Monatshefte für Chemie 127, 683–690 (1996)

Monatshefte für Chemie
Chemical Monthly

Stereoselective Epoxidation of 2-Arylidene-1-indanones and 2-Arylidene-1-benzosuberones[#]

W. Adam[1,*], J. Halász[2], Z. Jámbor[3], A. Lévai[3,*], C. Nemes[3], T. Patonay[3], and G. Tóth[2]

[1] Institute of Organic Chemistry, University of Würzburg, D-97094 Würzburg, Germany
[2] Technical Analytical Research Group of the Hungarian Academy of Sciences, Institute for General and Analytical Chemistry, Technical University, H-1111 Budapest, Hungary
[3] Department of Organic Chemistry, Lajos Kossuth University, H-4010 Debrecen, Hungary

Summary. Oxidation of the (*E*) and (*Z*) isomers of 2-arylidene-1-indanones (**1**) and 2-arylidene-1-benzosuberones (**4**) by alkaline hydrogen peroxide (method *i*) afforded the spiroepoxides *trans*-**2a–g** and *trans*-**5a–g** from both isomers as sole products in high yields. On the other hand, dimethyldioxirane epoxidation (method *ii*) of the (*E*) isomers **1a–g** and **4a–g** gave the corresponding *trans* spiroepoxides in good yields, whereas the (*Z*) isomers **1a, c, e** and **4a, c, e** led to the *cis* spiroepoxides in moderate yields. Dimethyldioxirane oxidation (method *ii*) of (*Z*)-**1c** and (*Z*)-**4c, e** gave diones **3c** and **6c, e** as by-products as well. Epoxidation of (*Z*)-**1a, c, e** and (*Z*)-**4a, c, e** by *m*-chloroperoxybenzoic acid (method *iii*) resulted in *ca.* 6:1 mixtures of *cis*-**2a, c, e** and *trans*-**2a, c, e** or *cis*-**5a, c, e** and *trans*-**5a, c, e** spiroepoxides.

Keywords. 2-Arylidene-1-indanones; 2-Arylidene-1-benzosuberones; Dimethyldioxirane; Stereoselective epoxidations; Epoxides.

Stereoselektive Epoxydierung von 2-Aryliden-1-indanonen und 2-Aryliden-1-benzosuberonen

Zusammenfassung. Oxidation der (*E*)- und (*Z*)-Isomeren von 2-Aryliden-1-indanonen (**1**) und 2-Aryliden-1-benzosuberonen (**4**) mit alkalischem Wasserstoffperoxyd (Methode *i*) liefert aus beiden Isomeren die Spiroepoxide *trans*-**2a–g** und *trans*-**5a–g** als einzige Produkte. Epoxidierung der (*E*)-Isomeren **1a–g** und **4a–g** mit Dimethyldioxiran (Methode *ii*) ergab die entsprechenden *trans*-Spiroepoxide in sehr guten Ausbeuten, während die (*Z*)-Isomeren **1a, c, e** und **4a, c, e** die *cis*-Spiroepoxide in nur mäßiger Ausbeute liefern. Oxidation von (*Z*)-**1c** und (*Z*)-**4c, e** mit Dimethyldioxiran (Methode *ii*) ergab die Dione **3c** und **6c, e** sowie einige Nebenprodukte. Wurden (*Z*)-**1a, c, e** und (*Z*)-**4a, c, e** einer Epoxidation mit *m*-Chlorperbenzoesäure (Methode *iii*) unterworfen, entstanden 6:1-Gemische der Spiroepoxide *cis*-**2a, c, e** und *trans*-**2a, c, e** oder *cis*-**5a, c, e** und *trans*-**5a, c, e**.

Introduction

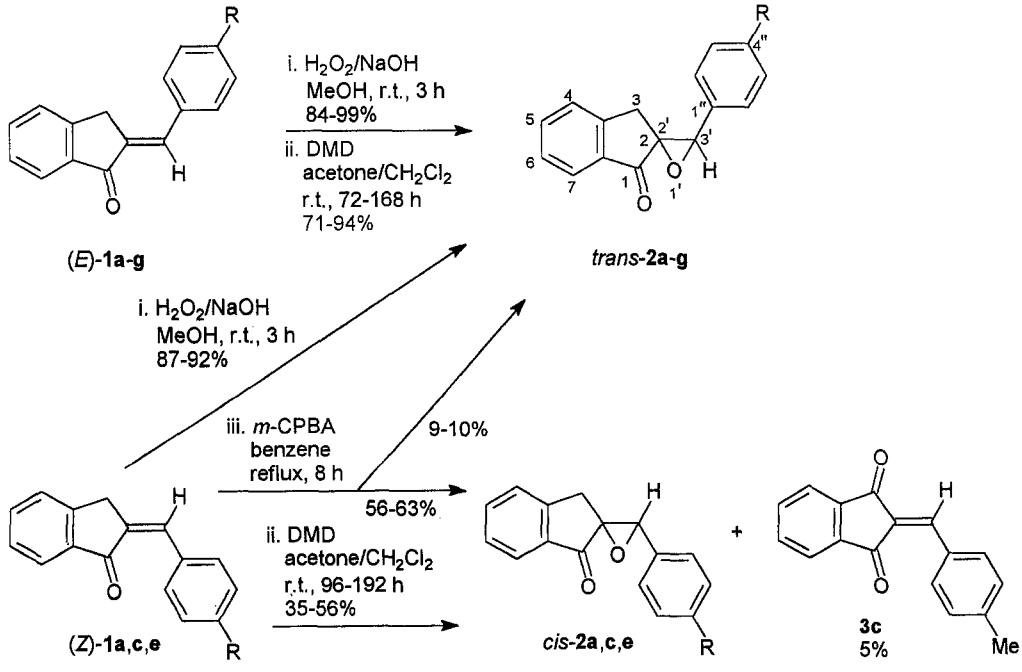
Both (*E*)- and (*Z*)-2-arylidene-1-indanones (**1**) are well-known compounds [1–9], but their epoxidation has only scarcely been investigated. To our knowledge, only

