glycol appear to be liquids, but its boiling point agrees with the recorded value.[12]

Hydrogenation of Ethyl Benzylmalonate.—Nineteen grams of the ester in 100 ml. of methyl alcohol was hydrogenated over 8 g. of copper–chromium oxide at 160° and 4900–5600 p. s. i. for six hours. The 2-benzyl-1,3-propanediol was collected by distillation and boiled at 143–145° at 0.5 mm. After standing, the glycol crystallized and was recrystallized from benzene, after which it melted at 68–70°. The yield was 3.3 g. (26%).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 72.26; H, 8.49. Found: C, 72.52; H, 8.44.

The *p*-nitrobenzoate of this glycol melted at 130–131° (from chloroform–ether).

Anal. Calcd. for $C_{24}H_{20}O_8N_2$: C, 62.06; H, 4.35; N, 6.03. Found: C, 61.88; H, 4.27; N, 6.06.

Hydrogenation of Ethyl *s*-Butylmalonate.—A solution of 53.7 g. of ethyl *s*-butylmalonate in 85 ml. of methyl alcohol was hydrogenated over 12.5 g. of copper–chromium oxide catalyst at 157–162° and 4700–6400 p. s. i. for ten hours.

The 2-*s*-butyl-1,3-propanediol, isolated as above, boiled at 92–105° at 0.5 mm. and weighed 7.9 g. The *p*-nitrobenzoate of this glycol melted at 101–102°.

Anal. Calcd. for $C_{21}H_{22}O_8N_2$: C, 58.60; H, 5.15; N, 6.51. Found: C, 58.68; H, 5.03; N, 6.55.

Hydrogenation of Ethyl Ethylmalonate.—A solution of 28.2 g. of ethyl ethylmalonate in 100 ml. of methyl alcohol was reduced at 160–162° for nine hours and then at 180° for fifteen hours at 4100–5500 p. s. i. over 8 g. of copper–chromium oxide. The 2-ethyl-1,3-propanediol, b. p. 86–87° at 0.5 mm., weighed 7.7 g. (49%).

Anal. Calcd. for $C_5H_{12}O_2$: C, 57.66; H, 11.62. Found: C, 57.02; H, 10.99.

The *p*-nitrobenzoate prepared from this glycol was recrystallized from methyl alcohol and melted at 88–89°.

Anal. Calcd. for $C_{19}H_{18}O_8N_2$: C, 56.72; H, 4.51; N, 6.96. Found: C, 56.81; H, 4.44; N, 7.09.

Acknowledgment.—The authors wish to express their appreciation to Mr. William B. Wright for technical assistance and Messrs. R. N. Boos, D. F. Hayman, Wilhelm Reiss, W. K. Humphrey, E. Thornton and Leonard Rosalsky, and Mrs. E. H. Meiss for carrying out the analyses.

Summary

Hydrogenation of β-oxygenated esters has been found to give rise to 1,3-glycols or their ethers by a lower temperature ester reduction method. When the malonic esters, acetoacetic ester, the β-hydroxy esters and β-alkoxy esters are hydrogenated at 160–180° over copper–chromium oxide, the corresponding glycols and their derivatives are produced.

By this method, ethyl acetoacetate, ethyl ethylacetoacetate and ethyl isobutylideneacetoacetate were converted into 1,3-butylene glycol, 2-ethyl-1,3-butylene glycol and 2-isobutyl-1,3-butylene glycol. Ethyl β-ethoxypropionate gave 3-ethoxy-1-propanol. The ethyl alkylmalonates (ethyl, *s*-butyl and benzyl) give the corresponding 2-alkyl-1,3-propanediols. The yields were 15–78%.

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[12] Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 1211 (1904).

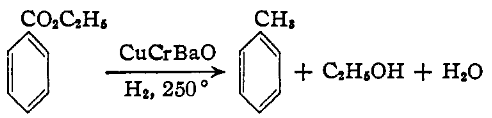
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK AND CO., INC.]

