Unprecedented Regio- and Stereoselective Conversion of 1-Cyclopropyl-3-ethoxycyclopentadienes to 3-(*E*)-Alkylidenecyclopentenes

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Cyclopropylalkynes **1** were converted into cyclopropyl-substituted 3-ethoxy-5-dimethylaminocyclopentadienes **4** via initially formed (*β*-dimethylaminoethenyl)carbene complexes **3** and their subsequent formal [3 + 2] cycloaddition to a second alkyne of type **1** (overall yields 51−59%). New regio- and stereoselective 1,7-addition and 1,6-substitution reactions have been developed that convert cyclopentadienes **4** into highly functionalized cyclopentenes **5** and **11**, respectively (yields 98−99% and 61%, respectively). An in situ domino reaction consisting of a [3 + 2] cycloaddition and subsequent 1,7-addition has also been achieved (86% overall yield).

Introduction

The unique electronic properties of the cyclopropyl group[1] in conjunction with its inherent ring strain[2] make it a valuable entity in composite functionalities[3] which are indispensable for efficient organic synthesis.[4] Among such cyclopropyl-group-containing building blocks with composite functionalities are cyclopropylalkynes and especially donor-substituted cyclopropylalkynes which have recently become easily accessible[5] even in enantiomerically pure form.[6] Our new method for the assembly of highly functionalized five-membered rings from an alkyne via an alkynylidenechromium complex by the 1,4-addition of dimethylamine and subsequent formal [3 + 2] cycloaddition of the resulting *β*-dimethylaminoalkenylidene complex to another alkyne,[7] when applied to 2-alkoxy-1-ethynylcyclopropanes, would yield a range of 1- and 5-cyclopropyl-substituted 3-ethoxy-5-dimethylaminocyclopentadienes **4** which ought to be prone to undergo interesting further transformations.

The (3-cyclopropylpropynylidene)pentacarbonylchromium complexes **2a**,**b**, as well as their dimethylamine Michael adducts **3a**,**b**, were readily prepared from hexacarbonylchromium and the corresponding alkynes **1a**,**b** according to previously published procedures.[8] As reported for the simple **3a**,[9] cyclopropyl-substituted (*β*-dimethylaminoethynyl)carbene complexes **3a**,**b** both undergo [3 + 2] cycloadditions without carbonyl insertion[10] when reacted with alkynes (Scheme 1). In this case, reactions of **3a**,**b** with cyclopropylalkynes **1a**−**c** were carried out in hexane solution with gentle heating (55 °C) to give the 1,5-dicyclopropyl-1,3-cyclopentadienes **4** in very good yields (82−95%). Compounds **4ab** and **4bc** were obtained as mixtures of diastereomers (1:1 and 2.5:2.5:1:1, respectively). The relatively low isolated yield of **3b** (48%) can be attributed to its decomposition upon chromatography on silica gel. When the crude product obtained by simple evaporation of the solvent and excess dimethylamine was treated with the cyclopropylalkyne **1c**, cycloadduct **4bc** was obtained in a good overall yield (75% from **2b**).

Upon treatment of cyclopentadienes **4ab** and **4bc** with ethanol under acid catalysis (aqueous HCl), 4-(dimethylamino)-1-ethoxy-3-[(*E*)-3′,3′-diethoxypropylidene]-1-cyclopentenes **5a**,**b** were formed rapidly in excellent yields (99% and 98%, respectively), apparently by regio- and stereoselective 1,7-addition of ethanol to the (3-ethoxy-

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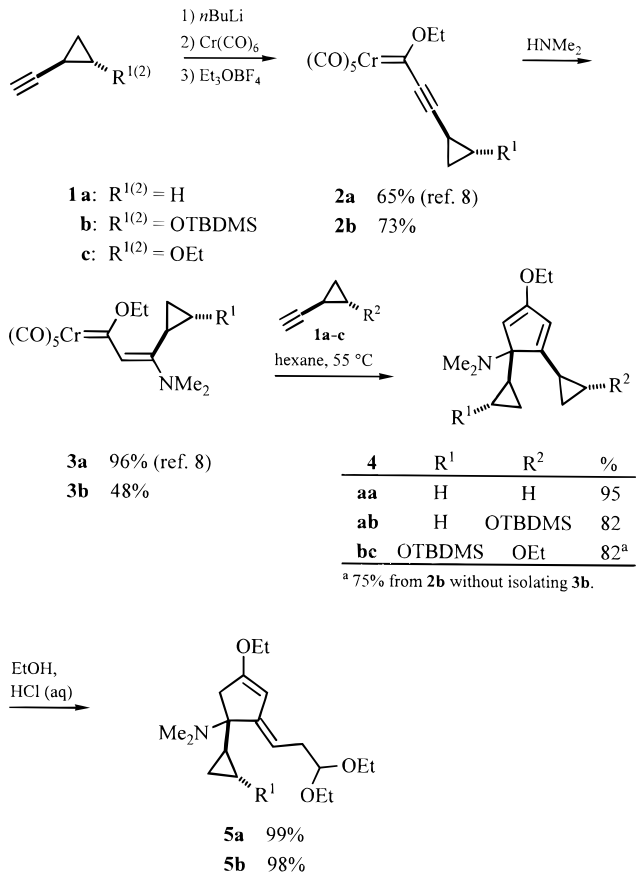
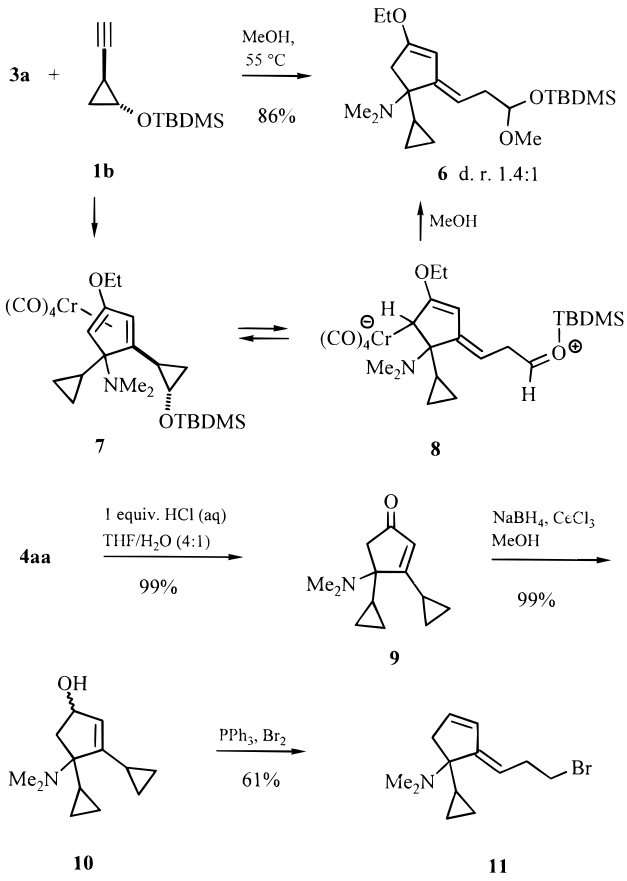
Scheme 1



