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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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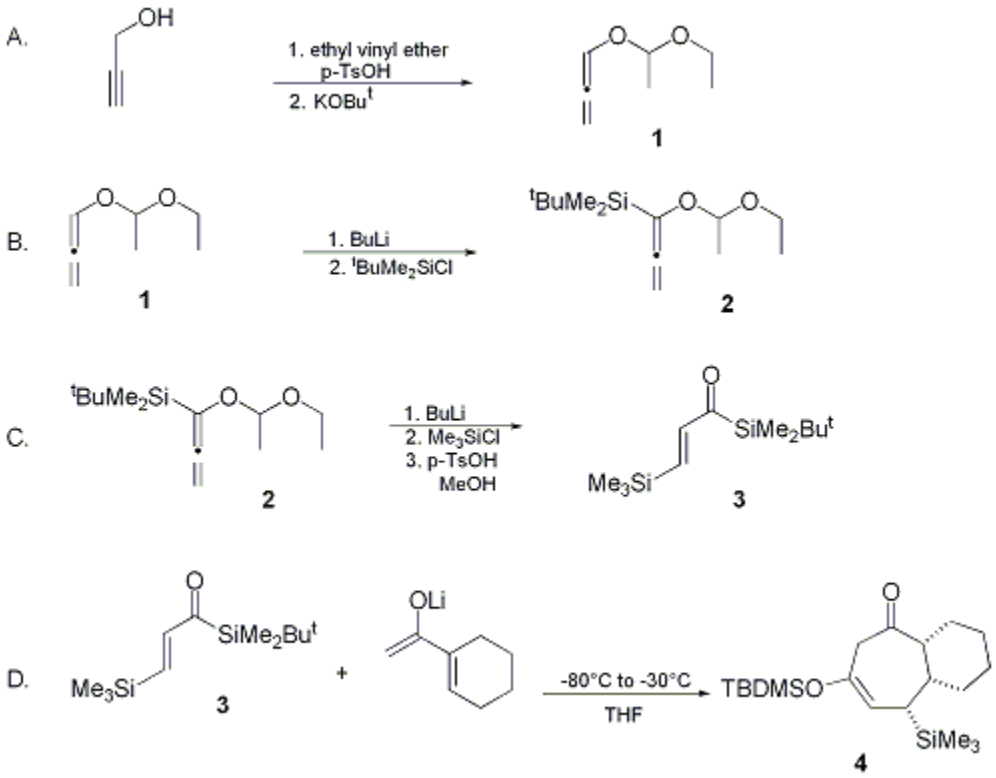
[3 + 4] ANNULATION USING A [β-(TRIMETHYLSILYL) ACRYLOYL]SILANE AND THE LITHIUM ENOLATE OF AN α,β-UNSATURATED METHYL KETONE: (1R,6S,7S)-4-(tert-BUTYLDIMETHYLSILOXY)-6-(TRIMETHYLSILYL)BICYCLO [5.4.0]UNDEC-4-EN-2-ONE



Submitted by Kei Takeda, Akemi Nakajima, Mika Takeda, and Eiichi Yoshii[1] .
Checked by Jing Zhang and Robert K. Boeckman, Jr..
Discussion Addendum *Org. Synth.* **2012**, *89*, 267

1. Procedure

Caution! Hexamethylphosphoric triamide has been identified as a carcinogen. Glove protection is required during the handling in Part B.

A. 1-(1-Ethoxyethoxy)-1,2-propadiene (**1**) (Note 1). A 300-mL, two-necked, round-bottomed flask is equipped with a magnetic stirring bar, a thermometer, and a 100-mL pressure-equalizing addition funnel fitted with a calcium chloride-filled tube. The flask is charged with 100 g (1.39 mol) of ethyl vinyl ether (Note 2) and 50 mg (0.26 mmol) of p-toluenesulfonic acid monohydrate (Note 3). The mixture is then stirred and cooled in an ice-salt bath while 56.1 g (1.00 mol) of propargyl alcohol (Note 4) is added dropwise via the addition funnel over 50 min; the rate of addition adjusted to maintain the temperature between 5°C and 10°C. After the addition is complete, the mixture is stirred at 0°C for 15 min and then quenched by adding of 3 mL of a aqueous saturated solution of potassium carbonate (K_2CO_3). The resulting mixture is dried over K_2CO_3, filtered, and excess ethyl vinyl ether is removed at reduced pressure using a rotary evaporator at temperatures below 25°C. Distillation of the residual liquid under reduced pressure affords 106 - 117 g (88 - 92%) of 3-(1-ethoxyethoxy)-1-propyne as a colorless clear oil, bp 37-41°C/11 mm (Note 5).