Hydrogenolysis of Aromatic Esters to Alcohols

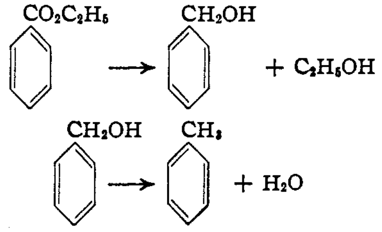
BY RALPH MOZINGO AND KARL FOLKERS

The hydrogenolysis of β-oxygenated esters and their ethers to 1,3-glycols and 1,3-glycol ethers[1] has lead to a reinvestigation of the hydrogenolysis of aromatic esters. While the hydrogenation of aromatic esters under the usual conditions[2] for ester hydrolysis leads to products in which the carboalkoxy group has been converted to a methyl group, it is possible by the low temperature technique previously described[1] to isolate the intermediate alcohol.

When an aromatic ester is hydrogenated at temperatures between 200 and 250° over a copper–chromium oxide catalyst[3] under 200 atmospheres of hydrogen it is converted rapidly into the corresponding methyl derivative. For example, ethyl benzoate gives toluene, ethanol and water.[2]



None of the corresponding alcohol has been obtained under these conditions and it has been suggested that the hydrogenolysis proceeds preferentially to the hydrocarbon.[4] However, it seems equally reasonable that the hydrogenation of an aromatic ester to the hydrocarbon may proceed stepwise.



This has now been found to be the case.

When hydrogenation is carried out between 125 and 175°, the exact temperature depending somewhat upon the ester, hydrogenolysis to the alcohol can be effected. For example, under these conditions ethyl benzoate (I, R = H) and its alkyl derivatives (I, R = CH_3, and II) and its

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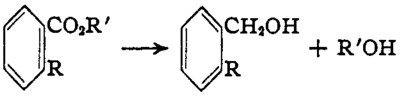
[1] Mozingo and Folkers, THIS JOURNAL, **70**, 227 (1948).

[2] Adkins, "Reaction of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 97–104.

[3] Connor, Folkers and Adkins, THIS JOURNAL, **53**, 2012 (1931).

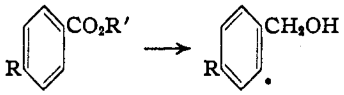
[4] Lazier, U. S. Patent 2,079,414 (May 4, 1937).

3,4-dimethyl derivative (III) are converted into benzyl alcohol (IV, R = H) and its alkyl derivatives (IV, V and VI).



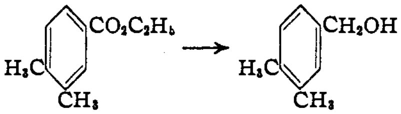
I IV

$(R = H, CH_3;\ R' = CH_3 \text{ or } C_2H_5)$



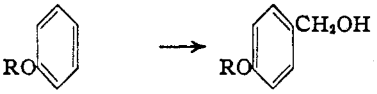
II V

$(R = H, CH_3 \text{ or } (CH_3)_2CH;\ R' = CH_3 \text{ or } C_2H_5)$



III VI

Similarly, the oxygenated derivatives may be converted into corresponding alcohols. Methyl anisate (VII, R = CH_3) is converted into *p*-methoxybenzyl alcohol (VIII, R = CH_3) and ethyl *p*-hydroxybenzoate (VII, R = H) is converted into *p*-hydroxybenzyl alcohol (VIII, R = H).



VII VIII

$(R = H \text{ or } CH_3;\ R' = CH_3 \text{ or } C_2H_5)$

The hydrogenolysis was carried out most successfully in methyl alcohol and, at the temperatures used here, decomposition of the methyl alcohol[4] apparently does not occur. With the aromatic esters the reduction is satisfactory, when pressures of 300 atm. or greater are used at temperatures in the range 125–175° with, in general, those near 160° giving the best yields of the alcohol. The yield of alcohol is greater when the reduction proceeds rapidly at a given temperature. Likewise, the amount of alcohol is usually greater when the reaction is interrupted at the point where its rate decreases markedly or the theoretical quantity of hydrogen has been consumed rather than when the reaction is allowed to proceed longer. Presumably, when the reaction is allowed to proceed beyond this point the benzyl alcohol is converted to the toluene derivative more rapidly than it is formed from the ester in the latter stages of the process.

