Synthesis and stereochemistry of the epoxides of 2-arylmethylidene-1-tetralones

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Oxidation of both the *E* and *Z* isomers of the 2-arylmethylidene-1-tetralones 1 by alkaline hydrogen peroxide afforded the spiroepoxides *trans*-2a–g as sole products in high yields. In contrast, the dimethyldioxirane epoxidation of the *E* isomers 1a–g gave the corresponding *trans* spiroepoxides in good yields, while the *Z* isomers 1a,c,e yielded the respective *cis* spiroepoxides in moderate yields. Epoxidation of (*Z*)-1a,c,e by *m*-chloroperoxybenzoic acid yielded *ca.* 6:1 mixtures of *cis*-2a,c,e and *trans*-2a,c,e spiroepoxides. Separation of the isomeric epoxides was achieved by silica gel chromatography and their structures, relative configurations and stereochemistry were elucidated by NMR spectroscopy.

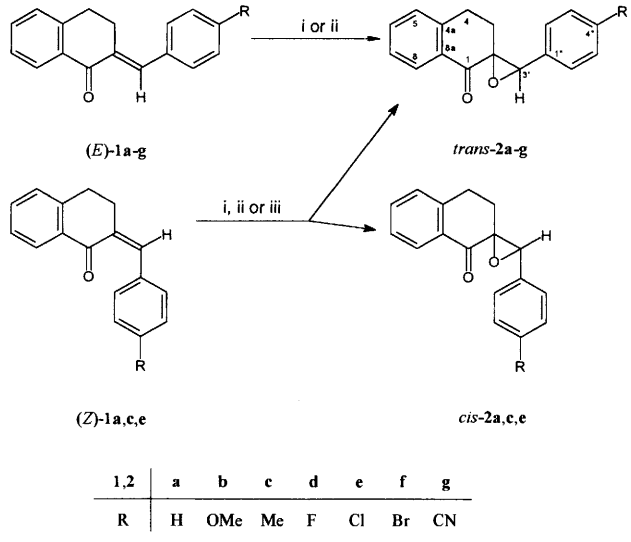
Although both (*E*)- and (*Z*)-2-arylmethylidene-1-tetralones† are well-known compounds,[1–3] their epoxidation has hitherto received little attention. Of the various epoxidation procedures only the alkaline hydrogen peroxide oxidation was utilized in the case of selected 2-arylmethylidene-1-tetralones and 2-arylmethylidene-4,4-dimethyl-1-tetralones to obtain the respective epoxides.[4–6] As an extension of our investigations on the epoxidation of exocyclic α,β-unsaturated ketones,[7–11] we have herein undertaken a comparative study of both (*E*) and (*Z*) isomers of 2-arylmethylidene-1-tetralones **1**, by employing alkaline hydrogen peroxide, dimethyldioxirane and *m*-chloroperoxybenzoic acid as oxygen transfer agents. The specific aim was to investigate the influence of the electronic character and the stereochemistry of the α,β-enones **1**, for which nucleophilic and electrophilic oxidants have been compared.

Results and discussion

Epoxidation of α,β-unsaturated ketones by alkaline hydrogen peroxide (Weitz–Scheffer reaction[12]) is frequently used for the preparation of the epoxides derived from electron-deficient olefins. As mentioned above, this is the only procedure used so far for the epoxidation of 2-arylmethylidene-1-tetralones. To check the utility of this method, both *E* and *Z* isomers of 2-arylmethylidene-1-tetralones (*E*)-**1a–g** and (*Z*)-**1a,c,e** (Scheme 1) have been subjected to alkaline hydrogen peroxide oxidation [method (*i*)].

NMR spectroscopic measurements (*vide infra*) revealed that *trans* spiroepoxides **2a–g**, in which the carbonyl and the aryl groups are located on the opposite sides of the epoxide ring, were obtained as sole products from both *E* and *Z* isomers in good yields (see Table 1). Thus, the simple and convenient alkaline hydrogen peroxide procedure can only be used for the preparation of *trans* epoxides of 2-arylmethylidene-1-tetralones.