Scheme 2



butadienyl)cyclopropane unit, attaching the second ethoxy group at the oxy-substituted cyclopropyl carbon. No reaction was observed for compound **4aa** in which R^2 = H. This is not surprising and reflects the activating effect that the donor substituents on the cyclopropane ring in **4ab** and **4bc** have in the regioselective opening of the cyclopropane ring. Apparently the *tert*-butyldimethylsilyloxy group in **4ab** is substituted for an ethoxy group, under acid catalysis, after the 1,7-addition of ethanol.

This formation of 3-(*E*)-alkylidene-4-(dimethylamino)-1-ethoxycyclopentenes **5** can be achieved even more efficiently by generating the cycloadduct of **3** with the alkyne **1b**,**c** in situ in an alcoholic solvent, as demonstrated by the reaction of **3a** with **1b** in methanol to give directly the mixed methyl trialkylsilyl acetal **6** with an (*E*)-alkylidenecyclopentene moiety equivalent to **5a** in 86% yield. In this reaction, most probably the strongly electron-withdrawing effect of the $(CO)_4Cr$ group in the transient chromium-complexed cyclopentadiene intermediate **7** induces ring opening in the polar solvent methanol to give **8**; subsequent addition of methanol with loss of the tricarbonylchromium fragment then gives **6**[11] (Scheme 2). Although a cyclopentadiene[12] (or a [2 + 2 + 1] cycloadduct[10]) bearing a chromiumcarbonyl fragment in the reaction of 1-alkoxy-3-aminoalkenylidenepentacarbonylchromium complexes with alkynes has never been isolated, as is usually observed in the normal Dötz reaction to give chromiumtricarbonyl complexed phenols,[13] it must be concluded that such complexes do form, as a direct result of cycloaddition, and then undergo decomplexation prior to and/or during workup of the reaction mixture. No addition of methanol was observed when the isolated cyclopentadiene **4ab** was heated in methanol at 60 °C for 48 h, and only starting material was recovered. The absence of a protic acid in this in situ process ensures the retention of the silyloxy group in **6** as part of a mixed acetal.

A different ring-opening possibility was uncovered in the case of **4aa** with R^1, R^2 = H. Hydrolysis of the enol ether moiety in **4aa** to give the cyclopentenone **9** and carbonyl reduction to give a 1:1 diastereomeric mixture of allyl alcohols **10** was achieved in very high overall yield. Treatment of **10** with the triphenylphosphane/bromine reagent led exclusively[14] to the homoallylic bromide 4-(dimethylamino)-3-[(*Z*)-3′-bromopropylidene]-1-cyclopentene **11** (61%) in an unprecedented S_N2'' type 1,6-substitution of the 3-cyclopropylallyl alcohol moiety.[15] This result is quite surprising since triphenylphosphane/bromine is the reagent of choice in the selective S_N2

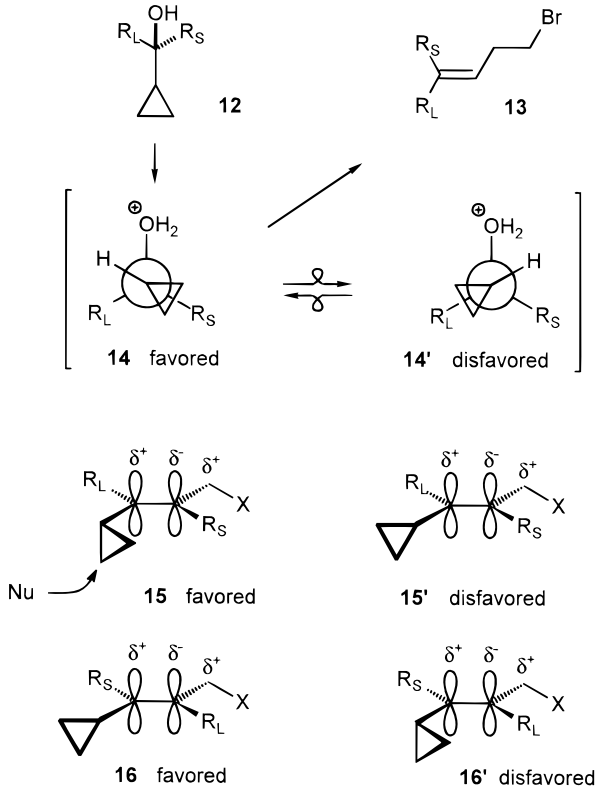
(11) We have taken advantage of a similar transient chromium-complexed cycloadduct in the migration of double bonds and the addition of water to the alternative carbonyl-inserted [2 + 2 + 1] cycloadducts. Cf. loc. cit. (10b).

