SYNTHESIS OF SILYLATED NAPHTHOPYRANS AND NAPHTHODIPYRANS

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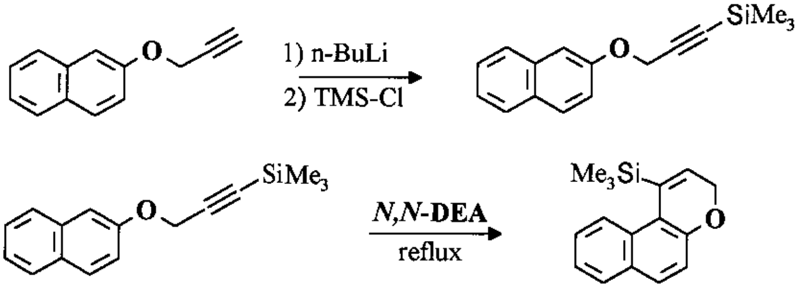
Abstract- Thermal Claisen rearrangement-cyclization of naphthyl trimethylsilylpropargyl ethers afforded silylated naphthopyrans and naphthodipyrans in good to moderate yields.

Synthesis of silylated compounds has found interest due to their synthetic use.[1] Up to now there are no reports of direct synthesis of silylated naphthopyrans and naphthodipyrans in the literature.

Since naphthopyrans and naphthodipyrans are known to be important intermediate in organic synthesis, introducing pyran rings into organic molecule such as benzene or naphthalene is important transformation.[2-6] Some of these reports indicate that benzopyrans and naphthopyrans can be synthesized by refluxing naphthyl or phenyl propargyl ethers in *N,N*-diethylaniline (*N,N*-DEA) for about four hours. Other reported methods required several steps or a Lewis acid as a catalyst for the rearrangment reaction. [7-8]

In this paper, we wish to report a procedure for introducing a trimethylsilyl (TMS) group into naphthopyrans and naphthodipyrans ring by Claisen rearrangement-cyclization reaction of naphthyl TMS-propargyl ethers. Naphthyl TMS-propargyl ethers were prepared by reaction of naphthyl propargyl ethers with n-butyllithium and then TMS-Cl, according to the Scheme 1. The crude products were purified by column chromatography.

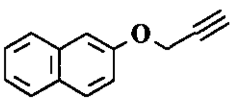
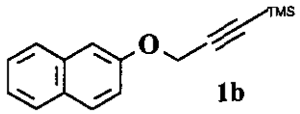
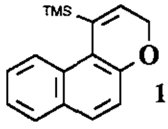
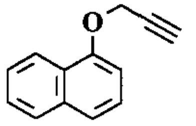
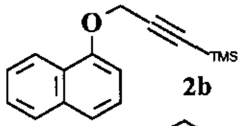
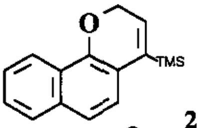
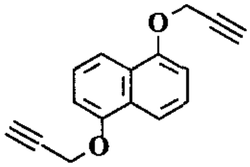
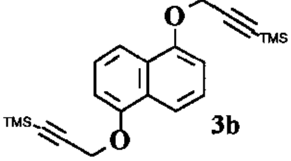
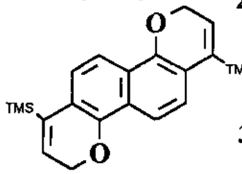
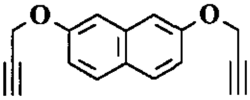
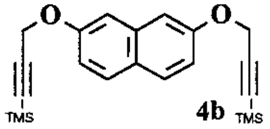
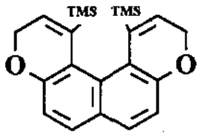
Thermal rearrangement of silylated naphthyl propargyl ethers at refluxing temperature in *N,N*-DEA gave the corresponding TMS-naphthopyran or TMS-naphthodipyran as a product in good to moderate yields. The results are shown in **Table 1**.



Scheme 1

Thermal reaction of naphthyl TMS-propargyl ether in the presence of sodium methoxide at refluxing temperature in *N,N*-DEA gave the desilylated naphthofuran, presumably, due to desilylation of the starting material or the product with sodium methoxide. [9]

Tabe 1. Structure of the starting materials and the products

	Starting ether	Trimethylsilyl ether	Product	Yield %
1		 **1b**	 **1c**	55
2		 **2b**	 **2c**	53
3		 **3b**	 **3c**	48
4		 **4b**	 **4c**	45

EXPERIMENTAL SECTION

Mp were recorded on a Gallenkamp unit and are uncorrected. Ir spectra were recorded on Matt Son 1000 Unicam FTIR spectrophotometers. ^{1}H- Nmr and ^{13}C- nmr spectra were recorded on Bruker AC 80 spectrometer in $CDCl_3$. Ms spectra were obtained on a Finnigan Mat model 8430, Varian MAT 311A and Varian MAT 111 spectrometers. Column chromatography was conducted on neutral silica gel 60, 70-230 mesh. Commercial TMS- Cl (Fluka) and *N,N*-DEA (Merck) were used. The organic extracts were dried over $CaCl_2$.

General procedure for the preparation of naphthyl TMS-propargyl ether.
Naphthyl ether (10 mmol) was dissolved in dry ether (15 ml) at room temperature and kept under atmosphere of nitrogen. n-BuLi (12.5 mmol, 5.3 g) of 15% solution in hexane was added slowly, and the reaction mixture was stirred for about 10 to 15 min. TMS-Cl (12.5 mmol, 1.36 g) was added and the reaction mixture was stirred for additional 1.5 h. Then water (20 ml) and ether (20 ml) were added, and the organic extract was dried. The solvent was evaporated, and the crude product was chromatographed on silica gel, eluting with light pet. ether.

