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# O-SILYLATED KETENE ACETAL CHEMISTRY[1]; DIVINYLOXYSILANE DERIVATIVES AS NOVEL AND USEFUL BIFUNCTIONAL PROTECTING AGENTS FOR H-ACIDIC MATERIALS

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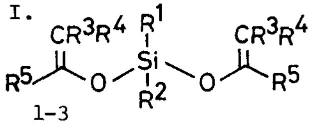
Summary: Novel reagents, bis(1-methoxy-2-methyl-1-propenyloxy)silanes (2a-d) have been shown to be very useful bifunctional protecting agents for various types of H-acidic materials, such as diols, dithiols, diacids and their combined materials. The reaction proceeds rapidly under mild conditions to give the corresponding silylene derivatives in almost quantitative yields.

Silylene derivatives have become very useful[2,3] as bifunctional protecting agents for H-acidic materials, such as diols, dithiols, diacids, and their combined materials. Generally, dichlorosilanes[2] and dimethoxysilanes[3] are well used for the conversion of these compounds into the corresponding siliconides, which are analogous to isopropylidene derivatives. These methods, however, have some disadvantages: i) Strong base, acid, or catalyst is required in the reactions, ii) Forceful reaction conditions (high temperature and a long period) are involved, iii) A large amount of side-product such as inorganic salt, amine-salt, or acid is produced with the moisture sensitive siliconides, and iv) The yields of the products are not always high. In our recent communication,[1c,1d] we have reported on the extremely useful silylating agents, ketene methyl trialkylsilyl acetals, which provide a ready silylation of H-acidic materials in the absence of base, and allow easy isolation of pure products without aqueous work-up in almost quantitative yields. As an extention of that work, we have explored a new approach to perform bifunctional protection of H-acidic materials using novel reagents, divinyloxysilane derivatives 1-3. Especially, the method using bis(1-methoxy-2-methyl-1-propenyloxy)silanes (2a-d) was found to be quite useful for bifunctional protection of H-acidic materials 4-15, leading to the corresponding siliconides 16-30.

Preparation of Divinyloxysilane Derivatives 1-3 Bis(1-methoxy-1-vinyloxy)silanes (1 and 2), which are thought to be ketene silyl acetal derivatives, were obtained by a similar method to that described for the preparation of ketene methyl trialkylsilyl acetals.[1c,1d] Thus, 2 equivalent amounts of methyl lithiopropionate or methyl lithioisobutyrate generated from methyl propionate or methyl isobutyrate and lithium diisopropylamide was allowed to react with 1 equivalent of dichlorosilanes at low temperature in THF to give the corresponding bis(1-methoxy-1-vinyloxy)silanes, 1[4] and 2a-d in reasonable yields. The related reagents, diisopropenyloxysilanes 3a,b were prepared by refluxing a mixture of acetone and the corresponding dichlorosilane in the presence of anhydrous manganese(II) chloride and triethylamine.[5] The structures of 1-3[6] were proved by microanalyses and IR and NMR spectral data. The results are summarized in Table I.



1-3

Table I. Preparation of Divinyloxysilanes 1-3

| Compd$^a$ | R$^1$ | R$^2$ | R$^3$ | R$^4$ | R$^5$ | Yield$^b$ % | Bp (mmHg)$^c$ °C | IR(CHCl$_3$) cm$^{-1}$ | $^1$H NMR (CDCl$_3$)$^d$: δ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Me | Me | Me | H | MeO | 54 | 96-97(7) | 1680,1260<br>1150,1015 | 3.86(2H,q,J=7,2×CH=),3.56(6H,s,2×MeO),1.52(6H,d,J=7,2×=CMe),0.32(6H,s,Me$_2$Si) |
| 2a | Me | Me | Me | Me | MeO | 82 | 89-90(6.5) | 1705,1260<br>1160,1030 | 3.44(6H,s,2×MeO),1.54(12H,br s,4×MeC=),0.28(6H,s,Me$_2$Si) |
| 2b | Me | Ph | Me | Me | MeO | 27 | 119-122 (2.5) | 1710,1260<br>1150,1025 | 7.25-7.8(5H,m,PhSi),3.45(6H,s,2×MeO),1.56(12H,br s,4×MeC=),0.56(3H,s,MeSi) |
| 2c | Et | Et | Me | Me | MeO | 33 | 100-101 (4.5) | 1710,1260<br>1160,1025 | 3.54(6H,s,2×MeO),1.56(12H,br s,4×MeC=),1.3-0.5(10H,m,Et$_2$Si) |
| 2d | i-Pr | i-Pr | Me | Me | MeO | 39 | 109-110(4) | 1705,1260<br>1170,1030 | 3.58(6H,s,2×MeO),1.58(12H,br s,2×Me$_2$C),1.13(14H,m,2×i-Pr) |
| 3a | Me | Me | H | H | Me | 42 | 59-60(6) | 1640,1260<br>1145 | 4.21(2H,br s,2×CH=),4.11(2H,br s,2×CH=),1.80(6H,s,2×MeC=),0.29(6H,s,Me$_2$Si) |
| 3b | Me | Ph | H | H | Me | 39 | 77-78(6) | 1640,1280<br>1260,1130<br>1050 | 7.2-7.8(5H,m,ArH),4.16(2H,br s,2×CH=),4.02(2H,br s,2×CH=),1.80(6H,s,2×MeC=),0.5(3H,s,MeSi) |

