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A NOVEL METHOD FOR SYNTHESIS OF NAPHTHOFURANS AND NAPHTHODIFURANS

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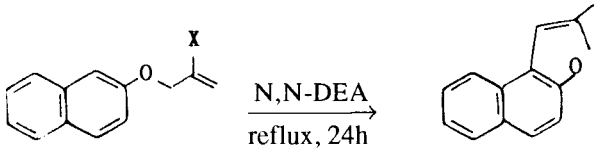
Abstract

Thermal rearrangement of propargyl naphthyl ethers produced naphthopyrans. In the presence of sodium methoxide, propargyl naphthyl ethers were converted easily to naphthofurans and naphthodifurans in good yields.

Introduction

The introduction of furan rings into organic molecules, such as benzene and naphthalene rings, is an important transformation, because furans provide convenient handles for the introduction of many other functional groups [1, 2]. In connection with studies on intramolecular thermal Claisen rearrangement, which has been used extensively for the preparation of benzofurans, naphthofurans, and naphthopyrans [3-10], Lewis acids or heat have been used to promote Claisen rearrangements of chloro- or bromopropenyl naphthyl ethers for the preparation of naphthofurans [3, 7, 9].



(1) X=Br (3)

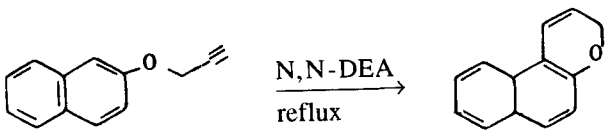
N, N-DEA=N,N-diethylaniline

(2) X=Cl $\xrightarrow{\text{polyphosphoric acid}}$ (3)

(1) $\xrightarrow[CH_2Cl_2]{TiCl_4}$ (3)

Chloro- or bromopropenyl naphthyl ethers are prepared from lachrymatory materials, and their preparations are more difficult than the propargyl naphthyl ethers [3, 6].

Direct heating of propargyl naphthyl ether (4) in N,N-diethylaniline gave only naphthopyran (5). Also, naphthyl ether (4) did not produce naphthofuran by using titanium tetrachloride in different solvents and at different temperatures [12].



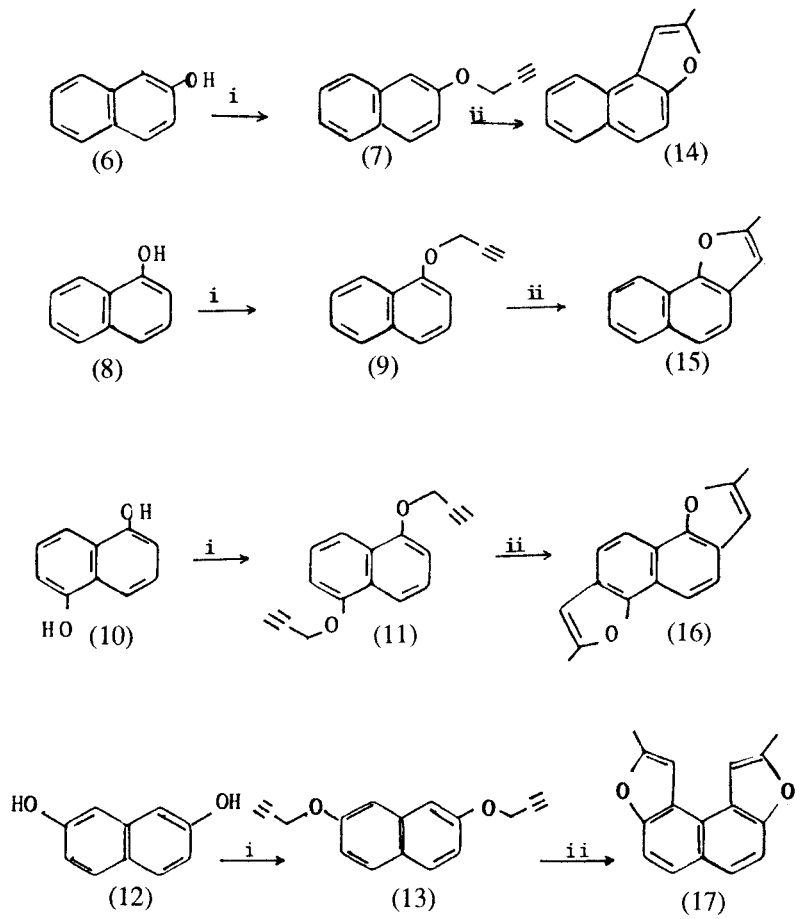
(4) (5)

In the present study, we report the feasibility of using propargyl naphthyl ethers, which can be prepared very easily, as a route to napthofurans, which are widespread in various natural products and have interesting properties [11].

