

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

RESEARCHES ON ALDEHYDES. IV. THE CATALYTIC REDUCTION OF SIMPLE AND OF SUBSTITUTED CINNAMIC ALDEHYDES

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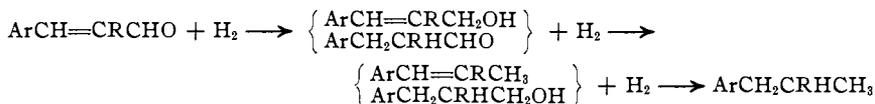
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Introduction

In previous papers we have reported on the synthesis of simple and of substituted 2-alkylcinnamic aldehydes,² and on the reduction of some of these to the corresponding unsaturated alcohols by the use of aluminum ethylate or of magnesium chloroethylate.³

The present contribution records the catalytic reduction of these cinnamic aldehydes to the corresponding saturated aldehydes, saturated alcohols and aryl paraffins.

Depending upon the amount of hydrogen taken up per mole of initial material, and excluding bimolecular reactions, the various products theoretically obtainable by reduction of a 2-alkylcinnamic aldehyde may be represented thus



In our experiments we followed the process of Skita,⁴ using colloidal palladium as the catalyst in most cases, since he found that with cinnamic aldehyde itself this process caused neither hydrogenation of the benzene nucleus nor formation of bimolecular compounds, under conditions similar to ours. With one mole of hydrogen per mole of cinnamic aldehyde, he reported that his product was nearly pure hydrocinnamic aldehyde.

Straus and Grindel⁵ repeated the experiment and stated that their products were the saturated alcohol, the propane and a little unsaturated alcohol, but no saturated aldehyde (except in one case), although pressure and proportion of hydrogen and of catalyst were varied considerably. Since they found that neither the saturated aldehyde nor the saturated alcohol separately could be reduced under these conditions, they suggested that the cinnamyl alcohol and phenylpropene were formed first and were

¹ Fritzsche Fellow for 1928-1929 at Columbia University. This investigation could not have been undertaken without the generous assistance of Mr. F. E. Watermeyer, President of Fritzsche Brothers, Inc., of New York, the donor of the Fellowship [M. T. B.].

² Bogert and Powell, *Am. Perfumer Ess. Oil Rev.*, **25**, 617 (1930).

³ Bogert and Powell, *THIS JOURNAL*, **53**, 1605 (1931).

⁴ Skita, *Ber.*, **48**, 1685 (1915).

⁵ Straus and Grindel, *Ann.*, **439**, 276 (1924).

then reduced to the saturated alcohol and phenylpropane, respectively, the velocity of these latter changes being greater than that of the reduction of the initial unsaturated aldehyde. This was their explanation of why little or none of these hypothetical intermediate products was detected.

Such a postulation, however, does not explain the formation of saturated aldehyde noted by Skita and by ourselves. It is true that the unsaturated alcohols are easily reduced under the conditions of the Skita process, while the saturated aldehydes are not, but the saturated aldehyde itself must be formed from its unsaturated progenitor either by direct saturation of the olefin bond, or by a 1,4-addition with subsequent rearrangement



It is suggested, therefore, that we may be dealing with several types of reactions taking place concurrently, the saturated aldehyde being formed as just indicated and the saturated alcohol and phenylpropane as postulated by Straus and Grindel, although it should be pointed out that because the saturated aldehyde and saturated alcohol cannot be readily reduced separately and individually by the Skita method, it does not follow necessarily that they may not undergo such a direct reduction under the catalytic effect of the other substances present in the mixture while the unsaturated aldehyde is being reduced.

Adams and Tuley⁶ have described a selective reduction of cinnamic aldehyde either to the unsaturated or the saturated alcohol, by suitable additions of small amounts of iron or zinc salts to their platinum-oxide platinum black catalyst, these additions promoting reduction of the aldehyde group and inhibiting the saturation of the olefin bond. The conditions for such selective reduction seem to be highly specific and likely to require prolonged experimentation in each case to learn the correct mixture for the purpose.

With the unsaturated aldehydes we were studying, the Skita process of reduction gave more satisfactory results than we were able to secure with the Adams methods.

