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An Unusual $AlCl_3$ Catalysed Aromatic Cyclisation Reaction : Novel Synthesis of Tetrahydronaphthoic Acids†

Raghao S. Mali*, Milind D. Sindkhedkar and Prakash G. Jagtap

Garware Research Centre, Department of Chemistry,
University of Pune, Pune-411 007, INDIA
(e-mail : rsmali@chem.unipune.ernet.in)

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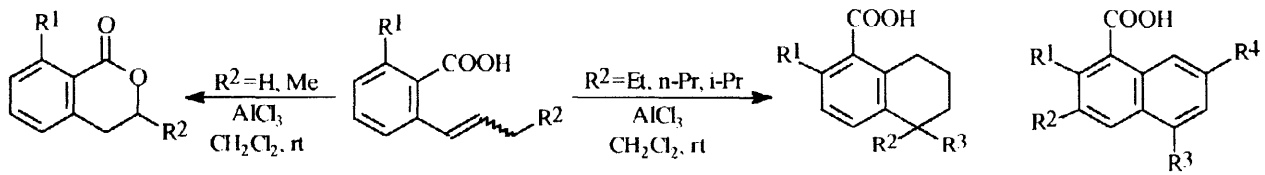
Abstract: An unusual $AlCl_3$ catalysed aromatic cyclisation reaction is described. This is used to develop a novel synthesis of 5,6,7,8-tetrahydro-5-alkyl-1-naphthoic acids (**1a-d**) from 2-vinylbenzoic acids (**3a-d**).

Tetrahydro-1-naphthoic acids like **1b** and naphthoic acids (**2a-b**) are reported to possess useful biological activities[1,2]. Tetrahydronaphthoic acid (**1d**) has been used as intermediate for the synthesis of naturally occurring pentacyclic phenanthrene hydrocarbons[3]. The 5-methyl-1-naphthoic acids (**2c** and **2d**) are also present as structural features in complex natural products[4] like azinomycins A and B and neocarzinostatin



4

4	R1	R2
a	OH	Me
b	H	Me
c	H	Et
d	OH	n-Pr

3

3	R1	R2
a	OMe	Et
b	H	Et
c	H	n-Pr
d	H	i-Pr
e	OMe	H
f	H	H
g	H	Me

1

1	R1	R2	R3
a	OMe	Me	H
b	H	Me	H
c	H	Et	H
d	H	Me	Me

2

2	R1	R2	R3	R4
a	H	H	Me	H
b	H	H	Et	H
c	H	OMe	Me	H
d	OH	H	Me	OMe

which are important antitumor antibiotics. In view of this various methods have been developed for their synthesis[3-5]. In this paper we describe an unusual $AlCl_3$ catalysed aromatic cyclisation reaction which has lead to a simple synthesis of 5,6,7,8-tetrahydro-5-alkyl-1-naphthoic acids (**1a-d**).

Recently[6] we have developed a novel method for the synthesis of 3-methyl- and 3-ethyl-3,4-dihydroisocoumarins (**4a-c**) from 2-vinylbenzoic acids (**3e-g**) using aluminium chloride. In this reaction,

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2-vinylbenzoic acid underwent a lactonisation reaction by addition of the carboxyl group across the double bond. In attempting the synthesis of 8-hydroxy-3-propyl-3,4-dihydroisocoumarin (**4d**) from 2-vinylbenzoic acid (E+Z, **3a**), using aluminium chloride in methylene chloride according to our procedure, surprisingly 5,6,7,8-tetrahydro-5-methyl-1-naphthoic acid (**1a**) was obtained in 65% yield instead of the desired isocoumarin **4d**. The novel observation of alkylation, instead of lactonisation, was also noticed in the synthesis of 5,6,7,8-tetrahydro-5-alkyl-1-naphthoic acids (**1b-d**) from 2-vinylbenzoic acids[7a,b] (**3b-d**), where the 1-naphthoic acids (**1b-d**) were obtained in 62-72% yield.

The tetrahydro-5-alkyl-1-naphthoic acids (**1b** and **1c**) on aromatisation using 10% Pd/C furnished the corresponding 1-naphthoic acids (**2a** and **2b**) in 62 and 66% yield respectively.

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References and Notes:

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8. **Typical Procedure** : Anhydrous $AlCl_3$ (0.4 g, 3 mmol) in dry methylene chloride (5 ml) was stirred for 15 min. and a solution of 2-vinylbenzoic acid (**3a**, 0.220 g, 1 mmol) in methylene chloride (5 ml) was added to it. It was stirred at room temperature for 1h, poured in ice cold HCl (1:1, 10 ml) and extracted with methylene chloride (2 x 10 ml). The combined organic layer was washed with water, dried (Na_2SO_4) and evaporated to give a solid which was chromatographed over silica gel using ethyl acetate:n-hexane (3:97) to afford naphthoic acid **1a**, (0.143 g, 65%); m.p. 142-43°C; ν_{max}/cm^{-1} (nujol) 3200-2700, 1698; δ_H ($CDCl_3$) 1.27 (3H, d, *J* 7.6Hz, CH_3), 1.38-2.0 (4H, m, $-CH_2CH_2-$), 2.70-3.04 (3H, m, $ArCH_2-$, ArCH-), 3.86 (3H, s, OCH_3), 6.82 (1H, d, *J* 8.9 Hz, Ar-H), 7.26 (1H, d, *J* 8.9 Hz, Ar-H).