A 200-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, a thermometer, a glass stopper, and a reflux condenser fitted with a nitrogen inlet/outlet adapter, is placed under a nitrogen atmosphere and charged with 98.6 g (0.769 mol) of 3-(1-ethoxyethoxy)-1-propyne and 8.63 g (76.9 mmol) of potassium tert-butoxide (Note 6). The flask is immersed in a preheated oil bath at 70°C with vigorous stirring of the mixture. The internal temperature is maintained at ca. 70°C for 40 min (there is an exothermic reaction; occasional removal of the heating bath may be necessary to moderate the reaction). The reaction mixture is transferred to a 500-mL separatory funnel containing 100 mL of ice-water, and the aqueous mixture is extracted three times with 100-mL portions of diethyl ether (Et_2O). The combined organic phases are washed three times with 100-mL portions of saturated brine , dried over K_2CO_3, filtered, and concentrated under reduced pressure using a rotary evaporator at temperatures below 25°C. The residual oil is distilled through a 10-cm Vigreux column under reduced pressure to afford 69.3-74.5 g (70 -75%) of 1-(1-ethoxyethoxy)-1,2-propadiene (**1**) as a colorless clear oil, bp 42-43°C/18 mm (Note 7) and (Note 8).

B. *1-(tert-Butyldimethylsilyl)-1-(1-ethoxyethoxy)-1,2-propadiene* (**2**) (Note 9). A 2-L, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, a thermometer, a rubber septum, and a 200-mL pressure-equalizing addition funnel fitted with a nitrogen inlet/outlet adapter, is purged with nitrogen and charged with 40.0 g (0.312 mol) of 1-(1-ethoxyethoxy)-1,2-propadiene (**1**), 350 mg of 4,4'-thiobis(2-tert-butyl-m-cresol) (Note 10), and 1 L of dry Et_2O (Note 11). The solution is stirred and cooled to −80°C with a hexane-liquid nitrogen bath, and then 220 mL (0.312 mol) of a 1.42 M hexane solution of butyllithium (BuLi) (Note 12) is added dropwise via a stainless steel cannula over 20 min. After the addition is complete, the mixture is stirred at −80°C for 1 hr, and a solution of 50.8 g (0.337 mol) of tert-butyldimethylsilyl chloride (Note 13) in 180 mL of dry Et_2O is added dropwise via the addition funnel over 20 min (the funnel is washed with 5 mL of dry Et_2O into the reaction mixture). After 10 min, a solution of 60 mL of hexamethylphosphoric triamide (Note 14) in 180 mL of dry Et_2O is added via a stainless steel cannula over 10 min. After 30 min, the cooling bath is removed, and the pale yellow solution is allowed to warm to 0°C over 90 min whereupon 31 mL of triethylamine (Note 15) is added. The reaction mixture is transferred to a 3-L separatory funnel containing 1 L of aqueous saturated sodium bicarbonate ($NaHCO_3$), and the organic phase is separated. The aqueous phase is extracted three times with 300-mL portions of Et_2O, and the combined organic phases are washed successively with 500 mL of water and 500 mL of saturated brine , dried over K_2CO_3, filtered, and concentrated at reduced pressure using a rotary evaporator. The residual liquid is distilled through a 10-cm Vigreux column under reduced pressure to afford 62.8 - 65.4 g (83-86%) of 1-(tert-butyldimethylsilyl)-1-(1-ethoxyethoxy)-1,2-propadiene (**2**) as a colorless clear oil, bp 60-62°C/0.5 mm (Note 8) and (Note 16).

