hexane, 1:1); $[\alpha]^{21}_D$ −65° (c 7.65 × 10^{-3}, CH_2Cl_2); IR ($CHCl_3$) ν_{max} 2955 (s), 2870 (s), 1770 (s), 1732 (s), 1669 (m), 1439 (m), 1385 (m), 1282 (s), 1265 (s), 1175 (s), 1138 (s), 980 (m), 920 (s), 877 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 4.76 (1 H, s, H17), 4.74 (1 H, s, H17′), 3.71 (3 H, s, CO_2CH_3), 2.93 (1 H, d, $J_{6,5}$ = 8.8 Hz, H6), 2.40 (1 H, dt, $J_{13,14\beta}$ = 5.7 Hz, $J_{13,12(12')}$ = 3.5 Hz, H13), 2.15 (1 H, m, H11α) 2.06 (1 H, d, $J_{5,6}$ = 8.8 Hz, H5), 2.05 (1 H, m, H1), 2.0 (1 H, m, H14β), 1.95 (1 H, s, br, H15), 1.9 (1 H, m, H11β), 1.82 (1 H, m, H2), 1.70 (1 H, m, H3), 1.62 (1 H, d, $J_{14\alpha,14\beta}$ = 11.5 Hz, H14α), 1.65–1.40 (5 H, m), 1.09 (3 H, s, H18); LRMS 328 (M^+, 12), 296 (2), 284 (44), 269 (31), 255 (13), 225 (100), 224 (45); HRMS found 328.1675 (M^+), $C_{20}H_{24}O_4$ requires 328.1675.

The *17,17-d_2* derivative of **34** (5.0 mg) was prepared with CD_2Br_2 in a completely analogous manner. The ^1H NMR spectrum was identical, except for the absence of signals from the 17-methylene gorup: LRMS 330 (M^+ 53), 286 (46), 271 (33), 257 (16), 243 (10), 227 (100), 226 (48). This material (2.0 mg) was demethylated with *n*-PrSLi/HMPT by the method described for the preparation of **3**.

Acknowledgment. We are grateful for the assistance and cooperation provided by numerous co-protagonists in the gibberellin and antheridiogen field, namely Professors MacMillan, Schraudolf, and Takahashi, and Drs. Gaskin, Nester, Takeno, and Yamane. The skilled assistance of Bruce Twitchin and the generous provision of fungal gibberellins by Abbott Laboratories have also been crucial to the success of this work.

Registry No. **2**, 34327-25-8; **3**, 114596-77-9; **3** methyl ester, 114596-83-7; **4**, 510-75-8; **4** MOM ether, methyl ester, 127472-82-6; **7**, 114596-78-0; **7** diacid, 127472-84-8; **8**, 114596-79-1; **8** (16-methylene derivative), 114613-99-9; **9**, 114673-20-0; **10**, 114614-20-9; **10** acetate, 127515-26-8; **10** mesylate, 114614-21-0; **11**, 114614-24-3; **12**, 114596-81-5; **13**, 114596-82-6; **13** (1,16-diol), 127472-70-2; **14**, 5508-48-5; **15**, 100769-73-1; **16**, 127472-74-6; **17**, 122054-19-7; **18**, 122054-20-0; **19**, 122054-21-1; **20**, 122054-22-2; **21**, 122054-23-3; **22**, 127472-75-7; **23**, 122054-24-4; **24**, 122054-26-6; **24** (16-methylene derivative), 122054-25-5; **26**, 110374-12-4; **27**, 127515-25-7; **28**, 127472-76-8; **29**, 127472-77-9; **30**, 127472-78-0; 3α-**30**, 127515-27-9; **31**, 127472-79-1; **32**, 127472-80-4; **32** (11,12-dihydro derivative), 127472-73-5; **32** 3-carbinol, 127472-85-9; **33**, 114614-22-1; **34**, 114614-23-2; **34**-17,17′-d_2, 127472-86-0; GA_4, 468-44-0; *ent*-2β-hydrazino-3α-(methoxymethoxy)-20-norgiberella-1(10),16-diene-7,19-dioic acid 7-(methyl ester) 19,*N*′-lactam, 127472-71-3; *ent*-2β-hydrazino-3α-(methoxymethoxy)-20-norgiberella-1(10),16-diene-7,9-dioic acid 19,*N*′-lactam, 127472-72-4; 1β,10α-dihydroxyantherida-6(8),16-diene-7,19-dioic acid 19,10-lactone methyl ester, 127472-81-5; 3-(methoxymethoxy)gibberellin A_4 methyl ester, 127472-83-7.

Supplementary Material Available: A table of more complete ^{13}C NMR spectral data (i.e. including unnumbered compounds) and copies of ^1H and ^{13}C NMR spectra for compounds **3** (methyl ester), **10–12**, **18**, **22–24**, **27**, **28**, **31**, **33**, **34**, and *17,17′-d_2*-**34** (37 pages). Ordering information is given on any current masthead page.

Synthesis of 2-Phenyldecahydroquinolin-4-ones via Imino Diels–Alder Reaction: Influence of the Imine Nitrogen Substituent on the Reaction Course and on the Heterocycle Conformation

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Reaction of acetylcyclohexene trimethylsilyl enol ether (1) with N-substituted phenyl imines **2** takes place in the presence of Lewis acids. When the N-substituent in **2** is phenyl, *p*-tolyl, or *p*-methoxyphenyl, the cycloaddition gives exo and endo enoxysilanes **5a–c** and **6a–c** in a 70/30 ratio under kinetic control and <2/98 under thermodynamic control, via a Diels–Alder ⇄ retro-Diels–Alder process. Starting from the *p*-(dimethylamino)phenyl, benzyl, or trimethylsilyl analogues, no stereoselection is observed whatever the conditions. Protonation of the enoxysilanes **5** and **6** by MeOH–Et_3N takes place from the exo side, leading to cis ring-fused N-substituted *exo*- or *endo*-2-phenyldecahydroquinolin-4-ones **7** and **8**; their conformation as determined by NMR and X-ray crystallography, as well as their stability in the case of endo isomers **8**, strongly depends on the planarity or pyramidality of nitrogen. Unexpectedly, the preferred conformation of the heterocycle, both in solution and in the crystal, of *N*-phenyl- and *N*-*p*-tolyl-substituted exo isomers **7a** and **7b** whose N atoms are planar is a boat with a quasi-axially located 2-phenyl substituent.

The synthetic utility of the Diels–Alder reaction has been increased through the use of the readily available silyloxy dienes, which exhibit high regioselectivity in their reactions with unsymmetrical dienophiles.[1] In the hetero-Diels–Alder field,[2] the condensation of these dienes with carbonyl compounds[3] continues to be an area of great synthetic activity, but there are few reports of their reactions with unactivated imines.[4]

Trimethylsilyl enol ether **1** of acetylcyclohexene is an interesting partner in Diels–Alder cycloadditions as it can lead to bicyclic compounds; recent papers are devoted to its reaction with carbon dienophiles.[5] Besides the problem

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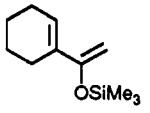
Table I. Reaction of 1 with Imines 2a–f

entry	imine	Lewis acid (equiv)	T, °C	reactn time	5/6[a]
1	2a	BF_3·Et_2O (0.1)	20	1 h 30 min	70/30[b]
2	2a	BF_3·Et_2O (1)	−78	5 min	67/33
3	2a	BF_3·Et_2O (1)	0	5 min	55/45
4	2a	$AlCl_3$ (1)	−10	3 h 30 min	70/30
5	2a	$AlCl_3$ (1)	20	5 min	55/45
6	2a	$AlCl_3$ (0.1)	20	3 h 30 min	55/45
7	2a	$AlCl_3$ (1)	20	1 h 30 min	10/90[b]
8	2a	Et_2AlCl (1)	20	1 h 30 min	70/30[b]
9	2a	$ZrCl_4$ (0.1)	20	18 h 30 min	c
10	2a	$ZrCl_4$ (1)	−40	5 min	70/30
11	2a	$ZrCl_4$ (1)	20	1 h	40/60
12	2a	$ZrCl_4$ (1)	20	4 h 30 min	1/99[b]
13	2a	$TiCl_4$ (1)	20	5 min	<2/98
14	2b	$AlCl_3$ (1)	−40	15 min	70/30[d]
15	2b	$AlCl_3$ (1)	20	1 h 30 min	<2/98[d]
16	2c	$AlCl_3$ (1)	−40	15 min	70/30[d]
17	2c	$AlCl_3$ (1)	20	1 h 30 min	<2/98[d]
18	2d	$AlCl_3$ (1)	−40	15 min	70/30
19	2d	$AlCl_3$ (1)	20	1 h 30 min or 4 h	50/50
20	2e	$AlCl_3$ (1)	−40	1 h	c
21	2e	$AlCl_3$ (1)	20	10 min or 1 h	53/47
22	2e	BF_3·Et_2O (1)	20	1 h	53/47[b]
23	2e	$ZrCl_4$ (1)	20	1 h	52/48
24	2e	$ZrCl_4$ (0.1)	20	1 h	c
25	2f	$ZrCl_4$ (1)	−50	1 h	c
26	2f	$ZrCl_4$ (1)	−10	2 min	43/57
27	2f	$ZrCl_4$ (1)	−10	10 min	50/40[e]
28	2f	$ZrCl_4$ (1)	20	2 h	28/57[b,e]
29	2f	ZnI_2 (1)	20	2 h	41/44[f]

[a] Determined by ^1H NMR (integration of H_2). [b] Yields in isolated ketones determined after MeOH/Et_3N treatment (see text): entry 1, 70%; entry 7, 80%; entry 8, 78%; entry 12, 50%; entry 21, 50%; entry 28, 85%. [c] Starting materials recovered. [d] The same result is obtained when the reaction mixture is treated by aqueous NH_4Cl or 0.1 N HCl for 2 min. [e] Presence of trans ketone **9g** (10%, entry 27, and 15%, entry 28). [f] Presence of trans ketone **10** (15%).

of the regioselectivity of its condensation, **1** presents two challenges from the stereochemical point of view, i.e., the stereoselectivity of the cyclocondensation and that of the protonation of the bicyclic enol ether adduct. Moreover, the mechanism of hetero-Diels–Alder reactions has given rise to much controversy.[2-6]

In the present paper, we report the stereochemical and mechanistic aspects of the reactions of silyloxy diene **1** with the *C*-phenyl imines **2a-f**.[7]



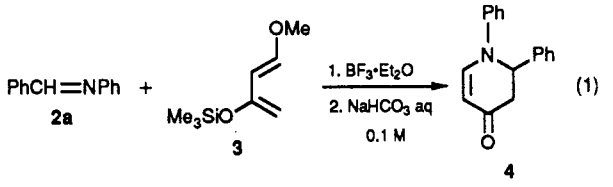
1

PhCH=NR

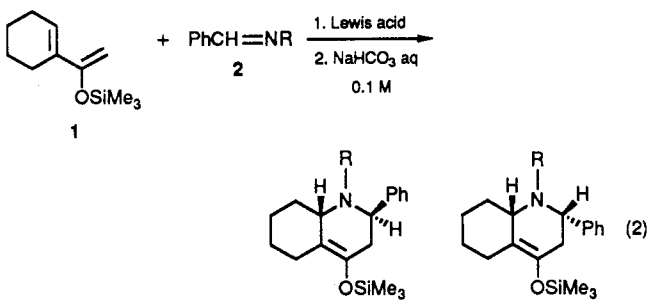
2a: R = Ph; **b**, R = *p*-$CH_3C_6H_4$; **c**, R = *p*-$CH_3OC_6H_4$; **d**, R = *p*-$(CH_3)_2NC_6H_4$; **e**, R = CH_2Ph; **f**; R = $SiMe_3$;

