169. The Diastereoselective Formation of 1,2,4-Trioxanes and 1,3-Dioxolanes by the Reaction of Endoperoxides with Chiral Cyclohexanones

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Dedicated to Professor *Dieter Seebach* on the occasion of his 60th birthday

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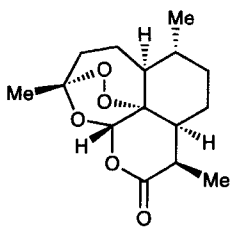
1,4-Diphenyl-2,3-dioxabicyclo[2.2.1]hept-5-ene (**2**), on treatment with a catalytic amount of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) in CH_2Cl_2 at −78°, reacts with excess (−)-menthone (**10**) to give (1*S*,2*S*,4'a*S*,5*R*,7'a*S*)-4'a,7'a-dihydro-2-isopropyl-5-methyl-6',7'-diphenylspiro[cyclohexane-1,3'-[7'*H*]cyclopenta-[1,2,4]trioxine] (**11**) and its (1*R*,2*S*,4'a*R*,5*R*,7'a*R*)-diastereoisomer **12** in a 1:1 ratio and in 21% yield. Repeating the reaction with 1.1 equiv. of Me_3SiOTf with respect to **2** affords **11**, **12**, and (1*S*,2*S*,3'a*R*,5*R*,6'a*S*)-3'a,6'a-dihydro-2-isopropyl-5-methyl-3'a-phenoxy-5'-phenylspiro[cyclohexane-1,2'-[4'*H*]cyclopenta[1,3]dioxole] (**13**) together with its (1*R*,2*S*,3'a*S*,5*R*,6'a*R*)-diastereoisomer **14** in a ratio of 3:3:3:1 and in 56% yield. (+)-Nopinone (**15**) in excess reacts with **2** in the presence of 1.1 equiv. of Me_3SiOTf to give a pair of 1,2,4-trioxanes (**16** and **17**) analogous to **11** and **12**, and a pair of 1,3-dioxolanes (**18** and **19**) analogous to **13** and **14**, in a ratio of 8:2:3:3 and in 85% yield. (−)-Carvone and racemic 2-(*tert*-butyl)cyclohexanone under the same conditions behave like **15** and deliver pairs of diastereoisomeric trioxanes and dioxolanes. In general, catalytic amounts of Me_3SiOTf give rise to trioxanes, whereas 1.5 equiv. overwhelmingly engender dioxolanes. Adamantan-2-one combines with **2** giving only (4'a*RS*,7'a*RS*)-4'a,7'a-dihydro-6',7'a-diphenylspiro[adamantane-2,3'-[7'*H*]cyclopenta[1,2,4]trioxine] in 98% yield regardless of the amount of Me_3SiOTf used. The reaction of 1,4-diphenyl-2,3-dioxabicyclo[2.2.2]oct-5-ene (**32**) with **10** and 1.1 equiv. of Me_3SiOTf produces only the pair of trioxanes **33** and **34** homologous to **11** and **12**. Treatment of the (*S*,*S*)-diastereoisomer **33** with Zn and AcOH furnishes (1*S*,2*S*)-1,4-diphenylcyclohex-3-ene-1,2-diol. The crystal structures of **11**–**13** and **16** are obtained by X-ray analysis. The reaction courses of **10** and the other chiral cyclohexanones with prochiral endoperoxides **2** and **32** to give trioxanes are rationalized in terms of the respective enantiomeric silylperoxy cations which are completely differentiated by the *si* and *re* faces of the ketone function. The origin of the 1,3-dioxolanes is ascribed to 1,2 rearrangement of the corresponding trioxanes, which occurs with retention of configuration of the angular substituent.

Introduction. – The discovery of the potent antimalarial agent, the naturally occurring tetracyclic 1,2,4-trioxane artemisinin (**1**), did much to encourage the development of synthetic methods for preparing simpler analogues which might posses similar biological activity [1]. We have previously shown that the reaction of certain allylic hydroper-



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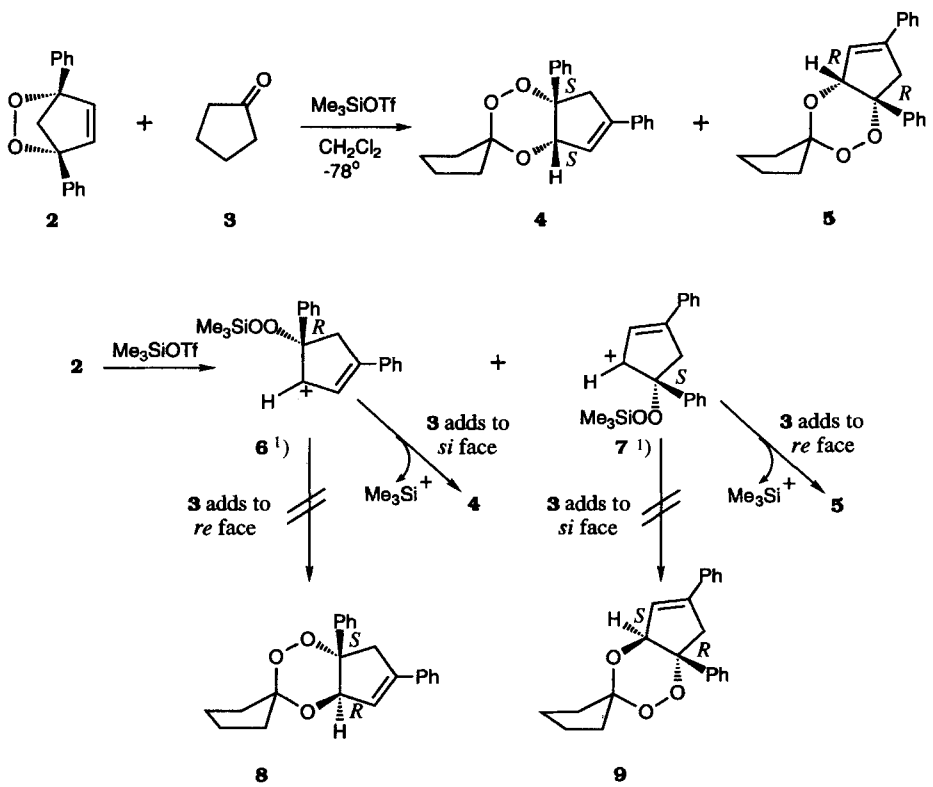
oxides, 1,2-dioxetanes, and endoperoxides with aldehydes and ketones provides a convenient means of preparing a wide variety of tricyclic, bicyclic, and monocyclic trioxanes [2], some of which surpass **1** in activity [3].

A typical synthesis is provided by the reaction of the symmetric endoperoxide, 1,4-diphenyl-2,3-dioxabicyclo[2.2.1]hept-5-ene (**2**) with cyclopentanone (**3**) [4]. Catalysis with trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) in CH_2Cl_2 at $-78°$ affords a racemic mixture of the *cis*-fused cyclopenta-1,2,4-trioxanes **4** and **5** in high yield as the sole products (*Scheme 1*). The result is explicable in terms of the pair of enantiomeric silylperoxy cations **6** and **7** that arise from **2** by attack of the trimethylsilyl cation on the peroxide bond[1]). They react equally efficiently with cyclopentanone (**3**), which itself is undoubtedly activated by the trimethylsilyl cation. Capture of **3** by the (*R*)-enantiomer **6** occurs in the expected electronic sense, but exclusively on the *si* face of the cationic center (→ **4**). Conversely, **3** combines with the (*S*)-configured cation **7** only on its *re* face (→ **5**). Hence, the new trioxane ring is formed uniquely with *cis*-fusion. Attack by **3** on the opposite sides of **6** and **7**, on the *re* and *si* faces, respectively, must be sterically prohibited or geometrically unfeasible, since the *trans*-fused trioxanes **8** and **9** are not

Scheme 1



[1]) The CIP descriptors of cations **6** and **7** refer to the delocalized cations.

observed. In other words, the reaction course is diastereoselective, which is a consequence of the prochiral nature of **2** and the steric requirements of the cations resulting therefrom. In order to further clarify the mechanism, it was decided to investigate the reaction of **2** with a chiral cyclohexanone partner. As the *si* and *re* faces of the carbonyl function of such a ketone are diastereotopic, diastereoselectivity would be expected to operate in both partners. Accordingly, (−)-menthone (**10**), (+)-nopinone (**15**), (−)-carvone (**20**), and 2-(*tert*-butyl)cyclohexanone (**25**) were selected as suitable chiral cyclohexanones. As an extension, the reaction of 1,4-diphenylcyclohexene 1,4-endoperoxide (**32**) with **10** was also examined. (For a preliminary report, see [5].)

Results. – The reaction of endoperoxide **2** with an excess of (−)-menthone (**10**) in the presence of a catalytic amount of Me_3SiOTf in CH_2Cl_2 at −78° gave just two products, **11** and **12**, in a ratio of 1:1 and in 21% yield (*Scheme 2*; *Table*, *Entry 1*). The molecular formula of both products revealed that one molecule each of **2** and **10** had combined. Unfortunately, their structures could not be elucidated by NMR spectroscopy owing to

Scheme 2

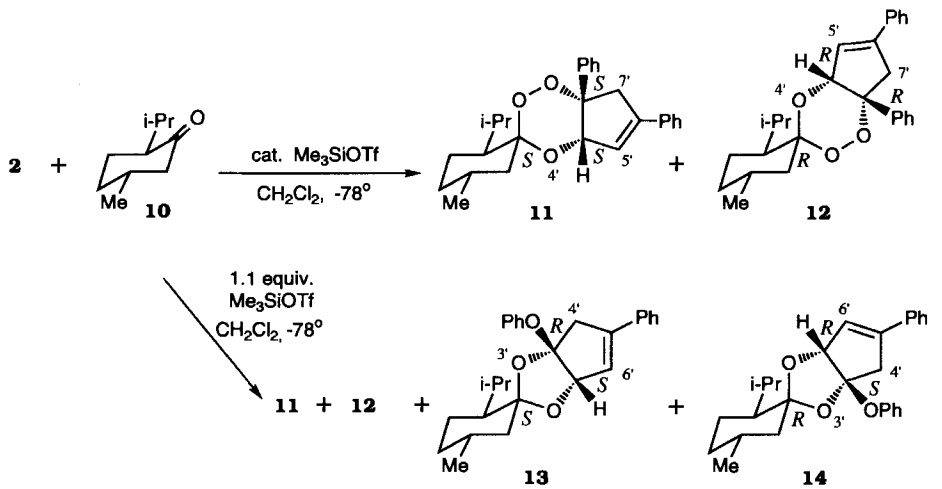


Table. *Me_3SiOTf-Catalysed Reaction of 1,4-Diphenyl-2,3-dioxabicyclo[2.2.1]hept-5-ene* (**2**) *with (−)-Menthone* (**10**) *to Give Diastereoisomeric 1,2,4-Trioxanes* (**11** and **12**) *and 1,3-Dioxolanes* (**13** and **14**)[a])

Entry	Me_3SiOTf[b]) [equiv.]	Yield [%]	Diastereoisomer ratio **11**/**12**/**13**/**14**[c])[d])	Trioxane: dioxolane ratio
1	0.033	21	50:50:0:0	100:0
2	0.5	30	55:43:1:1	98:2
3	1.1	56	30:30:30:10	60:40
4	1.3	31	3:35:46:16	38:62
5	1.5	27	0:0:50:50	0:100

[a]) The ratio **10**/**2** was 5:1 in all cases. [b]) Based on **2**. [c]) Determined by ^{1}H-NMR analysis of crude products. [d]) All reactions were carried out at −78° in CH_2Cl_2 for 4 h.