Dimethyldioxirane or DMD[13] (in acetone)[14] is a powerful and convenient oxidant for the epoxidation of various electron-deficient functionalized olefins. Recently we have found that (*E*)-3-arylmethylidenechromanones gave *trans* spiroepoxides and their *Z* isomers yielded *cis* spiroepoxides together with 3-aroylchromones on dimethyldioxirane oxidation,[8] while (*E*)-3-arylmethylideneflavanones afforded *trans,trans* spiroepoxides in high yields and complete diastereoselectivity.[9] Dimethyldioxirane epoxidation [method (*ii*)] of both (*E*)- and (*Z*)-2-arylmethylidene-1-tetralones **1** followed the procedure employed on the related exocyclic α,β-unsaturated ketones,[7–11] for which isolated dimethyldioxirane (*ca.* 0.1 mol dm^{-3} in acetone) in anhydrous CH_2Cl_2 at room temperature was used. The progress of the oxidation was monitored by thin-layer chromatography (TLC) and fresh batches of dimethyldioxirane solution were added at 24 h intervals until complete consumption of the starting 2-arylmethylidene-1-tetralones **1** was achieved (Scheme 1). According to the NMR spectroscopic investigations (*vide infra*) the 2-arylmethylidene-1-tetralones (*E*)-**1a–g** gave the spiroepoxides *trans*-**2a–g** in high yields (80–



1,2	a	b	c	d	e	f	g
R	H	OMe	Me	F	Cl	Br	CN

Scheme 1 *Reagents:* i, H_2O_2, NaOH; ii, DMD; iii, *m*-CPBA

† Tetralone is an abbreviated name for 3,4-dihydronaphthalen-1(2*H*)-one.

90%) and completely stereoselectively with DMD (1.5–2 equiv., 48–72 h; see Table 1), whereas the (*Z*)-**1a,c,e** isomers afforded the *cis*-**2a,c,e** spiroepoxides with complete stereoselectivity as well, but only in moderate yields (20–30%), and longer reaction times (120–240 h) and 3–5 equiv. of dimethyldioxirane were necessary. Longer reaction times were required as the electron-acceptor character of the R substituent increased, which would be expected of an electrophilic oxidant such as DMD.[8,9]

Since the dimethyldioxirane epoxidation of the (*Z*)-2-arylmethylidene-1-tetralones gave the *cis* spiroepoxides only in moderate yields, compounds (*Z*)-**1a,c,e** were oxidized by *m*-chloroperoxybenzoic acid [MCPBA, method (*iii*)] by way of comparison. This electrophilic oxidant provided a *ca.* 6:1 mixture of the *cis*-**2a,c,e** and *trans*-**2a,c,e** spiroepoxides (Scheme 1). Clearly, dimethyldioxirane is a more convenient oxidant for the stereoselective epoxidation of the (*Z*)-2-arylmethylidene-1-tetralones than *m*-chloroperoxybenzoic acid.

Table 1 Preparation of spiroepoxides **2**

Method	Starting material	Product	Ratio DMD:**1**	Reaction time (h)	Yield (%)
i	(*E*)-**1a**	*trans*-**2a**	—	8	81
i	(*Z*)-**1a**	*trans*-**2a**	—	8	78
ii	(*E*)-**1a**	*trans*-**2a**	1.5	48	79
ii	(*Z*)-**1a**	*cis*-**2a**	3.0	144	28
i	(*E*)-**1b**	*trans*-**2b**	—	8	94
ii	(*E*)-**1b**	*trans*-**2b**	1.5	48	85
i	(*E*)-**1c**	*trans*-**2c**	—	8	96
i	(*Z*)-**1c**	*trans*-**2c**	—	8	83
ii	(*E*)-**1c**	*trans*-**2c**	1.5	48	85
ii	(*Z*)-**1c**	*cis*-**2c**	3.0	120	23
i	(*E*)-**1d**	*trans*-**2d**	—	8	94
ii	(*E*)-**1d**	*trans*-**2d**	1.5	48	79
i	(*E*)-**1e**	*trans*-**2e**	—	8	90
i	(*Z*)-**1e**	*trans*-**2e**	—	8	91
ii	(*E*)-**1e**	*trans*-**2e**	2.0	72	81
ii	(*Z*)-**1e**	*cis*-**2e**	5.0	20	30
i	(*E*)-**1f**	*trans*-**2f**	—	8	93
ii	(*E*)-**1f**	*trans*-**2f**	2.0	72	89
ii	(*E*)-**1g**	*trans*-**2g**	2.0	72	83