Results

1. Study of the Condensation of Silyloxy Diene 1 with Imines 2. No reaction took place between **1** and **2a–f** under thermal conditions in various solvents (toluene, methylene chloride, acetonitrile) even at reflux. Danishefsky and al.[4a,c] have reported $ZnCl_2$-catalyzed cyclocondensation of silyloxy dienes with imines. We have shown that, instead of $ZnCl_2$ in tetrahydrofuran (THF), BF_3·Et_2O in CH_2Cl_2 at room temperature increased the rate of the reaction of **2a** with Danishefsky's diene **3**: a 60% yield in **4** was obtained after 15 min with BF_3·Et_2O instead of after 36 to 48 h with $ZnCl_2$.[4a]



These results prompted us to examine the reaction of **1** and **2a–f** in the presence of BF_3·Et_2O as well as with $AlCl_3$, Et_2AlCl, $ZrCl_4$, and $TiCl_4$. The reaction was performed by adding 0.1 to 1 equiv of Lewis acid to a solution of imine **2** in CH_2Cl_2, followed, after 30 min, by 1.1 equiv of diene **1** at different temperatures for various times. The reaction was quenched with 0.1 M aqueous $NaHCO_3$, saturated aqueous NH_4Cl, or 0.1 M HCl over a few minutes. Contrarily to recent literature results,[4f] after these workups, only starting materials and enoxysilanes **5** and **6** could be characterized by ^1H NMR in the crude reaction mixtures. The relative ratios **5a–c**/**6a–c** were dependent upon the reactions conditions, 70/30 to 2/98 (entries 1–17, Table I), while the **5d–g**/**6d–g** ratios changed only slightly, 70/30 to 60/40 (entries 18, 19, and 21–29, Table I). Moreover, from imines **2a–c**, crystalline enoxysilanes **5a–c** and **6a–c** have been obtained. Treatment of enoxysilanes



a, R = Ph; **b**, R = *p*-$CH_3C_6H_4$; **c**, R = *p*-$CH_3OC_6H_4$; **d**, R = *p*-$(CH_3)_2NC_6H_4$; **e**, R = CH_2Ph; **f**; R = $SiMe_3$; **g**, R = H (in **5** and **6**)

5 and **6** with MeOH/Et_3N at room temperature led to bicyclic ketones. **5a–e** and **6a,b** gave the cis ring-fused isomers **7a–e** and **8a,b** whatever the length of contact. On the other hand, **6c** gave the corresponding cis ketone **8c** after a 2-h reaction time while after a longer period (up to 15 h) only trans ring-fused ketone **9c** was obtained. This result was due, as shown by an independent experiment, to base-catalyzed isomerization of **8c**. Compounds **6d,e** also led to trans **9d,e** if treatment was extended long enough.

In the same manner, starting from trimethylsilyl imine **2f**, desilylation took place, leading to N-unsubstituted ketones **7g** and **9g**; these compounds were also obtained by catalytic hydrogenation of **7e** and **9e** over $Pd(OH)_2$.[8] Moreover, another trans ring-fused decahydroquinolin-4-one (**10**) was isolated (entry 29, Table I); it could also be prepared by base- or acid-catalyzed epimerization of **7g**.

N-Phenyl and *N*-*p*-tolyl trans ring-fused **9a,b** could be obtained by base (LDA or *n*-$Bu_4N^+F^-$) catalyzed equili-

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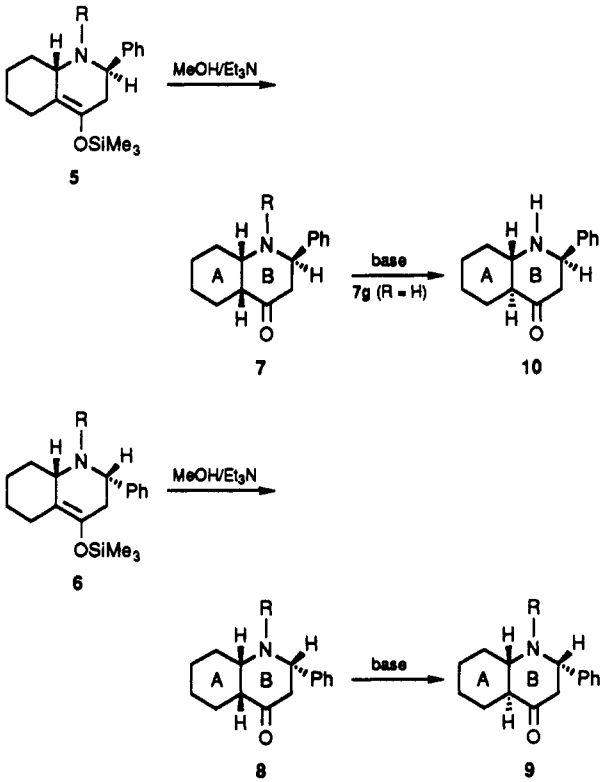
Table II

entry	starting compd	Lewis acid	reactn condtns time and temp[b]	products (ratio)[a]
30	**11a**	BF_3·Et_2O	1 h 30 min, rt	**11a**
31	**11a**	$TiCl_4$	1 h, rt	**7a**/**8a**/**9a**/**11a** = 25/25/35/15
32	**11a**	$TiCl_4$	15 h, rt	**9a**
33	**11b**	$AlCl_3$ + Me_3SiCl	10 min, −40 °C	**11b**

[a] Determined by ^1H NMR. [b] rt = room temperature.

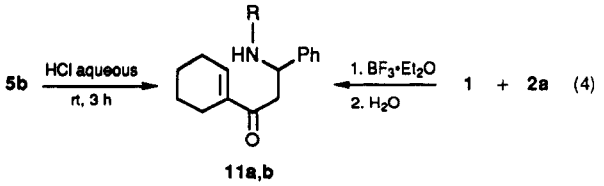
bration of **8a,b** or by n-$Bu_4N^+F^-$ treatment of enoxysilane **6a**. Furthermore, cis ring-fused **8c–e** were isomerized by SiO_2 chromatography into trans **9c–e**.



5 **7** **10** (3) **6** **8** **9**

a, R = Ph; **b**, R = p-$CH_3C_6H_4$; **c**, R = p-$CH_3OC_6H_4$; **d**, R = p-$(CH_3)_2NC_6H_4$; **e**, R = CH_2Ph; **f**, R = $SiMe_3$ (only for **5** and **6**); **g**, R = H

α,β-Unsaturated ketones **11** were isolated either from **2a** in the presence of BF_3·Et_2O followed by aqueous workup or when enoxysilanes **5b**,**6b** were treated with aqueous 0.1 N HCl at room temperature for 3 h. Ketones **7b**,**e** remained unchanged under these conditions, while ketone **8b** was isomerized into trans **9b**.



11a,b

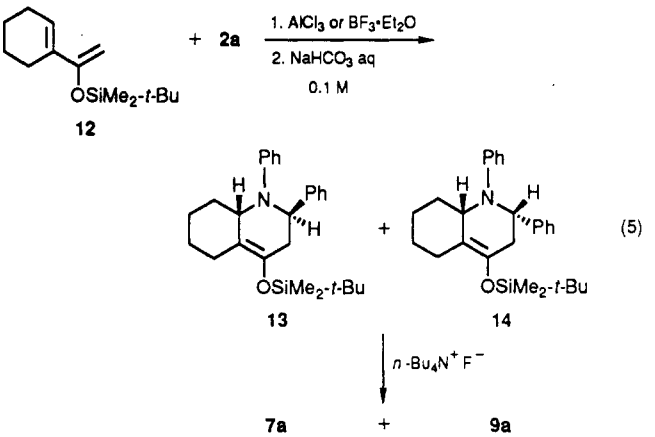
11 was recovered unchanged by action of BF_3·Et_2O or of $AlCl_3$ in the presence of Me_3SiCl (entries 30 and 33, Table II), while treatment of **11a** by $TiCl_4$ led to mixtures of bicyclic ketones **7a**, **8a**, and **9a** or only to **9a**, depending on the reaction conditions (entries 31 and 32, Table II).

Similar reactions were performed starting with imine **2a** and *tert*-butyldimethylsilyl enol ether of acetylcyclohexene **12** in the presence of $AlCl_3$ or BF_3·Et_2O: enoxysilanes **13** and **14** were formed in 70/30 or 2/98 ratios, depending, as previously, on the reaction conditions. Treatment of these mixtures by n-$Bu_4N^+F^-$ in THF for 2 h led to ketones **7a** and **9a** in a 70/30 ratio or to only trans ring-fused **9a**.

Table III. Main ^1H NMR Parameters of Decahydroquinolin-4-ones 7, 8, 9, and 10 ($CDCl_3$, 250 MHz)

compd	$\delta(H_2)$	$^3J_{H2-H3}$	δ(H-9) ($\omega_{1/2}$)	δ(H-10) ($\omega_{1/2}$)	$^3J_{H9-H10}$
7a[a]	5.09	5.3, 5.3	4.11 (21.0)	3.05 (10.0)	
7b	5.00	5.0, 5.0	4.10 (21.0)	3.10 (10.0)	4.6
7c	4.85	8.0, 5.4	3.90 (24.0)	3.20 (10.0)	5.6
7d	4.65	8.6, 6.3	3.70 (24.8)	3.00 (14.3)	
7e	4.10	10.6, 4.0	3.10	2.90 (13.0)	6.0
7g	4.35	8.5, 5.0	3.45 (23.0)	2.89 (15.0)	
8a	4.90	11.2, 4.5	3.9 (21.0)	2.85 (10.0)	
8b	4.70	11.6, 3.6	3.70 (21.4)	2.70 (10.0)	
8c	4.50	11.9, 3.5	3.60 (15.8)	2.70 (15.8)	
8d	4.50	11.9, 3.2	3.50 (18.7)	2.70 (13.5)	
8e	4.10	12.1, 3.5	3.05 (22.0)	2.90 (13.5)	
9a	4.35	10.0, 3.6	2.40	2.75	10.0
9b	4.35	10.0, 3.6	2.50	2.80	10.1
9c	4.25	11.0, 3.3	2.70	2.60	11.9
9d	4.25	14.2, 4.2	2.70	2.60	12.7
9e	3.80	12.2, 3.4	2.15	2.20[b]	9.5[b]
9g	4.05	11.0, 3.8	2.20	2.60	10.4
10	4.70	6.1, 3.6	2.15	2.50	10.5

[a] 500 MHz. [b] 500 MHz in C_6D_6.



2. Structural and Stereochemical Assignments. All the assignments rely upon IR and ^1H and ^{13}C NMR spectra, mass spectra, and elemental analysis for the crystalline compounds in conjunction with a single-crystal X-ray crystallographic determination of **5c**, **6c**,[9] **7a**, **7c**, **7e**, and **8a**.

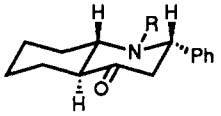
a. Decahydroquinolin-4-ones 7–10. The IR spectrum (ν(C=O) 1715 cm^{-1}) as well as the ^1H and ^{13}C NMR spectra of **7–10** are in agreement with a 2-phenyldecahydroquinolin-4-one structure (Tables III and IV). The cis or trans ring-fused stereochemistry was deduced from the values of the half bandwidth of the H-9 and H-10 protons or their coupling constants. The H-9 and H-10 signals were assigned in d-10 compounds obtained after MeOD/Et_3N treatment of the related enoxysilanes **5** and **6** (see Table III).

(9) Charpin, P.; Nierlich, M.; Le Coz, L.; Wartski, L. *Acta Crystallogr.* In press.

