[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

ACETYLENES. III. REACTIONS WITH LITHIUM ALUMINUM HYDRIDE[1]

WILLIAM J. BAILEY AND CHARLES R. PFEIFER[2]

Received May 20, 1955

Since a convenient one-step synthesis of allenes was developed by the treatment of commercially available acetylenic alcohols with hydrochloric acid and lithium aluminum hydride (1), we became interested in the reaction of other acetylene derivatives with lithium aluminum hydride. One of the main uses of this versatile reducing agent has been the reduction of olefin derivatives without the reduction of the carbon-to-carbon double bond. Very little information was available in the literature concerning the reaction of lithium aluminum hydride with derivatives containing a carbon-to-carbon triple bond. In the few cases reported, a triple bond that was conjugated with an unsaturated group was invariably reduced to a double bond. Thus Chanley and Sobatka (2) reduced 1-(1-cyclohexenyl)-1-butyn-3-ol to 1-(1-cyclohexenyl)-1-buten-3-ol with lithium aluminum hydride. Micovic and Mikhailovic (3) reduced a series of conjugated acetylenic acids to the corresponding olefin alcohols; for example, propiolic acid was converted to allyl alcohol. Similarly, Benedict and Russell (4) reduced acetylenedicarboxylic acid to *trans*-2-butene-1,4-diol.

With the exception of the propargyl halides (1, 5), no other acetylenic derivatives have been reduced with lithium aluminum hydride. In previous work (1) it was shown that a tertiary propargyl chloride could be reduced with lithium aluminum hydride either to a mixture of an allene and a small amount of an acetylene under mild conditions or to an olefin under vigorous conditions. Wotiz and co-workers (5) showed that primary and secondary propargyl bromides gave a mixture of allenes and acetylenes and in one case a pure acetylene.

In a research program to determine whether an isolated triple bond could be reduced by lithium aluminum hydride, the reaction with 1-hexyne, which has an active hydrogen, was studied. Even when the acetylene was heated at 60° for 6 days with a dioxane solution of the hydride, the triple bond was unaffected. It was also interesting that, at 0°, 4 days was required to effect the evolution of the theoretical amount of hydrogen in the reaction of hydride with 1-hexyne.

3-Hexyne also was unaffected by lithium aluminum hydride. This acetylene was recovered unchanged from an ether solution of hydride that had been heated under reflux for 10 days.

Since in the previous examples the product from the reduction of a conjugated acetylenic acid was an unsaturated alcohol, it was of interest to determine whether the triple bond could have been reduced after the carboxyl group was reduced to the alcohol derivative. Therefore, a dioxane solution of butynediol (I) was heated under reflux with lithium aluminum hydride for 30 hours. In order to

---

[1] Previous paper in this series, *J. Org. Chem.*, **20**, 95 (1955).

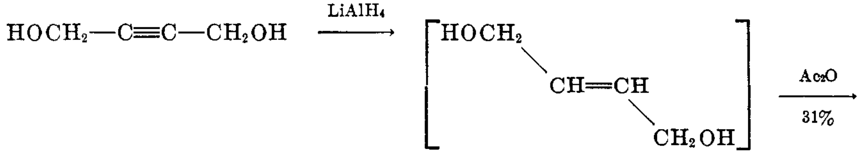
[2] Office of Naval Research Fellow, 1951–1953; Union Carbide Fellow, 1953–1954.

facilitate the isolation of the water-soluble diol from the inorganic salts, the procedure for reductive acetylation (6), in which the reduction mixture was heated for 2 days with acetic anhydride, was applied. With this procedure a 31% yield of *trans*-1,2-diacetoxy-2-butene (III) was obtained. This reaction, therefore, is an example of the reduction of an isolated triple bond with lithium aluminum hydride and shows that butynediol (I) could be an intermediate in the reduction of acetylenedicarboxylic acid. Since this work was completed, Bharucha and Weedon (7) reduced 2-butyn-1-ol with lithium aluminum hydride to *trans*-2-buten-1-ol, thus showing that the reduction of propargyl alcohols to allyl alcohols is fairly general. The reduction must be closely related to the reduction of cinnamyl alcohol with lithium aluminum hydride to 3-phenylpropanol (8).