Characteristic ^{1}H and ^{13}C NMR chemical shift data of the *trans*-**2** and *cis*-**2** spiroepoxides are summarized in Tables 2 and 3. In $CDCl_3$ the 3-H_2 and 4-H_2 protons gave a strongly coupled, overlapping spectrum, while in C_6D_6 the signals of these four protons are capable of first-order analysis; for this reason we used C_6D_6 as solvent in all NMR measurements. A common characteristic of the proton spectra is the extremely high chemical shifts of the 8-H signals as a consequence of the anisotropic effect of the *peri*-positioned C(1)=O carbonyl group.[15] Characteristic differences of the 3′-H and 2″,6″-H signals of the *trans* and *cis* isomers [δ_{trans}(3′-H) > δ_{cis}(3′-H) and δ_{trans}(2″,6″-H) < δ_{cis}(2″,6″-H)] also originate from the deshielding effect of the carbonyl group.[15]

The differentiation of the *trans* and *cis* isomers requires a detailed investigation of the conformational behaviour due to the flexibility of the annexed six-membered ring. Thus, in solution the conformational equilibrium among the halfchair **A**, envelope **A**, envelope **B** and halfchair **B** must be considered (Scheme 2), as in the case of the related spiroepoxides of the 3-arylmethylidenechromanones.[8]

In the halfchair conformers C-2 and C-3 and in the envelope ones C-3 are located out of the plane constituted by the other atoms of the ring. The orientation of the spiroepoxy oxygen atom is quasi-equatorial in the halfchair and envelope **A**

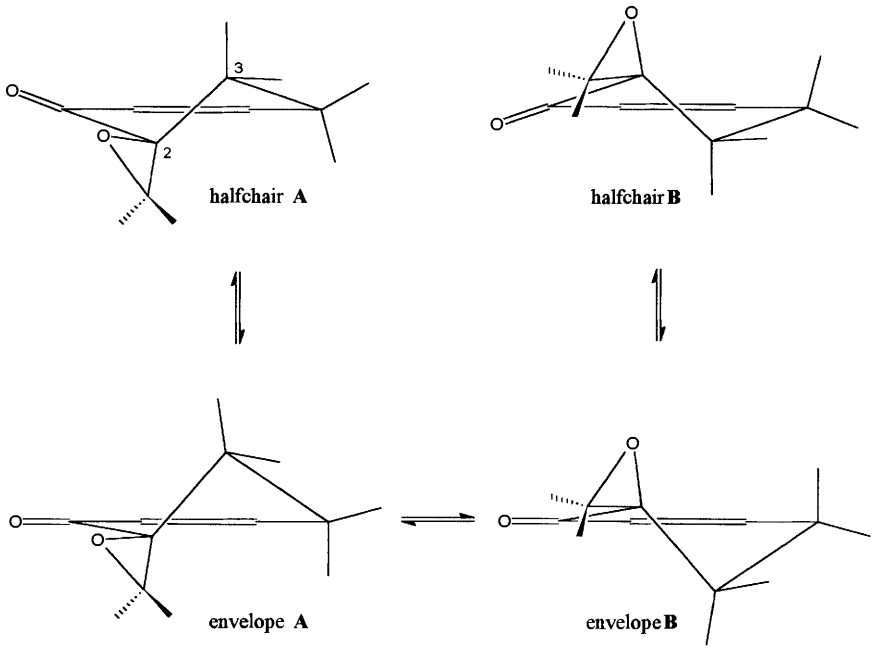
Table 2 ^{1}H NMR chemical shifts of spiroepoxides *trans*- and *cis*-**2** (400 MHz)

Proton	*trans*-**2a**	*trans*-**2b**	*trans*-**2c**	*trans*-**2d**	*trans*-**2e**	*trans*-**2f**	*trans*-**2g**	*cis*-**2a**[a]	*cis*-**2c**[a]	*cis*-**2e**[a]
3-H_{ax}	2.10	2.18	2.15	2.10	2.03	2.03	1.96	2.39	2.41	2.37
3-H_{eq}	1.69	1.78	1.77	1.60	1.54	1.53	1.39	1.58	1.62	1.56
4-H_{ax}	2.46	2.56	2.52	2.49	2.42	2.41	2.34	2.99	3.04	2.97
4-H_{eq}	2.28	2.38	2.33	2.39	2.32	2.32	2.34	2.59	2.64	2.61
5-H	6.75	6.86	6.82	6.88	6.84	6.83	6.83	6.89	6.91	6.91
6-H	7.18	7.22	7.19	7.22	7.20	7.18	7.19	7.07	7.10	7.10
7-H	7.08	7.11	7.10	7.11	7.10	7.09	7.09	6.84	6.86	6.88
8-H	8.36	8.33	8.35	8.30	8.32	8.33	8.33	8.00	8.02	8.00
3′-H	4.52	4.50	4.53	4.41	4.38	4.35	4.32	4.02	4.07	3.88
2″,6″-H		7.18	7.16	7.03	6.93	6.83	6.83	7.64	7.52	7.37
3″,5″-H	7.11–7.26	6.84	7.03	6.86	7.15	7.29	7.07	7.16	6.96	7.09
4″-H		—	—	—	—	—	—	7.06	—	—
Others		OMe	Me						Me	
		3.44	2.17						2.06	

[a] Measured at 250 MHz.

