small and varies with the conditions. In the dissociation, that atom which has the higher effective nuclear charge retains the extra electron. These assumptions together with certain other (specific) assumptions of the octet theory are used to interpret the properties of the double bond. Simple addition, selective addition, 1,4 addition, Markownikoff's rule, reduction, catalytic hydrogenation, and promoter action are discussed.

URBANA, ILLINOIS

THE UTILIZATION OF CASSIA OIL FOR THE SYNTHESIS OF CINNAMYL ALCOHOL[1]

BY ARTHUR J. HILL AND EDITH H. NASON

Cinnamyl alcohol has found fairly extensive use, either alone, or as a fixative, in the manufacture of perfumes.

The main source of this compound has been storax gum, in which it occurs as cinnamyl cinnamate, associated with other esters.

There is need, however, for a practical synthesis because of the many disadvantages attending the use of storax. Of the three[2] syntheses which have been recorded in the literature, that of Barbier appears to be the most practicable. This method involves first the reduction of cinnamyl diacetate (II) by means of iron and acetic acid, followed by saponification of the resulting acetate (III) with alcoholic sodium hydroxide.

$$C_6H_5CH=CHCHO \xrightarrow{(CH_3CO)_2O} C_6H_5CH=CH-CH(OCOCH_3)_2$$
$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$
$$C_6H_5CH=CHCH_2OH \xrightarrow{NaOH} C_6H_5CH=CH-CH_2-OCOCH_3$$
$$\text{IV} \qquad\qquad\qquad\qquad\qquad \text{III}$$

(with $\downarrow$ H$_2$ between II and III)
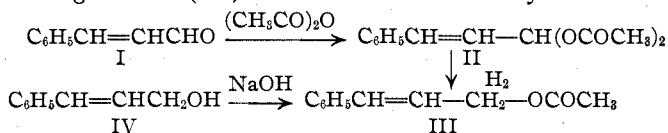
The yield is stated to be 20%. Unfortunately, however, the directions given by Barbier and Leser are rather inadequate and, as a result, have but little practical value in their present form. Indeed, they state that the method could undoubtedly be greatly improved by a study of the conditions of the reaction.

Cassia oil affords a comparatively cheap and abundant source of cinnamic aldehyde. Indeed, there are no methods involving the synthesis of the cinnamyl residue which so far would appear to compete successfully with this natural product. It has seemed desirable, therefore, to utilize this naturally occurring aldehyde for the preparation of cinnamyl alcohol, in particular through the medium of the Barbier method.

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[1] This paper is constructed from the dissertation presented by Edith H. Nason to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Barbier and Leser, *Bull. soc. chim.*, [3] **33**, 858 (1905). Rona, *Biochem. Z.*, **67**, 137 (1914). Skita, *Ber.*, **48**, 1692 (1915).

The investigation of this method necessitated, first, the isolation of pure cinnamic aldehyde from cassia oil. The usual method[3] employing sodium acid sulfite proved disadvantageous when quantities greater than 200 g. were used, on account of losses occasioned by polymerization and other reactions, of which the following was apparently one of the most prominent: $2C_6H_5CH:CH.CHOH.OSO_2Na = C_6H_5CH:CH.CHO + C_6H_5-CH(SO_3Na).CH_2.CHOH.SO_3Na$. It was also difficult to remove oily impurities from the voluminous precipitate of the addition product.

It was found, however, that pure cinnamyl diacetate could be directly prepared in large quantities and in excellent yields by the action of acetic anhydride on cassia oil. The laborious separation of cinnamic aldehyde was thus avoided, and at the same time a simple and more expedient method for its separation from cassia oil was effected, since cinnamyl diacetate is comparatively stable and can be readily hydrolyzed to cinnamic aldehyde without attendant polymerization and loss of material. The product is also superior to that obtained by the bisulfite method.

