Compound 19: R_f 0.39 (solvent system C); oil; FABMS (7 kV at 1.4 mA), *m/e* (relative intensity) 388 ([M+3]$^+$, 18), 386 ([M + 1]$^+$, 43), 350 ([M - Cl]$^+$, 54), 294 ([$C_{17}H_{16}N_3O_2$]$^+$, 100), 169 ([$C_{11}H_9N_2$]$^+$, 89); ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.51 (br s, 1 H, NH), 7.44-7.02 (m, 4 H, C(10)C(13)H), 6.24 (t, 1 H, ^3J = 5.7 Hz, C(8)*H*C(1')H_2), 4.50 (X part of ABX spectrum, 1 H, C(14a)*H*C(14)H_2), 4.20-3.28 (m, 3 H, C(5a)H and C(3)H_2), 3.53 and 2.81 (AB part of ABX spectrum, 2 H, ^2J = 15.6 Hz, ^3J = 4.8 Hz, ^3J = 11.1 Hz, C(14)H_2C(14a)H), 2.50-1.85 (m, 4 H, C(4)H_2C(5)H_2), 2.32 (d, 2 H, ^3J = 5.7 Hz, C(1')H_2C(8)H), 1.71 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3).

Registry No. (±)-**5**, 99708-07-3; **6**, 106211-91-0; (±)-**7**, 106211-87-4; **8**, 61350-60-5; **9**, 106211-89-6; **10**, 106211-90-9; **13**, 106211-88-5; **14**, 106292-67-5; **15**, 106292-68-6; **16**, 106211-93-2; **17**, 106292-69-7; **18**, 106211-92-1; **19**, 106292-70-0; **20**, 106211-94-3.

Furfural, a Convenient Precursor for Intramolecular Diels-Alder Reactions via Umpolung with Trimethylsilyl Cyanide[1]

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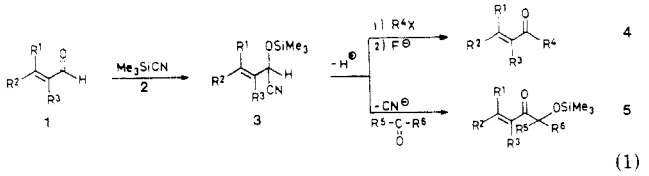
The deactivating effect of a 2-acyl group on the reactivity of furan as a diene in Diels-Alder reactions can be eliminated by protecting the carbonyl group. Therefore, the addition product **10** of trimethylsilyl cyanide and furfural offers a convenient starting material for intramolecular Diels-Alder reactions after deprotonation and reaction with suitable olefinic electrophiles (umpolung). In this way, 5-bromo-1-pentene and 1-hexen-5-one, respectively, were reacted with **10** and products **14** and **22** thermally transformed into cycloadducts **15** and **23**. Due to the mild conditions of the deprotection, cycloreversion can be suppressed so that the tricyclic ketones **19** and **25** can be obtained in high yields. Ketones **19** and **25** constitute the first examples of intramolecular Diels-Alder adducts with furan carrying a carbonyl group in the bridgehead position. On heating, these ketones cyclorevert in over 90% yields to **18** and **24**, demonstrating the usefulness of our approach.

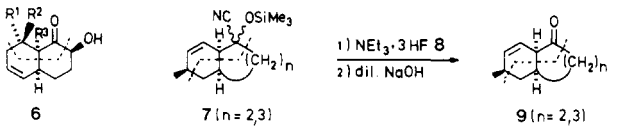
During the last decade, the intracular version of the Diels-Alder reaction has gained primary importance for the construction of bi- and polycyclic ring systems, especially for natural product synthesis.[3] Within certain limits the intramolecular [4 + 2] cycloaddition can be smoothly performed. Thus, the synthetic problem is essentially reduced to an efficient connection of the diene and dienophile precursors through a tether that carries the appropriately situated desired substituents.

By means of two different model systems, we have recently demonstrated that diene-dienophile precursors of a unique substituent pattern can be constructed by employing the well-developed method of umpolung of unsaturated aldehydes **1** with trimethylsilyl cyanide (**2**). Allowing the corresponding carbanions to react with alkylating agents produces ketones of type **4**[4] whereas with carbonyl compounds as electrophiles O-silylated acyloins **5** are obtained in high yield:[5]



(1)

Employing these principles resulted in the smooth synthesis of the new bicyclic ketones **6**[6] and **9**,[7] in which the diene and dienophile are delineated by the dotted lines. It should be stressed that so far intramolecular Diels-Alder reactions failed for tetrahydroindanones of type **9**[8] (n = 2) where instead of the expected octalones **9** (n = 3) only



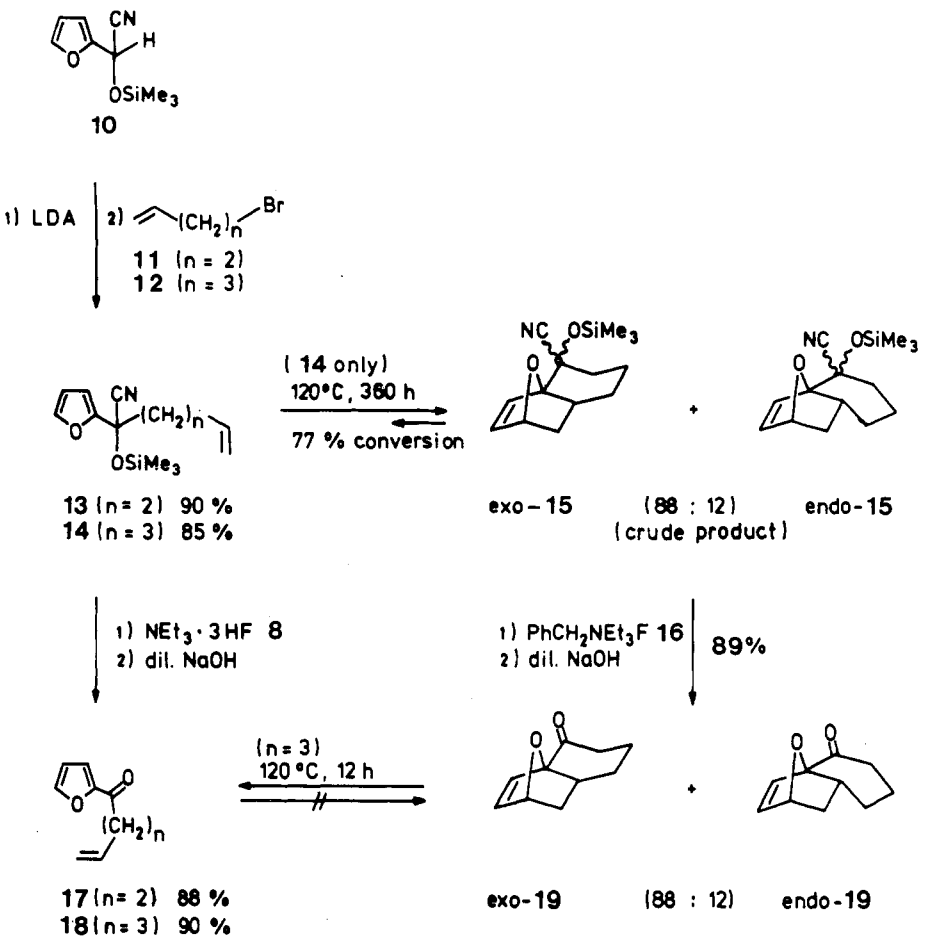
the isomers with a conjugated double bond could be isolated.[9] The key to smooth formation of **9** (n = 2, 3) lies in the mild conditions for both the cyclization of the precursor of **7** (n = 2, 3) and the desilylation by triethylamine dihydro-[10] or preferentially trihydrofluoride **8**.[11]

