further identified.

Hydrogenolysis of 1-phenylallyl alcohol (purified by v.p.c., 2.69 g., 20 mmoles) with 80 ml. (80 mmoles) of 1 *N* ethereal "dichloroaluminum hydride" for 4 hr. at room temperature gave, after the usual work-up, 1.52 g. (64%) of hydrocarbon collected at 55–60° (1–10 mm.). This mixture was analyzed by v.p.c. and the three components were isolated by preparative v.p.c. and identified by comparisons of their infrared spectra with those of authentic samples: 0.2% *n*-propylbenzene, 30% allylbenzene, and 70% 1-phenylpropene.

Distillation of the still-pot residue gave 0.39 g. of a hydrocarbon, b.p. 140–150° (2 mm.), $n^{20}\mathrm{D}$ 1.5756, apparently homogeneous by v.p.c. on Carbowax 20 M at 220°. Its composition and boiling point are consistent with its being dimeric. The ultraviolet spectrum was styrene-like, $\lambda_{\max}^{\mathrm{EtOH}}$ 252 mμ (ε 14,300), while the infrared spectrum indicated the presence of phenyl-, methyl-, and *trans*-olefin groups. The n.m.r. spectrum (p.p.m., relative to tetramethylsilane, in carbon tetrachloride) showed a doublet at 0.90 ($\mathrm{CH_3{-}\underset{|}{\overset{|}{C}}{-}H}$), a complex set of bands in the region 1.59–2.22 ($\mathrm{{-}\underset{|}{\overset{|}{C}}{-}H}$ and $\mathrm{{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}C{=}C}$), a set in the region 2.28–2.71 ($\mathrm{Ar{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}}$), a set of three at 6.0–6.22, almost identical in shape to those shown in this region by *trans*-1-phenylpropene ($\mathrm{Ar{-}\overset{\overset{H}{|}}{C}{=}\underset{\underset{H}{|}}{C}{-}}$), and one very strong band at 7.10 (phenyl). These peaks and regions indicated protons of the types shown above in the ratio 3:3:2:2:10, whence it seems probable that this substance is *trans*-1,2-diphenyl-4-methyl-1-pentene.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.46; H, 8.76.

Hydrogenolysis of Benzalacetone.—Fresh 3:1 mixed hydride reagent was prepared from 13 g. (100 mmoles) of anhydrous aluminum chloride in 40 ml. of ether and 27 ml. of a 1.27 *M* solution of lithium aluminum hydride in ether (34 mmoles). A solution of 5.0 g. (34 mmoles) of benzalacetone[22] in 15 ml. of ether was added dropwise and the mixture was then let stand 12 hr. at room temperature. Unchanged hydride was decomposed by dropwise addition of 5 ml. of ethyl acetate and then of 25 ml. of water to the cooled solution. The layers were separated and the aqueous layer was extracted with ether. The combined ether layer was dried over sodium sulfate, concentrated, and distilled to give, at 85–88° (22–25 mm.), 3.12 g. (69%) of hydrocarbon, $n^{21.5}\mathrm{D}$ 1.5310. V.p.c. on a Craig polyester product column gave *trans*-1-phenyl-1-butene, $n^{22}\mathrm{D}$ 1.5408 (lit.[23] $n^{16}\mathrm{D}$ 1.5414, lit.[24] $n^{20}\mathrm{D}$ 1.5387), dibromide m.p. 71–72° (lit.[25] m.p. 70–71°), and *trans*-1-phenyl-2-butene, $n^{22}\mathrm{D}$ 1.5104 (lit.[24] $n^{20}\mathrm{D}$ 1.5101). The infrared spectrum and retention time of the latter were the same as those of an authentic sample (Phillips Petroleum Co., $n^{22}\mathrm{D}$ 1.5110). Analysis of the product mixture by v.p.c. (polyadipate, 150°) indicated it to contain 67% of 1-phenyl-1-butene and 33% of 1-phenyl-2-butene, consistent with the refractive index of the mixture. Virtually the same mixture (66% 1-phenyl-1-butene and 34% 1-phenyl-2-butene) was obtained by reducing 1.0 g. (6.9 mmoles) of benzalacetone with 2:1 reagent from 10.3 mmoles of aluminum chloride and 5.2 mmoles of lithium aluminum hydride. It has been reported that this reduction gives some *n*-butylbenzene[5]; an authentic sample (National Bureau of Standards standard, $n^{22}\mathrm{D}$ 1.4886) showed a shorter retention time on polyadipate than did any of the components of our reduction product mixtures. Less than 1% of this material could have been detected.