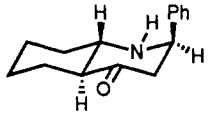
Table IV. Main X-ray Data of Decahydroquinolin-4-ones

angle	7a	7c	7e	8a
Selected Bond Angles (deg) for 7–8				
$C_9N_1C_2$	122.1 (9)	113.7 (2)	114.3 (2)	119.3 (2)
$C_9N_1C_{11}$	120.1 (9)	111.2 (2)	111.8 (2)	118.2 (2)
$C_2N_1C_{11}$	117.1 (9)	115.1 (2)	110.6 (3)	118.2 (2)
Σ	359.3	340.0	336.7	355.7
Selected Dihedral Angles (deg) for 7–8				
$C_{12}C_{11}N_1C_9$	-8.7	-70.0		-147.6
$C_{22}C_{21}C_2N_1$	9.6	137.6	-50.3	44.7
$H_2C_2C_3H_{31}$	-46.4	-60.2	-170.3	175.1
$H_2C_2C_3H_{32}$	71.6	178.3	-51.3	49.0
$C_9C_8H_{81}H_9$	54.1	-176.8	-55.4	-57.8
$C_9C_8H_{82}H_9$	175.6	-70.2	-175.1	179.4
$C_5C_6C_7C_8$	58.6	-56.5	-55.3	-56.8
$C_6C_7C_8C_9$	-59.3	58.7	59.9	54.9
$C_7C_8C_9C_{10}$	57.8	-56.4	-58.3	-53.2
$C_8C_9C_{10}C_5$	-53.5	52.4	54.5	52.7
$C_9C_{10}C_5C_6$	52.7	51.6	-52.1	-54.8
$C_{10}C_5C_6C_7$	-55.9	53.8	51.5	57.2
$N_1C_2C_3C_4$	-56.6	-52.9	-47.7	49.3
$C_2C_3C_4C_{10}$	28.9	54.6	50.1	31.3
$C_3C_4C_{10}C_9$	26.0	-53.9	-53.6	-19.8
$C_4C_{10}C_9N_1$	-52.8	55.5	56.9	54.6
$C_{10}C_9N_1C_2$	25.4	59.3	-59.0	37.5
$C_9N_1C_2C_3$	28.0	55.6	53.3	13.8

The configuration of the trans ring-fused compounds **9a–e,g** and **10** is unambiguous: the A and B rings are in chair conformations with an equatorial 2-phenyl substituent in **9** and an axial one in **10** as evidenced by the magnitude of $^3J_{H2-H3}$;[10a,b] however, for **10** the chair conformation of the B ring is flattened, as indicated by the magnitude of $^3J_{H2-H3}$.[11] Therefore **9a–e** and **9g** are endo isomers, with a trans relationship between C_8–C_9 and C_2–C_{21} bonds, while **10** is an exo isomer, the same bonds being in a cis relationship. These data are in line with previous literature results on NH analogues.[10c]



9a–e,g



10

The ^{1}H NMR data for the cis ring-fused isomers only indicate the equatorial location of the 2-phenyl ring in **8a–e,g** ($^3J_{H2-H3}$ = 11–12 Hz and 4 Hz) and the axial one in **7a,b** ($^3J_{H2-H3}$ = 5 and 5 Hz).[10] In the other cases, the location of the phenyl ring is less straightforward. However, by taking into account the cis → trans isomerization process, we have observed, i.e., **8a–e** being epimerized by various bases into **9a–e**, we can assign the endo configuration to these cis ring-fused ketones. Furthermore, **7a–e,g** being stereoisomers of **8a–e,g** at C-2, it seems logical to consider these compounds as cis ring-fused *exo*-2-phenyldecahydroquinolin-4-ones. The values of the half bandwidth of H-9 and H-10 ($w_{1/2}$(H-9) = 21–24 Hz; $w_{1/2}$(H-10) = 10–14 Hz) show that **7a–e** as well as **8a–e** lie in a highly predominant conformation, H-9 being axial and H-10 equatorial relative to the carbocyclic A ring. This is the case neither for **8c** ($w_{1/2}$(H-9) = $w_{1/2}$(H-10) = 15.8 Hz) nor for **8d** ($w_{1/2}$(H-9, H-10) = 18.7 and 13.5 Hz). The low-temperature (223 K) ^{1}H NMR spectrum of **8c** shows the presence of two slowly interconverting conformers **8c$_1$** and **8c$_2$** in a 1:1 ratio in which H_2 is axial or quasi-axial, H-9 being axial relative to the A ring in **8c$_1$** ($w_{1/2}$ = 25 Hz) and equatorial in **8c$_2$** ($w_{1/2}$ = 14 Hz). The easy **8d** → **9d** isomerization precluded such a low-temperature NMR study for **8d**.

Table V. Main ^{13}C NMR Parameters of *cis*-Decahydroquinolin-4-ones 7a–e,g and 8a–e and *trans*-Decahydroquinolin-4-ones 9a–e ($CDCl_3$, 62 MHz)

	δ in ppm				
compd	C-2	C-3	C-4	C-9	C-10
7a	56.1	47.7	209.0	59.4	49.6
7b	56.3	48.0	209.0	60.3	50.4
7c	57.9	50.0	209.3	64.0	55.3
7d	58.0	50.1	209.4	65.1	56.2
7e	61.9	49.8	210.1	58.4	50.1
7g	55.8	49.8	210.9	56.6	49.8
8a	59.6	48.3	210.3	62.0	49.9
8b	60.0	49.0	210.4	62.0	50.4
8c	61.3	48.2	210.9	64.0	54.3
8e	63.0	48.0	211.4	66.3	58.0
9a	67.2	49.4	209.4	53.9	65.3
9b	68.4	50.0	209.5	55.2	67.4
9c	68.8	50.8	209.6	55.2	67.5
9d	68.7	51.3	209.6	56.1	67.7
9e	68.4	49.8	209.6	53.5	68.4

The conformation of these cis ring-fused decahydroquinolin-4-ones was determined by a single-crystal X-ray diffraction study of **7a**, **8a**, **7c**, and **7e** (see Figure 1 and Table IV). In *N*-phenyl compounds **7a** and **8a**, the A ring is in a chair conformation, while the B ring is a boat, the cis-A/B ring junction thus being confirmed. Moreover, in **7a** there is a trans relationship between the C_8–C_9 and C_2–C_{21} bonds and the C-2 phenyl ring substituent is in a quasi-axial position. In **8a** this relationship is cis, the C-2 phenyl ring being quasi-equatorial. In these compounds the nitrogen atom in ring B is nearly planar due to conjugation with the phenyl group.[12]

In compound **7a**, the plane of the C-2 phenyl ring is perpendicular to the mean plane of the heterocycle, determined by C_2, C_{10}, and H_{10} atoms, this conformation relieving steric interactions between H-9 and H-10. Such behavior has been observed, from X-ray analysis, in molecules bearing axially located phenyl groups on cyclohexanes.[13] On the other hand, in ketone **8a** this C-2 phenyl plane exhibits a nearly gauche orientation, different from that observed for equatorial phenyl groups in chair-shaped cyclohexane or piperidine rings[10b,14] due to the interactions between the two aromatic rings. Molecular modeling[15] (Macromodel and Model) for **7a** and **8a** indicates preferred geometries in good agreement with these data, although for **7a** these calculations indicate the chair A–boat B conformer to be 3.14 kcal/mol higher in energy than the chair–chair one. As the ^{1}H NMR parameters of **7b** and **8b** are very close to those of **7a** and **8a**, their structures are certainly analogous.

In the *N*-(*p*-methoxyphenyl) (**7c**) and *N*-benzyl (**7e**) substituted cis ring-fused exo ketones, rings A and B adopt

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(15) Macromodel (Prof. W. C. Still) was used in Prof. Evans's Laboratory (Harvard University) with the help of Scott Miller and Joelle Gauchet to whom we are grateful. PC MODEL was given to us by Prof. Steliou, whose help was also greatly appreciated.

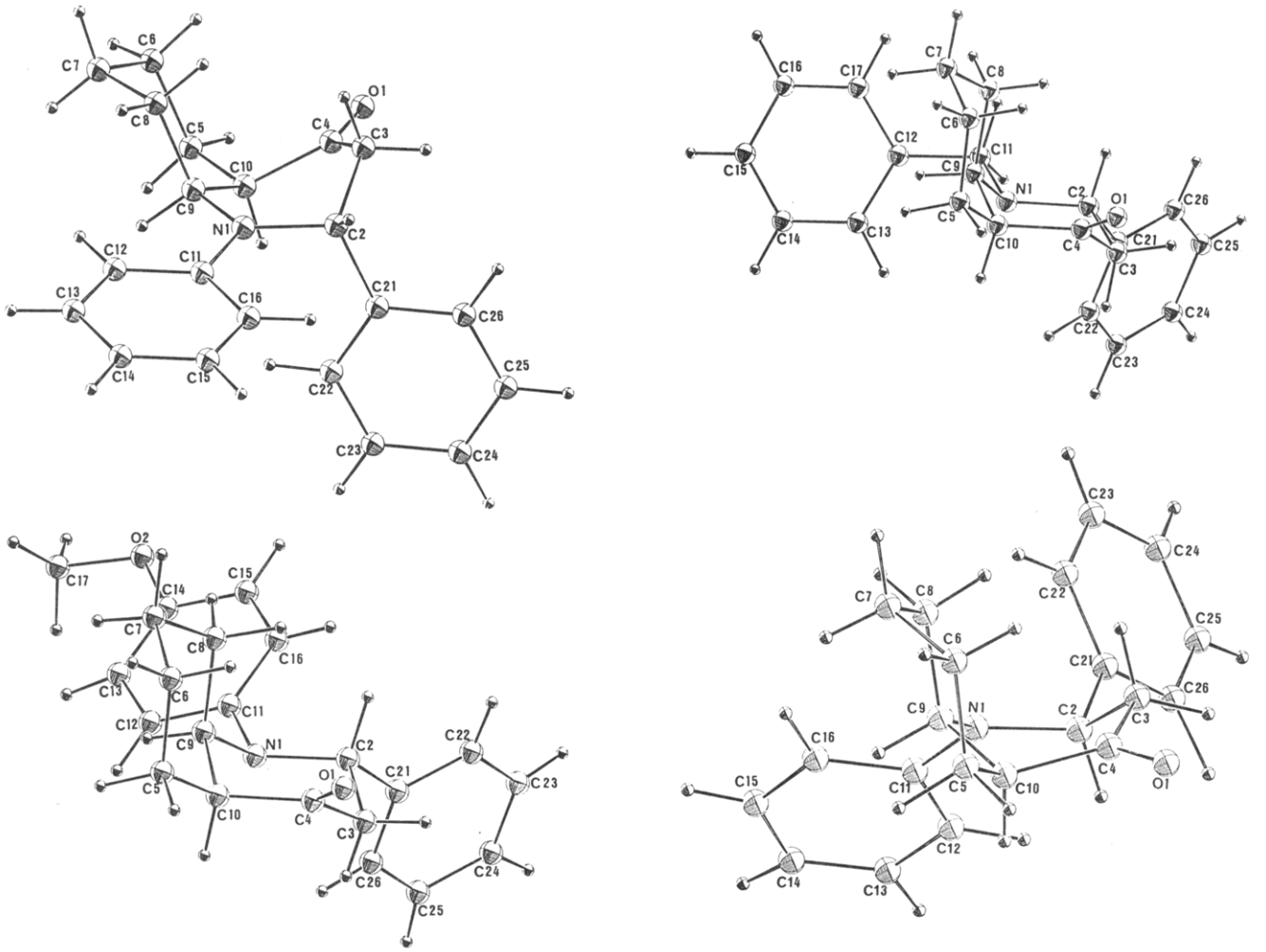

Figure 1. Single-crystal X-ray structure of **7a** (top left), **7c** (bottom left), **7e** (top right), and **8a** (bottom right).

a chair conformation and the N-atom is pyramidal. The C-2 phenyl is equatorial and the trans relationship of the C_8–C_9 and C_2–C_{21} bonds is confirmed. The C-2 phenyl ring plane is quasi-perpendicular to the mean plane of the heterocycles, as in substituted piperidines.[10b] The values of the $^3J_{H2-H3}$ coupling constants of all the compounds studied fit perfectly with the dihedral angles determined in the crystal structures,[11] thus showing the similarity of the preferred conformations in the solid state and in solution.