C. *(E)-1-(tert-Butyldimethylsilyl)-3-trimethylsilyl-2-propen-1-one* (**3**) (Note 17). A 200-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, a thermometer, a rubber septum, and a 10-mL pressure-equalizing addition funnel fitted with a nitrogen inlet/outlet adapter, is placed under a nitrogen atmosphere and charged with 10.0 g (41.2 mmol) of 1-(tert-butyldimethylsilyl)-1-(1-ethoxyethoxy)-1,2-propadiene (**2**), 100 mg of 4,4'-thiobis(2-tert-butyl-m-cresol) , and 80 mL of dry tetrahydrofuran (THF) (Note 18). The solution is stirred and cooled to −80°C with a hexane-liquid nitrogen bath, and 30 mL (44.1 mmol) of a 1.47 M hexane solution of BuLi is added dropwise via a stainless steel cannula over 30 min. The mixture is stirred at −80°C for 40 min, and 4.90 g (45.1 mmol) of trimethylsilyl chloride (Note 19) is added dropwise via the addition funnel over 10 min (the funnel is washed with 5 mL of dry THF into the reaction mixture). After 10 min, the cooling bath is removed, and the reaction mixture is allowed to warm to room temperature over 1 hr whereupon 4 mL of triethylamine is added. The reaction mixture is transferred to a 500-mL separatory funnel containing 100 mL of ice-cooled aqueous saturated $NaHCO_3$, and the organic phase is separated. The aqueous phase is extracted three times with 100-mL portions of Et_2O, and the combined organic phases are washed successively with 100 mL of water and 100 mL of saturated brine , dried over K_2CO_3, filtered, and concentrated at reduced pressure using a rotary evaporator to afford the crude 3-trimethylsilyl derivative of **2** as a colorless oil, which is used for the next reaction without further purification.

A 300-mL, one-necked, round-bottomed flask, equipped with a magnetic stirring bar, is charged with the above product, 1.58 g (8.24 mmol) of p-toluenesulfonic acid monohydrate , and 140 mL of methanol (Note 20). The mixture is stirred at room temperature for 15 min and then transferred to a 500-

mL separatory funnel containing 100 mL of ice-cooled aqueous saturated $NaHCO_3$. The mixture is extracted three times with 100-mL portions of pentane . The combined organic phases are washed with 100 mL of saturated brine , dried over magnesium sulfate ($MgSO_4$), filtered, and concentrated at reduced pressure using a rotary evaporator. The residual oil is distilled through a 10-cm Vigreux column under reduced pressure to afford 7.4 - 7.6 g (74 - 75% overall) of (E)-1-(tert-butyldimethylsilyl)-3-trimethylsilyl-2-propen-1-one (**3**) as an orange oil, bp 60-63°C/0.4 mm (Note 21) and (Note 22).

D. (1R,6S,7S)-4-(tert-Butyldimethylsiloxy)-6-(trimethylsilyl)bicyclo[5.4.0]-undec-4-en-2-one (**4**). A 100-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, a thermometer, a rubber septum, and a nitrogen inlet/outlet adapter, is placed under a nitrogen atmosphere and charged with 2.81 mL (2.17 g, 21.4 mmol) of diisopropylamine (Note 23) and 20 mL of dry THF. The solution is stirred and cooled with an ice-water bath while 13.7 mL (20.1 mmol) of a 1.47 M hexane solution of BuLi is added dropwise via a syringe over 5 min. After 10 min, the mixture is cooled to −80°C with a hexane-liquid nitrogen bath, and a solution of 2.58 mL (2.49 g, 20.1 mmol) of 1-acetyl-1-cyclohexene (Note 24) in 20 mL of dry THF is added dropwise via a stainless steel cannula over 15 min. The mixture is then stirred at the same temperature for an additional 30 min, and the solution is maintained at −80°C.

