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Research Article

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A facile synthesis of oxygen heterocycles from 1, 1'-bi-2-naphthols

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ABSTRACT

The Claisen rearrangement of 2, 2'-Bispropargyloxy-1, 1'-binaphthyl was refluxed in N, N-diethyl aniline for 8 h at 220 ºC to give 1,1'-bi-2-naphthols by using Ferric chloride oxidative coupling.

Keywords: - Claisen Rearrangement, Ferric chloride, 1, 1-bi-2-phenol and cyclic hemiketals.

INTRODUCTION

Natural and synthetic heterocyclic compounds play an important role in both drug discovery and chemical biology. The heterocycles are mainly of the classes of alkaloids, Chromones, Flavones, Isoflavones etc. The natural heterocyclics are plant secondary metabolites, which protect the plant from attack by pathogens, fungi, bacteria and insects. Several synthetic analogs of these heterocyclics show different bioactivity[1-5]. More than 50% of the drug used in the modern medicine is either derived from synthetic or natural heterocyclic systems.

Natural and synthetic binaphthols exhibit several biological properties. Diospyrol isolated from the fruits of Diospyros mollis show anti helmintic activity. The 1,1'-bi-2-naphthols is axially chiral and resolvable. Any heterocycle fused to it is also chiral. The resolved(S) or (R) -1,1,-bi-2-naphthol were used as the starting material for the synthesis of chiral macrocyclic crown ethers, the cavity in the chiral crown ethers has a particular size and shape and therefore can recognize and discriminate the enantiomers of a compounds as well as organic and inorganic cations of particular sizes and shapes.

EXEPERIMENTAL SECTION

General: - Melting points were determined in a sulfuric acid-bath and are uncorrected. IR spectra were recorded in KBr on a Shimadzu 435 spectrometer, ^{1}H NMR spectra on a Varian Gemini 200 MHz spectrometer with TMS as an internal standard and mass spectra on a Perkin Elmer Hitachi RDO-62 and MS-30 instrument.

1. General procedure for the synthesis of dinaphtho (2, 1-b: 1', 2'-d) pyrans (3a-e):

i.Dinaphtho [2,1-b:1',2'-d] pyran (3a):

2, 2'-Di-propargyloxy-1, 1'-binaphthyl **(2a)** (1.8 g, 5 m mol) was dissolved in N, N-diethylaniline (20 ml) and refluxed for 8 h at 220 ºC. The reaction mixture was cooled and neutralized with dilute HCl (10%, 100 ml) and extracted with ethyl acetate (3 x 100 ml). The solution was then successively washed with dil. HCl (10%, 2 x 100 ml) and water dried over anhydrous Sodium sulphate and concentrated. The crude product was chromatographed over silica gel (ACME, finer than 200 mesh) and eluted with petroleum ether: ethyl acetate (9:1 v/v) to yield di naphthol [2, 1-b: 1',2'-dpyran **(3a).**

yield 0.78 g, mp.180 ºC ; IR (KBr, cm^{-1}):3053, 2872, 1235, 863, 815.; ^1H NMR ($CDCl_3$): δ 4.98 and 5.20 (J=13 Hz, ABq-OCH_2), 7.20-7.90 (m, Ar-H).; ^{13}C NMR($CDCl_3$): δ 70.7(0-C), 115.8 (C-8', C-3), 116.5 (C-3', C- 1, C-5), 120.6 (C-6'), 123.7 (C-8), 125.7 (C-6', C-7'), 126.4 (C-5), 128 (C-7, C-4'), 129.3 (C-4, C- 8'a, C-2'), 129.5 (C-4a, C-4'a), 133.9 (C-8a), 134.3 (C-l'), 154.2 (C-2).; MS: 282 (Mt, 100%), 281 (82%), 252 (45%), 125 (8%).

ii. 6,6'-Dibromo-dinaphtho[2,1-b:1',2'-d]pyran (3b):
Yield 1.70g, mp. 165 °C.; IR (KBr, cm^{-1}**):** 3050, 2875, 1242, 874, 826.; ^1H NMR ($CDC1_3$): δ 5.00 and 5.25 (J=13 Hz, ABq, -OCH_2), 7.30-8.10 (m, Ar-H).; ^{13}C NMR ($CDC1_3$): 5 70.5 (0-C), 117.7 (C-8', C-3), 119.32 (C-3', C-1, C-5), 119.76; (C-6), 123.9 (C-8), 127.4 (C-6), 128.3 (C-7), 128.7 (C-5), 128.8(C-7), 129.3 (C-4'), 130.3 (C-4, C-8'a, C-2'), 130.44 (C-4a, C-4'a), 131.5 (C-8a), 133.9 (C-1'), 135.61(C-2); MS: 440 (Mt, 100), 359(30), 279 (60), 250 (35), 140 (30), 125 (25).