With the cis endo isomers **8c**, **8d**, **8e** being oils, such a study could not be performed. However, X-ray crystallographic analysis of enoxysilane **6c**,[9] precursor of **8c**, confirms the endo configuration of this compound.

The ^{13}C NMR analysis of these ketones (Table V), using 2D ^1H–^{13}C correlations, show that signals of C-2 and C-10 are shifted downfield in trans ring-fused ketones **9a–e** compared to the cis ring-fused analogues **8a–e**. The C-2 chemical shift is also displaced upfield in isomers **7a,b**, bearing axial substituents compared to **8a,b** having equatorial ones: these results can be easily explained by the related steric crowding and gauche effects in both types of molecules.[16] However, the carbonyl carbon resonates nearly at the same field whatever the configuration and the conformation of each isomer. These results thus strengthen the previous stereochemical assignments, although they are of no help in determining whether B ring is chair or boat shaped in cis ring-fused compounds.

b. Enoxysilanes 5 and 6. The IR spectra of enoxysilanes **5** and **6** exhibit characteristic absorption at 1660 cm^{-1} due to the C=C—O moiety.

Their configurations are the same as those of the corresponding cis ring-fused decahydroquinolin-4-ones (exo for isomers **5**, endo for **6**) and have been confirmed in two cases (**5c** and **6c**) by single-crystal X-ray diffraction studies.[9] Their ^1H and ^{13}C parameters are given in Table VI. From the $^3J_{H2-H3}$ coupling constants values in **5a–d** and **6a**, one might expect the possibility of the existence of two conformers in fast equilibrium. Low-temperature ^1H NMR experiments (175 K) on **5a** and **6a**, however, showed that this is not the case. Moreover, the dihedral angles determined by single-crystal X-ray crystallography on **5c**[8] are in agreement with the coupling constants determined in solution.

Discussion

Our results show that the Lewis acid catalyzed condensation of **1** and **2** is highly regioselective. However, its stereoselectivity depends upon the substituent on nitrogen: from *N*-phenyl, *N*-*p*-methyl- and *N*-(*p*-methoxyphenyl)-substituted imines **2a**, **2b**, and **2c**, cycloadducts **5a–c** and **6a–c** are formed in different ratios (70/30 to 2/98) according to the reaction conditions, while from *N*-[*p*-(dimethylamino)phenyl]- or *N*-benzyl-substituted imines **2d** and **2e**, a nearly 1:1 mixture of **5d,e**/**6d,e** is always obtained.

Two points will be discussed: (a) the hetero-Diels–Alder reaction mechanism and the stereochemistry of the pro-

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Table VI.

compd	δ in ppm, J and $\omega_{1/2}$ in hertz			
	H_2	$^3J_{H2-H3}$	H_9	$\omega_{1/2}$
Main ^1H NMR Parameters of Enoxysilanes 5 and 6 ($CDCl_3$, 250 MHz)				
5a	4.9	5.2 and 5.2	3.9	19.3
5b	4.8	5.2 and 5.2	3.8	18.6
5c	4.6	5.5 and 5.5	3.6	21.3
5d	4.5	5.9 and 5.9	3.6	20.9[a]
5e	4.2	9.7 and 4.8		a
5f/g	4.2	8.8 and 4.4	3.3	20.0[a]
6a	4.8	5.5 and 5.5	3.7	20.0
6b	4.5	8.7 and 4.3	3.5	19.5
6c	4.2	9.0 and 3.0	3.3	16.9
6d	4.2	12.8 and 4.4	3.3	23.5[a]
6e	4.1	10.9 and 4.2		a
6f/g	3.9	11.7 and 3.6	3.4	21.0[a]

Main ^{13}C Parameters of Enoxysilanes 5 and 6 ($CDCl_3$, 62 MHz)

compd	δ in ppm		
	C-2	C-3	C-9
5a	58.7	37.4	58.9
5b	58.8	37.5	59.3
5c	59.1	37.4	60.1
6a	59.0	37.2	60.9
6b	61.0	38.8	62.5
6c	63.5	40.7	64.3

[a] Observed as a mixture.

tonation of the resulting enoxysilanes; (b) the conformation of the cis ring-fused decahydroquinolin-4-ones.

1. Hetero-Diels–Alder Reaction Mechanism. Whatever the imine, the hetero-Diels–Alder reaction requires Lewis acid catalysis. It appears that under some reaction conditions the two enoxysilanes **5a–c** and **6a–c** are formed in a 70/30 ratio (entries 1, 2, 4, 8, 10, 14, 16), while when the reaction time is longer and/or the temperature higher, **6a–c** is highly predominant (entries 7, 12, 13, 15, 17), with intermediate ratios being also observed (entries 3, 5, 11). Thus, under kinetic control, the reaction is poorly stereoselective while, under thermodynamic control, **6a–c** are highly favored. The reaction conditions (temperature and time) under which kinetic or thermodynamic control are observed strongly depend upon the coordination ability of the Lewis acids, their efficiencies being $TiCl_4 > AlCl_3 > ZrCl_4 > Et_2AlCl > BF_3{\cdot}Et_2O$. *exo*-**5b**, treated with an equimolar amount of $AlCl_3$, gave a mixture of endo cycloadduct **6b**, imine **2b**, and bicyclic ketones **7**, **8**, and **9b**. Moreover, **5a** treated by an equimolar amount of Danishefsky's diene **3** and $AlCl_3$ gave adduct **4**, besides unchanged **5a**. Both experiments are indicative of a retro-Diels–Alder process. Such a Diels–Alder ⇄ retro-Diels–Alder pathway at room temperature has precedent in the literature in a few cases;[17] usually the retro Diels-Alder reaction takes place at higher temperature.[18] Recently, Schreiber[19] and Denmark[20] also noticed this possibility in intramolecular hetero-Diels–Alder condensations.

However, when starting from the *N*-(*p*-dimethylamino)-substituted imine **2d**, the **5d** ⇄ **6d** isomerization is considerably slower. After 4 h, decomposition of **5d** and **6d** takes place, so that it is difficult to assert if the 1:1 **5d/6d** ratio corresponds to the thermodynamic equilibrium. From *N*-benzyl or *N*-trimethylsilyl imine **2e** or **2f**, the reaction is also poorly stereoselective and nearly no change in the **5/6** ratio is observed under the different conditions used (entries 21–29); in this case, there is no compelling evidence for the nature of the control (kinetic or thermodynamic).

In all the cases studied, enoxysilanes **5** and **6** are the primary adducts: contrarily to recent results concerning the reaction of silyloxy dienes with imines[4f,6,21] and saturated[22] or α,β-unsaturated carbonyl compounds,[5c] neither α-enone **11** nor ketones **7**, **8**, or **9** were detected in the crude reaction mixtures. Moreover, **11** remains unchanged under conditions for which **5** and **6** were obtained (entries 30 and 33, Table II). Therefore, the cyclocondensation takes place via a concerted mechanism.[23,24] Midland[4d] and Simpkins[23b] have recently reached the same conclusion in related cases. As the reaction works better after precomplexation of the imine by the Lewis acid, its transition state involves silyloxy diene **1** and the complexed imine, lying in a trans geometry according to the literature.[21,23a] The regioselectivity is in agreement with FMO theory as the larger coefficients are on C-2 in complexed imine LUMO and on C-3 in the silyloxy diene HOMO;[26] it is the same as reported for imines[4] or carbonyl compounds[3,22] and other silyloxy dienes. The poor stereoselectivity observed under kinetic control is indicative of a nonsynchronous and loose[23,25] transition state. However, from Brassard's diene and imines, Midland[4d] observed a higher stereoselectivity, as well as Kraus and Gottschalk's from silyloxy diene **1** and 2-methylcyclohexenone. On the other hand, Richter and Otto[5b] observed, as did we, poor stereoselectivity from **1** and an α-enone. However, no evidence of kinetic control was presented in this case.

The formation of α-enone **11**, which is only obtained from cycloadducts in acidic medium, implies an acid-catalyzed ring opening of intermediate enoxysilanes.

$MeOH/Et_3N$ treatment of enoxysilanes **5a–e** and **6a–e**, under kinetic control under nonepimerizing conditions, always leads to cis ring-fused decahydroquinolin-4-ones **7a–e** and **8a–e** and, consequently, protonation at the ring junction takes place from the less hindered exo side. In several cases, from cis ring-fused endo ketones **8c–e**, longer treatment induces epimerization to the trans ring-fused endo isomers **9c–e**.

From *N*-silyl imine **2f**, desilylated **7g**, **9g**, and **10** are undoubtedly formed by similar processes (kinetics exo protonation eventually followed by isomerization).

2. Conformation of the Cis Ring-Fused Decahydroquinolin-4-ones. The geometry of the *cis-exo*-decahydroquinolin-4-ones **7** strongly depends upon the N substituent. Their ^1H NMR spectra indicate that the cyclohexane ring is in a chair conformation having H-9 in axial and H-10 in equatorial position at the ring junction. From the values of the $^3J_{H2-H3}$ coupling constants in **7a**, **7b**, **7c** and **7d**, a progressive change in location of the C-2 phenyl ring from a quasi-axial to equatorial position can

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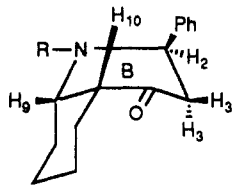
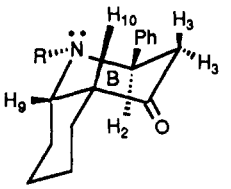
be deduced. The single-crystal X-ray determination of **7a** and **7c** confirms these assignments.

Furthermore, it appears that in **7a** the N atom is planar and the B heterocycle is a distorted boat while in **7c** the N atom is pyramidal and the B ring adopts a chair conformation (Table IV). This change in geometry of the N atom is in line with the well-known increase of aniline nitrogen inversion barriers by para electron donating substituents.[12b,c]

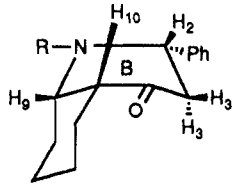
Examination of molecular models of **7a** shows that the chair conformation of ring B is highly disfavored by strong $A^{(1,3)}$[27] interactions developed between the planar *N*-phenyl moiety and an equatorial C-2 phenyl ring. Similar observations have been made in the case of monocyclic piperidine derivatives.[27] The unexpected boat conformation observed implies that a quasi-axial C-2 phenyl substituent is favored. In **7c**, with the (*p*-methoxyphenyl)-substituted N atom being pyramidal, such repulsive interactions are alleviated so that B ring adopts a chair conformation. The conformation of the *N*-benzyl compound **7e**, as determined by ^{1}H NMR and single-crystal X-ray analysis, is in agreement with these considerations, the B ring being slightly more flattened than in **7c**. All these conformations strongly contrast with those of *N*-alkyl-*cis*-decahydroquinolines.[10a] However, the boat conformation observed in **7a,b** with its two sp^2-hybridized sites in the 1,4 position, is comparable to that of cis decalin-1,4-dione.[28]



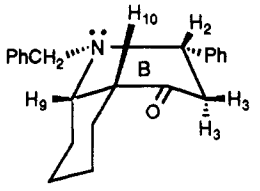
7a,b



7c,e



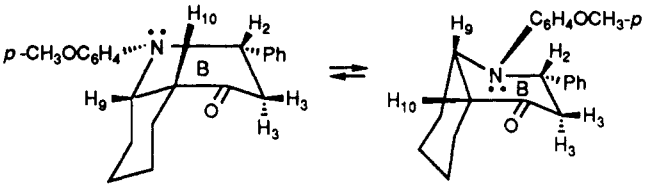
8a,b



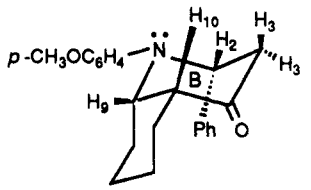
8e

The geometry of the *cis-endo*-decahydroquinolin-4-ones **8** is less obvious. The ^{1}H NMR analysis of all these compounds shows that the C-2 phenyl substituent is always located in the equatorial position. Examination of molecular models clearly indicates severe repulsions between the chair-shaped ring A and an axial endo substituent, thus disfavoring conformers II, whatever the N geometry.