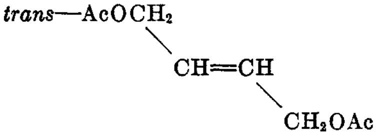
4-Chloro-2-butyn-1-ol (IV) (9), which is both a propargyl alcohol and a propargyl chloride, then was investigated in order to determine which functional group has the greatest influence on the course of the reduction. Treatment of IV with lithium aluminum hydride produced a 68% yield of 1,2-butadien-4-ol (V). Carothers and Berchet (10) had previously synthesized this very interesting allenic alcohol V in low yield by the addition of hydrogen chloride to vinylacetylene, followed by hydrolysis of the resulting chloride. The structure of V was confirmed by hydrogenation and determination of the infrared absorption spectrum. Thus V absorbed 2 moles of hydrogen to produce 1-butanol. V also showed strong bands in its infrared absorption spectrum at 853, 1020, 1440, 1980, 2950, and 3200 cm.$^{-1}$ and medium bands at 918, 1120, 1215, and 1707 cm.$^{-1}$. The starting chloro compound IV had absorption bands at 962, 1065, 1155, 1240, 1730, 2060, and 2210 cm.$^{-1}$.

A dichloroacetylene derivative, 2,5-dichloro-2,5-dimethyl-3-hexyne (VI), was reduced with lithium aluminum hydride to produce a 53% yield of 2,5-dimethyl-2,4-hexadiene (VII) and a 14% yield of the allene, 2,5-dimethyl-2,3-hexadiene (VIII). The solid diene VII had physical properties almost identical with those reported by Henne and Turk (11). The structure of VIII was indicated not only by its infrared absorption spectrum but also by agreement of its physical properties with those obtained by Krestinsky (12). VIII showed strong absorption bands at 848, 895, 1410, 1487, 1538, 1690, and 2960 cm.$^{-1}$ and medium intensity bands at 1049, 1152, 1230, and 1980 cm.$^{-1}$. The starting dichloro compound VI has strong absorption bands at 1164, 1232, 1298, and 2080 cm.$^{-1}$ and medium bands at 812, 1045, and 2240 cm.$^{-1}$.

The present work indicates that isolated triple bonds are not reduced by lithium aluminum hydride but that an acetylene with an *alpha* halogen group has a strong tendency to undergo allylic rearrangement during reduction, while an acetylene with an *alpha* hydroxyl group can be reduced to an olefinic alcohol.



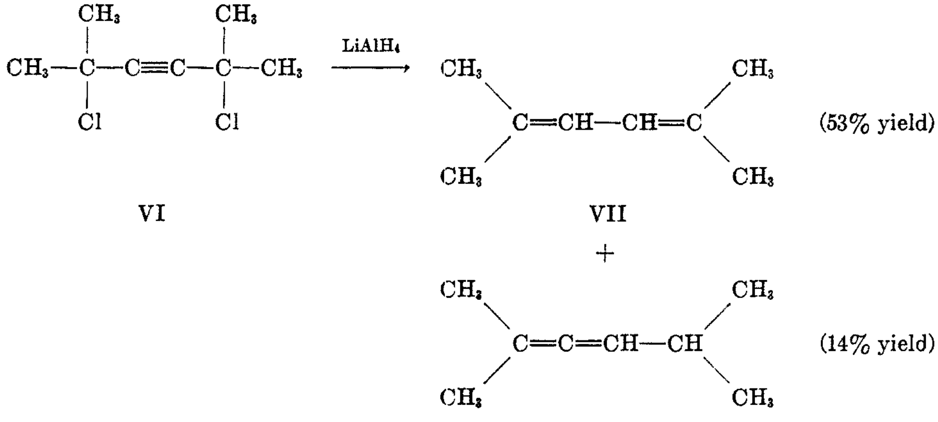
I II



III

$$ClCH_2—C\equiv C—CH_2OH \xrightarrow[68\%]{LiAlH_4} CH_2=C=CH—CH_2OH$$

IV V



VI VII VIII

EXPERIMENTAL[3]