The various factors influencing the reduction of cinnamyl diacetate by means of iron and acetic acid were then studied. During the first part of the investigation many of the reactions were incomplete, cinnamic aldehyde being the chief impurity in the reduction products. This necessitated the development of analytical methods for the quantitative estimation of the possible constituents in these mixtures. In consideration of the products formed in the reduction of other aldehydes by similar reagents[4] it appeared that the reduction products might contain one or more of the following substances, namely, the saturated and unsaturated aldehydes, alcohols and glycols, and the hydrocarbons, phenylpropane and phenylpropene.

A rapid method was developed for the determination of cinnamic aldehyde. This depends upon the quantitative precipitation of cinnamylphenylhydrazone in glacial acetic acid. This procedure was also applied to the estimation of the aldehyde in cassia oil. No evidence of the presence of hydrocinnamic aldehyde, or of the hydrocarbons, was obtained. A separation of cinnamyl from phenylpropyl alcohol was effected in the final product of hydrolysis by means of anhydrous calcium chloride, with which the former, and not the latter alcohol reacts. Glycols were readily sep-

[3] (a) *Ber.*, **24**, 1805 (1891); (b) **31**, 3302 (1898). (c) Schimmel and Co., "Semi-Annual Reports," Oct., **1896**, p. 12.

[4] *Monatsh.* (a) **1**, 825 (1880); (b) **4**, 21 (1883); (c) **7**, 55 (1886).

Action of reducing agents on cinnamic aldehyde: (d) *Ber.*, **24**, 1451 (1891); (e) **32**, 1296 (1899); (f) **48**, 1486 (1915); (g) **48**, 1692 (1915). (h) *J. Chem. Soc.*, **89**, 1512 (1906); (i) **101**, 1016 (1912). (j) *Compt. rend.*, **154**, 359 (1912).

Action of reducing agents on cinnamyl alcohol: (k) *Ber.*, **6**, 214 (1873); (l) **11**, 659 (1878); (m) **39**, 2587 (1906). (n) *J. Chem. Soc.*, **39**, 319 (1881). (o) *Compt. rend.*, **143**, 829 (1906).

arated by reason of their high boiling points. An accurate estimation or differentiation of these last-named compounds was not attempted.

After a very thorough investigation of all factors (quantity of iron and acetic acid, strength of acid, time and temperature) the writers were able to obtain yields of cinnamyl acetate corresponding to 64% of the calculated. The product, thus prepared, was aldehyde-free. The yield of cinnamyl acetate by the Barbier method was 20%, while 48% of the aldehyde was recovered unchanged.

The final step in the synthesis, the hydrolysis of cinnamyl acetate, was carefully studied with respect to the influence of time and the concentration of alkali. This saponification was finally accomplished in yields closely approaching the calculated, by digesting the acetate with an equimolecular proportion of 5% alcoholic sodium hydroxide.

A new method was developed for the purification of the crude product of hydrolysis, which contained small amounts of phenylpropyl alcohol. The purification was based on the observation, previously mentioned, that calcium chloride forms an addition product with cinnamyl alcohol, while phenylpropyl alcohol does not readily combine with the salt under the conditions developed.

An astonishing catalytic effect was observed when a small amount of nickel sulfate solution was added to the usual reduction mixture. The presence of this salt promoted the formation of phenylpropyl alcohol. This observation is in accord with the well-known catalytic effect of nickel to hydrogenate ethylenic linkages. Copper sulfate, on the other hand, inhibited the reduction of the diacetate.

Attempts were also made to obtain cinnamyl alcohol by the reduction of the diacetate with other metals. The instability of cinnamyl diacetate and aldehyde in the presence of moderately strong acid or alkali limited the choice of reducing agents.

Aluminum amalgam gave incomplete reduction, while zinc and zinc couples produced in every case the corresponding glycol, hydrocinnamoin, admixed with other sirupy by-products (presumably polymerized hydrocinnamic aldehyde and the saturated glycol). A similar observation was made by Thiele[4e] in the reduction of cinnamic aldehyde with zinc-copper couple and 33% alcohol. Cinnamyl acetate was *not obtained* by the writers when zinc in any form was employed.

According to Charon[5] there is a tendency for aldehydes containing the radical R.CH=CH—, and especially those in which R is C_6H_5—, to form glycols on reduction. Cinnamic aldehyde should readily yield hydrocinnamoin.