Experimental

Copper-Chromium Oxide Catalyst.—The catalyst was prepared according to the usual method.[3] The thermal decomposition was carried out at the lowest possible temperature. The catalyst contained barium, except in one case noted.

Purification of Esters.—The esters were heated in a solvent with, or distilled over, Raney nickel catalyst[5] before use.

Hydrogenation of Aromatic Esters.—A solution of the ester in reagent methyl alcohol was hydrogenated over copper-chromium-barium oxide at 125-165° and under 300-400 atm. of hydrogen until the rate of hydrogen absorption became slow or the theoretical amount had been taken up. The amount of material, time, etc., are listed under each ester.

The products were isolated, after removing the catalyst, in the following way. To the solution of products in methyl alcohol were added 1.5 equivalents of potassium hydroxide (based on the original amount of ester) and 100 ml. of water. After refluxing the mixture for five hours or longer, most of the methyl alcohol was distilled. The residue was diluted with 150 ml. of water and extracted repeatedly with chloroform or benzene to remove the aromatic alcohol. The water solution from the chloroform extraction was made strongly acid with concentrated hydrochloric acid, cooled to 0°, and the acid removed by filtration.

The chloroform extract was combined with the methyl alcohol distillate, dried over anhydrous magnesium sulfate and fractionated. For complete identification of the liquid alcohols a solid ester, usually the *p*-nitrobenzoate, was prepared in each case by the pyridine method.[6]

Hydrogenation of Ethyl Benzoate.—A solution of 50 g. of the ester in 75 ml. of methyl alcohol was hydrogenated at 155–160° over 7 g. of copper–chromium-barium oxide for three and one-quarter hours. Eleven grams (25%) of benzoic acid, m. p. 121–122°, and 22.7 g. (63%) of benzyl alcohol, b. p. 103–104° at 23 mm., were isolated as above. The *p*-nitrobenzoate of the benzyl alcohol melted at 84–85° (from methyl alcohol), its recorded melting point.[7]

Another reduction, using 150 g. of ethyl benzoate in 100 ml. of methyl alcohol with 30 g. of catalyst, was carried out at 125–132° for ten and one-third hours. The yield in this case was 53.4 g. (49%) of benzyl alcohol.

In one experiment, barium-free copper–chromium oxide catalyst was used. In this case 75 g. of ethyl benzoate in 75 ml. of methyl alcohol was hydrogenated at 125–134° over 7.5 g. of copper–chromium oxide catalyst containing no barium for fourteen and one-half hours. The yield of benzyl alcohol, b. p. 106–108° at 25 mm., was 12.1 g. (22%) together with 17 g. of liquid boiling at 191–193° at 25 mm. presumably benzyl benzoate since in this case the esters were not saponified before distillation of the reaction mixture.

Hydrogenation of Methyl *o*-Toluate.—A solution of 23 g. of the ester in 120 ml. of methyl alcohol was hydrogenated over 5 g. of copper–chromium-barium oxide for two hours at 159–162°, then was worked up as above.

The products were 13 g. (70%) of *o*-methylbenzyl alcohol,[8] b. p. 120–122° at 23 mm., and 1.3 g. (6%) of *o*-toluic acid, m. p. 104–105°.

The *p*-nitrobenzoate of *o*-methylbenzyl alcohol, m. p. 100–101° (from methyl alcohol), was analyzed.

Anal. Calcd. for $C_{15}H_{13}O_4N$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.49; H, 4.85; N, 4.95.