The advantage of this protocol becomes crucial if a 2-acylfuran is intended to serve as a diene moiety. In view of the well-known diminished reactivity of furan as a 4π component and the retro reaction of the Diels-Alder ad-

(1) Paper XIV of the series: Trimethylsilyl Cyanide—A Reagent for Umpolung. Paper XIII: See ref 6.
(2) Dissertation, University of Würzburg, 1985.
(3) (a) Oppolzer, W. *Angew. Chem.* **1977**, *89*, 10; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. (b) Oppolzer, W. In *New Synthetic Methods*; Verlag Chemie: Weinheim, 1979; Vol. 6, p 1f. (c) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (d) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. (e) Ciganek, E. *Org. React. (N.Y.)* **1984**, 32f. Taber, F. *Intramolecular Diels-Alder Reactions and Alder-Ene Reactions*; Springer Verlag: New York, 1984.
(4) Hertenstein, U.; Hünig, S.; Reichelt, H.; Schaller, R. *Chem. Ber.* **1986**, *119*, 722. Reichelt, H.; Hünig, S. *Chem. Ber.* **1986**, *119*, 1772.
(5) Hünig, S.; Öller, M. *Chem. Ber.* **1981**, *114*, 959.
(6) Fischer, K.; Hünig, S. *Chem. Ber.*, **1986**, *119*, 3344.
(7) Fischer, K.; Hünig, S. *Chem. Ber.* **1986**, *119*, 2590.
(8) (a) Oppolzer, W.; Fehr, L.; Warneke, J. *Helv. Chim. Acta* **1977**, *60*, 48. (b) Roush, W. R.; Gillis, H. R. *J. Org. Chem.* **1980**, *45*, 4283. Roush, W. R.; Pesckis, S. W. *J. Am. Chem. Soc.* **1981**, *103*, 6696. Roush, W. R.; Ko, A. I.; Gillis, H. R. *J. Org. Chem.* **1980**, *45*, 4264. Compare also ref 1.
(9) (a) Näf, F.; Decorzant, R.; Thommen, W. *Helv. Chim. Acta* **1979**, *62*, 114. Näf, F.; Decorzant, R.; Thommen, W. *Helv. Chim. Acta* **1982**, *65*, 2212. (b) Roush, W. R.; Hall, S. E. *J. Am. Chem. Soc.* **1981**, *103*, 5200. Compare also ref 1.
(10) Hünig, S.; Wehner, G. *Synthesis* **1975**, 391.
(11) Purchased from Riedel de Haen, Seelze, BRD; with this reagent the reaction stops exclusively at the cyanohydrin stage.

0022-3263/87/1952-0564$01.50/0

Scheme I



ducts at higher temperature,[12] the additional deactivating effect of a carbonyl group in the 2-position has to be eliminated by suitable protection.

Therefore, the addition product of trimethylsilyl cyanide on furfural represents a simple and inexpensive starting material for the introduction of a dienophile via umpolung and subsequent intramolecular [4 + 2] cycloaddition. This approach for the synthesis of thus far inaccessible tricyclic ketones **19** and **25** according to Schemes I and II is described in the present paper.

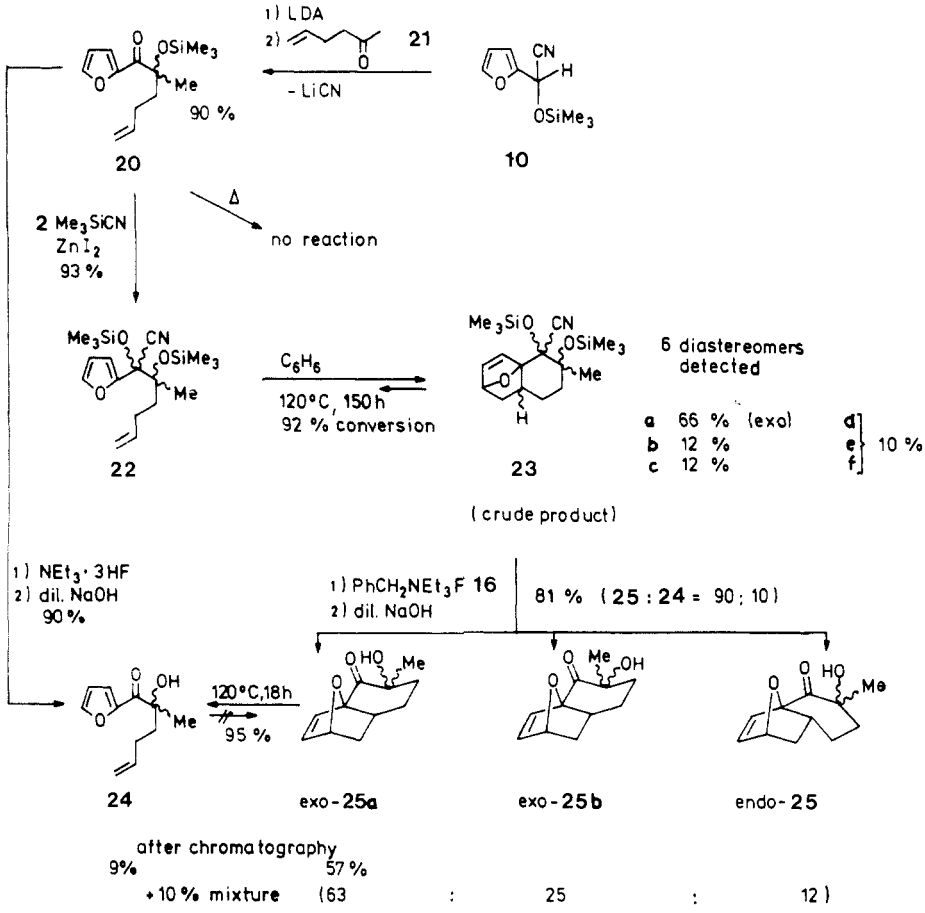
Results

Scheme I. The adduct **10** has been previously prepared in quantitative yield from furfural and trimethylsilyl cyanide, with zinc iodide as catalyst.[13] In the presence of tetrabutylammonium iodide, such additions proceed even more rapidly.[14] Deprotonation of **10** and alkylation with **11** or **12** yield the expected precursors **13** and **14**, of which only the latter undergoes cycloaddition to *exo*- and *endo*-**15** (88:12). On monitoring the reaction by ^{1}H NMR (C_6D_6), it became clear that the turnover is limited due to equilibration, which is reached at 120 °C after ca. 180 h (74% of **15**), at 150 °C after ca. 60 h (64% of **15**), and at 180 °C after ca. 24 h (41% of **15**). The preparative run with **14** (120 °C, 360 h) furnished 77% *exo*/*endo*-**15** (88:12), together with 23% starting material. **14**. After desilylation with benzyltriethylammonium fluoride **16**, which produced less side products than **8**, the isolated product (89% yield) contained the expected ketones **19** and **18** in exactly the same ratio (77:23). Moreover, the exo/endo ratio of **15** (88:12) was preserved in **19**. On flash chromatography, the product mixture yielded 23% **18** and 51% *exo*-**19**.