On the other hand, the Thiele hypothesis would suggest the formation of predominating quantities of hydrocinnamic aldehyde (or phenylpropyl

[5] Charon, *Compt. rend.*, **128**, 736 (1899).

alcohol). $C_6H_5CH:CHCH=O \xrightarrow{H_2} [C_6H_5CH_2CH=CHOH] \longrightarrow C_6H_5CH_2.CH_2.CHO.$
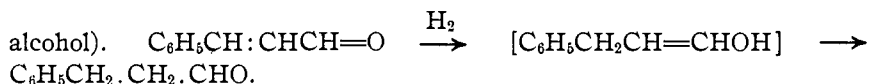
The reduction with iron and acetic acid does not conform to either of these theories, for neither hydrocinnamoin nor hydrocinnamic aldehyde was formed in any appreciable quantity in this reaction. This observation, and the fact that others[6] who have studied the action of iron and acetic acid on unsaturated aldehydes have also obtained the unsaturated alcohol, without appreciable glycol formation, suggests that metals not only function as a source of hydrogen, but are also able by means of their catalytic action to direct the course of the reduction of aldehydes. Thus, glycol formation appears to predominate when zinc is employed. Iron not only appears to inhibit glycol formation, but also to retard reduction of the ethylenic bond. Thus *allyl-p*-aminobenzoate[7] may be prepared by the action of iron and 30% hydrochloric acid upon *allyl-p*-nitrobenzoate.

Since completing the investigations outlined above, the writers have observed that another factor must be considered in the reduction with iron and acetic acid. When the ordinary cast iron or steel filings are used the product is aldehyde-free. Pure iron powder, however, gives a product containing 10% of aldehyde, while pure electrolytic iron produces considerable hydrocinnamoin. The difference in behavior of pure iron and zinc may not be as great as hitherto supposed.

The intrinsic directive effect of metals in reduction is apparently affected, not only by the acidity or alkalinity of the media in which they are used, but also by the catalytic influence of substances such as carbon, salts, etc. Further investigation is now being made of this factor.

So far as the writers are aware there is no record in the literature with regard to the preparation of cinnamyl alcohol from cinnamic aldehyde by means of a wet reduction method. When the procedure used for the reduction of cinnamyl diacetate was *directly* applied to either pure cinnamic aldehyde, or cassia oil, a surprisingly good yield of cinnamyl acetate was obtained. This observation is quite contrary to Barbier's experience. Indeed, the final yield of cinnamyl alcohol from either cinnamyl diacetate or cinnamic aldehyde is very nearly the same, namely, 55% and 50.9%, respectively. Obviously there is no practical advantage in using pure cinnamic aldehyde as the starting material when cassia oil is employed as the source of this compound, since the aldehyde is most conveniently isolated in the form of its diacetate. The direct utilization of cassia oil is of some advantage in that the natural impurity of cinnamyl acetate augments the final yield of alcohol. This is open, however, to one serious objection, in that it is somewhat difficult subsequently to remove certain

[6] Refs. 4 a, 4 b, 4 c. *Monatsh.*, **3**, 122 (1882).

[7] U. S. pat. 1,360,994.

aromatic constituents of the cassia oil which appear to be carried through to the alcohol stage.

In Table I are given data which serve to show the relative efficiencies of the three methods for the preparation of cinnamyl alcohol.

TABLE I

PREPARATION OF CINNAMYL ALCOHOL FROM CASSIA OIL, CINNAMIC ALDEHYDE AND CINNAMYL DIACETATE

Substance reduced	Substance reduced G.	Cinnamyl acetate G.	Reduction %	Hydrolysis product G.	Hydrolysis %	Cinnamyl alc. in hydrolysis product %	Total yield %
Cinnamyl diacetate	140	67	63.6	49	96.1	90	55
Cinnamic aldehyde	39	30	57.7	22	98	90	50.9
Cassia oil	104	80	80.5[a]	66	108[a]	80	70[a]

[a] Due to natural occurrence of cinnamyl acetate in cassia oil.