Hydrogenolysis of (+)-Carvone.—A sample of (+)-carvone (Matheson Coleman and Bell) was purified by v.p.c. on a preparative polyester column at 175° and had $\alpha^{20}\mathrm{D}$ +58.20° (1-dcm. capillary tube). The ketone (2.0 g., 13.3 mmoles) was added dropwise to 60 ml. (60 mmoles) of "dichloroaluminum hydride"

---

[16] J. H. Brewster, S. F. Osman, H. O. Bayer, and H. B. Hopps, *J. Org. Chem.*, **29**, 121 (1964).

[17] Unless otherwise specified, reductions were carried out with stock solutions of 3:1 mixed hydride reagent ("dichloroaluminum hydride").[2,3] Products were analyzed and, where possible, isolated and purified by vapor phase chromatography (v.p.c.) using an Aerograph Model A-90-C. Microanalyses were performed by Dr. C. S. Yeh, Mrs. I. Groten, and Mrs. V. Keblys. Infrared spectra were obtained by Mrs. M. Dilling and author H. O. B. Proton nuclear magnetic resonance (n.m.r.) spectra were obtained by Mr. W. Baitinger, using a Varian A-60 instrument (60 Mc.); δ-values in parts per million from tetramethylsilane.

[18] A. Klages, *Ber.*, **36**, 2574 (1903).

[19] (a) R. C. Huston and K. Goodemoot, *J. Am. Chem. Soc.*, **56**, 2432 (1934); (b) J. F. McKenna and F. J. Sowa, *ibid.*, **59**, 470 (1937).

[20] H. L. Goering and R. E. Dilgren, *ibid.*, **82**, 5744 (1960).

[21] H. L. Goering and R. E. Dilgren, *ibid.*, **81**, 2556 (1959).

[22] N. L. Drake and P. Allen, Jr., "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 77.

[23] A. Klages, *Ber.*, **37**, 2311 (1904).

[24] C. N. Riiber, *ibid.*, **44**, 2393 (1911).

[25] B. Radziszewski, *ibid.*, **9**, 261 (1876).

solution initially at 0° and the solution warmed almost to reflux as the ketone was added. The solution was let stand 2 hr. at room temperature, poured on ice, and worked up in the usual way to give, after distillation at 10–12 mm., 1.26 g. (70%) of crude limonene, $n^{20}\mathrm{D}$ 1.4722, $\alpha^{20}\mathrm{D}$ −2.26° (1 dcm.). This product was purified on a polyester preparative v.p.c. column at 85° and then had $n^{20}\mathrm{D}$ 1.4728 (lit.[26] $n^{18}\mathrm{D}$ 1.4727, lit.[12] $n^{20}\mathrm{D}$ 1.4720), $\alpha^{20}\mathrm{D}$ −1.56° (1 dcm.), infrared spectrum identical with a published one.[12] The carvone was about 96% optically pure[27] while the limonene was about 1.5% optically pure.[28]