Scheme II. The convenient route to α-trimethylsiloxy carbonyl derivatives according to the reaction sequence **1** → **3** → **5** is equally well applicable to (hetero)aromatic aldehydes.[15] Accordingly, from **10** and 5-hexen-2-one (**21**) the acyloin derivative **20** is readily formed. As expected, neither **20** nor the acyloin **24** itself undergoes cycloaddition even on prolonged heating. After reaction with **2**, however, the protected derivative **22** undergoes intramolecular Diels–Alder reaction to **23** rather easily. Again, equilibration is observed, but compared to the reaction **14** → **15**, the equilibrium lies more on the product side and is reached definitely faster, i.e., at 120 °C in ca. 120 h (92% of **23**), at 150 °C in ca. 24 h (86% of **23**), and at 180 °C in ca. 6 h (75% of **23**). Distillation of the preparative run with **22** (120 °C, 150 h) yielded **23** and **22** in the expected 92:8 ratio. Interestingly, in the residual starting material **22**, the ratio of diastereomers had dropped from 90:10 to 70:30, indicating different cycloaddition equilibria for the diastereomeric precursors. Of the eight diastereomers expected for product **23**, six were detected by 400 MHz ^{1}H NMR, in which one exo isomer of **23** predominates (66%). After desilylation of the product mixture with **16** and flash chromatography, in addition to 9% of unreacted acyloin **24** (from **22**), 57% of a single crystalline exo isomer of the tricyclic ketone **23** could be isolated. The remaining mixture contains mostly the same *exo*-**25** (a) but definitely

(12) Cf.: Dauben, W. G.; Krabbenhoft, H. O. *J. Am. Chem. Soc.* **1974**, *96*, 3664.
(13) Deuchert, K.; Hertenstein, U.; Hünig, S.; Wehner, G. *Chem. Ber.* **1979**, *112*, 2045.
(14) Schweeberg, W. Dissertation, University of Würzburg, 1983.
(15) Hünig, S.; Wehner, G. *Chem. Ber.* **1979**, *112*, 2062.

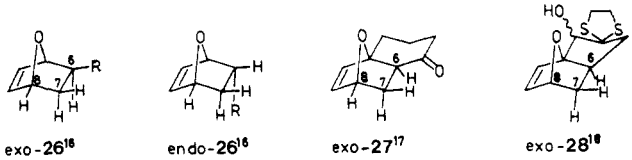
Scheme II



also one different *exo*-**25** (b), together with minor amounts of diastereomeric *endo*-**25**.

Unfortunately, an unambiguous assignment of the relative stereochemistry of the hydroxyl and methyl groups in these isomers could not be made by NMR. An attempted X-ray analysis of pure *exo*-**25** failed because of decomposition due to radiation. As expected from the cycloreversion **19** → **18** and the failure of [4 + 2] cycloaddition of **18** and **24**, the Diels–Alder products **25** cyclorevert quantitatively on heating to the acyloin **24**.

Characterization of Cycloadducts 15, 19, 23, and 25. By decoupling experiments most of the ^{1}H NMR spectra of the isomers from **15**, **19**, **23**, and **29** could be completely assigned. For the very similar cycloadducts **26**,[16] **27**,[17] and **28**,[18] the exo/endo geometry was definitively established



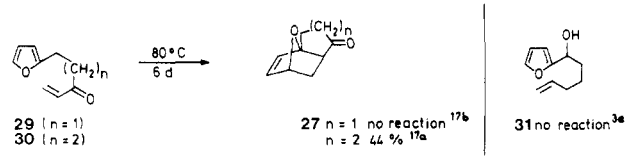
principally by means of the coupling constants of the hydrogen atoms 6-H and 7-H. The necessary differentiation between the exo and endo 7-H protons derives from their coupling constants with the 8-H proton ($J_{7\text{-exo-}8}$ = 4–5 Hz; $J_{7\text{-endo-}8}$ = 0 Hz).[16] Our data are in full accord with those values.

Discussion

The described intramolecular Diels–Alder reactions clearly demonstrate that so far inaccessible tricyclic ketones **19** and **25** can be obtained quite conveniently, which, however, undergo complete cycloreversion on heating. Even the protected derivatives **15** and **23** are not formed quantitatively from their precursors **14** and **22**. This phenomenon is well-documented for a variety of intramolecular cycloadditions involving the furan moiety.[17,19]

The thermal lability of the tricyclic ketones **19** and **25** requires an easily removable protecting group of the carbonyl function. Silylated cyanohydrins seem to be ideal for that purpose, especially since this group already introduced into furfural as in **10** provides a convenient tool for linking the diene and dienophile through umpolung.

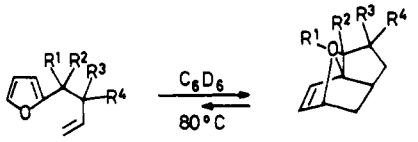
In all cases, the amount of cycloadduct formed at a certain temperature depends on the length of the tethering chain (n = 3, 2) and on its substitution pattern. It is known that a strongly activated dienophile as in **30** promotes smooth formation of the expected cycloadduct **27**[17a] (isomeric to **19**). However, for **29** no cycloaddition is



observed since a five-membered ring is to be annexed.[17b] It is, therefore, not surprising that **13**, which carries a nonactivated dienophile, does not form a cycloadduct.

(16) Nelson, W. L.; Allen, D. R. *J. Heterocycl. Chem.* **1972**, *9*, 561.
(17) (a) De Clercq, P. J.; Van Royen, L. A. *Synth. Commun.* **1979**, *9*, 771. (b) Van Royen, L. A.; Mijngheer, R.; De Clercq, P. J. *Tetrahedron Lett.* **1982**, *23*, 3283.
(18) Sternbach, D. D.; Rossana, D. M. *Tetrahedron Lett.* **1982**, *23*, 303.
(19) Gschwend, H. W.; Hillman, M. J.; Kisis, B.; Rodebaugh, R. K. *J. Org. Chem.* **1976**, *41*, 104.

Most remarkably, rather similar precursors lead to the expected cycloadducts with a new five-membered ring if appropriate substituents in the 2-position of the linking chain are present.



32 33

compd	R^1	R^2	R^3	R^4	33[a] % yield
32a[18]	CH_3	OH	H	H	0
b[20]	H	OH	CH_3	CH_3	<5
c[20]	H	OH	*n*-Pr	*n*-Pr	58
d[20]	H	OH	SEt	SEt	85
e[21]	H	H	CO_2Et	CO_2Et	40

[a] Turnover after equilibration (48–330 h).

The transformation **32** → **33** sheds some light on our findings. Whereas substituents at C-1 display no effect (**32a**,[18] **32b**[20]) and may even be absent (**32e**[21]), a remarkably strong gem effect at C-2 is observed, although only with rather bulky substituents (**32d,e**). *gem*-Dimethyl groups, which normally facilitate intramolecular Diels–Alder reactions,[19] are nearly ineffective in **32b**. This may be a reflection of the fact that the buttressing effect of these groups provides only a small incremental change in the ΔS^+ for a reaction that has an inherently large negative ΔS^+.[22] Since the increase in equilibration constants parallels the increase in rates of cycloaddition, the substituent effect presumably acts on the ground state, providing a higher population of the appropriate rotamers in the starting material.[20]

These arguments can be adopted to explain the higher equilibrium constants and cycloaddition rates of **22** compared to **14**. However, the number of new gauche interactions produced in the transition state may also be of importance as it has generally been stated for developing six-membered rings.[23]

These interactions may be reinforced also by substituents at C-1 of the linking chain. This would explain the high conversion of **14** to **15** compared to **31**, which is reported to refuse intramolecular cycloaddition.

