The precipitate changed from white to tan upon filtering and washing with petroleum ether. After drying it was analyzed for bromine and sulfur. The compound was soluble in toluene, xylene, benzene, chloroform, hot ethyl and hot methyl alcohol; insoluble in water, petroleum ether, and cold ethyl and methyl alcohol. Since the bromo-diacetyl-ditosyl glucose could not be obtained crystalline, a benzene solution was precipitated in 3 fractions to demonstrate homogeneity of the reaction product.

Anal. For bromo-diacetyl-ditosyl glucose $C_{24}H_{26}O_{11}S_2Br$:

	S, %	Br, %
Calcd.	10.21	12.75
Found: Fraction 1	10.20	12.59
Fraction 2	10.12	12.46
Fraction 3	10.17	12.65

Summary

1. The action of formic acid on starch produces an ester approximating a monoformate in composition.

2. Oxidation of the formate ester with periodic acid indicates that the formyl group is located primarily on carbon six of the glucose units.

3. Amorphous products analyzing as monoformyl-diacetyl starch and monoformyl-ditosyl starch were prepared.

4. Hydrolysis of the monoformyl-ditosyl starch yielded a compound which analyzed as bromo-diacetyl-ditosyl-glucose.

AMES, IOWA RECEIVED SEPTEMBER 27, 1940

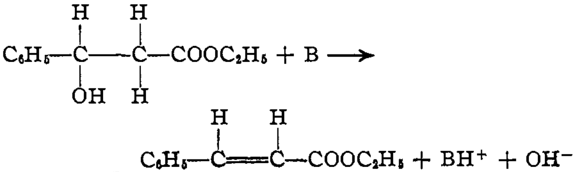
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Mechanism of Elimination of Water from Organic Compounds in the Presence of Bases[1]

BY CHARLES R. HAUSER AND DAVID S. BRESLOW

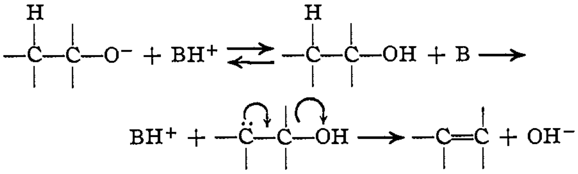
Apparently it is not generally recognized that bases can facilitate the elimination of water from organic compounds, although certain well-known reactions which presumably involve dehydration, for example, the aldol condensation of benzaldehyde with ketones or esters, are commonly effected by means of bases at ordinary temperatures.

Recently, we have stopped the reaction of benzaldehyde with ethyl acetate at the aldol stage.[2] It has now been shown that on standing with sodium triphenylmethyl in ether solution at room temperatures, the aldol, ethyl β-phenyl-β-hydroxypropionate, eliminates water to form ethyl cinnamate, whereas under comparable conditions but in the absence of the base the aldol appears to be quite stable. Also, it has been found that the elimination of water from ethyl β-phenyl-β-hydroxypropionate is facilitated by sodium ethoxide in ether. The elimination of water from the aldol by means of bases may be represented as follows, where B represents triphenylmethyl ion or ethoxide ion.



$$C_6H_5-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-COOC_2H_5 + B \longrightarrow C_6H_5-\overset{H}{C}=\overset{H}{C}-COOC_2H_5 + BH^+ + OH^-$$

It is suggested that the mechanism of elimination of the elements of water from organic compounds in the presence of bases is analogous to the mechanism of the removal of hydrogen halide from alkyl halides by means of these reagents. In the latter case it is generally considered[3] that the hydrogen is attacked and removed as a proton, accompanied or followed by the release of halogen as halide ion. With hydroxyl compounds, however, it is necessary to take into account the fact that the hydroxyl hydrogen is much more active than the hydrogen attached to the carbon. The reactions may be represented by the equations



$$-\overset{H}{\underset{|}{C}}-\underset{|}{C}-O^- + BH^+ \rightleftarrows -\overset{H}{\underset{|}{C}}-\underset{|}{C}-OH + B \longrightarrow$$

$$BH^+ + -\underset{|}{\ddot{C}}-\underset{|}{C}-OH \longrightarrow -\underset{|}{C}=\underset{|}{C} + OH^-$$

Although the hydroxyl hydrogen is much more active than the hydrogen attached to the β-carbon atom, the acid-base reaction involving the hydroxyl hydrogen is reversible. The acid-base reaction involving the hydrogen attached to the β-carbon atom also may be reversible, but the carbanion readily loses hydroxyl ion to give the olefinic double bond, the latter reaction being essentially irreversible. The removal of the proton

---

[1] This work was supported in part by a grant from the Duke University Research Council.

[2] Hauser and Breslow, THIS JOURNAL, 61, 793 (1939).

[3] See especially Hauser, *ibid.*, 62, 933 (1940).

from the β-carbon atom and the release of hydroxyl ion may be simultaneous processes.