In the case of **8a,b** in which the N atom is planar, the chair–chair conformer III, which bears an equatorial C-2 phenyl group (ring A being inverted), is also disfavored, in agreement with molecular modeling results, due, inter alia, to $A^{(1,3)}$ interactions. In the chair–boat conformation I, determined by X-ray analysis of **8a**, all these repulsive interactions are alleviated, the C-phenyl ring being further away as deduced from X-ray determination. However, for **8c**, low-temperature ^{1}H NMR has evidenced two rapidly interconverting conformers $\mathbf{8c_1}$ and $\mathbf{8c_2}$, whose conformation is similar to I and III, respectively. Assuming that in these species the N atom is pyramidal, as shown in **7c**, the examination of molecular models indicates very close steric interactions for each of them.



(6)



(II)

Concluding Remarks

We have shown that the reaction of enoxysilane **1** with imines **2** is a Lewis acid catalyzed concerted hetero-Diels–Alder cycloaddition leading to bicyclic enoxysilanes **5** and **6** as primary products. The stereoselectivity of the reaction depends upon the N substituent: poorly stereoselective under kinetic control, it may lead nearly exclusively to the endo adduct under thermodynamic control, when the N-substituent is phenyl, *p*-tolyl, or *p*-methoxyphenyl. Enoxysilanes **5** and **6** are protonated by MeOH/Et_3N from the exo side, giving stereoselectively cis ring-fused *exo*- and *endo*-2-phenyldecahydroquinolinones **7** and **8**, whose preferred conformation mainly depends upon the planarity or pyramidality of the nitrogen, according to the nature of its substituent.

A boat conformation of the heterocycle, with an axially located 2-phenyl substituent, has been shown in cis ring-fused exo ketones **7a,b**, whose N atom is planar.

Finally, depending on experimental conditions, cis or trans ring-fused decahydroquinolin-4-ones can be synthesized in good yields.

Experimental Section

X-ray Crystal Structure Determination. Crystallographic data are listed in Table IV. An empirical absorption correction was applied, using the Φ scan of two reflections.

The structures were solved by direct methods and subsequent Fourier maps. Hydrogens were found on difference maps and their positions refined in **7c** and **8a**; they were geometrically positioned in **7a** and **7e**. In the four compounds, hydrogen atoms were given an overall isotropic thermal parameter. For **7a**, the phenyl rings were isotopically refined as rigid groups, because of the small number of data, explained by the poor quality of crystals. All calculations were carried out with CRYSTALS.[29]

General. All cycloadditions were run in a three-necked flask equiped with a magnetic stirrer, a thermometer, a rubber septum cap, and an argon inlet. Methylene chloride (CH_2Cl_2) was purified by chromatography through an alumina column. Diethyl ether was distilled over lithium aluminum hydride ($LiAlH_4$). Dimethoxy-1,2-ethane and tetrahydrofuran (THF) were distilled under argon over $LiAlH_4$ or benzophenone–ketyl. Titanium chloride was distilled under argon and boron trifluoride etherate (BF_3·Et_2O) over calcium hydride. Aluminum chloride was purchased from Fluka and zirconium chloride from Janssen Chemica. Triethylamine and diisopropylamine were distilled over calcium hydride. *n*-Butyllithium in hexane and methyllithium in diethyl ether were purchased from Aldrich Chemical Co. and standardized by using diphenylacetic acid. Dienes **1** and **12** and imines **2** were

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prepared according to the literature;[30-33] diene 3 was purchased from Aldrich Chemical Co. Column chromatography was performed with silica gel SDS (70–200). The ^1H NMR spectra were recorded on a Bruker VM 500 (500 MHz), a Cameca (400 MHz), or a Bruker AM 250 (250 MHz) spectrometer. The ^{13}C NMR spectra (62 MHz) and heteronuclear shift correlated 2D NMR using polarization transfer from ^1H to C via $J(^{13}C-H)$ were recorded with a AM 250 Bruker spectrometer. The spectra are reported in ppm, from Me_4Si for ^1H NMR (internal standard Me_4Si) and for ^{13}C NMR (internal standard $CDCl_3$), and J values are in hertz. IR spectra were recorded on a Perkin-Elmer Model 682 infrared spectrophotometer and are given in cm^{-1}. Mass spectra were recorded on a mass spectrometer coupled with a Nermag R 10-10 capillary chromatograph. Melting points were obtained on a Mettler FP5 capillary melting point apparatus and are uncorrected.

1,2-Diphenyl-2,3-dihydropyridin-4(1*H*)-one (4). To a solution of benzylideneaniline (**2a**) (395 mg, 2.17 mmol) and diene **3** (570 μL, 2.91 mmol) in CH_2Cl_2 (21 mL) was added $BF_3{\cdot}Et_2O$ (300 μL, 2.38 mmol) under argon, at 20 °C. The reaction mixture was stirred for 15 min and then quenched with a 0.1 M $NaHCO_3$ aqueous solution (40 mL). After extraction with CH_2Cl_2, the organic layer was dried over $MgSO_4$. Flash chromatography of the crude product with ethyl acetate/hexane (1/1) affords **4** in a 60% yield. Recrystallization was performed from ethyl acetate/hexane (1/2): mp 96–97 °C; IR ($CDCl_3$) 1640, 1580, 1500; 400-MHz ^1H NMR ($CDCl_3$) 2.7 (dd, J = 3.0, 16.0 Hz, 1 H), 3.2 (dd, J = 7.5, 16.0 Hz, 1 H), 5.2 (m, 2 H), 6.9–7.4 (m, 10 H), 7.6 (d, J = 7.5 Hz, 1 H); MS, m/z 249 (M^+). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.92; H, 6.02; N, 5.65. Found: C, 81.23; H, 6.06; N, 5.65.

General Procedure for Cycloaddition Reactions of Imine 2 with Diene 1 Catalyzed by Lewis Acids. To a 0.1 M solution of imine **2** (1 equiv), in anhydrous methylene chloride, under N_2, was added the Lewis acid. After 30 min of stirring, the trimethylsilylenol ether of acetylcyclohexene (**1**) (1.1 equiv) was then added dropwise at different temperatures for various times (Table I). The reaction was quenched by addition of a 0.1 M $NaHCO_3$ aqueous solution and extracted with methylene chloride. The combined organic layers were washed with 0.1 M $NaHCO_3$ and brine, dried, and concentrated. **5a–c** and **6a–c** were purified by crystallization from MeOH. **5d–f** and **6d–f** mixtures were characterized by ^1H NMR spectra of the crude products.

Enoxysilane 5a: mp 82–83 °C; IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.2 (s, 9 H), 1.1–1.5 (m, 3 H), 1.6–1.9 (m, 3 H), 2.5 (m, 1 H), 2.9 (m, 1 H), 3.1 (m, 1 H), 3.9 (m, 1 H), 4.9 (t, J = 5 Hz, 1 H), 6.6–7.7 (m, 10 H); $w_{1/2}(H_9)$ = 19.3 Hz; ^{13}C NMR ($CDCl_3$) 0.5 (q), 25.2 (t), 26.5 (t), 27.1 (t), 32.6 (t), 37.4 (t), 58.7 (d), 58.9 (d), 115.3 (s), 120.3 (d), 122.3 (d), 125.3 (d), 127.5 (d), 128.3 (d), 128.6 (d), 133.4 (s), 144.3 (s), 149.6 (s); MS, m/z 377 (M^+). Anal. Calcd for $C_{24}H_{31}NOSi$: C, 76.34; H, 8.27; N, 3.71. Found: C, 76.37; H, 8.89; N, 3.25.

Enoxysilane 5b: mp 84–85 °C; IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.1 (s, 9 H), 1.3 (m, 3 H), 1.7 (m, 3 H), 2.0 (m, 1 H), 2.2 (s, 3 H), 2.4 (m, 1 H), 2.7 (m, 1 H), 3.0 (m, 1 H), 3.8 (m, 1 H), 4.8 (t, J = 5.2 Hz, 1 H), 6.7 (bd, 2 H), 6.9 (bd, 2 H), 7.1 (m, 5 H); $w_{1/2}(H_9)$ = 18.6 Hz; ^{13}C NMR ($CDCl_3$) 0.5 (q), 20.5 (q), 25.3 (t), 26.4 (t), 27.1 (t), 32.4 (t), 37.5 (t), 58.8 (d), 59.3 (d), 118.1 (s), 122.8 (d), 126.5 (d), 127.7 (d), 128.8 (d), 129.0 (d), 130.1 (s), 138.1 (s), 142.8 (s), 148.3 (s); MS, m/z 391 (M^+). Anal. Calcd for $C_{25}H_{33}NOSi$: C, 76.67; H, 8.49; N, 3.57. Found: C, 76.60; H, 8.53; N, 3.50.

Enoxysilane 5c: mp 85–86 °C; IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.2 (s, 9 H), 1.1–1.4 (m, 3 H), 1.5–1.9 (m, 4 H), 2.5 (m, 1 H), 2.8 (m, 1 H), 3.1 (m, 1 H), 3.6 (m, 1 H), 3.7 (s, 3 H), 4.6 (t, J = 5.5 Hz, 1 H), 6.6–6.9 (m, 4 H), 7.0–7.2 (m, 5 H); $w_{1/2}(H_9)$ = 21.3; ^{13}C NMR ($CDCl_3$) 0.7 (q), 25.5 (t), 26.2 (t), 27.0 (t), 32.1 (t), 37.4 (t), 55.3 (q), 59.1 (d), 60.1 (d), 113.4 (d), 118.1 (s), 125.6 (d), 126.5 (d), 127.8 (d), 138.5 (s), 142.1 (s), 142.3 (s), 154.6 (s); MS, m/z 407 (M^+). Anal. Calcd for $C_{25}H_{33}NO_2Si$: C, 73.66; H, 8.16; N, 3.43. Found: C, 73.81; H, 7.87; N, 3.43.

Enoxysilane 5d: IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.2 (s, 9 H), 1.1–1.4 (m, 3 H), 1.5–1.9 (m, 4 H), 2.2 (m, 1 H), 2.8 (s, 6 H), 2.9 (m, 2 H), 3.6 (m, 1 H), 4.5 (t, J = 5.9 Hz, 1 H), 6.5–6.8 (m, 4 H), 7–7.3 (m, 5 H); $w_{1/2}(H_9)$ = 20.9 Hz.

Enoxysilane 5e: IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 4.2 (dd, J = 8.8 and 4.4 Hz, 1 H); $w_{1/2}(H_9)$ = 20.0 Hz.

Enoxysilane 5f or 5g: 250-MHz ^1H NMR ($CDCl_3$) 3.3 (m, 1 H), 4.2 (dd, J = 8.8 and 4.4 Hz, 1 H); $w_{1/2}(H_9)$ = 20.0 Hz.