Table 3 ^{13}C NMR chemical shifts of spiroepoxides *trans*- and *cis*-**2** (62.5 MHz)

Carbon	*trans*-**2a**	*trans*-**2b**	*trans*-**2c**	*trans*-**2d**	*trans*-**2e**	*trans*-**2f**	*trans*-**2g**	*cis*-**2a**	*cis*-**2c**	*cis*-**2e**
C-1	192.7	192.9	192.8	192.5	192.4	192.3	191.8	190.0	190.1	189.9
C-2	64.2	64.4	64.3	64.2	64.1	64.1	64.2	67.7	67.8	67.7
C-3	25.5	25.6	25.6	25.4	25.4	25.4	25.3	32.6	32.6	32.4
C-4	27.2	27.4	27.3	27.2	27.2	27.2	27.0	29.1	29.2	29.0
C-4a	143.4	143.4	143.4	143.3	143.3	143.3	143.2	142.9	142.9	142.9
C-5	128.8	128.9	128.8	128.6	128.8	128.8	128.8	128.7	128.8	128.7
C-6	133.7	133.8	133.7	133.9	133.9	133.9	134.1	133.4	133.4	133.7
C-7	127.1	127.0	127.0	127.1	127.1	127.2	127.3	126.8	126.7	126.9
C-8	127.7	127.6	127.7	127.7	127.7	127.7	127.8	127.5	127.4	127.5
C-8a	133.4	133.5	133.5	133.3	133.3	133.3	133.2	133.8	133.9	133.7
C-3′	63.9	63.9	64.0	63.2	63.1	63.1	62.8	65.3	65.4	64.6
C-1″	135.0	126.8	132.1	130.7	133.5	134.0	139.6	133.9	131.0	132.3
C-2″,6″	126.7	128.2	126.9	128.8	128.3	128.6	127.3	127.6	127.5	129.0
C-3″,5″	128.4	114.0	129.1	115.3	128.6	131.5	131.8	128.0	128.8	128.2
C-4″	128.2	160.1	123.9	162.9	134.2	122.4	112.4	128.2	137.8	134.1
Others		OMe	Me				CN		Me	
		54.9	21.1				118.5		21.0	



Scheme 2

conformers and quasi-axial in the halfchair and envelope **B** conformers. In the envelope conformers C(1)=O and 8-H are coplanar and, therefore, $\delta(8\text{-H}_{envelope}) > \delta(8\text{-H}_{halfchair})$. As far as conjugation is concerned, the envelope conformation is favoured but it is destabilized by the unfavourable steric interaction between the 8-H and the *peri*-positioned C(1)=O. These results suggest that in the case of the *trans* isomers the envelope and for the *cis* ones the halfchair conformation is favoured. On ring inversion of the envelope conformers **A** and **B** the axial and equatorial protons are interchanged. The $^3J_{H,H}$ coupling constant values (11.6–13.2 Hz) of the *trans* 3-H and 4-H protons refer to their antiperiplanar orientation and suggest that the conformational equilibrium between **A** and **B** is considerably shifted in one direction (Table 4). This is corroborated by the $^3J_{C\text{-}4a,3\text{-}H}$ coupling constants (Table 5) determined by 2D semiselective INEPT measurements.[16] From the characteristic Karplus-type relationship between the $^3J_{C,H}$ coupling constants and the dihedral angles, the latter is estimated to be 160–175° between the C-4a and 3-H_{eq} atoms and for the 3-H_{ax} proton it is 70–80°, as confirmed by inspection of the Dreiding model and AM1 calculations. The coupling constants of the 3-H methylene proton (lower chemical shift) and the C-4a atom is 8.4 Hz for the *trans*-**2a** and 9.5 Hz for the *cis*-**2a** isomer, which refers to an equatorial orientation of this proton. In the case of *cis*-**2a** the J values of $J_{3\text{-}H_{ax},4\text{-}H_{ax}}$ 13.1 and $J_{3\text{-}H_{eq},4\text{-}H_{eq}}$ 2.7 Hz indicate that the conformational equilibrium is considerably shifted in one direction.