Hydrogenolysis of 1,5-Dimethylcyclohexen-3-one.—A sample of the ketone, prepared by Dr. G. Asato, had $n^{20}\mathrm{D}$ 1.4843 after purification by v.p.c. on a preparative column. Purified ketone (2.48 g., 20 mmoles) was added to 80 ml. (80 mmoles) of ice-cold "dichloroaluminum hydride" in ether. The solution was let stand at room temperature for 2 hr. and worked up as usual to give 1.42 g. (65%) of hydrocarbon distillate. Analysis by v.p.c. on oxyadiponitrile–silver nitrate at 30° indicated the presence of three monoolefins (A, 15%; B, 3%; C, 70%) as well as three dienes which, together, constituted about 12% of the product. The monoolefins were separated into two fractions by preparative v.p.c., the two lesser components being collected together ($n^{20}\mathrm{D}$ 1.4383) and the major (slower-running) component being isolated pure, $n^{20}\mathrm{D}$ 1.4465.[29]

The n.m.r. spectrum (Varian A-60 instrument, carbon tetrachloride with tetramethylsilane as internal reference) showed three well resolved peaks (p.p.m.): a doublet centered at 0.85 (H—C—CH_3), a sharp singlet at 1.65 (=C—CH_3), and a peak at 5.35 (=$\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}$—), with integrated areas in the ratio 3:3:1. Signals for seven more protons formed a broad "hill" in the region 0.60–2.15 p.p.m. This spectrum indicates that this product is 1,5-dimethylcyclohexene. The mixture of minor products was hydrogenated over platinum oxide to give a mixture of two components which could be separated by preparative v.p.c. The fast-moving major component (*ca.* 80%) was identified as *cis*-1,3-dimethylcyclohexane, $n^{20}\mathrm{D}$ 1.4228 (lit.[30] $n^{20}\mathrm{D}$ 1.4229) by comparison of its infrared spectrum with a published one (API-1570).

Vinylcyclohexanol.—A solution of vinylmagnesium bromide in tetrahydrofuran was prepared from 32 g. (0.30 mole) of vinyl bromide and 7.3 g. (0.30 g.-atom) of magnesium according to the procedure of Goering and Dilgren.[20] To this was added dropwise 24.5 g. (0.25 mole) of cyclohexanone. The reaction mixture was stirred overnight and then decomposed with 50 ml. of a cold solution containing 33 g. of ammonium chloride. The organic layer was decanted and the viscous aqueous layer was extracted with four portions of ether. The combined organic solution was dried over sodium sulfate and then over magnesium sulfate, concentrated at the water pump and distilled to give 18.1 g. boiling at 55–56° (7 mm.). This product, as analyzed by v.p.c. on Carbowax 20 M, contained about 70% of one alcohol and 30% of another. Fractionation on a Carbowax preparative column at 155° gave a sample of the main component, vinylcyclohexanol, $n^{23}\mathrm{D}$ 1.4761 (lit.[31] $n^{20}\mathrm{D}$ 1.4777, lit.[32] 1.4755). The other component had $n^{24}\mathrm{D}$ 1.4729 and was not further investigated.

Ethyl Cyclohexylideneacetate.—The procedure of Wittig and Haag[33] for the condensation of carbethoxymethyl–triphenylphosphonium bromide with benzaldehyde was adapted for this preparation. A solution of 43 g. (0.10 mole) of carbethoxymethyl–triphenylphosphonium bromide in 100 ml. of absolute ethanol was added to a solution of 0.10 mole of sodium ethoxide (prepared from 2.3 g. of sodium) in about 100 ml. of ethanol. After 9.8 g. (0.10 mole) of freshly distilled cyclohexanone had been added the mixture was stored at room temperature for 3 days. The solution was filtered and concentrated in a Rinco evaporator and the residue was taken up in pentane. Distillation gave 2.0 g. of unchanged cyclohexanone and 4.4 g. (55%) of a mixture of esters, collected at 62–64° (1 mm.). Analysis and fractionation by v.p.c. on Carbowax 20 M at 150° gave ethyl cyclohexenylacetate (64%), $n^{20}\mathrm{D}$ 1.4623 (lit.[34] $n^{18}\mathrm{D}$ 1.4639), ethyl cyclohexylideneacetate (28%), $n^{20}\mathrm{D}$ 1.4790 (lit.[34] $n^{18}\mathrm{D}$ 1.4799), and about 8% of an unknown substance, $n^{21}\mathrm{D}$ 1.4511.