(12) The recently developed reaction conditions are highly selective for the formation of 5-dialkylamino-3-ethoxycyclopentadienes from the cycloaddition of alkynes even to 3-(dimethylamino)-2-propenylidene chromium complexes not bearing a cyclopropyl group at the C3 position. Cf. loc. cit. (7).

(13) For reviews on the Dötz reaction, see: (a) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. D.; Tang, P.-C.; Chan, K.-S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813.

(14) Although the mass balance of this reaction is not very high, the ^{1}H NMR spectrum of the crude reaction mixture (obtained by evaporation of the solvent acetonitrile) only revealed resonances attributable to **11** and triphenylphosphane oxide. The incomplete mass balance of this reaction is attributed to the partial decomposition of **11** upon workup or chromatography.

Scheme 3



substitution of allyl alcohols without allylic rearrangement[16] and of cyclopropyl carbinols without opening of the cyclopropane ring.[17]

The (*E*)-configuration of all methylenecyclopentenes **5**, **6**, and **11** was assigned on the basis of ^{1}H NMR NOESY spectra, in which intense NOEs between the olefinic hydrogen on the ring and the exocyclic allylic hydrogens were observed in all cases. Also, in no case did the two olefinic hydrogens exhibit an NOE as would have been expected for the (*Z*)-isomer.

This stereoselective ring opening of the above vinyl- **10** and dienylcyclopropanes **4** can be rationalized with essentially the same model as developed by Johnson et al.[18] for the stereoselective opening of cyclopropylmethanols **12** with hydrobromic acid to give homoallylic bromides **13** (Scheme 3), but for vinylogous cases. The Johnson model contends that protonation of the hydroxy group in **12** to give **14**/**14′** further polarizes the C−O bond, which increases its interaction with the electron-donating C−C bonds of the cyclopropyl group prior to the S_N2' type attack of the bromide. Of the two possible conformers, **14** and **14′**, **14** is of the lowest energy as a result of the greater steric interaction between the cyclopropyl ring and the large group R_L in **14′** compared to that between the cyclopropyl group and R_S in **14** (Scheme 3). In the vinylogous cases demonstrated here, polarization of the double bond by an approaching electrophile or an adjacent leaving group in the vinylcyclopropanes **15**/**15′** increases the interaction between the π-orbitals of the double bond and the cyclopropane C−C bonds. The preferred conformer is again determined by the relative size and distance of the geminal and (*Z*)-positioned vicinal groups R_L and R_S, respectively, in **15**/**15′**.[19] In all cases encountered here, the geminal group is large (a tetrahedral quaternary center) and the (*Z*)-vicinal group is small (a hydrogen), thereby favoring ring opening from the *synclinal* conformer **15** to give the homoallylic system with a (*Z*)-configuration relative to the position of the leaving group in the precursor molecule. On the basis of this model, it would be predicted that when the geminal group is sufficiently small and the (*Z*)-vicinal group sufficiently large as in **16**/**16′**, similar ring openings would give homoallylic systems with the opposite configuration.

Other than providing an efficient means for the conversion of the readily accessible 3-ethoxy-5-dialkylaminocyclopentadienes **4** to methylenecyclopentenes **5**, **6**, and **11**, these rare examples of stereoselective ring opening of vinyl- and dienylcyclopropane derivatives via 1,5-substitution and 1,7-addition steps are of intrinsic interest.[15,20] As do the chromium-template-assisted [3 + 2] cycloadditions,[9,10] these stereoselective transformations offer new possibilities for highly substituted carbon skeletons making use of the "umpolung" effect of a cyclopropyl group.[1]

Experimental Section

All operations were performed under argon unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium/benzophenone. Hexane was freshly distilled from sodium. Ethanol and methanol were dried by addition of sodium (30.0 g/L) and subsequent distillation vented with a $CaCl_2$ drying tube. Column chromatography was carried out using silica gel (230−400 mesh) or on neutral alumina (ICN Alumina N, Super I, deactivated to activity grade Super II). Melting points are uncorrected. High-resolution masses were determined with preselected ion peak matching R ≫ 10 000 to be within ±2 ppm of the exact mass. Elemental analyses were performed by Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Universität Göttingen.