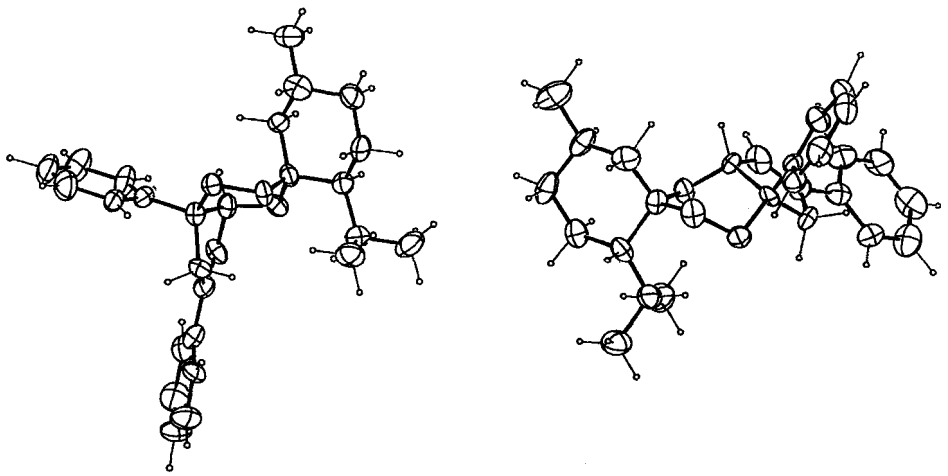


Fig. 1. *Perspective drawings of the X-ray structures of 1,2,4-trioxanes* **11** *and* **12**

their high O-content. However, both gave crystals suitable for X-ray analysis. X-Ray revealed that **11** and **12** are spirocyclic 1,2,4-trioxanes attached to a menthane ring (see *Fig. 1*) [5]. The trioxane ring in **11** adopts a chair conformation, and as expected, is *cis*-fused to the cyclopentene moiety. All the three newly generated chiral centers have the (*S*)-configuration. The trioxane ring in **12** is also *cis*-fused, but adopts a twist-boat conformation, while each of the three new chiral centers has the (*R*)-configuration. Trioxanes **11** and **12** are also distinguishable by the ^{1}H-NMR chemical shift of the methine proton H–C(4'a) (**11**: 4.83 ppm; **12**: 0.465 ppm).

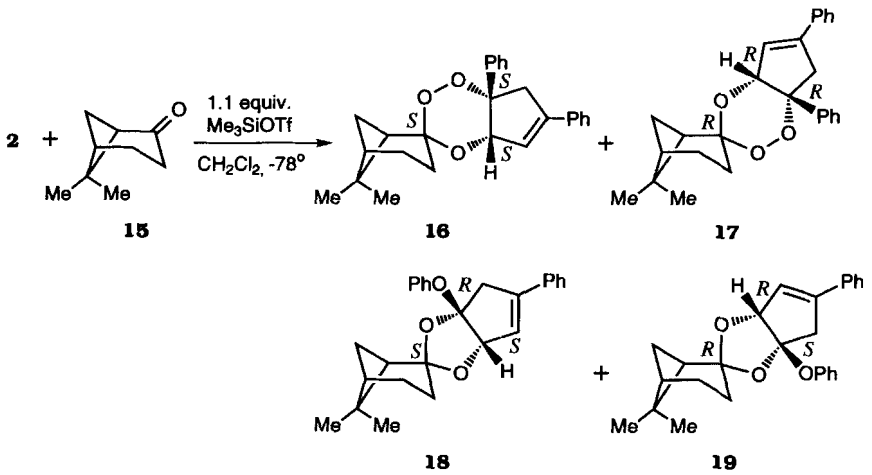
When **2** (1 equiv.) was allowed to react with excess **10** in the presence of 1.1 mol-equiv. of Me_3SiOTf in CH_2Cl_2 at $-78°$, four products were obtained in an overall yield of 56% (*Scheme 2*). This time, besides the aforementioned 1,2,4-trioxanes **11** and **12**, two unknown isomeric products **13** and **14** were formed in a ratio of 3:3:3:1. One of them, **13**, was obtained as a crystalline solid. Unfortunately, its structure is disordered. Nonetheless X-ray analysis revealed that the central ring in **13** is not a 1,2,4-trioxane, but a 1,3-dioxolane bearing a phenoxy substituent[2]). Like **11**, the dioxolane moiety is *cis*-fused. Moreover, the configurations of the new chiral centers in **13** correspond to those of **11**. The phenoxy substituent in **13** is easily distinguished by its ^{1}H-NMR signals (1 H_o at 7.02 ppm). The signal at 5.47 ppm characterizes the methine proton H–C(3'a) attached to the dioxolane structure. The minor product **14**, which was inextricably contaminated with **13**, was inferred to be the 1,3-dioxolane diastereoisomer on the basis of the complementarity of its NMR spectrum with that of **13**. When 1.3 and 1.5 mol-equiv. of Me_3SiOTf were used, the trioxanes diminished and were overtaken by dioxolanes which finally became the sole products (*Table*, *Entries 4* and *5*).

The other chiral cyclic ketones behaved exactly like (–)-menthone (**10**) in the presence of 1.1 mol-equiv. of Me_3SiOTf. (+)-Nopinone (**15**) gave four products, trioxanes **16** and **17** and dioxolanes **18** and **19**, in a ratio of 8:2:3:3 and in an overall yield of 85%

[2]) A perspective view of dioxolane **13** is shown in [5].

(*Scheme 3*). The major product **16** was isolated and its structure determined by X-ray (*Fig. 2*). The trioxane ring adopts a boat conformation and is *cis*-fused to its original cyclopentene component. All the new chiral centers are of the (*S*)-configuration. Its (all-*R*)-configured diastereoisomer **17** could not be isolated, but its presence was deduced from the NMR spectrum of the reaction mixture. The dioxolane counterparts **18** and **19** were separated and their configurations, which correspond to the related trioxanes, were assigned on the basis of their NMR spectra.

Scheme 3



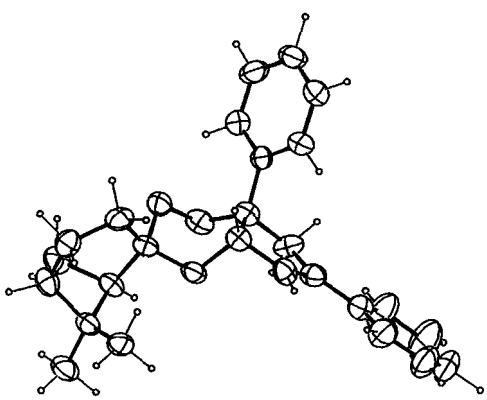
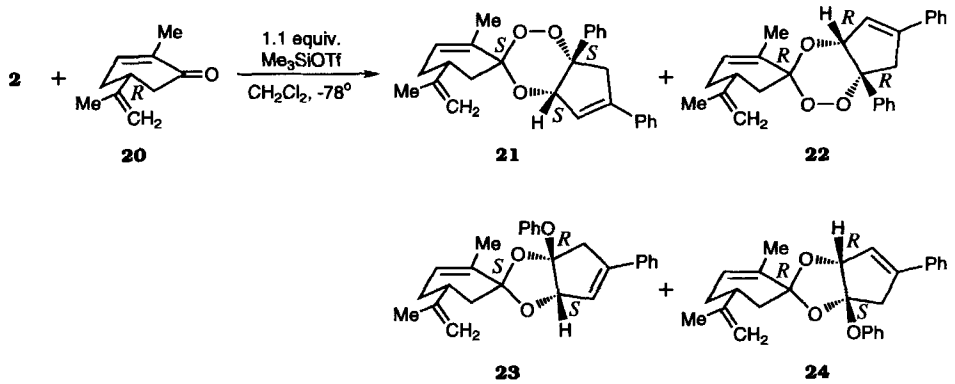


Fig. 2. *Perspective drawing of the X-ray structure of 1,2,4-trioxane* **16**

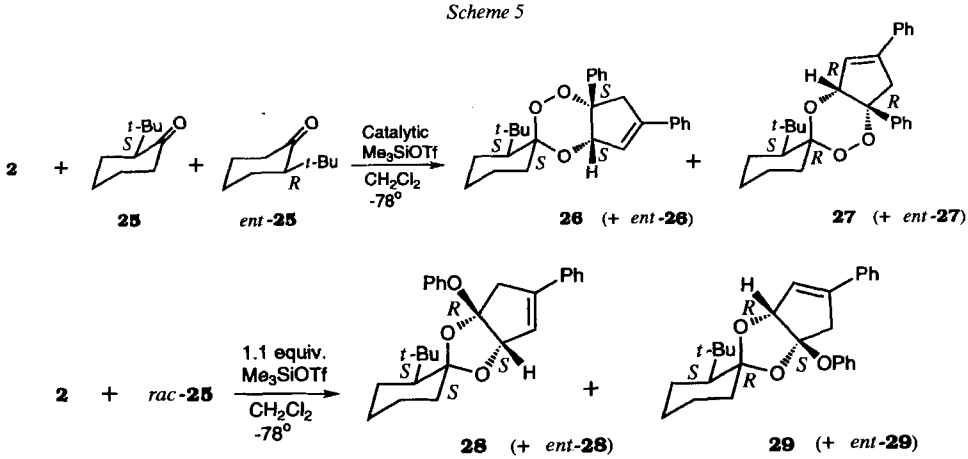
(−)-Carvone (**20**) also afforded four products **21**–**24** in 58% yield in a ratio of 5:4:18:15 (*Scheme 4*). Subsequent chromatographic separation afforded the diastereoisomer pair of 1,3-dioxolanes **23** and **24**. The minor components, the corresponding trioxanes **21** and **22**, were lost during purification and could not be isolated.

