[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE REDUCTION OF CINNAMIC ALDEHYDE TO CINNAMYL ALCOHOL IN THE PRESENCE OF PLATINUM-OXIDE PLATINUM BLACK AND PROMOTERS. XI

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Recent work from this Laboratory[1b] has shown that aldehydes can be reduced to alcohols in the presence of pure platinum-oxide platinum black and hydrogen only if the catalyst is repeatedly reactivated with air, or better if some promoter such as ferrous chloride is present in the reaction mixture. Most of the substances tested which acted as promoters in the reduction of aldehydes acted as poisons to the catalyst in the reduction of olefins;[1i] the speed of reduction of the olefins was decreased and in the presence of traces of certain salts the reaction was stopped completely. It was of interest, therefore, to determine whether in compounds containing both an olefin and an aldehyde group, the aldehyde might be reduced with platinum-oxide platinum black in the presence of certain salts to the corresponding alcohol without affecting the olefin group at all. This paper describes the study of the reduction of cinnamic aldehyde in the presence of platinum-oxide platinum black under various conditions, with the result that a very satisfactory method for the selective reduction[2] of the aldehyde group, and consequently for the production of cinnamyl alcohol was found.

The catalytic reduction of cinnamic aldehyde has been investigated by others. In every instance the ultimate product has been phenyl propyl alcohol but in no instance was it possible to obtain any reasonable amount of cinnamyl alcohol[3] as a reaction product. Vavon[4] studied

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Previous articles in this field are, (a) Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922); (b) Carothers and Adams, *ibid.*, **45**, 1071 (1923); (c) Adams and Shriner, *ibid.*, **45**, 2171 (1923), preparation of catalyst; (d) Kaufmann and Adams, *ibid.*, **45**, 3029 (1923); (e) Carothers and Adams, *ibid.*, **46**, 1675 (1924); (f) Shriner and Adams, *ibid.*, **46**, 1684 (1924); (g) Carothers and Adams, *ibid.*, **47**, 1047 (1925); (h) Pierce and Adams, *ibid.*, **47**, 1098 (1925); (i) Kern, Shriner and Adams, *ibid.*, **47**, 1147 (1925); (j) Heckel and Adams, *ibid.*, **47**, 1712 (1925).

[2] For some previous cases of selective reduction, see Ref. 1 d; 1 i; Richardson, Knuth and Milligan, *Ind. Eng. Chem.*, **17**, 80 (1925); Hilditch and Moore, *J. Soc. Chem. Ind.*, **42**, 15 (1923); Vavon, *Compt. rend.*, **175**, 277 (1922); Rosenmund, *Ber.*, **51**, 578, 585 (1918); Armstrong and Hilditch, *J. Soc. Chem. Ind.*, **44**, 701 (1925).

[3] Armstrong and Hilditch, *Chim. Ind.*, **12**, 211 (1924).

[4] Vavon, *Compt. rend.*, **154**, 359 (1912).

the reaction with platinum black and isolated only phenylpropyl alcohol. Skita[5] reduced cinnamic aldehyde using colloidal platinum and isolated in succession after absorption of one molecular equivalent of hydrogen, phenylpropionaldehyde; after two molecular equivalents, phenylpropyl alcohol; and after five molecular equivalents, hexahydrophenylpropyl alcohol. Traces of cinnamyl alcohol and phenylpropane were also found. It is particularly noticeable that the olefin double bond is reduced first to the practical exclusion of reduction of the aldehyde group.

When cinnamic aldehyde is reduced with pure platinum-oxide platinum black in the presence of hydrogen (Table I) the reduction goes to only a very slight extent before it stops. This might be predicted from previous results with benzaldehyde. About 0.15 molecular proportion of hydrogen is absorbed before the catalyst becomes entirely inactive. Only by reactivation with air will the reduction proceed, and many reactivations are necessary before the reduction is complete with the absorption of two molecular equivalents of hydrogen and formation of phenylpropyl alcohol. If the reaction mixture is worked up after the absorption of one molecular equivalent of hydrogen it is found that there exists a mixture of products; unchanged cinnamic aldehyde, phenylpropionaldehyde, cinnamyl alcohol and phenylpropyl alcohol. It was possible to extract about 25% of such a mixture with sodium bisulfite whereas the remaining 75% consisted chiefly of cinnamyl alcohol and a little phenylpropyl alcohol.

