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A CONVENIENT METHOD FOR THE PREPARATION OF 3-TRIMETHYLSILYL-2,5-DIHYDROFURANS AND THEIR CONVERSION TO FURANS

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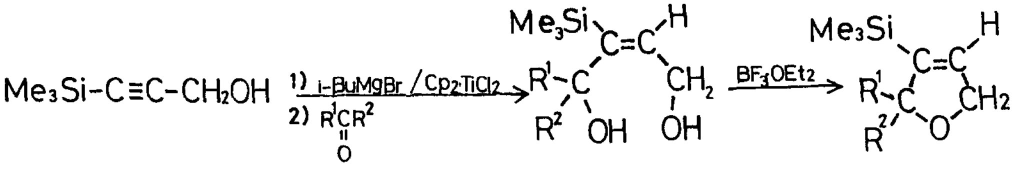
Summary: Hydromagnesiation of 3-trimethylsilyl-2-propyn-1-ol (1) followed by reaction with aldehydes or ketones affords (E)-3-trimethylsilyl-2-alken-1,4-diols (2), which can be readily dehydrated to 3-trimethylsilyl-2,5-dihydrofurans (3) by treatment with BF_3OEt_2. The compounds 3 are converted to furans (5) by epoxidation and subsequent treatment with H_2SO_4.

We report here a facile method for the preparation of 3-trimethylsilyl-2,5-dihydrofurans (3) from 3-trimethylsilyl-2-propyn-1-ol (1) via hydromagnesiation, and also their conversion to furans (5).

Hydromagnesiation of 1 followed by treatment with aldehydes or ketones afforded (E)-3-trimethylsilyl-2-alken-1,4-diols (2) in excellent yields.[1,2] When the compounds 2 thus prepared were treated with BF_3OEt_2 in CH_2Cl_2, dehydration to 3 occurred readily (Eq 1 and Table 1).[3] This observation is

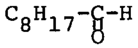
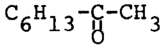
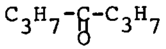
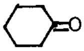
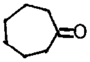


(1)

1 2 3

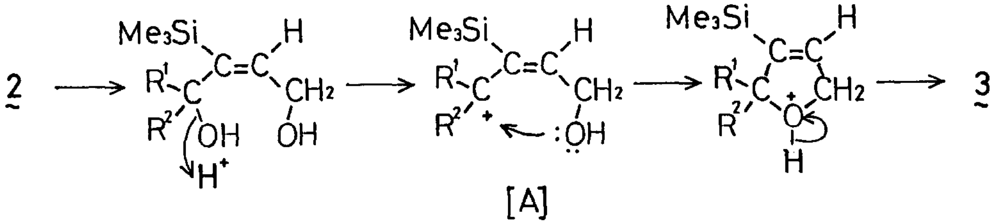
particularly noteworthy, because numerous reports show that substituted 2-butene-1,4-diols are dehydrated not to 2,5-dihydrofurans but to unsaturated carbonyl compounds in the presence of acids via isomerization of the double bond and dehydration.[4,5] In fact, treatment of (Z)-2-dodecene-1,4-diol, which was prepared by protodesilylation[6] of the corresponding **2**, with BF_3OEt_2 did not produce any conceivable amount of the 2,5-dihydrofuran.

Table 1. PREPARATION OF **2** BY THE REACTION OF **1** WITH CARBONYL COMPOUNDS AND THEIR CONVERSION TO **3**

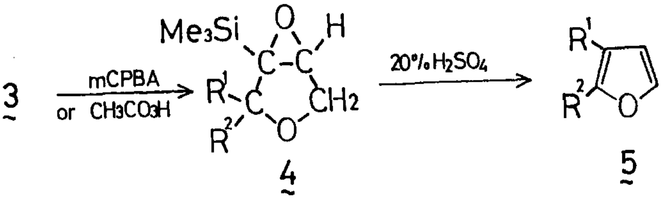
Entry	Carbonyl compound	Product **2** Yield (%)[a]	Product **3** Yield (%)[b]
1	 $C_8H_{17}-\underset{O}{\underset{\|}{C}}-H$	84	84
2	 $C_6H_{13}-\underset{O}{\underset{\|}{C}}-CH_3$	83	90
3	 $C_3H_7-\underset{O}{\underset{\|}{C}}-C_3H_7$	80	88
4		88	90
5		85	92

[a]Isolated yield based on **1**. [b]Isolated yield based on **2**.

The mechanism shown below may account for the present dehydration reactions. Presumably, $SiMe_3$ group either prevents the isomerization of the double bond or stabilizes the intermediate A.

