[Contribution from the George Herbert Jones Laboratory, The University of Chicago]

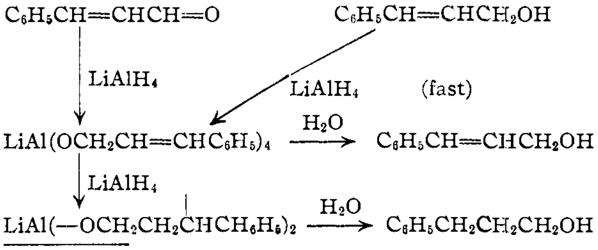
Addition of Lithium Aluminum Hydride to Double Bonds

By F. A. Hochstein and Weldon G. Brown

Although lithium aluminum hydride normally has no action on carbon–carbon double bonds, there are now several known[1] examples in which the reduction of a polar functional group is accompanied by reduction of an adjacent double bond. Many of these examples are of the type, $C_6H_5CH{=}CHX$, where X may be NO_2, COOH, CHO, COR, etc., but reduction of the double bond does not occur with styrene itself (R = H).[2] This pattern of behavior suggests that the first stage in these reductions might be a 1,4 addition of the metal hydride. However, the new experimental evidence here presented excludes this possibility and an interpretation introducing a novel type of metallo-organic compound is offered.

It is found, first, that whereas the normal reduction procedure, as applied to cinnamaldehyde, furnishes hydrocinnamyl alcohol,[1] the reverse mode of addition, carried out by adding the calculated amount of hydride solution to a solution of cinnamaldehyde at temperatures below 10°, results in an excellent yield of cinnamyl alcohol. Secondly, it is found that cinnamyl alcohol reacts with lithium aluminum hydride at room temperature, liberating a quantity of hydrogen gas which corresponds with the replacement of the hydroxyl hydrogen in a very fast reaction, and this is followed by reaction at a moderate rate with an additional equivalent (0.25 mole) of the hydride. Hydrolytic decomposition of the resulting material liberates hydrocinnamyl alcohol in very good yield.

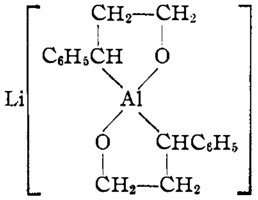
It is thus evident that reduction of the unsaturated aldehyde occurs in two successive stages and that the attack upon the double bond takes place as a slower reaction which follows the reduction of the carbonyl group. The successful reduction of purely aliphatic α-β unsaturated aldehydes, acids, etc., to unsaturated alcohols is a consequence of the fact that these alcohols undergo further reduction relatively more slowly than does cinnamyl alcohol. Thus allyl alcohol is not reduced at room temperature but at elevated temperatures is partially converted to propyl alcohol by the action of lithium aluminum hydride.



From purely stoichiometrical considerations it can be concluded that one of the two hydrogen atoms required for the conversion of cinnamyl alcohol to hydrocinnamyl alcohol is supplied by the hydrolyzing agent acting upon a carbon–metal bond in the intermediate complex. The stoichiometry also requires that the carbon–metal bonds must be predominantly carbon–aluminum, and since it is found that the complex does not react with carbon dioxide the presence of carbon–lithium bonds is unlikely.

The presence, and also the location, of the carbon–metal bond is clearly demonstrated in tracer experiments employing deuterium. Decomposition of the complex by the addition of amyl alcohol containing deuterium in the hydroxyl group, followed by acid hydrolysis (in natural water),[3] generates hydrocinnamyl alcohol having deuterium in the methylene group adjacent to the benzene ring. The proof of position is based upon conversion of the alcohol to allylbenzene, and to hydrocinnamic acid, without loss of deuterium; the methylene group adjacent to the ring is the only one of the three originally present which remains intact through both of these transformations.