Our first run was always made on a 1.5 mole reduction basis, *i. e.*, until 1.5 moles of hydrogen per mole of initial unsaturated aldehyde had been absorbed. The results obtained in that run determined what changes, if any, were desirable in subsequent runs. The saturated aldehydes and saturated alcohols were the principal products with a one or two mole hydrogenation, the propanes being formed in small amounts only. The limit of hydrogenation, with repeated use of catalyst, was not far from two moles of hydrogen, and the amount of hydrogen absorbed in proportion to catalyst varied according to the unsaturated aldehyde used. The yield of saturated aldehyde was favored by restricting the quantity of hydrogen absorbed, while that of the propane was improved by increasing

⁶ Adams and Tuley, *THIS JOURNAL*, **47**, 3061 (1925).

the gas pressure. In one experiment, only the saturated alcohol and aryl paraffin were found. In all other cases, both these and the saturated aldehyde were produced. No unsaturated alcohols or aryl olefins were detected in any of the runs.

The palladous chloride used for the preparation of the catalyst contained traces of platinum, rhodium and hydrochloric acid. The catalyst was not poisoned by the addition of traces of iron, cobalt or nickel salts.

Skita reported that the reduction of cinnamic aldehyde by colloidal palladium yielded mainly hydrocinnamic aldehyde and that the further reduction of the latter was accomplished better with platinum than with palladium. We have found the same to be true in the case of the substituted hydrocinnamic aldehydes prepared by us, namely, that they are either not at all, or certainly not easily, reduced by the usual Skita process with colloidal palladium.

In addition to the products already mentioned, the catalytic reduction of these unsaturated aldehydes always gave higher boiling products, which remained in the distilling flasks after the removal of propanes, saturated aldehydes and saturated alcohols, in the order named, but which have not yet been identified.

Commercial hydrogen from cylinders was used in all of the reductions. The unsaturated aldehyde was subjected to the action of the gas in an Adams hydrogenator. Practically all of the distillations were conducted under diminished pressure and in an atmosphere of nitrogen, to guard against oxidation.

While this investigation was in progress, a French patent⁷ appeared, claiming improvement in color and in odor of perfumes by subjection to reduction by hydrogen in the presence of a nickel catalyst, by aluminum amalgam, zinc dust, etc., and citing ionones, geraniol and others as examples of perfumes improved by such reduction, but it does not specifically cover any of the field reported in the following pages.

The saturated aldehydes were colorless, mobile liquids which boiled lower than the corresponding saturated alcohols or unsaturated aldehydes. They all possessed agreeable odors, which varied with the nature of the side chains.

In general, their reactions were normal. The ability of the 2-amyl derivatives to form bisulfite compounds seems doubtful. The other saturated aldehydes prepared all gave bisulfite compounds, although in some instances they formed very slowly.

When this research was begun, the only aldehyde of this type in the literature was the 2-methyldihydrocinnamic aldehyde of Miller and Rohde.⁸

⁷ I. G. Farbenind. A.-G., French Patent 643,352 (Nov. 4, 1927); *Chem. Abstracts*, 23, 1475 (1929).

⁸ Miller and Rohde, *Ber.*, 23, 1080 (1890).

The saturated alcohols were colorless, more or less viscous liquids and, with the exception of the hydrocinnamic series, practically odorless. They were recovered from the middle fractions of the reduced unsaturated aldehydes, after oximation to remove all aldehydes. In the case of some of the higher homologs, their isolation as acetate or as dinitrobenzoate proved more satisfactory than as the free alcohol.

The aryl paraffins were found in the first runnings of the distillate from the mixture obtained by reduction of the unsaturated aldehyde. Aldehydic impurities were removed by oximation when necessary. The purified propanes were all colorless, mobile liquids. They were all fragrant, the aroma of some of them being quite potent. The scent of 2-benzyl-*n*-butane may be likened to that of safrole containing a little citral. Dihydrosafrole has been described⁹ as having only a weak safrole odor, whereas in our judgment it possesses fully as strong if not a stronger odor than safrole itself. The 2-substituted dihydrosafroles all exhaled a strong safrole aroma but rather sweeter than safrole, and the scent of the substituted dihydroanetholes was strongly reminiscent of anethole. The odor of 2-ethyl-3-*p*-anisylpropane was of anethole type, but also somewhat stronger and sweeter.

