SYNTHESIS OF FUNCTIONAL SILYLATED ACYLALKYNES

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ABSTRACT : *Functional trimethylsilylacetylenes 2(a-i) with different functional groups were synthesized from their corresponding acyl chloride (1) in good yields.*

KEY WORDS : *Trimethylsilylacetylenes, Acyl chloride, Functional groups.*

INTRODUCTION :

Synthesis of new organosilicon, specially functional silylated compounds continues to attract much attention. Functional acyltrimethylsilylacetylenes can serve as precursors for many chemical transformations, and they possess many interesting biological properties, which are characteristic of functionalized acetylenes [1-7].

In connection with our work on synthesis of silylated acetylenic amines, and the synthesis of monoacyltrimethylsilylacetylenes [8,9], in this paper, we would like to report synthesis of new and functional trimethylsilylacetylenes.

Reaction of substituted acyl chloride *(1)* with bis (trimethylsilyl) acetylene in the presence of anhydrous aluminium trichloride in dichloromethane gave polyfunctional monoacyltrimethylsilylacetylenes *(2)*, under mild conditions, in good yields.

$$\underset{1(a\text{-}i)}{X\text{-}CH_2COCl} + (CH_3)_3SiC{\equiv}CSi(CH_3)_3 \xrightarrow{AlCl_3,CH_2Cl_2} \underset{2(a\text{-}i)}{X\text{-}CH_2COC{\equiv}CSi(CH_3)_3}$$

In these reactions, acyl chloride with a double bond, furan and thiophen ring, puls other functional groups were used. The results are shown in Table 1.

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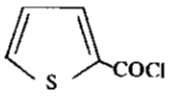
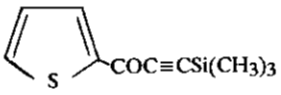
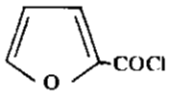
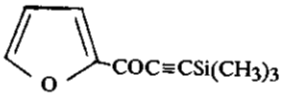
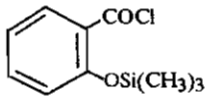
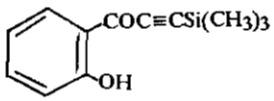
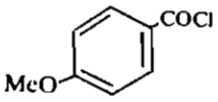
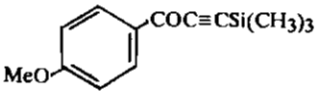
Table 1: The structure of the starting materials and the products.

Entry	Staring Material	Product	%Yield
1	 *(1-a)*	 *(2-a)*	77
2	 *(1-b)*	 *(2-b)*	58
3	$C_6H_5CH=CHCOCl$ *(1-c)*	$C_6H_5CH=CHCOC\equiv CSi(CH_3)_3$ *(2-c)*	70
4	 *(1-d)*	 *(2-d)*	74
5	 *(1-e)*	 *(2-e)*	90
6	$CH_2ClCH_2CH_2COCl$ *(1-f)*	$CH_2ClCH_2CH_2COC\equiv CSi(CH_3)_3$ *(2-f)*	90
7	$CH_2CH_2CHBrCOBr$ *(1-g)*	$CH_2CH_2CHBrCOC\equiv CSi(CH_3)_3$ *(2-g)*	54
8	$(CH_3)_3CCH_2COCl$ *(1-h)*	$(CH_3)_3CCH_2COC\equiv CSi(CH_3)_3$ *(2-h)*	98
9	CH_3CH_2COCl *(1-i)*	$CH_3CH_2COC\equiv CSi(CH_3)_3$ *(2-i)*	65

EXPERIMENTAL :

CH_2Cl_2 was distilled over anhydrous calcium chloride. The yields in the Table 1 are the isolated yields and were calculated based on the amount of acyl chloride (the limiting reagent) used. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a *Bruker* AC 80 spectrometer. IR spectra were recorded on a *Perkin Elmer* model 883 and *Magna* 750 *Nicolet* spectrometer. The starting materials *1-a*, *1-b*, and *1-d* were prepared from the corresponding carboxilic acids and $SOCl_2$. Bis (trimethylsilyl) acetylene was prepared by the procedure described in the literature [10]. Other starting materials were

purchased from *Fluka,* A.G., Switzerland.

General procedure for the preparation of silylated acylalkynes

2.9 mmol acyl chloride *(1)* was placed in a flask fitted with a magnetic stirrer and ice-bath, and then 2.9 mmol bis (trimethylsilyl) acetylene in 10mL methylene chloride was added. The mixture was stirred at 0°C for 5 min. and 2.9 mmol anhydrous aluminium chloride was added. After three h. stirring, the product was poured into a mixture of HCl/ice. After extraction of the organic materials with methylene chloride (20mL), washing the methylene chloride solution with 5% sodium bicarbonate solution (20mL, two times), and with water, the organic layer was dried over anhydrous $CaCl_2$, the pure product was collected as a liquid. The new compounds displayed satisfactory analyses. The spectral data of these compounds are given below.