TABLE I

REDUCTION WITH PURE CATALYST

Aldehyde, g.	95% alcohol, cc.	Catalyst, g.	Reaction time		Product	
			1 *mol. eq.*	2nd *mol. eq.*	after 1 *mol. eq.*	after 2 *mol. eq.*
26.4	100	0.2	0.0378 mole in 70 min. .0432 mole in 295 min.			
52.8	200	.4	10 hrs.		46.8 g. not solid at —5°	
52.8	200	.4	9.5 hrs.	14 hrs. (10 reactivations)		43 g. phenylpropyl alcohol

A mixture of such products would be expected from a consideration of previous work on substituted olefins and aldehydes.[1b,1i] The olefin linkage of a symmetrical disubstituted olefin such as cinnamic aldehyde would not be reduced very readily as compared with many other types of olefins, and the presence of the aldehyde would especially affect the catalyst so as to cause the reaction to proceed very much more slowly or to stop completely. The aldehyde group, on the other hand, if the catalyst is frequently reactivated with air should be reduced readily. It is not surprising, therefore, that a large proportion of cinnamyl alcohol is formed. The separation of pure cinnamyl alcohol from the other prod-

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[5] Skita, *Ber.*, **48,** 1685 (1915).

ucts, however, is impossible by simple distillation and therefore the method is not a feasible one for producing a pure cinnamyl alcohol.

When 2 moles of cinnamic aldehyde are reduced with 0.20 g. of catalyst in 100 cc. of 95% alcohol in the presence of various amounts of ferrous chloride it is possible to carry the reaction completely to phenylpropyl alcohol without any reactivations with air (Table II). An increase in the amount of ferrous chloride has very little effect upon the speed of reduction. The ferrous chloride is obviously, therefore, a promoter in the reduction of cinnamic aldehyde as it is with other aldehydes. If such a reduction is stopped as soon as one molecular equivalent of hydrogen is absorbed it is found that only traces of aldehydes are present. The product is cinnamyl alcohol, the purity depending to a certain extent on the amount of ferrous salt present. Thus the use of 0.01 to 0.02 millimole gave the best results, with the production of a cinnamyl alcohol which melted at 22–24°. Large amounts of ferrous salt up to 0.5 millimole allowed the absorption of one molecular equivalent of hydrogen to take place in approximately the same time, but in every instance gave a product melting somewhat lower, 14–19°. If the reaction was not stopped after one molecular equivalent of hydrogen was absorbed, more hydrogen was always absorbed and the absorption of the second molecular equivalent was much slower than for the first.

Table II

Reduction of 26.4 G. of Cinnamic Aldehyde in 100 Cc. of 95% Alcohol with 0.2 G. of Catalyst and Ferrous Chloride

Moles of $FeCl_2$	Reaction time		Product after 1 mol. eq.		Product after 2 mol. eq.
	For 1st mol. eq., min.	For 2nd mol. eq., hrs.	Wt., g.	M. p., ° C.	Phenyl propyl alcohol, g.
0.0005	168		20	16–18	
.0005	180	6[a]			21.5
.0002	160	75% of 2nd mole in 26 hours			
.0001	155		20	18–19	
.00002	165		23	23–24	
.00002	143		22	22–23	
.00001	195		23	22–23	
.000006	600	12			22

[a] Two reactivations of the catalyst were necessary before the reduction was complete.

The presence of zinc acetate in the catalytic reduction of benzaldehyde led to interesting results; with extremely small amounts no noticeable effect could be noted, a greater amount acted as an excellent promoter, while still greater amounts poisoned the catalyst completely. The zinc acetate was a poison in the reduction of olefins. The reduction of cinnamic aldehyde in the presence of 0.02 millimole of zinc acetate (Table III) indicated that the zinc acetate in that concentration was a promoter, since