Of the intramolecular [4 + 2] cyclization products containing a furan moiety, only the exo isomers are reported[3e] (e.g., **27**, **28**, **33**). In these mobile cycloaddition equilibria,[17,19] presumably the exo isomers are thermodynamically more favored. For **19** and **25** we observe for the first time small amounts of endo isomers, which seem to be only 1.5–2 kcal/mol less stable than their exo counterparts.

Conclusion

Umpolung of furfural with trimethylsilyl cyanide (**2**) and reaction with suitable olefinic alkylating agents (Scheme I) create the linking chain between the diene and the dienophile moiety, providing simultaneous protection of the carbonyl function and activation of the diene. For carbonyl compounds as electrophiles (Scheme II), a subsequent treatment with **2** is necessary for the intramolecular Diels–Alder reaction to proceed. The products of type **14** and **22** can easily be equilibrated in high yield with their intramolecular [4 + 2] cyclization products **15** and **23**. Desilylation of **15** or **23** with fluoride ions requires only very mild and chemoselective conditions. The novel tricyclic ketones **19** and **25** can, therefore, be isolated without any cycloreversion to the furan derivatives **18** and **24**, which are quantitatively formed on heating. On the basis of reported substituent effects for derivatives of **32**, it can be expected that in the models discussed the linking chain can be shortened from four to three carbon atoms without losing the propensity of intramolecular cycloadditions, provided the central atom of the chain is suitably substituted.

Experimental Section

Melting points, taken on a Kofler microscope, are corrected. Boiling points correspond to the oven temperature of a Büchi Kugelrohr apparatus. IR spectra were run on a Beckman Acculab 4 spectrometer and ^1H NMR spectra at 90 MHz on a Varian EM 390 spectrometer and at 400 MHz or ^{13}C NMR spectra at 100.6 MHz on a Bruker WM 400 spectrometer. Known compounds were either purchased from commercial suppliers or prepared according to published methods and purified to match reported physical constants and spectral data. All metalation reactions were performed in dry solvents under nitrogen and with magnetic stirring.

2-(2-Furyl)-2-(trimethylsiloxy)-5-hexenenitrile (13). A solution of 4.88 g (25.0 mmol) of 2-(2-furyl)-2-(trimethylsiloxy)-acetonitrile (**10**)[13] in 5 mL of THF was slowly added to 28 mmol of LDA in 25 mL of THF at −78 °C, followed after 30 min by 4.88 g (25.0 mmol) of 4-bromobutene-1 (**11**) in 5 mL of THF. After the reaction mixture had reached room temperature (5–6 h), it was quenched by the addition of 20 mL of saturated NH_4Cl solution. The aqueous phase was extracted with 3 × 10 mL of petroleum ether. The combined organic phases were extracted with aqueous NH_4Cl solution and dried over $MgSO_4$, and the solvent was removed in vacuo. The oily residue (6.02 g (97%)) gave on distillation 5.61 g (90%) of **13**: bp 60–65 °C (0.1 Torr); IR (film) 3150, 3120, 3080, 1635, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.07 (s, 9 H, OSi*Me*$_3$), 2.18 (m, 4 H, 3-H, 4-H), 4.92–5.13 (m, 2 H, 6-$H_{a/b}$), 5.78 (m, 1 H, $J_{5,6a}$ = 17.10 Hz, $J_{5,6b}$ = 9.60 Hz, 5-H), 6.37 (dd, 1 H, $J_{4',3'}$ = 3.30 Hz, $J_{4',5'}$ = 1.80 Hz, 4-H), 6.52 (dd, 1 H, $J_{3',5'}$ = 1.20 Hz, 3-H), 7.42 (dd, 1 H, 5-H). Anal. Calcd for $C_{13}H_{19}NO_2Si$ (249.4): C, 62.61; H, 7.68; N, 5.62. Found: C, 62.69; H, 7.98; N, 5.44.

2-(2-Furyl)-2-(trimethylsiloxy)-6-heptenenitrile (14). By a procedure as for **13**, 3.91 g (20.0 mmol) of **10**,[13] 22 mmol of LDA, and 3.28 g (22 mmol) of 5-bromoheptene-1 (**12**) yielded 4.48 g (85%) of **14**: bp 70–75 °C (0.1 Torr); IR (film) 3140, 3110, 3060, 1640, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.12 (s, 9 H, OSi*Me*$_3$), 1.25–1.92 (m, 4 H, 3-H, 4-H), 2.12 (q, 2 H, $J_{5,6}$ = $J_{5,4}$ = 6.30 Hz, 5-H), 4.88–5.12 (m, 2 H, 7-$H_{a/b}$), 5.77 (ddt, 1 H, $J_{6,7a}$ = 17.10 Hz, $J_{6,7b}$ = 9.60 Hz, 6-H), 6.37 (dd, 1 H, $J_{4',3'}$ = 3.30 Hz, $J_{4',5'}$ = 1.80 Hz, 4-H), 6.52 (d, 1 H, 3-H), 7.42 (dd, 1 H, $J_{5',3'}$ = 1.10 Hz, 5-H). Anal. Calcd for $C_{14}H_{21}NO_2Si$ (263.4): C, 63.84; H, 8.04; N, 5.32. Found: C, 63.72; H, 8.28; N, 5.24.

1-(2-Furyl)-4-penten-1-one (17). A solution of 1.78 g (7.14 mmol) of **13** and 1.15 g (7.14 mmol) of $NEt_3 \cdot 3HF$[9] (**8**) in 15 mL of THF was stirred at room temperature for 1 h. After addition of 10 mL of H_2O and 30 mL of ether, the organic phase was separated and extracted with 2 × 5 mL of 1 N NaOH. The organic layer was washed with saturated NH_4Cl solution, dried, and evaporated. From the residue (1.05 g (98%)) was distilled 940 mg (88%) of **17**: bp 80 °C (0.5 Torr); IR (film) 3140, 3080, 1670, 1635, 1560 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.40 (m, 2 H, 3-H), 2.87 (mc, 2 H, $J_{2,3}$ = 7.00 Hz, 2-H), 4.87–5.12 (m, 5-$H_{a/b}$), 5.82 (ddt, 1 H, $J_{4,5a}$ = 17.10 Hz, $J_{4,5b}$ = 9.90 Hz, $J_{4,3}$ = 6.30 Hz, 4-H), 6.47 (dd, 1 H, $J_{4',3'}$ = 3.60 Hz, $J_{4',5'}$ = 1.80 Hz, 4-H), 7.08 (d, 1 H, 3-H), 7.52 (dd, 1 H, $J_{5',3'}$ = 1.10 Hz, 5-H). Anal. Calcd for $C_9H_{10}O_2$ (150.2): C, 71.99; H, 6.71. Found: C, 71.24; H, 6.61.

