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

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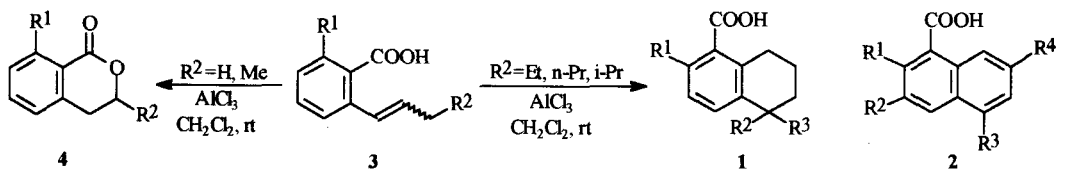
Abstract: An unusual $AlCl_3$ catalysed aromatic cyclisation reaction is described. This is used to develop a novel synthesis of 5,6,7,8-tetrahydro-5-alkyl-1-naphthoic acids (**1a-d**) from 2-vinylbenzoic acids (**3a-d**).

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

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

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

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

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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1. Thomson, R. H. *Naturally Occurring Quinones III: Recent Advances*; Chapman and Hall; London and New York, 1987.
2. (a) Fujita, T.; Koshimizu, K.; Imai, T.; Mitsui, T.; Kato, J. *Agr. Biol. Chem.* **1961**, *25*, 710. (b) Fujita, T.; Komazawa, T.; Koshimizu, K.; Mitsui, T. *Agr. Biol. Chem.* **1961**, *25*, 719. (c) Starovoitov, I. I.; Pshirkov, S. Yu.; Nefedova, M. Yu.; Yakovlev, G. I.; Adanin, V. M.; Skryabin, G. K. *Dokl. Akad. Nauk. SSSR* **1973**, *213*, 1210, (*Chem. Abstr.* 80:106843u, 1973).
3. Greiner, A. Ch.; Spyckerelle, C.; Albrecht, P. *Tetrahedron* **1976**, *32*, 257.
4. (a) Shishido, K.; Omodani, T.; Shibuya, M. *J. Chem. Soc., Perkin Trans. I* **1992**, 2053. (b) Meyers, A. G.; Subramaniam, V.; Hammond, M. *Tetrahedron Lett.* **1996**, *37*, 587.
5. (a) Wightman, R. H.; Laycock, D. E.; Avdovich, H. W. *J. Org. Chem.* **1978**, *43*, 2167. (b) Meyers, A. I.; Reuman, M.; Gabel, R. A. *J. Org. Chem.* **1981**, *46*, 783. (c) Tanis, S. P.; Abdallah, Y. M. *Synth. Commun.* **1986**, *16*, 251. (d) Parlow, J. *Tetrahedron* **1994**, *50*, 3297.
6. Mali R. S.; Jagtap. P. G.; Patil, S. R.; Pawar, P. N. *J. Chem. Soc., Chem. Commun.* **1992**, 883.
7. (a) Mali R. S.; Patil, S. R.; Kulkarni, B. K.; Yeola, S. N. *Ind. J. Chem.* **1990**, *29B*, 319. (b) Mali, R. S.; Patil, S. R. *Synth. Commun.* **1990**, *20*, 167.
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).