



A new direct synthesis of cinnamic acids from aromatic aldehydes and aliphatic carboxylic acids in the presence of sodium borohydride

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Abstract—Cinnamic acids have been prepared in 59–86% yields by a new direct synthesis from aromatic aldehydes and aliphatic carboxylic acids in the presence of sodium borohydride and *N*-methyl-2-pyrrolidinone (NMP) as solvent, at reflux (185–190°C), for 9–12 hours. Without sodium borohydride, this reaction is not possible. © 2003 Published by Elsevier Science Ltd.

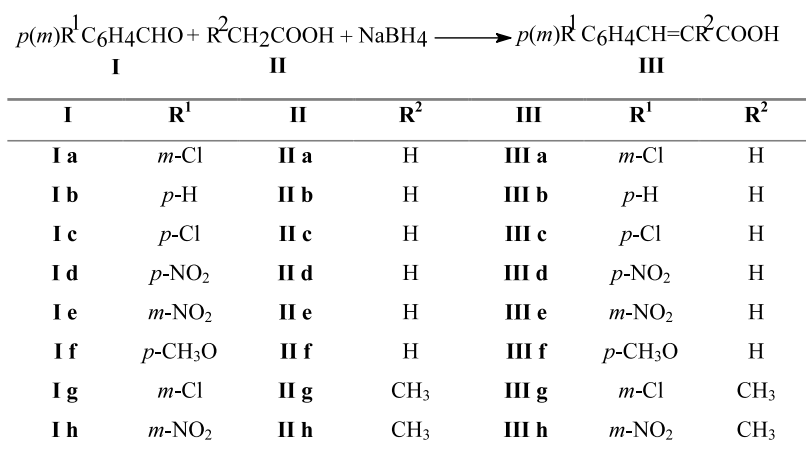
Cinnamic acids can be prepared from aromatic aldehydes and aliphatic anhydrides, in the presence of bases, particularly with sodium or potassium salts of the carboxylic acids corresponding to the anhydrides used in the reaction (the Perkin reaction).¹

Thus, potassium acetate can be used for the reaction between acetic anhydride and benzaldehyde, yields are 70–72% at 180°C in 8 h. With sodium acetate, the yields are lower under the same conditions.² This reaction is not suitable for aliphatic aldehydes.³

If the aliphatic carboxylic anhydrides are replaced by the corresponding aliphatic carboxylic acids, the reaction is not successful.

We have now found that this reaction is possible with aliphatic carboxylic acids in the presence of sodium borohydride.

It is known that the aliphatic carboxylic acids can react with sodium borohydride resulting in different products. For example, when using acetic acid the following reactions take place:



Scheme 1.

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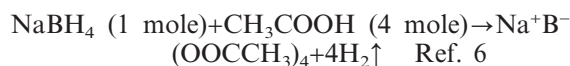
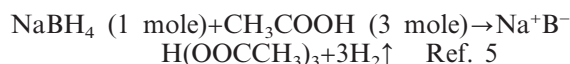
Table 1. Cinnamic acids obtained by direct synthesis in the presence of sodium borohydride

Cinnamic acids ^a	Yield ^b (%)	Reaction time (h)	M.p. ^c (°C)	Literature m.p. (°C)
III a	74	10	176–177	175–177 ⁷
III b	66	12	131–133	132–133 ⁸
III c	83	9	248–250	249–250 ⁷
III d	86	9	285–286	284–286 ⁹
III e	81	10	195–197	196–197 ¹⁰
III f	59	12	173–175	173–175 ⁸
III g	72	10	105–107	106–107 ⁹
III h	77	10	195–197	196–197 ⁹

^a The cinnamic acids obtained were identified by comparison of their m.p. and IR spectra with authentic samples.

^b Yields calculated based on the aromatic aldehydes **I** employed.

^c After recrystallization.



We found that this last compound **3**, prepared in situ in acetic acid solution, can react with aromatic aldehydes to give the corresponding cinnamic acids.

By stepwise investigations, we established that aromatic aldehydes **I** can react with aliphatic carboxylic acids **II** in the presence of sodium borohydride, in the mole ratio 1: excess: 1.33, resulting in cinnamic acids **III**, as presented in Scheme 1.

Using a mole ratio between the aldehyde **I** and NaBH₄ of 1:1.33, good yields for this reaction were obtained.

Without a suitable solvent, this reaction is difficult to perform. We tested many solvents, such as DMSO, DMF, *N*-methyl-2-pyrrolidinone (NMP), HMPTA etc. From these solvents, we selected NMP because it is a good solvent for our products, is stable under the reaction conditions and has a high boiling point (202°C).

The synthesis necessitates high temperatures (reflux at 180–190°C), during 9–12 h (Table 1). At lower temperatures, the yields decrease. For example, the yield for product **IIIa** decreased to 45–48% when the reaction was performed at 145–150°C, for 6 h.

As can be seen in Table 1, cinnamic acids **III** were obtained in yields which ranged from 59 to 86% depending on the reaction conditions and structure of the aldehyde. The cinnamic acid **III f** was obtained with the lowest yield. Cinnamic acids with electron-withdrawing groups were obtained in good yields.¹¹

The detailed mechanism of this reaction will be discussed in a separate communication.

In conclusion, we have found a new synthesis for the direct preparation of cinnamic acids from aromatic aldehydes and aliphatic carboxylic acids in the presence of sodium borohydride. This method is a very effective alternative

to the classical Perkin synthesis. Without the sodium borohydride, the synthesis is not possible.

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- General procedure for the synthesis of cinnamic acids: In a 100 mL three-necked Claisen flask fitted with a mechanical stirrer, 0.14 mole (excess) of aliphatic carboxylic acid **II** was added. Then, 1 g (0.0266 mole) of sodium borohydride was added slowly in small portions, under stirring and cooling with ice, in order to maintain the temperature in the flask at 20–30°C. Then, the solution obtained was stirred for 1 h at room temperature, and then for 1 h at 90–100°C. To this solution, at 70–90°C, 0.02 mole of aromatic aldehyde **I** was added and then 2 mL of NMP as solvent. The solution obtained was stirred for 2–3 min. The mechanical stirrer was replaced with a condenser and the excess of compound **II** was removed by distillation, until the temperature in the flask increased to 185–187°C. Then, the distillation set was replaced with an air-cooled reflux condenser 30 cm long and 2.9 cm in diameter, which was extended with a water-cooled reflux condenser. This solution was heated under reflux, at 185–190°C, for 9–12 h (see Table 1). At the end of the reaction, the final solution was treated with 70–80 mL water and then with NaOH solution 20%, to pH=9–10. From this solution, the unreacted aromatic aldehyde **I** was distilled with water under vacuum (30–40 mm Hg), until the distillate was no longer cloudy. The solution was diluted with water until a volume of 80–90 mL was obtained which was then filtered at 30–40°C. The filtrate was treated with HCl solution 15–20%, until pH=1–2, when cinnamic acid **III** precipitated. After 2–3 h of stirring under cooling with ice, the final product **III** obtained was filtered, washed with 15–20 mL cold water and dried. Yields ranged from 59 to 86% (Table 1).