Scheme 4



In a similar manner, racemic 2-(*tert*-butyl)cyclohexanone (**25**/*ent*-**25**) was allowed to react with endoperoxide **2** in the presence of a catalytic amount of Me_3SiOTf in CH_2Cl_2. Only two racemic pairs of 1,2,4-trioxanes, **26** (and *ent*-**26**) and **27** (and *ent*-**27**), were formed in a ratio of 1:1.3 and in 31% yield (*Scheme 5*). As previously observed for the chiral ketones, increasing the amount of Me_3SiOTf to 1.1 mol-equiv. brought about dioxolane formation. Just two racemic pairs of 1,3-dioxolanes, **28** (and *ent*-**28**) and **29** (and *ent*-**29**), were obtained in 27% yield and in a ratio of 2:1 (*Scheme 5*). As before, the constitution and configurations of *rac*-**26**–**29** were readily assigned by comparing their NMR spectral data with those of the X-ray structures, namely, **11**, **12**, **13**, and **16**.

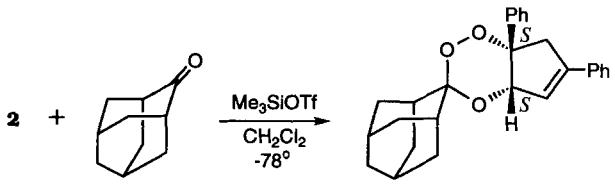
Scheme 5



It was further found that in the case of the other chiral cyclohexanones, the ratio of trioxanes to dioxolanes varied with the amount of Me_3SiOTf used. Catalytic amounts invariably led to trioxanes as the sole products, whereas concentrations of 1.5 mol-equiv. favored dioxolanes. These results stand in contrast to the behavior of the achiral, but bulky ketone adamantan-2-one (**30**). It reacted with **2** in the presence of catalytic or

equivalent amounts of Me_3SiOTf giving the racemic pair 1,2,4-trioxane **31**/*ent*-**31** as the sole products in high yield (*Scheme 6*). No trace of dioxolane was detected.

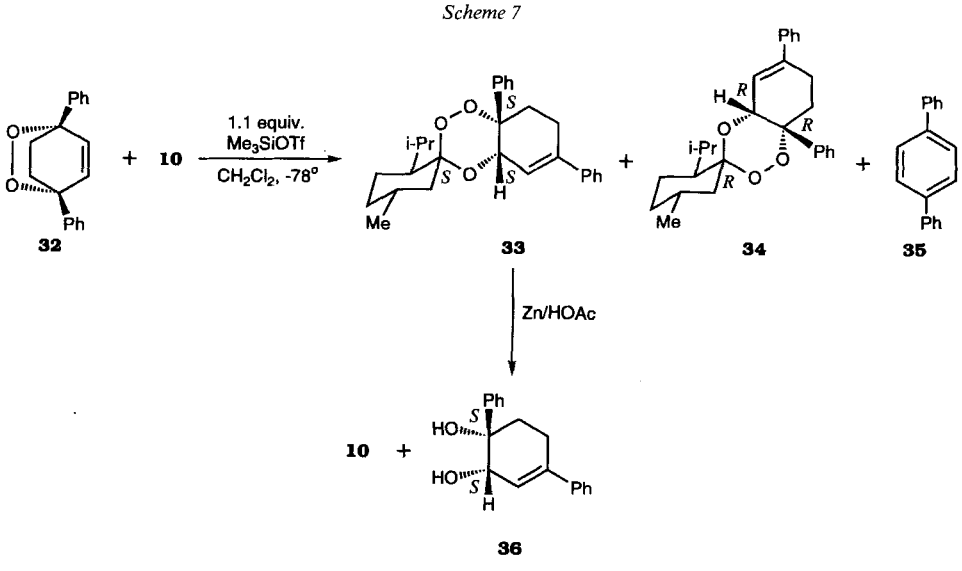
Scheme 6



At this juncture, it is appropriate to emphasize that the spectral markers for the trioxanes and dioxolanes are unambiguous. The methine proton H–C(4'a) in 1,2,4-trioxanes give a ^{1}H-NMR signal at *ca.* 4.65–5.20 ppm, whereas the signal H–C(3'a) in 1,3-dioxolanes appears between 5.26 and 5.47 ppm. Furthermore, all dioxolanes are easily distinguished by a signal at *ca.* 7.00 ppm for a single aromatic proton that is indicative of the phenoxy substituent. In the ^{13}C-NMR spectra, the quaternary C-atom C(7'a) in trioxanes usually resonates at 85–104 ppm, whereas the signal for the corresponding C(6'a) in dioxolanes lies in the region of 110–120 ppm. The mass spectra are also characteristic. All trioxanes and dioxolanes give rise to base peaks at 105 and 157, respectively.

Lastly, the reaction of 1,4-diphenyl-2,3-dioxabicyclo[2.2.2]oct-5-ene (**32**) with (–)-menthone (**10**) was assayed in the presence of 1.1 mol-equiv. of Me_3SiOTf (*Scheme 7*). The NMR spectrum of the reaction mixture revealed that the diastereoisomeric trioxanes **33** and **34** were formed in 75% yield and in a ratio of 2:1, together with 7% of *p*-terphenyl (**35**). Chromatography delivered **33** as a pure product, but failed to separate **34**. The assignment of configuration to **33** was made by comparing its NMR spectrum with those of **11** and **12**. The values of the resonances for the quaternary

Scheme 7

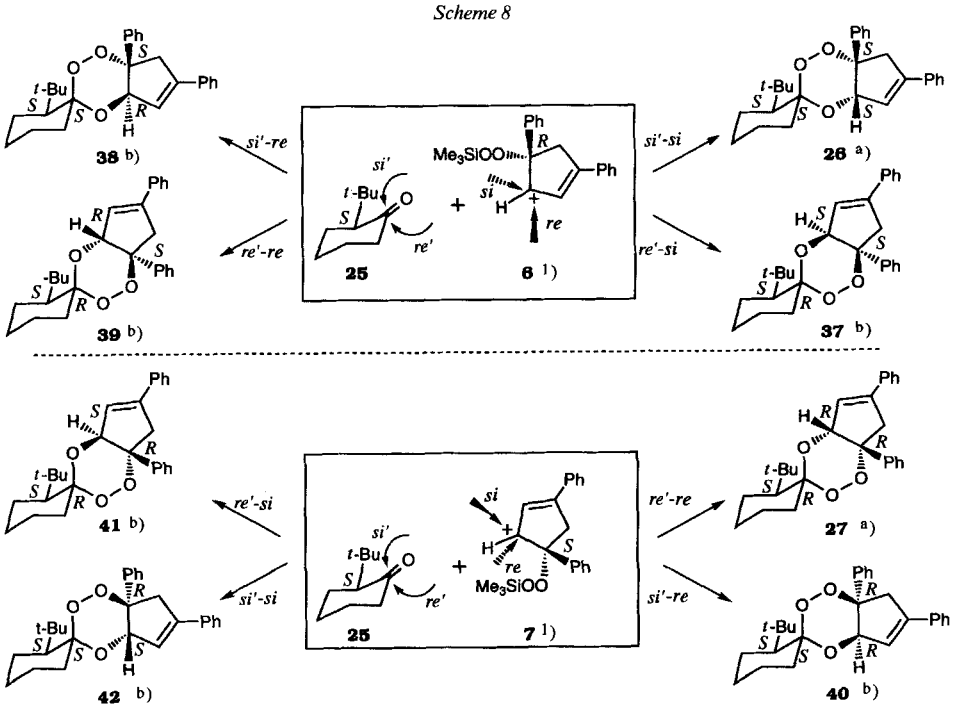


C-atoms and the H–C(4'a) signal were a better match with those of **11**. Treatment of **33** with Zn powder in AcOH gave the *cis*-1,2-diol **36** in 53% yield [9].

Discussion. – All the chiral cyclohexanones behave essentially the same way towards the endoperoxide **2** in the presence of a catalytic amount of Me_3SiOTf. The results can be conveniently discussed by taking 2-(*tert*-butyl)cyclohexanone (**25**) of the (*S*)-configuration as the example. In principle, the combination of **25** and **2** could give rise to eight diastereoisomeric trioxanes (*Scheme 8*). However, in practice, just two were formed (**26** and **27**). In other words, the reaction is diastereoselectively controlled. The factors responsible may be evaluated in terms of the reactivity of the (*R*)- and (*S*)-(trimethylsilyl)peroxy cations **6** and **7** arising from **2** by silylation. Each enantiomeric cation can combine with **25** in four different ways. Construction of the trioxane ring entails two crucial bond-making steps at the trigonal centers which may or may not be synchronous. As a nucleophile, the peroxy group of the cation **6** or **7** can attack either the *si'* or *re'* face of the cyclic ketone **25**. The erstwhile ketone O-atom then has the choice of annihilating the positive charge on the *si* or *re* face of the attached cationic center. Formation of the *trans*-fused trioxanes **38** and **39** from **6**, and **41** and **42** from **7** is prohibited, probably for geometric reasons, as mentioned earlier.

By default, the four *cis*-fused trioxanes are more accessible. However, the transition states leading to **26**, **37**, **27**, and **40** are clearly subject to other steric constraints. Assum-

Scheme 8



a) Formation experimentally established. b) Formation prohibited.

ing that the transition states are late, and therefore product-like, it is seen that the bulk of the *tert*-butyl substituent plays a dual role. Firstly, it anchors the attached cyclohexane ring in a rigid chair conformation thanks to its unequivocal equatorial orientation. Secondly, it compels the newly formed spirocyclic trioxane to adopt the least encumbered of the two possible chair conformations (*Fig. 3*). In fact, these conformational preferences are readily apparent from the X-ray structures of the related trioxanes **11** and **12** (*Fig. 1*). Consequently, the cooperative formation of the peroxide bond on the *si'* face of **25** and of the ether link on the *si* face of **6** to create **26** encounters no unfavorable nonbonded interactions, because the 'vinyl' bond of the *cis*-fused cyclopentene ring takes up an equatorial (eq) position on the trioxane ring (*Fig. 3*, *C*-**26**). If **6** opts for peroxidation on the *re'* face of **25**, then closure on the *si* face of the cationic center to form **37** is obstructed by the energetically costly 1,3-diaxial interaction arising between the methylene group of the cyclohexane ring and the 'vinyl' bond of the cyclopentene ring (*Fig. 3*, *C*-**37**).