Experimental Part

Reduction of Piperonylidene Acetaldehyde, $(\text{CH}_2\text{O})_2[3,4]\text{C}_6\text{H}_3\text{CH}=\text{CHCHO}$

Dihydrosafrole, $(\text{CH}_2\text{O})_2[3,4]\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{CH}_3$.—Piperonylideneacetaldehyde (3,4-methylenedioxcinnamic aldehyde) was reduced by the method of Skita.⁴

To a solution of 12 g. of the unsaturated aldehyde in 125 cc. of 95% alcohol and 40 cc. of water, there were added 20 cc. of a 2% aqueous solution of gum arabic and 10 cc. of a 1% aqueous palladous chloride solution, and the mixture was immediately treated with hydrogen at 3 atmospheres' pressure in the Adams hydrogenator. After forty-five minutes, the absorption of hydrogen ceased abruptly. It was found that two moles of hydrogen had been absorbed and the pressure had fallen to two atmospheres.

The solution was filtered from the catalyst, the filtrate diluted largely with water, extracted with ether and the ether extract treated with 4–6 volumes of saturated sodium bisulfite solution for a day with frequent shaking, to remove aldehydes. This ether solution usually contained 15–25% of the reduction products, and these were the conditions employed in the case of other reductions as well for the separation of the aldehyde bisulfites, the only important variation being in the length of time required for such compounds to separate.

The bisulfite compound precipitated was removed, washed thoroughly with ether and the washings added to the filtrate. The ether layer in this filtrate was separated, washed with a sodium carbonate solution, then with water, dried, the ether distilled off and the residue fractionated under diminished pressure in an atmosphere of nitrogen. The first fraction was dihydrosafrole, without admixture with any safrole or isosafrole, which on rectification boiled at 226–228° (uncorr.). The odor of this dihydro derivative, as mentioned in the introductory portion of this paper, was fully as powerful as that of safrole itself. It was unchanged by digestion with strong potassium hydroxide solution; yield, about 10%.

⁹ Ciamician and Silber, *Ber.*, **23**, 1162 (1890).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.13; H, 7.37; for $C_{10}H_{10}O_2$ (safrole or isosafrole); C, 74.04; H, 6.22. Found: C, 73.41; H, 7.55.

The higher boiling fraction, after removal of the dihydrosafrole, contained the saturated alcohol.

Attempts to carry out this same reduction with the Adams and Tuley⁶ platinum-oxide platinum black catalyst were less satisfactory, for it was found necessary to re-activate the catalyst thrice before the two mole hydrogenation could be completed. As far as our examination went, the reduction products seemed to be the same as with palladium.

In the palladium reductions, variations in the pressure (1.3, 2, 2.5 or 3 atmospheres) of the hydrogen, did not alter the fact that exactly two moles of hydrogen was absorbed in every case. It affected only the rate of this absorption, which naturally increased with the pressure.

2-Piperonylethanol, $(CH_2O)_2[3,4]C_6H_3CH_2CH_2CH_2OH$, as mentioned above, was found in the second fraction from the distillation of the reduction products of the 3,4-methylenedioxcinnamic aldehyde. It was a colorless, odorless, viscous liquid, b. p. 149–150° (uncorr.) at 6 mm.; n_D^{21} 1.54427; yield, about 70%.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.64; H, 6.72. Found: C, 66.63; H, 6.69.

Acetate.—From the alcohol digested two hours with fused sodium acetate and excess of acetic anhydride; colorless liquid, of faint but agreeable odor, b. p. 145° (uncorr.) at 4 mm.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.83; H, 6.35. Found: C, 64.92; H, 6.58.