A 500-mL, three-necked, round-bottomed flask, equipped with a stirring bar, a thermometer, a rubber septum, and a nitrogen inlet/outlet adapter, is charged under a nitrogen atmosphere with 5.34 g (22.0 mmol) of (E)-1-(tert-butyldimethylsilyl)-3-trimethylsilyl-2-propen-1-one (**3**) and 150 mL of dry THF. The mixture is cooled to −80°C with a hexane-liquid nitrogen bath, and the THF solution of the lithium enolate of 1-acetylcyclohexene, which was prepared above and kept at −80°C, is added via a stainless steel cannula over 2 min (the enolate-containing flask is washed twice into the reaction mixture with 2-mL portions of dry THF). The reaction mixture is allowed to warm to −30°C over 70 min, and a solution of 1.22 g (20.3 mmol) of acetic acid in 10 mL of dry THF is added rapidly in one portion via a cannula. The resulting mixture is transferred to a 1-L separatory funnel containing 200 mL of aqueous saturated ammonium chloride , and the organic phase is separated. The aqueous phase is extracted twice with 100-mL portions of Et_2O. The combined organic phases are washed with 100 mL of saturated brine , dried over $MgSO_4$, filtered, and concentrated at reduced pressure using a rotary evaporator. The residual crude product is purified by column chromatography (150-325 mesh silica gel, 400 g; elution with hexane-AcOEt = 40:1) to afford 5.8 - 6.0 g (79 - 82%) of **4** as a pale yellow oil crude product, which solidifies on storage in a refrigerator. This material is ~95% pure based upon ^1H NMR spectroscopic analysis. Higher purity material may be obtained by recrystallization of this sample from a minimum amount of Et_2O-hexane affording colorless prisms, mp 74 - 75 °C (Note 25) and (Note 26).

2. Notes

1. This procedure was reported by Hoff, Brandsma and Arens.[2]
2. Ethyl vinyl ether was purchased from Wako Pure Chemical Co., Ltd. or Aldrich Chemical Company, Inc. and freshly distilled.
3. p-Toluenesulfonic acid monohydrate was purchased from Kanto Chemical Co., Inc. or Aldrich Chemical Company, Inc. and used without purification.
4. Propargyl alcohol was purchased from Nakalai Tesque, Inc. or Aldrich Chemical Company, Inc. and distilled.
5. This material has the following spectral properties: ^1H NMR (500 MHz, $CDCl_3$) δ: 1.17 (t, 3 H, J = 7.1, CH_2 Me), 1.29 (d, 3 H, J = 5.3, CHMe), 2.38 (t, 1 H, J = 2.6, H-1), 3.44-3.51 (m, 1 H, CH $_2$Me), 3.58-3.65 (m, 1 H, CH $_2$Me), 4.16 (d, 2 H, J = 2.6 H-3), 4.82 (q, 1 H, J = 5.3, OCHMe) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 15.3 (CH_2 Me), 19.7 (CHMe), 52.5 (C-3), 60.8 (CH $_2$Me), 73.9 (C-1), 80.1 (C-2), 98.7 (OCHO) . The checkers obtained material having bp 61-62°C/30 mm.
6. Potassium tert-butoxide was purchased from E. Merck and used as received.
7. This material has the following spectral properties: ^1H NMR (500 MHz, $CDCl_3$) δ: 1.20 (t, 3 H, J = 7.1, CH_2 Me), 1.36 (d, 3 H, J = 5.1, CHMe), 3.46-3.52 (m, 1 H, CH $_2$Me), 3.72-3.79 (m, 1 H, CH $_2$Me), 4.92 (q, 1 H, J = 5.1, OCHMe), 5.34 (dd, 1 H, J = 6.0, 8.5, H-3), 5.37 (dd, 1 H, J = 6.0, 8.5, H-3), 6.68 (t, 1 H, J = 6.0, H-1) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 15.3 (CH_2 Me), 20.4 (CHMe), 62.9 (CH $_2$Me), 89.2 (C-3), 99.9 (OCHO), 117.2 (C-1), 201.6 (C-2) . The checkers obtained material having bp 55-56° C/35 mm.
8. This compound can be stored in the presence of a trace amount of radical inhibitor such as 4,4'-

thiobis(2-tert-butyl-m-cresol) in a freezer for several months without significant decomposition. The checkers recommend that **1** be used as soon as practicable, as they observed significant amounts of polymerization upon storage for 1 month, even in the presence of the radical inhibitor. However, the checkers found that **2** is stable for 3 months in the presence of the inhibitor.

9. This procedure was reported by Reich, Kelly, Olson, and Holtan.[3]

10. 4,4'-Thiobis(2-tert-butyl-m-cresol) was purchased from Tokyo Kasei Kogyo Co., Inc. or Aldrich Chemical Company, Inc. and used as received.