Hydrogenation of Methyl *p*-Toluate.—A mixture of 50 g. of methyl *p*-toluate, 200 ml. of methyl alcohol and 10 g. of copper–chromium–barium oxide catalyst was agitated under hydrogen at 126–130° for eleven and one-quarter hours. The *p*-methylbenzyl alcohol,[9] m. p. 57–58° (from petroleum ether, b. p. 30–60°), weighed 28.4 g. (70%). The 3,5-dinitrobenzoate of the *p*-methylbenzyl alcohol melted at 117–118° (from ethyl alcohol).

Anal. Calcd. for $C_{15}H_{12}O_6N_2$: C, 56.96; H, 3.80; N, 8.86. Found: C, 57.00; H, 4.07; N, 8.91.

Hydrogenation of Methyl *p*-Isopropylbenzoate.[10]—When 26.9 g. of this ester, 120 ml. of methyl alcohol and 5 g. of copper–chromium–barium oxide catalyst were allowed to react with hydrogen at 156–160° for eight hours, the amount of *p*-isopropylbenzoic acid, m. p. 109–110°, isolated after hydrolysis was 4.0 g. (16%). The *p*-isopro-

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[5] "Organic Syntheses," **21**, 15 (1941).

[6] Einhorn and Hollandt, *Ann.*, **301**, 95 (1898).

[7] Kothe, *ibid.*, **266**, 313 (1891).

[8] Law, *J. Chem. Soc.*, **91**, 748 (1907).

[9] Cannizzaro, *Ann.*, **124**, 252 (1862).

[10] Bert, *Bull. soc. chim.*, **37**, 1397 (1925).

pylbenzyl alcohol,[11] b. p. 135-136° at 26 mm., weighed 18.4 g. (81%) and gave a 3,5-dinitrobenzoate melting at 91-92°[12] (from petroleum ether, b. p. 60-70°).

Anal. Calcd. for $C_{17}H_{16}O_6N_2$: C, 59.30; H, 4.68; N, 8.14. Found: C, 59.20; H, 4.57; N, 8.37.

Hydrogenation of Ethyl 3,4-Dimethylbenzoate.—A solution of 89 g. of ethyl 3,4-dimethylbenzoate in 60 ml. of methyl alcohol was allowed to react with hydrogen over 10 g. of copper-chromium-barium oxide catalyst at 128-132° for twenty-four hours. The 3,4-dimethylbenzoic acid,[13] m. p. 165-166°, weighed 17.3 g. (23%). The 3,4-dimethylbenzyl alcohol,[14] m. p. 61-62° (from ethyl alcohol) amounted to 43.2 g. (64%).

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.24; H, 8.79.

The *p*-nitrobenzoate of this alcohol melted at 78-79° (from methyl alcohol).

Anal. Calcd. for $C_{16}H_{15}O_4N$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.38; H, 5.57; N, 4.81.

Hydrogenation of Methyl *o*-Methoxybenzoate.—A solution of 36 g. of the ester in 90 ml. of methyl alcohol was reduced over 5 g. of copper-chromium-barium oxide for six and one-third hours at 160-162°. The products were 4.5 g. (14%) of *o*-methoxybenzoic acid, m. p. 100-102°, and 16.7 g. (56%) of *o*-methoxybenzyl alcohol,[15] b. p. 134-135° at 20 mm. The *p*-nitrobenzoate of this alcohol melted at 81-82° (from methyl alcohol).

Anal. Calcd. for $C_{15}H_{13}O_4N$: C, 62.72; H, 4.56; N, 4.88. Found: C, 62.90; H, 4.77; N, 5.02.

When reduction of 33.2 g. of methyl *o*-methoxybenzoate, with the same amounts of other reactants as above, was carried out for three and one-third hours, 8 g. (26%) of the acid and 15.6 g. (57%) of the alcohol were isolated.