Reduction of 2-Piperonylidene-propionaldehyde, $(CH_2O)_2[3,4]C_6H_3CH=C(CH_3)CHO$

2-Piperonylpropane, $(CH_2O)_2[3,4]C_6H_3CH_2CH(CH_3)_2$.—A mixture of 10 g. of the unsaturated aldehyde, 150 cc. of 95% alcohol, 5 cc. of the catalyst solution, 20 cc. of gum arabic solution and 30 cc. of water, was treated with hydrogen at atmospheric pressure until 1.25 moles of hydrogen had been absorbed per mole of aldehyde. Several runs were made with these proportions and the accumulated reduction mixtures then worked up as described for the reduction of the piperonylidene acetaldehyde. The bisulfite compound separated was decomposed by agitation with sodium carbonate solution and ether, until the solid had all disappeared. The ether layer was removed, washed with water, dried and the solvent evaporated. The residue was almost pure initial unsaturated aldehyde (oxime, m. p., 124–126°, uncorr.).

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.44; H, 5.30. Found: C, 69.38; H, 5.44.

After the removal of the aldehyde bisulfite from the original reduction mixture, the ether extracts, as before, were washed with sodium carbonate solution, then with water, dried and distilled. After removal of the ether, two fractions were collected, one of boiling point around 120° at 4 mm., and the other at about 150° at 4 mm.

The first fraction on redistillation yielded a colorless mobile oil, b. p. 238–240° (uncorr.) at 760 mm., n_D^{23} 1.51841, of safrole odor, and proved to be the expected arylpropane.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.85. Found: C, 73.99; H, 7.82.

From a similar reduction, with acetic acid as solvent in place of alcohol, the bisulfite separation yielded a mixture of aldehydes, b. p. 140–158° (uncorr.) at 4.5 mm., of an odor quite different from that of the initial unsaturated aldehyde, and which presumably contained some of the saturated aldehyde. The amount of material available, however, was insufficient to enable us to isolate the latter pure.

A preliminary experiment, using 5 g. of the unsaturated aldehyde in place of 10, and the other ingredients of the mixture as already stated, with hydrogen at ordinary

pressure, showed that after two moles of hydrogen had been absorbed, the absorption ceased abruptly. As it was believed that this might be carrying the reduction too far, in view of the results obtained by a two-mole reduction of piperonylidene-acetaldehyde, we investigated the piperonylidene-propionaldehyde chiefly from the standpoint of a 1.25-mole reduction as outlined above.

2-Piperonylpropanol, $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$.—The higher boiling fraction (b. p. around 150° at 4 mm.) referred to above, after taking off the arylpropane in the first runnings, was dissolved in aqueous alcohol and refluxed for one and one-half hours with hydroxylamine, to remove any aldehydes present. The product of this oximation was diluted with water, extracted with ether, the ether extracts washed with dilute hydrochloric acid, to remove any excess of hydroxylamine, then repeatedly with water, with sodium carbonate solution and finally with water again. The ether was removed and the residue, as usual, distilled under diminished pressure in an atmosphere of nitrogen, collecting the fraction of b. p. $147\text{--}148^\circ$ (uncorr.) at 4 mm. The alcohol thus purified formed an odorless, colorless, viscous liquid, $n_D^{22.5}$ 1.54054, which did not absorb bromine in carbon tetrachloride solution.

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3$: C, 68.0; H, 7.27. Found: C, 68.08, 67.97; H, 7.41, 7.40.

Reduction of 2-Piperonylidene-butyraldehyde, $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CHO}$

2-Piperonyl-butyraldehyde, $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CHO}$.—A mixture of 10.2 g. of the unsaturated aldehyde, 65 cc. of glacial acetic acid, 30 cc. of water, 7 cc. of gum arabic solution and 5 cc. of the catalyst solution absorbed 1.6 moles of hydrogen in two hours at ordinary pressure. A mixture of 10.2 g. of the unsaturated aldehyde, 100 cc. of 95% alcohol, 20 cc. of water, 10 cc. of gum arabic solution and 5 cc. of the catalyst solution, absorbed 1.8 moles of hydrogen in one and one-half hours at ordinary pressure. This latter reduction mixture was worked up in the manner already described.

Decomposition of the bisulfite precipitate yielded the pure saturated aldehyde as a colorless liquid, b. p. 136° (uncorr.) at 3 mm., of weak but agreeable odor.

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.86; H, 6.85. Found: C, 70.21; H, 6.82.

