

A NOVEL METHOD FOR SYNTHESIS OF SUBSTITUTED NAPHTHOFURANS AND NAPHTHOPYRANS[☆]

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ABSTRACT: *Substituted naphthofurans and naphthopyrans were constructed at high temperature from allyl or propargyl naphthyl ethers via Claisen rearrangement in moderate to good yields. Also, substituted (trimethylsilyl)-naphthofurans were synthesized from the corresponding naphthofurans.*

KEY WORDS: *Novel, Synthesis, Naphthofurans, Naphthopyrans.*

INTRODUCTION

Intramolecular Claisen cyclization is a topic of interest in synthetic organic chemistry and has been used as one of the useful techniques for the formation of heterocycles [1-4]. Many of benzo- and naphthofuran or naphthopyran derivatives have been used in synthesis as intermediate in many organic transformations [5]. Also, due to their biological importance, they have also earned considerable attention, leading to their synthesis by several groups [5b-6]. Some of the substituted naphthopyrans are naturally occurring compounds (such as lapachenole from *paratecoma-alba*) [7]. Dihydronaphthofurans are known to be important intermediate as well. These compounds were prepared in several steps or by Claisen rearrangement-cyclization reaction [8]. Also, the electrochemical synthesis of phenyl-substituted naphthofurans was reported in the presence of lithium perchlorate in acetic acid/acetonitrile solution (Eq. 1) [9].

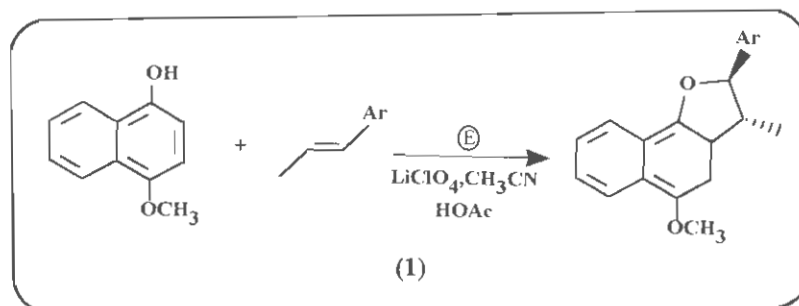
The light-promoted cyclization of α - or β -naphthol carrying allyl group gave mixture of methyl naphthodihydrofuran, naphthodihydropyran and methyl naphthofuran [10]. Later works have shown that heating of propargyl naphthyl ether in *N,N*-diethylaniline (*N,N*-DEA) alone and in the presence of sodium methoxide selectively gave naphthopyran and naphthofuran, respectively. Reaction time for these conversions are 30 minutes to several hours with good to moderate yields [11]. In this paper, we would like to report a simple and direct approach to the synthesis of substituted naphthofurans and naphthopyrans. The method involves thermal cyclization of allyl and propargyl naphthyl ethers to naphthofurans and naphthopyrans. Due to the importance of silylated furans [12], (trimethylsilyl)naphthofurans were also reported from corresponding naphthofurans.

[☆] Dedicated to Professor Abbas Shafiee on the occasion of his 60th birthday.

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5/\$2.50



EXPERIMENTAL

Melting points were recorded on a Gallenkamp unit and are uncorrected. IR spectra were recorded on Unicam Mattson 1000 and Bruker IFS88. ^1H -NMR and ^{13}C NMR spectra were recorded on a Bruker Ac 80 spectrometer in CDCl_3 . Column chromatography was run on neutral silica gel 70-230 mesh. Naphthyl ethers were prepared according to those reported in the literature [8c,13].

General procedure for the preparation of substituted naphthofurnas.

A solution of naphthyl allyl ether (5 mmol) and 0.06 g (7.5 mmol) of sodium methoxide in N,N -DEA (5 mL) was stirred and refluxed for 1.5 hours. After acidic work up the product was chromatographed eluting with petroleum ether. The products were characterized by IR, NMR and C&H analysis (see below).

General procedure for the preparation of trimethylsilyl-substituted dihydronaphthofuran

$n\text{-BuLi}$ in hexane 1.7 mL, (1.7 M in hexane, 2.5 mmol) was added to the solution of dihydronaphthofuran 0.46 g (2.5 mmol), in diethyl ether. After stirring at room temperature for 30 minutes, TMS-Cl 0.30 g (2.8 mmol) was added and the mixture stirred at room temperature for additional 1.5 hours. The mixture was diluted with water (20 mL) and the product extracted with light petroleum ether (3×20 mL). Purification of the crude reaction product on silica gel column, eluting with light petroleum ether gave the pure product. The products were characterized by IR, NMR, and C&H analysis (see below).

trans-2-Methyl-3-phenyl-2,3-dihydronaphtho [1,2-*b*] furan (2a)