Experimental Part

Isolation of Pure Cinnamic Aldehyde from Cassia Oil

1. Sodium Bisulfite Method

As the result of preliminary experiments, the following process was adopted as being the most satisfactory.

A solution containing 90 g. of sodium acid sulfite in 180 cc. of water was added slowly to a well-cooled solution of 100 g. of cassia oil in 100 cc. of 95% alcohol. The solution was cooled during the reaction and continuously shaken or stirred. The solid, colorless addition product was filtered off, washed well with alcohol, and transferred to a flask suitable for steam distillation. After the cautious addition of 140 cc. of 50% sulfuric acid, the mixture was warmed on the steam-bath for a short time and then steam distilled. The cinnamic aldehyde, which came over slowly in an emulsoid state, was extracted with ether, dried over anhydrous sodium sulfate and distilled under diminished pressure (b. p., 139.5°, 24 mm.).

2. Diacetate Method

A. The Diacetate of Cinnamic Aldehyde.—A few drops of concd. sulfuric acid were added to an equimolecular mixture of cinnamic aldehyde and acetic anhydride, which had previously been cooled to 10°. There was an immediate reaction, the temperature rising to 40°. When the reaction mixture had cooled below 20°, the solid mass was neutralized with dil. sodium carbonate solution, the acetate filtered off and washed with cold alcohol. The yield, based on the product thus obtained (m. p., 86°), was 85.7%.

This method was found satisfactory for the direct preparation of cinnamyl diacetate from cassia oil. The preparation of the substance in large quantities offered no difficulties. It was found more expedient in large scale productions to crystallize the crude diacetate from alcohol, rather than to attempt removal of impurities by washing with this solvent.

B. The Preparation of Cinnamic Aldehyde from Cinnamyl Diacetate.—One liter of 10% sulfuric acid was added to 475 g. of cinnamyl diacetate, and the mixture cautiously heated on a steam-bath for a short time. The aldehyde, which separated as a colorless oil, was then steam distilled and removed from the distillate by extraction with

ether. After drying over fused sodium sulfate, the aldehyde was distilled under diminished pressure; yield, 260 g., or 96% of pure aldehyde.

Analysis of Cinnamic Aldehyde in the Reduction Product.—An aliquot portion, 1 g., of the reduction product was treated with an equimolecular quantity, 0.9 g., of phenylhydrazine, which was dissolved in 3 cc. of glacial acetic acid. The completeness of the reaction was insured by allowing the solution to stand for twelve hours, after which the phenylhydrazone was filtered off, washed with a small amount of glacial acetic acid, dried and weighed, and the results were calculated in terms of cinnamic aldehyde. The determination of the amount of cinnamic aldehyde in cassia oil was made similarly. The reliability of the method was shown by the fact that pure cinnamic aldehyde when subjected to the same procedure gave the calculated amounts of cinnamyl-phenylhydrazone. This method of analysis proved to be more practicable for the purpose of the present investigation than either the oxamazide,[8] or the bisulfite[3c] method.

It is important to note, in this connection, that the majority of *aldehyde-free* reduction products gave on hydrolysis almost quantitative yields of cinnamyl alcohol. Moreover, when unchanged aldehyde was present, its hydrazone was pure cinnamyl-phenylhydrazone. It seems probable, therefore, that hydrocinnamic aldehyde is not an end-product of the iron-acetic acid reduction.

The Reduction of Cinnamyl Diacetate with Iron and Acetic Acid.—

Barbier and Leser treated cinnamyl diacetate with four to five parts of 80% acetic acid and an *indefinite* amount of iron filings. When the vigor of the reaction had subsided, the reduction mixture was placed on a steam-bath and digested for twelve hours. The excess of iron was then removed by filtration and thoroughly washed with hot water. The cinnamyl acetate was extracted with ether, dried, and distilled under diminished pressure. According to Barbier, the product, which was the acetic ester of cinnamyl alcohol, boiled at 120–160° (14 mm.).

