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The Effect of the Benzene Ring on 1,5-Electrocyclizations: Synthesis and Thermolysis of Optically Active Benzohomofuran, Benzohomothiophene, N-Carbmethoxyhomoindole, Benzohomophosphole and Homoindene.

Dedicated to Professor Günther Snatzke

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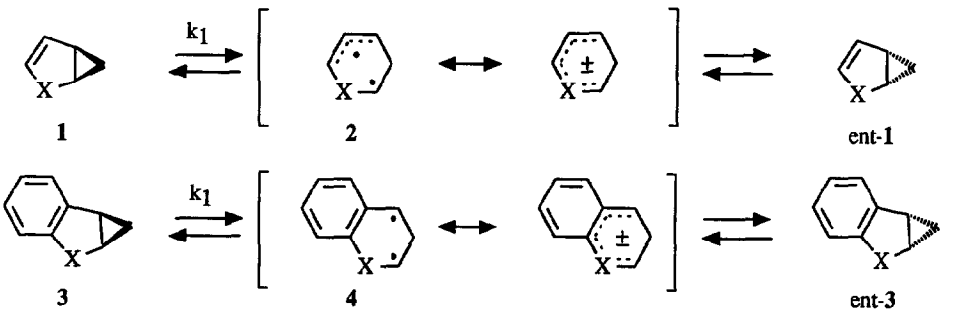
Abstract: *Carbonyl ylide-like intermediates are involved in the 1,5-electrocyclization of the benzo-heterocycles* ***3a-d*** *mentioned in the title. The activation barriers analyzed by the time- and temperature-dependence of the racemisation of the optically active derivatives turned out to be higher by* $\Delta\Delta G^{\neq} = 13 \pm 2$ *kcal/mol than those determined for the parent systems* ***1a-d*** *whereas for the corresponding carbocycles* ***3d*** *and* ***1d*** *the difference is only* $\Delta\Delta G^{\neq} \approx 4$ *kcal/mol as expected from the difference between the bond dissociation energies of toluene and propene (*$\Delta BDE = 3.2$ *kcal/mol). This result can be considered as an evidence for the electrocyclic character of the ring-opening in the heterocycles* ***1a-d*** *and* ***3a-d.*** *The difference between the Gibbs activation enthalpies found for the ring-opening of homofuran* ***1a*** *and homothiophene* ***1b*** *(*$\Delta\Delta G^{\neq} = 8.7$ *kcal/mol) can be attributed to the heteroatom effect on the ground state.*

Introduction



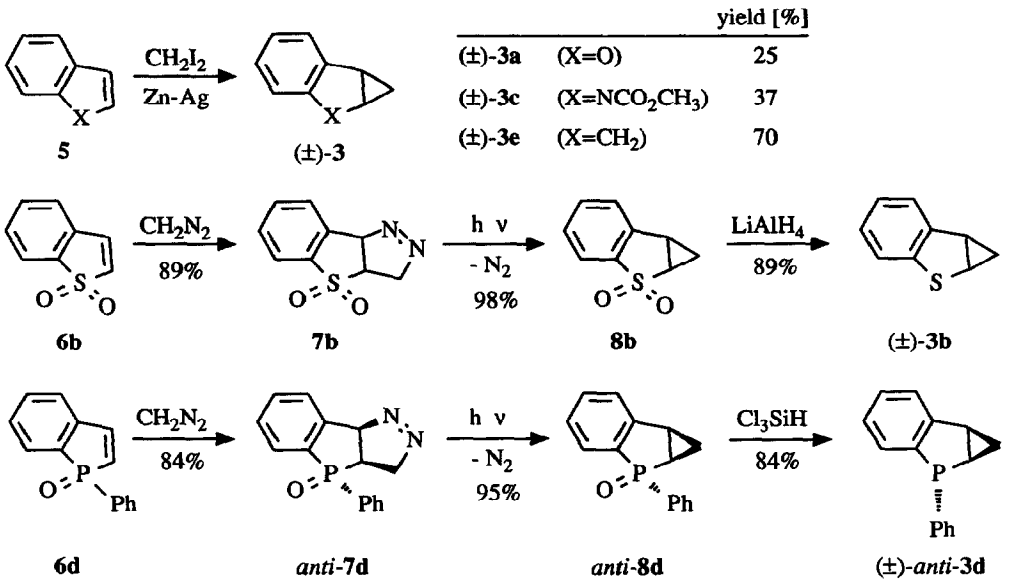
X: O, S, N-CO_2CH_3, P-Ph, CH_2
a **b** **c** **d** **e**

Carbonyl ylides, thiocarbonyl ylides and azomethine ylides - formally the products of the oxirane, thiirane or aziridine ring-opening - have attracted great attention (e.g. as reaction partners in 1,3-dipolar cycloadditions)[2]-[6]. The corresponding ylides **2a-d** were recently shown to be involved in the 1,5-electrocyclization of the heterocycles **1a-d**[7],[8]. At 120°C the ring-opening of homothiophene **1b** and homopyrrole **1c** proceeds 63100 and 72 times, respectively, faster and that of homophosphole **1d**-4,5-$(CH_3)_2$ slower by a factor of 0.0016 than that of homofuran **1a**. These results seem to be an evidence that the

heteroatoms (N, O, P, and S) stabilize carbonyl ylide-like intermediates very differently. Here we report on the ring-opening of the corresponding benzo-substituted heterocycles **3a-d**. The comparison of the parent and benzosubstituted heterocycles **1a-d** and **3a-d** with the corresponding carbocyclic system **1e** and **3e** provides an information on the nature of the surprisingly large heteroatom-effect and on the electrocyclic character of the ring-opening in the heterocyclic systems.