1-(2-Furyl)-5-hexen-1-one (18). By a procedure as for **17**, 1.58 g (6.00 mmol) of **14** and 0.97 g (6.00 mmol) of **6** yielded 890 mg (90%) of **32**: bp 75 °C (0.1 Torr); IR (film) 3140, 3080, 1680, 1640, 1570 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.00 (m, 4 H, 3-H, 4-H),

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(21) Parker, K. A.; Adamchuk, M. R. *Tetrahedron Lett.* **1978**, *19*, 1689.
(22) (a) Boeckman, R. K., Jr.; Koo, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1033. (b) Gschwend, H. W.; Lee, A. D.; Meier, H.-P. *J. Org. Chem.* **1973**, *38*, 2169.
(23) (a) Allinger, N. L.; Zalkow, V. *J. Org. Chem.* **1960**, *25*, 701. (b) Dale, J. *J. Chem. Soc.* **1963**, 93.

2.85 (t, 2 H, $J_{2,3}$ = 7.20 Hz, 2-H), 4.90–5.12 (m, 2 H, 6-$H_{a/b}$), 5.83 (m, 1 H, $J_{5,6a}$ = 17.10 Hz, $J_{5,6b}$ = 9.60 Hz, $J_{5,4}$ = 6.30 Hz, 5-H), 6.53 (dd, 1 H, $J_{4',3'}$ = 3.60 Hz, $J_{4',5'}$ = 1.80 Hz, 4-H), 7.18 (d, 1 H, 3-H), 7.57 (dd, 1 H, $J_{5',3'}$ = 1.10 Hz, 5-H). Anal. Calcd for $C_{10}H_{12}O_2$ (164.2): C, 73.15; H,m 7.37. Found: C, 72.90; H, 7.76.

***exo*- and *endo*-2-Cyano-2-(trimethylsiloxy)-11-oxatricyclo[6.2.1.0^{1,6}]-9-undecene (*exo*-15/*endo*-15 Mixture of Diastereomers).** In a sealed tube, 2.54 g (9.64 mmol) of **14** in 9.7 mL of benzene and a trace of hydroquinone were heated for 360 h at 120 °C. After evaporation of the solvent, the brown residue yielded 2.43 g (96%) (bp 75 °C (0.5 Torr)) of a 77:21:2 mixture of **15**, **14**, and **18** (^{1}H NMR (C_6D_6, 400 MHz)) as a colorless liquid. Compound **15** consisted of 88% exo and 12% endo isomers as diastereomers a/b: *exo*-**15** (65:35), *endo*-**15** (67:33). The mixture was desilylated without further purification. ^{1}H NMR (C_6D_6, 400 MHz): *exo*-**15a** δ 0.32 (s, 9 H, 2-OSi*Me*$_3$), 1.04–1.20, 1.47–2.27 (m, 7 H, $J_{6\text{-endo},7\text{-endo}}$ = 6.65 Hz, $J_{6\text{-endo},7\text{-exo}}$ = 2.35, 3-H–6-H), 1.26 (*AB*, 1 H, $J_{7\text{-exo},8}$ = 4.40 Hz, 7-H_{exo}), 1.31 (*AB*, 1 H, $J_{7\text{-endo},7\text{-exo}}$ = 11.10 Hz, $J_{7\text{-endo},8}$ = 0 Hz, 7-H_{endo}), 4.71 (dd, 1 H, $J_{8,9}$ = 1.65 Hz, 8-H), 6.11 (dd, 1 H, $J_{9,10}$ = 5.70 Hz, 9-H), 6.44 (d, 1 H, 10-H); *exo*-**15b** δ 0.36 (s, 9 H, 2-OSi*Me*$_3$), 1.04–1.20, 1.47–2.27 (m, 7 H, $J_{6\text{-endo},7\text{-endo}}$ = 7.05 Hz, $J_{6\text{-endo},7\text{-exo}}$ = 2.10 Hz, 3-H–6-H), 1.28 (*AB*, 1 H, $J_{7\text{-exo},8}$ = 4.50 Hz, 7-H_{exo}), 1.34 (*AB*, 1 H, $J_{7\text{-endo},7\text{-exo}}$ = 11.05 Hz, $J_{7\text{-endo},8}$ = 0 Hz, 7-H_{endo}), 4.79 (dd, 1 H, $J_{8,9}$ = 1.7 Hz, 8-H), 6.21 (dd, 1 H, $J_{9,10}$ = 5.80 Hz, 9-H), 6.35 (d, 1 H, 10-H); *endo*-**15a** δ 0.42 (s, 9 H, 2-OSi*Me*$_3$) 1.04–1.20, 1.47–2.27 (m, 7 H, 3-H–6-H), 4.67 (dd, 1 H, $J_{8,9}$ = 1.80 Hz, 8-H), 6.18 (dd, 1 H, $J_{9,10}$ = 5.85 Hz, 9-H), 5.96 (d, 1 H, 10-H); *endo*-**15b** δ 0.43 (s, 9 H, 2-OSi*Me*$_3$), 1.04–1.20, 1.47–2.27 (m, 7 H, 3-H–6-H), 4.65 (dd, 1 H, $J_{8,9}$ = 1.80 Hz, 8-H), 6.27 (dd, 1 H, $J_{9,10}$ = 5.80 Hz, 9-H), 5.94 (d, 1 H, 10-H). The resonances 7-H_{exo} and 7-H_{endo} of *endo*-**15a**/**b** are covered by resonances of the exo isomers. ^{13}C NMR (C_6D_6, 100 MHz): *exo*-**15a** δ 1.91 (q, 3 C, 2-OSi*Me*$_3$), 23.33 (t, C-4), 36.30 (d, C-6), 73.78 (s, C-2; exchangeable for C-2 of *exo*-**15b**, 79.59 (d, C-8), 90.15 (s, C-1), 120.99 (s, 2-CN), 134.38 (d, C-9), 138.25 (d, C-10); *exo*-**15b** δ 1.20 (q, 3 C, 2-OSi*Me*$_3$), 25.78 (t, C-4), 32.94 (d, C-6), 70.10 (s, C-2), 79.74 (d, C-8), 88.48 (s, C-1), 120.48 (s, 2-CN), 133.77 (d, C-9), 138.74 (d, C-10); *endo*-**15a** δ 1.63 (q, 3 C, 2-OSi*Me*$_3$), 24.39 (t, C-4), 39.92 (d, C-6; exchangeable for C-6 of *endo*-**15b**), 73.38 (s, C-2), 79.00 (d, C-8), 91.94 (s, C-1), 119.57 (s, 2-CN), 130.50 (d, C-9), 138.86 (d, C-10); *endo*-**15b** δ 1.40 (q, 3 C, 2-OSi*Me*$_3$), 21.51 (t, C-4), 39.79 (d, C-6), 131.76 (d, C-9), 140.19 (d, C-10). Resonances of C-1, C-2, C-8, and C-10 of *endo*-**15b** are hidden or have too low intensities to be observed.

