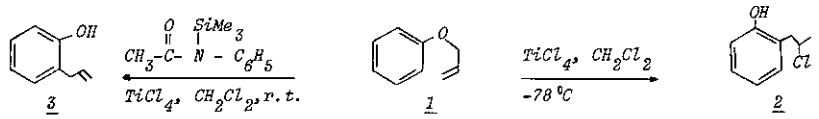
REARRANGEMENT OF NAPHTHYL ETHERS PROMOTED BY TITANIUM TETRACHLORIDE SYNTHESIS OF NAPHTHO{b}FURANS AND 1,2-DIHYDRONAPHTHO{b}FURANS

Mohammad Reza Saidi[1]

Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

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]

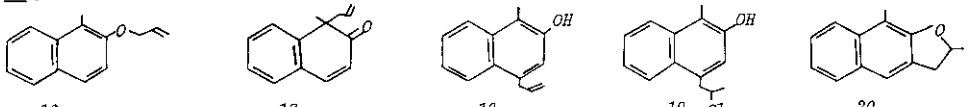


3 1 2

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]

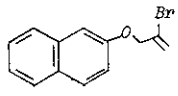
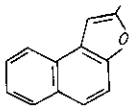
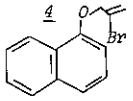
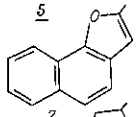
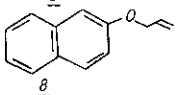
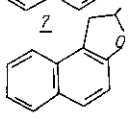
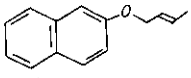
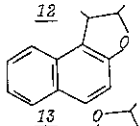
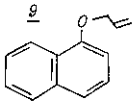
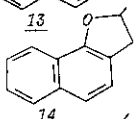
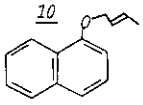
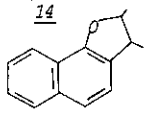


16 17 18 19 20

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 approach 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.

ACKNOWLEGEMENT

The author wishes to thank the staff of Institute of Chemistry at University of Mazandaran, especially Professor J. Ipacktschi.

REFRENCES AND NOTES

1. *This work was done during the leave at Institute of Chemistry, University of Mazandaran, Babolsar, Iran.*
2. *K. Narasaka, E. Bald, and T. Mukaiyama, Chem. Lett., 1041 (1975).*
3. *Acid-catalyzed Claisen rearrangement of 2-(2-chloroprop-2-enyl)phenols give 2-methylbenzo-[b]furans; W. K. Anderson, E. J. LaVoie, and J. C. Bottaro, J. Chem. Soc. Perkin 1, 1 (1976).*
4. *K. D. Kaufmann and L. E. Hewitt, J. Org. Chem. 45, 738 (1980).*
5. *T. Hosokawa, H. Ohkata, and I. Moritani, Bull. Chem. Soc. Jap., 48, 1533 (1975).*
6. *B. Miller and M. R. Saidi, Tet. Lett., 4391 (1972); M. R. Saidi, Ph. D. Dissertation, University of Massachusetts, 1975; B. Miller and M. R. Saidi, J. Amer. Chem. Soc., 98, 2227 (1976).*
7. *Compound 12: PMR δ1.49 (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 δ1.16 (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 δ1.46 (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 δ1.32 (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 δ1.44 (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).*

Received, 15th March, 1982