Synthesis of optically active 3a-e

Racemic benzohomofuran (±)-**3a**, homoindole (±)-**3c**, and homoindene (±)-**3e** can be prepared by the addition of methylene to benzofuran **5a**, indole **5c**[9] and indene **5e** using the Simmons-Smith reagent modified by Conia[10]. Since methylene generated under various conditions (Simmons-Smith reagent, CH_2N_2/CuCl or CH_2N_2/$Pd(OAc)_2$) does not add to benzothiophene **5b** or benzophosphole **5d** in satisfactory yields[11], we synthesized the desired benzohomothiophene (±)-**3b** and benzohomophosphole (±)-*anti*-**3d** by a detour. The oxidation products of **5b** and **5d**, **6b** and **6d**[12], reacts with diazomethane leading to the 1,3-dipolar cycloadduct **7b** or *anti*-**7d**. Photochemically induced N_2-elimination of **7b** and *anti*-**7d** gives the oxides **8b** and *anti*-**8d**, which can be reduced by $LiAlH_4$ or Cl_3SnH to give (±)-**3b** and (±)-*anti*-**3d** in an over all yield of 78% and 67%, respectively.



		yield [%]
(±)-3a	(X=O)	25
(±)-3c	(X=NCO_2CH_3)	37
(±)-3e	(X=CH_2)	70

Racemic (±)-**3a**, (±)-**3c**, (±)-**3d** and (±)-**3e** could be partially separated into their enantiomers by HPLC on triacetylcellulose. The enantiomers of (±)-**3b** could not be resolved by HPLC, but a partial separation of enantiomers of the diazomethane-adduct (±)-**7b** could be achieved. Thus, optically active **3b** was also available on the route described above starting with optically active **7b**. The enantiomeric excess (e.e.) could be determined by GC on octakis-(3-O-butyryl-2,6-O-di-pentyl)-γ-cyclodextrin[13] in the case of **3a**, **3b** and **3e** and by HPLC on tribenzoylcellulose in the case of **3c**, as shown in figure 1.

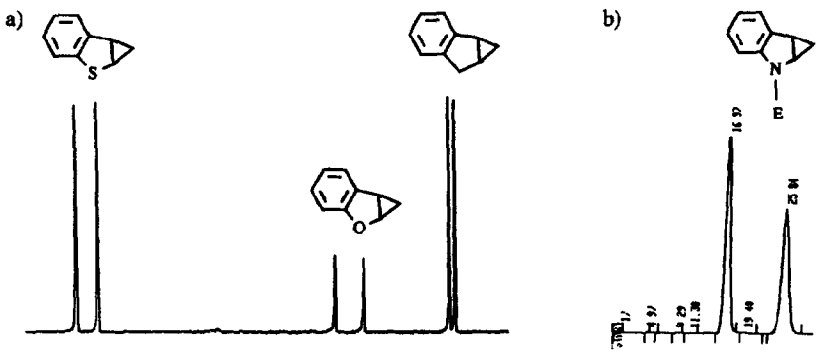


Figure 1: Separation of enantiomers a) (±)-**3a**, (±)-**3b** and (±)-**3e** (GC: Octakis-(3-O-butyryl-2,6-di-O-pentyl)-γ-cyclodextrin[14]); b) (±)-**3c** (HPLC: Cellulosetribenzoate, methanol-water 95 : 5)

Thermolysis of optically active 3a-e

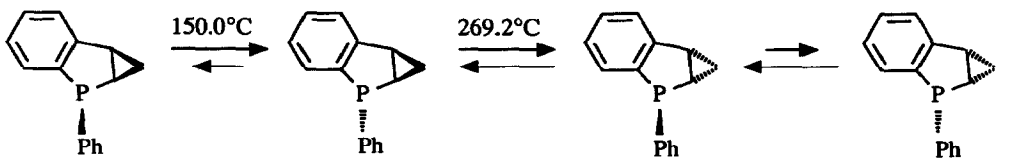
The rate of the ring-opening in **3a-e** can be determined by measuring the rate of racemization in the optically active systems ($k_{rac} = k_1$). At temperatures above 150°C optically active benzohomofuran **3a**, benzohomothiophene **3b** and homoindole **3c** racemize without any side reaction. In these cases the rate constants listed in table 1 could be determined easily by measuring the decrease of the enantiomeric excess with time at various temperatures using GC or HPLC. From the temperature-dependence of the rate constants one can calculate the activation parameters listed in table 3.

Table 1: Temperature-dependent rate constants of racemization $k_{rac} \times 10^5$ [s^{-1}]; a) (+)-**3a**, $(e.e.)_0$ = 15.4%; b) (-)-**3a**, $(e.e.)_0$ = 17.1% (in decaline); c) (+)-**3b**, $(e.e)_0$ = 94.5% (in n-heptane); d) (+)-**3c**, $(e.c.)_0$ = 94.0% (in n-heptane)

T [°C]	172.02	181.80	186.50	191.29	202.25
a)	1.545 ± 0.030	3.702 ± 0.203	5.767 ± 0.148	9.360 ± 0.178	22.94 ± 0.159
b)	1.483 ± 0.089	3.841 ± 0.043	6.193 ± 0.054	9.131 ± 0.239	22.76 ± 0.485
T [°C]	154.66	165.14	175.22	184.63	194.89
c)	2.036 ± 0.020	5.554 ± 0.036	14.16 ± 0.126	31.53 ± 0.249	72.97 ± 0.643
T [°C]	197.14	207.03	216.43	226.22	235.58
d)	0.839 ± 0.012	2.045 ± 0.013	4.613 ± 0.022	10.44 ± 0.044	22.18 ± 0.159

On thermolysis of optically active benzohomophosphole (+)-*anti*-**3d** at temperatures between 145 and 190°C the specific rotation decreases approaching a limit not equal to zero. By ^{1}H-NMR spectroscopy this reaction could be monitored leading to an equilibrium mixture of *syn*- and *anti*-**3d** and not to a racemization of the starting material. From the ^{1}H-NMR analysis of the time-dependent (syn:anti) ratio the optical rotation of *syn*-**3d** having the same enantiomeric excess as the starting material (+)-*anti*-**3d** could be calculated to be $(\alpha_{syn})_{t=0} = [(\alpha)_t - (\alpha_{anti})_{t=0}\,[anti\text{-}\mathbf{3d}]_t] / [syn\text{-}\mathbf{3d}]_t = -(22.2 \pm 0.8)°$; $(\alpha_{anti})_{t=0} = +15.5°$ (figure 2). The activation parameters for the equilibration *anti*-**3d** ⇌ *syn*-**3d** which is due to the inversion of the

phosphorous can be obtained from the temperature-dependence of the rate constants (table 2) measured by the time-dependent decrease of the optical rotation of (+)-*anti*-**3d** (table 2). The equilibrium mixture consisting of (+)-*anti*-**3d** and (-)-*syn*-**3d** racemizes substantially only at temperatures above 250°C. The rate of racemization was determined at 269.2°C to be $k_{rac} = (1.87\pm0.08)\times10^{-5}$ s^{-1}[17]. According to the optically active homophosphole *anti*-**1d**-4,5-$(CH_3)_2$ (≡ **1d***) where the racemization is faster than the inversion of the phosphorous to *syn*-**1d**-4,5-$(CH_3)_2$ we assume that the racemization in the benzohomophosphole occurs only starting from *anti*-**3d**, too.