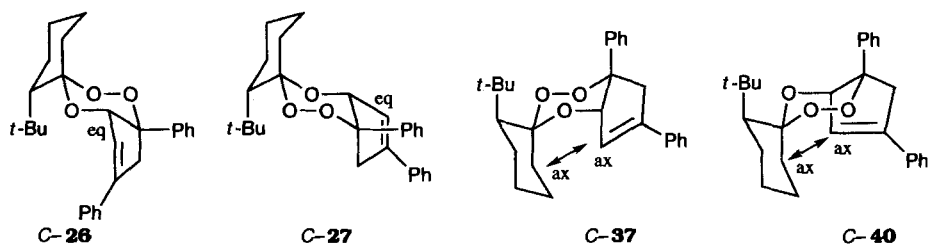


Fig. 3. *Chair conformations of spirocyclic trioxanes revealing 1,3-diaxial interactions* (*C*-**37** and *C*-**40**) *and alignment of Ph group with O–O bond* (*C*-**26** and *C*-**27**)

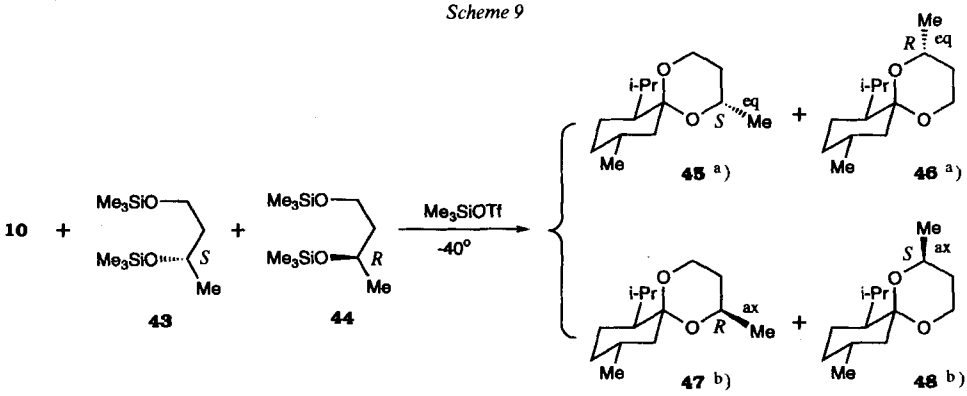
Similar arguments are valid for the enantiomeric cation **7** and its combination with **25**. Assembly of the *cis*-fused trioxane **27** is unimpeded and therefore easy (*Fig. 3*, *C*-**27**), whereas access to **40** is blocked owing to the severe 1,3-diaxial interaction (*C*-**40**). The essential finding is that a chiral cyclohexanone, *e.g.* **25**, differentiates between the enantiomeric peroxy cations; **6** gives uniquely the (*S*,*S*)-*cis*-fused trioxane **26**, and **7** the (*R*,*R*)-diastereoisomer **27**.

As already mentioned, (–)-menthone (**10**) behaves just like **25**. The isopropyl and methyl substituents lock the cyclohexane ring into a chair conformation. The isopropyl substituent by virtue of its bulk forces the spirocyclic 1,2,4-trioxane into the least constrained of the two possible chair conformations, thereby accounting for the formation of the trioxanes **11** and **12** in each of which the 'vinyl' bond of the cyclopentene ring occupies an equatorial position. The methyl and isopropenyl substituents of (–)-carvone (**20**), although differently positioned, anchor the parent ring in a half-chair conformation and exert stereocontrol on cyclopenteno-trioxane formation. The nopinane skeleton confers the same conformational bias to favor trioxanes **16** and, presumably, **17**.

The aforementioned enantioselective differentiation displayed by the chiral ketones towards the prochiral endoperoxide finds precedent in the stereochemically biased formation of spiroacetals from (–)-menthone (**10**) and racemic 1,3-diols. For example, **10** on catalysis with Me_3SiOTf reacts with the trimethylsilyl derivatives **43** and **44** of racemic butane-1,3-diols to give just two of the four possible diastereoisomeric 1,3-dioxanes

(*Scheme 9*) [6][7]. As explained above, the spirocyclic six-membered rings adopt the most comfortable chair conformations. As a result, only equatorially substituted methyl-1,3-dioxanes are allowed to form, namely **45** and **46**, arising from the (*S*) and (*R*)-diol derivatives, **43** and **44**, respectively. Their axial methyl counterparts, **47** and **48**, would be badly strained and thus are not obtained.

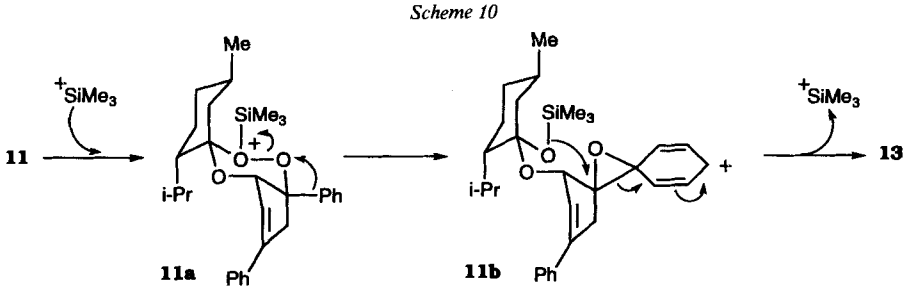
Scheme 9



a) Formation experimentally established. b) Formation prohibited.

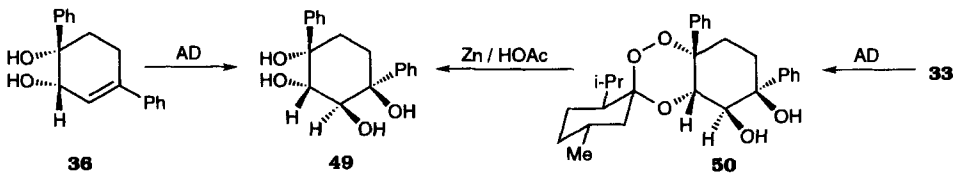
The 1,3-dioxolanes are obviously secondary products. They arise only from chiral cyclic ketones when Me_3SiOTf is employed in reagent quantities. Prior rearrangement of the endoperoxide **2** can, therefore, be ruled out. More reagent leads to more dioxolane. It also seems from the product ratios that dioxolane is formed at the expense of trioxane (*Table*). The simplest explanation of their origin is to invoke further reaction of the initially formed trioxanes. Their propensity to rearrangement probably depends on their inherent strain and their ability to attain the requisite geometry. Inspection of the conformations of **26** and **27** (*Fig. 3*, *C*-**26** and *C*-**27**) reveals that the Ph group is perfectly lined up with the peroxide bond for dyotropic rearrangement [8]. Trioxane **11** assumes the same conformation as that of *C*-**26**. Breakage of the peroxide bond by silylation (**11** → **11a**) triggers a 1,2-shift of the Ph group to the adjacent O-atom (**11a** → **11b**) while the other O-atom substitutes with inversion on the terminus of the epoxy phenonium cation (*Scheme 10*, **11** → **13**). The process causes minimal disturbance of the skeleton; the trioxane smoothly transforms itself into a dioxolane ring with retention of configuration of the angular substituent.

Scheme 10



Conclusion. – The foregoing results demonstrate that a prochiral cyclic endoperoxide (*e.g.* **2**) is desymmetrized by a chiral cyclohexanone such as (–)-menthone (**10**). More or less equal amounts of the diastereoisomeric 1,2,4-trioxanes **11** and **12** are obtained. Apart from the menthane component, the substituted trioxane entities are, of course, enantiomeric to each other. Consequently, further chemical transformation of **11** or **12** could ultimately give enantiomerically pure derivatives of the trioxane portion. Clearly, such desymmetrization would have synthetic potential [7]. A pertinent indication is provided by the six-membered peroxide **32**. It reacts with (–)-menthone (**10**) just like its lower homologue **2** (*Scheme 7*). Surprisingly, no dioxolanes are formed with 1 equiv. of Me_3SiOTf, only diastereoisomeric trioxanes **33** and **34**. Be that as it may, reductive deoxygenation of **33** with Zn and AcOH, which works well with trioxanes in general [9], disengages **10** and furnishes the enantiomerically pure *cis*-1,2-diol **36**. The overall process amounts to the regio- and diastereoselective *cis*-1,2-dihydroxylation of 1,4-diphenylcyclohexa-1,3-diene and opens an avenue to conduritol-like molecules [10]. Although not performed, osmium-catalyzed asymmetric dihydroxylation (AD) [11] of either **36** or **33** through the dihydroxylated trioxane **50** would provide a route to the pure enantiomeric tetrol **49** (*Scheme 11*). Other 1,4-dienes, through their endoperoxides, should be amenable to similar conversion to diastereoisomeric menthone-derived trioxanes and thence to enantiomerically pure *cis*-1,2-diol and *r*-1,*c*-2,*t*-3,*t*-4-tetrol derivatives.

Scheme 11



36 **49** **50**

Experimental Part

1. *General.* All solvents were redistilled before use. Anh. CH_2Cl_2 was purchased from the *Aldrich Chemical Company, Inc.* All glassware was flame-dried prior to use. Column chromatography (CC): silica gel *60* (230–400 mesh ASTM *Merck*); *Florisil* (100–200 mesh, *Fluka*). Flash chromatography (FC): silica-gel column 20 × 4 cm [12]. Melting points (m.p.): *Reichert* hot-stage microscope, uncorrected. Optical rotation: *Perkin-Elmer-241* polarimeter. IR: CCl_4 soln.; in cm^{-1}; *Perkin-Elmer-681* spectrometers. ^1H- and ^{13}C-NMR: *Varian-XL-200* or *Bruker-AMX-400* spectrometers, chemical shifts δ in ppm rel. to internal SiMe (= 0 ppm), coupling constants J in Hz; commercial $CDCl_3$ was used without further purification, for ^{13}C, APT was used and signals are designated as o (odd) for C-atoms attached to 1 or 3 H-atoms and e (even) for C-atoms bearing 0 or 2 H-atoms. MS: *m/z* (intensities in % rel. to base peak); *Vacuum-Generators VG-7070, CH-4 MAT*, and *Finnigan GC/MS-4023* using the INCOS data collection system. Elemental analyses were performed by Dr. *H. J. Eder*, Service de Microchimie, Département de Chimie Pharmaceutique, Université de Genève.