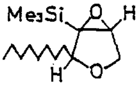
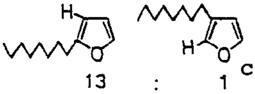
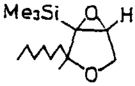
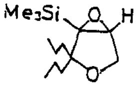
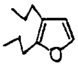
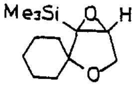
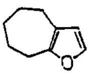
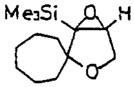
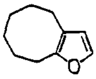


Epoxidation of **3** with mCPBA or CH_3COOOH, and treatment of the resulting epoxides **4** with 20% H_2SO_4 in methanol at 50°C furnished the corresponding furans **5**[7] (Eq 2 and Table 2).



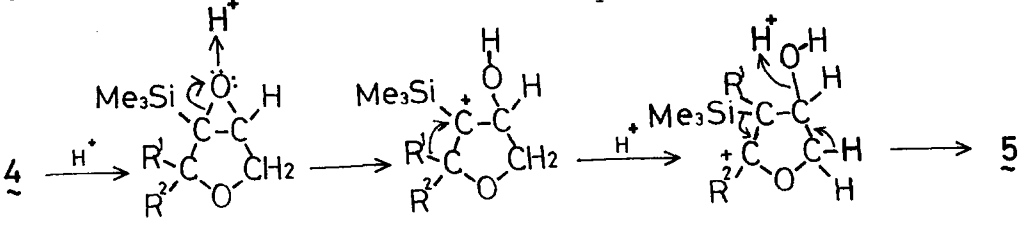
(2)

Table 2. CONVERSION OF 4 TO 5

Entry	Compound 4[a]	Product 5 Distribution	Total yield[b] (%)
1		 13 : 1[c]	49
2		 3 : 1[c]	80
3			95
4			92
5			95

[a] Prepared by epoxidation of 3 with mCPBA or CH_3COOOH in 82-90% yields. [b] Isolated yield based on 4. [c] The ratio was determined by ^1H nmr (200 MHz).

Possible mechanism for the production of 5 from 4 is as follows. Addition of proton on the epoxide oxygen of 4 followed by epoxide ring opening yields the cation B.[8] Rearrangement of R^1 (or R^2) affords more stable cation C, which changed to 5 via Peterson olefination and dehydration.



[B]

[C]

In cases of compounds **4** where the substituent R^1 and R^2 is same, the reaction affords only one product in excellent yields, thus making this reaction useful for preparation of furans such as shown in entries 3, 4 and 5. It is also noteworthy that hydrogen migrates more readily than an alkyl group (see entry 1).

References and Notes

1) F. Sato, H. Watanabe, Y. Tanaka, and M. Sato, J. Chem. Soc., Chem. Commun., 1126(1982).
2) Typical procedure for preparation of **2** is as follows: To a solution of isobutylmagnesium bromide in ether (36 ml of 1.25 M solution, 45 mmol) was added $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (0.25 g, 1mmol) at 0°C, and the mixture was stirred for 5 min at that temperature under argon. To this solution was added **1** (3 ml, 20 mmol) dropwise, and the mixture was stirred at 25°C for 6 h. An aldehyde or ketone (21 mmol) was then added to this solution at 0°C and the mixture was stirred for 30 min at room temperature. The usual workup and column chromatography on silica gel gave **2**.
3) Dehydration of **2** to **3** was carried out as follows: The compound **2** (2.7 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a solution of BF_3OEt_2 (8 mmol) in CH_2Cl_2 (10 ml) with stirring under argon at room temperature. After 30 min, aqueous $NaHCO_3$ was added and the product was extracted with CH_2Cl_2 repeatedly. The combined CH_2Cl_2 layers was dried and concentrated in vacuo to give a pale yellow oil, which was subjected to column chromatography on silica gel to afford **3**.
4) M. Bartok and A. Molnar, in "The Chemistry of Ethers, Crown ethers, Hydroxyl groups and Their sulphur analogues" ed. S. Patai, Interscience, New York, 1980, Suppl. E, part 2, chapter 16, pp 751-752.
5) In the case of 2-butene-1,4-diol, formation of 2,5-dihydrofuran was found; N.O. Brace, J. Amer. Chem. Soc., 77, 4157 (1955) and references cited therein.
6) F. Sato, Y. Tanaka, and M. Sato, J. Chem. Soc., Chem. Commun., 165(1983).
7) Conversion of **4** to **5** was carried out as follows: To a solution of **4** (0.8 mmol) in MeOH (3 ml) was added 20% H_2SO_4 (3 ml) dropwise with stirring at 50°C. The reaction mixture was stirred at 50°C for 1-3 h, then brought to room temperature, poured into water and the product was repeatedly extracted with ether. The combined ethereal layers was washed with aqueous $NaHCO_3$ and brine, dried, and concentrated in vacuo to give an oil, which was subjected to column chromatography to afford **5**.
8) F. Sato, Y. Tanaka, and H. Kanbara, J. Chem. Soc., Chem. Commun., 1024(1983).

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