syn-**3d** *anti*-**3d** ent-*anti*-**3d** ent-*syn*-**3d**

Table 2: Rate constants and activation parameters for the inversion at the phosphorous $kx10^5$ [s^{-1}]; a) (-)-*syn*-**3d** → (+)-*anti*-**3d**, b) (+)-*anti*-**3d** → (-)-*syn*-**3d**, c) $K = [anti\text{-}3d]_\infty/[syn\text{-}3d]_\infty$

T [°C]	147.5	158.8	168.6	179.1	188.8
a) k	1.178	3.023	6.788	15.28	29.00
b) k	0.213	0.605	1.420	3.325	7.036
c) K	5.531	5.000	4.780	4.595	4.122

a) $k = 5.67 \times 10^{10} \exp [-(30.18 \pm 1.06)$ kcal mol $^{-1}/ R T] [s^{-1}]$

b) $k = 2.10 \times 10^{11} \exp [-(32.70 \pm 0.55)$ kcal mol $^{-1}/ R T] [s^{-1}]$

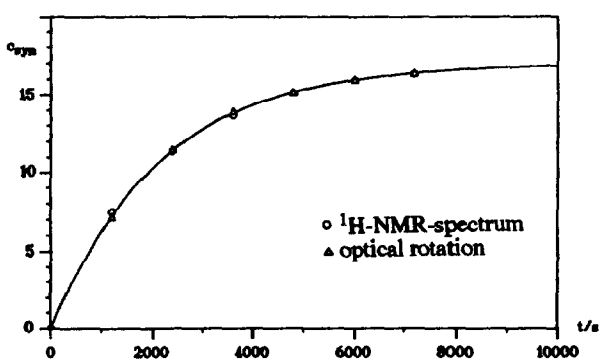
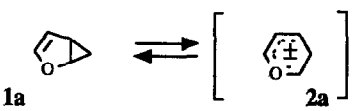
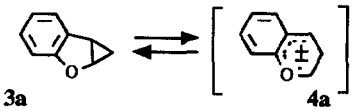
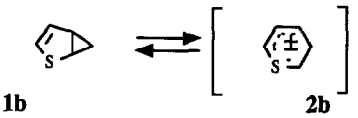
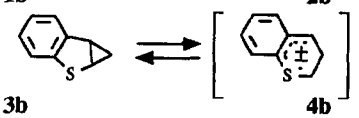
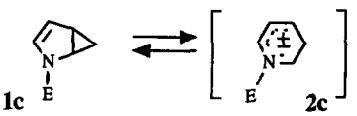
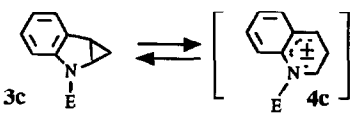
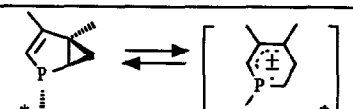
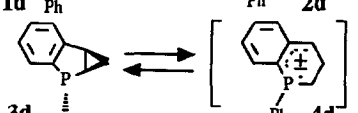
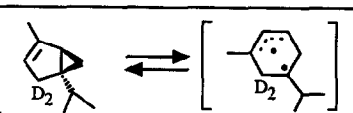
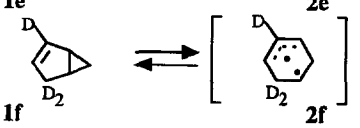
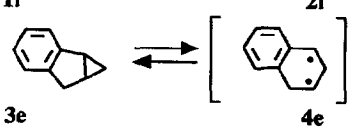


Figure 2: Time-dependence of the formation of (-)-*syn*-**3d** starting from (+)-*anti*-**3d** calibrated by ^{1}H-NMR.

On thermolysis at 264.5°C optically active homoindene (-)-**3e** undergoes a racemization accompanied by the formation of naphthaline and 1,2-dihydronaphthaline to a minor extent (ca 5%). All reactions of (-)-**3e** could be followed by GC. From the time-dependent decrease of the enantiomeric excess of (-)-**3e** the rate constant of racemization was determined to be $k_{rac} = (1.98\pm0.03)\times10^{-5}$ s^{-1} at 264.5°C.

Table 3: Comparison between the activation parameters of bicyclo[3.1.0]hexenes and their benzo-substituted derivatives (E_A, $\Delta G^{\neq}$ and $\Delta\Delta G^{\neq}$ in kcal/mol)

	E_A	logA	$\Delta G^{\neq}$ (T[°C])	$\Delta\Delta G^{\neq}$	Lit.
 **1a** **2a**	28.35 ±0.17	13.57 ±0.05	27.2 (120.0)	**9.1**	[7]
 **3a** **4a**	37.98 ±0.92	13.83 ±0.44	36.3 (120.0)		
 **1b** **2b**			18.5 (120.0)	**16.0**	[7]
 **3b** **4b**	35.53 ±0.58	13.41 ±0.28	34.5 (120.0)		
 **1c** **2c**	24.52 ±0.28	13.28 ±0.10	23.8 (120.0)	**15.2**	[7]
 **3c** **4c**	40.42 ±0.09	13.71 ±0.04	39.0 (120.0)		
 **1d*** **2d***	32.01 ±0.55	12.83 ±0.30	32.2 (269.2)	**12.0**	[8]
 **3d** **4d**			44.2 (269.2)		
 **1e** **2e**	43.4	14.33	40.2 (264.5)		[15]
 **1f** **2f**			39.6 (317.4)	**3.5** **4.1**	[16]
 **3e** **4e**			43.7 (264.5)		

Conclusions

In the benzocycles **3a-d** studied here the heteroatom effect on the rate of the ring-opening is less pronounced than it is in the parent systems **1a-d**. At 120°C the ring-opening in benzohomothiophene **3b** is faster only by a factor of 8.7 and in homoindole **3c** even slower by a factor of 0.04 than that in benzohomofuran **3a** contrary to the results obtained for homothiophene **1b**, homopyrrole **1c** and homofuran **1a** mentioned in the introduction. These findings indicate, that the different rates observed for ring-opening in the parent heterocycles **1a-c** may largely result from ground-state effects. In order to obtain more information about the influence of the heteroatoms on the ground-state we calculated the enthalpies of the isodesmic reactions shown in table 4 using the known enthalpies of formation ($\Delta H°_f$)[18].