1-(2-Furyl)-5-hexen-1-one (18), (1*R,6*S**,8*R**)-11-Oxatricyclo[6.2.1.0^{1,6}]-9-undecen-2-one (*exo*-19), and (1*R**,6*R**,8*R**)-11-Oxatricyclo[6.2.1.0^{1,6}]-9-undecen-2-one (*endo*-19).** The mixture from the preceding experiment (890 mg, 3.38 mmol) was allowed to react with 572 mg (3.38 mmol) of BTAF (**16**) in 7 mL of CH_2Cl_2 for 1 h. After addition of 10 mL of CH_2Cl_2 and 5 mL of H_2O, the mixture was stirred with 5 mL of 1 N NaOH for 5 min. The organic layer was washed with saturated NH_4Cl solution, dried, and evaporated. The resulting yellow oil (500 mg (89%)) contained **18**, *exo*-**19**, and *endo*-**19** in the ratio 32:68:9 (^{1}H NMR (C_6D_6, 400 MHz)). Flash chromatography of 300 mg on silica gel (SiO_2 Woelm 32–63 μm, CH_2Cl_2) yielded two fractions. Fraction 1: 110 mg of colorless liquid from which 75.0 mg (23%) of **18** was distilled, bp 65 °C (0.1 Torr), identical (^{1}H NMR, IR) with product **18** described above; ^{13}C NMR (C_6D_6, 400 MHz) δ 23.29 (t, C-3), 33.37 (t, C-4), 37.67 (t, C-2), 112.08, 115.91 (d, C-3, C-4), 115.17 (t, C-6), 138.26 (d, C-5), 145.56 (d, C-5), 153.67 (s, C-2), 188.39 (s, C-1). Fraction 2: 200 mg of colorless liquid. Kugelrohr distillation furnished 170 mg (51%) of *exo*-**19**: bp 65 °C (0.1 Torr); IR (film) 3090, 1720 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.29 (*AB*, 1 H, $J_{7\text{-endo},7\text{-exo}}$ = 10.95 Hz, $J_{7\text{-endo},8}$ = 0 Hz, 7-H_{endo}), 1.35 (*AB*, 1 H, $J_{7\text{-exo},8}$ = 4.30 Hz, 7-H_{exo}), 1.38–1.50 (m, 2 H, 4-H), 1.60–1.74 (m, 3 H, $J_{6\text{-endo},7\text{-endo}}$ = 6.90 Hz, $J_{6\text{-endo},7\text{-exo}}$ = 2.50 Hz, 5-H, 6-H_{endo}), 4.41 (mc, 1 H, $J_{3\text{-eq},4\text{-ax.}}$ = 3.20 Hz, $J_{3\text{-eq},4\text{-eq.}}$ = 3.20 Hz, $J_{3\text{-eq},5\text{-eq}}$ = 1.60 Hz, 3-H_{eq}), 2.57 (mc, 1 H, $J_{3\text{-ax.},3\text{-eq}}$ = 13.50 Hz, $J_{3\text{-ax.},4\text{-ax.}}$ = 13.50 Hz, $J_{3\text{-ax.},4\text{-eq}}$ = 5.15 Hz, 3-H_{ax}), 4.82 (dd, 1 H, $J_{8,9}$ = 1.65 Hz, 8-H), 6.08 (dd, 1 H, $J_{9,10}$ = 5.80 Hz, 9-H), 6.60 (d, 1 H, 10-H); ^{13}C NMR (C_6D_6, 100 MHz) δ 27.12 (t, C-4), 31.45 (t, C-5; exchangeable for C-7), 36.10 (t, C-7), 40.55 (t, C-3), 42.29 (d, C-6), 80.61 (d, C-8), 90.38 (s, C-1), 132.75 (d, C-9), 137.31 (d, C-10), 205.94 (s, C-2). Anal. Calcd for $C_{10}H_{12}O_{12}$ (164.2): C, 73.15; H, 7.37. Found: C, 73.04; H, 7.58.

With these data at hand, the following signals of the product mixture can be attributed to *endo*-**19**: ^{1}H NMR (C_6D_6, 400 MHz) δ 4.71 (dd, 1 H, $J_{8,7\text{-exo}}$ = 4.25 Hz, $J_{8,7\text{-endo}}$ = 0 Hz, $J_{8,9}$ = 1.80 Hz, 8-H), 5.90 (d, 1 H, $J_{10,9}$ = 5.65 Hz, 10-H), 6.19 (dd, 1 H, 9-H); ^{13}C NMR (C_6D_6, 100 MHz) δ 28.05, 29.46, 30.97 (t, C-4, C-5, C-7), 40.10 (t, C-3), 45.68 (d, C-6), 78.99 (d, C-8), 91.80 (s, C-1), 132.03 (d, C-9), 138.68 (d, C-10).

***Formation of* 18 *by Cycloreversion of exo*-19.** In a sealed NMR tube, 110 mg (0.67 mmol) of *exo*-**19** in 0.5 mL of C_6D_6 were heated at 120 °C until the ^{1}H NMR signals of *exo*-**19** had disappeared. After evaporation of the solvent, 102 mg (93%) of **18** (IR, ^{1}H NMR) were obtained on distillation, bp 70 °C (0.1 Torr).

1-(2-Furyl)-2-methyl-2-(trimethylsiloxy)-5-hexen-1-one (20). In 15 mL of THF, 5.86 g (30.0 mmol) of **10**[13] were lithiated with 30.0 mmol of LDA in THF at 78 °C. After 30 min, 2.94 g (30.0 mmol) of 5-hexene-2-one (**21**) in 15 mL of THF was slowly added. After reaching 0 °C (ca. 6 h), the reaction mixture was treated with 30 mL of saturated NH_4Cl solution and worked up as described for **13**. From 8.28 g of an orange oil was isolated 7.17 g (90%) of **20** by fractional distillation: bp 91–92 °C (0.04 Torr); IR (film) 3140, 3080, 1670, 1640, 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.18 (s, 9 H, 2-OSi*Me*$_3$), 1.55 (s, 3 H, 2-C*H*$_3$), 1.62–2.22 (m, 4 H, 3-H, 4-H), 4.82–5.03 (m, 2 H, 6-$H_{a/b}$), 5.72 (mc, 1 H, $J_{5,6a}$ = 17.10 Hz, $J_{5,6b}$ = 10.20 Hz, 5-H), 6.47 (dd, 1 H, $J_{4,3}$ = 3.60 Hz, $J_{4',5'}$ = 1.80 Hz, 4-H), 7.42 (d, 1 H, 3-H), 7.57 (dd, 1 H, $J_{5',3'}$ = 1.10 Hz, 5-H). Anal. Calcd for $C_{14}H_{22}O_3Si$ (266.4): C, 63.12; H, 8.32. Found: C, 63.33; H, 8.54.

1-(2-Furyl)-2-hydroxy-2-methyl-5-hexen-1-one (24). In 10 mL of THF, 870 mg (5.39 mmol) of **6** and 1.30 g (4.88 mmol) of **20** were reacted for 1 h. After addition of 5 mL of water and 20 mL of ether, the organic phase was separated, washed with water, dried, and evaporated. The crude product (980 mg) yielded 850 mg (90%) of **24**: bp 90 °C (0.01 Torr); IR (film) 3460, 3140, 3080, 1650, 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.52 (s, 3 H, 2-C*H*$_3$), 1.75–2.22 (m, 4 H, 3-H, 4-H), 3.97 (s, 1 H, 2-O*H*), 4.80–5.00 (m, 2 H, 6-$H_{a/b}$), 5.72 (mc, 1 H, $J_{5,6a}$ = 17.10 Hz, $J_{5,6b}$ = 10.20 Hz, 5-H), 6.55 (dd, 1 H, $J_{4',3'}$ = 3.60 Hz, $J_{4',5'}$ = 1.80 Hz, 4'-H), 7.37 (d, 1 H, 3'-H), 7.63 (dd, 1 H, $J_{5',3'}$ = 1.10 Hz, 5'-H). Anal. Calcd for $C_{11}H_{14}O_3$ (194.2): C, 68.02; H, 7.27. Found: C, 67.82; H, 7.48.