To assign a structure to the intermediate metallo-organic compound is perhaps premature, since its isolation in crystalline form has not yet been accomplished, but the evidence thus far cited, together with the further observations that it is colorless and ether-soluble, and that on oxidation 1-phenyl-1,3-propanediol is formed, is consistent with the structure shown



The proposal of a cyclic structure rests largely on the solubility of the material in ether; the alternative polymeric structure would doubtless represent an insoluble material. It remains for future study to determine if the cyclization, made possible by the position of the oxygen atom with respect to the original double bond, is really an essential condition for the addition of hydride to the double bond.

Presumably the same intermediate complex is eventually formed irrespective of whether the starting material is cinnamyl alcohol or a related

---

[1] Nystrom and Brown, This Journal, **69**, 1197, 2548 (1947); and forthcoming papers.

[2] Unpublished observation by R. F. Nystrom.

[3] This sequence of alcoholysis and hydrolysis, rather than direct hydrolysis in deuterated water, was employed in order to secure maximum utilization of the limited quantity of deuterium at hand.

compound (cinnamaldehyde, cinnamic acid, etc.) which would first be reduced to the cinnamyl alcohol stage.

Experimental

Reduction of Cinnamaldehyde to Cinnamyl Alcohol.—To a solution of 31 g. (0.23 mole) of cinnamaldehyde in 80 ml. of ether, cooled to −10° in an ice–salt-bath, was added dropwise a solution of lithium aluminum hydride (0.065 mole, 10% excess) (product of Metal Hydrides, Inc.) in ether with continued stirring over a period of thirty minutes. At the end of the addition the temperature had risen to +10°. Ten minutes later water was added to the suspension and then 80 ml. of 10% sulfuric acid. The product, after isolation in the conventional manner, consisted of 28 g. (90% of theory) of cinnamyl alcohol, m.p. 33–34°.

Reduction of Cinnamyl Alcohol to Hydrocinnamyl Alcohol.—This reduction, following the usual order of addition,[1] was carried out by adding 27.5 g. (0.205 mole) of cinnamyl alcohol (Eastman Kodak Co. "White Label" Grade, previously redistilled), dissolved in 75 ml. of ether, to 80 ml. of an ether solution containing 0.127 mole of lithium aluminum hydride. The white precipitate which formed after half of the alcohol had been added redissolved after heating the mixture under reflux for one-half hour. After two hours water was added to the clear solution which resulted in the evolution of 2.02 l. (N.T.P.) of hydrogen gas (0.025 mole of unreacted hydride). It was noted that an exothermic reaction continued after evolution of hydrogen gas had ceased. Dilute sulfuric acid was added and the reaction product was worked up in the usual way to yield 26.0 g. (0.191 mole, 93%) of hydrocinnamyl alcohol, b.p. 132° (21 mm.), 237.5° (750 mm.), $n^{20}\text{D}$ 1.5278.

Reduction of Allyl Alcohol.—Allyl alcohol was found to react with lithium aluminum hydride at room temperature only by replacement of the active hydroxyl hydrogen. To effect a reaction at a higher temperature and to avoid the necessity of separating the reaction products from water, the following modified procedure was employed. A mixture, prepared by the addition of 6.8 g. (0.12 mole) of dry allyl alcohol to a solution of 0.075 mole of lithium aluminum hydride in 250 ml. of dibutyl ether, was heated to 100° for three hours. Diethyleneglycol (22 g., 0.21 mole) was added and the volatile products were removed by distillation through a 24" wire spiral column. Two fractions were collected at 97–98° and 98–141°, of which the first was shown by a rough bromine titration to contain about 40% allyl alcohol. The two fractions were combined and a solution of bromine in dibutyl ether was added, at room temperature, until the bromine color persisted for one minute. This mixture was then subjected to fractional distillation at 80 mm. pressure furnishing a fraction (1.7 g.) of impure propyl alcohol ($n^{20}\text{D}$ 1.3981, lit. $n^{20}\text{D}$ 1.3852). The 3,5-dinitrobenzoate prepared from this material melted at 72°, not depressed by admixture of an authentic specimen of *n*-propyl 3,5-dinitrobenzoate melting at 73°.