Table 4: Estimation of the conjugative interaction between a C-C double bond and the heteroatom oxygen and sulfur, respectively, by calculating enthalpies of isodesmic reactions ΔH_R [kcal/mol] from enthalpies of formation $\Delta H°_f$ [kcal/mol][18]

					ΔH_R
$\Delta H°_f$	-60.3	- 5.1	-33.7	- 35.1	- 3.4
$\Delta H°_f$	-53.4	- 1.2	-29.9	-29.5	- 4.8
$\Delta H°_f$	-60.3	1.9	-24.3	-35.1	- 1.0
$\Delta H°_f$	- 8.2	8.1	21.7	-18.3	+3.5
$\Delta H°_f$	-20.0	1.9	18.4	-35.1	+1.4

Accordingly the conjugative interaction between oxygen and a double bond leads to a stabilization of the enolether by about -4 kcal/mol whereas the corresponding reaction between sulfur and a double bond destabilizes the thioenolether by +3.5 kcal/mol. Similar but considerably smaller effects can be calculated for the interaction between oxygen or sulfur and a benzene ring. With these data one can extrapolate that the difference in the activation barriers of the ring-opening of homofuran **1a** and homothiophene **1b** ($\Delta\Delta G^{\neq}$ = 8.7 kcal/mol) largely results from their different ground-state enthalpies (3.5 - (-4.0) = 7.5 kcal/mol) (figure 3). Taking these ground-state effects into consideration the activation barriers for the ring-opening in the benzosubstituted heterocycles **3a-d** can be calculated to be higher by $\Delta\Delta G^{\neq}$ = 13 ± 2 kcal/mol than those

found for the ring-opening in the corresponding parent heterocycles **1a-d**. This $\Delta\Delta G^{\neq}$value is exceedingly larger than that found for the carbocyclic systems **3e** and **1e** ($\Delta\Delta G^{\neq} \approx 4$ kcal/mol) which is in accord with the difference between the bond dissociation energies of toluene and propene (ΔBDE = 3.2 kcal/mol) derived from the recently determined enthalpies of formation of benzyl- and allyl-radical[18],[19]. The larger differences between the heterocycles **3a-d** and **1a-d** reveal the electrocyclic character of these ring-openings. In the transition state involved in these reactions the resonance energy of the annelated benzene ring is obviously consumed to a larger extent than in that for the carbocyclic homoindene **3e**, which is an ordinary homolytic cyclopropane bond dissociation.

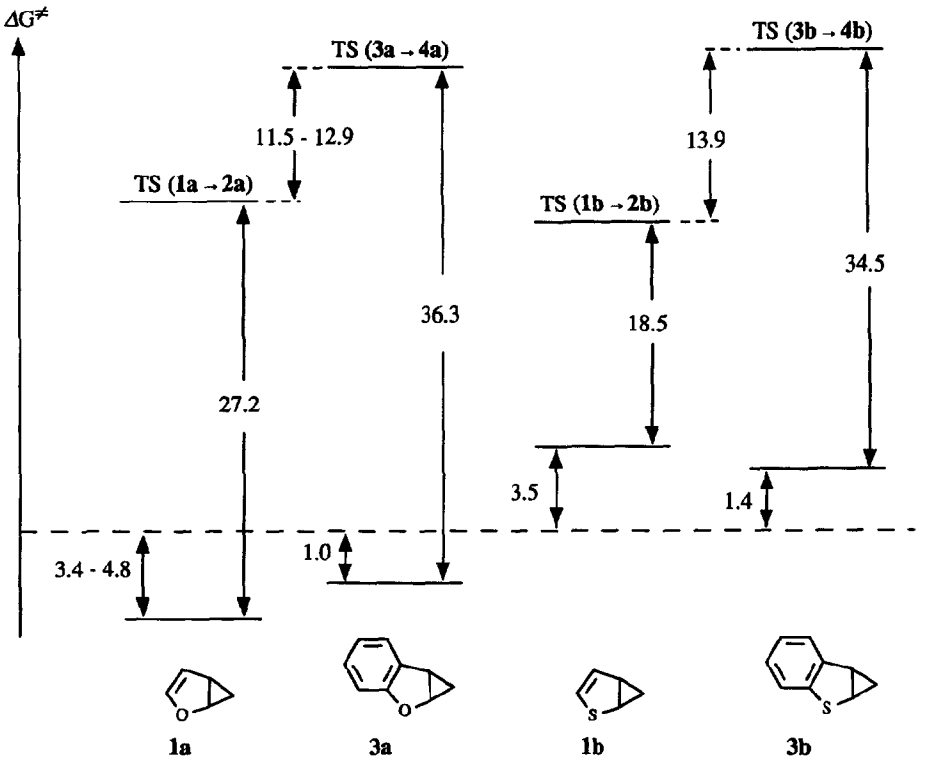


Figure 3: Energy diagram for ring-opening of **1a**, **3a** and **1b**, **3b** including ground-state effects

Experimental Section

General methods: melting points and boiling points are uncorrected. - ^{1}H-NMR spectra and ^{13}C-NMR spectra: WP-80 or AM-400 (Bruker); chemical shifts in $CDCl_3$ are reported in δ relative to tetramethylsilane as an internal standard; x- indicates protons standing *exo*, n- indicates protons standing *endo*. - IR: Infrarot-Gitter-Spektrometer 681 (Perkin-Elmer). - UV: Cary 1 (Varian). - MS: CH-5 MAT (Varian), 70 eV; CH-7 MAT (Varian), 15 eV. - GC-analyses: IGC 120 FB (Intersmat), carrier gas: helium; column A: 25 m

