Synthesis of *vic*-Bromotrimethylsiloxyalkenes (α-Bromoenol Trimethylsilyl Ethers)

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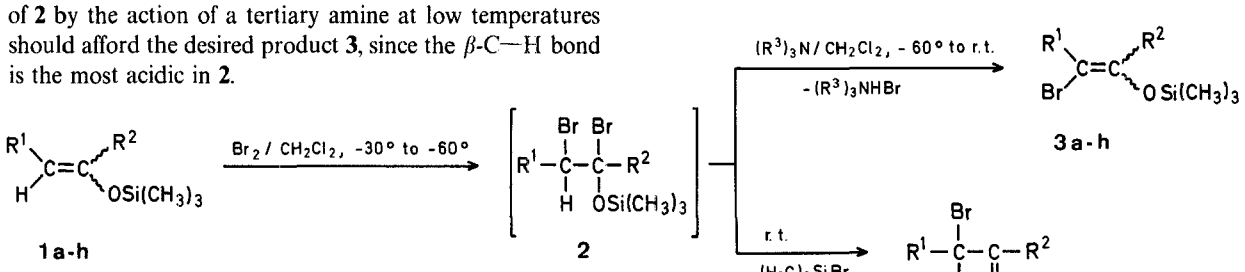
In connection with other studies[1], we needed trimethylsilyl analogs of β-bromovinyl ethyl ether, the title compounds (**3** in Scheme **A**). Only three such compounds have previously been prepared by House et al.[2] using α-chloroalkyl ketones as the starting material, but the preparation and manipulation of the latter compounds themselves are rather hard. Recent reports[3,4] described that α-bromo carbonyl compounds can be prepared regioselectively from the corresponding silyl enol ethers via bromination at low temperatures followed by spontaneous β-elimination of volatile bromotrimethylsilane (see Scheme **A**). The intermediate formation of 1,2-dibromoalkyl trimethylsilyl ether **2** in this reaction strongly suggested the possibility that dehydrobromination of **2** by the action of a tertiary amine at low temperatures should afford the desired product **3**, since the β-C—H bond is the most acidic in **2**.



Scheme **A**

The reaction indeed proceeded smoothly and **3** was obtained in satisfactory yield as shown in the Table. As expected, the dehydrobromination occurred in the direction of producing α-bromoenol silyl ethers **3**, and no β-siloxyallyl bromide derivatives were formed in the cases of **3d**, **3g**, and **3h**. Interestingly, the present dehydrobromination proceeds in a highly stereoselective fashion. Thus, only a (*Z*)-isomer of **3a** was obtained and the isomer ratios in other products (**3b–f**) are 90:10 to 95:5 (by G.L.C.), probably with the (*Z*)-isomers predominating. Triethylamine or triethylenediamine was used as a tertiary amine in all cases except for **3f**, for which was used 1,5-diazabicyclo[5,4,0]undecene-5 (DBU), because the use of other amines resulted in the competitive β-elimination of trimethylbromosilane to give the α-bromo ketone.

The present procedure affords a simple route to α-bromoenol silyl ethers, not requiring lachrymatory α-halo ketones as a starting material.

The starting silyl enol ethers were prepared as described by House et al.[5], except for **1a** which was prepared according to the method described in a patent claim[6].

Preparation of α-Bromoenol Trimethylsilyl Ethers (3); General Procedure:

Bromine (1 equiv) in dichloromethane (20 ml) is added to a stirred solution of a silyl enol ether (100 mmol) in dichloromethane (20 ml) at a given temperature. The addition is controlled at such a rate that the solution always remains colorless to pale orange. Subsequently, a tertiary amine (1.5 equiv) is added rapidly to the solution and the mixture is allowed to stand at room temperature. After evaporation of the solvent under reduced (aspirator) pressure, the resulting slurry is hydrolyzed at 0° by addition of water. The aqueous solution is extracted quickly with petroleum ether. The extract is dried over sodium sulfate, and then distilled in vacuo to afford the product as a colorless to pale yellow liquid.

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Table. Preparation of vic-Bromotrimethylsiloxyalkenes (**3**)

Product No.	R^1	R^2	Reaction temperature[a]	Yield [%]	b.p./torr	^{1}H-N.M.R. (CCl_4, 60 MHz) δ [ppm]	Molecular formula[c]
3a	H	H	−30°	50	48–49°/15	0.24 (s, 9H), 5.23 (d, 1H), 6.66 (d, 1H)	$C_5H_{11}BrOSi$ (195.1)
3b	CH_3	H	−60°	71	71–75°/22	0.22 (s, 9H), 2.12 (d, 3H),[b] 6.40 (broad, 1H)	$C_6H_{13}BrOSi$ (209.1)
3c	C_2H_5	H	−60°	78	52–53°/6	0.20 (s, 9H), 1.10 (t, 3H, J=8 Hz), 2.31 (q, 2H, J=8 Hz), 6.39 (broad, 1H)	$C_7H_{15}BrOSi$ (223.2)
3d	H	CH_3	−60°	48	58–59°/18	0.24 (s, 9H), 1.90 (broad, 3H),[b] 5.20 (broad, 1H)	$C_6H_{13}BrOSi$ (209.1)
3e	H	C_6H_5	−30°	62	100–104°/4	0.20 (s, 9H), 5.87 (s, 1H), 7.33 (m, 5H)	$C_{11}H_{15}BrOSi$ (271.2)
3f	CH_3	C_6H_5	−30°	47	92–95°/2	0.03 (s, 9H), 2.27 and 2.35 (two s, total 3H),[b] 7.31 (m, 6H)	$C_{12}H_{17}BrOSi$ (285.3)
3g	—$(CH_2)_3$—		−60°	30	97–99°/22	0.23 (s, 9H), 1.7–2.7 (m, 6H)	$C_8H_{15}BrOSi$ (235.2)
3h	—$(CH_2)_4$—		−60°	47	93–100°/5	0.17 (s, 9H), 1.5–1.8 (m, 4H), 2.0–2.3 (m, 4H)	$C_9H_{17}BrOSi$ (249.2)

[a] The temperature at which bromine and the amine were added.

[b] Both configurations are present in the product.

[c] All products gave satisfactory microanalyses (C ±0.54%, H ±0.29%).

[1] K. Tamao, M. Zembayashi, M. Kumada, *Chem. Lett.* **1976** 1239.
[2] H. O. House, W. F. Fischer, Jr., M. Gall, T. E. McLaughlin N. P. Peet, *J. Org. Chem.* **36**, 3429 (1971).
[3] R. H. Reuss, A. Hassner, *J. Org. Chem.* **39**, 1785 (1974).
[4] L. Blanco, P. Amice, J. M. Conia, *Synthesis* **1976**, 194.
[5] H. O. House, L. J. Czuba, M. Gall, H. D. Olmstead, *J. Org Chem.* **34**, 2324 (1969).
[6] *Belgium Patent* 670, 769, Rhone-Poulenc S. A., (1966); *C. A* **65**, 5487 (1966).