Chinese Chemical Letters Vol. 10, No. 1, pp. 11–12, 1999

Acyldesilylation of 5-Trimethylsilyl-2-furancarboxaldehyde

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Abstract: Acyldesilylation of 5-trimethylsilyl-2-furancarboxaldehyde with acyl chlorides was investigated and the unexpected 5-acyl-2-dichloromethylfuran were obtained as main products. The expected 5-acyl-2-furancarboxaldehydes were also found after hydrolyzing of the corresponding dichloro-compounds.

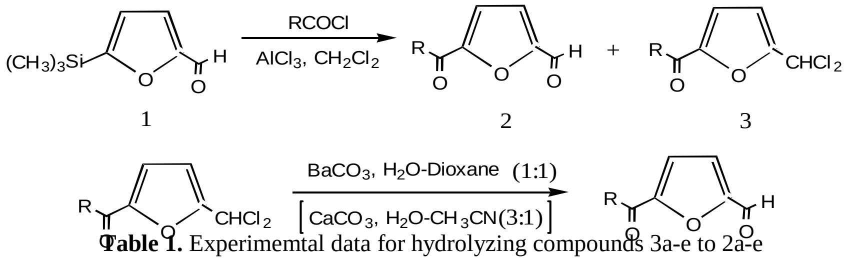
Keywords: 2-Acyl-5-dichloromethylfuran, 5-Acyl-2-furancarboxaldehyde, 5-Trimethylsilyl-2-furancarboxaldehyde, Acyldesilylation.

5-Acyl-2-furancarboxaldehydes **2** are important intermediates[1] for synthesizing naturally occurring furanoid fatty acids which have antioxidant effects and antineoplastic activities in biological systems[2]. Nakayama *et al*[3] reported successful halodesilylation of ethyl 5-trimethylsilyl-2-furoate. In the present paper, the authors wish to report acyldesilylation of 5-trimethylsilyl-2-furan carboxaldehyde **1** with several acyl chlorides was reported.

When compounds **1** reacted with acetyl chloride in the presence of aluminum chloride in dichloromethane, an unexpected compound **3a** was obtained as the main product (78%), while the expected compound **2a** was obtained only as a minor product (20%) after chromatography. Acyldesilylation of **1** with various other acyl chlorides (propionyl chloride, pentanoyl chloride, benzoyl chloride and 3, 3-dimethylacryloyl chloride) were also examined to afford corresponding products **2b-e** and **3b-e**. Hydrolysis of **3a-e** as shown in **Table 1** gave rise to the desired **2a-e** in moderate yields (**Scheme 1**).

A general procedure for acyldesilylation **1** with acetyl chloride: To a suspension of anhydrous aluminum chloride (20.0g, 0.25mole) in anhydrous dichloromethane (40ml) was added dropwise a solution of **1** (8.4g, 0.05mole) in anhydrous dichloromethane (20ml) at 0-5℃ under argon, and the mixture was allowed to stir for 30min at the same temperature. To the resulting mixture, a solution of acetyl chloride (19.6g, 0.25mole) in anhydrous dichloromethane (20ml) was added dropwise at 2-5℃. After stirring for 1 h at room temperature and refluxing 4 h, the mixture was cautiously poured over ice-water and extracted with dichloromethane. The extract was washed with water, saturated $NaHCO_3$ solution and brine, dried into $MgSO_4$ and concentrated *in vacuo.* The residue was chromatographed on silica gel (hexane/EtoAc, 20:1) to give analytically pure products **2a** (20%, mp 94-95℃[4]) and **3a** (78%, mp 38-39℃).

Sheme 1



R=CH_3, CH_3CH_2, $CH_3(CH_2)_3$, $(CH_3)_2C=CH_2$, C_6H_5

Table 1. Experimemtal data for hydrolyzing compounds 3a-e to 2a-e

Compd.	R	Reaction Condition	Temp (℃)	Time (h)	Yield (%)
2a	CH_3	H_2O-acetonitrile (3:1), $CaCO_3$	50	3	70
2b	CH_3CH_2	H_2O-acetonitrile (3:1), $CaCO_3$	50	3	71
2c	$CH_3(CH_2)_3$	H_2O-acetonitrile (3:1), $CaCO_3$	50	3	70
2d	$(CH_3)_2C=CH_2$	H_2O-dioxane (1:1), $BaCO_3$	60	0.5	90
2e	C_6H_5	H_2O-dioxane (1:1), $BaCO_3$	60	5	85

Belen'kii *et al*[4] reported direct acetylation of furfural at 5-position with acetyl chloride in the presence of aluminum chloride in chloroform to give **2a** in 45% yield. However, they did not find any dichloro-compound, **3a** of when we stirred the mixture of **2a** under the same conditions **3a** was detected by TLC. It is possible that compound **2a** was the product fo hydrolyzation of **3a.**

The mass spectrum of **3a** shows the molecular ion m/z 196/194/192 (relative intensity 1.4:7.8:11.8) indicating the presence of two chlorine atoms, and ^{1}H-NMR spectrum of **3a** indicates that there is no aldehyde group but the signal of the proton of dichloromethyl group (1H, s, δ =6.66) is observed. From the above spectral data combined with the IR spectrum and elemental analysis **3a** is assigned the structure of 5-acetyl-2-dichloromethylfuran, to which we have paid great attention for further application.

References

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Received 9 July 1998