Cyclohexylideneethanol.—A mixture (1.10 g., 6.6 mmoles) containing 90% of ethyl cyclohexylideneacetate and 10% of ethyl cyclohexenylacetate was obtained from the above mixture by preparative gas chromatography. This was dissolved in 15 ml. of anhydrous ether and the solution was cooled in ice while 10 ml. of 1 *M* lithium aluminum hydride in ether was added dropwise (2 hr.). The solution was then let stand 8 hr. at room temperature and hydrolyzed by dropwise addition of water. Aluminum hydroxide was removed by filtration; the solid was washed several times with ether. The ether solution was dried over sodium sulfate and concentrated. Analysis of the crude product by v.p.c. indicated the presence of two compounds in the ratio of the constituents of the starting material. The major product was isolated and purified by v.p.c. on a preparative Carbowax 20 M column to give 0.52 g. of cyclohexylideneethanol, $n^{20}\mathrm{D}$ 1.4955 (lit.[32] $n^{20}\mathrm{D}$ 1.4910).

Anal. Calcd. for $C_8H_{14}O$: C, 76.17; H, 11.18. Found: C, 76.27; H, 11.50.

Hydrogenolysis of Vinylcyclohexanol and Cyclohexylideneethanol.—"Dichloroaluminum hydride" solution (3.2 ml., 3.2 mmoles) was cooled in ice and 0.10 g. (0.8 mmole) of vinylcyclohexanol was added. The solution was let stand 4 hr. at room temperature, treated with water, dried over anhydrous potassium carbonate, and analyzed by v.p.c. on oxyadiponitrile–silver nitrate at 62°. As analyzed in this way, the product contained, in addition to *ca.* 1% of a fast moving component, two substances, A (15%) and B (35%), with relative retention times of 0.68 and 1.00 and a third substance, C (50%), with a relative (to B) retention time of 2.20; neither vinylcyclohexanol nor cyclohexylideneethanol were present. Identical results were obtained with a reaction time of 15 min. at 45°. The same products were obtained in parallel and concurrent reductions of cyclohexylideneethanol: A, 20%; B, 47%; C, 32%. The individual products from vinylcyclohexanol were isolated in 64% combined yield by v.p.c. on a preparative Carbowax column. Component A was identified as vinylcyclohexane, $n^{20}\mathrm{D}$ 1.4456 (lit.[35] $n^{20}\mathrm{D}$ 1.4462), infrared spectrum identical with a published one (API 1830). Component B was identified as ethylidenecyclohexane, $n^{20}\mathrm{D}$ 1.4620 (lit.[36] $n^{20}\mathrm{D}$ 1.4626, lit.[35] 1.4623), infrared spectrum identical with a published one (API 1962). The third component is believed to be the expected dehydration product, 1-vinylcyclohexene, since its infrared spectrum shows bands at 6.05, 6.2, 10.1, 10.9, and 11.2 μ consistent with this structure. Its refractive index, $n^{19}\mathrm{D}$ 1.5112, is, however, considerably higher than that reported for products obtained by dehydration of vinylcyclohexanol, lit.[37] $n^{20}\mathrm{D}$ 1.4915 (lit.[31] $n^{20}\mathrm{D}$ 1.4952). The isolated components also were used in v.p.c. identification of the products obtained on hydrogenolysis of acetylcyclohexene, where compounds with retention times identical with those of B and C were formed.