Hydrogenation of Methyl Anisate.—Eighty-three grams of methyl anisate in 60 ml. of methyl alcohol was hydrogenated over 10 g. of copper-chromium-barium oxide at 130-140° for twenty-three hours. A fore-run in the distillation, b. p. 84-85° at 27 mm., consisted of *p*-cresol methyl ether and weighed 4.0 g. (6.6%). The yield of anisyl alcohol, b. p. 150-151° at 27 mm., was 61.3 g. (89%). The *p*-nitrobenzoate of the anisyl alcohol melted at 93-94° (from 95% ethyl alcohol).

Anal. Calcd. for $C_{15}H_{13}O_5N$: C, 62.72; H, 4.53; N, 4.88. Found: C, 62.81; H, 4.65; N, 4.90.

Hydrogenation of Methyl Veratrate.[16]—A solution of 19.6 g. of methyl veratrate in 130 ml. of methyl alcohol was hydrogenated for three and two-thirds hours at 155-160° over 5 g. of copper-chromium-barium oxide. The recovered acid, m. p. 179-180°, amounted to 0.4 g. (2%). The 3,4-dimethoxybenzyl alcohol,[17] b. p. 135-140° at 1 mm., amounted to 14.4 g. (86%) and gave a *p*-nitrobenzoate melting at 108-109° (from methyl alcohol).

Anal. Calcd. for $C_{16}H_{15}O_6N$: C, 60.56; H, 4.77; N, 4.41. Found: C, 60.57; H, 4.76; N, 4.46.

Hydrogenation of Ethyl *p*-Hydroxybenzoate.—A mixture of 49.8 g. of ethyl *p*-hydroxybenzoate, 75 ml. of methyl alcohol and 10 g. of copper-chromium-barium oxide catalyst was submitted to hydrogenation at 155-160° for nineteen hours. In this case the phenol was separated from the acid by extracting the acid from a chloroform solution of the two with bicarbonate solution. The *p*-hydroxybenzoic acid, m. p. 205-207°, amounted to 7 g. (17%). The solid phenol after recrystallization from benzene weighed 22.5 g. (60%) and melted at 124-125°; the recorded melting point of *p*-hydroxybenzyl alcohol is 124-125°.[18]

Acknowledgment.—The authors wish to express their appreciation to Mr. William Wright for technical assistance and to Messrs. Richard Boos, D. F. Hayman, Wilhelm Reiss, H. S. Clark, W. K. Humphrey and E. Thornton for carrying out the microanalyses.

Summary

Several aromatic esters have been converted into the corresponding benzyl alcohols by catalytic hydrogenation over copper-chromium-barium oxide at 125 to 160° in 50-90% yield. Methyl alcohol has been found to be a suitable solvent for these reductions.

Using this method, it has been found that alkyl and alkoxy benzoic acid esters containing one or more substituents as well as the unsubstituted benzoic esters can be converted into the corresponding alcohols. Likewise, ethyl *p*-hydroxybenzoate gives *p*-hydroxybenzyl alcohol.

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[11] Bert, *Bull. soc. chim.*, **37**, 1252 (1925).

[12] Cooke, Gillespie and Macbeth (*J. Chem. Soc.*, 1825 (1938)) report the melting point of this derivative as 107° (from methyl alcohol). The melting point of the compound obtained here could not be raised by repeated recrystallization of the pure material from methyl alcohol. Recrystallization of the crude ester from methyl alcohol gave methyl 3,5-dinitrobenzoate, m. p. 106-107°, undepressed by admixture with methyl 3,5-dinitrobenzoate prepared directly from methyl alcohol.

[13] Lellmann and Benz, *Ber.*, **24**, 2115 (1891)

[14] Sommelet, *Compt. rend.*, **157**, 1443 (1913).

[15] Späth, *Monatsh.*, **34**, 1965 (1913).

[16] Sabalitschka and Tietz, *Arch. Pharm.*, **269**, 545 (1931).

[17] Decker and Pschorr, *Ber.*, **37**, 3396 (1904).

[18] Auwers and Daiche, *ibid.*, **32**, 3374 (1899).