2-Piperonylbutane, $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_3$.—After removal of the aldehyde bisulfite, the ether extracts were distilled and, following the evaporation of the ether, a fraction of b. p. up to 130° at 3 mm. was collected and then a second one, b. p. about 150° at 2 mm. The lower fraction carried the arylbutane, the upper one the saturated alcohol.

The piperonylbutane on rectification boiled at $255\text{--}260^\circ$ (uncorr.) at 760 mm., mainly at 257° , and its odor was very faint. It was a colorless mobile oil.

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.95; H, 8.39. Found: C, 74.73; H, 8.28.

2-Piperonylbutanol, $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$.—From the fraction above the piperonylbutane, the butanol was isolated in the same way as noted for the analogous piperonylpropanol, removing aldehydic contaminants by oximation. After repeated distillation, it was obtained as a colorless, odorless, viscous liquid, b. p. $148\text{--}150^\circ$ (uncorr.) at 2 mm., n_D^{22} 1.53853.

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_3$: C, 69.19; H, 7.75. Found: C, 68.89; H, 7.57.

Reduction of 2-Ethylcinnamic Aldehyde, $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CHO}$

2-Ethylhydrocinnamic Aldehyde (β -Benzyl-*n*-butyraldehyde), $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CHO}$.—The mixture used for reduction was composed of 23 g. of the unsaturated aldehyde, 110 cc. of 95% alcohol, 30 cc. of water, 10 cc. of gum arabic solution and 10 cc. of the palladous chloride solution. At ordinary temperature and pressure, this ab-

sorbed less than one mole of hydrogen per mole of aldehyde in forty-five minutes. After the addition of 10 cc. more of the catalyst solution, the absorption rose to 1.25 moles of hydrogen and was increasing so slowly that it was interrupted and the reduction products examined as described under the reduction of piperonylidene-acetaldehyde.

Hydrolysis of the bisulfite compound yielded the pure saturated aldehyde as a colorless liquid, b. p. 115–116° (uncorr.) at 12.5 mm., n_D^{22} 1.50839, which formed a mirror with ammoniacal silver solutions. Its odor was agreeable, but not very strong.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.42; H, 8.70. Found: C, 81.32; H, 8.67.

It was not reduced by the Skita process under the conditions which caused reduction of the unsaturated aldehyde, but was reduced by hydrogen under pressure in the presence of the platinum-oxide platinum black catalyst.

2-Benzyl-*n*-butane, $C_6H_5CH_2CH(C_2H_5)CH_3$.—After the separation of the above saturated aldehyde, the solvent was removed from the ether extracts and the residue fractionated under diminished pressure in an atmosphere of nitrogen. The first fraction contained the hydrocarbon, the second the saturated alcohol. Both were freed from aldehyde impurities by oximation.

The benzylbutane present in the first fraction (b. p. 98–100° at 30 mm.), was isolated as a liquid, b. p. 190° (uncorr.) at 710 mm., of a weak saffrole-type of odor. It has been reported before by Dumesnil,¹⁰ who gave its b. p. as 102° at 15 mm., and by Glattfeld and Cameron,¹¹ who prepared it by five different methods and found an approximate boiling point of 192° at 710–720 mm.

2-Benzyl-*n*-butanol, $C_6H_5CH_2CH(C_2H_5)CH_2OH$.—This saturated alcohol, as separated from the higher boiling fraction of the above reduction mixture, was a colorless, viscous liquid, with a faint sweetish odor, b. p. 105–107° (uncorr.) at 4 mm., or about 256–257° (corr.) at 755 mm.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.43; H, 9.83. Found: C, 80.19; H, 9.63.

It has been prepared previously by other methods, by Guerbet,¹² who recorded its b. p. as 258–261° (corr.) and its odor as lilac-like, and by Von Braun, Rohmer and co-workers,¹³ who found a boiling point of 134–135° at 13 mm., and described its fragrance as rose-like.

Reduction of 2-*n*-Amylcinnamic Aldehyde, $C_6H_5CH=C(C_6H_{11})CHO$

2-Amyl- γ -phenylpropane, $C_6H_5CH_2CH(C_6H_{11})CH_3$, was isolated by fractional distillation of accumulated reduction products of the amylocinnamic aldehyde, being found in the first runnings. It was a colorless mobile oil, b. p. 128–130° (uncorr.) at 16 mm., of not very pleasant odor.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.34; H, 11.66. Found: C, 86.95; H, 11.92.