Results and Discussion

Heating of propargyl naphthyl ethers (7), (9), (11), and (13) in N,N-diethylaniline in the presence of sodium methoxide afforded naphthofurans (14) - (17) in good yields. These naphthofurans were the only products (Scheme 1). Table 1 shows the condition and the

Keywords: Synthesis; Naphthofurans; Naphthodifuran



i, Br-CH_2 C=CH , K_2 CO_3 , acetone
ii, N,N-DEA, reflux, CH_3ONa

Scheme 1

yields of naphthofurans.

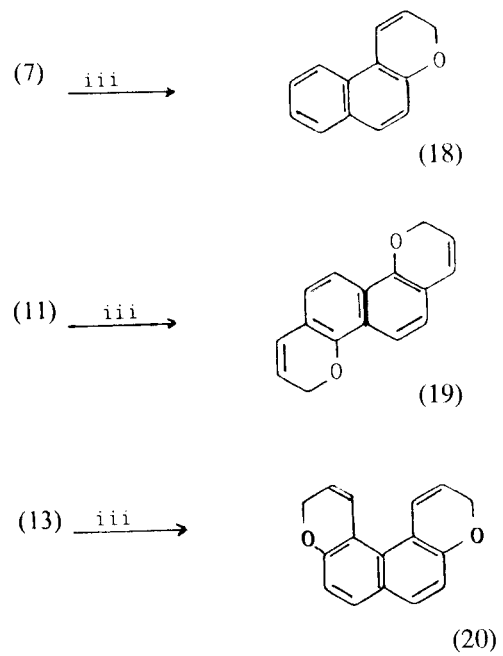
Heating the propargyl naphthyl ethers (7), (11), and (13) in N,N-diethylaniline in the absence of sodium methoxide, gave naphthopyrans (18) - (20), Scheme 2. Table 2 shows the condition and the yields of products (18) - (20).

Table 1

Entry	Starting material	Time, min.	Product	%Yield
1	ether 7	40	furan 14	80
2	ether 9	50	furan 15	70
3	ether 11	40	furan 16	75
4	ether 13	40	furan 17	67

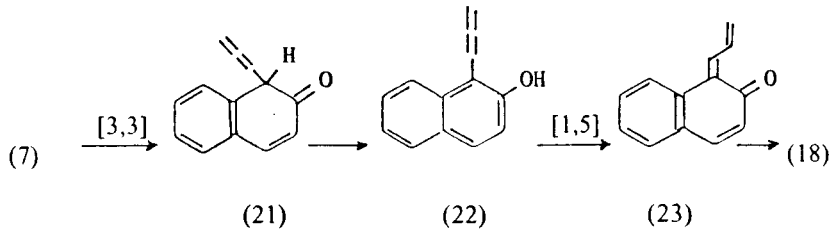
Table 2

Entry	Starting material	Time, min.	Product	%Yield
5	ether 7	45	pyran 18	40
6	ether 11	40	pyran 19	42
7	ether 13	50	pyran 20	60



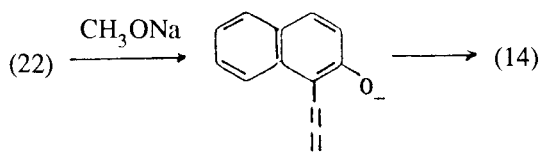
Scheme 2

As was shown by Schmid and co-workers, naphthyl ethers undergo thermal Claisen rearrangement to give intermediate allenylnaphthalene such as (21), which, after enolization, [1,5]-H shift, and electrocyclic reaction, affords naphthopyrans [13], Scheme 3.