Pentacarbonyl{3-[(*E*)-2′-*tert*-butyldimethylsilyloxycyclopropyl]}-1-ethoxy-2-propyn-1-ylidene)]chromium (2b). To a solution of 2-[(*E*)-*tert*-butyldimethylsilyloxy]-1-ethynylcyclopropane (**1b**)[5c] (2.77 g, 14.1 mmol) in diethyl ether (60 mL) kept at −78 °C was added *n*BuLi (6.26 mL, 14.4 mmol, 2.3 M in hexanes) over a period of 5 min. To this solution were added hexacarbonylchromium (3.52 g, 16.0 mmol) and THF (20.0 mL), and the slurry was allowed to warm and was stirred at room temperature for 3 h. The resulting clear bright yellow solution was cooled to 0 °C, and triethyloxonium tetrafluoroborate (3.05 g, 16.0 mmol) was added, upon which the solution immediately turned dark red-brown. This reaction

(15) To the best of our knowledge, this is the first example of a 1,5-substitution on a 3-cyclopropylallyl alcohol. The denotion of this reaction as S_N2'' is based on the fact that the triphenylphosphane/bromine reagent normally substitutes alcohols in a concerted manner: Wiley G. A.; Rein, B. M.; Hershkowitz R. L. *Tetrahedron Lett.* **1964**, 2509. However, this assignment is tentative, and the proof of concertedness of this reaction will require further investigation.

(16) (a) Wijnberg J. B. P. A.; Wiering, P. G.; Stenberg, H. *Synthesis* **1981**, 901. (b) Schaefer, J. P.; Higgins, J. G.; Shenov, P. K. *Org. Synth.* **1968**, *48*, 51.

(17) Hrubiec, R. T.; Smith, M. B. *J. Org. Chem.* **1984**, *49*, 431.

(18) Brady, S. F.; Ilton, M. A.; Johnson, W. S. *J. Am. Chem. Soc.* **1968**, *90*, 2882.

(19) In unsubstituted vinylcyclopropane, the conformational equilibrium is between a *synclinal* (*gauche*) and an *antiperiplanar* (*s-trans*) conformer with the latter predominating: de Meijere, A.; Lüttke, W. *Tetrahedron* **1969**, *25*, 2047. Traetteberg, M.; Bakken, P.; Almenningen, A.; Lüttke, W. *J. Mol. Struct.* **1988**, *189*, 357.

(20) To the best of our knowledge, the only other example of a 1,7-conjugate addition involving a cyclopropane ring is the addition of cuprates to 1-acyl-2-vinylcyclopropanes: Miyaura, N.; Itoh, M.; Sasaki, S.; Suzuki, A. *Synthesis* **1975**, 317. Miyaura, N.; Itoh, M.; Suzuki, A. *Tetrahedron Lett.* **1976**, 255. Addition of cuprates to β-cyclopropyl-substituted α,β-unsaturated ketones occurs selectively in a 1,4-mode: Casey C. P.; Cesa, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4236.

mixture was allowed to warm to room temperature over 20 min, filtered through a short plug of silica gel, and rinsed with ether. The filtrate was concentrated under reduced pressure without heating. Purification of the residue was achieved by flash chromatography (200 g of silica gel, pentane) to give **2b** (4.60 g, 73%) as a deep red-brown liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.05, 0.09 (2 s, 6 H), 0.92 (s, 9 H), 1.19 (dd, $^2J = {}^3J$ = 7.2 Hz, 1 H), 1.45 (t, ^3J = 7.1 Hz, 3 H), 1.54 (m, 1 H), 1.80 (m, 1 H), 3.88 (m, 1 H), 4.59 (q, ^3J = 7.1 Hz, 2 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.20, −5.12, 12.55, 14.82, 18.00, 21.92, 25.66, 59.12, 75.72, 83.82, 147.97, 216.54, 225.16, 314.17. IR (KBr) ν (cm^{-1}): 2150, 2059, 1939. MS (70 eV) *m*/*z* (%): 444 (1) [M^+], 304 (5), 73 (100). Anal. Calcd for $C_{19}H_{24}CrO_7Si$: C, 51.34; H, 5.44. Found: C, 51.50; H, 5.61.

Pentacarbonyl{(2*E*)-3-[(*E*)-2′-*tert*-butyldimethylsilyloxycyclopropyl)-3-(dimethylamino)-1-ethoxy-2-propen-1-ylidene]}chromium (3b). Through a stirred solution of **2b** (210 mg, 0.47 mmol) in diethyl ether (15 mL) was passed a slow stream of dimethylamine for 5−10 s, whereupon the dark red-brown solution turned bright yellow. The solution was concentrated under reduced pressure without heating, and the residue was subjected to flash chromatography on silica gel (pentane/CH_2Cl_2 9:1) to give **3b** (110 mg, 48%) as a yellow semisolid. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.11, 0.12 (2 s, 6 H), 0.89 (s, 9 H), 1.25 (m, 2 H), 1.47 (t, ^3J = 7.0 Hz, 3 H), 1.57 (m, 1 H), 3.18 (s, 6 H), 3.46 (m, 1 H), 4.64 (q, ^3J = 7.0 Hz, 2 H), 5.93 (s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.06, −4.84, 15.71, 18.00, 19.70, 24.74, 25.71, 42.11, 56.68, 73.22, 116.38, 161.25, 219.57, 224.42, 284.35. IR (KBr) ν (cm^{-1}): 2044, 1908, 1558. MS (70 eV) *m*/*z* (%): 489 (0.8) [M^+], 349 (10). Anal. Calcd for $C_{21}H_{31}CrNO_7Si$: C, 51.52; H, 6.38. Found: C, 51.33; H, 6.35.