2. *1,4-Diphenyl-2,3-dioxabicyclo[2.2.1]hept-5-ene* (**2**) [4]. A soln. of 1,4-diphenylcyclopenta-1,3-diene (2.01 g, 9.23 mmol) in CCl_4 (100 ml) was photooxygenated at 0° for 5 h by using tetraphenylporphin (tpp; 2 mg) as sensitizer. Workup afforded **2** (2.28 g, 99%). ^1H-NMR (200 MHz): 2.57 (*AB*, J = 8.8, 1 H); 2.68 (*AB*, J = 8.8, 1 H); 6.82 (*s*, 2 H); 7.24–7.64 (*m*, 10 H). ^{13}C-NMR (100 MHz): 61.13 (e); 96.16 (e); 126.89 (o); 128.69 (o); 128.78 (o); 129.13 (o); 137.91 (e).

3. *Reaction of* **2** *with (–)-Menthone* (**10**); *Standard Procedure.* Me_3SiOTf (494 mg, 2.23 mmol) was added dropwise to a stirred soln. of **2** (506 mg, 2.0 mmol) and **10** (2.90 g, 18.8 mmol) in CH_2Cl_2 (15 ml), at –78° under N_2. After stirring the mixture for 4 h, dry Et_3N (225 mg, 2.23 mmol) was added to quench the reaction. The mixture was washed (H_2O), dried ($MgSO_4$), filtered, and evaporated. Traces of tpp were removed by filtration

through a short column of *Florisil* to give **11**–**14** as a colorless oil in 56% yield. The ratio **11**/**12**/**13**/**14** 3:3:3:1 was determined from the ^{1}H-NMR spectrum of the crude mixture by using cyclooctatetraene as the internal standard (see *Entry 3*, *Table 1*). The products **11**–**14** were separated by FC (CH_2Cl_2/hexane 1:5).

(1S,2S,5R,4'aS,7'aS)-4'a,7'a-Dihydro-2-isopropyl-5-methyl-6',7'a-diphenylspiro[cyclohexane-1,3'-[7'H]cyclopenta[1,2,4]trioxine] (**11**): 38 mg. Colorless crystals. M.p. 103–106° (from EtOH). $[\alpha]_D^{20} = -4.9$ ($c = 0.31$, $CHCl_3$). IR: 2960*s* (br.), 1500*m*, 1450*m*, 1380*w*, 1340*w*, 1305*w*, 1265*w*, 1170*w*, 1100*m*, 1075*s*, 1000*w*, 930*w*, 690*s*. ^{1}H-NMR (400 MHz): 0.87 (*d*, $J = 7.2$, 3 H); 0.91 (*d*, $J = 7.2$, 3 H); 0.92 (*m*, 1 H); 0.93 (*d*, $J = 6.0$, 3 H); 1.05–1.08 (*t*, $J = 12.2$, 1 H); 1.42–1.84 (*m*, 5 H); 2.43 (*sept.* $J = 7.2$, 1 H); 2.70 (*d*, $J = 12.2$, 1 H); 3.03 (*AB*, $J = 16.0$, 1 H); 3.70 (*ABd*, $J = 16.0$, 2.0, 1 H); 4.83 (*d*, $J = 2.7$, 1 H); 6.30 (*dd*, $J = 2.7$, 2.0, 1 H); 7.25–7.56 (*m*, 10 H). ^{13}C-NMR (100 MHz): 19.03 (o); 22.18 (o); 22.20 (e); 23.67 (o); 24.22 (o); 29.35 (o); 34.86 (e); 40.82 (e); 42.96 (e); 51.19 (o); 76.28 (o); 86.77 (e); 103.45 (e); 122.50 (o); 125.52 (o); 126.16 (o); 127.96 (o); 128.38 (o); 128.59 (o); 128.68 (o); 135.00 (e); 141.80 (e); 148.25 (e). MS: no M^+, 251 (1.25), 233 (6), 218 (15), 157 (11), 105 (100), 77 (40), 69 (38), 55 (38). Anal. calc. for $C_{27}H_{32}O_3$ (404.55): C 80.16, H 7.97; found: C 79.92, H 7.99.

(1R,2S,4'aR,5R,7'R)-4'a,7'a-Dihydro-2-isopropyl-5-methyl-6',7'a-diphenylspiro[cyclohexane-1',3'-[7H]cyclopenta[1,2,4]trioxine] (**12**): 96 mg. Colorless crystals. M.p. 105–110° (from EtOH). $[\alpha]_D^{20} = -34.2$ ($c = 1.18$, $CHCl_3$). IR: 2960*s* (br.), 1500*m*, 1451*s*, 1390*w*, 1370*w*, 1350*w*, 1305*m*, 1265*m*, 1215*w*, 1170*m*, 1110*m*, 1095*m*, 1080*s*, 1060*m*, 700*s*. ^{1}H-NMR (200 MHz): 0.88 (*d*, $J = 7.0$, 3 H); 0.90 (*d*, $J = 7.0$, 3 H); 0.91 (*d*, $J = 6.2$, 3 H); 0.92 (*m*, 2 H); 1.35–1.90 (*m*, 5 H); 2.26 (*m*, 1 H); 2.55 (*m*, 1 H); 2.98 (*ABd*, $J = 16.2$, 0.9, 1 H); 3.54 (*ABm*, $J = 16.2$, 1 H); 4.65 (*dd*, $J = 2.7$, 1.4, 1 H); 6.35 (*ddd*, $J = 2.7$, 2.6, 0.9, 1 H); 7.20–7.60 (*m*, 10 H). ^{13}C-NMR (50 MHz): 18.13 (o); 21.84 (e); 22.07 (o); 23.33 (o); 25.40 (o); 29.83 (o); 34.61 (e); 38.78 (e); 43.00 (e); 51.08 (o); 87.90 (o); 104.67 (e); 117.99 (e); 122.46 (o); 124.81 (o); 126.12 (o); 127.55 (o); 128.41 (o); 128.62 (o); 128.70 (o); 134.86 (e); 143.24 (e); 148.07 (e). MS: 404 (5, M^+), 233 (50) 218 (40), 105 (100) 77 (37). Anal. calc. for $C_{27}H_{32}O_3$ (404.55): C 80.16, H 7.97; found: C 79.96, H 7.86.

(1S,2S,3'aR,5R,6'aS)-3'a,6'a-Dihydro-2-isopropyl-5-methyl-3'a-phenoxy-5'-phenylspiro[cyclohexane-1,2'-[4H]cyclopenta[1,3]dioxole] (**13**): 167 mg. Colorless crystals. M.p. 111–114° (from EtOH). $[\alpha]_D^{20} = -63.1$ ($c = 0.91$, $CHCl_3$) IR: 2960*s*, 1600*w*, 1495*s*, 1450*w*, 1340*w*, 1325*w*, 1305*w*, 1225*m*, 1200*m*, 1160*m*, 1120*s*, 1100*w*, 1060*m*, 1040*m*, 1000*w*, 970*w*, 935*m*, 920*m*, 690*s*. ^{1}H-NMR (200 MHz): 0.72 (*d*, $J = 6.4$, 3 H); 0.73 (*d*, $J = 6.8$, 3 H); 0.87 (*d*, $J = 7.0$, 3 H); 0.88 (*m*, 1 H); 1.12 (*t*, $J = 12.6$, 1 H); 1.23–1.75 (*m*, 5 H); 2.10–2.33 (*m*, 2 H); 3.01 (*ABd*, $J = 16.9$, 1.8, 1 H); 3.34 (*ABdd*, $J = 16.9$, 1.7, 1.7, 1 H); 5.47 (*dd*, $J = 1.7$, 1.6, 1 H); 6.17 (*ddd*, $J = 1.6$, 1.7, 1.8, 1 H); 7.03 (*m*, 1 H); 7.19–7.49 (*m*, 9 H). ^{13}C-NMR (50 MHz): 18.20 (o); 21.96 (o); 23.35 (e); 23.52 (o); 24.41 (o); 30.49 (o); 34.53 (e); 42.94 (e); 46.36 (e); 48.81 (o); 91.04 (o); 114.67 (e); 116.34 (e); 118.25 (o); 121.86 (o); 122.60 (o); 125.90 (o); 126.00 (o); 128.40 (o); 129.31 (o); 135.09 (e); 143.17 (e); 155.35 (e). MS: 404 (2, M^+), 311 (26), 250 (78), 233 (19), 157 (100), 141 (8), 128 (9). Anal. calc. for $C_{27}H_{32}O_3$ (404.55): C 80.16, H 7.97; found: C 79.90, H 7.80.

(1R,2S,3'aS,5R,6'aR)-3'a,6'a-Dihydro-2-isopropyl-5-methyl-3'a-phenoxy-5'-phenylspiro[cyclohexane-1',2'-[4H]cyclopenta[1,3]dioxole] (**14**): 18.5 mg (mixed with **13**). Colorless crystals. M.p. 105–111° (from EtOH). IR: 2860*s* (br.), 1550*m*, 1540*w*, 1445*s*, 1400*m*, 1338*w*, 1315*w*, 1294*m*, 1280*w*, 1255*m*, 1210*w* (br.), 1176*m*, 1155*m*, 1110*m*, 1060*s*, 1024*m*, 1012*m*, 1000*m*, 988*s*, 950*m*, 930*w*, 920*w*, 880*m*, 830*w*, 640*s*. ^{1}H-NMR (200 MHz; data from **13**/**14** 1:1): 0.77 (*d*, $J = 7.0$, 3 H); 0.82 (*d*, $J = 7.0$, 3 H); 0.83 (*d*, $J = 7.0$, 3 H); 0.85 (*d*, $J = 7.0$, 3 H); 0.87 (*d*, $J = 7.0$, 3 H); 0.90 (*d*, $J = 7.0$, 3 H); 1.00–1.78 (*m*, 14 H); 1.95–2.10 (*m*, 2 H); 2.25–2.38 (*m*, 2 H); 3.06 (*ABdd*, $J = 16.8$, 1.0, 2.0, 1 H (**14**)); 3.28 (*ABdd*, $J = 16.8$, 2.0, 2.0, 1 H (**14**)); 3.08 (*ABd*, $J = 16.8$, 2.2, 1 H (**13**)); 3.35 (*ABdd*, $J = 16.8$, 2.0, 2.0, 1 H (**13**)); 5.42 (*m*, 2 H); 6.18 (*ddd*, $J = 2.0$, 2.0, 1.8, 1 H (**14**)); 6.21 (*ddd*, $J = 2.0$, 2.0, 1.9, 1 H (**13**)); 7.05 (*m*, 2 H); 7.20–7.43 (*m*, 18 H). ^{13}C-NMR (50 MHz; data from **13**/**14** 1:1): 17.99 (o); 18.58 (o); 22.17 (o); 22.17 (o); 23.07 (e); 23.38 (e); 23.51 (o); 23.57 (o); 24.27 (o); 24.42 (o); 30.57 (o); 30.64 (o); 34.50 (e); 34.56 (e); 42.88 (e); 43.55 (e); 45.92 (e); 48.35 (o); 48.75 (e); 49.90 (o); 91.49 (o); 91.92 (o); 114.23 (e); 114.54 (e); 116.65 (e); 118.22 (e); 118.65 (o); 118.78 (o); 122.09 (o); 122.63 (o); 124.24 (o); 124.24 (o); 125.97 (o); 126.01 (o); 128.41 (o); 128.49 (o); 128.52 (o); 128.54 (o); 129.34 (o); 129.36 (o); 135.10 (e); 135.25 (e); 142.55 (e); 143.08 (e); 155.43 (e); 155.80 (e). MS: no M^+, 311 (29), 250 (10), 233 (20), 157 (100), 141 (38), 128 (48), 115 (13), 103 (10), 94 (20), 77 (17), 69 (25), 55 (30). Anal. calc. for $C_{27}H_{32}O_3$ (404.55): C 80.16, H 7.97; found: C 80.11, H 7.96.