A dark brown viscous liquid after chromatography,

0.78 g. ^1H NMR(CDCl_3), δ , 1.42, (d, $J=6.35$ Hz, 3H), 3.36-3.73(m, 1H), 5.32(d, $J=7.70$ Hz, 1H), 6.91-8.09(m, 11H). IR(film); 3053, 1584, 1269, 1110 cm^{-1} . Calcd. for $\text{C}_{19}\text{H}_{16}\text{O}$; C, 87.66, H, 6.19. Found C; 87.77, H, 6.36.

trans-2-Methyl-3-phenyl-2,3-dihydronaphtho [2,1-*b*] furan (2b)

A white crystalline solid after chromatography, 0.84 g, mp 92-94 °C. ^1H NMR(CDCl_3), δ , 1.58(d, $J=6.76$ Hz, 3H), 3.59-3.81(m, 1H), 5.32(d, $J=8.10$ Hz, 1H), 7.09-7.81(m, 11H). ^{13}C NMR(CDCl_3), δ , 156.93 (C), 142.18(C), 130.85(C), 129.97(C), 129.73(CH), 129.19(CH), 128.74(CH), 126.71(CH), 120.71(CH), 125.51 (CH), 122.87(CH), 122.32(CH), 112.26(CH), 92.37(CH), 45.54(CH), 20.98(CH_3).

2,2-Dimethyl-2,3-dihydronaphtho [1,2-*b*] furan (2c)

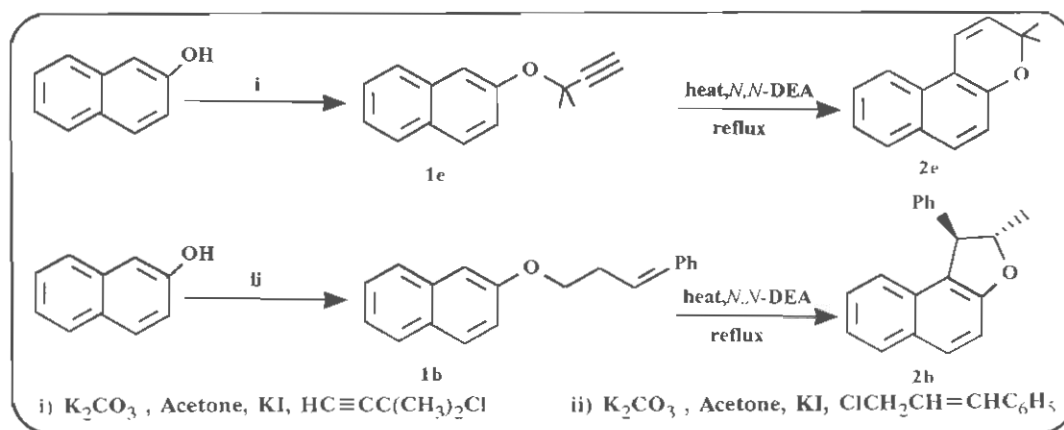
A yellow viscous liquid after chromatography, 0.93 g. ^1H NMR(CDCl_3), δ , 1.49(s, 6H), 3.05(s, 2H), 7.11-7.99(m, 6H). IR(film); 3053, 1630, 1269 cm^{-1} . Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}$; C, 84.81; H, 7.12. Found; C, 84.57; H, 7.44.

2,2-Dimethyl-2,3-dihydronaphtho [2,1-*b*] furan (2d)

A yellow viscous liquid after chromatography, 1.0 g. ^1H NMR(CDCl_3), δ , 1.41(s, 6H), 3.13(s, 2H), 6.89-7.81(m, 6H). IR(film); 3053, 1630, 1269 cm^{-1}

2,2-Dimethylnaphtho [2,1-*b*] pyran (2e)

A white crystalline solid after chromatography, mp 60-61 °C. ^1H NMR(CDCl_3), δ , 1.55(s, 6H), 5.72 (d, $J=9.2$ Hz, 1H), 7.12(d, $J=9.2$ Hz, 1H), 7.3-8.15(m, 6H). IR(film); 1630, 1261 cm^{-1} Calcd. for $\text{C}_{15}\text{H}_{14}\text{O}$; C, 85.68, H, 6.71. Found; C, 85.51; H, 6.92.



Scheme 1

2,2-Dimethylnaphtho [1,2-b] pyran (2f)

A white crystalline solid after chromatography, mp. 42-43°C. ^1H NMR(CDCl_3), δ , 1.42(s, 6H), 5.55(d, $J=9.8$ Hz, 1H), 6.40(d, $J=9.8$ Hz, 1H), 7.3-8.15(m, 6H), IR(film); 1632, 1253 cm^{-1} .

2-Methyl-3-phenyl-3-(trimethylsilyl)-2,3-dihydro-naphtho [1,2-b] furan (3b)

A yellow viscose liquid after chromatography. ^1H -NMR(CDCl_3), δ , 0.19(s, 9H), 1.56(d, $J=6.3$ Hz, 3H), 3.75-4.01(m, 1H), 7.12-8.05(m, 11H). IR(film); 1261.5, 861.5 cm^{-1} .