11. Diethyl ether was distilled over calcium hydride and dried over 4 Å molecular sieves.

12. Butyllithium was purchased from Kanto Chemical Co., Inc. or Aldrich Chemical Company, Inc. and standardized by titration using 1,3-diphenylacetone p-tosylhydrazone as an indicator.[4]

13. tert-Butyldimethylsilyl chloride was purchased from Aldrich Chemical Company, Inc. and used as received.

14. Hexamethylphosphoric triamide was purchased from Aldrich Chemical Company, Inc. or Tokyo Kasei Kogyo Co., Inc. and distilled over calcium hydride and then dried over 4 Å molecular sieves.

15. Triethylamine was purchased from Nakalai Tesque, Inc. and distilled over calcium hydride. The checkers used triethylamine purchased from Aldrich Chemical Company, Inc. as received.

16. This material has the following spectral properties: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.02 (s, 3 H, $SiMe_2$), 0.03 (s, 3 H, $SiMe_2$), 0.91 (s, 9 H, t-Bu), 1.16 (t, 3 H, J = 7.1, CH_2 Me), 1.28 (d, 3 H, J = 5.1, CHMe), 3.38-3.45 (m, 1 H, CH $_2$Me), 3.68-3.74 (m, 1 H, CH $_2$Me), 4.92 (q, 1 H, J = 5.1, CHMe), 5.00 (d, 1 H, J = 8.5, H-3), 5.06 (d, 1 H, J = 8.5, H-3) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ −6.5 ($SiMe_2$), −6.6 ($SiMe_2$), 15.4 (CH_2 Me), 17.5 (CMe_3), 20.5 (CHMe), 26.8 (CMe_3), 63.1 (CH $_2$Me), 84.4 (C-3), 100.1 (OCHO), 125.8 (C-1), 203.0 (C-2) . The checkers obtained material having bp 108-109°C/8 mm.

17. This procedure is a modification of Reich's method[3] for the synthesis of 1,3-bis(trimethylsilyl)-2-propen-1-one.

18. Tetrahydrofuran was distilled over calcium hydride and dried over 4 Å molecular sieves.

19. Trimethylsilyl chloride was purchased from Nakalai Tesque, Inc. or Aldrich Chemical Company, Inc. and distilled over calcium hydride.

20. Methanol was purchased from Wako Pure Chemical Co., Ltd. or Aldrich Chemical Company, Inc. and used as received.

21. This material (E)-**3** has the following physical properties: R_f = 0.52 (hexane- Et_2O = 10:1). IR (neat) cm^{-1}: 1655, 1250 ; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.09 (s, 9 H, $SiMe_3$), 0.18 (6 H, $SiMe_2$), 0.87 (s, 9 H, t-Bu), 6.64 (d, 1 H, J = 19.2, H-2), 6.80 (d, 1 H, J = 19.2, H-3) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: −5.8 ($SiMe_2$), −1.7 ($SiMe_3$), 16.7 (CMe_3), 26.7 (CMe_3), 145.1 (C-3), 147.1 (C-2), 236.3 (C-1) . The checkers obtained material having bp 110-112°C/8 mm.

22. A mixture of **3** and its (Z)-isomer is obtained when trifluoroacetic acid is used for the removal of the 1-ethoxyethyl protective group. A solution of crude 1-(tert-butyldimethylsilyl)-1-(1-ethoxyethoxy)-3-(trimethylsilyl)-1,2-propadiene obtained from 38.7 g (160 mmol) of **2** in 300 mL of THF-water (5:1) is cooled with an ice-water bath, and 91 mL (135 g, 1.18 mol) of trifluoroacetic acid is added in one portion. The mixture is then placed in a refrigerator (ca. 4°C) and, after 12 hr, transferred to a 1-L separatory funnel containing 200 mL of water. The whole is extracted three times with 100-mL portions of pentane . The combined organic phases are washed thoroughly with aqueous saturated $NaHCO_3$ to remove trifluoroacetic acid completely, and then with 100 mL of saturated brine . The pentane solution is dried over $MgSO_4$, filtered, and concentrated at reduced pressure using a rotary evaporator. The residue is subjected to column chromatography (150-325 mesh silica gel, 1 kg; elution with hexane-Et_2O, 40:1) to afford 9.89 g (27%) of (Z)-**3** and 17.72 g (46%) of (E)-**3** . (Z)-**3** : bp 60°C/0.45 mm, an orange oil; IR (neat) cm^{-1}: 1655, 1245 ; R_f = 0.67 (hexane-Et_2O, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.10 (s, 9 H, $SiMe_3$), 0.18 (6 H, $SiMe_2$), 0.91 (s, 9 H, t-Bu), 6.01 (d, 1 H, J = 14.1, H-2), 7.30 (d, 1 H, J = 14.1, H-3) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: −7.0 ($SiMe_2$), −0.5 ($SiMe_3$), 17.0 (CMe_3), 26.7 (CMe_3), 144.6 (C-2), 144.9 (C-3), 238.0 (C-1) .

