

A Convenient Method for Reduction of α,β -Unsaturated Carboxylic Acids

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There are many methods for reduction of α,β -unsaturated carboxylic acids. The most commonly used is the catalytic hydrogenation, especially with Raney-Ni as the catalyst. In an interesting paper Schwenk *et al.*¹ have shown that cinnamic acid among other acids can be reduced in strongly alkaline water solution at atmospheric pressure by means of Raney-Ni/Al alloy, where the aluminium by reaction with sodium hydroxide gives the desired hydrogen. However, the method has some disadvantages as aluminium hydroxide often contaminates the reduced acid in the final separation from the mother liquor. The mixture of the reduced acid and aluminium hydroxide is difficult to separate, especially when the acid is a solid.

In order to avoid these difficulties the author looked for other systems having a reducing power, without the disadvantages mentioned above. Such a system is hydrazine hydrate and Raney-Ni in ethanol which, however, is said to reduce only nitro groups, leaving α,β -unsaturated carboxylic acids unaffected. For example, *p*-nitrocinnamic acid is reduced to *p*-aminocinnamic acid². From the work of Schwenk *et al.* one might presume that as a rule the sodium salts of α,β -unsaturated acids are more readily reduced than the corresponding free acids. Therefore, reduction of these acids in the form of their sodium salts might be achieved by hydrazine and Raney-Ni in water.

Experiments have shown that reduction is achieved in this way if the hydrazine is added slowly. Experimental data are given for the reduction of cinnamic acid to 3-phenylpropionic acid.

In Table 1 are summarized further examples of the reduction. Physical data of the acids prepared are in good agreement with those known from the literature.

Table 1.

Acid reduced	Acid isolated	Yield %	B.p. °C/mm Hg M.p. °C
α -Methylcinnamic ^a	2-Methyl-3-phenylpropionic	93	152–154°/8
Maleic	Succinic	70 ^b	188–189
Fumaric	Succinic	71 ^b	188–189

a. *Trans* isomer.

b. Isolated by filtration from the acidified and chilled water solution.

Preparation of 3-phenylpropionic acid. 300 g (2.02 moles) of *trans*-cinnamic acid is dissolved in a solution of 85 g (2.12 moles) of sodium hydroxide in 2 liters of water. A teaspoonful of Raney-Ni W6 is added. The mixture is agitated and heated to 90°C, at which temperature 260 ml (4.5 moles) of 85 % hydrazine hydrate is added within 2 h. When all the hydrazine hydrate has been added the temperature is held at 90°C until no more gas is evolved. The catalyst is then filtered off and the solution is acidified. The liberated acid is extracted from the water layer with two portions of chloroform. The chloroform layer is dried with magnesium sulfate and the chloroform is evaporated. The residue is distilled under reduced pressure. A fraction is collected boiling at 146–148°C/8 mm Hg, weighing 257 g (85 %) with a m.p. of 47.5°–48.5°C. No melting point depression was observed when the acid was mixed with an authentic sample of 3-phenylpropionic acid.

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