2,3-Bis(trimethylsiloxy)-2-(2-furyl)-3-methyl-6-heptenenitrile (22). A mixture of 4.53 g (17.0 mmol) of **20**, 1.86 g (18.7 mmol) of trimethylsilyl cyanide, and catalytic amounts of ZnI_2 was allowed to react for 24 h at room temperature, affording 5.75 g (93%) of **22** (diastereomers 90:10): bp 90 °C (0.02 Torr); IR (film) 3140, 3110, 3070, 1640, 1495 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) **22a** (90% diastereomer) δ 0.23 (s, 9 H, 3-OSi*Me*$_3$), 0.33 (s, 9 H, 2-OSi*Me*$_3$), 1.55 (*AB*, 1 H, $J_{4a,4b}$ = 13.45 Hz, $J_{4a,5}$ = 11.55 Hz, 5.55 Hz, 4-H_a), 1.57 (s, 3-CH_3), 1.88 (*AB*, 1 H, $J_{4b,5}$ = 11.45 Hz, 5.25 Hz, 4-H_b), 2.22 (mc, 2 H, $J_{5,6}$ = 6.65 Hz, $J_{5,7a}$ = 1.60 Hz, $J_{5,7b}$ = 1.10 Hz, 5-H), 5.01 (mc, 1 H, 7-H_b), 5.09 (mc, 1 H, $J_{7a,7b}$ = 1.75 Hz, 7-H_a), 5.79 (ddt, 1 H, $J_{6,7a}$ = 17.00 Hz, $J_{6,7b}$ = 10.20 Hz, 6-H), 6.11 (dd, 1 H, $J_{4',5'}$ = 1.80 Hz, 4'-H), 6.56 (dd, 1 H, $J_{3',4'}$ = 3.30 Hz, $J_{3',4}$ = 0.75 Hz, 3'-H), 7.07 (dd, 1 H, 5'-H); **22b** (10% diastereomer) δ 0.19 (s, 9 H, 3-OSi*Me*$_3$), 0.22 (s, 9 H, 2-OSi*Me*$_3$), 1.42 (s, 1 H, 3-CH_3), 2.36 (mc, 2 H, $J_{5,6}$ = 6.65 Hz, $J_{5,7a}$ = 1.60 Hz, $J_{5,7b}$ = 1.15 Hz, 5-H), 5.05 (mc, 1 H, 7-H_b), 5.16 (mc, 1 H, $J_{7a,7b}$ = 1.75 Hz, 7-H_a), 5.86 (ddt, 1 H, $J_{6,7a}$ = 17.15 Hz, $J_{6,7b}$ = 10.25 Hz, 6-H), 6.13 (dd, 1 H, $J_{4',5'}$ = 1.80 Hz, 4'-H), 6.57 (dd, 1 H, $J_{3',4'}$ = 3.35 Hz, $J_{3',4'}$ = 0.75 Hz, 3'-H), 7.10 (dd, 1 H, 5'-H); ^{13}C NMR (C_6D_6, 100 MHz) **22a** (90% diastereomer) δ 0.93 (q, 3 C, 3-OSiMe_3), 3.17 (q, 3 C, 2-OSiMe_3), 22.46 (q, 3-CH_3), 29.19 (t, C-4), 38.33 (t, C-5), 79.87 (s, C-3, exchangeable for C-2), 81.94 (s, C-2), 111.45 (d, C-4 Anal. Calcd for $C_{18}H_{31}NO_3Si_2$ (356.6): C, 59.13; H, 8.55; N, 3.83. Found: C, 59.16; H, 8.56; N, 4.15.

2,3-Bis(trimethylsiloxy)-2-cyano-3-methyl-11-oxatricyclo[6.2.1.0^{1,6}]-9-undecene (23) (diastereomers). In 8.5 mL of benzene, 3.07 g (3.41 mmol) of **22** and a trace of hydroquinone were heated for 150 h at 120 °C, yielding 2.90 g (94%) of a colorless liquid, bp 75 °C (0.05 Torr), containing **23** and **22** (92:8, ^{1}H NMR). The mixture was desilylated without purification. ^{1}H NMR (C_6D_6, 400 MHz): **23a** (66% diastereomer) δ 0.30, 0.43 (s, 18 H, 2/3-OSi*Me*$_3$), 1.23 (AB, 1 H, $J_{7\text{-exo},8}$ = 4.65 Hz, 7-H_{exo}), 1.32 (*AB*, 1 H, $J_{7\text{-endo},7\text{-exo}}$ = 11.20 Hz, $J_{7\text{-endo},8}$ = 0 Hz, 7-H_{endo}), 1.54 (s, 3 H, 3-C*H*$_3$), 1.63–1.75 (m, 3 H, $J_{6\text{-endo},7\text{-endo}}$ = 7.25 Hz, $J_{6\text{-endo},7\text{-exo}}$ = 2.65 Hz, 5-H, 6-H), 1.82 (ddt, 1 H, $J_{4\text{-eq},5\text{-ax.}}$ = 3.50 Hz, $J_{4\text{-eq},5\text{-eq}}$ = 3.50 Hz, 4-H_{eq}), 2.12 (ddt, 1 H, $J_{4\text{-ax.},4\text{-eq}}$ = 13.55 Hz, $J_{4\text{-ax.},5\text{-ax.}}$ = 13.70

Hz, $J_{4\text{-ax.},5\text{-eq}}$ = 3.70 Hz, 4-$H_{ax.}$), 4.68 (dd, 1 H, $J_{8,9}$ = 1.65 Hz, 8-H), 6.11 (dd, 1 H, $J_{9,10}$ = 5.75 Hz, 9-H), 6.50 (d, 1 H, 10-H); **23b** (12% diastereomer) δ 0.26 (s, 18 H, 2/3-OSiMe_3), 1.58 (s, 3 H, 3-CH_3), 4.77 (dd, 1 H, $J_{8,9}$ = 1.85 Hz, 8-H), 6.18 (dd, 1 H, $J_{9,10}$ = 5.85 Hz, 9-H), 6.34 (d, 1 H, 10-H); **23c** (12% diastereomer) δ 0.40 (s, 18 H, 2/3-OSiMe_3), 1.49 (s, 3 H, 3-CH_3), 4.65 (dd, 1 H, $J_{8,9}$ = 1.60 Hz, 8-H), 6.37 (dd, 1 H, $J_{9,10}$ = 5.75 Hz, 9-H), 6.75 (d, 1 H, 10-H); **23d–f** (10% three diastereomers) δ 0.27, 0.287, 0.295, 0.42, 0.46 (s, 18 H, 2/3-OSiMe_3), 4.75 (dd, 1 H, $J_{8,9}$ = 1.65 Hz, 1.75 Hz, 1.65 Hz, 8-H), 6.08, 6.26 (dd, 1 H, $J_{9,10}$ = 5.75 Hz, 5.75 Hz, 5.75 Hz, 9-H), 6.44, 6.45, 6.63 (d, 1 H, 10-H).