Deuterium Analyses.—Analyses for deuterium were performed by density measurements,[4] using a quartz float and observing the temperature of flotation, on the water produced by combustion of the sample. The combustions were carried out in some instances by the lamp technique, in others with the aid of a copper oxide-filled quartz combustion tube. Each water sample was subjected to treatment with potassium permanganate and anhydrous sodium carbonate at 200° for one hour in a sealed tube.

Hydrocinnamyl Alcohol-*d*.—In this experiment, amyl alcohol containing deuterium in the hydroxyl group was to be used to convert the intermediate metallo-organic product from the reaction of cinnamyl alcohol with lithium aluminum hydride to a mixed lithium aluminum alkoxide which could later be subjected to hydrolysis in natural water. The required amyl alcohol-*d* was prepared by mixing 13.4 g. (0.152 mole) of amyl alcohol with 3 g. (0.15 mole) of deuterium oxide (99%), shaking the mixture vigorously for ten minutes, and eventually drying the alcohol layer over a small quantity of calcium hydride. This alcohol should have contained 66.3 mole % of $C_5H_{11}OD$, corresponding to 5.53 mole % D_2O in the water of combustion; the observed value was 7.52 mole % D_2O, the discrepancy being doubtless due to the presence of water in the alcohol as the result of inadequate drying.

The reduction of cinnamyl alcohol was carried out essentially as described above, taking 13.4 g. (0.1 mole) of the compound and 0.055 mole of lithium aluminum hydride. After refluxing the mixture for five hours, 12.0 g. (0.136 mole) of amyl alcohol-*d* was added dropwise, causing a marked exothermic reaction until nearly the end of the addition. The solution remained clear but became very viscous. During this addition 400 ml. of hydrogen gas was evolved (0.004 mole of unreacted hydride). The solution was allowed to stand at room temperature for ten hours and then subjected to hydrolysis by the addition of 70 ml. of 20% sulfuric acid. The aqueous layer was twice extracted with ether and after drying the combined ether solutions over potassium carbonate the product was recovered by distillation under reduced pressure; yield 12.3 g., 90% of theory.

The quantity of material was deemed inadequate for the subsequent operations and it was therefore diluted with ordinary hydrocinnamyl alcohol in the ratio of 10.7 g. of the deuterated alcohol to a final weight of 32.5 g. To ensure normalization of the hydroxyl hydrogen the resulting material was twice treated with 50-ml. portions of ethanol, which were removed by distillation, and, finally, the hydrocinnamyl alcohol was distilled under reduced pressure, b.p. 131.5–132° (20 mm.).

Analysis for deuterium showed 17.2 mole % $C_9H_{11}DO$ whereas the predicted value, assuming no isotopic discrimination in the reaction with (excess) amyl alcohol-*d*, is 21.8%.

Hydrocinnamic Acid-*d*. (a) By Potassium Hydroxide Fusion.—Following the procedure of Guerbet,[5] 5 g. of hydrocinnamyl alcohol-*d* and 7.2 g. of powdered potassium hydroxide (previously fused at red heat) were heated at 245–255° for three hours. The volume of hydrogen gas evolved during the reaction was found to be 1.45 liters (88%). The solid residue furnished 4.9 g. (88%) of hydrocinnamic acid-*d*, m.p. 47.5°, which on combustion gave water containing 1.18 mole % D_2O, and thus contained 11.8 mole % $C_9H_9DO_2$. This result signified either that 37% of the deuterium originally present in the hydrocinnamyl alcohol was present in the carbinol group, or that deuterium originally present in other positions was lost, to the extent of 37%, through exchange with potassium hydroxide.