The writers repeated the procedure described above without modification, in so far as it was possible. Barbier does not stipulate the amount of iron which he used. In repeating his procedure and employing the quantity of iron later found to be most efficient, the yield of cinnamyl acetate was not above 28%, and the product contained 48% of unchanged aldehyde.

A study was then made of the factors influencing the course of this reaction, with the object of obtaining the maximum yield of aldehyde-free cinnamyl acetate. During the study of one factor, as for example the strength of acid, all other conditions were kept constant. In each experiment 35 g. of cinnamyl diacetate was reduced under a reflux condenser on a steam-bath for twelve hours. Upon completion of the reaction 500 cc. of hot water was added, the excess of iron filtered off and carefully washed with hot water and ether. The reduction product was extracted from the combined filtrates, dried over anhydrous sodium sulfate and distilled under diminished pressure. The so-called reduction product of all the experiments represents the total amount of material which distilled at 135–150° at 20 mm. of which the greater part boiled at 140–145° (20 mm.).

[8] *Chem. Zentr.*, **1903**, II, 1091.

The factors[9] investigated were the following: strength of acid, quantity of iron and acetic acid, and time of reduction.

Strength of Acid.—This was varied from 20 to 99.7% acetic acid. The maximum yield (61%) was obtained with 60% acid, while further dilution occasioned a slight decrease. Subsequent experience has shown that with some grades of iron it is advisable to use somewhat less than 60% acid. The optimum strength varies, therefore, from 50 to 60%. With 80% acid, the strength employed by Barbier and Leser, the yield of cinnamyl acetate was but 28%, and 48% of the aldehyde was recovered unchanged. Considerable polymerization of the aldehyde occurred when 99.7% acid was used, and the reduction was only 18% complete.

Amount of Iron.—The calculated quantity of iron necessary for the reduction of 35 g. of cinnamyl diacetate is 9 g. (1 molecular equivalent). The minimum amount necessary to give an aldehyde-free acetate was nearly eight times that calculated, or 7.7 molecular equivalents (70 g.). A slightly greater yield was obtained with 8.3 molecular equivalents (75 g.), but this was not continued by further addition. The increase of iron from 1 to 8.3 molecular equivalents caused a steady decrease of unchanged aldehyde from 81.5 to 0%.

Amount of Acid.—Amounts of 50–60% acetic acid above 300 cc. caused a surprising increase in unchanged cinnamic aldehyde. A similar effect was also produced by the addition of small amounts (2 cc. to 15 cc.) of sulfuric acid. The amounts of unchanged aldehyde were 3.1% and 20.4%, respectively, in these cases.

Time.—A period of twelve hours seemed most efficient; when this was shorter the time allotted the reduction of cinnamyl diacetate was extremely important, but beyond that, it had no appreciable effect, either on the yield of reduced product, or on the percentage of unchanged material. Apparently, ferrous acetate does not function in this reduction. When the time was decreased to eight hours, for example, the product, previously aldehyde-free, contained 23.5% of cinnamic aldehyde.

Temperature.—In view of the influence of time on the progress of the reaction, it was not considered advisable to attempt reduction at a lower temperature. One carried out at 110° gave results similar to those at 100°.

As a result of the foregoing experiments, the following procedure was found to be productive of the maximum yield of cinnamyl acetate.

Cinnamyl Acetate.—A mixture of 75 g. of iron filings and 35 g. of cinnamyl diacetate in 300 cc. of 50% acetic acid was heated on a steam-bath under a reflux condenser for twelve hours, at the end of which time, 500 cc. of hot water was added. The excess of iron was filtered by suction,

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[9] Space has not permitted the presentation of all data relating to the investigation of these factors. Suffice it to say that numerous experiments were carried out in order to define the most favorable condition in each case.

washed with hot water and finally ether. The filtrate was then extracted with ether, dried over anhydrous sodium sulfate and distilled under diminished pressure (b. p., 135–150°, 20 mm.). The product, cinnamyl acetate, obtained in a yield of 60.7%[10] contained no aldehyde, and gave on hydrolysis an oil containing more than 90% of cinnamyl alcohol.