Ni-R-Cam fused silica OV 110. HP-5890 (Hewlett-Packard), column B: 31 m glass capillary, OV 1701/ octakis(3-O-butyryl-2,6-di-O-pentyl)-γ-cyclodextrin 6:1, carrier gas: H_2; column C: 25 m quarz capillary, OV 17, carrier gas: He. - GC-seperations: Aerograph 90 P (Varian), column D: 3 m DC 200 20%, carrier gas: He. - HPLC-enantiomeric-seperations: Waters-Solvent-Delivery-System 6000A with injection-system U6K (Waters), UV-Photometer 153 (Altex, 254 nm), Polarimeter P 241 (Perkin-Elmer); column E: Chiral Triacel 250/10 (Macherey-Nagel); column F: Chiral Triacel 250/20 (Macherey-Nagel); column G: CTA 250/10 (Merck). - HPLC-analyses: L 5000-LC-Controller (Merck-Hitachi), Liquid Chromatograph 655A-12 (Merck-Hitachi) UV-Spectrophotometric-Detector SPD-6A (Shimadzu), Integrator 3390 (Hewlett-Packard); column H: Chiral Tribencel 250/8/4 (Macherey-Nagel).

***Cyclopropanation using Simmons-Smith procedure*[10]:**

General Procedure: To a degassed, stirred mixture of zinc-silver couple and a piece of silver wool in anhydrous ether diiodomethane was added and heated at reflux for 1 h. After dropwise addition of the alkene heating at reflux was continued for the time given below. Then the same amount of zinc-silver couple and diiodomethane was added and the stirred reaction mixture was heated at reflux for an additional time given below. In some cases the addition of zinc-silver couple and diiodomethane and the heating was repeated one more time. The reaction mixture was worked up by partitioning between water and ether. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo (20 Torr). The residue was purified either by LC or GC.

3,4-Benzo-2-oxa-bicyclo[3.1.0]hex-3-ene 3a: The mixture of 8.50 g (130 mmol) zinc-silver couple, a piece of silver wool, 20.10 g (75 mmol) diiodomethane and 5.80 g (75 mmol) **5a** in 60 ml ether prepared according to the general procedure was heated for 65 h. After the addition of another 8.50 g zinc-silver couple and 20.1 g CH_2I_2 heating was continued for 48 h. After the work-up LC (silica gel, pentane - ether 20:1) of the residue gave 1.60 g **3a** (25%) as an colourless oil.[20]: - ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.30 (ddd, 1H, 6-Hn, $J_{6n,6x}$ = 6.0 Hz, $J_{6n,1}$ = 2.0 Hz, $J_{6n,5}$ = 4.0 Hz); 1.00 (ddd, 1H, 6-Hx, $J_{6x,1}$ = 5.5 Hz, $J_{6x,5}$ = 9.0 Hz); 2.60 (ddd, 1H, 5-H, $J_{5,1}$ = 5.5 Hz); 4.80 (td, 1H, 1-H); 6.85 (dd, td, 2H, arom-H); 7.10 (td, 1H, arom-H); 7.35 (dd, 1H, arom-H); - ^{13}C-NMR (100 MHz, DEPT, $CDCl_3$): δ = 10.01 (CH_2, C-6); 19.73 (CH, C-5); 61.43 (CH, C-1); 110.24, 120,33, 123.81, 126.89 (CH, C-7/C-8/C-9/C-10); 131.17, 159.28 (C, C-3, C-4); - IR (film): ν/cm^{-1} = 3060 (ν C-H, cyclopropane); 2980 (ν C-H); 1610 (ν C=C); 1470, 1460 (δ C-H); 1220, 1015 (ν C-O); - UV (acetonitrile): $\lambda_{max}(\epsilon)$ = 211 nm (5381); 285 nm (2178); 280 nm (2250); - MS (70 e): m/z (%) = 132 (40) [M^+]; 131 (100) [M^+-1]; 77 (34) [$C_6H_5^+$]; 51 (40) [$C_4H_3^+$]; C_9H_8O: calc.: 132.0573; exp.: 132.0563 (MS).

2-Aza-3,4-benzo-N-carbmethoxy-bicyclo-[3.1.0]hex-3-ene 3c: The mixture of 2.20 g zinc-silver couple, a piece of silver wool, 5.40 g (20 mmol) diiodomethane and 2.20 g (12.5 mmol) **5c**[9] in 50 ml ether prepared according to the general procedure was heated for 24 h. After the addition of the same amount of zinc-silver couple and diiodomethane heating was continued for another 24 h. After the work-up LC (silica gel, pentane - ether 10:1) of the residue gave 0.52 g **3c** (33%) as white crystals. mp.: 81°C; - ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.26 (m(b), 1H, 6-Hn); 1.06 (m(b), 1H, 6-Hx); 2.62 (ddd, 1H, 5-H, J = 4.0 Hz, 7.0 Hz, 9.0 Hz); 3.85 (s, 3H, O-CH_3); 4.16 (s(b), 1H, 1-H); 6.93 (td, 1H, arom-H); 7.15 (t, 1H, arom-H); 7.30 (d, 1H, arom-H); 7.82 (s(b), 1H, arom-H); - ^{13}C-NMR (100 MHz, DEPT, $CDCl_3$): δ = 11.38 (CH_2, C-6); 19.05 (CH, C-5); 38.30 (CH, C-1); 53.00 (CH_3, O-CH_3); 119.78, 122.64, 124.25, 127.10 (CH, C-7/C-8/C-9/C-10); - IR (KBr): ν/cm^{-1} = 3051 (ν C-H, cyclopropane); 3010 (ν C=C-H); 2957, 2861 (ν C-H); 1712 (ν C=O); 1602 (ν C=C); 1482, 1465, 1445 (δ C-H); 1399 (δ C-H, methylester); 1309 (ν C-O); - UV (acetonitrile): $\lambda_{max}(\epsilon)$ =

215 nm (13814); 264 nm (6776); 308 nm (2506); - MS: m/z (%) = 189 (40) [M^+]; 188 (38) [M^+-1]; 174 (35) [M^+-CH_3]; 130 (100) [M^+-CO_2CH_3]; 103 (35) [$C_8H_7^+$]; 77 (50) [$C_6H_5^+$]; $C_{11}H_{11}NO_2$: calc.: 189.0790; exp.: 189.0788 (MS).