5-(Dimethylamino)-1,5-dicyclopropyl-3-ethoxy-1,3-cyclopentadiene (4aa). Through a slurry of **3a**[8a] (310 mg, 0.86 mmol) in *n*-hexane (4.0 mL) in a thick-walled Pyrex bottle equipped with a magnetic stirrer was passed a slow stream of argon for 2 min. Cyclopropylethyne (**1a**)[5c] (228 mg, 3.45 mmol) was then added, and the sealed bottle (screw cap) was suspended in an oil bath heated to 55 °C. After 20 h, consumption of **3a** was complete (TLC). The black slurry was cooled to room temperature, diluted with diethyl ether (10 mL), and allowed to stand open to the air for 30 min. The slurry was then filtered through Celite (washing with pentane/diethyl ether 1:1). The filtrate was concentrated under reduced pressure and chromatographed [alumina II, eluting sequentially with pentane, pentane/CH_2Cl_2 (5:1), pentane/diethyl ether (10:1), (5:1), (1:1)] to yield **4aa** (191 mg, 95%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ −0.36 (m, 1 H), 0.12 (m, 1 H), 0.35 (m, 1 H), 0.51 (m, 1 H), 0.57 (m, 2 H), 0.79 (m, 2 H), 1.05 (m, 1 H), 1.27 (t, ^3J = 7.0 Hz, 3 H), 1.48 (m, 1 H), 2.30 (s, 6 H), 3.76, 3.78 (2 q, ^3J = 7.0 Hz, 2 H), 4.32 (d, ^4J = 1.8 Hz, 1 H), 5.22 (dd, ^4J = 1.8, ^4J = 2 Hz, 1 H). ^{13}C NMR + DEPT (62.9 MHz, $CDCl_3$): δ −0.81 (−), 6.88 (−), 7.81 (−), 8.14 (+), 9.70 (−), 14.31 (+), 16.26 (+), 40.41 (+), 64.39 (−, O*C*H_2CH$_3$), 77.48 (C_{quat}, C-5), 87.94 (+, C-4), 115.74 (+, C-2), 161.14, 162.01 (2 C_{quat}). IR (film) ν (cm^{-1}): 3079, 1696, 1634, 1582. MS (70 eV) *m*/*z* (%): 233 (18) [M^+], 204 (100), 188 (58). Anal. Calcd for $C_{15}H_{23}NO$: C, 77.20; H, 9.93. Found: C, 77.27; H, 9.80.

1-[(*E*)-2′-*tert*-Butyldimethylsilyloxycyclopropyl)]-5-cyclopropyl-5-(dimethylamino)-3-ethoxy-1,3-cyclopentadiene (4ab). A mixture of **3a**[8a] (210 mg, 0.59 mmol) and **1b** (460 mg, 2.34 mmol) in *n*-hexane (6.0 mL) was reacted, and the product was purified in accordance with the procedure described above for the formation of **4aa** (from **3a** and **1a**), giving both diastereomers of **4ab** in equal amounts (86 + 89 = 175 mg, 82%) as slightly tanned oils. **1st diastereomer.** ^{1}H NMR (250 MHz, $CDCl_3$): δ −0.30 (m, 1 H), 0.07 (m, 1 H), 0.10 (s, 6 H), 0.32 (m, 1 H), 0.65 (m, 1 H), 0.73 (dq, ^3J = 6.9, ^2J = 2.0 Hz, 1 H), 0.89 (s, 9 H), 1.10 (m, 2 H), 1.30 (t, ^3J = 7.1 Hz, 3 H) 1.67 (m, 1 H), 2.33 (s, 6 H), 3.50 (m, 1 H), 3.80, 3.81 (2 q, ^3J = 7.1 Hz, 2 H), 4.36 (d, ^4J = 1.8 Hz, 1 H), 5.25 (dd, ^4J = 1.8, ^4J = 1.9 Hz, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.06, −4.88, 7.82, 14.38, 15.26, 17.96, 18.03, 19.51, 28.16, 40.46, 51.43, 64.50, 77.63, 88.39, 116.62, 158.70, 161.81. IR (film) ν (cm^{-1}): 1632, 1581. MS (70 eV) *m*/*z* (%): 363 (2) [M^+], 318 (62). Anal. Calcd for $C_{21}H_{37}NO_2Si$: C, 69.37; H, 10.26. Found: C, 69.10; H, 10.33. **2nd diastereomer.** ^{1}H NMR (250 MHz, $CDCl_3$): δ −0.31 (m, 1 H), 0.06, 0.07 (2 s, 6 H), 0.08 (m, 1 H), 0.31 (m, 1 H), 0.65 (m, 1 H), 0.72 (dq, ^3J = 6.6, ^2J = 2.0 Hz, 1 H), 0.86 (s, 9 H), 1.10 (m, 2 H), 1.29 (t, ^3J = 7.0 Hz, 3 H), 1.68 (m, 1 H), 2.30 (s, 6 H), 3.36 (m, 1 H), 3.77, 3.78 (2 q, ^3J = 7.0 Hz, 2 H), 4.34 (d, ^4J = 1.8 Hz, 1 H), 5.13 (dd, ^4J = 1.8, ^4J = 2.0 Hz, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −4.97, −4.82, −0.62, 7.97, 14.46, 15.86, 18.06, 18.08, 18.35, 25.85, 40.53, 56.95, 64.57, 77.52, 87.83, 115.76, 159.54, 162.05. IR (film) ν (cm^{-1}): 1632, 1582. MS (70 eV) *m*/*z* (%): 363 (1) [M^+], 318 (49).