TABLE III

REDUCTION OF 26.4 G. OF ALDEHYDE IN 100 CC. OF SOLVENT WITH 0.2 G. OF CATALYST AND ZINC ACETATE

Moles of $ZnAc_2$	Time for 1 mol. eq., hrs.	Time for 2nd mol. eq., hrs.	Product after 1 mol. eq.	Product after 2 mol. eq.
0.0004	0.1370 mole of H_2 in 10 hrs.			
.0003	15	10		
.0003	14	10		
.00002	8	not recorded		23 g. of phenylpropyl alcohol
.00002	11		23 g. not solid at —10°	

the cinnamic aldehyde could be reduced under these conditions completely though slowly to phenylpropyl alcohol without reactivation of the catalyst with air. The reduction was very slow and the zinc acetate in the amount used was consequently not as effective a promoter as the iron salt in the amount used. Increasing the amount of zinc acetate 0.6 millimole inhibited the reduction completely. If the reaction was stopped after the absorption of one molecular equivalent of hydrogen, the reaction mixture yielded a cinnamyl alcohol which did not solidify at —5° and was, therefore, contaminated with phenylpropyl alcohol, no aldehyde being detectable. After one molecular equivalent of hydrogen had been absorbed, further absorption of hydrogen took place with not much change in rate.

A combination of iron and zinc salts gave surprising results (Table IV). The hydrogen was readily absorbed until one molecular equivalent had reacted, after which the hydrogen was taken up only very slowly, more slowly than when zinc salt or iron salt alone was used, or not taken up at all. When the proper proportions, 0.1 mole of alde-

TABLE IV

REDUCTION OF 26.4 G. ALDEHYDE IN 100 CC. OF SOLVENT WITH 0.2 G. OF CATALYST AND A MIXTURE OF FERROUS CHLORIDE AND ZINC ACETATE

Moles of $FeCl_2$	Moles of $ZnAc_2$	Time for 1 mol. eq., min.	Product after 1 mol. eq. absorbed Yield, g.	M. p., ° C.
0.0002 3 runs	0.00002 3 runs	156–165[a]	21–23[b]	25–26
.0002 5 runs	.00003 5 runs	275–390[a]	22–23[c]	22–23 to 26–28
.0002	.00004	349	22	25–27
.0004	.00002	209	23	21–23

[a] Rather wide variation occurred in these reductions, far greater than any in reductions previously studied. The temperature was that of the room and was not carefully controlled; this may account for part of the variation.

[b] Almost stopped after 1 mol. eq. absorption.

[c] Stopped completely after 1 mol. eq. absorption.

hyde in 100 cc. of solvent, 0.2 g. of platinum-oxide platinum black, 0.2 millimole of ferrous chloride and 0.03 millimole of zinc acetate were used the reduction stopped completely after one molecular equivalent had been absorbed, the cinnamyl alcohol thus produced was of very high purity, m. p. 25–30°, and contained no aldehyde.

The reaction is very specific and for each amount of aldehyde and platinum used it is necessary to find the proper amount of iron and zinc salts (Table V). When the amount of aldehyde, platinum and solvent was doubled (0.4 mole of aldehyde and 0.4 g. of platinum black in 200 cc. of solvent), the most advantageous combination of iron and zinc salts was 0.4 millimole of ferrous chloride and 0.1 millimole of zinc acetate. This reduction required nine hours for completion and yielded an alcohol melting at 24–26°. An even higher melting point was obtained if 0.12 millimole of zinc acetate was used but the time for reduction was increased to 21 hours; 26.4 g. of aldehyde in 100 cc. of solvent and 0.2 g. of catalyst with 0.0002 g. of ferrous chloride and 0.0002 g. of zinc acetate required nine hours, or with 0.0002 g. of ferrous chloride and 0.00025 g. of

Table V

Reduction of 52.8 G. of Aldehyde in 200 Cc. of Solvent with 0.4 G. of Catalyst and a Mixture of Ferrous Chloride and Zinc Acetate

Moles of $FeCl_3$	Moles of $ZnAc_2$	Time for 1 mol. eq., min.	Product after 1 mol. eq. absorbed Yield, g.	M. p., ° C.
0.0004	0.00004	205	17[a]	15–18
.0004	.00008	269	44[b]	24–26
.0004	.00010	542	43[c]	24–25
.0004	.00012	1260	44[d]	27–30

[a] Warmed to 45°; did not stop after 1 mol. eq. absorption.