2,3-Benzobicyclo[3.1.0]hex-2-ene 3e: The mixture of 8.60 g (132 mmol) zink-silver couple, a piece of silver wool, 18.40 g (69 mmol) diiodomethane and 5.00 g (43 mmol) **5e** in 100 ml ether prepared according to the general procedure was heated for 48 h. After the addition of another 8.60 g zinc-silver couple and 18.40 g CH_2I_2 heating was continued for 48 h. After the work-up destillation of the residue in vacuo (20 Torr, 85°C) afforded a crude product, which could be partially seperated by GC (column D, 110°C) to give pure **3e** as colourless liquid. **3e** was identified by means of its ^{1}H-NMR-spectrum[21].

Synthesis of 3,4-Benzo-2-thiabicyclo[3.1.0]hex-3-ene 3b:

a) Benzothiophene-S,S-dioxide 6b: To a stirred solution of 6.50 g (49 mmol) **5b** in 60 ml ethanol was added 35.00 g (70 mmol) magnesium monoperoxyphthalate MMPP in 250 ml water. After the reaction was warmed to 50°C for 4 h, crystals of **6b** were filtered by suction. Additional **6b** was obtained by extraction of the aqueous phase with CH_2Cl_2 (100 ml); the organic phase was dried ($MgSO_4$) and concentrated in vacuo (20 Torr). The combined solids were recrystallized from ethanol to give 6.00 g of **6b** (74%). mp.: 143°C (lit.[22]: 143°C).

b) 3,4-Benzo-6,7-diaza-2-sulfoxy-bicyclo[3.3.0]octa-3,6-diene 7b: The mixture of 2.21 g (13 mmol) **6b** and 64 mmol diazomethane[23] in 150 ml ether was kept in the dark for 2 d. After removal of the ether in vacuo (20 Torr) the residue was recrystallized from ethanol to give 2.50 g **7b** (89%). mp.: 137°C; - ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.91 (ddd, 1H, 1-H, $J_{1,5}$ = 8.5 Hz, $J_{1,8n}$ = 4.0 Hz, $J_{1,8x}$ = 10.0 Hz); 4.98 (ddd, 1H, 8-Hx, $J_{8x,8n}$ = 19.5 Hz, $J_{8x,5}$ = 2.0 Hz); 5.46 (ddd, 1H ,8-Hn, $J_{8n,5}$ = 2.0 Hz); 6.42 (d(b)), 1H, 5-H); 7.61 (tm, 1H, arom-H); 7.72 (m, 2H, arom-H); 7.98 (dm, 1H, arom-H); - ^{13}C-NMR (100 MHz, DEPT, $CDCl_3$): δ = 54.78 (CH, C-5); 79.06 (CH_2, C-8); 93.87 (CH, C-1); 122.16, 127,87, 131.22, 134.35 (CH, C-9/C-10/C-11/C-12); 113.64, 137.71 (C, C-3/C-4); - IR (KBr): ν/cm^{-1} = 3017 (ν C=C-H); 1580 (ν N=N); 1308, 1152 (ν O=S=O); 1470 (δ C-H); - UV (acetonitrile): $\lambda_{max}(\epsilon)$ = 214 nm (10852); 266 nm (571); 318 nm (338); - MS (70 eV): m/z (%) = 180 (0.3) [M^+-N_2]; 115 (100) [$C_9H_7^+$].

c) 3,4-Benzo-2-sulfoxy-bicyclo[3.1.0]hex-3-ene 8b: A solution of 2.45 g (12 mmol) **6b** in 300 ml toluene was irradiated (Hg high-pressure lamp Philipps HPK, 125 W, Pyrex vessel) for 27 h at -78°C. The mixture was evaporated to dryness in vacuo and the residue was chromatographed (silica gel, pentane - ether 1 : 3) to give 1.12 g **8b** (52%) as white crystals. mp.: 63°C; - ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.28 (td, 1H, 6-Hn, $J_{6n,1}$ = 5.0 Hz, $J_{6n,5}$ = 5.0 Hz, $J_{6n,6x}$ = 6.0 Hz); 1.65 (td, 1H, 6-Hx, $J_{6x,1}$ = 8.0 Hz, $J_{6x,5}$ = 8.0 Hz); 3.04 (ddd, 1H, 5-H, $J_{5,1}$ = 7.0 Hz); 3.18 (ddd, 1H, 1-H); 7.02 (td, 1H, arom-H); 7.12 (m, 2H, arom-H); 7.33 (dm, 1H, arom-H); - ^{13}C-NMR (100 MHz, DEPT, $CDCl_3$): δ = 21.48 (CH, C-5); 22.29 (CH_2, C-6); 34.32 (CH, C-1); 122.54, 126.48, 128.85, 133.13 (CH, C-7/C-8/C-9/C-10); 138.44 (C, C-3/C-4); - IR (KBr): ν/cm^{-1} = 3060 (ν C-H, cyclopropane); 1595 (ν C=C); 1470 (δ C-H); 1300,1144 (ν O=S=O); - UV (acetonitrile): $\lambda_{max}(\epsilon)$ =214 nm (6517); 272 nm (823); - MS (70 eV): m/z (%) = 180 (7) [M^+]; 155 (100) [$C_9H_7^+$]; $C_9H_8O_2S$: calc.: 180.0245; exp.: 180.0245 (MS).