As would be expected on the basis of the above mechanism, the elements of water are removed from organic compounds by bases much less readily than the elements of hydrogen halide are removed from alkyl halides by these reagents. Thus, for example, hydrogen bromide is removed readily from 2-phenyl-1-bromopropane by means of potassium amide in liquid ammonia at −33°,[4] whereas an analogous compound, phenylbenzylcarbinol, has been found to be stable in the presence of sodium amide even when the reaction mixture is allowed to stand in a sealed tube at room temperature for a week. In fact, water is eliminated readily from organic compounds in the presence of even strong bases apparently only when the hydrogen on the β-carbon atom is relatively highly activated (as when a carbonyl group is present).

As is well known, water is eliminated from organic compounds in the presence of acids generally more easily than in the presence of bases. However, when the hydrogen on the β-carbon atom is especially highly activated, as in the aldol obtained from the condensation of methyl benzoylformate and methyl cyanoacetate[5] (activation by both a carbonyl and a nitrile group), water appears to be eliminated in the presence of bases as readily as in the presence of acids.

Experimental

Dehydration of Ethyl β-Phenyl-β-hydroxypropionate with Sodium Triphenylmethyl.—Ethyl β-phenyl-β-hydroxypropionate was prepared by a Reformatsky reaction from benzaldehyde and ethyl bromoacetate using a modification[6] of the method of Blaise and Herman[7]; b. p. 149–151° at 11 mm. To a sodium triphenylmethyl solution prepared as previously described[8] from 63 g. (0.227 mole) of triphenylchloromethane dissolved in 1500 cc. of ether and 1500 g. of 1% sodium amalgam was added 25.2 g. (0.13 mole) of ethyl β-phenyl-β-hydroxypropionate dissolved in a small amount of ether. After standing at room temperature for twenty-four hours, the mixture was acidified with 20 cc. of glacial acetic acid in 75 cc. of ether, extracted with dilute sodium carbonate solution until alkaline and dried over "Drierite." The alkaline solution on acidification yielded 1.0 g. of cinnamic acid, m. p. 132.5–133.5°, after recrystallization from hot water.

The residue from the ether solution was distilled twice at 11–12 mm., collecting 3.6 g. at 130–140° (plus a few drops at 140–160°). Hydrolysis of 2 g. of this material gave 1.52 g. of cinnamic acid melting at 129–132° (133–134° after recrystallization). The acidic filtrate was made alkaline and extracted with ether. The ethereal solution on evaporation left a negligible residue, showing that the hydrolysis was essentially complete. The total yield of ethyl cinnamate, based on the crude cinnamic acid (m. p. 129–132°) obtained from the hydrolysis and the pure cinnamic acid isolated from the original carbonate solution, was 4.5 g. (20%).

A blank was run with the same amount of ethyl phenylhydroxypropionate in 1500 cc. of ether. It was worked up in the same way as the above experiment. On hydrolysis of 2.0 g. of the residue obtained by evaporation of the ether, 0.05 g. of cinnamic acid (only one-thirtieth of the amount obtained in the presence of the base) was obtained, m. p. 129–131°. Thus it was shown that essentially no decomposition of the hydroxy-ester to ethyl cinnamate took place in working up the reaction products.

Dehydration of Ethyl β-Phenyl-β-hydroxypropionate with Sodium Ethoxide.—Sodium ethoxide was prepared from 4.6 g. (0.20 mole) of sodium and excess absolute alcohol as described previously.[6] To a suspension of the sodium ethoxide in 250 cc. of dry ether was added with cooling 38.8 g. (0.20 mole) of ethyl β-phenyl-β-hydroxypropionate and the mixture shaken for several hours. A copious precipitate formed and the liquid turned deep brown. The mixture was allowed to stand at room temperature with occasional shaking for a week. It was then hydrolyzed with 250 cc. of ice water, the alkaline solution extracted with ether and the combined ether solutions dried over "Drierite."

The alkaline solution was cooled and acidified with hydrochloric acid. The resulting precipitate was crystallized from ligroin (b. p. 100–120°), yielding 8.5 g. of cinnamic acid. The residue from the ether extract of the filtrate was crystallized from warm water, yielding 7 g. of impure β-phenyl-β-hydroxypropionic acid, m. p. 88–90°.[9]

The residue from the dried ether solution was distilled at 11 mm., collecting 10.7 g. at 133–135°. It was identified as ethyl cinnamate by hydrolysis to cinnamic acid as described in the preceding experiment.

The total yield of dehydration product calculated as ethyl cinnamate was 20.8 g. or 75.0% of the theoretical amount (based on the ethyl phenylhydroxypropionate started with minus that recovered as phenylhydroxypropionic acid).

Attempted Dehydration of Phenylbenzylcarbinol with Sodium Amide.—To 25 cc. of liquid ammonia and sodium amide (prepared from 3.45 g. of sodium) contained in a Carius tube was added a dry ether solution (25 cc.) of 9.9 g. of Eastman Kodak Co. phenylbenzylcarbinol (m. p. 65–66°). The tube was sealed and allowed to stand a week at room temperature. The ammonia was allowed to evaporate, water added to the residue, and the mixture extracted with ether. The residue from the dried ether solution gave no test for unsaturation with bromine in carbon tetrachloride. Recrystallization of the residue gave 8.9 g. (90% recovery) of phenylbenzylcarbinol melting at 65–66°.