Enoxysilane 6a: mp 110–111 °C; IR C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.3 (s, 9 H), 1.0–2.0 (m, 7 H), 2.5 (m, 1 H), 2.7 (m,1 H), 3.7 (m, 1 H), 4.8 (t, J = 5.5 Hz, 1 H), 6.6–7.7 (m, 10 H); $w_{1/2}(H_9)$ = 20.0 Hz; ^{13}C NMR ($CDCl_3$) 0.6 (q), 25.2 (t), 25.8 (t), 26.1 (t), 32.8 (t), 37.2 (t), 59.0 (d), 60.9 (d), 116.7 (s), 121.1 (d), 121.7 (d), 126.5 (d), 127.6 (d), 128.0 (d), 128.5 (d), 138.5 (s), 143.0 (s), 149.7 (s); MS m/z 377 (M^+). Anal. Calcd for $C_{24}H_{31}NOSi$: C, 76.34; H, 8.27; N, 3.71. Found: C, 76.82; H, 8.78; N, 3.26.

Enoxysilane 6b: mp 127–128 °C; IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.2 (s, 9 H), 1.1 (m, 3 H), 1.6 (m, 4 H), 2.2 (s, 3 H), 2.3 (dd, J = 4.3 and 16.0 Hz, 1 H), 2.6 (m, J = 8.7 and 16.0 Hz), 2.9 (m, 1 H), 3.5 (m, 1 H), 4.5 (dd, J = 8.7 and 4.3 Hz, 1 H), 7.0–7.3 (m, 9 H); $w_{1/2}(H_9)$ = 19.5 Hz; ^{13}C NMR ($CDCl_3$) 0.6 (q), 20.8 (q), 25.2 (t), 25.7 (t), 26.3 (t), 33.5 (t), 38.8 (t), 61.0 (d), 62.5 (d), 117.1 (s), 124.2 (d), 126.4 (d), 127.7 (d), 128.3 (d), 129.0 (d), 131.9 (s), 138.8 (s), 143.4 (s), 147.7 (s); MS m/z 391 (M^+). Anal. Calcd for $C_{25}H_{33}NOSi$: C, 76.67; H, 8.49; N, 3.57. Found: C, 76.53; H, 8.30; N, 3.40.

Enoxysilane 6c: mp 129–130 °C; IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.2 (s, 9 H), 1.0–1.3 (m, 3 H), 1.5–1.8 (m, 4 H), 2.1–2.3 (m, J = 3.0 and 17.0 Hz, 1 H), 2.5–2.7 (m, J = 9.0 and 17.0 Hz, 1 H), 2.9–3.0 (m, 1 H), 3.3 (m, 1 H), 3.6 (s, 3 H), 4.2 (dd, J = 3.0 and 9.0 Hz, 1 H), 6.7 (bd, 2 H), 6.9–7.2 (m, 7 H); $w_{1/2}(H_9)$ = 16.9 Hz; ^{13}C NMR ($CDCl_3$) 0.8 (q), 25.0 (t), 25.4 (t), 26.3 (t), 34.0 (t), 40.7 (t), 55.1 (q), 63.5 (d), 64.3 (d), 113.3 (s), 117.3 (s), 126.4 (s), 127.7 (d), 128.5 (d), 139.2 (s), 143.4 (s), 156.2 (s); MS, m/z 407 (M^+). Anal. Calcd for $C_{25}H_{33}NOSi$: C, 73.66; H, 8.16; N, 3.16. Found: C, 73.57; H, 8.00; N, 3.16.

Enoxysilane 6d: IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.2 (s, 9 H), 1.0–1.9 (m, 6 H), 2.2 (m, 1 H), 2.4 (m, 1 H), 2.5 (m, 1 H), 2.7 (s, 6 H), 2.8 (, 2 H), 3.3 (m, 1 H), 4.2 (dd, J = 12.8 and 4.4 Hz, 1 H), 6.5 (bd, 2 H), 6.8 (bd, 2 H), 7.0–7.3 (m, 5 H); $w_{1/2}(H_9)$ = 23.5 Hz.

Enoxysilane 6e: IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 4.1 (dd, J = 10.9 and 4.2 Hz).

Enoxysilane 6f or 6g: 250-MHz ^1H NMR ($CDCl_3$) 3.4 (m, 1 H), 3.9 (dd, J = 3.6 and 11.7 Hz); $w_{1/2}(H_9)$ = 21 Hz.

Enoxysilane 13: IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.3 (s, 6 H), 1.2 (s, 9 H), 1.2–1.5 (m, 3 H), 1.7–1.9 (m, 4 H), 2.4 (m, 1 H), 2.7–3.0 (m, 1 H), 3.0 (m, 1 H), 3.9 (m, 1 H), 7.0–7.5 (m, 10 H).

Enoxysilane 14: IR ($CDCl_3$) C=C—O 1660; 250-MHz ^1H NMR ($CDCl_3$) 0.2 (s, 6 H), 1.1 (s, 9 H), 1.2–1.6 (m, 3 H), 1.6–1.9 (m, 4 H), 2.4 (m, 1 H), 2.6 (dd, 1 H), 3.0 (m, 1 H), 3.6 (m, 1 H), 4.7 (dd, 1 H), 7.0–7.9 (m, 10 H).

General Procedure for Protonation of Enoxysilanes. MeOH (250 mL) and Et_3N (250 mL) were added to pure or mixtures of enoxysilanes (210 mg). The mixture was stirred for various times at room temperature. Either a precipitate was formed (immediately or not), isolated, and recrystallized or an oil was obtained after evaporation of the solvent and purified by column chromatography.

1,2-Diphenyldecahydroquinolin-4-one (7a): obtained from pure **5a** ($MeOH/Et_3N$ treatment, 15 h) and crystallized from ethyl acetate/hexane (1/2), in a 70% yield; mp 167–168 °C; IR ($CDCl_3$) CO 1720; 250-MHz ^1H NMR ($CDCl_3$) 1.3 (m, 4 H), 1.5 (m, 1 H), 1.8 (m, 1 H), 2.2 (m, 1 H), 2.4 (m, 1 H), 2.9 (dd, J = 5.3 and 17.0 Hz, 1 H), 4.1 (m, $w_{1/2}$ = 21 Hz, 1 H), 5.1 (t, J = 5.3 Hz, 1 H), 6.5–7.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) 21.9 (t), 25.0 (t), 25.1 (t), 28.4 (t), 47.7 (t), 49.6 (d), 56.1 (d), 59.4 (d), 116.1 (d), 118.2 (d), 127.0 (d), 127.7 (d), 128.7 (d), 129.0 (d), 142.4 (s), 147.4 (s), 209.0 (s); MS, m/z 305 (M^+). Anal. Calcd for $C_{21}H_{23}NO$: C, 82.62; H, 7.54; N, 4.59. Found: C, 82.51; H, 7.69; N, 4.89.

1-(*p*-Methylphenyl)-2-phenyldecahydroquinolin-4-one (7b): obtained from pure **5b** ($MeOH/Et_3N$ treatment, 15 h) and crystallized from MeOH, in a 78% yield; mp 123–124 °C; IR

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($CDCl_3$) CO 1720; 250-MHz ^1H NMR ($CDCl_3$) 1.3 (m, 3 H), 1.5 (m, 2 H), 1.7 (m, 1 H), 2.1 (m, 1 H), 2.2 (s, 3 H), 2.4 (m, 1 H), 2.8 (dd, J = 5.0 and 16.9 Hz, 1 H), 2.9 (dd, J = 5.0 and 16.9 Hz, 1 H), 3.1 (m, 1 H), 4.1 (m, $w_{1/2}$ = 21.0 Hz, 1 H), 5 (t, J = 5.0 Hz, 1 H), 6.6 (bd, 2 H), 6.9 (bd, 2 H), 7.1 (m, 5 H); ^{13}C NMR ($CDCl_3$) 20.6 (q), 22.3 (t), 25.0 (t), 25.7 (t), 26.3 (t), 48.0 (t), 50.4 (d), 56.3 (d), 60.3 (d), 116.0 (d), 120.4 (d), 128.0 (d), 128.4 (d), 129.0 (d), 131.5 (s), 138.8 (s), 143.4 (s), 209.0 (s); MS, m/z 319 (M^+). Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.63; H, 7.98; N, 4.40.

1-(*p*-Methoxyphenyl)-2-phenyldecahydroquinolin-4-one (7c): obtained from pure **5c** ($MeOH/Et_3N$ treatment, 15 h) and crystallized from EtOH, in a 62% yield; mp 126–127 °C; IR ($CDCl_3$) CO 1720; 250-MHz ^1H NMR ($CDCl_3$) 1.1–1.5 (m, 4 H), 1.6–1.7 (m, 1 H), 1.8–1.9 (m, 1 H), 2.3–2.4 (m, 1 H), 2.7–2.8 (m, 2 H), 3.2 (m, 1 H), 3.7 (s, 3 H), 3.8–3.9 (m, $w_{1/2}$ = 24.0 Hz, 1 H), 4.8 (dd, J = 5.4 and 8.0 Hz, 1 H), 6.6–6.8 (AA'BB' system, 4 H), 7.0–7.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) 21.8 (t), 24.8 (t), 24.9 (t), 25.2 (t), 50.0 (t), 50.3 (q), 55.3 (d), 57.8 (d), 64.0 (d), 113.7 (d), 122.9 (d), 126.7 (d), 128.4 (d), 141.7 (s), 143.0 (s), 153.9 (s), 209.2 (s); MS m/z 335 (M^+). Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.52; N, 4.17; O, 9.54. Found: C, 78.58; H, 7.36; N, 3.71; O, 9.70.

1-[*p*-(Dimethylamino)phenyl]-2-phenyldecahydroquinolin-4-one (7d): obtained from mixture **5d/6d** ($MeOH/Et_3N$ treatment, 15 h) and crystallized from cyclohexane in a 55% yield; mp 132–133 °C; IR (C_6D_6) CO 1720; 250-MHz ^1H NMR (C_6D_6) 0.9–1.4 (m, 3 H), 1.4–1.5 (m, 1 H), 1.5–1.9 (m, 4 H), 2.4 (s, 6 H), 2.5–2.6 (m, J = 8.6 and 15.0 Hz, 1 H), 2.7–2.8 (dd, J = 6.3 and 15.0 Hz, 1 H), 3.0 (m, 1 H), 3.7 (m, $w_{1/2}$ = 24.8 Hz, 1 H), 4.6 (dd, J = 8.6 and 6.3 Hz, 1 H), 6.5 (dd, 2 H), 6.8–7.1 (m, 7 H); ^{13}C NMR (C_6D_6) 21.9 (t), 23.8 (t), 24.9 (t), 27.7 (t), 50.1 (t), 50.2 (q), 56.2 (d), 58.7 (d), 65.1 (d), 113.5 (d), 122.1 (d), 125.3 (d), 127.6 (d), 140.3 (s), 143.2 (s), 154.5 (s), 209.1 (s); MS, m/z 348 (M^+). Anal. Calcd for $C_{23}H_{28}NO_2$: C, 79.27; H, 8.09; N, 8.03; O, 4.58. Found: C, 79.13; H, 8.00; N, 7.98; O, 4.47.

