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A SIMPLE ONE POT SYNTHESIS OF 1-ARYLTETRALINS

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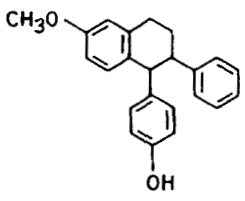
ABSTRACT : Synthesis of 1-aryltetralins is described by the Fridel-Crafts arylation of 1-tetrols with phenol.

Synthesis of 1-Aryltetralins is challenging because they possess a wide spectrum of biological activities. Tetrahydronapthalins eg. 1 are important fungicidal[1] agents, inhibitor-antifertility[2] agents and possess hypercholesterolemic activity[3]. The aryltetralin derivative 2 is a hypolipidermic agent[4]. The biologically important lignan podophyllotoxin 3 and its congeners posses aryltetralin skeleton.



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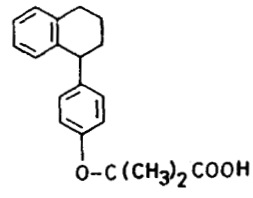

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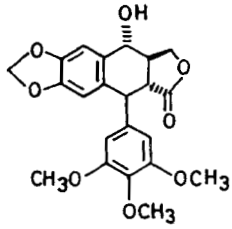

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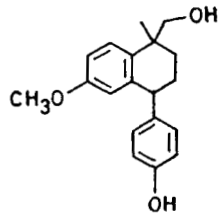
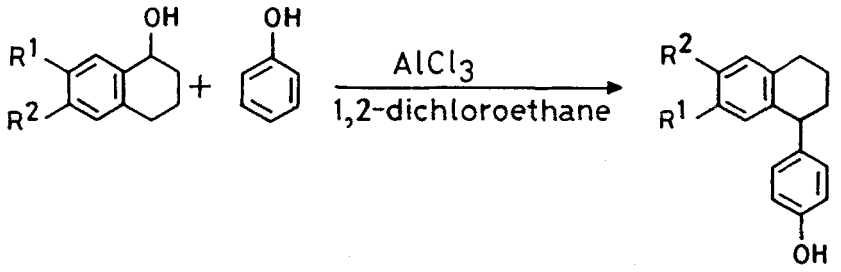


4

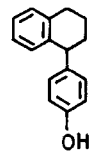
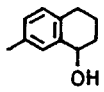
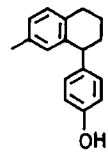
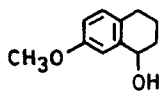
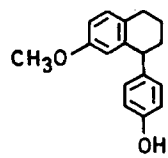
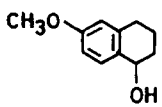
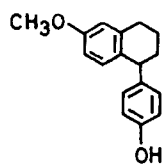
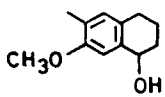
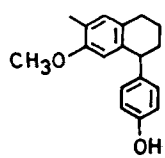
Aryltetralins are generally prepared by the intramolecular cationic cyclisation of the corresponding benzyl alcohols using either protic[5] or lewis acid[6] catalysts. In continuation of our work on the total synthesis[7] of aromatic steroids, we required the phenyltetralin derivative 4 and examined a suitable method for its preparation. We now describe a simple, efficient and convenient synthesis of 1-aryltetralins using the Fridel-Crafts reaction as shown in *scheme-1*.



Scheme -1

A typical reaction procedure involves the addition of a solution of 1-tetrol[8] and anhydrous $AlCl_3$ to a solution of the phenol in 1,2-dichloroethane during 45 to 60 min., to furnish 1-aryltetralins. The reaction is rapid and high yielding (Table-1). The yield of the aryltetralin seems to depend on many factors like the controlled addition of the tetrol, the reactivity of the aromatic ring of the tetrol etc. Rapid addition of the tetrol reduces the yield of the reaction product. In the case of tetrols having less activating substituents on the aromatic ring, the yields are very good (entries 1, 2 & 3). But in the case of tetrols having highly

Table-1

Entry	Substrate	Product	Time (min.)	Yield (%)
1	 5	 10	60	85
2	 6	 11	60	83
3	 7	 12	75	75
4	 8	 13	75	56
5	 9	 14	75	50

activated aromatic ring, yields are moderate due to the competing side reactions like self arylation (entries 4 & 5). In such cases the tetrol and $AlCl_3$ were added very slowly to minimize the side reactions.

A similar procedure for the preparation of aryltetralin 10 has been reported by Bencze et al[4]. However, this method suffers from long reaction time and low yield compared to the present method which affords the same tetralin in excellent yield.

In summary, the present communication describes a simple one pot and efficient method for the synthesis of 1-aryltetralins in excellent yields.