The experiment was repeated with a catal. amount (0.033 equiv.) or with 0.5, 1.3, or 1.5 equiv. of Me_3SiOTf. In each case, a corresponding amount of Et_3N was used for quenching. Various amounts of **11**–**14** were obtained (see *Table*).

4. *Reaction of* **2** *with (+)-(1R)-Nopinone* (**15**). According to the *Standard Procedure*, Me_3SiOTf (103 mg, 0.46 mmol), **2** (105 mg, 0.42 mmol), and **15** (392 mg, 2.84 mmol) in CH_2Cl_2 (3 ml) were allowed to react for 2 h, whereupon dry Et_3N (110 mg, 1.08 mmol) was added. Workup gave a colorless oil (142 mg, 85% overall). The

ratios **16**/**17**/**18**/**19** 8:2:3:3 was estimated from the ^{1}H-NMR spectrum of the crude mixture. Separation by FC (CH_2Cl_2/hexane 1:15 → 1:10) gave **16**, **18**, and **19** (**17** being irrecoverable).

(1R,2S,4'aS,5R,7'aS)-4'a,7'-Dihydro-6,6-dimethyl-6',7'a-diphenylspiro[bicyclo[3.1.1]heptane-2,3'-[7H]cyclopenta[1,2,4]trioxine] (**16**): 52.7 mg. Colorless crystals. M.p. 85–90° (from EtOH). $[\alpha]_D^{20} = -109.4$ ($c = 0.87$, $CHCl_3$). IR: 2926*s* (br.), 2360*w*, 1500*m*, 1462*w*, 1450*m*, 1390*w*, 1370*w*, 1350*m*, 1310*w*, 1290*w*, 1255*w* (br.), 1230*m*, 1165*w*, 1120*s*, 1095*s*, 1060*s*, 915*w*, 880*w*, 700*s*, 690*s*. ^{1}H-NMR (200 MHz): 1.07 (*s*, 3 H); 1.26 (*m*, 1 H); 1.30 (*s*, 3 H); 1.68–2.00 (*m*, 5 H); 2.20 (*m*, 1 H); 2.87 (*m*, 1 H); 2.94 (*ABdd*, $J = 16.8$, 1.8, 1.5, 1 H); 3.10 (*ABdd*, $J = 16.8$, 1.8, 1.5, 1 H); 5.20 (*ddd*, $J = 2.2$, 1.5, 1.5, 1 H); 6.27 (*ddd*, $J = 2.2$, 1.8, 1.8, 1 H); 7.23–7.50 (*m*, 8 H); 7.57–7.70 (*m*, 2 H). ^{13}C-NMR (50 MHz): 22.74 (e); 23.27 (o); 26.14 (e); 27.24 (o); 27.73 (e); 37.47 (e); 40.46 (o); 44.90 (e); 47.43 (o); 79.43 (o); 87.35 (e); 108.33 (e); 125.36 (o); 125.76 (o); 125.81 (o); 127.45 (o); 128.28 (o); 128.39 (o); 128.51 (o); 134.84 (e); 141.83 (e); 142.5 (e). MS: no M^+, 295 (0.57), 250 (1), 233 (7), 218 (40), 157 (31), 105 (100), 95 (15), 83 (33), 77 (38), 55 (36). Anal. calc. for $C_{26}H_{38}O_3$ (388.50): C 80.38, H 7.26; found: C 80.10, H 7.35.

(1R,2S,3'aR,5S,6'aS)-3'a,6'a-Dihydro-6,6-dimethyl-3'a-phenoxy-5'-phenylspiro[bicyclo[3.1.1]heptane-2,2'-[4H]cyclopenta[1,3]dioxole] (**18**): 8 mg. Colorless crystals. M.p. 125–129° (from EtOH). $[\alpha]_D^{20} = +60.0$ ($c = 0.24$, $CHCl_3$). IR: 2927*s* (br.), 1600*w*, 1500*m*, 1347*w* (br.), 1255*w*, 1228*m*, 1204*m*, 1160*w*, 1125*s*, 1100*m*, 1050*s*, 924*w* (br.), 690*s*. ^{1}H-NMR (200 MHz): 1.02 (*s*, 3 H); 1.21 (*s*, 3 H); 1.24–1.35 (*m*, 1 H); 1.78–1.98 (*m*, 3 H); 2.00–2.34 (*m*, 3 H); 2.45 (*m*, 1 H); 3.00 (*ABdd*, $J = 16.7$, 2.0, 0.6, 1 H); 3.24 (*ABdd*, $J = 16.7$, 1.7, 1.7, 1 H); 5.35 (*ddd*, $J = 2.0$, 1.7, 0.6, 1 H); 6.23 (*ddd*, $J = 2.0$, 2.0, 1.7, 1 H); 7.05 (*m*, 1 H); 7.18–7.46 (*m*, 9 H). ^{13}C-NMR (50 MHz): 22.80 (o); 23.01 (e); 26.72 (e); 26.88 (o); 30.67 (e); 37.83 (e); 40.19 (o); 42.72 (e); 50.22 (o); 91.46 (o); 113.83 (e); 118.99 (e); 119.07 (o); 122.18 (o); 122.89 (o); 125.91 (o); 125.91 (o); 128.39 (o); 129.25 (o); 134.96 (e); 143.11 (e); 155.44 (e). MS: no M^+, 295 (2.5), 250 (6), 234 (6), 157 (100), 139 (14), 128 (15), 55 (16). Anal. calc. for $C_{26}H_{28}O_3$ (388.50): C 80.38, H 7.26; found: C 80.21, H 7.42.

(1R,2R,3'aS,5S,6'aR)-3'a,6'a-Dihydro-6,6-dimethyl-3'a-phenoxy-5'-phenylspiro[bicyclo[3.1.1]heptane-2,2'-[4H]cyclopenta[1,3]dioxole] (**19**): 23 mg. Colorless crystals. M.p. 60–64° (from EtOH). $[\alpha]_D^{20} = -73.5$ ($c = 0.19$, $CHCl_3$). IR: 2940*m* (br.), 1600*m*, 1590*m*, 1500*s*, 1460*w*, 1450*w*, 1360*w*, 1345*w*, 1330*w*, 1260*w*, 1230*m*, 1200*m*, 1175*w*, 1165*w*, 1110*s*, 1100*s*, 1065*m*, 1050*s*, 920*m*, 690*s*. ^{1}H-NMR (200 MHz): 0.73 (*s*, 3 H); 1.00 (*s*, 3 H); 1.20–1.37 (*m*, 1 H); 1.76–1.92 (*m*, 3 H); 1.98–2.32 (*m*, 3 H); 2.40 (*m*, 1 H); 3.09 (*ABd*, $J = 16.8$, 2.0, 1 H); 3.38 (*ABdd*, $J = 16.8$, 1.9, 1.7, 1 H); 5.26 (*dd*, $J = 2.1$, 1.9, 1 H); 6.19 (*ddd*, $J = 2.1$, 2.0, 1.9, 1 H); 7.01 (*m*, 1 H); 7.10–7.50 (*m*, 9 H). ^{13}C-NMR (50 MHz): 22.49 (o); 22.81 (e); 26.39 (e); 26.59 (o); 30.09 (e); 37.76 (e); 39.89 (o); 43.49 (e); 49.78 (o); 90.28 (o); 114.39 (e); 118.17 (o); 118.75 (e); 121.63 (o); 122.38 (o); 125.91 (o); 128.39 (o); 128.42 (o); 129.07 (o); 134.96 (e); 143.41 (e); 154.79 (e). MS: no M^+, 295 (3), 250 (6), 233 (7), 157 (100), 139 (11), 128 (11). Anal. calc. for $C_{26}H_{28}O_3$ (388.50): C 80.38, H 7.26; found: C 80.49, H 7.24.

5. *Reaction of* **2** *with (–)-Carvone* (**20**). According to the *Standard Procedure*, Me_3SiOTf (233 mg, 1.05 mmol), **2** (240 mg, 0.96 mmol), and **20** (959 mg, 6.38 mmol) in CH_2Cl_2 (1 ml) were allowed to react for 2 h. The ^{1}H-NMR spectrum of the crude mixture revealed **21**/**22**/**23**/**24** in a ratio of 5:4:18:15. Workup gave a greenish oil which was purified by FC (Et_2O/hexane 1:5): colorless crystals (224 mg, 58%). Recrystallization from EtOH afforded **23** and **24**; but **21** and **22** could not be isolated owing to their paucity.

(1S,3'aR,5R,6'S)-3'a,6'a-Dihydro-5-isopropenyl-2-methyl-3'a-phenoxy-5'-phenylspiro[cyclohex-2-ene-1,2'-[4H]cyclopenta[1,3]dioxole] (**23**): 34 mg. Colorless crystals. M.p. 130–132° (from EtOH). $[\alpha]_D^{20} = +23.3$ ($c = 0.15$, $CHCl_3$). IR: 2920*m* (br.), 2370*w*, 1650*w*, 1600*m*, 1500*s*, 1450*m*, 1375*w*, 1345*w*, 1330*w*, 1295*w*, 1250*w*, 1230*m*, 1205*m*, 1170*s*, 1135*s*, 1113*m*, 1075*m*, 1050*vs*, 1030*s*, 950*m*, 925*m*, 900*m*, 800*w*, 770*m* (br.), 685*s*. ^{1}H-NMR (200 MHz): 1.56 (*s*, 3 H); 1.65 (*m*, 1 H); 1.70 (*s*, 3 H); 1.90 (*m*, 1 H); 2.15 (*m*, 1 H); 2.42 (*m*, 1 H); 2.55 (*m*, 1 H); 3.07 (*ABd*, $J = 16.8$, 2.1, 1 H); 3.33 (*ABdd*, $J = 16.8$, 1.8, 1.8, 1 H); 4.70 (*m*, 2 H); 5.45 (*dd*, $J = 1.8$, 1.8, 1 H); 5.78 (*m*, 1 H); 6.18 (*ddd*, $J = 1.8$, 1.8, 2.1, 1 H); 7.06 (*m*, 1 H); 7.20–7.47 (*m*, 9 H). ^{13}C-NMR (50 MHz): 15.65 (o); 20.64 (o); 30.74 (e); 39.73 (o); 40.01 (e); 42.68 (e); 91.23 (o); 109.19 (e); 112.41 (e); 115.27 (e); 118.73 (o); 122.21 (o); 122.30 (o); 125.94 (o); 128.45 (o); 128.50 (o); 129.32 (o); 129.55 (o); 132.72 (e); 134.87 (e); 143.41 (e); 148.48 (e); 155.37 (e). MS: no M^+, 307 (1.08), 250 (3), 157 (100), 141 (3), 128 (16), 109 (4), 95 (2), 77 (6), 65 (4). Anal. calc. for $C_{27}H_{28}O_3$ (400.52): C 80.97, H 7.05; found: C 80.70, H 7.05.