Materials. 2,5-Dichloro-2,5-dimethyl-3-hexyne (VI), b.p. 56–57° (9 mm.), n_D^{25} 1.4597 [reported (13) b.p. 62° (14 mm.), n_D^{20} 1.4603], was prepared in a 45% yield by the treatment of 2,5-dimethyl-3-hexyne-2,5-diol[4] with gaseous hydrogen chloride, according to the procedure of Hennion and Banigan (13).

2-Butyne-1,4-diol (I) was obtained as a 35% aqueous solution from the General Aniline and Film Corp. Evaporation of the water, followed by distillation of the residue under reduced pressure, produced the colorless diol I, b.p. 115° (0.15 mm.), m.p. 56–57° [reported (14) m.p. 57.5°].

4-Chloro-2-butyn-1-ol (IV), b.p. 50° (0.5 mm.), n_D^{25} 1.4976 [reported (8) b.p. 50° (0.5 mm.), n_D^{25} 1.4980], was prepared from 2-butyne-1,4-diol (I) and thionyl chloride in a 48% yield.

3-Hexyne, b.p. 80.4–80.5° (759 mm.), n_D^{25} 1.4090 [reported (15) b.p. 81.9°, n_D^{25} 1.4092], was obtained by distillation of a commercial sample (Farchan Research Laboratories) through a 6-inch, helix-packed column.

1-Hexyne, b.p. 70.0–70.6°, n_D^{20} 1.4001 [reported (16) b.p. 70–72°, n_D^{20} 1.3990], was also obtained by distillation of a commercial sample (Farchan Research Laboratories) through the same column.

Attempted reduction of 1-hexyne. A mixture of 44.0 g. (0.536 mole) of 1-hexyne and 14.0 g. (0.368 mole) of lithium aluminum hydride in 150 ml. of dioxane was stirred at 0° for 4 days.

---

[3] The authors are indebted to Kathryn Gerdeman for the analysis and to Joseph Wenograd, Franklin Byers, Kathyrn Gerdeman, and Dr. Robert A. Spurr for the infrared absorption spectra. A Perkin-Elmer model 12-C infrared spectrophotometer, modified for double pass operation, was used.

[4] The authors are grateful to the Air Reduction Co. for a generous supply of this acetylenic glycol.

Hydrogen was still being evolved after 3 days. The complex was decomposed as usual and the volatile hydrocarbon was removed by extraction with toluene. Distillation of the dried toluene extracts through a 6-inch, helix-packed column produced 38.9 g. (88%) of the 1-hexyne, b.p. 69–71°, n_D^{20} 1.4004, with no evidence of any reduction to the corresponding olefin or paraffin.

When equivalent quantities of 1-hexyne and lithium aluminum hydride in dioxane were heated for 6 days at 60° and the reaction mixture was worked up in the same way, the 1-hexyne was again recovered unchanged.

Attempted reduction of 3-hexyne. A mixture of 45.6 g. (0.556 mole) of 3-hexyne and 21.2 g. (0.557 mole) of lithium aluminum hydride in 250 ml. of anhydrous ether was heated under reflux with stirring for 10 days. After the reaction mixture was worked up in the usual way, distillation of the dried ether solution of the hydrocarbon through a 6-inch, helix-packed column produced 40.4 g. (88.5%) of 3-hexyne, b.p. 79–81°, n_D^{25} 1.4088. No evidence of the formation of any 3-hexene or *n*-hexane was found.

