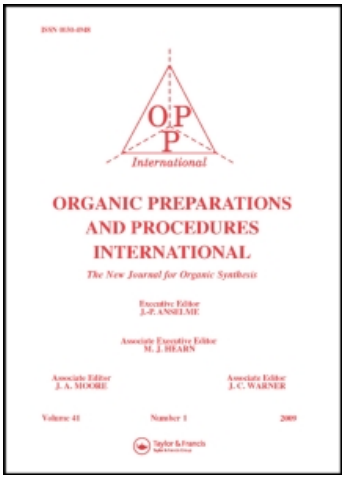

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A NEW CERIUM(III)-CATALYSED ROUTE TO CINNAMYL ALCOHOLS

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A NEW CERIUM(III)-CATALYSED ROUTE TO CINNAMYL ALCOHOLS

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Cinnamyl alcohols occur in nature e.g. in Storax, Peru, Balsam, Cinnamon leaves and hyacinth. Besides this, some cinnamyl alcohols are suggested to be possible liver metabolites in mice and rats. p-Methoxycinnamyl alcohol is believed to be the most toxic of the possible metabolites.[1] Our interest in the chemical simulation of neoflavanoids, required various substituted cinnamyl alcohols.

Several routes are available for the synthesis of these alcohols, e.g. the LAH reduction of the corresponding cinnamic acid esters[2] or the acid-catalysed rearrangement of 3-aryl-1-propenol derivatives. A one-pot reaction for the synthesis of various cinnamyl alcohols from the oxidation of substituted 3-phenylpropenes with selenium dioxide;[1] the yields of cinnamyl alcohols obtained by this method range from 25-35%. An alternative route involves the sodium borohydride reduction of the acids in the presence of N,N-dimethylchloromethyleneimminium chloride.[3] Metal-catalysed borohydride reductions have been employed for the reduction of acid halides to the corresponding aldehydes, using the complex $CdCl_2 \cdot 1.5$ DMF as the catalyst.[4] Sodium borohydride catalysed by cerous chloride (hexahydrate) have been used for the reduction of 2-alkenals to the corresponding allyl alcohols.[5] Advantage was taken of these two observations to develop a novel synthesis of cinnamyl alcohols *via* the acid chlorides using anhydrous cerous chloride and sodium borohydride.

$$ArCH{=}CHCOCl + NaBH_4 \xrightarrow[MeCN]{CeCl_3} ArCH{=}CHCH_2OH$$

Thus, treatment of acid halides with sodium borohydride and cerous chloride in hexamethylphosphoramide and acetonitrile gave only moderate yields of the corresponding alcohols, while in the absence of hexamethylphosphoramide, good yields of the cinnamyl alcohols were obtained.

TABLE 1. Reduction of Cinnamoyl Chlorides to Cinnamyl Alcohols with $NaBH_4(Ce^{+++})$

Cinnamoyl Chloride	Yield[a] (%)	mp./bp. (°C) (lit. data)
Parent	85	100-110/3 mm (95-110/3 mm)
p-Methoxy	85	76-77(76-78)
3,4-Methylenedioxy	80	74-75(74-75)
p-Nitro	82	124-126(124-126)
p-Methyl	75	120-130/6 mm (115-130/6 mm)

a) The reported compounds exhibited satisfactory spectral data; yields of products obtained in the presence of HMPA range from 60-70%.

Under these conditions, the double bond remains unaffected (NMR). This reduction is rapid and has the advantage of being free from side-products and the conditions employed are mild.

EXPERIMENTAL SECTION

The substituted cinnamic acids were obtained by condensation of appropriate benzaldehydes and malonic acids according to the procedure of Vogel.[6] The acid chlorides were obtained by refluxing the acids with freshly distilled thionyl chloride. Anhydrous cerous chloride was obtained by heating cerous chloride hexahydrate at 200-250° for 2 hrs. Melting points were determined by the open capillary method and are uncorrected. Yields mentioned are of

isolated pure products and are not optimised. The NMR spectra of crude products indicated the absence of conjugate addition products.

General Procedure.- Sodium borohydride (1 mmol) in acetonitrile (5 ml) was stirred at -10 to -15° for 5 min., then cerous chloride (0.1 mmol) was added and the milky mass was stirred for 30 min. The acid chloride (1 mmol) in acetonitrile (2 ml) was added and the whole mixture was stirred for 5 min. The reaction was worked up the decomposing the excess sodium borohydride with dilute hydrochloric acid (5%) and extracting the alcohol into ether or dichloromethane. The product was purified by crystallisation or distillation.

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