(b) By Chromic Acid Oxidation.—Oxidation of 4.0 g. of hydrocinnamyl alcohol-*d*, dissolved in 25 ml. of glacial acetic acid, by the gradual addition of 3.80 g. of powdered anhydrous chromic oxide to the cooled and vigorously stirred solution, provided 0.55 g. (13% of theory[6]) of hydrocinnamic acid-*d*, m.p. 47.5°, which was found to contain 17.5 mole % $C_9H_9DO_2$. It is therefore concluded that no deuterium was present in the carbinol group of the hydrocinnamyl alcohol.

Formation of Allylbenzene.—For the purposes of this work it was necessary to find a method for converting hydrocinnamyl alcohol to allylbenzene which would not at the same time form propenylbenzene because any process giving rise to the latter in substantial amounts would be suspect on the grounds of possible deuterium exchange. The thermal decomposition of hydrocinnamyl sulfite is reported[7] to give only allylbenzene but our experience with this process was highly unsatisfactory. Other methods for the dehydration of hydrocinnamyl alcohol, *e.g.*, dehydration over activated silica[8] and dehydration by way of tri-

---

[4] The assistance of Mr. Frank B. Colton in making these measurements is gratefully acknowledged.

[5] Guerbet, *Bull. soc. chim.*, [4] **11**, 164 (1912).

[6] The procedure is essentially that of Fittig and Rugheimer [*Ann.*, **172**, 124 (1874)] who did not report their yield.

[7] Ramart-Lucas and Amagat, *Bull. soc. chim.*, [4] **51**, 121 (1932).

[8] Ramart-Lucas and Amagat, *Compt. rend.*, **188**, 638 (1929).

methylhydrocinnamylammonium hydroxide,[9] are known to furnish principally propenylbenzene and not more than traces of allylbenzene.

In view of the known capacity of strong alkali in causing the isomerization of allylbenzene to propenylbenzene,[10] it seemed probable that the formation of the latter in the thermal decomposition of trimethylcinnamylammonium hydroxide is a consequence of the strongly alkaline nature of the material. If so, the thermal decomposition of neutral salts of this base would be expected to form allylbenzene. This was realized for both the bromide and the iodide. The acetate decomposed smoothly at 275° but the product, formed in good yield, was dimethylhydrocinnamylamine. The bromide decomposition was used in the dehydration of the deuterated hydrocinnamyl alcohol.

Preparation and Thermal Decomposition of Trimethylhydrocinnamylammonium bromide-*d*.—The alcohol, 14.1 g., was first converted to hydrocinnamyl bromide-*d* (yield, 18.9 g.) by treatment with hydrobromic acid.[11] This product was heated under reflux for six hours with 10.8 g. of trimethylamine in 100 ml. of absolute ethanol. Concentration of the resulting solution caused separation of the quaternary bromide (17.3 g.) as colorless crystalline plates, m.p. 150.5–152°. Without further purification, 15.8 g. of this material was heated in a distilling flask at 280–320°. An ether extract of the distillate, which consisted of liquid hydrocarbon and solid trimethylamine hydrobromide, was washed successively with water, dilute hydrochloric acid, sodium bicarbonate solution and again with water, and was then subjected to fractional distillation. The allylbenzene was collected in two fractions, 3.20 g. in the range 156–158°, $n^{20}\text{D}$ 1.5104, and 0.70 g. in the range 158–160°, $n^{20}\text{D}$ 1.5176 (lit.[10a] $n^{20}\text{D}$ 1.5143), which together constitute a yield of 68%. A further fraction, 0.55 g., b.p. 160–167°, $n^{20}\text{D}$ 1.5295, doubtless contained some additional allylbenzene as well as some propenylbenzene ($n^{20}\text{D}$ 1.5492). Analysis of the first fraction for deuterium showed 17.2 mole % C_9H_9D.

Attempted Carbonation of the Product from Cinnamyl Alcohol and Lithium Aluminum Hydride.—A solution containing the product of the interaction of cinnamyl alcohol and lithium aluminum hydride, prepared as described earlier, was treated with carbon dioxide at 35°. No evidence of a reaction was noted, and upon hydrolysis of the mixture hydrocinnamyl alcohol was isolated in substantially the same yield as before. Likewise a solution of the intermediate product in tetrahydrofuran showed no evidence of a reaction when treated with carbon dioxide at 65°.

