REARRANGEMENT OF NAPHTHYL ETHERS PROMOTED BY TITANIUM TETRACHLORIDE
SYNTHESIS OF NAPHTHO{b}FURANS AND 1,2-DIHYDRONAPHTHO{b}FURANS

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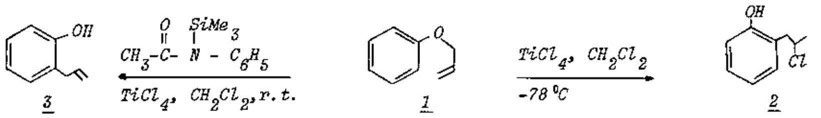
Abstract - Rearrangement of {(β-bromoallyl)oxy}naphthalenes and allyl naphthyl ethers promoted by titanium tetrachloride produced naphtho{b}furans and 1,2-dihydronaphtho{b}furans, respectively.

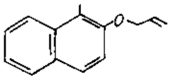
The Claisen rearrangement is generally effected by prolonged heating (180-200°C) of naphthyl ethers in solvent such as N,N-dimethylaniline. Further, it is also known that Lewis acids cause the acid-catalyzed Claisen rearrangement under milder condition. However, when allyl phenyl ether , 1 , was treated with an equimolar amount of titanium tetrachloride in dichloromethane at -78°C, phenol 2 was obtained. When the reaction was carried out in the presence of N-trimethylsilylacetanilide at room temperature, phenol 3 was obtained in 88% yield.[2]



We have found that Claisen rearrangement of naphthyl ethers promoted by titanium tetrachloride did not produce naphthols but the cyclized product.[3]

Treatment of 2-naphthol with 2,3-dibromopropene gave 2-{(β-bromoallyl)}naphthalene, 4 , in good yield.[4,5] Compound 6 was also prepared with the same procedure in excellent yeild. when compound 4 and 6 were treated with two equimolar amounts of titanium tetrachloride in dichloromethane, 2-methylnaphtho{2,1-b}furan, 5 , and 2-methylnaphtho{1,2-b}furan, 7 , were obtained, respectively. In addition, the rearrangement of naphthyl ethers 8 - 11 with titanium tetrachloride in dichloromethane, at 0°C, gave 1,2-dihydronaphtho{b}furans 12 - 15 (Table 1).

Acid-catalyzed rearrangement of ether 16 is known to give naphthol 18 via naphthalenone 17.[6] However, when ether 16 was treated with two equimolar amounts of titanium tetrachloride in dichloromethane, naphthol 19 was obtained after 1 h at 0°C. No 2,3-dihydro-2,9-dimethylnaphtho{2,3-b}furan , 20 , could be isolated.[11]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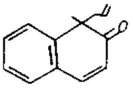
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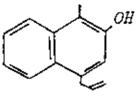

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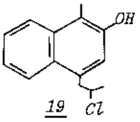

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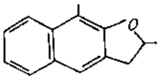

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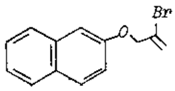
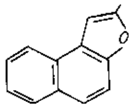
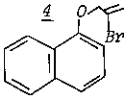
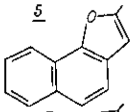
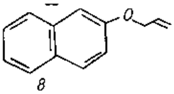
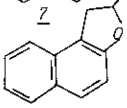
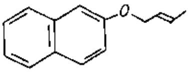
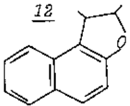
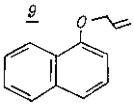
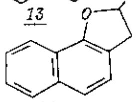
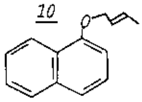
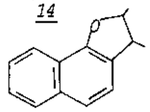
To decide whether the rearrangements proceed via the naphthols, 1-allyl-2-naphthol was treated with titanium tetrachloride in dichloromethane at 0°C. After 30 min compound 12 was obtained in 82% yield.

The results suggest a general appraoch to the synthesis of a methylfuran ring fused to naphthalene system, as well as the 1,2-dihydronaphtho{b}furan rings, in two steps from naphthols, in good yields.

Table 1

Naphthyl ether	Equimolar $TiCl_4$ used	Reaction Time; Temperature	Product	Isolated Yield(%)	Ref.
 4	2	18 h; 40°C	 5	56	4
 6	2	15 h; r.t.	 7	38	5
 8	2	1/2 h; 0°C	 12	84	7
 9	1.5	1/2 h; 0°C	 13	54	8
 10	1.5	1/2 h; 0°C	 14	64	9
 11	1.5	1/2 h; 0°C	 15	56	10

EXPERIMENTAL

PMR spectra were determined in CCl_4 with TMS as internal standard on a Varian EM 360 instrument. (β-Bromoallyl)naphthalenes 4 and 6 were prepared by reaction of 2,3-dibromopropene and anhydrous potassium carbonate with 2-naphthol or 1-naphthol in acetone, respectively. Naphthyl ethers 8 -11 were prepared with the same procedure using 3-bromo-1-propene or trans-1-bromo-2-butene. Their PMR spectra were identical with those reported in the literature.[6] PMR of 1-{(β-bromoallyl)}naphthalene , 6 , showed peaks at δ4.86 (s, 2H), 5.63 (d, J= 2Hz, 1H), 6.02 (d, J = 2Hz, 1H), 6.51-6.8 (m, 1H), 7.13-7.92 (m, 5H), 8.11-8.49 (m, 1H).

General procedure for the rearrangement of naphthyl ethers:

Naphthyl ether (10 mmol) was dissolved in dry dichloromethane (40 ml) and kept under atmosphere of nitrogen. Titanium tetrachloride in CH_2Cl_2 (10 ml) was added slowly, and the reaction mixture was stirred (or was refluxed). Then water was added and after normal work-up, the dark brown liquid was chromatographed on neutral alumina, eluting with light petroleum ether. The temperature and the condition of the reaction are given in Table 1.

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REFRENCES AND NOTES

1. This work was done during the leave at Institute of Chemistry, University of Mazandaran, Babolsar, Iran.
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7. Compound 12: PMR δ 1.49 (d, J = 6Hz, 3H), 2.72-3.66 (m, 2H), 4.7-5.2 (m,1H), 6.9-7.8 (m, 6H).
8. Compound 13: PMR δ 1.16 (d, J = 6Hz, 3H), 1.45 (d, J = 6Hz, 3H), 3.28-3.76 (m, 1H), 4.6-5.07 (m, 1H), 6.98-7.78 (m, 6H).
9. Compound 14: PMR δ 1.46 (d, J = 6Hz, 3H), 2.60-3.56 (m, 2H), 4.71-5.3 (m, 1H), 7.02-7.51 (m, 4H), 7.52-8.1 (m, 2H).
10. Compound 15: PMR δ 1.32 (d, J = 6Hz, 3H), 1.51 (d, J = 6Hz, 3H), 2.92-3.39 (m, 1H), 4.22-4.67 (m, 1H), 7.02-7.47 (m, 4H), 7.51-8.1 (m,2H).
11. Compound 19: PMR δ 1.44 (d, J = 3Hz, 3H), 2.43 (s, 3H), 2.9-3.62 (m, 2H), 3.96-4.51 (m, 1H), 6.78 (s, 1H at C_3), 7.1-7.56 (m, 3H), 7.66-7.98 (m, 2H).

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