Scheme 3

But, in the presence of sodium methoxide, naphthol (22) gives naphthofuran (14).



Experimental Section

M.p.s were recorded on a Gallenkamp unit and are uncorrected. IR spectra were recorded on Perkin Elmer model 883, and Matt Son 1000 Unicam FTIR spectrophotometers. ^{1}H NMR spectra were recorded on a Bruker AC 80 spectrometer in $CDCl_3$. MS spectra were recorded on a Finigan incos 500 spectrometer. Column chromatography was conducted on neutral alumina 70-230 mesh. Commercial ally and propargyl bromide (Fluka) and N,N-DEA (Merck) were used. The organic extracts were dried over $CaCl_2$. IR, ^{1}H NMR, and MS spectral data of the products are given in Table 3.

Propargyl naphthyl ethers (7), (9), and (13)

These ethers were prepared according to those reported in the literature. Their ^{1}H NMR and IR spectra were the same as those reported [10].

1,5-Bis (2'-Propynyloxy)naphthalene (11)

A solution of 2,7-dihydroxynaphthalene (8.0 g, 50 mmol), propargylbromide (17.8 g, 150 mmol), and anhydrous potassium carbonate (27.0 g, 200 mmol), in dry acetone (200 ml) was stirred and refluxed for 5h. After cooling and normal work up, it was purified with column chromatography, eluting with pet. ether. The pure product was 10.3 g (87%) with m.p. of 144-145°C.

2,7-Dimethylnaphtho [1,2-b; 5,6-b] difuran (16)

A solution of bispropargylnaphthyl ether (11) 1.0 g (4.2 mmol) and 0.7 g (13 mmol) sodium methoxide in N,N-DEA (10 ml) was stirred and refluxed for 40 min. After normal acidic work up, the product was chromatographed, eluting with pet. ether. The yield was 0.75 g (75%) with m.p. of 188-189°C.

2,5-Dimethylnaphtho [2,1-b; 7,8-b] difuran (17)

A solution of bispropargyl naphthyl ether (13) 1.2 g (5 mmol) and 0.7 g (13 mmol) sodium methoxide in N,N-DEA was stirred and refluxed for 40 min. After

Table 3. Spectral data of products

Product	ν_{max} cm^{-1}	δppm	m/z
11	3277,2131,1600,1515,1415,1377 1269,1215,1054,777,708,661	7.91(2H,d,**J** 8.6), 7.38(2H,t,**J** 8), 6.98(2H,d,**J** 7.6), 4.87(4H,d,**J** 2.4) 2.52(2H,t,**J** 2.4)	
16	3116,3082,2922,1611,1540,1450 1387,1318,1266,1030,941,825,709	8.05(2H,d,**J** 8.4), 7.63(2H,d,**J** 8.4) 6.5(2H,q,**J** 1),2.56(6H,d,**J** 1)	236(M+100%), 237(M+1),17.5% 238(M+2), 1.9%
17	3003,2950,2915,1592,1431,1375, 1269,1161,1116,1080,1000,937,	7.75(2H,d,**J** 8.9),7.54(2H,d,**J** 8.9) 6.99(2H,q,**J** 0.8),2.58(6H,d,**J** 0.8)	236(M+100%), 237(M+1)17.5% 238(M+2) 1.9%
19	3077,2896,1650,1503,1418,1333, 1233,1102,1020,816,664	7.72(2H,d,**J** 8.4),7.05(2H,d,**J** 8.4) 6.51(2H,d, of t,**J** 1.7,9.6),5.78(2H, d of t,**J** 3.6,9.6),4.95(4H,d of d,**J** 3.6,1.7)	236(M+100%), 237(M+1),17.4% 238(M+2),1.9%

acidic work up and chromatography, 0.8 g (67%) of difuran (17) was obtained with m.p. of 210-211°C.

Naphtho [1,2-b; 5,6-b] dipyran (19)

A solution of bispropargyl naphthyl ether (11) 1.2 g (5 mmol) in N,N-DEA (20 ml) was stirred and refluxed for 40 min. After acidic work up and chromatography, 0.5 g (42%) of (19) was obtained with m.p. of 125-126°C.

Acknowledgements

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