EXPERIMENTAL SECTION:

M.p's are uncorrected. IR spectra were recorded on a Perkin-Elmer model 781 spectrometer in nujol mull. ^{1}HNMR (90MHz) and ^{13}CNMR (22.5MHz) spectra were recorded on a JEOL FX 90Q FT NMR spectrometer in $CDCl_3$ using TMS as internal standard.

General procedure for Fridel-Crafts Arylation:

To an ice cold solution of the phenol (470 mg, 5 mmol) in 1,2-dichloroethane (30 ml) was added simultaneously the 1-tetrol(1 mmol) in 1,2-dichloroethane (10 ml) and anhydrous $AlCl_3$ (266 mg, 2 mmol) for 45 to 60 min. The reaction mixture was stirred for a further period of 15 min and poured into ice cold 10% HCl (20 ml). The organic layer was separated and the aqueous layer was extracted with methylenechloride (2 X 20 ml). The combined extracts were washed with water, Na_2Co_3, water , brine, and dried over Na_2So_4 and evaporated to give the crude product. Which was further purified by chromatography to furnish pure 1-aryltetralin (50-85%).

1-(p-Hydroxyphenyl)-1,2,3,4-tetrahydronaphthalene (5):

m.p. 127°C (lit[4]. 127-28°C) ν_{max}. 3172,1605 cm^{-1}, δ_H 1.5-2.3(m,4H,2xCH_2), 2.88 (t,J=5.4Hz,ArCH_2),4.08(t, J=6Hz,1H, CH), 4.64(s,1H,OH), 6.6-7.3(m,8H,ArH).

1-(p-Hydroxyphenyl)-7-methyl-1,2,3,4-tetrahydronaphthalene (6): m.p. 122-23°C; ν_{max} 3316,1611cm^{-1}; δ_H 1.6-2.2 (m,4H,2XCH_2), 2.19(s,3H,ArCH_3), 2.81(t, J=5.4 Hz,2H Ar-CH_2), 4.0(t,J=6.3Hz,1H,CH), 4.73(s,1H,OH), 6.5-7.3(m, 7H, ArH); δ_C 21.0(q), 20.9(t), 29.4(t), 33.4(t), 44.7(d), 115.2(d), 126.8(d), 128.9(d), 130.0(d), 130.6(d), 134.5(s), 134.6(s), 139.4(s), 140.0(s), 153.3(s).

1-(p-Hydroxyphenyl)-7-methoxy-1,2,3,4-tetrahydro naphthalene (7): m.p.129-30°C; ν_{max} 3382,1608cm^{-1}; δ_H 1.6-2.3(m,4H,2XCH_2), 2.79(t,J=5.4Hz,2H,ArCH_2), 3.65(s,3H,OCH_3) 4.0(t,J=6.3Hz,1H,CH), 4.68(s,1H,OH), 6.3-7.1(m,7H,ArH); δ_C 21.2(t), 29.0(t), 33.3(t), 45.1(d), 55.4(q), 112.5(d), 115.0(d), 115.2(d), 129.9(d), 130.1(s), 139.4(s), 141.0(s), 153.9(s), 157.3(s).

1-(p-Hydroxyphenyl)-6-methoxy-1,2,3,4-tetrahydro-naphthalene (8): m.p.108-9°C;ν_{max}3160,1605cm^{-1}; δ_H 1.7-2.3 (m,4H,X CH_2), 2.83(t,J=5.4Hz,2H,ArCH_2), 3.79(s,3H,OCH_3), 3.98(t,J=5.4Hz,1H, CH), 4.76(s,1H,OH), 6.5-7.2(m,7H,ArH).

δ_C 20.9(t), 30.0(t), 33.5(t), 44.0(d), 55.3(q), 112.0(d), 113.3(d), 115.1(d), 129.7(d), 131.1(d), 132.2(s), 138.7(s), 139.9(s), 153.6(s), 157.2(s).

1-(p-Hydroxyphenyl)-7-methoxy-6-methyl-1,2,3,4-tetra hydronaphthalene(9):m.p.106^{0}C;ν_{max} 3280,1611cm^{-1} δ_H 1.5-2.2(m,4H,2XCH_2), 2.73(t,J=5.4Hz,12H,ArCH_2),3.6(s,3H,OCH_3), 4.0(t,J=6.3Hz,1H,OH), 6.2-7.3(m,6H,ArH); δ_C 15.8(q), 20.9(t), 28.9(t),33.5(t), 44.8(d), 55.5(q), 111.8(d), 115.1(d), 124.6(s), 129.5(s), 129.8(d), 131.1(d), 137.6(s),139.9(s),153.6(s), 155.6(s).

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8. The tetrols were prepared by the $NaBH_4$ reduction of the corresponding tetralones.

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