5-[(*E*)-2″-*tert*-Butyldimethylsilyloxycyclopropyl]-5-(dimethylamino)-3-ethoxy-1-[(*E*)-2′-ethoxycyclopropyl]-1,3-cyclopentadiene (4bc). Variant A. A mixture of **3b** (256 mg, 0.52 mmol) and 2-[(*E*)-ethoxy]-1-ethynylcyclopropane (**1c**)[5a] (236 mg, 2.14 mmol) in *n*-hexane (6.0 mL) was reacted, and the product was purified in accordance with the procedure described above for the formation of **4aa** (from **3a** and **1a**), giving a 2.5:2.5:1:1 ratio of all four possible diastereomers of **4bc** (61 + 64 + 23 + 27 = 175 mg, 82%) as slightly tanned oils. **1st Stereoisomer.** ^{1}H NMR (250 MHz, $CDCl_3$): δ −0.21 (q, ^3J = 6.9 Hz, 1 H), 0.06, 0.09 (2 s, 6 H), 0.44 (m, 1 H), 0.87 (s, 9 H), 1.12 (m, 3 H), 1.13 (t, ^3J = 7.0 Hz, 3 H), 1.28 (t, ^3J = 7.0 Hz, 3 H), 1.68 (m, 1 H), 2.32 (s, 6 H), 3.07, 3.23 (m, 2 H), 3.58, 3.63 (2 q, ^3J = 7.0 Hz, 2 H), 3.75, 3.76 (2 q, ^3J = 7.0 Hz, 2 H), 4.82 (bs, 1 H), 5.22 (bs, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −4.94, −4.76, 9.46, 14.35, 15.07, 16.57, 18.05, 24.62, 25.77, 30.91, 40.43, 54.11, 61.53, 64.54, 65.94, 74.20, 88.27, 116.24, 157.86, 161.47. IR (film) ν (cm^{-1}): 1631, 1581. MS (70 eV) *m*/*z* (%): 407 (<1) [M^+], 318 (57). Anal. Calcd for $C_{23}H_{41}NO_3Si$: C, 67.76; H, 10.14. Found: C, 67.47; H, 10.16. **2nd stereoisomer.** ^{1}H NMR (250 MHz, $CDCl_3$): δ −1.17 (q, ^3J = 6.9 Hz, 1 H), 0.05, 0.08 (2 s, 6 H), 0.36 (m, 1 H), 0.86 (s, 9 H), 1.11 (m, 3 H), 1.16 (t, ^3J = 7.0 Hz, 3 H), 1.28 (t, ^3J = 7.0 Hz, 3 H), 1.73 (m, 1 H), 2.30 (s, 6 H), 3.13 (m, 2 H), 3.54, 3.62 (2 q, ^3J = 7.0 Hz, 2 H), 3.76, 3.77 (2 q, ^3J = 7.0 Hz, 2 H), 4.31 (bs, 1 H), 5.14 (bs, 1 H). **3rd stereoisomer.** ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.01, 0.02 (2 s, 6 H), 0.59 (m, 1 H), 0.84 (s, 9 H), 0.88 (m, 1 H), 1.16 (t, ^3J = 7.0 Hz, 3 H), 1.17−1.37 (m, 3 H), 1.28 (t, ^3J = 7.2 Hz, 3 H), 1.73 (m, 1 H), 2.29 (s, 6 H), 2.59 (m, 1 H), 3.27 (m, 1 H), 3.64 (2 q, ^3J = 7.0 Hz, 2 H), 3.79, 3.80 (2 q, ^3J = 7.2 Hz, 2 H), 4.32 (bs, 1 H), 5.21 (bs, 1 H). **4th stereoisomer.** ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.01, 0.02 (2 s, 6 H), 0.60 (m, 1 H), 0.84 (s, 9 H), 0.88 (m, 1 H), 1.16 (t, ^3J = 7.1 Hz, 3 H), 1.17−1.37 (m, 3 H), 1.27 (t, ^3J = 7.2 Hz, 3 H), 1.80 (m, 1 H), 2.27 (s, 6 H), 2.63 (m, 1 H), 3.27 (m, 1 H), 3.64 (2 q, ^3J = 7.1 Hz, 2 H), 3.79, 3.80 (2 q, ^3J = 7.2 Hz, 2 H), 4.32 (bs, 1 H), 5.22 (bs, 1 H).

Variant B. A solution of **2b** (210 mg, 0.473 mmol) in diethyl ether (7.0 mL) was treated with dimethylamine as described above for the formation of **3b**. The resultant ether solution of **3b** was concentrated under reduced pressure without heating, the residue was transferred to a Pyrex bottle (washing with CH_2Cl_2), and the solvent was removed under a stream of argon without heating. This crude residue was reacted with **1c** (288 mg, 2.62 mmol) as described above for the formation of **4aa** (from **3a** and **1a**), giving **4bc** (144 mg, 75%) as a mixture of all four possible stereoisomers (not separated).