The measured $J_{C,H}$ values of $J_{4a,3eq}$ 9.5 and $J_{4a,3ax}$ 1.8 Hz are reference values for this conformer. On the basis of these ^3J data for the *trans*-**2a** isomer, the dominant conformer is populated at 85%; therefore, the axial and equatorial designations can be used for both isomers.

For carbohydrates a Karplus type relationship exists between the C–O–C-1–H J value and the corresponding dihedral angle, where a value of 7 Hz is expected for the 1-H_{eq} (Φ *ca.* 180°) and 2 Hz for the 1-H_{ax} (Φ *ca.* 60°).[17–19] Parella *et al.*[20] found that for 1-hydroxycyclohexane derivatives the two respective values are 6 and 1 Hz, *viz.* in the C–X–C–H fragment, the replacement of X = O with X = CH_2 results in a *ca.* 1 Hz decrease. Comparison of the J values for the C–X–C–H units of the *cis*-**2a** and the related chromanone epoxides[8] showed that the replacement of X = O by X = CH_2 brought about a 1 Hz increase in the vicinal coupling constant, which is in contradiction with the above-mentioned literature data. This alteration may be a consequence either of the fact that in compounds **2** the carbon atom in the γ-position is sp^2 rather than sp^3 or that the geometry of the ring with the carbonyl group is slightly different. Dihedral angles of the 3-H_{eq}–C–X–C= fragments obtained by AM1 calculations are within error limits (167° for the *cis*-**2a** tetralone and 163° for the analogous chromanone).

1D NOE measurements have been performed (Table 6) to determine the quasi-equatorial (type **A**) or quasi-axial (type **B**) orientation of the oxygen atom of the spiroepoxy moiety of the six-membered ring (Scheme 2) in the dominant conformer. These measurements allowed an unambiguous differentiation between the *trans*-**2** and *cis*-**2** isomers, since spatial proximity of the 3′-H and 3-H_2 methylene protons is possible only in the *cis*

Table 4 ^{1}H–^{1}H coupling constants of spiroepoxides *trans*- and *cis*-**2a** [$J_{H,H}$ (Hz)][a]

	trans-**2a**	*cis*-**2a**
$^2J_{3ax,3eq}$	13.5	13.1
$^2J_{4ax,4eq}$	16.4	16.8
$^3J_{3ax,4ax}$	11.9	13.1
$^3J_{3ax,4eq}$	4.5	4.6
$^3J_{3eq,4ax}$	4.5	4.6
$^3J_{3eq,4eq}$	4.4	2.7

[a] The variation in coupling constants for the *trans*-**2** and *cis*-**2** series is max. 0.5 Hz.

Table 5 Results of the 2D semiselective INEPT measurements of spiroepoxides *trans*-**2a** and *cis*-**2a**,**e** [$J_{C,H}$ (Hz)]

	trans-**2a**	*cis*-**2a**	*cis*-**2e**
$^3J_{1,3ax}$		1.2	
$^3J_{4a,3ax}$		1.8	
$^3J_{3',3ax}$		3.8	
$^3J_{1,3eq}$	5.4	5.7	
$^2J_{2,3eq}$		7.1	
$^2J_{4,3eq}$		3.8	
$^3J_{4a,3eq}$	8.4	9.5	
$^3J_{3',3eq}$	6.5	3.1	
$^2J_{2,3'}$			2.5
$^2J_{1'',3'}$	5.6		5.0
$^3J_{2'' \text{ or } 6'',3'}$	2.2		2.3

Table 6 Results of 1D NOE measurements for spiroepoxides *trans*-**2a**,**f** and *cis*-**2a**,**e** (250 MHz)