2,2-Dimethyl-3-(trimethylsilyl)-2,3-dihydronaphtho [1,2-b] furan (3d)

A yellow viscose liquid after chromatography. ^1H -NMR(CDCl_3), δ , 0.15(s, 9H), 1.60(s, 6H), 3.60(s, 1H), 6.80-7.62(m, 6H). IR(film); 1261.0, 853.8 cm^{-1} . Calcd. for $\text{C}_{17}\text{H}_{22}\text{OSi}$; C, 75.50, H, 8.20. Found; C, 75.11, H, 8.50.

3-Methyl-3-(trimethylsilyl)-2,3-dihydronaphtho [1,2-b] furan (3g)

A yellow viscose liquid after chromatography. ^1H -NMR(CDCl_3), δ , 0.2(s, 9H), 1.51(d, $J=5.9$ Hz, 3H), 3.05-3.46(m, 1H), 4.80-5.15(m, 1H), 7.10-7.80(m, 6H). IR(film); 1253.8, 815.3 cm^{-1} . Calcd. for $\text{C}_{16}\text{H}_{20}\text{OSi}$; C, 74.95, H, 7.86. Found; C, 74.51, H, 7.33.

RESULTS AND DISCUSSION

One of the important method developed during the past several decades for C-C bond formation

through highly ordered cyclic transition state, involves the Claisen rearrangement. The Claisen rearrangement of naphthyl propargyl ethers and naphthyl allyl ethers in high boiling solvents has found useful applications as a method for the synthesis of naphthofurans and naphthopyrans. The course of the rearrangement is markedly dependent upon the solvent, Lewis acid catalyst and the presence or absence of added base [14].

Treatment of 1-naphthol or 2-naphthol with alkenyl or propargyl halide, gave the corresponding naphthyl ethers 1(a-f) by the known methods [11,13]. Heating of naphthyl ethers 1(a-f) in N,N' -diethylaniline in (N,N -DEA) afforded naphthofurans and naphthopyrans 2(a-f), Scheme 1. The reaction conditions and the yields of the products are shown in the Table 1. The mechanism for these type of transformation was reported before [3,15].

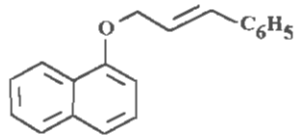
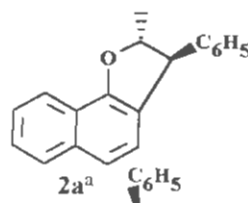
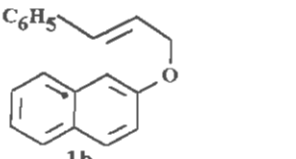
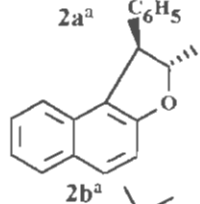
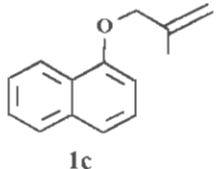
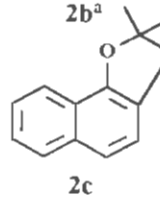
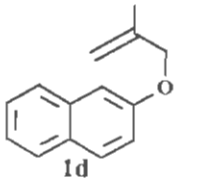
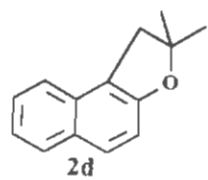
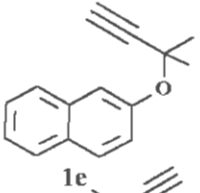
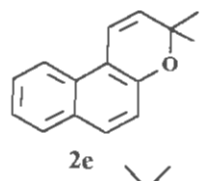
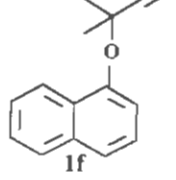
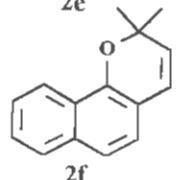
In order to prepare trimethylsilyl-substituted naphthofurans, compounds 2b, 2d and 2g were treated with $n\text{-BuLi}$ and then with chlorotrimethylsilane (TMS-Cl). After normal work up, TMS-substituted naphthofurans 3b, 3d and 3g were isolated with moderate yields. The results are shown in Table 2.

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Table 1 : Synthesis of naphthofurans and naphthopyrans

Entry	Substrate	Product	Time/h(yield%)
1	 1a	 2a ^a	8.0(60)
2	 1b	 2b ^a	6.0(65)
3	 1c	 2c	0.5(47)
4	 1d	 2d	0.5(64)
5	 1e	 2e	6.0(65)
6	 1f	 2f	8.0(60)

a : The stereochemistry of these compounds established by comparison of their ¹H NMR with those reported in ref. [9].

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Table 2 : Synthesis of silylated naphthofurans

Entry	Substrate	Product	Time/h(yield%)
1			6.0(62)
2			6.0(60)
3			6.0(70)

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