(1R,3'aS,5R,6'aR)-3'a,6'a-Dihydro-5-isopropenyl-2-methyl-3'a-phenoxy-5'phenylspiro[cyclohex-2-ene-1,2'-[4H]cyclopenta[1,3]dioxole] (**24**): 25 mg. Colorless crystals. M.p. 120–125° (from EtOH). $[\alpha]_D^{20} = -208.1$ ($c = 0.66$, $CHCl_3$). IR: 2930*m* (br.), 2370*w*, 2350*w*, 1640*w*, 1600*m*, 1500*s*, 1450*m*, 1370*w*, 1345*w*, 1330*w*, 1290*w*, 1260*w*, 1225*m*, 1200*m*, 1170*s*, 1130*vs*, 1110*s*, 1070*m*, 1030*vs*, 940*s*, 925*m*, 885*m*, 800*w*, 775*w*, 690*s*. ^{1}H-NMR (200 MHz): 1.45 (*s*, 3 H); 1.55–1.72 (*m*, 4 H); 1.85–2.20 (*m*, 2 H); 2.28–2.60 (*m*, 2 H); 3.06 (*ABdd*, $J = 16.8$, 2.1, 0.64, 1 H); 3.38 (*ABdd*, $J = 16.8$, 1.7, 1.7, 1 H); 4.50 (*m*, 1 H); 4.59 (*m*, 1 H); 5.55 (*ddd*, $J = 1.7$, 1.7, 0.64, 1 H); 5.76 (*m*, 1 H); 6.21 (*ddd*, $J = 1.7$, 1.7, 2.1, 1 H); 7.02 (*m*, 1 H); 7.20–7.48 (*m*, 9 H). ^{13}C-NMR (50 MHz): 16.35 (o);

20.49 (o); 30.42 (e); 39.64 (o); 40.52 (e); 42.75 (e); 92.22 (o); 108.89 (e); 112.83 (e); 114.50 (e); 118.48 (o); 122.12 (o); 122.80 (o); 125.91 (o); 125.91 (o); 128.46 (o); 129.29 (o); 129.59 (o); 133.02 (e); 134.87 (e); 142.98 (e); 148.24 (e); 155.06 (e). MS: no M^+, 307 (0.89), 250 (3.10), 157 (100), 141 (3.72), 128 (18.12), 109 (4.33), 95 (1.25), 77 (5.99), 65 (5.78). Anal. calc. for $C_{27}H_{28}O_3$ (400.52): C 80.97, H 7.05; found: C 80.73, H 6.88.

6. *Reaction of* **2** *with 2-(*tert*-Butyl)cyclohexanone* (*rac*-**25**). To a soln. of **2** (423.2 mg, 1.69 mmol) and *rac*-**25** (1.305 g, 8.46 mmol) in dry CH_2Cl_2 (5 ml), Me_3SiOTf (12.25 mg, 0.0552 mmol) was added under N_2 at $-78°$. After stirring for 4 h, Et_3N (5.58 mg, 0.0552 mmol) and H_2O (5 ml) were successively added. Workup as described in *Exper. 3* gave an oil which by ^{1}H-NMR revealed two products (239.5 mg, 35%) in a ratio of 1:1. CC (silica gel, hexane/Et_2O 50:1) gave trioxanes *rac*-**26** and *rac*-**27**.

*(1*RS,*2*RS,*4'a*RS,*7'a*RS*)-2-(*tert*-Butyl)-4'a,7'a-dihydro-6',7'a-diphenylspiro[cyclohexane-1,3'-[7*H*]cyclopenta[1,2,4]trioxine]* (*rac*-**26**): 96 mg. Colorless crystals. M.p. 124–126° (from $(iPr)_2O$/hexane). IR: 2959*s*, 1495*w*, 1448*m*, 1260*s*, 1089*s*, 1014*s*, 812*s*, 776*m*, 736*s*, 695*m*. ^{1}H-NMR (400 MHz): 0.94 (*s*, 9 H); 1.10–1.80 (*m*, 8 H); 2.79 (*d*, *J* = 13.2, 1 H); 3.02 (*AB*, *J* = 16.2, 1 H); 3.77 (*ABd*, *J* = 16.2, 2.2, 1 H); 4.73 (*d*, *J* = 2.9, 1 H); 6.17 (*dd*, *J* = 2.2, 2.9, 1 H); 7.16–7.49 (*m*, 10 H). ^{13}C-NMR (100 MHz): 23.05 (e); 25.54 (e); 26.47 (e); 30.74 (o); 32.85 (e); 33.93 (e); 40.98 (e); 54.73 (o); 75.34 (o); 85.90 (e); 104.80 (e); 122.64 (o); 125.51 (o); 126.11 (o); 128.02 (o); 128.38 (o); 128.57 (o); 128.57 (o); 135.18 (e); 141.47 (e); 147.90 (e). MS: 404 (90, M^+), 347 (50), 299 (100), 284 (48), 218 (20), 105 (100), 77 (31), 57 (12). Anal. calc. for $C_{27}H_{32}O_3$ (404.55): C 80.16, H 7.97; found: C 79.99, H 7.98.

*(1*RS,*2*SR,*4'a*RS,*7'a*RS*)-2-(*tert*-Butyl)-4'a,7'a-dihydro-6',7'a-diphenylspiro[cyclohexane-1,3'-[7*H*]cyclopenta[1,2,4]trioxine]* (rac-**27**): 96 mg. Colorless crystals. M.p. 113–115° (from $(iPr)_2O$/hexane). IR: 2938*s*, 1494*m*, 1447*m*, 1366*w*, 1332*w*, 1257*m*, 1115*m*, 1070*s*, 1000*m*, 947*m*, 874*w*, 815*w*, 694*s*. ^{1}H-NMR (400 MHz): 1.02 (*s*, 9 H); 1.20–1.83 (*m*, 8 H); 2.83 (*m*, 1 H); 3.10 (*AB*, *J* = 16.2, 1 H); 3.84 (*ABd*, *J* = 16.2, 2.2, 1 H); 4.67 (*d*, *J* = 2.6, 1 H); 6.30 (*dd*, *J* = 2.2, 2.6, 1 H); 7.25–7.38 (*m*, 10 H). ^{13}C-NMR (100 MHz): 23.14 (e); 25.17 (e); 26.33 (e); 30.50 (o); 31.75 (e); 33.81 (e); 41.32 (e); 54.21 (o); 75.35 (o); 85.88 (e); 105.21 (e); 122.67 (o); 125.45 (o); 126.11 (o); 127.92 (o); 128.35 (o); 128.56 (o); 128.56 (o); 135.18 (e); 141.68 (e); 147.95 (e). MS: 404 (3, M^+), 218 (70), 105 (100), 77 (41), 57 (18). Anal. calc. for $C_{27}H_{32}O_3$ (404.55): C 80.16, H 7.97; found: C 79.99, H 7.92.

7. *Reaction of* **2** *with 2-(*tert*-Butyl)cyclohexanone* (*rac*-**25**). Repetition of *Exper. 6* with Me_3SiOTf (136.8 mg, 0.62 mmol), **2** (140 mg, 0.56 mmol), and *rac*-**25** (691 mg, 4.48 mmol) in CH_2Cl_2 (3 ml) for 4 h, followed by addition of Et_3N (62.74 mg, 0.62 mmol), and the usual workup furnished an oil. Purification by CC (Et_2O/hexane 1:40) gave dioxolanes *rac*-**28**/*rac*-**29** (58.64 mg, 26%) in a 2:1 ratio (by ^{1}H-NMR). Separation was effected by FC (Et_2O/hexane 1:50).

*(1*RS,*2*RS,*3'a*SR,*6'a*RS*)-2-(*tert*-Butyl)-3'a,6'a-dihydro-3'a-phenoxy-5'-phenylspiro[cyclohexane-1,2'-[4*H*]-cyclopenta[1,3]dioxole]* (*rac*-**28**): Colorless crystals. M.p. 113–117° (from EtOH). IR: 2937*s*, 1597*m*, 1494*s*, 1447*m*, 1367*w*, 1341*m*, 1286*w*, 1248*m*, 1190*m*, 1120*s*, 1063*m*, 1035*s*, 1002*w*, 922*m*, 868*w*, 691*s*. ^{1}H-NMR (400 MHz): 0.96 (*s*, 9 H); 1.08–1.69 (*m*, 8 H); 2.36 (*dm*, *J* = 12.5, 1 H); 3.03 (*ABd*, *J* = 16.9, 1.8, 1 H); 3.30 (*ABdd*, *J* = 16.9, 1.8, 1.8, 1 H); 5.42 (*dd*, *J* = 1.84, 1.7, 1 H); 6.19 (*ddd*, *J* = 1.7, 1.8, 1.8, 1 H); 7.02 (*m*, 1 H); 7.20–7.41 (*m*, 9 H). ^{13}C-NMR (100 MHz): 23.96 (e); 26.49 (e); 26.49 (e); 30.17 (o); 33.69 (e); 38.26 (e); 43.43 (e); 52.80 (o); 91.09 (o); 113.75 (e); 117.44 (e); 118.04 (o); 121.73 (o); 122.31 (o); 126.01 (o); 128.42 (o); 128.42 (o); 129.36 (o); 135.03 (e); 143.62 (e); 155.49 (e). MS: 404 (72, M^+), 311 (100), 250 (22), 233 (60), 157 (100), 128 (12), 57 (10). Anal. calc. for $C_{27}H_{32}O_3$ (404.55): C 80.16, H 7.97; found: C 80.16, H 8.08.