4-Cyclopropyl-4-(dimethylamino)-3-[(*Z*)-3′,3′-diethoxypropylidene]-1-ethoxy-1-cyclopentene (5a). To a solution of **4ab** (83.6 mg, 0.23 mmol, mixture of diastereomers) in anhydrous ethanol (5.0 mL) was added a drop (~50 μL) of aqueous HCl (0.5 M), and the solution allowed to stand at room temperature for 20 min, after which time complete consumption of starting material was observed (TLC). The solution was diluted with diethyl ether (50 mL), washed once with saturated aqueous $NaHCO_3$ solution (30 mL) and once with water, and dried over $MgSO_4$. After filtration, the solution was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel [pentane/diethyl ether (1:1), diethyl ether, diethyl ether/methanol (20:1)] giving **5a** (73.5 mg, 99%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.13 (m, 1 H), 0.28 (m, 2 H), 0.45 (m, 1 H), 1.03 (dt, 2 × ^3J = 5.7 Hz, 1 H), 1.17, 1.19 (2 m, 6 H), 1.32 (t, ^3J = 7.1 Hz, 3 H), 1.57 (d, ^2J = 17.1 Hz, 1 H), 2.25 (s, 6 H), 2.41 (dd, 2 × ^3J = 7.1

Hz, 2 H), 2.43 (d, ^2J = 17.3 Hz, 1 H), 3.49, 3.62 (2 m, 4 H), 3.85 (q, ^3J = 7.1 Hz, 2 H), 4.49 (t, ^3J = 7.0 Hz, 1 H), 5.04 (bt, ^3J = 6.8 Hz, 1 H), 5.26 (bs, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −0.58, 3.39, 14.47, 15.32, 19.57, 30.01, 33.92, 39.48, 61.05, 61.14, 65.05, 68.40, 98.34, 102.95, 109.19, 151.47, 163.85. IR (film) ν (cm^{-1}): 1652, 1612. MS (70 eV) *m*/*z* (%): 323 (19) [M^+]. $C_{19}H_{33}NO_3$: calcd 323.2460 (correct HRMS).

4-[(*E*)-2″-*tert*-Butyldimethylsilyloxycyclopropyl]-4-(dimethylamino)-3-[(*Z*)-3′,3′-diethoxypropylidene]-1-ethoxy-1-cyclopentene (5b). Cyclopentadiene **4bc** (69.2 mg, 0.170 mmol, mixture of first two diastereomers) was reacted with a catalytic amount of HCl and ethanol (4.0 mL) and purified in the same manner as described above for the formation of **5a** (from **4ab**), giving **5b** (75.4 mg, 98%, single diastereomer) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.18, 0.33 (2 s, 6 H), 0.54 (m, 2 H), 0.85 (s, 9 H), 1.11 (m, 1 H), 1.12, 1.22 (2 m, 6 H), 1.32 (t, ^3J = 7.1 Hz, 3 H), 1.76 (d, ^2J = 17.1 Hz, 1 H), 2.23 (s, 6 H), 2.37 (dd, 2 × ^3J = 7.1 Hz, 2 H), 2.63 (d, ^2J = 17.3 Hz, 1 H), 3.15 (m, 1 H), 3.46, 3.63 (2 m, 4 H), 3.83 (q, ^3J = 7.1 Hz, 2 H), 4.46 (t, ^3J = 7.0 Hz, 1 H), 4.87 (bt, ^3J = 6.9 Hz, 1 H), 5.22 (bs, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.19, −4.94, 9.26, 14.41, 15.29, 15.33, 17.96, 25.76, 28.97, 32.35, 33.77, 39.28, 52.15, 60.92, 61.13, 64.99, 67.56, 98.24, 102.86, 109.67, 146.53, 163.93. IR (film) ν (cm^{-1}): 1612. MS (70 eV) *m*/*z* (%): 453 (10) [M^+]. Anal. Calcd for $C_{25}H_{47}NO_4Si$: C, 66.18; H, 10.44. Found: C, 66.22; H, 10.46.

3-[(*Z*)-3′-*tert*-Butyldimethylsilyloxy-3′-ethoxypropylidene]-4-cyclopropyl-4-(dimethylamino)-1-ethoxy-1-cyclopentene (6). A solution of **3a** (100 mg, 0.28 mmol) and **1b** (219 mg, 1.12 mmol) in methanol (6.0 mL) was reacted, and the product was purified in accordance with the procedure described above for the formation of **4aa** (from **3a** and **1a** in *n*-hexane), giving both diastereomers (inseparable, ∼1.4:1 by ^{13}C NMR) of **6** (95 mg, 86%) as a slightly tanned oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.08, 0.09, 0.10, 0.11 (4 s, 6 H), 0.10 (m, 1 H), 0.22 (m, 2 H), 0.43 (m, 1 H), 0.86, 0.87 (2 s, 9 H), 1.16 (m, 1 H), 1.33 (t, ^3J = 7.1 Hz, 3 H), 1.50, 1.61 (2 d, ^2J = 17.1 Hz, 1 H), 2.24 (s, 6 H), 2.33−2.48 (m, 3 H), 3.28, 3.29 (2 s, 3 H), 3.87 (q, ^3J = 7.1 Hz, 2 H), 4.64 (m, 1 H), 5.03 (bt, ^3J = 6.9 Hz, 1 H), 5.23, 5.25 (2 bs, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −4.60, −4.55, −0.44, 3.26, 3.36, 14.31, 17.99, 19.27, 19.43, 25.70, 30.18, 30.64, 37.18, 37.42, 39.31, 39.40, 53.41, 53.66, 64.94, 68.57, 98.31, 98.45, 99.42, 99.48, 109.58, 147.65, 163.63, 163.77. IR (film) ν (cm^{-1}): 1652, 1612. MS (70 eV) *m*/*z* (%): 395 (14) [M^+]. Anal. Calcd for $C_{22}H_{41}NO_3Si$: C, 66.79; H, 10.44. Found: C, 66.93; H, 10.46.