The efficiency of this procedure as compared with Barbier's is shown in Table II. That of Barbier gives a product highly contaminated with cinnamic aldehyde and the yield of the reduction product is only 28% of the calculated amount.

<div align="center">TABLE II</div>
<div align="center">COMPARATIVE REDUCTIONS OF CINNAMYL DIACETATE</div>

Diacetate G.	Iron G.	Acetic acid %	Acid Cc.	Time Min.	Temp. °C.	Product G.	Aldehyde G.	Reduction %
35[a]	?	80	187	12	100	14	48	28
35	75	50–60	250–300	12	100	15	0	60.7[b]

[a] Barbier's procedure.

[b] 64% with larger amounts of diacetate.

The Effect of Metallic Salts on the Reduction.—Attempts were made to catalyze the reduction by means of metallic salts. It is well known that iron does not form couples with other metals. The effect of a couple is often produced when metallic salt solutions are added to an iron reduction mixture. Two experiments of this nature, made with copper and nickel sulfate solutions, gave rather surprising results. In both experiments, 100 cc. of a 10% solution of the sulfate was added gradually to a reduction mixture containing 65 g. of iron, 300 cc. of 60% acetic acid and 35 g. of cinnamyl diacetate. The temperature, time and manipulation were those previously shown to give optimum results.

The addition of cupric sulfate increased the amount of unchanged aldehyde to 14%, while nickel sulfate appeared to make the reduction more complete. An examination in each case of the crude alcohol revealed the interesting facts that cupric sulfate merely decreased the amount of reduction, while nickel sulfate produced considerable phenylpropyl alcohol, with no unchanged aldehyde.

Action of Aluminum Amalgam on Cinnamyl Diacetate.—Aluminum amalgam, containing 30 g. of aluminum, was added to 35 g. of cinnamyl diacetate, dissolved in 300 cc. of 50% acetic acid. The reduction was carried out in the usual way. The reduction product contained 85.7% of unchanged cinnamic aldehyde.

Action of the Zinc-Copper Couple on Cinnamyl Diacetate in Neutral Medium.—A solution of 35 g. of cinnamyl diacetate in 300 cc. of 60% alcohol was added to 30 g. of a zinc-copper couple. After eight hours on the steam-bath, the mixture became cloudy, due to the precipitation of zinc hydroxide. At the end of twelve hours the alcohol was removed by vacuum distillation on a steam-bath and the product extracted as usual.

[10] When a larger amount of cinnamyl diacetate (140 g.) is reduced by the same method, the yield is increased to 63.7%.

When the product was distilled at 11 mm. it decomposed. The experiment was then re-peated to the point of distillation and the material thus obtained placed in a vacuum desiccator over sulfuric acid for a few days. The crystals, which formed slowly, were filtered off and washed with alcohol. The compound was found to be identical with the hydrocinnamoin prepared by Thiele[46] by the reduction of cinnamic aldehyde with zinc-copper couple and 33% alcohol.

When the reduction described above was carried out with the zinc-copper couple in alcohol, slightly acidified with acetic acid, the results were the same as those above.

Zinc-Nickel Couple.—When a zinc-nickel couple was used in place of the copper-zinc, glycol was again formed.

Zinc and Acetic Acid.—Thirty-five g. of cinnamyl diacetate was reduced with 30 g. of zinc in 175 cc. of 80% acetic acid for twelve hours on the steam-bath. The product, isolated in the usual way, did not distil under diminished pressure. A repetition of the experiment to the point of distillation gave a sweet-smelling substance from which no crystals deposited, although it was allowed to stand in a vacuum desiccator over sulfuric acid for several weeks. The sirupy consistency of the product together with the fact that zinc couples in both acid and neutral media produced hydrocinnamoin suggested the presence of glycols in this reaction product. The odor of this material was also in-dicative of hydrocinnamic aldehyde, or its polymerization products.