1-Acetylcyclohexene.—Ethynylcyclohexanol was converted to acetylcyclohexene by the method of Chanley.[38] From 13 g. (0.10 mole) of starting material there was obtained 8.2 g. of nearly pure (by v.p.c. analysis) acetylcyclohexene, b.p. 63–65° (5 mm.), $n^{20}\mathrm{D}$ 1.4917. A pure sample, $n^{20}\mathrm{D}$ 1.4913 (lit.[38] $n^{20}\mathrm{D}$ 1.4900), was obtained by v.p.c. on a preparative Carbowax column.

Hydrogenolysis of 1-Acetylcyclohexene.—In the usual manner, 3.10 g. (25 mmoles) of 1-acetylcyclohexene was hydrogenolysed with 100 ml. of 1 *M* "dichloroaluminum hydride" in ether for 3 hr. at room temperature to give 1.96 g. (71%) of hydrocarbon distillate. V.p.c. analysis on oxyadiponitrile–silver nitrate at 45° indicated the presence of four constituents. The two principal

---

(26) F. Richter and W. Wolff, *Ber.*, **63**, 1725 (1930).

(27) Based on the values $[\alpha]^{20}\mathrm{D}$ 62.93° [H. Rupe, *Ann.*, **409**, 354 (1915)] and $d^{20}{}_4$ 0.9608 [J. W. Brühl, *Ber.*, **32**, 1224 (1899)].

(28) Based on the value $\alpha^{20}\mathrm{D}$ 55° (5 dcm.): J. von Braun and G. Lemke, *ibid.*, **56B**, 1563 (1923).

(29) O. Wallach [*Ann.*, **396**, 271 (1913)] gives $n^{21}\mathrm{D}$ 1.4466 for a product described as 1,5-dimethylcyclohexene, prepared by dehydration of 1,3-dimethylcyclohexanol.

(30) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," A. P. I. Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953, p. 51 (*trans* isomer has $n^{20}\mathrm{D}$ 1.4309).

(31) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, **20**, 1187 (1955).

(32) I. N. Nazarov, I. N. Azerbaev, and V. N. Rakcheeva, *Bull. acad. sci. URSS, classe sci. chim.*, 419 (1946); *Chem. Abstr.*, **42**, 7730 (1948).

(33) G. Wittig and W. Haag, *Ber.*, **88**, 1664 (1955).

(34) G. A. R. Kon and R. P. Linstead, *J. Chem. Soc.*, 1278 (1929).

(35) J. R. van der Bij and E. C. Kooyman, *Rec. trav. chim.*, **71**, 840 (1952).

(36) O. Wallach and E. Evans, *Ann.*, **360**, 45 (1908).

(37) I. N. Nazarov and T. D. Nagibina, *J. Gen. Chem. USSR* (Eng. Transl.), **23**, 599 (1953).

(38) J. D. Chanley, *J. Am. Chem. Soc.*, **70**, 244 (1948).

ones, A (49%) and B (34%), had similar short retention times while the minor constituents, C (9.5%) and D (7.3%), had longer but similar retention times. Comparisons with samples obtained in the reduction of vinylcyclohexanol indicated that B was ethylidenecyclohexane and C was vinylcyclohexene. The two major components were not resolved on a preparative Carbowax column, but a sample of a mixture of the two, n^{20}_{D} 1.4588, could be obtained. The infrared spectrum contained the bands shown by ethylcyclohexene (API No. 1958) (lit.[39] n^{20}_{D} 1.4576) and by ethylidenecyclohexane (API No. 1962), n^{20}_{D} 1.4260.