Reaction with Oxygen.—Solutions containing the product of the reaction of cinnamyl alcohol with lithium aluminum hydride were found to absorb oxygen readily. Highly concentrated preparations, obtained as viscous liquids or glass-like solids upon evaporation of the solvent, fumed and heated strongly upon exposure to air but did not inflame. The nature of the oxidation product was established in the following experiment. A solution was prepared by the addition of 9 g. (0.067 mole) of cinnamyl alcohol to 0.034 mole of lithium aluminum hydride in ethyl ether solution and the resulting suspension was stirred at room temperature (under nitrogen) for two hours, whereupon a clear solution was formed. Upon passing dry air through the solution a white precipitate formed. The passage of air was continued for eight hours. Aqueous sulfuric acid was then added and the organic product was isolated by ether extraction. Upon attempted distillation at 8 mm. pressure evidence of decomposition was noted; the residue was then transferred to a Hickman alembic and the distillation was conducted at 100° and 0.2 mm. pressure. The product, 2.5 g. of a colorless viscous oil, $n^{20}\text{D}$ 1.5451, was identified as 1-phenyl-1,3-propanediol by conversion to the di-*p*-nitrobenzoate,[12] m.p. 110°.

Summary

It is shown that the reduction of cinnamaldehyde to hydrocinnamyl alcohol by lithium aluminum hydride occurs in two stages, of which the first, giving rise to cinnamyl alcohol, is realized exclusively by performing a reversed addition at lowered temperatures. The further reduction of cinnamyl alcohol is a slower reaction which occurs by addition of metal hydride to the double bond, the metal being replaced by hydrogen during the subsequent hydrolysis. This, as well as the location of the carbon–metal bonds, is shown by tracer studies employing deuterium. The intermediate metallo-organic compound is formulated as a lithium aluminate in which the aluminum is bound, with a coördination number of four, to two carbon atoms and two oxygen atoms. The analogous reduction of allyl to propyl alcohol is found to occur only at higher temperatures.

CHICAGO, ILLINOIS RECEIVED MAY 5, 1948

---

[9] von Braun, *Ann.*, **382**, 47 (1911).

[10] (a) Tiffeneau, *Compt. rend.*, **139**, 482 (1904); (b) Klages, *Ber.*, **39**, 2590 (1906).

[11] Norris, Watt and Thomas, THIS JOURNAL, **38**, 1078 (1916).

[12] St. Pfau and Plattner, *Helv. Chim. Acta*, **15**, 1250 (1932).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF FLORIDA]

Dimercaptols of Acetonylacetone

BY EDWARD G. RIETZ, RICHARD D. CHAPMAN AND JAMES B. FERNANDEZ

Considerable has been published on the chemistry of the simple mercaptols but relatively little on the dimercaptols of the 2,5-diketones. Posner observed the reaction of ethyl,[1] *i*-amyl,[1] benzyl[2] and phenyl[2] mercaptans on acetonylacetone but he was interested in the sulfones and paid little attention to the mercaptols.

Inasmuch as acetonylacetone is now readily available, it was decided to prepare a series of dimercaptols and to study them more adequately. Accordingly, the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl and *n*-dodecyl mercaptols were prepared as well as the mercaptol from thioglycolic acid. All of these compounds, with the exception of the ethyl derivative, are new to the literature. The latter compound was described by Posner as a liquid; we have obtained it as a solid, melting at 27°, although it may be supercooled without difficulty.

All of the compounds were prepared by the interaction of the mercaptan and acetonylacetone at room temperature under the influence of hydro-

---

[1] Posner, *Ber.*, **33**, 2983–2993 (1900).

[2] Posner, *ibid.*, **35**, 493–495 (1902).