[b] Almost stopped after 1 mol. eq. absorption.

[c] Stopped after 1 mol. eq. absorption

[d] Stopped after 1 mol. eq. absorption.

Table VI

Consecutive Reductions with the Same Catalyst Using 26.4 G. of Aldehyde in 100 Cc. of Solvent

	Moles of $FeCl_3$	Moles of $ZnAc_2$	Time for 1 mol. eq.	Product after 1 mol. eq. absorbed G.	M. p., ° C.
A	0.0002	0.00003	272 min.	23[a]	24–26
B			400 min.	23[b]	23–25
C		additional .00001	15 hrs.	24[c]	23–25
D			15 hrs. (reactivated once)	24[d]	26–28

[a] Decanted product and added new aldehyde in alcohol without further addition of salts.

[b] Did not stop as definitely as A.

[c] With an additional 0.00001 mole of $ZnAc_2$. Stopped after absorption of 1 mol. eq.

[d] Added 50 cc. of alcohol and shook catalyst with air for five minutes; then added 26.4 g. of aldehyde in 50 cc. of alcohol.

zinc acetate required 11.5 hours for absorption of 1 molecular equivalent of hydrogen. Smaller amounts of zinc acetate greatly reduced the time necessary but with too rapid reductions, the product was not pure.

To show that the method might be one of practical importance in the synthesis of cinnamyl alcohol the results of a number of runs using the same catalyst are given in Table VI.

The temperature at which the reduction is carried out is an important factor in the yield of product. When the temperature of the reaction mixture rises to 40–50° or above, the speed of reduction is increased but the product is always contaminated with high-boiling material, probably polymerized cinnamic aldehyde or alcohol. As a consequence, larger amounts of platinum and smaller amounts of poison cannot be used to cause the reaction to take place more rapidly, because of the accompanying rise in temperature. If the amount of poison is sufficient to cause the reaction to take place sufficiently slowly or if other conditions are modified to give the same effect, the temperature does not rise and a pure reaction product is obtained.

The character of the catalyst also has a marked effect. Previous investigations have shown that platinum oxide when reduced in the presence of the substance to be reduced frequently gives a platinum black of different activity from that formed in the absence of the substance to be reduced. Experiments with cinnamic aldehyde also showed that the catalyst under these latter conditions was apparently more finely divided and it required more poisoning in the form of salts in order to give the same results as those obtained when the platinum oxide was reduced in the absence of the aldehyde. With catalyst made in this way conditions were not found whereby the reduction would stop completely after the absorption of one molecular equivalent of hydrogen. Nevertheless it was possible to obtain a very good grade of cinnamyl alcohol by working up the reaction mixture after one molecular equivalent of hydrogen had been absorbed.

It is obvious that the reductions which have just been described are extremely specific and it has not yet been determined whether satisfactory results can be obtained with homologous aldehydes. Preliminary experiments with crotonaldehyde indicated that it was possible to obtain croton alcohol although contaminated with a certain amount of *n*-butyl alcohol. A discussion of the effect of the zinc or iron salts, alone or in combination, upon the catalyst in the reduction of α,β-unsaturated aldehydes will be reserved until more experimental results are available.

Experimental Part

Cinnamic Aldehyde.—The cinnamic aldehyde used in this work was prepared by the fractional distillation under diminished pressure of the ordinary commercial grade of pure cinnamic aldehyde, and a fraction boiling over a range of not more than 2° was collected. The aldehyde prepared in this way probably contained from 0 to 2% of cinnamic acid[6] but no variation in the rate of reduction of different portions of the same sample or different samples of aldehyde was observed. The presence of small amounts of cinnamic acid is, therefore, not considered as an important factor in the reductions.

Ferrous Chloride and Zinc Acetate.—The ferrous chloride solution was prepared by a method previously described in this series of papers.[1b]

A 0.2 *M* solution of zinc acetate was prepared by dissolving 9.50 g. of Kahlbaum's zinc acetate in boiled, distilled water and diluting to 200 cc.

Reduction Experiments.—The apparatus used in the reductions was similar to that described previously in this series of papers.