Hydrogenolysis of Pulegone.—Pulegone, as purified on a Carbowax 20 M preparative column at 150°, had n^{19}_{D} 1.4878 (lit.[40] n^{19}_{D} 1.4880) and α^{20}_{D} $+20.87°$ (neat, 1 dcm.) (lit.[41] $[\alpha]^{15}_{\mathrm{D}}$ $+23.60°$). Reduction of 2.0 g. (13 mmoles) with 50 ml. (50 mmoles) of 3:1 reagent for 4 hr. at room temperature gave a crude product, containing (by v.p.c.) 83% of hydrocarbon, 7% of menthone and isomenthone, and four components of higher retention time which may be alcohols. The hydrocarbon distillate (1.20 g., 71%) was analyzed and fractionated on a Carbowax 20 M column to give four products which were identified by their refractive indices, optical rotations, and infrared spectra[42,43]: 3-menthene (41%), n^{20}_{D} 1.4522, $[\alpha]^{20}_{\mathrm{D}}$ $+112°$ (*c* 1.00, chloroform) (lit.[42] n^{20}_{D} 1.4519, lit.[44] 1.4523, lit.[44] $[\alpha]^{20}_{\mathrm{D}}$ 114.5°, homogeneous); 4(8)-menthene (35%), n^{20}_{D} 1.4682, optically inactive (lit.[42] n^{20}_{D} 1.4689); 3,8-menthadiene (13%), n^{20}_{D} 1.4930, $[\alpha]^{20}_{\mathrm{D}}$ $+159°$ (*c* 0.898 chloroform) (lit.[43] n^{20}_{D} 1.4936, lit.[12] 1.4893, lit.[41] $[\alpha]^{14}_{\mathrm{D}}$ $+140.6°$); 2,4(8)-menthadiene (12%), n^{20}_{D} 1.5037, $[\alpha]^{20}_{\mathrm{D}}$ $+63°$, (*c* 0.312, chloroform) (lit.[43] n^{20}_{D} 1.5050, lit.[12] 1.5030).

Hydrogenolyses of Linalool, Nerol, and Geraniol.—Commercial linalool (Eastman Kodak, white label) was found to be about 98% pure by v.p.c. on Carbowax 20 M at 130° and was used directly. The alcohol (3.08 g., 20 mmoles) was added dropwise over a 10-min. period to 80 ml. (80 mmoles) of "dichloroaluminum hydride" cooled in an ice bath. The solution was let stand 5 hr. at room temperature and then poured on ice and worked up in the usual way. Flash distillation under vacuum gave 2.26 g. (*ca.* 81%) of hydrocarbon mixture; this mixture was analyzed by v.p.c. on Carbowax 20 M and oxyadiponitrile–silver nitrate (see Table I). Commercial nerol (Fluka), found to contain 39% of geraniol by v.p.c., gave 2.15 g. (77%) of hydrocarbon mixture in a fully parallel experiment.

A sample of pure nerol, n^{20}_{D} 1.4748 (lit.[45] n_{D} 1.4754), was obtained by repetitive gas chromatography at 160° on a Carbowax 20 M analytical column; this product gave a single peak on v.p.c. analysis. Practical grade geraniol (Eastman Kodak) was partially purified by conversion to the crystalline calcium chloride complex[46] and then further purified by v.p.c. on Carbowax 20 M at 180° to give a product with n^{20}_{D} 1.4777 (lit.[47] n^{20}_{D} 1.4766). These two alcohols were separately reduced in parallel runs; 30 mg. (0.2 mmole) of alcohol was added to 0.80 ml. (0.8 mmole) of "dichloroaluminum hydride" in ice-chilled screwcap vials. The vials were closed and held at room temperature for 5 hr. Then several drops of water were added and the ether solutions were transferred to separate vials and dried over potassium carbonate and then sodium sulfate. These mixtures were analyzed by v.p.c. without concentration (see Table I). Assuming 100% material balance in the analysis, it was found that about 10% of alcohol had not reacted in each case; the residual alcohol was, in each case, apparently pure starting material. Infrared spectra were obtained for all substances for which refractive indices are reported; they were identical with those of authentic samples or comparable to published ones.

Commercial citral was fractionated by v.p.c. on Carbowax 20 M at 125°[48] to give a sample of neral, n^{22}_{D} 1.4852 (lit.[49] n^{20}_{D} 1.4869). This substance gave a mixture virtually identical with that obtained from nerol on hydrogenolysis with 3:1 reagent.