c) 3,4-Benzo-2-thia-bicyclo[3.1.0]hex-3-ene 3b: To a stirred solution of 2.50 g (6.7 mmol) lithium aluminium hydride in 40 ml anhydrous ether a solution of 1.20 g (6.7 mmol) **8b** in 150 ml anhydrous benzene was dropped at 0°C. After heating at reflux for 1 h the mixture was cooled to 0°C and 5 ml of water were added dropwisely just sufficiently to form a flaky precipitate of aluminium hydroxyde. The precipitate was filtered and washed with ether (50 ml). The combined organic phases were dried ($MgSO_4$) and

concentrated in vacuo. Bulb-to-bulb destillation of the residue at 0.1 Torr afforded 0.82 g **3b** (89%) as colourless oil. - ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.41 (td, 1H, 6-Hn, $J_{6n,6x}$ = 5.0 Hz, $J_{6n,5}$ = 4.0 Hz, $J_{6n,1}$ = 4.0 Hz); 1.32 (ddd, 1H, 6-Hx, $J_{6x,1}$ = 7.0 Hz, $J_{6x,5}$ = 8.5 Hz); 2.92 (ddd, 1H, 5-H, $J_{5,1}$ = 7.0 Hz); 3.04 (td, 1H, 1-H); 7.01 (td, 1H, arom-H); 7.10 (m, 2H, arom-H); 7.33 (dm, 1H, arom-H); - ^{13}C-NMR (100 MHz, DEPT, $CDCl_3$): δ = 12.94 (CH_2, C-6); 23.10 (CH, C-5); 27.83 (CH, C-1); 122.34, 123.88, 124.82, 126.91 (CH, C-7/C-8/C-9/C-10); 140.73, 140.97 (C, C-3/C-4); - IR (film): ν/cm^{-1} = 3064 (ν C-H, cyclopropane); 3020 (ν C=C-H); 2960,2840 (ν C-H); 1585 (ν C=C); 1464 (δ C-H); - UV (acetonitrile): $\lambda_{max}(\epsilon)$ = 220 nm (12335); 250 nm (5433); 268 nm (4376); - MS: m/z (%) = 148 (46) [M$^+$]; 147 (100) [M$^+$-1]; 115 (10) [$C_9H_7^+$]; C_9H_8S: calc.: 148.0347; exp.:148.0343 (MS).

Synthesis of 3,4-Benzo-2-phenyl-2-phosphabicyclo[3.1.0]hex-3ene anti-3d:

a) 3,4-Benzo-6,7-diaza-2-phenyl-2-phosphabicyclo[3.3.0]octa-3,6-diene-2-oxide anti-7d: The mixture of 3.00 g (13 mmol) **6d**[12] and ca. 64 mmol diazomethane in 150 ml ether was kept in the dark for 2 h. The adduct *anti*-**7d** precipated. The excess of diazomethane was evaporated by a stream of N_2 and the solvent decanted from the crystalline residue, which was washed with a small amount of pentane to give 3.00 g *anti*-**7d** (84%). mp.: 125°C; - ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.72 (dddd, 1H, 1-H, $J_{1,5}$ = 9.5 Hz, $J_{1,8n}$ = 6.5 Hz, $J_{1,8x}$ = 11.5 Hz, $J_{1,P}$ = 1.0 Hz); 5.03 (dddd, 1H, 8-Hx, $J_{8x,8n}$ = 19.0 Hz, $J_{8x,P}$ = 13.5 Hz, $J_{8x,5}$ = 1.0 Hz); 5.28 (ddt, 1H, 8-Hn, $J_{8n,P}$ = 19.0 Hz, $J_{8n,5}$ = 2.5 Hz); 7.40-7.55 (m, 6H, arom-H); 7.60-7.81 (m, 2H, arom-H); 8.00 (m, 1H, arom-H); - ^{13}C-NMR (100 MHz, DEPT, $CDCl_3$): δ = 32.53 (CH, C-1); 78.08 (CH_2, C-8); 96.23 (CH, C-5); 127.30, 128.89, 129.90, 130.32, 130.51, 132.31, 133.76 (CH, C-Ph/C-9/C-10/C-11/C12); - IR (KBr): ν/cm^{-1} = 3040, 3035 (ν C=C-H); 2980, 2930 (ν C-H); 1590 (ν C=C); 1550 (ν N=N); 1445, 1430, 1425 (ν P-Ph); 1200, 1180 (ν P=O); - MS: m/z (%): = 267 (12) [M$^+$-H]; 240 (100) [M$^+$-N_2]; 191 (20) [M$^+$-Ph]; 163 (18) [M$^+$-N_2-Ph]; 115 (40) [$C_9H_7^+$]; $C_{15}H_{13}N_2OP$ calc.: 268.0766; exp.: 268.0753 (MS).

b) 3,4-Benzo-2-phenyl-2-phosphabicyclo[3.1.0]hex-3-ene-2-oxide anti-8d: A solution of 3.00 g (11 mmol) *anti*-**7d** in 500 ml toluene was irradiated (Hg high-pressure lamp Philipps HPK, 125 W, Pyrex vessel) for 13 h at room temperature. The mixture is evaporated to dryness in vacuo and the residue was chromatographed (silica gel, chloroform - acetone 3:2) to give 2.60 g *anti*-**8d** (95%). - ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.33 (m, 1H, 6-Hn, $J_{6n,P}$ = 14.5 Hz, $J_{6n,6x}$ = 5.0 Hz, $J_{6n,1}$ = 5.5 Hz, $J_{6n,5}$ = 14.5 Hz); 1.46 (m, 1H, 6-Hx, $J_{6x,P}$ = 10.5 Hz, $J_{6x,1}$ = 9.5 Hz, $J_{6x,5}$ = 7.0 Hz); 1.75 (m, 1H, 1-H, $J_{1,P}$ = 12.5 Hz, $J_{1,5}$ = 6.5 Hz); 2.88 (m, 1H, 5-H, $J_{5,P}$ = 9.0 Hz); 7.20-7.30 (m, 1H, arom-H); 7.35-7.75 (m, 5H, arom-H); 7.60-7.70 (m, 3H, arom-H); - ^{13}C-NMR (100 MHz, DEPT, $CDCl_3$): δ = 13.11 (CH, C-1); 19.89 (CH_2, C-6); 23.6 (CH, C-5); 125.92, 128.21, 128.83, 130.95, 131.06, 132.11, 132.64 (CH, C-Ph/C-7/C-8/C-9/C-10); 129.49, 133.91, 148.44 (C, C-3/C-4/C-P); - IR (KBr): ν/cm^{-1} = 3060 (ν C=C-H); 3000-2950 (ν C-H); 1595 (ν C=C); 1435 (ν P-Ph); 1200, 1180 (ν P=O); - MS: m/z (%) = 240 (100) [M$^+$]; 115 (40) [$C_9H_7^+$]; $C_{15}H_{13}OP$: calc.: 240.0704; exp.: 240.0705 (MS).

