

Summary

1. A procedure for the preparation of *p*-nitrophenylcarbonyl chloride has been worked out.

2. The *p*-nitrophenyl urethans of the common aliphatic alcohols are described.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 643]

THE SYNTHESIS OF SIMPLE AND OF SUBSTITUTED 2-ALKYLCINNAMIC ALCOHOLS, INCLUDING A MONOMOLECULAR CUBEBIN

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RECEIVED FEBRUARY 11, 1931

PUBLISHED APRIL 6, 1931

Introductory

The appearance of the recent articles by Gomberg and Bachmann² and by Shankland and Gomberg,³ lead us to publish some closely related work, carried out in 1929, reported at the Annual Convention of the American Manufacturers of Toilet Articles, New York, last April, and published last spring as part of the Dissertation submitted by the junior author for the Ph.D. degree at Columbia University.

The problem of reducing unsaturated aldehydes to the corresponding unsaturated alcohols has occupied the attention of organic chemists for many years and is a subject of considerable practical importance to the perfume industry.

Iron and acetic acid have been used on aldehydes⁴ or on their diacetates,⁵ but the methods are tedious and the yields unsatisfactory.

The reducing action of aliphatic Grignard reagents on aldehydes and ketones has been known for many years. Marshall's experiments,⁶ supported by the work of Meisenheimer⁷ and of Shankland and Gomberg,⁸

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 Gomberg and Bachmann, *THIS JOURNAL*, **52**, 4967 (1930).

³ Shankland and Gomberg, *ibid.*, **52**, 4973 (1930).

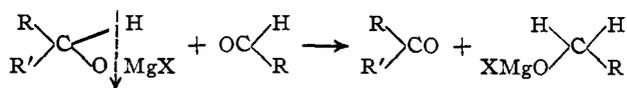
⁴ (a) Herzig, *Monatsh.*, **3**, 123 (1882); (b) Lieben and Zeisel, *ibid.*, **4**, 28 (1883); (c) *ibid.*, **7**, 55 (1886).

⁵ (a) Barbier and Leser, *Bull. soc. chim.*, [3] **33**, 858 (1905); (b) Hill and Nason, *THIS JOURNAL*, **46**, 2236 (1924); (c) Pauly, Schmidt and Böhme, *Ber.*, **57B**, 1329 (1924).

⁶ (a) Marshall, *J. Chem. Soc.*, **105**, 527 (1914); (b) **107**, 509 (1915); (c) **127**, 2184 (1925).

⁷ Meisenheimer, *Ann.*, **446**, 76 (1926).

make it clear that is not the Grignard reagent itself which functions as the reducing agent in such cases, but the addition product formed by the reagent with the aldehyde, $RCH(OMgX)R'$, which is then oxidized by the excess of aldehyde, the latter being compensatingly reduced



Lüttringhaus⁸ patented a process of reducing aldehydes to alcohols by the action of ethyl alcohol in the presence of activated magnesium, the alcohol being oxidized simultaneously to aldehyde, and claimed the successful reduction of citronellal, geraniol (citral) and cinnamic aldehydes to the corresponding alcohols.

Meerwein and Schmidt⁹ discovered that $Al(OR)_3$, or $ROMgX$, in the presence of some free ROH , acting on aldehydes at moderate temperatures, gave 80 to 90% yields of the corresponding alcohols, the aldehyde and alcohol groups exchanging partners, the equilibrium being kept moving to the right by the removal of the aldehydic by-product as fast as it formed



Among the alcohols they secured in this way from their aldehydes, were geraniol and hydroxycitronellol.

Ponndorf,¹⁰ by the use of a similar method, successfully prepared cinnamic alcohol, geraniol and nerol, carveol and other alcohols, from the corresponding aldehyde or ketone. As pointed out by Gibson and Simonsen,¹¹ *dl*-piperitol can thus be prepared readily from *dl*-piperitone.

Inasmuch as a compensating oxidation and reduction seems to be involved in the change, it has been likened⁹ to the Cannizzaro Reaction.

The noteworthy fact remains, however, that when $Al(OR)_3$ acts upon mixtures of aldehydes and alcohols, the products are the same as when $ROMgX$ is the catalyst, although aluminum does not form organic complexes of exactly the same type as magnesium.

Child and Adkins¹² carried out an interesting series of experiments, using aluminum ethoxide as catalyst to convert aldehydes into esters, $2RCHO \longrightarrow RCOOCH_2R$.

Adams and his co-workers¹³ obtained an excellent yield of cinnamic alcohol by reducing cinnamic aldehyde with hydrogen in the presence of their platinum oxide-platinum black catalyst. Our experience with this method, however, has been that the conditions determining a satisfactory

⁸ Lüttringhaus, German Patent 384,351 (1924).

⁹ Meerwein and Schmidt, *Ann.*, **444**, 221 (1925).

¹⁰ Ponndorf, *Z. angew. Chem.*, **39**, 138 (1926).