*(1*RS,*2*SR,*3'a*SR,*6'a*RS*)-2-(*tert*-Butyl)-3'a,6'a-dihydro-3'a-phenoxy-5'-phenylspiro[cyclohexane-1,2'-[4*H*]-cyclopenta[1,3]dioxole]* (*rac*-**29**): Colorless crystals. M.p. 153–156° (from EtOH). IR: 2937*m*, 1587*w*, 1494*s*, 1341*w*, 1261*m*, 1226*m*, 1199*m*, 1113*s*, 1088*s*, 1059*s*, 1036*s*, 921*m*, 871*w*, 735*s*. ^{1}H-NMR (400 MHz): 0.88 (*s*, 9 H); 1.00–1.85 (*m*, 8 H); 2.35 (*dd*, *J* = 13.24, 1.11, 1 H); 2.97 (*ABd*, *J* = 16.9, 1.8, 1 H); 3.26 (*ABdd*, *J* = 16.9, 1.8, 1.8, 1 H); 5.29 (*m*, 1 H); 6.15 (*m*, 1 H); 6.95 (*m*, 1 H); 7.08–7.35 (*m*, 9 H). ^{13}C-NMR (100 MHz): 24.13 (e); 26.32 (e); 26.65 (e); 30.07 (o); 33.76 (e); 37.57 (e); 43.20 (e); 51.99 (o); 90.86 (o); 114.11 (e); 117.46 (e); 118.34 (o); 121.86 (o); 122.43 (o); 126.03 (o); 128.53 (o); 128.53 (o); 129.34 (o); 135.07 (e); 143.71 (e); 155.20 (e). MS: 404 (2, M^+), 375 (10), 233 (34), 157 (100), 128 (16), 57 (22). Anal. calc. for $C_{27}H_{32}O_3$ (404.55): C 80.16, H 7.97; found: C 80.04, H 7.89.

8. *(4'a*RS,*7'a*RS*)-4'a,7'a-Dihydro-6',7'a-diphenylspiro[adamantane-2,3'-[7*H*]cyclopenta[1,2,4]trioxine]* (*rac*-**31**). *Exper. 7* was repeated with **2** (64.8 mg, 0.27 mmol), adamantan-2-one (**30**; 77.9 mg, 0.52 mmol), and Me_3SiOTf (61.3 mg, 0.28 mmol), thereby giving *rac*-**31**. Colorless crystals (96.8 mg, 93%). M.p. 92–95° (from EtOH). IR: 3060*w*, 3030*w*, 2910*s*, 2860*m*, 1600*w*, 1490*m*, 1470*w*, 1450*m*, 1380*w*, 1340*w*, 1320*w*, 1260*m*, 1220*m*, 1110*s*, 1080*s*, 1010*w*, 920*w*, 910*w*, 875*w*, 700*s*. ^{1}H-NMR (200 MHz): 0.08–1.00 (*m*, 1 H); 1.20–2.20 (*m*, 12 H); 2.60 (*m*, 1 H); 3.00 (*ABdd*, *J* = 17.0, 1.6, 1.6, 1 H); 3.28 (*ABdd*, *J* = 17.0, 2.0, 2.0, 1 H); 5.20 (*ddd*, *J* = 1.6, 2.0, 2.0, 1 H); 6.36 (*ddd*, *J* = 1.6, 2.0, 2.0, 1 H); 7.20–7.70 (*m*, 10 H). ^{13}C-NMR (100 MHz): 26.94 (o); 27.23 (o); 33.65 (e);

33.71 (e); 33.74 (e); 34.01 (o); 34.34 (o); 34.70 (o); 37.26 (e); 44.23 (e); 79.09 (o); 87.18 (e); 104.59 (e); 125.01 (o); 125.93 (o); 126.14 (o); 127.61 (o); 128.30 (o); 128.36 (o); 128.53 (o); 134.93 (e); 142.29 (e); 144.61 (e). MS: 400 (10, M^+), 295 (10), 250 (20), 234 (75), 218 (18), 150 (30), 105 (100), 91 (10), 77 (80), 67 (15), 51 (22). Anal. calc. for $C_{27}H_{28}O_3$ (400.51): C 80.97, H 7.05; found: C 80.78, H 7.12.

9. *1,4-Diphenylcyclohexa-1,3-diene*. Prepared by dehydration of the corresponding 1,4-diphenylcyclohexane-1,4-diol by using AcOH and concentrated H_2SO_4 [13]. IR: 3060*m*, 3032*m*, 2941*m*, 2874*m*, 2828*m*, 1600*m*, 1495*s*, 1446*m*, 1373*w*, 1265*w*, 1074*m*, 1034*m*, 846*s*. ^{1}H-NMR (400 MHz): 2.79 (*s*, 4 H); 6.53 (*s*, 2 H); 7.25–7.65 (*m*, 10 H). ^{13}C-NMR (100 MHz): 26.11 (e); 121.63 (o); 124.90 (o); 127.06 (o); 128.43 (o); 135.95 (e); 140.75 (e). MS: 232 (93, M^+), 215 (15), 154 (18), 141 (37), 115 (30), 91 (100), 77 (35), 63 (12), 51 (30).

10. *1,4-Diphenyl-2,3-dioxabicyclo[2.2.2]oct-5-ene* (**32**). Prepared by tpp-sensitized photo-oxygenation of 1,4-diphenylcyclohexa-1,3-diene [14]. ^{1}H-NMR (400 MHz): 1.90–2.50 (*m*, 2 H); 2.62–2.80 (*m*, 2 H); 6.88 (*s*, 2 H); 7.34–7.69 (*m*, 10 H).

11. *(1S,2S,4'aS,5R,8'aS)-4'a,7',8',8'a-Tetrahydro-2-isopropyl-4-methyl-6',8'a-diphenylspiro[cyclohexane-1,3'-cyclohexa[1,2,4]trioxine]* (**33**). To a soln. of **32** (201.3 mg, 0.76 mmol) and (–)-menthone (**10**; 588.1 mg, 3.8 mmol) in CH_2Cl_2 (2 ml), Me_3SiOTf (185.6 mg, 0.836 mmol) was added with stirring at –78° under Ar. After 2 h further stirring, Et_3N (84.6 mg, 0.836 mmol) was added. Workup gave a colorless oil. CC (silica gel, ArOEt/hexane 1:70) gave pure **33** (114 mg, 51%), together with **34** mixed with terphenyl (**35**) in a 2:1 ratio (by ^{1}H-NMR). Further CC gave **35** (12.3 mg, 7%). Trioxane **34** could not be obtained pure. **33**: Colorless crystals. M.p. 188–190° (from MeOH). $[\alpha]_D^{20} = +13.2$ (*c* = 0.30, $CHCl_3$). IR: 2970*s*, 1500*w*, 1450*m*, 1370*w*, 1310*w*, 1270*w*, 1220*m*, 1160*m*, 1100*m*, 1080*s*, 1030*m*, 1020*m*, 700*s*. ^{1}H-NMR (400 MHz): 0.86 (*d*, *J* = 6.3, 3 H); 0.91 (*d*, *J* = 7.0, 3 H); 0.92 (*m*, 2 H); 0.93 (*d*, *J* = 7.0, 3 H); 1.31–1.82 (*m*, 5 H); 1.98 (*dddd*, *J* = 12.1, 12.1, 4.4, 1.8, 1 H); 2.11 (*dd*, *J* = 5.2, 12.1, 1 H); 2.59 (*dd*, *J* = 12.1, 4.4, 1 H); 2.62 (*m*, 1 H); 2.96 (*dd*, *J* = 11.4, 2.0, 1 H); 3.05 (*ddd*, *J* = 5.2, 12.1, 1 H); 5.05 (*d*, *J* = 5.5, 1 H); 6.38 (*dd*, *J* = 5.5, 1.8, 1 H); 7.25–7.50 (*m*, 10 H). ^{13}C-NMR (100 MHz): 18.86 (o); 21.15 (e); 22.02 (o); 23.33 (o); 23.70 (o); 26.78 (e); 27.07 (e); 29.00 (o); 34.47 (e); 38.44 (e); 50.95 (o); 64.11 (o); 80.41 (e); 105.39 (e); 120.95 (o); 125.26 (o); 126.14 (o); 127.87 (o); 128.23 (o); 128.30 (o); 128.68 (o); 137.42 (e); 139.81 (e); 142.57 (e). MS: 418 (3, M^+), 232 (80), 144 (45), 105 (100), 77 (27). Anal. calc. for $C_{28}H_{34}O_3$ (418.25): C 80.35, H 8.19; found: C 80.05, H 8.01.

p-*Terphenyl* (**35**). Colorless crystals. M.p. 210–212°. IR and ^{1}H-NMR correspond to those reported [15]. MS: 230 (100, M^+), 115 (10).

12. *(1S,2S)-1,4-Diphenylcyclohex-3-ene-1,2-diol* (**36**). Trioxane **33** (49.8 mg, 0.12 mmol), AcOH (1.5 ml), and Zn powder (50 mg) were stirred together at r.t. After 12 h, the mixture was filtered over *Celite* and evaporated. The residue was purified by CC (silica gel, CH_2Cl_2): **36** (16.9 mg, 53%). Colorless crystals. M.p. 115–118° (from AcOEt/hexane). $[\alpha]_D^{20} = -60.0$ (*c* = 0.31, $CHCl_3$). IR: 3620*m*, 3590*m*, 3090*m*, 3060*m*, 2960*s*, 1510*s*, 1460*s*, 1275*m*, 1220*w*, 1060*s*, 890*m*, 710*vs*. ^{1}H-NMR (400 MHz): 1.98 (*d*, *J* = 5.3, 1 H); 2.12–2.26 (*m*, 2 H); 2.43 (*dm*, *J* = 17.3, 1 H); 2.84 (*m*, 1 H); 2.87 (*s*, 1 H); 4.69 (*dd*, *J* = 2.5, 5.3, 1 H); 6.06 (*m*, 1 H); 7.24–7.90 (*m*, 10 H). ^{13}C-NMR (100 MHz): 24.76 (e); 34.29 (e); 72.93 (o); 73.10 (e); 124.13 (o); 125.16 (o); 125.36 (o); 127.23 (o); 127.63 (o); 128.35 (o); 128.42 (o); 139.69 (e); 140.34 (e); 145.32 (e). MS: 266 (4, M^+), 249 (2), 230 (2), 219 (4), 146 (82), 145 (100), 131 (24), 105 (27), 91 (22), 77 (43), 51 (19). Anal. calc. for $C_{18}H_{18}O_2$ (266.34): C 81.17, H 6.81; found: C 81.15, H 6.80.

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