iii.6, 6'-Di-(2-oxobuty1)-dinaphtho[2,1-b : 1',2'd] pyran (3c):
Yield 1.8 g, mp 86 °C.; IR (KBr, cm^{-1}):3051, 2922, 1274, 1708, 887, 817.; ^1H NMR ($CDC1_3$): 5 2.10 (s, CH_3-3'), 2.80 (t, H-1'), 3.05 (t, J=7 Hz, H-2'), 4.95-5.20 (ABq, OCH_2), 7.15-7.85 (m, Ar-H).; MS: 422 (Mt, 100%), 364 (25), 305 (22), 293 (15), 186 (10), 148 (70), 120 (60).

iv. Methyl-2-(13-methyloxycarbonylmethy1-4H-benzo [f]naphtha [2,1-c] chromen-8-y1) acetate (3d) :
Yield 1.8 g, mp 92 °C.; IR (KBr, cm^{-1}): 3028, 2936, 1736, 1277, 889, 819.; ^1H NMR**:** δ 1.50 (d, J=8Hz, -CH_3), 3.65 (s, OCH_3), 3.85 (m, CH), 4.90-5.20 (J=13 Hz, ABq, OCH_2), 7.20-7.90 (m, Ar-H).; MS: 454 (Mi), 100%, 396 (20), 367 (15), 308 (30), 168 (5).

v.6,6 '-Di-(ethyl 2-propanoate)-dinaphtho[2, 1-b: 1', 2 'd] pyran (3e):
Yield 1.6 g, mp. 89 ºC.; IR (KBr, cm^{-1}): 3025, 2932, 1735, 1268, 880, 816.; ^1H NMR ($CDCl_3$): δ 1.23 (t, J=10 Hz, CH_2CH_3), 1.64 (d, J=8Hz, CH_3), 3.82 (q, J=8 Hz, CH), 4.10 (q, J=7 Hz, CH_2CH_3), 4.92-5.18 (ABq, -OCH_2), 7.20-8.00 (m, Ar-H).

II. Genersl procedur for the synthesis of 2, 2'-di-(allyloxy)-1, 1'-binaphthyls (4a-e):
vi.2,2 '-Diallyoloxy-1, 1 '-Binaphthyl (4a):
A solution of 1,1'-bi-2-naphthol **(1a)** (1.4g, S m mol) and allyl bromide (0.8 ml, 10 m mol) in acetone (100 ml) containing anhydrous potassium carbonate (15g) was refluxed 8-10 h. The mixture was cooled, filtered and the filtrate evaporated to give 2, 2'-di allyloxy-1,1'-bi naphthyl **5a** which was recrystallised from benzene as colorless crystals. yield 1.78 g, mp. 92 °C.

IR (KBr, cm^{-1}): 2840, 1647 (C=C), 1589, 1260.; ^1H NMR ($CDCl_3$): δ 4.50 (d, J=-6Hz, H-1"), 5.00 (m, H-3"), 5.85 (m, H-2"), 7.10-7.97 (m, Ar-H).; ^{13}C NMR ($CDC1_3$): δ 69.9 (C-1"), 115.7 (C-3"), 116.3 (C-2"), 120.4 (C-3), 123.5 (C-1), 125.4 (C-8), 126.1 (C-6), 127.8 (C-7), 129.1 (C-5), 129.3 (C-4a), 133.7 (C-4), 134.1 (C-8a), 154.1 (C-2).
MS: 366 (Mt, 100), 325 (31), 284 (52), 41(15).

Under similar procedure mentioned compound **1a-4a, 4b-be** were obtained from **1b-1e**.

vii..6, 6'-Dibromo-2, 2'-di-allyoxy-1, 1'-binaphthyl (4b):
Yield 2.5 g, mp. 136 °C.; IR (KBr cm^{-1}): 3068, 1640, 1278, 988, 874.; ^1H NMR ($CDCl_3$): 8 4.45 (d, J=6Hz, H-1"), 5.00 (m, H-3"), 5.70 (m, H-2"), 6.95-8.00 (m, Ar, H).

viii.6,6'-Di-(2-oxobuty1)-2,2'-diallyloxy-1,1'-binaphthyl (4c):
Yield 2.4 g, mp. 98 °C.; IR (KBr, cm^{-1}): 3052, 1712, 1642, 1274, 825.; ^1H NMR ($CDCl_3$, 200 MHz): δ 2.25 (s, CH_3), 2.85 (t, J=7 Hz, CH_2-3'), 3.20 (t, J=7 Hz, CH_3-4', 4.40 (d, J=6 Hz, H-i"), 5.10 (m, H-3"), 5.75 (m, H-2"), 7.15-8.00 (m, Ar-H).

ix.6,6'-Di-(methyl 2-propanoate)- 2,2'-diallyloxy- 1,1 '-binaphthyl (4d):
Yield 2.5g, mp. 96 °C.; IR (KBr, cm^{-1}): 3058, 1731, 1640, 1275, 832.; ^1H NMR ($CDCl_3$): δ 1.65 (d, J=4Hz, CH-CH_3), 3.75 (s, OCH_3), 3.92 (q, J=7 Hz, CH), 4.60 (d, J'6 Hz, H- 1'), 5.05 (m, H-3"), 5.80 (m, H-2"), 7.15-8.0 (m, ArH).