¹¹ Gibson and Simonsen, *Chem. Industry*, **49**, 540 (1930).

¹² Child and Adkins, *THIS JOURNAL*, **45**, 3013 (1923).

¹³ Adams and Tuley, *ibid.*, **47**, 3061 (1925); etc.

yield are highly specific, small variations in the proportions of the catalyst mixture, or changes in its activity, affecting the results profoundly, so that considerable experimentation would have been necessary to ascertain the optimum conditions in the case of each aldehyde.

For the reduction of certain cinnamic aldehydes we had on hand, the method of Meerwein and Schmidt⁹ proved entirely satisfactory and in this way 2-ethyl and 2-isoamyl cinnamic alcohol, 2-methyl-3-*p*-tolylallyl alcohol and 2-piperonylidene-ethanol, were prepared. The products were practically free from unchanged initial aldehydes, for simple fractional distillation under diminished pressure sufficed to give a pure alcohol, without any previous special chemical treatment for the removal of aldehydes.

The 2-piperonylidene-ethanol prepared by this method was not identical with the product obtained by Pauly, Schmidt and Böhme^{5c} by reduction of the same aldehyde with iron and acetic acid, and to which they assigned the same formula. The reason for this discrepancy is under investigation and the results will be published later.

Natural cubebin was at one time assumed to be the 2-piperonylidene-ethanol, but recent researches, especially those of Mameli,¹⁴ make it clear that its formula is much more complicated and, in support of this, the 2-piperonylidene-ethanol obtained by Pauly, Schmidt and Böhme, and the one prepared by us, are totally different from natural cubebin.

In general, these unsaturated alcohols decolorized a carbon tetrachloride solution of bromine much more rapidly than the corresponding unsaturated aldehydes, the color being discharged promptly until near the saturation point.¹⁵

Their boiling points were generally higher than those of the corresponding saturated or unsaturated aldehydes, saturated alcohols or propanes. Their odors were of the cinnamic alcohol type.

Experimental

2-Ethylcinnamyl Alcohol, $C_6H_5CH=C(C_2H_5)CH_2OH$.—A solution of 5.5 g. of dry hydrogen chloride in 100 cc. of absolute alcohol was prepared in a flask provided with a reflux condenser which carried a calcium chloride guard tube, and to this solution there was added 4 g. of clean magnesium ribbon. The reaction was completed by refluxing the mixture until all the metal was dissolved (one hour or longer). The air in the apparatus was then displaced by a current of dry nitrogen and, while this gas was kept passing through the refluxing mixture, 30 cc. of α -ethylcinnamic aldehyde was added through the condenser. The water in the condenser was not changed during this reaction and upon its completion had become sufficiently heated by the refluxing condensate so that the calcium chloride tube was removed and 40 cc. of alcohol was carried out in this way by the stream of nitrogen gas. After refluxing for about seven hours, the mixture was cooled, thrown into excess of water, the whole acidified with acetic acid, ether added, the

¹⁴ Mameli (a) *Gazz. chim. ital.*, **37**, II, 483 (1907); (b) **39**, I, 477 (1909); (c) **39**, I, 494 (1909); (d) **42**, II, 546 (1912); (e) **42**, II, 551 (1912); (f) **51**, II, 353 (1921).

¹⁵ Compare Reich, van Wijck and Waelle, *Helv. Chim. Acta*, **4**, 242 (1921).

mass filtered from a small amount of resinous impurities, the ether layer separated, washed with sodium carbonate solution, to remove all acetic acid, then with water, dried and the solvent removed. The residue was fractioned under reduced pressure in an atmosphere of nitrogen and 22 cc. of a nearly colorless oil was collected at 127–137° (mostly at 137°) at 8 mm., leaving a viscous residue in the flask. When the fraction collected was redistilled (in nitrogen), practically all passed over at 131–132° (corr.) at 9 mm., as a colorless oil.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.42; H, 8.70. Found: C, 81.28; H, 8.86.

In this preparation, chloromagnesium ethylate was found to be far superior to aluminum ethylate. Meerwein and Schmidt⁹ record a similar experience in the production of cinnamic alcohol from the aldehyde.

The viscous by-product remaining in our flask after taking off the fraction of b. p. 127–137° (8 mm.) yielded, with incipient decomposition, a fraction boiling at about 200° (4 mm.), containing 79.39% of carbon and 8.92% of hydrogen, but which was not investigated further.

The alcohol instantly decolorized carbon tetrachloride solutions of bromine, with no observable evolution of hydrogen bromide, whereas the corresponding unsaturated aldehydes take from seconds to minutes to discharge the color of such bromine solutions. The odor was weak but agreeable, similar in type to that of cinnamic alcohol itself. The alcohol was easily reduced to the corresponding 2-ethylhydrocinnamyl alcohol (2-ethyl-3-phenylpropyl alcohol) and 2-ethyl-3-phenylpropane (3-methyl-4-phenylbutane), by hydrogen in the presence of palladium (Skita method). It discharged the color of a dilute aqueous potassium permanganate solution when shaken with it.

p-Nitrobenzoate.—This was prepared from *p*-nitrobenzoyl chloride and the alcohol in the presence of pyridine; m. p. 110–111° (corr.).