---

(4) R. D. Bright, Ph.D. Thesis, Duke University, 1939, p. 94.

(5) Kohler and Corson, THIS JOURNAL, **45**, 1975 (1923).

(6) Hauser and Breslow, *ibid.*, **62**, 595 (1940).

(7) Blaise and Herman, *Ann. chim. phys.*, [8] **23**, 532 (1911).

(8) Hauser and Renfrow, THIS JOURNAL, **59**, 1823 (1937).

(9) The melting points reported in the literature range from 92 to 96°.

Summary

Ethyl β-phenyl-β-hydroxypropionate has been dehydrated in the presence of either sodium triphenylmethyl or sodium ethoxide at room temperature.

It has been shown that phenylbenzylcarbinol is not dehydrated by sodium amide at room temperature.

The mechanism of elimination of water from organic compounds by means of bases is discussed.

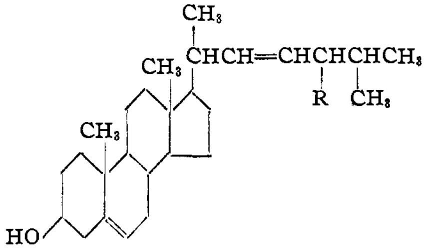
DURHAM, NORTH CAROLINA RECEIVED JULY 26, 1940

[CONTRIBUTION FROM THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH, DIVISION OF ORGANIC CHEMISTRY]

Preparation of 22,23-Dihydrostigmasterol and 22,23-Dihydrobrassicasterol

BY ERHARD FERNHOLZ AND WILLIAM L. RUIGH

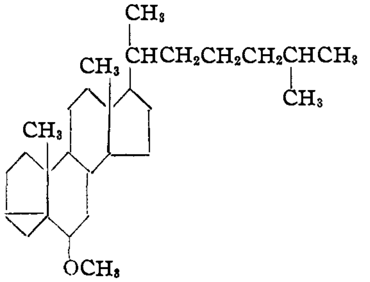
Bernstein and Wallis[1] showed that the double bond in the side-chain of stigmasterol (Ia) could be selectively reduced by means of palladium and hydrogen. Evidence was brought by the same authors to show the identity of 22,23-dihydrostigmasterol with β-sitosterol from cottonseed oil.



I. (a) $R = C_2H_5$; (b) $R = CH_3$.

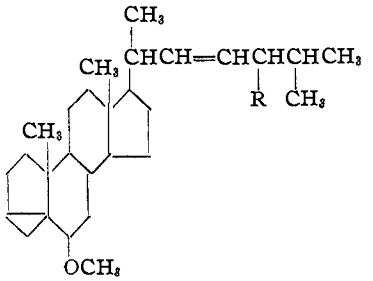
After the elucidation of the structure of brassicasterol,[2] we were interested in the application of such a partial hydrogenation to this sterol so that the properties of 22,23-dihydrobrassicasterol might become known and its isolation from natural sources thus be facilitated. In the attempt to reproduce the experiments of Bernstein and Wallis, however, it became apparent that the selectivity of our palladium catalyst was not great enough, and in following the directions closely we obtained a 22-23-dihydrostigmasterol undoubtedly contaminated with a certain amount of stigmasterol.

It occurred to us at this point that our objective might be reached with much greater ease and certainty if the 5,6-double bond could be blocked by conversion into the *i*-ether prior to hydrogenation. In a noteworthy series of articles Wallis and his school[3,4,5,6] demonstrated that the abnormal cholesteryl ether of Stoll,[7] which is formed when cholesteryl *p*-toluenesulfonate is boiled in methanol in presence of potassium acetate, has structure II.



II

The *i*-cholesteryl ether is without a double bond. If stigmasterol and brassicasterol underwent the same type of abnormal ether formation, it would leave the double bond in the side chain free for hydrogenation. The conversion of stigmasterol and brassicasterol into the *i*-ethers (III) was readily accomplished. When a weak palladium catalyst was used, the reaction stopped sharply after one mole of hydrogen was absorbed, giving the reduced ethers in good yields. Treatment with zinc acetate in boiling acetic acid[8] led to rearrangement with the formation of the normal



III

---

(1) Bernstein and Wallis, *J. Org. Chem.*, **2**, 341 (1937).

(2) Fernholz and Stavely, THIS JOURNAL, **62**, 1875 (1940).

(3) Wallis, Fernholz and Gephart, *ibid.*, **59**, 137 (1937).

(4) Ford and Wallis, *ibid.*, **59**, 1415 (1937).

(5) Ford, Chakravorty and Wallis, *ibid.*, **60**, 413 (1938).

(6) Ladenburg, Chakravorty and Wallis, *ibid.*, **61**, 3483 (1939).

(7) W. Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

(8) Beynon, Heilbron and Spring, *J. Chem. Soc.*, 406 (1937).