a The microanalyses for all compounds were in satisfactory agreement with the calculated values except for compound 1. b Distilled yields are given. c Uncorrected boiling points are given. d J values are given in hertz.

## Bifunctional Protection of H-Acidic Materials 4-15 with Divinyloxysilanes 1-3

The reactivity of these reagents with H-acidic materials was examined by the rate of the formation of dimethyldibenzyloxysilane (16) from 4. Although bis(1-methoxy-1-propenyloxy)dimethylsilane (1) is active enough to react with 4 at 20°C in an inert solvent without any catalyst, the reagent 1 itself contains a small amount of an inseparable side-product and it could not be removed from the siliconide (16). Bis(1-methoxy-2-methyl-1-propenyloxy)dimethylsilane (2a) was found to be the best reagent for bifunctional protection of 4 because of the ready preparation of the reagent (no C-silylated material), high reactivity, and no side-product besides the volatile methyl isobutyrate. Dimethyldiisopropenyloxysilane (3a) is not active enough to react with 4 under the same conditions as employed for the reaction of the reagents (1 and 2a).

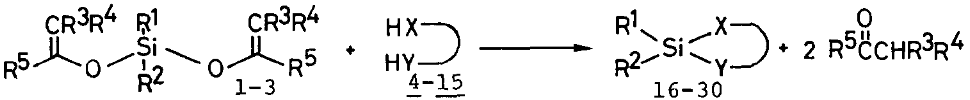
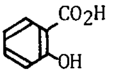
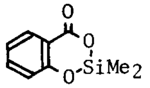
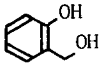
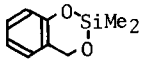
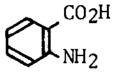
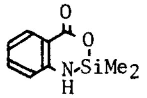
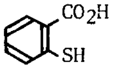
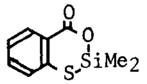
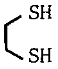
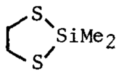
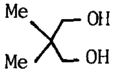
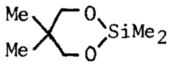
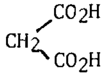
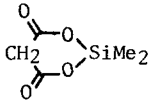
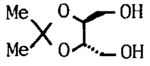
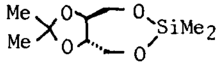
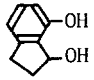
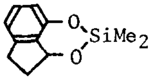