23. Diisopropylamine was purchased from Nakalai Tesque, Inc. or Aldrich Chemical Company, Inc. and distilled over calcium hydride .

24. 1-Acetyl-1-cyclohexene was purchased from Aldrich Chemical Company, Inc. and distilled before use.

25. The checkers found that recovery of pure material from the recrystallization is low (~30%) unless care is taken to use the minimum amount of total solvent and the minimum amount of ether. The checkers found use of pure hexanes more satisfactory in terms of recovery; however, the material

obtained was pale yellow in color.
26. This material has the following physical properties : R_f = 0.47 (hexane-ethyl acetate (AcOEt) = 15:1); IR (KBr) cm^{-1}: 1705, 1645, 1250 ; ^1H NMR (500 MHz, C_6D_6) δ: 0.08 (s, 9 H, $SiMe_3$), 0.21 (s, 3 H, $SiMe_2$), 0.26 (s, 3 H, $SiMe_2$), 1.00 (s, 9 H, t-Bu), 1.06 (dddd, 1 H, J = 3.9, 4.3, 13.0, 13.5, H-11), 1.21 (ddddd, 1 H, J = 4.7, 4.7, 13.5, 13.5, 13.5, H-9), 1.42-1.45 (m, 2 H, H-8), 1.52 (br d, 1 H, J = 13.5, H-10), 1.71 (br d, 1 H, J = 13.5, H-9), 1.79 (d, 1 H, J = 7.1, H-6), 2.05 (ddddd, 1 H, J = 3.9, 3.9, 13.5, 13.5, 13.5, H-10), 2.13 (br ddd, 1 H, J = 3.9, 3.9, 11.5, H-7), 2.27 (br d, 1 H, J = 13.0, H-11), 2.38 (br dd, 1 H, J = 3.9, 3.9, H-1), 2.85 (dd, 1 H, J = 1.9, 12.2, H-3), 3.67 (dd, 1 H, J = 1.9, 12.2, H-3), 5.00 (ddd, 1 H, J = 1.9, 1.9, 7.1, H-5) ; ^{13}C NMR (125 MHz, C_6D_6) δ: −4.3, −4.2, −1.8, 18.2, 22.2, 25.8, 26.9, 27.6, 28.8, 31.3, 46.3, 51.3, 57.7, 106.0, 149.9, 203.3. Anal Calcd. for $C_{20}H_{38}O_2Si_2$: C, 65.51; H, 10.45, Found C, 65.26; H, 10.56 . The structure was determined by X-ray crystallographic analysis.[5]

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

The procedure described here illustrates an efficient preparation of cis-6-alkyl-5-trimethylsilyl-3-siloxy-3-cycloheptenones by reaction of (E)-(β-(trimethylsilyl)acryloylsilane (**3**) with the kinetic lithium enolate of an α,β-unsaturated methyl ketone generated with lithium diisopropylamide in tetrahydrofuran (Table).[5] This new [3 + 4] annulation[6] is also effective with 1-cyclopentenyl and 1-cyclohexenyl methyl ketones, affording all-cis bicyclic cycloheptenones in comparable yields as shown in the scheme. It is remarkable that reaction of **3** with 2'-bromoacetophenone enolate produces benzocycloheptenone, albeit in low yield, showing that a benzenoid unsaturation can also participate in the [3 + 4] annulation. In sharp contrast to the case of (E)-**3** , the reaction of (Z)-**3** under the same conditions is quite slow and affords only 5,6-trans isomer in much lower yield. The stereospecificity in the annulation has been rationalized by intermediacy of cis-1,2-divinylcyclopropanediolate (**6**), which is generated from 1,2-adduct (**5**) by way of a Brook rearrangement/cyclopropanation sequence in a concerted manner. Compound **6** is expected rapidly to undergo a stereospecific oxyanion-accelerated Cope rearrangement to **7**. The low yields in the reaction of (Z)-**3** is attributed to slowness in the initial 1,2-addition step since substantial amount of the starting material is recovered.