Anal. Calcd. for $C_{18}H_{17}O_4N$: H, 5.5. Found: H, 5.68. Through an accident, the carbon determination was lost, and there remained insufficient material for purification and another combustion.

A phenylurethan also was produced by heating equal moles of the alcohol and phenyl isocyanate together in a sealed tube for six hours at 100°. By the addition of petroleum ether (b. p. 40–60°) to the reaction product, crystals were obtained, m. p. 63–64° (corr.), whose melting point was unchanged by recrystallization from 75% alcohol.

2-*n*-Amylcinnamyl alcohol, $C_6H_5CH=C(C_8H_{11})CH_2OH$, was prepared similarly. The refluxing was continued for eleven and one-half hours, and the crude product separated as before and distilled in nitrogen, gave a main fraction, b. p. 144–165° (6 mm.). This was redistilled and the fraction, b. p. 141–143° (5 mm.) was a colorless oil of faint odor recalling that of cinnamic alcohol; yield, 50%.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.29; H, 9.88. Found: C, 82.15; H, 10.0.

The properties of this alcohol, so far as tested, were the same as those of the corresponding 2-ethyl derivative.

Phenylurethan.—A mixture of the alcohol with a slight excess of phenyl isocyanate was heated in a sealed tube for two and one-quarter hours at 100°. The excess of isocyanate was removed from the product by heating at 100° and reducing the pressure to 16 mm. Addition of petroleum ether to the residue precipitated a solid, which crystallized from dilute alcohol in colorless crystals, m. p. 61–62° (uncorr.).

2-Methyl-3-*p*-tolylallyl alcohol, $p\text{-}CH_3C_6H_4CH=C(CH_3)CH_2OH$, from 3.5 g. of magnesium, 5 g. of hydrogen chloride in 225 cc. of absolute alcohol, and 25 cc. of 2-methyl-3-*p*-tolylacrolein, refluxed for seven and one-half hours in an atmosphere of nitrogen, was worked up as in the case of the other alcohols and finally distilled. The

portion coming over below 160° at 10 mm. on rectification gave a fraction, b. p. $142-143^{\circ}$ (11 mm.), as a colorless oil, whose odor and other properties resembled those already described; yield, 60%.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.42; H, 8.70. Found: C, 81.39; H, 8.97.

2-Piperonylidene-ethanol (Monomolecular "Cubebin") was prepared from 4 g. of magnesium, 5.5 g. of dry hydrogen chloride in 225 cc. of absolute alcohol, and 23 g. of piperonylidene-acetaldehyde (m. p. $83-84^{\circ}$; b. p. $162-163^{\circ}$ (5 mm.)). After refluxing for four hours (in nitrogen), the crude product was separated and distilled at 5 mm. pressure. Above 200° , considerable decomposition was evident. The distillate collected below this point yielded, on rectification, a fraction, b. p. $167-168^{\circ}$ (5 mm.), which gave colorless crystals from benzene or alcohol, m. p. $78-78.8^{\circ}$ (corr.).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 67.39; H, 5.66. Found: C, 67.17; H, 5.95. Molecular weight (in camphor): Calcd., 178. Found: 173.

The yield before final purification was only about 20% (4 g.), but this was raised to approximately 30% when aluminum ethylate was used in place of the chloromagnesium ethylate.

Its reactions were similar to those of the other alcohols described in this paper. It decolorized instantly a carbon tetrachloride solution of bromine, or an aqueous permanganate solution. Reduced catalytically, the odor of dihydrosafrole was pronounced, one mole of hydrogen being absorbed in about ten minutes.

Benzoate.—The alcohol was condensed with benzoyl chloride in the presence of pyridine, and the purified product formed fine long colorless needles, m. p. $96-97^{\circ}$ (corr.), which decolorized bromine solutions less rapidly than the alcohol itself.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.31; H, 5.0. Found: C, 72.21; H, 5.22.

Phenyl Urethan.—A mixture of the alcohol with an excess of phenyl isocyanate was heated in a sealed tube for four hours at 100° . As the tube cooled, the contents solidified. The crude product was dissolved in benzene, reprecipitated by the addition of petroleum ether and the precipitate then crystallized from a mixture of these two solvents. Small colorless needles were obtained, m. p. $96-97^{\circ}$ (uncorr.).

Anal. Calcd. for $C_{17}H_{16}O_4N$: C, 68.66; H, 5.1. Found: C, 68.98; H, 5.11.

Summary

1. The 2-alkylated cinnamic aldehydes are very satisfactorily reduced to the corresponding cinnamic alcohols by the use of chloromagnesium ethylate or aluminum ethylate.

2. The monomolecular "cubebin" prepared in this way differs from that recorded in the literature, which was obtained by reduction with iron and acetic acid.

NEW YORK, N. Y.