The low figure for carbon suggests that the product was not quite pure.

2-Amyl-3-phenylpropanol (2-Amyl-dihydrocinnamic Alcohol), $C_6H_5CH_2CH(C_6H_{11})CH_2OH$.—Using the same proportions of ingredients as noted above for the reduction of 2-ethylcinnamic aldehyde, a 1.6 mole reduction product (34 g.) was refluxed for forty-five minutes with 100 g. of acetic anhydride and 3 g. of fused sodium acetate. Distillation of the product gave a principal fraction, b. p. 134–135° (uncorr.) at 3.5 mm., which proved to be the acetate of the saturated alcohol.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.36; H, 9.74. Found: C, 77.85; H, 9.82.

¹⁰ Dumesnil, *Ann. chim.*, [9] 8, 91 (1916).

¹¹ Glattfeld and Cameron, *THIS JOURNAL*, 49, 1043 (1927).

¹² Guerbet, *Compt. rend.*, 146, 1406 (1908); *Bull. soc. chim.*, [4] 3, 944 (1908).

¹³ Von Braun, Rohmer and co-workers, *Ann.*, 451, 50 (1926).

This *acetate* was hydrolyzed by refluxing it for an hour with a 5% alcoholic potassium hydroxide solution. The alcohol was a colorless, viscous liquid, b. p. 119–120° (uncorr.) at 2.5 mm., of weak but rather pleasing odor.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.48; H, 10.76. Found: C, 81.68; H, 10.54.

3,5-Dinitrobenzoate.—The saturated alcohol present in a one-mole reduction product of the amylocinnamic aldehyde was converted to its 3,5-dinitrobenzoate, a reddish, viscous liquid, hydrolysis of which yielded the saturated alcohol, in an impure form (C, 82.15; H, 10.56), but which contained no unsaturated alcohol (no bromine absorption).

Reduction of 2-Methyl-*o*-methoxycinnamic Aldehyde, $o\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$

2-Methyl-3-*o*-anisyl-propionaldehyde, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$.—A mixture of 21 g. of the unsaturated alcohol, 150 cc. of 95% alcohol, 30 cc. of water, 10 cc. of gum solution and 12 cc. of catalyst, when subjected to the action of hydrogen at an average pressure of 2.5 atmospheres, absorbed 1.9 moles of hydrogen exothermally in an hour.

The bisulfite compound separated from the reduction mixture gave the pure saturated aldehyde when hydrolyzed, as a colorless liquid, of a weak sweet odor, b. p. 113–114° (uncorr.) at 5.25 mm., which formed a mirror with ammoniacal silver solutions.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.11; H, 7.93. Found: C, 74.11; H, 8.16.

2-Methyl-3-*o*-anisylpropane, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$.—Fractionation of the residual ether solution after removal of the above bisulfite compound gave a fraction, b. p. near 90° at 9 mm., which contained the propane. This hydrocarbon was isolated in the pure state by rectification, without requiring oximation, and was a colorless liquid, b. p. 111–112° (corr.) at 31.25 mm., of agreeable aromatic odor.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.81. Found: C, 80.34; H, 9.77.

2-Methyl-3-*o*-anisylpropanol, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$.—The fraction boiling just above that containing the anisylpropane carried the saturated alcohol. Its boiling point was around 130° at 6 mm. It was oximated, to remove a small amount of aldehyde present, and was then purified by distillation. It was a colorless, odorless oil, b. p. 131.5–132.5° (corr.) at 8.75 mm.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.29; H, 8.94. Found: C, 72.95; H, 8.82.

Reduction of 2-Ethyl-*o*-methoxycinnamic Aldehyde, $o\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CHO}$

2-Ethyl-3-*o*-anisylpropionaldehyde, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CHO}$.—A mixture of 20 g. of the unsaturated aldehyde, 150 cc. of 95% alcohol, 30 cc. of water, 10 cc. of gum solution and 10 cc. of the catalyst, was reduced with hydrogen at an average pressure of 2.5 atmospheres, and approximately one mole of hydrogen was absorbed.