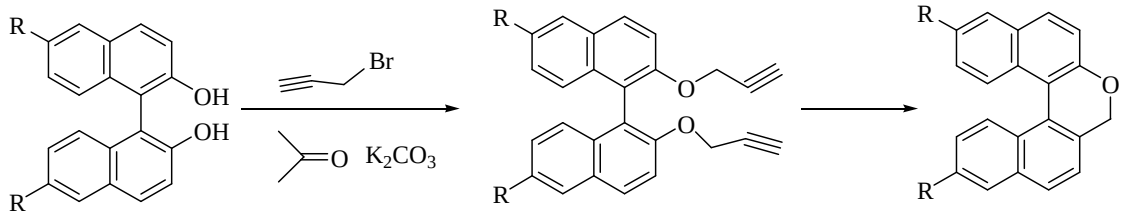
x.6, 6-Di-(ethyl 2-propanoate)- 2,2 '-diallyloxy-1,l '-binaphthyl (4e):
Yield 2.7g, mp. 89 ºC.; IR (KBr, cm^{-1}): 3042, 1734, 1642, 1261, 835.; ^1H NMR ($CDCl_3$): δ 1.20 (t, J=7 Hz, $2CH_3$), 4.35 (q, CH), 4.40 (d, J=811z, H-l'), 5.10 (m, H-3'), 5.80 (m, H-2"), 7.15-8.10 (m, Ar-H).

RESULTS AND DISSCUSSION

Synthesis of diallyl ethers of 1, 1'-bi-2-naphthols (5a-e)
The reaction of 1,1'-bi-2-naphtho!s **(1a-e)** with two equivalents of allyl bromide in dry acetone K_2CO_3 afforded 2,2'-bis-allyloxy-1,1'-binaphthyls **(5a-e).** The IR spectrum of 2,2'-bis-allyloxy-1,1-binaphthyl **5a** showed peaks at 1647 (C=C), 1618 (aromatic C=C), 1260 (0-C) cm^{-1}. Its ^1H NMR spectrum **5a** indicated symmetrical structure and showed multiplets at δ 5.85 and δ 5.00 are due to the H-2" and H-3" of olefinic group, and the methylene protons (H-1") appeared as the doublet at δ 4.50 (J=6 Hz). The aromatic protons appeared as two complex multiplets in the region 6 7.10-7.97. The ^{13}C NMR spectrum recorded in $CDC1_3$ **5a,** 50.3 MHz,) showed 13 carbons. The methylene carbon appeared at δ 69.9 (C-1") and olefinic carbons at116.3 (C-2") and 115.7 (C-3"). The aromatic carbons resonated at δ 154.1 (C-2), 134.1 (C-8a), 133.7 (C-4), 129.3 (C-4a), 129.1 (C-5), 127.8 (C-7), 126.1 (C-6), 125.4 (C-8), 123.5 (C-1) and 120.4 (C-3).

The EI mass spectrum of 2,2'-diallyloxy-1,1'-binaphthyl **5a** showed molecular ion at m/z 366 as the base peak. It loses an allyl radical to give a peak at m/z 325 which by further loss of another allyl radical gave a peak at m/z 284.

Scheme-1

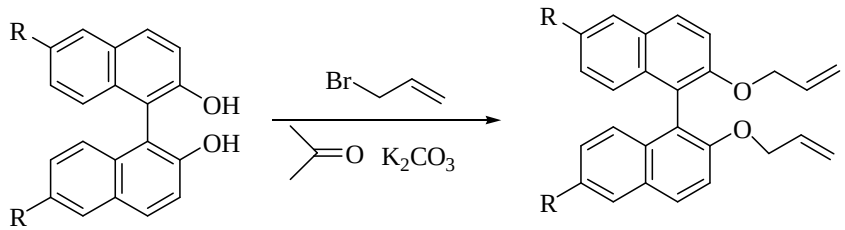


1a-e **2a-e** **3a-e**

a) R = H b) R = Br c) R = $CH_2CH_2COCH_3$

d= $CH(CH_3)CO_2CH_3$ e) R = $CH(CH_3)CO_2C_2H_5$

Scheme-2



1a-e **4a-e**

a) R = H b) R = Br c) R = $CH_2CH_2COCH_3$

d= $CH(CH_3)CO_2CH_3$ e) R = $CH(CH_3)CO_2C_2H_5$

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