3,4-Dicyclopropyl-4-(dimethylamino)-2-cyclopenten-1-one (9). To a solution of **4aa**[8a] (275 mg, 1.18 mmol) in THF/water (4:1, respectively, 4.0 mL) was added aqueous HCl (2 M, 0.6 mL). After less than 1 min, consumption of starting material was complete (TLC). The solution was diluted with diethyl ether (40 mL) and washed once with aqueous NaOH (10%, 40 mL) solution and once with H_2O, and the combined aqueous phases were extracted once with diethyl ether. The combined organic phases were dried over $MgSO_4$ and filtered, and the filtrate was concentrated under reduced pressure. The resultant residue was purified by flash chromatography [pentane/diethyl ether (1:1), diethyl ether, diethyl ether/methanol (20:1)] giving **9** (240 mg, 99%) as a colorless crystalline solid, mp 59−60 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ −0.30 (m, 1 H), 0.41 (m, 2 H), 0.74 (m, 3 H), 1.19 (m, 3 H), 1.27 (d, ^2J = 16.6 Hz, 1 H), 1.88 (m, 1 H), 2.17 (d, ^2J = 16.6 Hz, 1 H), 2.24 (s, 6 H), 5.33 (s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 0.24, 6.43, 9.84, 12.22, 14.15, 17.22, 30.88, 40.01, 71.76, 120.68, 191.42, 206.12. IR (KBr) ν (cm^{-1}): 3076, 1692, 1612. MS (70 eV) *m*/*z* (%): 205 (52) [M^+], 161 (100). Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33. Found: C, 76.13; H, 9.22.

1,5-Dicyclopropyl-5-(dimethylamino)-1-cyclopenten-3-ol (10). To a solution of **9** (120 mg, 0.585 mmol) in methanol (3.0 mL) was added a solution of $CeCl_3 \cdot 7H_2O$ in ethanol (0.4 M, 1.5 mL), upon which a milky suspension formed. To this suspension was added sodium borohydride (23.7 mg, 0.63 mmol) in several portions over 1 min, and the clear reaction mixture was stirred for 30 min at room temperature. A solution of NaOH (20%, 20 mL) was added, and the mixture was extracted four times with diethyl ether. The combined organic phases were washed once with water, dried over $MgSO_4$, and filtered, and the filtrate was concentrated under reduced pressure. The resultant residue was purified by flash chromatography [pentane/diethyl ether (1:1), diethyl ether, diethyl ether/methanol (10:1)] giving **10** (1:1 mixture of diastereomers, 120 mg, 99%) as a colorless crystalline solid, mp 70−71 °C. **1st diastereomer.** ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.05 (m, 1 H), 0.35 (m, 2 H), 0.55 (m, 3 H), 0.68 (m, 1 H), 0.78 (m, 2 H), 1.22 (m, 1 H), 1.38 (m, 1 H), 1.68 (bs, 1 H), 2.05 (dd, ^2J = 16.1, ^3J = 7.0 Hz, 1 H), 2.22 (s, 6 H), 4.66 (m, 1 H), 5.06 (m, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 0.84, 4.78, 7.39, 7.61, 9.88, 17.47, 29.18, 39.01, 74.51, 76.24, 121.84, 156.21. IR (KBr) ν (cm^{-1}): 3481, 3102, 1675. MS (70 eV) *m*/*z* (%): 207 (22) [M^+], 190 (8), 163 (100). $C_{13}H_{21}NO$: calcd 207.1623 (correct HRMS). **2nd diastereomer.** ^{1}H NMR (250 MHz, $CDCl_3$): δ −0.29 (m, 1 H), 0.47 (m, 2 H), 0.59 (m, 3 H), 0.71 (m, 1 H), 0.87 (m, 2 H), 1.24 (m, 1 H), 1.31 (m, 1 H), 1.63 (bs, 1 H), 2.10 (dd, ^2J = 16.1, ^3J = 7.0 Hz, 1 H), 2.18 (s, 6 H), 4.41 (m, 1 H), 5.05 (m, 1 H).

4-Cyclopropyl-4-(dimethylamino)-3-(3′-bromopropylidene)-1-cyclopentene (11). To a solution of triphenylphosphane (159 mg, 0.61 mmol) in acetonitrile (2.0 mL) was added a solution of bromine (64 mg, 0.40 mmol) in acetonitrile (0.7 mL). The alcohol **10** (80 mg, 0.39 mmol, mixture of diastereomers) was added to this solution portionwise over 1 min, and the resultant reaction mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel [pentane/diethyl ether (1:1), diethyl ether] giving **11** (single isomer, 64 mg, 61%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ −0.43 (m, 1 H), 0.25 (m, 2 H), 0.45 (m, 1 H), 0.97 (m, 1 H), 1.52 (dd, ^2J = 17.1, ^3J = 1.9 Hz, 1 H), 2.21 (s, 6 H), 2.35 (d, ^2J = 17.3 Hz, 1 H), 2.72 (dt, 2 × ^3J = 7.0 Hz, 2 H), 3.38 (m, 2 H), 5.23 (bt, ^3J = 6.8 Hz, 1 H), 5.94 (m, 1 H), 6.29 (m, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −0.84, 3.47, 19.74, 29.87, 32.75, 32.82, 39.55, 69.53, 116.92, 129.59, 135.69, 151.72. IR (film) ν (cm^{-1}): 1642, 1617. MS (70 eV) *m*/*z* (%): 271/269 (56/53) [M^+], 190 (98), 162 (100). $C_{13}H_{20}BrN$: calcd 269.0779 (correct HRMS).

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