1-(2-Furyl)-2-hydroxy-2-methyl-5-hexen-1-one (24), (1*R,6*S**,8*R**)-3-Hydroxy-3-methyl-11-oxatricyclo-[6.2.1.$0^{1,6}$]-9-undecen-2-one (*exo*-25a and *exo*-25b), and (1*R**,6*R**,8*R**)-3-Hydroxy-3-methyl-11-oxatricyclo-[6.2.1.$0^{1,6}$]-9-undecen-2-one (*endo*-25).** The product mixture of **23** and **22** (1.03 g, 2.82 mmol) was treated with 954 mg (5.64 mmol) of BTAF in 6 mL of CH_2Cl_2 for 1 h. Workup similar to that for **19** yielded 445 mg (81%) of **25/24**, 90:10 (^{1}H NMR). Flash chromatography (SiO_2 Woelm 32–63 m, CH_2Cl_2, after the first two fractions acetone). Fraction 1: 36 mg (9%) of **24** (IR, ^{1}H NMR). Fraction 2: 225 mg of *exo*-**25a** (55%), colorless crystals, mp 48–49 °C. Fraction 3: 40 mg (10%) of a mixture of *exo*-**25a**, *exo*-**25b**, and *endo*-**25** (63:25:12, ^{1}H NMR, 400 MHz). *exo*-**25a**: IR (film) 3540, 3090, 1720 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.22 (AB, 1 H, $J_{7\text{-endo},7\text{-exo}}$ = 11.10 Hz, $J_{7\text{-endo},8}$ = 0 Hz, 7-H_{endo}), 1.28 (A*B*, 1 H, $J_{7\text{-exo},8}$ = 4.30 Hz, 7-H_{exo}), 1.44–1.52 (m, 2 H, 5-$H_{ax.}$, 5-H_{eq}), 1.58–1.69 (m, 1 H, $J_{6\text{-endo},7\text{-endo}}$ = 7.00 Hz, $J_{6\text{-endo},7\text{-exo}}$ = 2.65 Hz, 4-H_{eq}, 6-H_{endo}), 1.63 (s, 3 H, 3-CH_3), 1.84 (dt, 1 H, $J_{4\text{-ax.},4\text{-eq}}$ = 12.60 Hz, $J_{4\text{-ax.},5\text{-ax.}}$ = 13.85 Hz, $J_{4\text{-ax.},5\text{-eq}}$ = 3.20 Hz, 4-$H_{ax.}$), 2.07 (dd, 1 H, $J_{4\text{-eq},5\text{-ax.}}$ = 3.75 Hz, $J_{4\text{-eq},5\text{-eq}}$ = 3.0 Hz, 4-H_{eq}), 4.20 (s, 1 H, 3-O*H*), 4.77 (dd, 1 H, $J_{8,9}$ = 1.65 Hz, 8-H), 6.02 (dd, 1 H, $J_{9,10}$ = 5.85 Hz, 9-H), 6.56 (d, 1 H, 10-H); ^{13}C NMR (C_6D_6, 100 MHz) δ 23.95 (t, 3-CH_3), 28.29 (t, C-5, exchangeable for C-7), 35.79 (t, C-7), 41.87 (t, C-4), 43.08 (d, C-6), 77.25 (s, C-3), 81.04 (d, C-8), 90.50 (s, C-1), 133.21 (d, C-9), 136.81 (d, C-10), 209.45 (s, C-2).

With these data at hand, the following signals of the product mixture were assigned: ^{1}H NMR (C_6D_6, 400 MHz) *exo*-**25b** δ 1.15 (mc, 1 H, $J_{7\text{-endo},7\text{-exo}}$ = 10.95 Hz, $J_{7\text{-endo},6\text{-endo}}$ = 7.00 Hz, $J_{7\text{-endo},8}$ = 0 Hz, 7-H_{endo}), 1.58 (s, 3 H, 3-CH_3), 4.74 (dd, 1 H, $J_{8,7\text{-exo}}$ = 4.60 Hz, $J_{8,9}$ = 1.85 Hz, 8-H), 6.27 (dd, 1 H, $J_{9,10}$ = 5.70 Hz, 9-H), 6.96 (d, 1 H, 10-H); ^{13}C NMR (C_6D_6, 100 MHz) *exo*-**25b** δ 24.89 (q, 3-CH_3), 25.78, 31.50 (t, C-5, C-7), 46.05 (d, C-6), 77.13 (s, C-3), 78.55 (d, C-8), 134.11 (d, C-9), 138.31 (d, C-10); ^{1}H NMR (C_6D_6, 400 MHz) *endo*-**25** δ 1.44 (s, 3 H, 3-CH_3), 4.67 (dd, 1 H, $J_{8,7\text{-exo}}$ = 4.50 Hz, $J_{8,9}$ = 1.75 Hz, 8-H), 5.94 (dd, 1 H, $J_{9,10}$ = 5.85 Hz, 9-H), 6.59 (d, 1 H, 10-H); ^{13}C NMR (C_6D_6, 100 MHz) *endo*-**25** δ 23.05 (q, 3-CH_3), 26.47, 36.05 (t, C-5, C-7), 41.53 (t, C-4), 42.88 (d, C-6), 81.83 (d, C-8), 132.46 (d, C-9).

Formation of 24 by Cycloreversion of *exo*-25a. Compound *exo*-**25a** (110 mg, 0.57 mmol) in 0.45 mL of C_6D_6 was treated as described for *exo*-**19**, yielding 105 mg (95%) of **24**, bp 85 °C (0.01 Torr) (IR, ^{1}H NMR). Anal. Calcd for $C_{11}H_{14}O_3$ (194.2): C, 68.2; H, 7.26. Found: C, 68.04; H, 7.49.

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Registry No. **8**, 73602-61-6; **10**, 40861-56-1; **11**, 5162-44-7; **12**, 1119-51-3; **13**, 106161-85-7; **14**, 106161-86-8; *exo*-**15a**, 106247-63-6; *endo*-**15a**, 106161-82-4; *exo*-**15b**, 106247-64-7; *endo*-**15b**, 106247-62-5; **17**, 59304-43-7; **18**, 106161-87-9; *exo*-**19**, 106247-65-8; *endo*-**19**, 106161-83-5; **20**, 106191-38-2; **21**, 109-49-9; **22a**, 106161-88-0; **22b**, 106161-84-6; **23**, 106161-89-1; **24**, 106161-90-4; *exo*-**25a**, 106161-91-5; *exo*-**25b**, 106247-66-9; *endo*-**25**, 106247-67-0; TMSCN, 7677-24-9; Furfural, 98-01-1.

Two Approaches to Angularly Fused Triquinanes via Intramolecular Pauson–Khand Cyclization

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The Pauson–Khand reaction has been used to form angularly fused triquinanes via the cyclization of derivatives of 1-(4-pentynyl)cyclopentene in the presence of $Co_2(CO)_8$. Precursor enynes were prepared in two ways: the key to the first method involved addition of 1,4-bis-Grignard reagents to butyrolactone, while the second utilized addition of regioselectively prepared 5-methyl-1-cyclopentenyllithium to a suitable substrate. Tri- but not tetrasubstituted alkenes could be induced to cyclize. Extensive NMR analyses of the products allowed determination of product stereochemistry and generalization of some useful spectroscopic characteristics of these compounds.

Introduction

Interest in the intramolecular Pauson–Khand reaction[1] as a route to polycyclopentanoid intermediates for natural product synthesis has increased dramatically in the past several years. Syntheses of bicyclo[3.3.0]octanes,[2] tricyclo[6.3.0.$0^{1,5}$]undecanes,[3] tricyclo[5.2.1.$0^{4,10}$]undecanes,[4] and heteroatom-containing analogues[5] using this methodology[6] have been reported. We describe herein two simple approaches toward cyclization precursors for angularly fused triquinanes (tricyclo[6.3.0.$0^{1,5}$]undecanes). The first affords the unsubstituted ring system in only four steps from

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