The platinum oxide catalyst was made from pure chloroplatinic acid by the method[1c] already described. In all but the last series of experiments, the platinum oxide was reduced to platinum black before the substance to be reduced or any salt was added. In order to get uniform results, the oxide must be completely reduced before the aldehyde is added.

Procedure.—The weighed amount of catalyst was placed in the reaction flask with 50 cc. of 95% alcohol and after evacuation of the flask was shaken with hydrogen under pressure for five minutes. The ferrous chloride or zinc acetate solution was then added from a capillary pipet and then the aldehyde with the additional amount of solvent. The reductions were carried out under a pressure of from two to three atmospheres.

Isolation of the Products.—The platinum was filtered off and the solvent removed by distillation under atmospheric pressure in a modified Claisen flask.[7] The residue was distilled under diminished pressure (20–30 mm.). A small amount of tarry residue always remained in the flask after the distillation. Cinnamyl alcohol boils at 254° (745 mm.) and 135–137° (25 mm.). Phenylpropyl alcohol boils at 235° (745 mm.) and 129–130° (20 mm.).

Summary

1. Cinnamic aldehyde cannot be reduced completely with hydrogen and platinum-oxide platinum black unless the catalyst is reactivated frequently with air.

2. In the presence of small amounts of zinc or iron salts the reduction goes completely to phenylpropyl alcohol without the necessity of reactivation. When iron salt is used and the reduction is stopped after one molecular equivalent of hydrogen has been absorbed the product is almost pure cinnamyl alcohol.

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[6] Phillips, *Pharm. J.*, **93**, 129 (1914).

[7] Noyes, This Journal, **39**, 2718 (1917).

3. In the presence of both zinc and iron salts in proper proportions, cinnamic aldehyde is reduced to pure cinnamyl alcohol and no more than one molecular equivalent of hydrogen is absorbed.

4. A discussion of the effect of changing other conditions is given.

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THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS. II. THE DISSOCIATING INFLUENCE OF THE CYCLOHEXYL GROUP

BY J. B. CONANT AND L. F. SMALL

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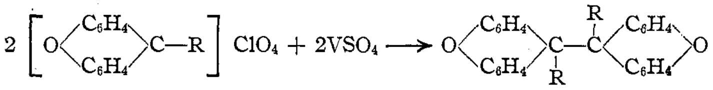
The discovery that many carbinols and their halochromic salts are quantitatively reduced to ethanes by vanadous salts[1] has opened the way to the preparation of derivatives of dixanthyl of Type I, where R is a *non-aromatic* residue. A study of such compounds is of particular interest in connection with the problem of the existence of free radicals with other than aromatic or unsaturated groups attached to the central carbon atom. As a continuation of our study of the effect of different groups on the dissociation of such substituted dixanthyls we have now prepared by our method the following compounds: di(*p*-chlorobenzyl)-dixanthyl ($R{=}ClC_6H_4CH_2—$); di-*iso*-amyl-dixanthyl($R{=}(CH_3)_2CH—CH_2—CH_2—$); di(*n*-hexyl)-dixanthyl($R{=}C_6H_{13}—$) and dicyclohexyl-dixanthyl($R{=}C_6H_{11}$).



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Like dibenzyl-dixanthyl,[1b] the *p*-chlorobenzyl derivative shows the characteristic properties of an ethane which dissociates into a free radical. The absorption of oxygen is very rapid. The degree of dissociation is too small to be detected by the molecular-weight determinations in freezing benzene. A solution of the dixanthyl when warmed to 80–100° loses its ability to absorb oxygen, presumably because of the usual intramolecular oxidation and reduction.

The study of the chlorobenzyl compound thus confirms our previous conclusions that an aromatic residue in the *β position* is effective in causing dissociation in the dixanthyl series, a conclusion that goes far towards disproving the postulates of the Werner-Thiele theory of valence as applied to the dissociation of ethanes.[2]

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[1] Conant and Sloan, (a) THIS JOURNAL, **45**, 2466 (1923); (b) **47**, 572 (1925). (c) For the discussion of the electrochemistry of this reaction, see *ibid.*, **47**, 1959 (1925).

[2] Compare Ref. 1b, p. 576, and Schlenk and Mark, *Ber.*, **55B**, 2285–2289 (1922).