1-Benzyl-2-phenyldecahydroquinolin-4-one (7e): obtained from mixture **5e/6e** ($MeOH/Et_3N$ treatment, 15 h) and crystallized from ethyl acetate/hexane (1/2) in a 58% yield; mp 158–159 °C; IR ($CDCl_3$) CO 1720; 250-MHz ^1H NMR ($CDCl_3$) 0.9–1.3 (m, 5 H), 1.8 (m, 1 H), 1.9 (m, 1 H), 2.2 (m, 1 H), 2.5 (dd, J = 4.0 and 14.6 Hz, 1 H), 2.6 (dd, J = 10.6 and 14.6 Hz, 1 H), 2.9 (m, $w_{1/2}$ = 13 Hz, 1 H), 3.1 (td, J = 6.1 and 4.4 Hz, 1 H), 3.3 (d, J = 13.3 Hz, 1 H), 3.6 (d, J = 13.3 Hz, 1 H), 4.1 (dd, J = 4.0 and 10.6 Hz, 1 H), 7.1–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) 21.0 (t), 22.1 (t), 24.7 (t), 25.3 (t), 49.8 (t), 50.1 (d), 51.8 (t), 58.4 (d), 61.9 (d), 126.9 (d), 127.4 (d), 128.7 (d), 128.4 (d), 128.9 (d), 139.8 (s), 143.2 (s), 210.1 (s); MS, m/z 319 (M^+). Anal. Calcd for $C_{22}H_{25}NO$: C, 82.75; H, 7.83; N, 4.38. Found: C, 81.64; H, 7.70; N, 4.55.

2-Phenyldecahydroquinolin-4-one (7g): obtained from mixture **5f/6f** ($MeOH/Et_3N$ treatment, 15 h) and SiO_2 chromatography (eluent ethyl acetate/hexane 7/3); oil; R_f 0.35; IR ($CDCl_3$) NH 3420, CO, 1710; 250-MHz ^1H NMR ($CDCl_3$) 0.7–2.4 (m, 9 H), 2.4–2.5 (m, 2 H), 2.8 (m, $w_{1/2}$ = 15.0 Hz, 1 H), 3.4 (m, $w_{1/2}$ = 23.0 Hz, 1 H), 4.3 (dd, J = 8.5 and 5.0 Hz, 1 H), 7.3–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) 21.7 (t), 24.5 (t), 25.0 (t), 29.9 (t), 49.8 (t, d), 55.8 (d), 56.6 (d), 126.6 (d), 127.4 (d), 127.7 (d), 128.7 (d), 210.9 (s), 142.8 (s). MS, m/z 229 (M^+).

1,2-Diphenyldecahydroquinolin-4-one (8a): obtained from pure **6a** ($MeOH/Et_3N$ treatment, 15 h) and crystallized from ethyl acetate/hexane (1/2), in a 45–50% yield; mp 156–157 °C; IR ($CDCl_3$) CO 1715; 250-MHz ^1H NMR ($CDCl_3$) 1.5 (m, 5 H), 1.9 (m, 1 H), 2.2 (m, 1 H), 2.7 (dd, J = 4.5 and 16 Hz, 1 H), 2.8 (bdd, J = 11.2 Hz, 16 Hz, 2 H), 3.9 (m, $w_{1/2}$ = 21 Hz, 1 H), 4.9 (dd, J = 4.5 and 11.2 Hz, 1 H), 6.6–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) 22.6 (t), 24.5 (t), 25.6 (t), 34.5 (t), 48.3 (t), 49.9 (d), 59.6 (d), 62.0 (d), 118.6 (d), 120.0 (d), 126.4 (d), 127.2 (d), 128.7 (d), 128.8 (d), 143.8 (s), 149.9 (s), 210.3 (s); MS m/z 305 (M^+). Anal. Calcd for $C_{21}H_{23}NO$: C, 82.62; H, 7.54; N, 4.59. Found: C, 82.48; H, 7.71; N, 4.78.

1-(*p*-Methylphenyl)-2-phenyldecahydroquinolin-4-one (8b): obtained from pure **6b** ($MeOH/Et_3N$ treatment, 15 h) and crystallized from EtOH, in a 57% yield; mp 103–104 °C; IR ($CDCl_3$) CO 1715; 250-MHz ^1H NMR ($CDCl_3$) 1.4 (m, 4 H), 1.7 (m, 2 H), 2.0 (m, 1 H), 2.1 (s, 3 H), 2.4 (m, 1 H), 2.6 (dd, J = 3.6 and 17.2 Hz, 1 H), 2.8 (m, 2 H), 3.7 (m, $w_{1/2}$ = 21.4 Hz, 1 H), 4.7 (dd, J = 3.6 and 11.6 Hz, 1 H), 6.7 (dd, 1 H), 6.9 (dd, 1 H), 7.1 (m, 5 H); ^{13}C NMR ($CDCl_3$) 20.4 (q), 22.3 (t), 25.1 (t), 25.4 (t), 33.7 (t), 49.1 (t), 50.6 (d), 61.3 (d), 63.5 (d), 117.7 (d), 121.3 (d), 126.8 (d), 127.7 (d), 128.8 (d), 128.9 (d), 132.6 (s), 140.8 (s), 147.3 (s), 210.7 (s); MS, m/z 319 (M^+). Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.70; H, 7.91; N, 4.39.

1-(*p*-Methoxyphenyl)-2-phenyldecahydroquinolin-4-one (8c): obtained from pure **6c** ($MeOH/Et_3N$ treatment, 2 h); oil; IR ($CDCl_3$) CO 1720; 250-MHz ^1H NMR ($CDCl_3$) 1.2–1.6 (m, 5 H), 1.6–1.9 (m, 3 H), 2.5–2.6 (m, 1 H), 2.8–3 (dd, J = 11.9 and 16.3 Hz, 1 H), 3.5–3.6 (m, $w_{1/2}$ = 15.8 Hz, 1 H), 3.7 (s, 3 H), 4.5 (dd, J = 11.9 and 3.5 Hz, 1 H), 6.6 (bd, 2 H), 6.9 (bd, 2 H), 7.0–7.3 (m, 5 H); 500-MHz ^1H NMR ($CDCl_3$, at 223 K) $8c_1$ and $8c_2$ are characterized by the following signals, $8c_1$ 4.8 (m, 1 H), 3.7 (m, $w_{1/2}$ = 25.0 Hz, 1 H); $8c_2$ 3.9 (m, 1 H), 3.2 (m, $w_{1/2}$ = 14.0 Hz, 1 H).

1-[*p*-(Dimethylamino)phenyl]-2-phenyldecahydroquinolin-4-one (8d): obtained from mixture **5d/6d** ($MeOH/Et_3N$ treatment, 2 h). The ^1H NMR spectrum of the filtrate shows the presence of **8d** and **9d** in a 50/50 ratio; **8d** was characterized in the presence of **9d**. 250-MHz ^1H NMR ($CDCl_3$): 2.7 (m, 1 H), 3.5 (m, $w_{1/2}$ = 18.7 Hz, 1 H), 4.5 (dd, J = 11.9 and 3.2 Hz, 1 H).

1-Benzyl-2-phenyldecahydroquinolin-4-one (8e): obtained from **5e/6e** mixture ($MeOH/Et_3N$ treatment, 2 h) by Al_2O_3 chromatography (eluent cyclohexane/methylene chloride 1/9) in a 3% yield; oil; R_f 0.5; IR ($CDCl_3$) CO 1710; 250-MHz ^1H NMR ($CDCl_3$) 0.7–1.7 (m, 9 H), 2.5 (dd, J = 3.5 and 18.0 Hz, 1 H), 2.6 (dd, J = 12.1 and 18.0 Hz, 1 H), 2.9 (m, 1 H), 3.0 (m, $w_{1/2}$ = 22.0 Hz, 1 H), 3.5 (d, 1 H), 3.8 (d, 1 H), 4.1 (dd, J = 12.1 and 3.5 Hz, 1 H), 7.1–7.6 (m, 10 H); ^{13}C NMR ($CDCl_3$) 22.2 (t), 24.7 (t), 25.0 (t), 35.4 (t), 48.0 (t), 58.2 (d), 59.3 (t), 63.0 (d), 66.3 (d), 127.0 (d), 127.4 (d), 128.0 (d), 128.7 (d), 129.0 (d), 139.3 (s), 144.0 (s), 211.4 (s).

Preparation of Trans Ketones 9a and 9b by *n*-$Bu_4N^+F^-$ Treatment of Enoxysilanes 6a and 6b. A solution of **6a** or **6b** (1 mmol) in 4 mL of dry THF was treated with 2.9 mmol of tetra-*n*-butylammonium fluoride (1 M in THF) under an argon atmosphere for 2 h at room temperature. The mixture was diluted with ether, washed with water, and dried over $MgSO_4$. After removal of solvents under reduced pressure the crude residue **9a** or **9b** was recrystallized from ethylacetate/hexane (1/2).

1,2-Diphenyldecahydroquinolin-4-one (9a): mp 144–145 °C; IR ($CDCl_3$) CO 1715; 250-MHz ^1H NMR ($CDCl_3$) 0.8–1.3 (m, 4 H), 1.4–1.7 (m, 3 H), 1.9–2.0 (m, 1 H), 2.4 (td, J = 10.1 and 2.7 Hz, 1 H), 2.5 (dd, J = 3.6 and 14.6 Hz, 1 H), 2.8 (dd, J = 10.0 and 14.6 Hz, 2 H), 4.3 (dd, J = 10.0 and 3.6 Hz, 1 H), 6.4–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) 24.4 (t), 24.7 (t), 33.0 (t), 49.4 (t), 53.9 (d), 65.3 (d), 67.2 (d), 124.3 (d), 125.8 (d), 127.0 (d), 127.7 (d), 128.2 (d), 128.5 (d), 142.3 (s), 148.9 (s), 209.4 (s); MS, m/z 305 (M^+). Anal. Calcd for $C_{21}H_{23}NO$: C, 82.62; H, 7.54; N, 4.59. Found: C, 82.44; H, 7.47; H, 4.77.

1-(*p*-Methylphenyl)-2-phenyldecahydroquinolin-4-one (9b): yield 75%; mp 121–122 °C; IR ($CDCl_3$) CO 1715; 250-MHz ^1H NMR ($CDCl_3$) 1.0–1.4 (m, 1 H), 1.5–1.7 (m, 2 H), 1.8 (m, 1 H), 2.1 (m, 1 H), 2.2 (s, 3 H), 2.5 (td, J = 10.1 and 3.0 Hz, 1 H), 2.6 (dd, J = 3.6 and 14.4 Hz, 1 H), 2.8–3.0 (m, J = 10.4 and 14.4 Hz, 2 H), 4.3 (dd, J = 10.4 and 3.6 Hz, 1 H), 6.9–7.3 (m, 9 H); ^{13}C NMR ($CDCl_3$) 20.2 (q), 24.3 (t), 24.8 (t), 34.0 (t), 50.0 (t), 55.2 (d), 67.4 (d), 68.4 (d), 125.4 (d), 126.3 (d), 127.2 (d), 128.3 (d), 132.4 (s), 143.4 (s), 147.2 (s), 209.7 (s); MS, m/z 319 (M^+). Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.63; H, 7.83; N, 4.30.

Preparation of Trans Ketones 9c–e,g by $MeOH/Et_3N$ Treatment of Enoxysilanes 5c–g and 6c–g. General Procedure. To pure **6c** or **5d–g/6d–g** mixtures (1 mmol) were added respectively 250 μL of Et_3N and 250 μL of MeOH. The solution was stirred for 15 h at room temperature. In the case of **9c**, the precipitate was filtered, washed with ether, and crystallized from ether. **9d–g** ketones were purified by SiO_2 chromatography of the crude product.

1-(*p*-Methoxyphenyl)-2-phenyldecahydroquinolin-4-one (9c): yield 80%; mp 124–125 °C; IR ($CDCl_3$) CO 1715; 250-MHz ^1H NMR ($CDCl_3$) 1.0–1.5 (m, 5 H), 1.6–1.7 (m, 1 H), 1.7–1.8 (m, 1 H), 2.0–2.1 (m, 1 H), 2.5–2.6 (m, 2 H), 2.8 (td, J = 11.9 and 3.4 Hz, 1 H), 2.9 (dd, J = 11.0 and 13.1 Hz, 1 H), 3.7 (s, 3 H), 4.2 (dd, J = 11.0 and 3.3 Hz, 1 H), 6.6 (bd, 2 H), 6.9 (bd, 2 H) 7.0–7.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) 24.0 (t), 24.7 (t), 24.8 (t), 33.2 (t), 50.8

(t), 54.8 (q), 55.2 (d), 67.5 (d), 68.8 (d), 113.6 (d), 127.0 (d), 127.9 (d), 128.2 (d), 128.5 (d), 141.5 (s), 142.3 (s), 157.0 (s), 209.6 (s); MS, m/z 335 (M^+). Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.52; N, 4.17; O, 9.54. Found: C, 78.64; H, 7.39; N, 4.03; O, 9.63.