	Proton irradiated	Protons for which NOE observed (%)
trans-**2a**	3_{ax}	3_{eq} (20.3)
	3_{eq}	3_{ax} (17.8); 4_{ax} (2.5); 4_{eq} (1.6); 3′ (0.8); 2″ and 6″ (3.0)
	4_{ax}	3_{eq} (1.9); 5 (1.1)
	4_{eq}	3_{eq} (1.7); 4_{ax} (> 7.0); 5 (3.3)
trans-**2f**	3′	2″ and 6″ (2.0)
	3_{ax}	3_{eq} (24.9)
	3_{eq}	3_{ax} (27.4); 4 (5.8); 2″ and 6″ (6.7)
cis-**2a**	3_{ax}	3_{eq} (23.2)
	3_{eq}	3_{ax} (27.3); 4_{ax} (2.7); 4_{eq} (2.0); 3′ (10.2)
	3′	3_{eq} (5.6); 4_{ax} (1.5); 2″ and 6″ (5.2)
cis-**2e**	3′	3_{eq} (5.8); 4_{ax} (< 1); 2″ and 6″ (6.3)

Table 7 ^{1}H–^{13}C long-range correlations for spiroepoxides *trans*- and *cis*-**2** by semiselective 1D INEPT measurements ($J_{C,H}$ 7 Hz)

	Proton	Carbon
trans-**2a**	4_{eq}	2; 4a; 5; 8a
	5	4; 7; 8a
trans-**2c**	3′	1″; 2″,6″
trans-**2e**	5	4; 7; 8a
	3′	1″; 2″,6″
trans-**2f**	3′	1″; 2″,6″
cis-**2a**	4_{eq}	2; 4a; 5; 8a
	3′	2; 1″; 2″,6″
	2″,6″	3′
cis-**2c**	3′	3; 3′; 1″; 2″,6″
cis-**2e**	4_{eq}	2; 3; 4a; 5; 8a
	3′	2; 1″; 2″,6″

isomers. Since the signal intensity was enhanced for the 3-H_{eq} methylene proton on irradiation of the 3′-H signal of *cis*-**2a**,**e**, the dominant conformer is the halfchair **A**, corroborated by the characteristic δ values for 8-H as well (Table 2). In the case of *cis*-**2a**, irradiation of 3′-H produced an NOE at 4-H_{ax}, as expected for the type **A** conformers. In the case of the *trans*-**2a** and **2f** derivatives, irradiation of 3-H_{eq} resulted in an enhanced intensity for the 2″,6″-H signal. These experiments suggest that the dominant conformer of the *trans*-**2** isomers is the envelope **A**.

Semiempirical AM1 (MOPAC-6 version 1990)[21] calculations have been performed for the conformers of the *trans*-**2a** and *cis*-**2a** isomers. Dihedral angles obtained by these calculations are 160–175° for (3-H_{eq})–(C-3)–(C-4)–(C-4a) and 70–80° for (3-H_{ax})–(C-3)–(C-4)–(C-4a). In the case of *cis*-**2a**, such calculations showed that the halfchair **A** is more stable by 3.0 kcal mol^{-1} ‡ than the halfchair **B** conformer, which is in agreement with the results of our conformational analysis. In the *trans*-**2a** isomer, however, these calculations revealed that the envelope **A** and **B** conformers are present in comparable amounts, since their energy difference is only 0.1 kcal mol^{-1}. In the *trans* isomers the dihedral angle of 2–3° for the O–(C-1)–(C-8a)–(C-8) unit corresponds to an envelope conformer, while the 13–19° values indicate a halfchair conformer in the *cis* isomers.

^{1}H NMR chemical shifts (Table 2) indicate that the chemical shifts of the 3-H_{eq} signals are lower than those of the axial ones within the geminal pairs both in the *trans* and *cis* isomers, which is a consequence of the diamagnetic effect of the three-membered ring.[22] The *ca.* 0.3 ppm diamagnetic difference in the chemical shifts of the axial 3-H protons of the *trans*-**2** isomers, compared to those measured for the respective *cis*-**2** isomers, reveals that in the envelope **A** conformer of the *trans* isomers the 3-H_{ax} proton is closer to the aromatic ring of the tetralone moiety, which is reflected in a more pronounced diamagnetic effect. Moreover, the assignments of the ^{1}H and ^{13}C NMR signals have been further corroborated by two-dimensional C,H COSY measurements.

In the ^{13}C NMR spectra the quaternary C-4a and C-8a signals were unambiguously assigned (Table 5) by means of 2D semiselective INEPT measurements since the polarization transfer from 3-H_{eq} differentiates between these two carbon atoms. The C-2″,6″ and C-3″,5″ signals were identified by means of 1D semiselective INEPT[23] measurements optimized for the 7 Hz coupling constant of the 3′-H signal (Table 7). These measurements reveal carbon atoms which are located two or three bonds distant from the irradiated proton. Further corroboration of the assignment of the C-3, C-4, C-7 and C-8 signals has been performed by the polarization transfer derived from the respective protons.