trans-1,4-Diacetoxy-2-butene (III). To a stirred slurry of 28.5 g. (0.75 mole) of lithium aluminum hydride in 350 ml. of anhydrous dioxane was added through a dropping-funnel over a period of 1.5 hours a solution of 43.0 g. (0.50 mole) of 2-butyne-1,4-diol (I) in 120 ml. of anhydrous dioxane. After the mixture had been stirred and heated under reflux for an additional 28 hours, the excess hydride was decomposed by the addition of 36 g. of water in 40 ml. of dioxane. Acetic anhydride (300 ml.) then was added dropwise to produce an extremely thick reaction mixture. However, after the mixture had been stirred and heated under reflux for 44 hours, it became quite fluid. The mixture then was cooled to approximately 60° and was filtered rapidly through a Büchner funnel. The insoluble salts were washed with two 25-ml. portions of acetic anhydride, and the washings were combined with the original filtrate. After the filtrates were concentrated to about 150 ml. by vacuum distillation of the solvents at 40° through a 6-inch, helix-packed column, the cold residue was washed with a cold, saturated sodium bicarbonate solution until the washings remained basic to litmus paper. The aqueous washings were re-extracted with three 100-ml. portions of ether, and the combined ether layers plus the original organic layer were dried overnight with potassium carbonate. After the ether was removed by distillation, the residue was fractionated through a 6-inch, helix-packed column to yield 26.5 g. (31%) of *trans*-1,4-diacetoxy-2-butene (III), b.p. 62–63° (0.28 mm.), n_D^{20} 1.4430, m.p. 13.5–15.5° [reported b.p. 116° (12 mm.) (17), n_D^{20} 1.4435 (17), m.p. 14–16° (18)].

1,2-Butadien-4-ol (V). To a stirred slurry of 23.0 g. (0.605 mole) of lithium aluminum hydride in 800 ml. of anhydrous ether was added dropwise, over a period of 1.3 hours, 30.0 g. (0.287 mole) of 4-chloro-2-butyn-1-ol (IV) in 200 ml. of anhydrous ether. After the mixture was heated under reflux for an additional 2 hours, the excess hydride was decomposed with water and enough 20% hydrochloric acid was added to lower the *p*H of the solution to 2. The water layer was extracted continuously for 3 days with 200 ml. of ether, and this extract was combined with the original ether layer. After the combined ether solution was dried over potassium carbonate, the ether was removed by distillation and the residue was fractionated through a 10-inch, helix-packed column to produce 13.8 g. (68%) of 1,2-butadien-4-ol (V), b.p. 68–69° (45 mm.), n_D^{25} 1.4754, d_4^{20} 0.913 [reported (10) b.p. 68–70° (53 mm.), n_D^{20} 1.4759, d_4^{20} 0.916].

Anal. Calc'd for C_4H_6O: C, 68.60; H, 8.57.

Found: C, 68.54; H, 8.52.

A larger run, made by the use of 104.5 g. (1.0 mole) of the chlorohydrin IV, 47.5 g. (1.25 moles) of lithium aluminum hydride, and 1400 ml. of ether, yielded 38.5 g. (56%) of the allenic alchol V.

Hydrogenation of 1.136 g. (0.0162 mole) of 1,2-butadien-4-ol (V) in 70 ml. of distilled water in the presence of 0.50 g. of Adams catalyst (PtO_2) at 23° and 763 mm. resulted in the absorption of 766 ml. (97.8%) of hydrogen in 44 hours. The *n*-butyl alcohol formed in the reduction was identified as its 3,5-dinitrobenzoate, m.p. 64–64.5° [reported (19) m.p. 64°]. A mixture melting point determination with an authentic sample of *n*-butyl 3,5-dinitrobenzoate showed no depression.