1-[*p*-(Dimethylamino)phenyl]-2-phenyldecahydroquinolin-4-one (9d): eluent cyclohexane (9/1); R_f = 0.6; yield 45%; mp 130–131 °C; IR ($CDCl_3$) CO 1715; 250-MHz ^1H NMR ($CDCl_3$) 1.0–1.4 (m, 5 H), 1.5–1.8 (m, 1 H), 2.0–2.1 (m, 2 H), 2.5–2.6 (m, 2 H), 2.7 (td, J = 12.7 and 3.3 Hz, 1 H), 2.8 (s, 6 H), 2.9 (t, J = 14.2 Hz, 1 H) 4.2 (dd, J = 14.2 and 4.2 Hz, 1 H), 6.6 (bd, 2 H), 6.9 (dd, 2 H) 7.0–7.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) 24.2 (t), 24.4 (t), 25.2 (t), 51.3 (t), 56.1 (d), 67.7 (d), 68.7 (d), 127.4 (d), 127.7 (d), 128.3 (d), 129.4 (d), 141.1 (s), 143.1 (s), 144.0 (s), 209.6 (s); MS, m/z 348 (M^+). Anal. Calcd for $C_{23}H_{28}N_2O$: C, 79.27; H, 8.09; N, 8.03; O, 4.58. Found: C, 78.97; H, 8.05; N, 7.95; O, 4.50.

1-Benzyl-2-phenyldecahydroquinolin-4-one (9e): eluent CH_2Cl_2/hexane (9/1); yield 50%; R_f 0.3; mp 158–159 °C; 250-MHz ^1H NMR ($CDCl_3$) 1.0–1.4 (m, 4 H), 1.6–1.8 (m, 2 H), 1.9–2.1 (m, 2 H), 2.4–2.5 (m, 3 H), 2.8 (t, J = 12.2 Hz, 1 H), 3.5 (d, J = 16.2 Hz, 1 H), 3.8 (dd, J = 12.2 and 3.4 Hz, 1 H), 3.9 (d, J = 16.2 Hz, 1 H), 7.1–7.4 (m, 10 H); 500-MHz ^1H NMR (C_6D_6) 0.8–1.1 (m, 3 H), 1.2–1.6 (m, 3 H), 1.7–1.8 (m, 1 H), 2.0–2.1 (m, 2 H), 2.2 (td, J = 9.5 and 3.6 Hz, 1 H), 2.4 (dd, J = 12.0, 3.6 Hz, 1 H), 2.5 (t, J = 12 Hz, 1 H), 3.2 (d, J = 16.5 Hz, 1 H), 3.5 (dd, J = 12.0 and 3.6 Hz, 1 H), 3.7 (d, J = 16.5 Hz, 1 H), 6.9–7.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) 24.3 (t), 24.6 (t), 25.2 (t), 33.7 (t), 49.8 (t), 53.5 (d), 53.9 (t), 68.4 (d), 126.3 (d), 127.5 (d), 127.6 (d), 128.0 (d), 128.4 (d), 128.8 (d), 141.1 (s), 143.1 (s), 209.6 (s); MS, m/z 319 (M^+). Anal. Calcd for $C_{22}H_{25}NO$: C, 82.75; H, 7.83; N, 4.38. Found: C, 82.17; H, 7.78; N, 4.16.

2-Phenyldecahydroquinolin-4-one (9g): eluent AcOEt/hexane (1/2); mp 100–101 °C; IR ($CDCl_3$) NH 3400, CO 1710; 250-MHz ^1H NMR ($CDCl_3$) 1.1–1.6 (m, 4 H), 1.7–2.0 (m, 5 H), 2.2 (td, J = 10.4 and 3.5 Hz, 1 H), 2.6 (m, 3 H), 4.0 (dd, J = 11 and 3.8 Hz, 1 H), 7.2–7.4 (m, 5 H); 250-MHz (pyridine-d_6) 1.1–1.7 (m, 7 H), 1.8–2.0 (m, 1 H), 2.0–2.1 (m, 1 H), 2.1 (td, J = 11.0 and 3.5 Hz, 1 H), 2.5 (td, J = 11.0 and 3.5 Hz, 1 H), 2.6 (dd, J = 11.0, 4.8 Hz, 1 H), 2.7 (t, J = 11.0 Hz, 1 H), 4.0 (dd, J = 11.0, 4.8 Hz, 1 H), 7.0–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) 23.4 (t), 24.6 (t), 25.0 (t), 33.9 (t), 50.6 (t), 55.4 (d), 61.7 (d), 61.8 (d), 126.2 (d), 127.8 (d), 128.8 (d), 142 (s), 209.8 (s); MS, m/z 229 (M^+). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.60; H, 8.29; N, 6.11. Found: C, 78.32; H, 7.99; N, 6.12.

2-Phenyldecahydroquinolin-4-one (10): oil; R_f 0.2; IR ($CDCl_3$) NH 3400, CO 1710; 250-MHz ^1H NMR ($CDCl_3$) 1.0–1.4 (m, 4 H), 1.7 (m, 4 H), 2.0 (m, 1 H), 2.1 (td, J = 10.5 and 3.6 Hz, 1 H), 2.5 (td, J = 10.5 and 3.6 Hz, 1 H), 2.9 (m, 2 H), 4.7 (dd, J = 6.1 and 3.6 Hz, 1 H), 7.2–7.4 (m, 5 H); MS, m/z 229 (M^+).

1-Cyclohexenyl 2-Anilino-2-phenylethyl Ketone (11a). To a solution of benzylideneaniline (**2a**) (181 mg, 1.0 mmol) and diene **1** (235 mg, 1.2 mmol) in CH_2Cl_2 (10 mL) was added $BF_3{\cdot}Et_2O$ (125 μL, 1.0 mmol) at 20 °C under argon. The reaction mixture was stirred for 30 min and then quenched with water (20 mL). Usual workup gave an oil, which was treated with MeOH (20 mL) for 2 h. The precipitate was filtered and washed with hexane. Recrystallization from hexane/ethyl acetate (2/1) leads to **11a** in a 65–70% yield: mp 141–142 °C; IR ($CDCl_3$) NH 3420, CO 1670; 400-MHz ^1H NMR ($CDCl_3$) 1.4 (m, 4 H), 2.0 (m, 4 H), 2.9 (dd, J = 8.0 and 15.0 Hz, 1 H), 3.1 (dd, J = 7.0 and 15.0 Hz, 1 H), 4.7 (dd, J = 7.0 and 8.0 Hz, 1 H), 6.5–7.4 (m, 11 H); MS, m/z 305 (M^+). Anal. Calcd for $C_{21}H_{23}NO$: C, 82.62; H, 7.54; N, 4.59. Found: C, 82.51; H, 7.52; N, 4.59.

1-Cyclohexenyl 2-(*p*-Methylanilino)-2-phenylethyl Ketone (11b). To a solution of pure **5b** (100 mg) in CH_2Cl_2 was added 10 mL of HCl (0.1 M). The reaction mixture was stirred for 3 h and extracted with methylene chloride. The combined organic layers were washed with brine, dried, and concentrated. The resulting precipitate was filtered and washed with EtOH to give an 80% yield: recrystallization from EtOH; mp 148–149 °C; IR ($CDCl_3$) NH 3420, CO 1670; 250-MHz ^1H NMR ($CDCl_3$) 1.5–1.7 (m, 4 H), 2.1–2.3 (m, 7 H), 3.0–3.1 (dd, J = 7.6 and 15.3 Hz, 1 H), 3.1–3.2 (dd, J = 5.1 and 15.3 Hz, 1 H), 4.8 (dd, J = 7.6 and 5.1 Hz, 1 H), 6.5 (dd, 2 H), 6.9 (m, 3 H), 7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$) 20.2 (t), 21.3 (t), 21.7 (t), 22.8 (t), 26.1 (q), 44.7 (t), 55.7 (d), 114.0 (d), 126.3 (d), 126.8 (d), 127.1 (d), 128.7 (d), 129.3 (d), 139.3 (s), 141.3 (s), 143.2 (s), 144.8 (s), 199.5 (s).

Under similar conditions **7b** and **7e** remained unchanged, while **8b** was isomerized into **9b**.

Cyclization of 11a by $TiCl_4$. To a solution of compound **11a** (305 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added a 1 M solution of $TiCl_4$ (1 mL) in the same solvent under argon at room temperature. The mixture was stirred for 18 h and then quenched with a 0.1 M $NaHCO_3$ aqueous solution (20 mL). After usual workup, column chromatography on silica gel with CH_2Cl_2/hexane (9/1) and recrystallization from ethyl acetate/hexane (1/2), **9a** was obtained in a 60–65% yield.

Debenzylation Experiments. Decahydroquinolin-4-one **7e** or **9e** (100 mg, 0.3 mmol) was dissolved into 10 mL of MeOH/CH_2Cl_2 (1/1); 0.15 mg of 20% $Pd(OH)_2$ on carbon (Aldrich) was added and the mixture was stirred under an H_2 atmosphere until absorption no longer took place (about 30 h). The mixture was filtered over Celite, the solvents were evaporated, and the residue was chromatographed on SiO_2: purified yield in **7g** from **7e** 40% (eluent AcOEt/hexane (7/3)), in **9g** from **9e** 80% (eluent MeOH/CH_2Cl_2 (1/1)).

Base Isomerization of 8a into 9a. To a solution of diisopropylamine (45 mL, 0.32 mmol) in DME (0.5 mL), cooled with an ice bath, was added dropwise *n*-BuLi (210 mL, 1.5 M, 0.31 mmol) under argon. After the addition was complete, the yellow solution was stirred at room temperature for 5 min. A solution of ketone **7a** and **8a** (**7a**/**8a** 2/8) (100 mg, 0.33 mmol) in DME (1 mL) was then added rapidly. The reaction was stirred for 4 h and quenched with H_2O (0.5 mL). Usual workup leads to a mixture of compounds **7a**, **8a**, and **9a** in the 20/10/70 ratio determined by ^1H NMR.

Retro-Diels–Alder Process Experiments. To a 0.1 M solution of pure **5b** in CH_2Cl_2 was added 1 equiv. of $AlCl_3$ under argon at room temperature. After stirring for 15 mm[a] or 2 h[b], washing with a 0.1 M NaHCO aqueous solution, and usual workup **2b**, **5b**, **6b**, **7b**, **8b**, and **9b** were characterized by ^1H NMR in the following ratios: **2b**/**5b**/**6b**/**7b**/**8b**/**9b** = (a) 5/11/25/38/5/16, (b) 2/19/2/20/9/48.

To a 0.1 M solution of the pure **5a** in CH_2Cl_2 was added diene **3** (1 equiv) and then 1 equiv of $AlCl_3$ under argon at room temperature. The mixture was stirred for 2.5 h and then washed with a 0.1 M $NaHCO_3$ aqueous solution. After usual workup **4** was characterized by ^1H NMR comparison to unchanged **5a**.

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Supplementary Material Available: Tables of X-ray data for **7a**, **7c**, **7e**, and **8a** and ^1H NMR spectra **5d**,**e**,**g**/**6d**,**e**,**g**, **7g**, **8d**/**9d**, **8e**, **11b**, and **13**/**14** (24 pages). Ordering information is given on any current masthead page.