2-Naphthyl trimethylsilylpropargyl ether (1b): A pale yellow liquid after chromatography (2.03 g, 80%). ^{1}H-Nmr δ 0.19 (s, 9H), 4.79 (s, 2H), 7.12-7.85 (m, 7H); ir 2173, 1259, 848 cm^{-1}; ms m/z 254 (M$^+$, 52.4), 165 (33.8), 73 (100).Anal. Calcd for: $C_{16}H_{18}OSi$: C, 75.54; H, 9.44. Found: C, 75.23 ; H, 9.94.

1-Naphthyl trimethylsilyl propargyl ether (2b): A yellow liquid after chromatography (1.9 g,75%).^{1}H -Nmr δ 0.2 (s, 9H), 4.70 (s, 2H), 6.80-8.20 (m, 7H); ir 2176, 1268, 853 ; ms m/z 254 (M$^+$), 73 (base peak).Anal. Calcd for: $C_{16}H_{18}OSi$: C, 75.54; H, 9.44. Found: C, 75.59 ; H, 9.62.

1,5-Naphthyl bis(trimethylsilylpropargyl) ether (3b): A red crystaline solid after chromatography (2.77 g, 73%). mp 60-62 °C. ^{1}H-Nmr δ 0.2 (s, 9H), 4.9 (s, 4H), 6.90 - 7.70 (m, 6H); ir 2169, 1253, 846 cm^{-1}; Anal. Calcd for: $C_{22}H_{28}O_2Si_2$: C, 69.42; H, 7.41. Found: C, 69.96 ; H, 7.23.

2,7-Naphthyl bis(trimethylsilylpropargyl) ether (4b): A pale yellow crystalline solid after chromatography (2.85 g, 75%). mp 52-54 °C. ^{1}H-Nmr δ 0.08 (s, 9H), 4.70 (s, 4H), 6.75-7.85 (m, 6H); ir 2194, 1255, 853 cm^{-1}; ms m/z 380 (M$^+$), 73 (base peak); Anal. Calcd for: $C_{22}H_{28}O_2Si_2$: C, 69.42; H, 7.41. Found: C, 69.01 ; H, 7.68.

General procedure for the Claisen rearrangement of silylated naphthyl ethers.

Naphthyl TMS-propargyl ether (5 mmol) in *N,N*-DEA (5ml) was stirred and refluxed for 1.5 h. After acidic work-up, the crude product was chromatographed on silica gel, eluting with light pet. ether. The yields are given in **Table 1**.

4-Trimethylsilylnaphtho[2,1-*b*]pyran (1c): A brown liquid after chromatography (0.7 g, 55%). ^{1}H-Nmr δ 0.13 (s, 9H), 4.43 (d, J = 5.07 Hz, 2H), 6.28 (t, J = 5.07 Hz, 1H), 6.98-8.01 (m, 6H); ^{13}C-Nmr δ 136.96 (C), 131.68 (CH), 129.92 (C), 129.14 (C), 128.97 (CH), 128.36 (CH), 125.48 (CH), 125.19 (CH), 124.51 (C), 123.49 (CH), 117,91 (CH), 111.51 (C), 64.16 (CH_2), 1.13 (CH_3); ms m/z 254 (M$^+$), 73 (base peak). Hrms Calcd. for : $C_{16}H_{18}OSi$: 254.1129, found : 254.1069.

4-Trimethylsilylnaphtho[1,2-*b*]pyran (2c): A dark brown liquid after chromatography (0.67 g, 53%).^{1}H-Nmr δ 0.15 (s, 9H), 4.65 (d, J = 7.05 Hz, 2H), 6.00 (t, J = 7.05 Hz, 1H), 7.00 - 8.30 (m, 6H); ir 1261, 853 cm^{-1} ; ms m/z 254 (M$^+$), 73 (base peak). Hrms Calcd for: $C_{16}H_{18}OSi$: 254.1129, found: 254.1102.

4,4'-Bis(trimethylsilyl)naphtho[2,1-*b*;5,6-*b*]dipyran (3c): A dark red solid (0.9 g, 48%). mp 191-193 °C. ^{1}H-Nmr δ 0.1 (s, 9H), 4.63 (d, J = 7.0 Hz, 2H), 6.00 (t, J = 7.0 Hz, 1H), 7.02-7.55 (m, 4H);ir 1250, 841 cm^{-1} ; ms m/z 380 (M$^+$, 100), 73 (78). Anal. Calcd for: $C_{22}H_{28}O_2Si_2$: C, 69.42; H, 7.41. Found: C, 69.86 ; H, 7.19.

4,4'-Bis(trimethylsilyl)naphtho[2,1-*b*;7,8-*b*]dipyran (4c): A pale yellow liquid after chromatography (0.85 g, 45%). ^{1}H-Nmr δ 0.1 (s, 9H), 4.29 (d, J = 5.02 Hz , 2H), 6.22 (t, J = 5.02 Hz, 1H), 6.88- 7.25 (m, 4H); ir 1265, 855 cm^{-1}. Anal. Calcd for: $C_{22}H_{28}O_2Si$: C, 69.42; H, 7.41. Found: C, 69.30; H, 7.90.

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