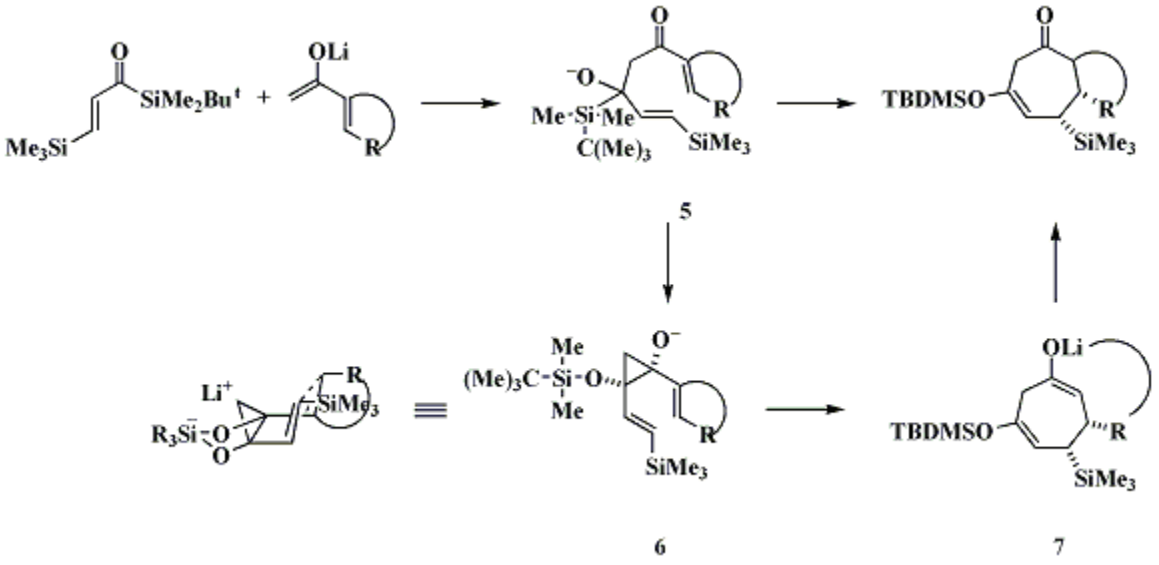
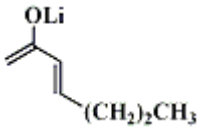
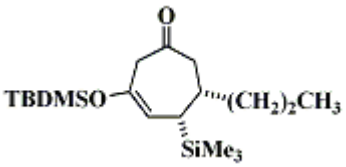
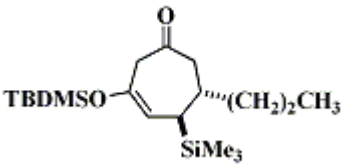
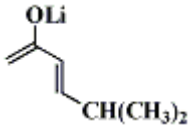
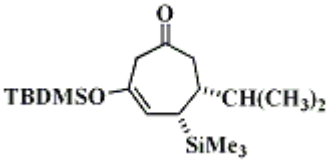
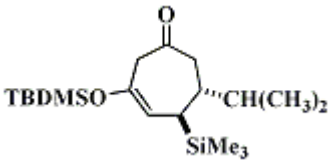
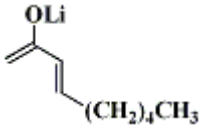
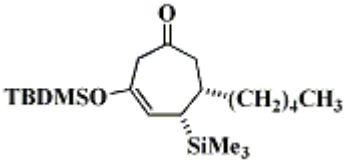
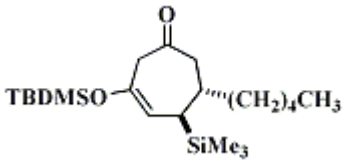
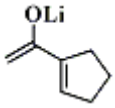
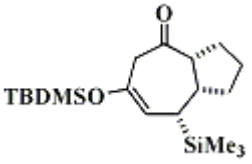
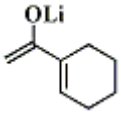
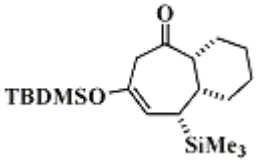
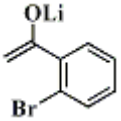
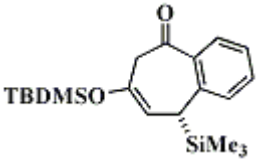