Cinnamyl Acetate

By the Action of Iron and Acetic Acid on Pure Cinnamic Aldehyde.—Thirty-nine g. of pure cinnamic aldehyde was heated on a steam-bath for twelve hours with 600 cc. of 50% acetic acid and 160 g. of iron filings; 30 g. of an aldehyde-free distillate was obtained; b. p., 135–150° (18 mm.). The yield of the cinnamyl acetate thus obtained was 57% of that calculated, a result practically as good as that obtained by the reduction of cinnamyl diacetate.

By the Action of Iron and Acetic Acid on Cassia Oil.—Twenty-seven g. of cassia oil, containing 19.5 g. of cinnamic aldehyde, was treated with 85 g. of iron filings and 300 cc. of 50% acetic acid under the usual conditions. The product of the reaction boiling at 127–143° (11 mm.) was aldehyde-free, and represented a 77% yield of crude cinnamyl acetate. Although aldehyde-free, the ester was contaminated with some of the impuri-ties of the cassia oil. The purity of the cinnamyl alcohol obtained by the hydrolysis of this material will be discussed later.

Cinnamyl Alcohol

The Hydrolysis of Cinnamyl Acetate.—A few preliminary experiments with several hydrolytic agents, such as hydrochloric acid, sulfuric acid, barium hydroxide, potassium carbonate and sodium hydroxide, demonstrated the unfeasibility of all but sodium hydroxide in an alcoholic medium. A more detailed investigation of the latter was then made, and the most favorable conditions resulting from this have been incorporated in the following description. A mixture of 67 g. of cinnamyl acetate and one molecular proportion of a 5% alcoholic solution of sodium hydroxide was digested on the steam-bath for 45 minutes. The solution was then diluted with 3 volumes of water, and the cinnamyl alcohol extracted with ether, dried over anhydrous sodium sulfate, and dis-tilled. The boiling point of the purest product, thus obtained, was 148–153° at 20 mm.; yield, 49 g., or 96%. A new method of purification is described below.

When smaller quantites of the acetate are used, the time of hydrolysis may be shortened to 30 minutes. Extension of time beyond 45 minutes, as well as the use of larger amounts of alkali, occasions some polymerization and consequent loss of the al-cohol. This point is being further investigated.

Purification.—The purification by fractional distillation of the cinnamyl alcohol resulting from the hydrolysis described above was found to be somewhat unsatisfactory. The crude product boiled within 15° (20 mm.), 83% distilling within 5°. The larger fraction (b. p., 147–153°; 20 mm.) solidified in ice and remained solid up to 30° (the melting point of the pure alcohol is 33°). The smaller fraction solidified when cooled in ice water, thus showing the presence of a relatively large amount of the alcohol, but the melting point of this fraction was about 20°. Attempts to better the alcohol content of this fraction by distillation were unsuccessful.

Purification by alternate freezing and pressure filtration was found to entail large mechanical losses.

It is well known that calcium chloride forms addition compounds with certain alcohols. An application of this principle to the purification of cinnamyl alcohol was successful, after preliminary tests had shown that pure cinnamyl alcohol could be quantitatively recovered by this procedure.

Five parts by weight of cinnamyl alcohol were treated with 35 parts of anhydrous ether and 10 parts of powdered anhydrous calcium chloride. The addition product which was completely formed after twelve hours, was filtered off, washed thoroughly with dry ether and decomposed by treatment with cold water. The cinnamyl alcohol was then extracted with ether, dried and weighed.

Since phenylpropyl alcohol was the probable impurity in the crude cinnamyl alcohol, the same process was repeated with this compound. No addition occurred. Furthermore, when a known mixture of cinnamyl and phenylpropyl alcohols was similarly treated, the cinnamyl alcohol was obtained from the filtered and washed calcium chloride addition product in 90% yield, and the phenylpropyl alcohol was recovered on evaporation of the ether washings.

This method was applied to the alcohol obtained by the hydrolysis of the cinnamyl acetate from the three sources, namely cinnamyl diacetate, cinnamic aldehyde and cassia oil. When cinnamyl diacetate and cinnamic aldehyde were the sources of the acetate, the products of the hydrolysis contained 90% of cinnamyl alcohol, while that obtained from the reduction of cassia oil contained but 80%. This lower percentage in the latter case was due to impurities contained in the original cassia oil, and which modify the odor of the crude cinnamyl alcohol resulting from this source.