c) 3.4-Benzo-2-phenyl-2-phosphabicyclo[3.1.0]hex-3-ene anti-3d: The stirred solution of 2.55 g (11 mmol) *anti*-**8d** and 4.27 g (32 mmol) trichlorsilane in 100 ml anhydrous benzene was heated at reflux for 1 h under Ar. The organic layer was extracted twice with degassed aqueous NaOH (2 N) and washed with degassed water until the mixture was neutral. After drying over Na_2SO_4 the solution was concentrated in vacuo (20 Torr, 20°C) and the residue purified by LC (silica gel, pentane). The product was recrystallized from ethanol - water 96 : 4 to give 2.00 g *anti*-**3d** (84%). mp.: 65°C; - ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.19 (dddd, 1H, 6-Hn, $J_{6n,1}$ = 5.8 Hz, $J_{6n,6x}$ = 4.8 Hz, $J_{6n,P}$ = 8.2 Hz, $J_{6n,5}$ = 3.5 Hz); 1.42 (dddd, 1H, 6-Hx, $J_{6x,1}$ = 9.5 Hz,

$J_{6x,P}$ = 11.0 Hz, $J_{6x,5}$ = 8.0 Hz); 1.80 (dddd, 1H, 1-H, $J_{1,P}$ = 12.0 Hz, $J_{1,5}$ = 6.0 Hz); 2.92 (m, 1H, 5-H, $J_{5,P}$ = 2.0 Hz); 7.15-7.40 (m, 7H, arom-H); 7.50-7.60 (m, 2H, arom-H); - ^{13}C-NMR (100 MHz, DEPT, $CDCl_3$): δ = 18.03 (CH_2 , C-6); 19.08 (CH, C-1); 27.82 (CH, C-5); 124.69, 126,26, 128.37 (CH, C-Ph/C-7/C-8/ C-9/C-10); 140.32, 150.26 (C, C-3/C-4); - IR (KBr) ν/cm^{-1} = 3060, 3040 (ν C=C-H); 2960 (ν C-H); 1950 (ν C=C); 1445, 1430 (ν P-Ph); - MS: m/z (%) = 224 (100) [M$^+$]; 146 (30) [M$^+$-PhH]; 115 (45) [$C_7H_9^+$]; 91 (80) [$C_7H_7^+$]; $C_{15}H_{13}P$: calc.: 224.0755; exp.: 224.0753 (MS).

HPLC seperations of enantiomers (triacetylcellulose, ethanol - water 96:4):

a) (±)-3a: 400 mg (±)-**3a** was seperated into three fractions (column E). The first and third one contained (+)-**3a** and (-)-**3a**, respectively, and were worked up seperately by dilution with water and extraction with pentane. The pentane extracts were dried ($MgSO_4$) and concentrated in vacuo (20 Torr) at room temperature. Each residue was seperated into two fractions by HPLC for a second time and was worked up as described above. The e.e. of both samples was determined by GC (column A, 80°C) to be 15.4% ((+)-**3a**) and 17.1% ((-)-**3a**).

b) (±)-3b: 160 mg (±)-**7b** was seperated into two fractions (column F), first fraction (+)-**7b**, second fraction (-)-**7b**. The solvent of each fraction was removed in vacuo (20 Torr) and each residue consisting of (+)-**7b** and (-)-**7b**, respectively, was transfered to (+)-**3b** and (-)-**3b** using the procedures described above for the synthesis of (±)-**3b**. 20 mg (+)-**3b** (e.e. = 94.5%) and 28 mg (-)-**3b** (e.e.= 41.4) were obtained. The values were determined by GC (column B, 100°C).

c) (±)-3c: 54 mg (±)-**3c** was seperated into two fractions (column G), first fraction (-)-**3c**, second fraction (+)-**3c**. After removal of the solvent in vacuo (20 Torr) the e.e. of both fractions was determined by HPLC (column H) to be 94.0% ((+)-**3c**) and 84.7% ((-)-**3c**).

d) (±)-anti-3d: 500 µl of a saturated solution of *anti*-**3d** in ethanol was seperated into two fractions, first fraction (+)-**3d**, second fraction (-)-**3d** (column F). The solvent of each fraction was evaporated in vacuo. During these procedures (+)-*anti*-**3d** and (-)-*anti*-**3d** were oxidized by air to the corresponding optically active oxides (+)-*anti*-**8d** and (-)-*anti*-**8d** which were reduced by Cl_3SiH leading to (+)-*anti*-**3d** and (-)-*anti*-**3d** in a yield of 50 and 44%, respectively.

e) (±)-3e: 70 mg (±)-**3e** was seperated into two parts (column G), first fraction (-)-**3e**, second fraction (+)-**3e**. Each fraction was diluted with water and extracted with pentane. The organic layers were dried ($MgSO_4$) and concentrated in vacuo (20 Torr) by room temperature. They were seperated for a second time by HPLC and worked up as described above. The e.e. of each sample was determined by GC (column B, 55°C) to be 10.1% ((+)-**3e**) and 14.2% ((-)-**3e**), respectively.

Kinetics of racemization: Solutions of (+)-**3a**, (-)-**3a** (each 1% in decaline), (+)-**3b** (0.5% in n-heptane), (+)-**3c** (0.5% in n-heptane), (+)-**3d** (c = 0.041 g/ml toluene, $(\alpha^{546})_{t=0}$ = +15.51°, after thermolysis at 183.2°C, t = 2.0 h: $(\alpha^{436})_t$ = +9.32°), and (-)-**3e** (0.5% in n-heptane) in sealed glass tubes (dia.: 1.6 mm; length: 75 mm) were heated at constant temperatures (± 0.1°C) for appropriate periods. For each sample the e.e. was analysed by GC, HPLC (five times, columns see above), or decrease of optical rotation; the resulting rate constants are listed in table 1 and 2).

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