Reduction of 2,5-dichloro-2,5-dimethyl-3-hexyne (VI). To a stirred slurry of 25.0 g. (0.650 mole) of lithium aluminum hydride in 1 liter of anhydrous ether was added dropwise over a period of 1.2 hours 116 g. (0.648 mole) of 2,5-dichloro-2,5-dimethyl-3-hexyne (VI). After the mixture was heated under reflux for an additional 20 hours, the excess hydride was decomposed by the addition of cyclohexanone, and enough 20% hydrochloric acid was added to produce a clear solution. The aqueous layer was extracted with three 150-ml. portions of ether, and the extracts were combined with the original ether layer. This ether solution was dried for 4 hours with calcium chloride and then was dried overnight with Drierite and potassium carbonate. After the ether was removed by distillation, the residue was fractionated through a 6-inch, helix-packed column to yield 9.85 g. (14%) of 2,5-dimethyl-2,3-hexadiene (VIII), b.p. 120–122.5°, n_D^{25} 1.4505 [reported (12) b.p. 119–123°, n_D^{20} 1.45054], and 37.6 g. (53%) of slightly impure 2,5-dimethyl-2,4-hexadiene (VII), b.p. 132–134° (747 mm.), n_D^{25} 1.4731. Fractional crystallization of this diene produced a highly purified sample of VII, n_D^{25} 1.4752, m.p. 13.6–13.7° [reported (11) b.p. 134.5°, m.p. 13.94°, n_D^{20} 1.4781].

SUMMARY

Although the simple acetylenes, 1-hexyne and 3-hexyne, could be recovered unchanged from lithium aluminum hydride solutions, 2-butyne-1,4-diol was, in effect, reductively acetylated with lithium aluminum hydride and acetic anhydride to yield 1,4-diacetoxy-2-butene. The very interesting allenic alcohol, 1,2-butadien-4-ol, was synthesized in a 68% yield by reduction of 4-chloro-2-butyn-1-ol. Lithium aluminum hydride reduced 2,5-dichloro-2,5-dimethyl-3-hexyne to 2,5-dimethyl-2,3-hexadiene plus 2,5-dimethyl-2,4-hexadiene.

COLLEGE PARK, MARYLAND

REFERENCES

(1) BAILEY AND PFEIFER, *J. Org. Chem.*, **20,** 95 (1955).
(2) CHANLEY AND SOBATKA, *J. Am. Chem. Soc.*, **71,** 4140 (1949).
(3) MICOVIC AND MIKHAILOVIC, *Bull. soc. chim. Belgrade*, **16,** 19 (1951).
(4) BENEDICT AND RUSSELL, *J. Am. Chem. Soc.*, **73,** 5444 (1951).
(5) WOTIZ, *J. Am. Chem. Soc.*, **73,** 693 (1951); SAMMUL, HOLLINGSWORTH, AND WOTIZ, *J. Am. Chem. Soc.*, **75,** 4856 (1953).
(6) BAILEY AND ECONOMY, *J. Am. Chem. Soc.*, **77,** 433 (1955).
(7) BHARUCHA AND WEEDON, *J. Chem. Soc.*, 1584 (1953).
(8) HOCHSTEIN AND BROWN, *J. Am. Chem. Soc.*, **70,** 3484 (1948).
(9) BAILEY AND FUJIWARA, *J. Am. Chem. Soc.*, **77,** 165 (1955).
(10) CAROTHERS AND BERCHET, *J. Am. Chem. Soc.*, **55,** 2807 (1933).
(11) HENNE AND TURK, *J. Am. Chem. Soc.*, **64,** 826 (1942).
(12) KRESTINSKY, *Ber.*, **55,** 2754 (1922).
(13) HENNION AND BANIGAN, *J. Am. Chem. Soc.*, **68,** 1202 (1946).
(14) HENNION AND KUPIECKI, *J. Org. Chem.*, **18,** 1601 (1953).
(15) EGLOFF, *Physical Constants of Hydrocarbons*, Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 366.
(16) VAUGHN, HENNION, VOGT, AND NIEUWLAND, *J. Org. Chem.*, **2,** 1 (1937).
(17) PUDOVIK, *J. Gen. Chem. (U.S.S.R.)*, **19,** 1179 (1949) [*Chem. Abstr.*, **44,** 1005 (1950)].
(18) ARBUZOV AND ZOROASTROVA, *Compt. rend. acad. sci. (U.S.S.R.)*, **53,** 41 (1946) [*Chem. Abstr.*, **41,** 3751 (1947)].
(19) SHRINER AND FUSON, *Systematic Identification of Organic Compounds*, John Wiley and Sons, New York, N. Y., 1948, p. 226.