TABLE
PREPARATION OF CYCLOHEPTENONES USING (3 + 4) ANNULATION

(*E*)-**3**	(*Z*)-**3**

Ketone Enolate	Product	Yield	Product	Yield
		73%		31%
		84%		11%
		84%		29%
		73%		
		82%		
		30%		

The present [3 + 4] annulation methodology for the synthesis of seven-membered carbocycles involves a straightforward procedure that also provides the product functionalities (e.g., masked and unmasked ketone carbonyl and trimethylsilyl groups) that can be transformed to hitherto inaccessible or difficult-to-prepare cycloheptane structures. The prior approach,[7,8,9,10] based on Cope rearrangement of cis-1,2-divinylcyclopropane, bears an intrinsic drawback in that there exist a limited number of methods for stereoselective preparation of the substrate.

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Hexamethylphosphoramide HIGHLY TOXIC:
Phosphoric triamide, hexamethyl- (8,9); (680-31-9)

1-(1-Ethoxyethoxy)-1,2-propadiene:
1,2-Propadiene, 1-(1-ethoxyethoxy)- (9); (20524-89-4)

Ethyl vinyl ether:
Ether, ethyl vinyl (8);
Ethene, ethoxy- (9); (109-92-2)

p-Toluenesulfonic acid monohydrate (8);
Benzenesulfonic acid, 4-methyl-, monohydrate (9); (6192-2-5)

Propargyl alcohol:
2-Propyn-1-ol (8,9); (107-19-7)

3-(1-Ethoxyethoxy)-1-propyne:
1-Propyne, 3-(1-ethoxyethoxy)- (9); (18669-04-0)

Potassium tert-butoxide:
tert-Butyl aclohol, potassium salt (8);
2-Propanol, 2-methyl-, potassium salt (9); (865-47-4)

4,4'-Thiobis(2-tert-butyl-m-cresol):
Phenol, 4,4'-thiobis[2-(1,1-dimethylethyl)-3-methyl- (8);
m-Cresol, 4,4'-thiobis[2-tert-butyl- (9); (4120-97-2)

Butyllithium:
Lithium, butyl- (8,9); (109-72-8)

tert-Butyldimethylsilyl chloride:
Silane, chloro(1,1-dimethylethyl)dimethyl- (9); (18162-48-6)

Triethylamine (8);

Ethanamine, N,N-diethyl- (9); (121-44-8)

(E)-1-(tert-Butyldimethylsilyl)-3-trimethylsilyl-2-propen-1-one:
Silane, (1,1-dimethylethyl)dimethyl[1-oxo-3-(trimethylsilyl)-2-propenyl]- (E)- (11); (83578-66-9)

Trimethylsilyl chloride:
Silane, chlorotrimethyl- (8,9); (75-77-4)

Diisopropylamine (8);
2-Propanamine, N-(1-methylethyl)- (9); (108-18-9)

1-Acetyl-1-cyclohexene:
Ethanone, 1-(1-cyclohexen-1-yl)- (9); (932-66-1)

Acetic acid (8,9); (64-19-7)

1,3-Diphenylacetone p-tosylhydrazone:
p-Toluenesulfonic acid, (α-benzylphenethylidene)hydrazide (8);
Benzenesulfonic acid, 4-methyl-, [2-phenyl-1-(phenylmethyl)ethylidene]hydrazide (9); (19816-88-7)

Trifluoroacetic acid:
Acetic acid, trifluoro- (8,9); (76-05-1)