---

(39) O. Wallach and P. Mendelsohn-Bartholdy, *Ann.*, **360**, 50 (1908).

(40) J. Doeuvre and H. Perret, *Bull. soc. chim. France*, [5] **2**, 301 (1935).

(41) W. J. Grubb and J. Read, *J. Chem. Soc.*, 242 (1934).

(42) R. L. Frank and R. E. Berry, *J. Am. Chem. Soc.*, **72**, 2985 (1950).

(43) H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955).

(44) A. J. van Pelt and J. P. Wibaut, *Rec. trav. chim.*, **60**, 62 (1941).

(45) A. Béhal, *Bull. soc. chim. France*, [4] **25**, 452 (1919).

(46) J. Bertram and E. Gildemeister, *J. prakt. Chem.*, [2] **53**, 225 (1896); **56**, 506 (1897).

(47) F. Tiemann and F. W. Semmler, *Ber.*, **26**, 2711 (1893).

(48) G. Ohloff [*Tetrahedron Letters*, **11**, 10 (1960)] reports that citral is isomerized at temperatures above 130°; v.p.c. of citral at higher temperatures gave products which were always found to be mixtures on reanalysis.

(49) Y.-R. Naves, *Bull. soc. chim. France*, [5] **19**, 521 (1952).

Hydrogenolyses with Chloroaluminum Hydrides. IV. Saturated and Homobenzylic Alcohols[1]

JAMES H. BREWSTER, STANLEY F. OSMAN, HORST O. BAYER, AND HARVEY B. HOPPS

Department of Chemistry, Purdue University, Lafayette, Indiana

Received June 7, 1963

Saturated alcohols react with "dichloroaluminum hydride" at 60–80° in higher-boiling ethers to give hydrocarbons. Wholly aliphatic secondary and tertiary alcohols give some reduction but large amounts of olefins are formed. β-Phenyl alcohols give predominating reduction of the hydroxy group. Rearrangements suggestive of carbonium ion processes are observed in several instances.

Evidence indicating that hydrogenolyses with mixtures of aluminum chloride and lithium aluminum hydride occur with the formation of carbonium ions[2-5] suggested the possibility that conditions might be found for the hydrogenolysis of saturated alcohols. Orientation experiments (in which the products were analyzed by gas chromatography, but in which individual products were not actually isolated) indicated that saturated secondary and tertiary alcohols do indeed react with "dichloroaluminum hydride"[3-5] in di-*n*-butyl ether or in diphenyl ether at 60–80° to give small amounts of paraffins together with large amounts of olefins. Phenyl-2-propanone gave nearly pure *n*-propylbenzene while benzyldimethylcarbinol gave nearly equal amounts of isobutylbenzene and a mixture of olefins. No hydrocarbons were, however, obtained from 1-hexanol, which was recovered on hydrolysis of the reaction mixture.

In experiments in which pure products were isolated and identified by comparisons of infrared spectra with authentic samples, several other homobenzylic alcohols gave principally products of reduction rather than of elimination. Thus, *trans*-2-phenylcyclopentanol gave phenylcyclopentane containing about 11% of 1-phenylcyclopentene, while 2-phenylcyclohexanol (mixed isomers) gave a 1:2:1 mixture of benzylcyclopentane, phenylcyclohexane, and 1-phenylcyclohexene. Reduction of 1,1-diphenyl-2-propanone, or of the corresponding alcohol, gave 1,2-diphenylpropane.

---

(1) The authors are grateful for financial support from the National Science Foundation (Grant NSF-G 10051).

(2) E. L. Eliel, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **22**, 129 (1961).

(3) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105 (1964).

(4) J. H. Brewster, H. O. Bayer, and S. F. Osman, *ibid.*, **29**, 110 (1964).

(5) J. H. Brewster and H. O. Bayer, *ibid.*, **29**, 116 (1964).