Cinnamyl p-Nitrobenzoate, $C_6H_5CH:CHCH_2$—$OCOC_6H_4NO_2(p)$.—Twenty g. of cinnamyl alcohol was heated on the steam-bath with 100 cc. of anhydrous ether and 52 g. of solid sodium carbonate; 200 cc. of an ether solution containing 30 g. of p-nitrobenzoyl chloride was then added and the digestion continued for ten hours. After removal of the ether the reaction product was separated from inorganic material by solution in ethyl acetate. After evaporation of this solvent, the p-nitrobenzoic acid and the cinnamyl ester were separated completely by the use of ligroin, in which the acid is insoluble. The cinnamyl ester of p-nitrobenzoic acid was thus obtained in a yield of 78%. It crystallizes from ligroin in almost colorless leaflets; m. p., 78°.

Anal. Calc. for $C_{16}H_{13}O_4N$: C, 67.6; H, 5.05; N, 4.95. Found: C, 67.8; H, 4.59; N, 4.72.

Summary

1. Cinnamyl diacetate has been prepared by the action of acetic anhydride on cinnamic aldehyde, or cassia oil, in yields averaging 85.7%.

2. Pure cinnamic aldehyde is readily prepared in 96% yield by hydrolysis of cinnamyl diacetate.

3. Under appropriate conditions of temperature and concentration of

reagents, cinnamyl diacetate may be reduced to cinnamyl acetate by means of iron and acetic acid, in 60.7% yield.

4. Pure cinnamic aldehyde and cassia oil may likewise be reduced to cinnamyl acetate with good yields.

5. The addition of copper or nickel salts to the iron and acetic acid reducing medium does not catalyze the formation of cinnamyl acetate.

6. Aluminum amalgam, zinc-copper couple, zinc-nickel couple, or zinc and acetic acid with cinnamyl diacetate give *glycols*, and not *cinnamyl acetate*.

7. Cinnamyl acetate is hydrolyzed in 98% yield by 5% alcoholic sodium hydroxide.

8. Cinnamyl alcohol forms an addition compound with calcium chloride which may be used for the purification of the crude alcohol.

9. Cinnamyl alcohol reacts with *p*-nitrobenzoyl chloride to form the characteristic ester, cinnamyl *p*-nitrobenzoate.

NEW HAVEN, CONNECTICUT

STERIC HINDRANCE IN THE MIGRATION OF ACYL FROM NITROGEN TO OXYGEN

BY L. CHAS. RAIFORD AND CHAS. M. WOOLFOLK

Previous work published from this Laboratory[1] has shown that the migration of acetyl from nitrogen to oxygen, which occurs when an *o*-acetyl-aminophenol is benzoylated by the Schotten-Baumann method, is not prevented by the presence of acid-forming (halogen) or certain other substituents attached to the phenol nucleus. In view of the fact, however, that many well-known reactions are hindered to a greater or less degree, depending apparently on the weight and space occupied by the radicals adjacent to the reacting groups,[2] it became a matter of interest to us to study the behavior of acetyl-benzoyl derivatives of aminophenols in which the positions *ortho* to both amino and hydroxyl groups were occupied by heavy radicals. For this purpose the bromine derivatives of *o*-amino-*p*-cresol and *o*-amino-*o*-cresol (OH = 1) were selected. 2-Amino-3,6-di-bromo-4-methylphenol, obtained by reduction of the corresponding nitro compound which, in turn, was prepared by nitration of 2,3,6-tribromo-*p*-cresol,[3] was acetylated in the usual way. Though hydrolysis of this

[1] THIS JOURNAL, **45**, 1738 (1923), gives a list of papers.

[2] For a bibliography of the subject see Stewart, "Stereochemistry," Longmans, Green and Co., **1907**, p. 261.

[3] (a) Zincke, *J. prakt. Chem.*, [2] **61**, 564 (1900). (b) Zincke and Emmerich, *Ann.*, **341**, 312 (1905).