Further support for the assignment of the *trans*-**2** and *cis*-**2** isomers was possible through the characteristic value of $\Delta\delta$ = 7 of the C-3 signals, which is a consequence of the γ-gauche arrangement between the C-3 and the aryl group connected to C-3′ in the *trans* isomers. A further characteristic is the decrease of $\Delta\delta$ = *ca.* 1.5 for C-3′ in the *trans*-**2** *vs.* *cis*-**2** isomers, which we have also observed for analogous spirocyclopropanes[24] and spiroepoxides.[8] In the *trans*-**2** isomers this is the consequence of the γ-steric interaction between the carbonyl oxygen and the C-3′-H moiety, which results in a diamagnetic shift, while in the *cis* epoxides the carbonyl oxygen is in spatial proximity to the C-3′–C-1″ bond.

The stereochemical outcome of the epoxidations, as established by the NMR methods can be rationalized by the known mechanisms of these reactions. Since the Weitz–Scheffer nucleophilic epoxidation with alkaline peroxide is a two-step process to afford an intermediate enolate, fast epimerization at the α-carbon atom in the latter should lead preferentially to the thermodynamically favoured *trans* epoxides from both *E* and *Z* isomers of the α,β-enone substrates. A control experiment established that *Z*→*E* isomerization did not take place under the employed alkaline reaction conditions. In contrast, dimethyldioxirane, an electrophilic oxidant, reacts with these α,β-unsaturated ketones according to the known[13] "butterfly mechanism" to give the *trans*-**2** epoxides from (*E*)-**1** and the *cis*-**2** epoxides from (*Z*)-**1** as sole products. Similarly, for the electrophilic epoxidation by *m*-chloroperoxybenzoic acid oxygen transfer with *syn* stereochemistry would also be expected.[25] Therefore, the formation of the spiroepoxides *cis*-**2a**,**c**,**e** and *trans*-**2a**,**c**,**e** from (*Z*)-**1a**,**c**,**e** as a *ca.* 6:1 mixture may be attributed to an initial *Z*→*E* acid-catalysed isomerization.[26] Indeed, a control experiment established that addition of a fresh portion of the *cis*-olefin to a spent *m*-CPBA epoxidation mixture led to appreciable isomerization.

In summary, two convenient procedures, namely Weitz–Scheffer epoxidation of both (*E*)-**1** and (*Z*)-**1** and dimethyldioxirane epoxidation of (*E*)-**1** have been developed for the synthesis of the *trans* epoxides of 2-arylmethylidene-1-tetralones. *cis*-Epoxides are produced stereoselectively by the dimethyldioxirane epoxidation of (*Z*)-2-arylmethylidene-1-tetralones. Despite the fact that in the latter procedure the *cis* epoxides are obtained only in moderate yields (20–30%), presumably due to decomposition, this is the only method for the stereoselective synthesis of *cis* epoxides. *m*-Chloroperoxybenzoic acid [method (*iii*)] is not a suitable reagent for the stereoselective synthesis of *cis* epoxides of 2-arylmethylidene-1-tetralones since *cis*–*trans* mixtures of epoxides were obtained.

‡ 1 kcal = 4.184 J.

Table 8 Physical constants, analytical and IR spectral data of spiroepoxides **2**

Compound	Appearance	Mp (°C)[a] (Lit. mp)	νC=O (cm^{-1})	Overall formula	Required (%) C	Required (%) H	Found (%) C	Found (%) H
trans-**2a**	P	76–77 (77–77.5)[4]	1690	$C_{17}H_{14}O_2$	81.6	5.65	81.8	5.7
trans-**2b**	P	105–106	1686	$C_{18}H_{16}O_3$	77.15	5.75	77.35	5.8
trans-**2c**	N	145–146	1690	$C_{18}H_{16}O_2$	81.8	6.1	81.8	6.15
trans-**2d**	P	88–89	1686	$C_{17}H_{13}FO_2$	76.25	4.9	76.4	4.85
trans-**2e**	N	141–142 (137–138)[5]	1686	$C_{17}H_{13}ClO_2$	71.7	4.6	71.5	4.5
trans-**2f**	P	138–140	1686	$C_{17}H_{13}BrO_2$	62.2	3.95	62.3	3.9
trans-**2g**	P	151–152	1690	$C_{18}H_{13}NO_2$	78.5	4.75	78.35	4.7
cis-**2a**	P	113–114	1690	$C_{17}H_{14}O_2$	81.6	5.65	81.75	5.6
cis-**2c**	P	107–108	1690	$C_{18}H_{16}O_2$	81.8	6.1	81.7	6.2
cis-**2e**	N	115–116	1690	$C_{17}H_{13}ClO_2$	71.7	4.6	71.6	4.7