On working up the reduced mixture, the aldehyde bisulfite separated very slowly. Its hydrolysis yielded the pure saturated aldehyde as a colorless liquid, b. p. 144–145° (uncorr.) at 16 mm., of faint but not unpleasant odor.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.95; H, 8.39. Found: C, 74.70; H, 8.64.

2-Ethyl-3-*o*-anisylpropane, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_3$.—The ether filtrate from the aldehyde bisulfite separation was distilled and the following fractions collected: (1) near 100° at 9 mm., and (2) near 135° at 6 mm.

Redistillation of Fraction (1) gave the propane as a colorless, mobile oil, b. p. 100.5–102.5° (corr.) at 9 mm., with an odor like that of the lower homolog described above.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.19. Found: C, 80.27; H, 10.37.

2-Ethyl-3-*o*-anisylpropanol, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$.—Fraction (2) noted in the last preparation and boiling at about 135° at 6 mm. consisted mainly of unchanged initial unsaturated aldehyde but, after its removal as oxime, a small amount of the

saturated alcohol was isolated, as a colorless, odorless liquid, b. p. 132–134° (corr.) at 5.5 mm.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.17; H, 9.35. Found: C, 74.17; H, 9.43.

Reduction of 2-Ethyl-*p*-methoxycinnamic Aldehyde, $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CHO}$

2-Ethyl-3-*p*-anisyl-propionaldehyde, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CHO}$.—The mixture used was 14 g. of the unsaturated aldehyde, 100 cc. of 95% alcohol, 30 cc. of water, 10 cc. of the gum solution and 10 cc. of the catalyst. The hydrogen was applied at an average pressure of two atmospheres. The absorption ensued exothermally and in thirty minutes about two moles of hydrogen was taken up. With a larger proportion of catalyst, somewhat more hydrogen was absorbed. The reduction product was worked up as in the other cases.

Hydrolysis of the bisulfite precipitate gave the saturated aldehyde practically pure, as a colorless liquid, b. p. 116–117° (uncorr.) at 3 mm., n_D^{23} 1.51673, which formed a mirror with ammoniacal silver solutions. Its odor resembled that of the 2-ethylhydrocinnamic aldehyde.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.95; H, 8.39. Found: C, 74.61; H, 8.55.

2-Ethyl-3-*p*-anisylpropane (β -Ethylidihydroanethole), $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{-CH}_3$.—As usual, after separation of the above aldehyde bisulfite, the ether extracts were distilled and after removal of the ether two fractions were collected, the first one containing the hydrocarbon and the second the saturated alcohol. Both fractions were oxidized, to remove any aldehyde still present.

The first fraction was collected at 105–110° at 10 mm., and yielded the pure hydrocarbon as a colorless mobile liquid, b. p. 135–136° (uncorr.) at 29 mm., of anethole odor.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.19. Found: C, 80.15; H, 9.92.

2-Ethyl-3-*p*-anisylpropanol, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$.—The higher boiling fraction referred to above was collected at about 140° at 3 mm., and from it was recovered the saturated alcohol, as a colorless, odorless oil, b. p. 129–130° (uncorr.) at 2.5 mm., n_D^{22} 1.52398.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.17; H, 9.35. Found: C, 74.42; H, 9.64.

In the above reduction, 36 g. of crude reduction product (from several runs) yielded 4 g. of the saturated aldehyde, 4 g. of the hydrocarbon and 10 g. of the saturated alcohol.

Summary

1. The following have been reduced catalytically: piperonylideneacetaldehyde, its 2-methyl- and 2-ethyl-derivatives; 2-ethyl- and 2-amylcinnamic aldehydes; 2-methyl- and 2-ethyl-*o*-methoxycinnamic aldehydes and 2-ethyl-*p*-methoxycinnamic aldehyde.

2. The reduction products isolated were the corresponding saturated aldehyde, saturated alcohol and arylparaffin. No unsaturated alcohols or arylelefins were detected.

3. Most of the products described are new. Their physical and chemical properties are recorded, as well as their odors.

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