Table II. Bifunctional Protection of H-Acidic Materials

| Entry | Starting Materials | Conditions[a] | Products[b,c] | Yield[d] % |
|---|---|---|---|---|
| 1 | $PhCH_2OH$ 4 | 1/2 1, $CH_3CN$, 20°C, 0.5h[e]; 1/2 2a, $CH_3CN$, $CH_2Cl_2$ or THF, 20°C, 0.5h or 5min[f]; 1/2 3a, $CH_3CN$, 20°C, 0.5h[f] | $(PhCH_2O)_2SiMe_2$ 16 | 93-98<br>(77-85) |
| 2 | 4 | 1/2 2b, $CH_3CN$, 80°C, 5h or 20°C, 0.5h[f]; 1/2 3b, $CH_3CN$, 20°C, 2h[f] | $(PhCH_2O)_2Si{<}^{Me}_{Ph}$ 17 | 82-97<br>(82-94) |
| 3 | 4 | 1/2 2c, $CH_3CN$, 80°C, 5h or 20°C, 0.5h[f] | $(PhCH_2O)_2SiEt_2$ 18 | 90(81) |
| 4 | 4 | 1/2 2d, $CH_3CN$, 80°C, 5h or 20°C, 0.5h[f] | $(PhCH_2O)_2Si(i\text{-}Pr)_2$ 19 | 90(60) |
| 5 | PhOH 5 | 1/2 2a, $CH_2Cl_2$, 20°C, 0.5h | $(PhO)_2SiMe_2$ 20 | 98(82) |
| 6 | $PhCO_2H$ 6 | 1/2 2a, $CH_2Cl_2$, 20°C, 0.5h | $(PhCO_2)_2SiMe_2$ 21 | 96(61) |
| 7 |  7 | 1.0 2a, $CH_3CN$, 20°C, 0.5h |  22 | 98(80) |
| 8 |  8 | 1.0 2a, $CH_2Cl_2$, 20°C, 1h |  23 | 97(85) |
| 9 |  9 | 1.0 2a, THF, 20°C, 0.5h |  24 | 95[g] |
| 10 |  10 | 1.0 2a, THF, 20°C, 0.5h |  25 | 94[g] |
| 11 |  11 | 1.1 2a, $CH_3CN$, 80°C, 5h or $CH_2Cl_2$, 20°C, 5 min[f] |  26 | 90(58) |
| 12 |  12 | 1.1 2a, THF:$CH_2Cl_2$=1:1, 20°C, 0.5h[f] |  27 | 90(57) |
| 13 |  13 | 1.1 2a, THF, 20°C, 0.5h |  28 | 92[g] |
| 14 |  14 | 1.1 2a, THF, 20°C, 1h[f] |  29 | 95(64) |
| 15 |  15 | 1.1 2a, $CH_3CN$, 20°C, 1h[f] |  30 | 95[g] |

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[a] The number indicated is the reagent/starting material ratio. [b] All spectroscopic data (NMR and IR) are in good agreement with the proposed structures. [c] Uncorrected boiling points (°C/mmHg) are as follows: 16: 155-160/3; 17: 225-230/2.5 (bath); 18: 102-110/4; 19: 120-125/14; 20: 90-95/3 [lit.[7] 107/1]; 21: 160-161/1 [lit.[7] 160-161/1]; 22: 100/1 (bath) [lit.[7] 104/2, lit.[2k] 85-115/0.1]; 23: 125-130/10 (bath) [lit.[2c] 89/10]; 26: 73-78/12 [lit.[2b] 75-77/12, lit.[8] 188]; 27: 65-75/50 [lit.[2a] 24-25/5]; 29: 125-135/4 (bath). [d] Yields were based on the H-acidic materials and the purity of the products (>95%) was determined by GLC, NMR, and TLC. Distilled yields carried out on an 1-3 mmol scale of H-acidic materials are given in parentheses. [e] Less than 5% yield of an inseparable side-product was contaminated in the distilate. [f] The reaction was performed in the presence of a 0.02-0.1 equimolar amount of the corresponding dichlorosilane. [g] The siliconide was readily cleaved during the purification on silica gel or distillation.

The reaction of the bis(1-methoxy-2-methyl-1-propenyloxy)silanes 2a-d with H-acidic materials (4-15) is generally carried out by employing a slight excess of the reagent in an inert solvent such as methylene chloride or acetonitrile and usually brought to completion to give a high yield of the corresponding siliconides 16-30, respectively. Furthermore, addition of catalytic amounts (0.02-0.1 equivalent) of the corresponding dichlorosilane induced a slightly exothermal reaction leading to the ready formation of the siliconides. A wide range of 1,2-, 1,3-, and 1,4-functions reacted with the reagent 2 to give the corresponding siliconides in high yields. All products have been characterized by $^1$H NMR, IR, and GLC data. The reaction conditions, yields, and physical data are summarized in Table II. The advantages of these reagents are found in the mild reaction conditions, the high yields, the absence of base or acid, easiness of procedures, and formation of volatile isobutyrate as a single product.[9]

## REFERENCES AND NOTES

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3 M. R. Jenner and R. Khan, *J. Chem. Soc. Chem. Commun.*, 1980, 50.

4 Less than 5% yield of an inseparable side-product (probably C-silylated compound) was contaminated in the distilate of 1.

5 The preparation of dimethyldiisopropenyloxysilane (3a) was reported in the patent: T. Okamoto and K. Kunimoto, *Japan Tokkyo Koho*, 1980, 55-19201 [*C. A.*, 85, 12345f (1980)].

6 These reagents are stable enough to be allowed to stand at room temperature for a few weeks or to be stored in the refrigerator for more than several months after the reagent bottle is flushed with nitrogen or argon.

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9 Recently we have reported analogous types of useful amino-protecting reagents using enol-keto transformations: Y. Kita, J. Haruta, H. Yasuda, K. Fukunaga, Y. Shirouchi, and Y. Tamura, *J. Org. Chem.*, 47, 2697 (1982) and references cited therein.

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