A NOVEL TRIMETHYLSILYL GROUP MIGRATION: FORMATION OF ETHYL 5-CHLORO-4-TRIMETHYLSILYL-2-FUROATE WITH SULFURYL CHLORIDE IN DICHLOROMETHANE[1]

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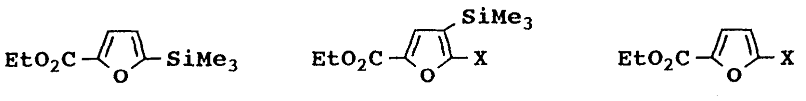
The reaction of ethyl 5-trimethylsilyl-2-furoate (1) with sulfuryl chloride in dichloromethane afforded an unexpected product, ethyl 5-chloro-4-trimethylsilyl-2-furoate (2a), through a novel trimethylsilyl group migration.

KEYWORDS ethyl 5-trimethylsilyl-2-furoate; ethyl 5-chloro-4-trimethylsilyl-2-furoate; sulfuryl chloride; trimethylsilyl migration; halodesilylation; chlorodesilylation

In the previous paper,[2] the authors reported that the halodesilylation of ethyl 5-trimethylsilyl-2-furoate (1) with various halogenating reagents in acetonitrile afforded the expected ethyl 5-halo-2-furoates (3a-c) in high yields, while the reactions of 1 with sulfuryl chloride and bromine in carbon tetrachloride gave ethyl 5-chloro-2-furoate (3a) and ethyl 5-bromo-2-furoates (3b) together with unidentified compounds (2a) and (2b), respectively, in small amounts. The authors reacted 1 with sulfuryl chloride in dichloromethane in order to improve the yield of 2a and determine the structure of 2a, and it was proved that the structure of 2a was ethyl 5-chloro-4-trimethylsilyl-2-furoate which underwent 1,2 C-C trimethylsilyl group migration on furan ring. Regarding silyl group migration of C-trialkylsilylated aromatic compounds, Seyferth[3] and Vollhardt[4] have reported that the treatments of 1,2-bis(trimethylsilyl)benzene with trifluoroacetic acid and of 4,5-bis(trimethylsilyl)benzocyclobutene with bromine afforded 1,3-bis(trimethylsilyl)benzene and 4-bromo-3,5-bis(trimethylsilyl)benzocyclobutene, respectively. More recently, Keay[5] has reported that trialkylsilylated furans undergo C-O or O-C silyl group migration in the presence of base. However, to our knowledge, there is no information on the C-C trialkylsilyl group migration on furan ring. Then, the authors wish to report here a novel trimethylsilyl group migration on furan ring. In the first place, 1 was allowed to react with sulfuryl chloride in dichloromethane at room temperature for one and a half hours to give a mixture of 2a and 3a in a ratio of ca. 7:3. A similar reaction also gave a mixture of 2a and 3a in a ratio of ca. 7:3 in either chloroform or 1,2-dichloroethane. 2a was isolated as colorless liquid (bp 142-144°C / 13mmHg) in 65% yield from the mixture by fractional distillation.[6] The IR spectrum of 2a showed the ester group ($\nu_{c=o}$) at 1730 cm^{-1} and the trimethylsilyl group (ν_{si-c}) at 850 cm^{-1}. The ^{1}H-NMR spectrum of 2a showed the trimethylsilyl group at δ 0.9 (s, 9H), ethyl group at δ 1.35 (t, 3H, J=7Hz) and δ 4.2 (q, 2H, J=7Hz), and furan ring proton at δ 6.89 (s, 1H). The mass spectrum of 2a showed the molecular ion m/z 248 and 246, indicating the presence of one chlorine atom, and the base peak m/z 233 and 231, indicating loss of one methyl group from the



1

2
a: X=Cl
b: X=Br

3
a: X=Cl
b: X=Br
c: X=I

Chart 1

Table I. Halogenation of 1 with Various Halogenating Reagents

Entry	Halogenating reagent	Solvent	Reaction conditions		Reaction products
			Temp.(°C)	Time (h)	[(%) [a)]] [b)]
1	SO_2Cl_2	CH_2Cl_2	Room temp.	/ 1.5	2a (69.5) [55][b)], 3a (30.5)
2	SO_2Cl_2	CH_2Cl_2	Reflux	/ 0.3	2a (76) [65][b)], 3a (24)
3	SO_2Cl_2	$ClCH_2CH_2Cl$	Reflux	/ 0.5	2a (75.2), 3a (24.8)
4	SO_2Cl_2	$CHCl_3$	Reflux	/ 0.5	2a (72), 3a (28)
5	Br_2	CH_2Cl_2	Reflux	/ 1.0	2b, (14.7), 3b (85.3) [60][b)]
6	ICl	CH_2Cl_2	Room temp.	/ 1.0	3a (15), 3c (85) [52][b)]

a) Relative yields were shown in parenthesis by means of GLC. b) Square brakets were the isolated yields of 2a, 3a and 3c, respectively.