[a] Crystallized from CH_3OH, P = powder, N = needles.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were measured with a Perkin-Elmer 16 PC instrument as KBr discs. The ^1H (400 and 250 MHz) and ^{13}C (100 and 62.5 MHz) NMR spectra were obtained on Bruker AC-400 and AC-250 spectrometers in deuteriobenzene with tetramethylsilane as the internal standard at room temperature. *J* Values are given in Hz. Elemental analyses were performed in-house. All solvents were purified by following standard literature methods. Caroate (potassium monoperoxosulfate), the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was used as received. Dimethyldioxirane (*ca.* 0.1 mol dm^{-3} in acetone) was prepared according to the published procedure[14] and its peroxide content was determined by iodometric titration. The dimethyldioxirane solutions were stored over molecular sieves (4 Å) at −20 °C. Substrates (*E*)- and (*Z*)-**1** were prepared according to known procedures.[1–3] Chromatography was performed on silica gel 60 (Merck) with hexane–acetone (8:2) or hexane–benzene (3:2) as eluents.

General procedures for the preparation of spiroepoxides 2

Method (*i*). Hydrogen peroxide (30%; 1.0 cm^3, 8.82 mmol) was added to a cooled and stirred mixture of the appropriate 2-arylmethylidene-1-tetralone **1** (1.00 g, 3.19–4.27 mmol) and NaOH (2 mol dm^{-3}, 4.0 mmol) in methanol (20 cm^3). The stirring was continued at ambient temperature for 8 h (or as specified in Table 1), after which the mixture was diluted with water and the precipitated material was filtered off, washed with water and dried to give the epoxides **2** (Tables 1 and 8).

Method (*ii*). The required amount of the dimethyldioxirane (in acetone) was added rapidly to a cooled and stirred solution of the appropriate 2-arylmethylidene-1-tetralone **1** (0.50 g, 1.86–2.13 mmol) in dry CH_2Cl_2 (5.0 cm^3) and stirred in the dark. The stirring was continued for 24 h and another quantity of dimethyldioxirane was rapidly added. The dioxirane administration was continued at 24 h intervals until consumption of the starting material **1** was complete. The mixture was evaporated under reduced pressure (*ca.* 20 mmHg) and the residue was recrystallized from CH_3OH to afford the corresponding *trans*-**2a–g** spiroepoxides. In the case of (*Z*)-**1a,c,e**, silica gel chromatography with hexane–acetone (8:2) as the eluent was used to produce spiroepoxides *cis*-**2a,c,e**.

Method (*iii*). The appropriate (*Z*)-2-arylmethylidene-1-tetralone (0.70 g, 2.61–2.99 mmol) and *m*-CPBA (0.60 g, 3.49 mmol) were dissolved in benzene (30 cm^3) and heated under reflux for 8 h. The mixture was left to stand overnight at room temperature, the precipitated *m*-chlorobenzoic acid was filtered off and the filtrate washed with 10% aq. $NaHCO_3$ and water. The mixture was dried over $CaCl_2$ and evaporated under reduced pressure (*ca.* 20 mmHg) after which the residue was chromatographed on silica gel with hexane–acetone (8:2) as the eluent to yield both *cis*- and *trans*-**2a,c,e** epoxides. Thus, (*Z*)-**1a** gave *trans*-**2a** (10%) and *cis*-**2a** (60%), (*Z*)-**1c** gave *trans*-**2c** (8%) and *cis*-**2c** (48%), whilst (*Z*)-**1e** gave *trans*-**2e** (8%) and *cis*-**2e** (56%).

Alkaline treatment of (*Z*)-2-(4-methylbenzylidene)-1-tetralone (*Z*)-1c. To a stirred mixture of (*Z*)-**1c** (0.50 g, 2.01 mmol) and methanol (20 cm^3), NaOH (2 mol dm^{-3}; 1.0 cm^3, 2.0 mmol) was added. The stirring was continued for 8 h at *ca.* 20 °C, after which TLC analysis and ^1H NMR spectroscopy showed that *ca.* 10% of the starting (*Z*)-**1c** had isomerized into (*E*)-**1c**.

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