(2a): IR (film, cm^{-1}), 2154.4, 1628.1, 1270.2, 863.2.

^{1}H-NMR ($CDCl_3$, δ), 0.04(s, 9H), 6.79-6.99(m, 2H), 7.35-7.73(m, 2H).

^{13}C-NMR($CDCl_3$, δ), $-0.83(CH_3)$, 98.88(C), 100.41(C), 128.26(CH), 135.33(CH), 135.38(CH), 144.54(C), 169.18(C).

(2b): IR(film, cm^{-1}), 2158.9, 1638.3, 1253.8, 850.0.

^{1}H-NMR($CDCl_3$,δ), 0.05(s, 9H), 6.39(m, 1H), 7.05-7.47(m, 2H).

^{13}C-NMR($CDCl_3$, δ), $0.90(CH_3)$, 99.08(C), 100.14(C), 112.51(CH), 121.38(CH), 148.80(CH), 152.99(C), 164.07(C).

(2c): IR(film, cm^{-1}), 2158.8, 1631.8, 1253.4, 848.2.

^{1}H-NMR($CDCl_3$, δ), 0.30(s, 9H), 7.44-7.93(m, 7H).

^{13}C-NMR($CDCl_3$, δ), $0.71(CH_3)$, 91.39(C), 98.31(C), 128.22(CH), 128.62(CH), 128.99(CH), 131.09(CH), 134.04(C), 148.68(CH), 177.84(C).

(2d): IR(film, cm^{-1}), 3233.4, 2153.6, 1693.1, 1251.3, 848.2.

^{1}H-NMR($CDCl_3$, δ), 0.08(s, 9H), 7.42(m, 5H).

^{13}C-NMR($CDCl_3$, δ), $-1.04(CH_3)$, 101.41(C), 111.94(C), 117.71(CH), 119.50(CH), 126.54(CH), 129.39(C), 130.84(CH), 162.08(C), 175.19(C).

(2e): IR(film, cm^{-1}), 2153.5, 1640.7, 1256.6, 845.4.

^{1}H-NMR($CDCl_3$, δ), 0.24(s, 9H), 3.81(s, 3H), 6.88(d, J=8.8Hz, 2H), 8.04(d, J=8.8Hz, 2H).

^{13}C-NMR($CDCl_3$, δ), $-0.72(CH_3)$, $55.46(CH_3)$, 99.39(C), 113.78(CH), 114.19(C), 131.94(CH), 133.69(C), 164.47(C), 176.19(C).

(2f): IR(film, cm^{-1}), 2151.4, 1678.7, 1253.8, 848.3.

^{1}H-NMR($CDCl_3$, δ), 0.00(s, 9H), 1.73- 2.01(m, 2H), 2.37-2.72(m, 2H), 3.22-3.55(m, 2H).

^{13}C-NMR($CDCl_3$, δ), $-0.91(CH_3)$, $26.42(CH_2)$, $42.07(CH_2)$, $43.73(CH_2)$, 98.34(C), 101.68(C), 177.77(C).

(2g): IR(film, cm^{-1}), 2157.7, 1680.4, 1254.8, 849.1.

^{1}H-NMR($CDCl_3$, δ), 0.20(s, 9H), 1.1(t, J=7.3Hz, 3H), 1.9-2.2(m, 2H), 4.23(t, J=7.13, 1H).

^{13}C-NMR($CDCl_3$, δ), $-0.97(CH_3)$, $11.64(CH_3)$, $27.12(CH_2)$, 56.05(CH), 99.17(C), 101.91(C), 180.69(C).

(2h): IR(film, cm^{-1}), 2151.7, 1674.6, 1257.2, 860.8.

^{1}H-NMR($CDCl_3$, δ), 0.00(s, 9H), 0.83(s, 9H), 2.25(s, 2H).

^{13}C-NMR($CDCl_3$, δ), $-0.97(CH_3)$, $29.56(CH_3)$, 31.42(C), 57.85(CH_2), 96.83(C), 103.70(C).

(2i): IR(film, cm^{-1}), 2153.1, 1687.4, 1258.3, 851.0.

^{1}H-NMR($CDCl_3$, δ), 0.00(s, 9H), 0.90(t, J= 7.3Hz, 3H), 2.34(q, J=7.3Hz, 2H).

^{13}C-NMR($CDCl_3$, δ), $0.89(CH_3)$, $7.80(CH_3)$, $38.47(CH_2)$, 97.45(C), 101.80(C), 188.05(C).

CONCLUSIONS :

Since the silylated acetylene compounds are being used for various purposes and the fact that trimethylsilyl can be used as a protecting group, this method allows the preparation of functional silylated acylalkynes in good yields as a way for further transformations in organic synthesis.

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