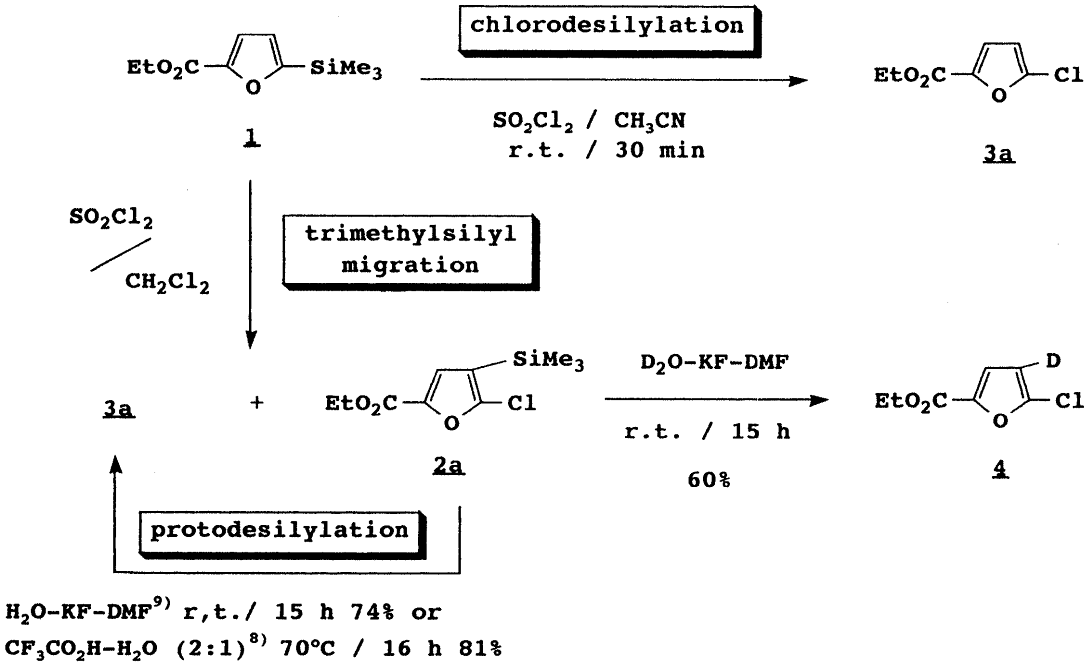


Chart 2

molecular ion. Based on the above spectral data and the elemental analysis, the structure of 2a could be assumed to be ethyl 4-chloro-5-trimethylsilyl-2-furoate, which was chlorinated at the 4-position of 1. To confirm the structure by chemical conversion, 2a was allowed to react with CF_3COOH / H_2O (2:1) [70°C / 16 h] or N,N-dimethylformamide (DMF) / potassium fluoride (KF) / H_2O [room temp. / 15 h] to give ethyl 5-chloro-2-furoate (3a).[7)] From the above results, it was proved that the chloro group of 2a was situated in the 5-position of the furan ring. Further, in order to confirm the position of the trimethylsilyl group of 2a, 2a was treated with potassium fluoruide (KF) in N,N-dimethylformamide (DMF) containing deuterium oxide to produce ethyl 5-chloro-4-deuterio-2-furoate (4) (by ^{1}H-NMR). It was confirmed by ^{1}H-NMR that the deuterium had been added at the 4-position on the furan ring of 4; of the two furan ring protons in the ^{1}H-NMR spectrum of 3a (δ 7.03, d, J=3 Hz (3-H) and δ 6.26, d, J=3 Hz (4-H)), the upfield signal had disappeared in the ^{1}H-NMR spectrum of 4. Therefore, the structure of 2a was determined to be ethyl 5-chloro-4-trimethylsilyl-2-furoate, although the detailed mechanism for the formation of 2a by reaction of 1 with sulfuryl chloride in dichloromethane is not clear, a possible mechanism for the formation of 2a is proposed in Chart 3. It has been reported that sulfuryl chloride formed chloronium ion in the presence of Lewis acid.[10)] Thus, it can be presumed that the silicon atom of the trimethylsilyl group of 1, which is assumed to behave like a Lewis acids,[11)] is acted on by sulfuryl chloride to

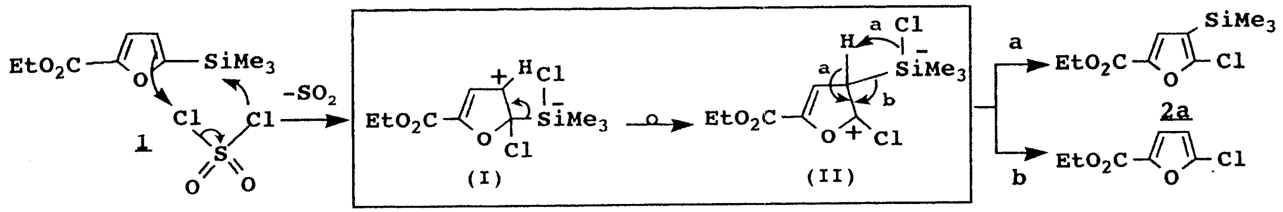


Chart 3

form an intermediate [I] bearing the pentacoordinated silyl group. Then [I] is converted into an intermediate [II], which is formed by migration of the pentacoordinated silyl group from 5-position to 4-position of [I], followed by [II] giving 2a (route a) and 3a (route b) through loss of hydrogen chloride and trimethylsilyl chloride, respectively (Chart 3). Thus, it has become apparent that the reaction of 1 with sulfuryl chloride in dichloromethane provided ethyl 5-chloro-4-trimethylsilyl-2-furoate (2a), via a novel trimethylsilyl group 1,2-migration on the furan ring with the chlorination at the 5-position of 1. The reaction of 1 with bromine in dichloromethane provided a mixture of 2b and the migrated compound 3b in a ratio of ca. 3:7 as well as chlorination of 1. On the other hand, the treatment of 1 with iodine monochloride in dichloromethane only furnished a 1:7 mixture of 3a and 3c. In conclusion, the authors show that the reaction of 1 with sulfuryl chloride in dichloromethane afforded ethyl 5-chloro-4-trimethylsilyl-2-furoate (2a) which is interesting as an intermediate of the β-substituted furans synthesis.12) This provides the first example of the trimethylsilyl group 1,2 migration on the furan ring. Further work on preparation of trisubstituted furans using 2a is in progress.

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