[#] Dedicated to Prof. *W. Fleischhacker* on the occasion of his 65th birthday

2-benzylidene-1-indanone (**1a**) has hitherto been epoxidized by alkaline hydrogen peroxide [2, 10]. A few examples of 2-arylidene-1-benzosuberones (**4**) are described in the literature [8, 11, 12], particularly their (*E*) isomers. Neither the preparation of the (*Z*) isomers nor the epoxidation of these α,β-unsaturated ketones has been reported in the literature. Since the epoxides of α,β-enones are potentially valuable synthetic intermediates, we here report a comparative study of both (*E*) and (*Z*) isomers of 2-arylidene-1-indanones (**1**) and 2-arylidene-1-benzosuberones (**4**) employing alkaline hydrogen peroxide, dimethyldioxirane, and *m*-chloroperoxybenzoic acid as oxygen donors as a continuation of our previous detailed investigations on the epoxidation of exocyclic α,β-unsaturated ketones [13–16].

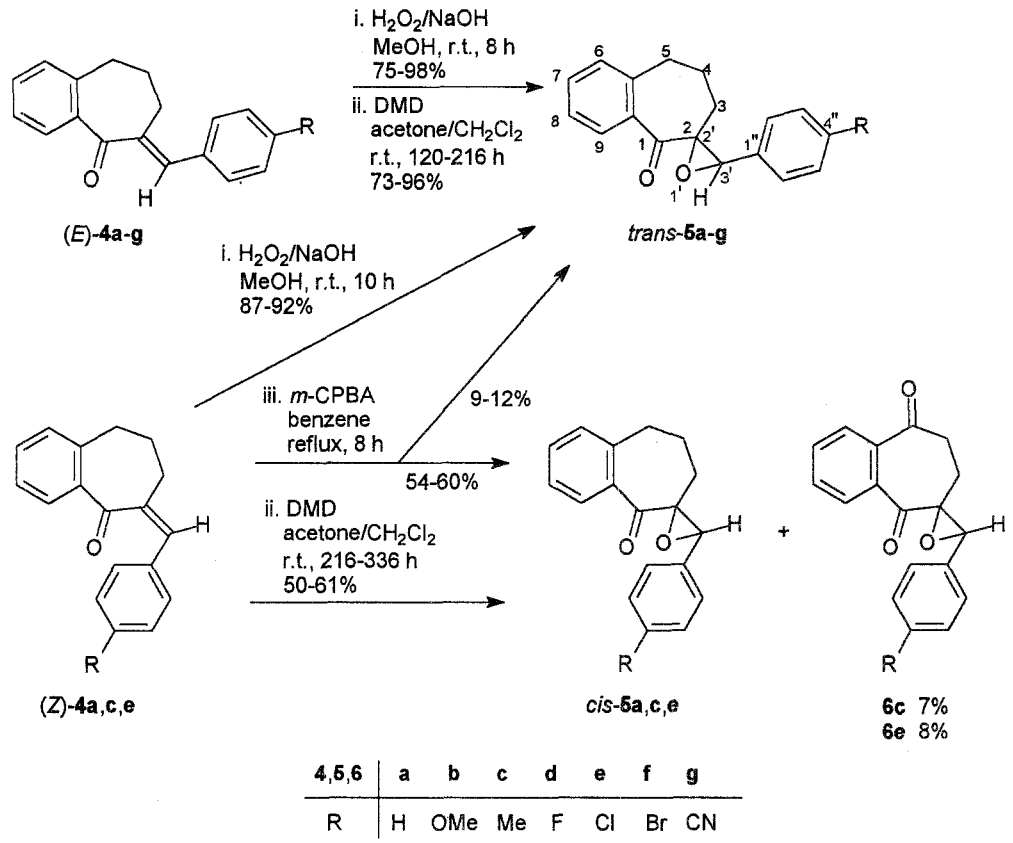
Results and Discussion

Alkaline hydrogen peroxide oxidation (*Weitz-Scheffer* reaction [17]) is a frequently used procedure for the preparation of epoxides of electron-poor olefins. In our present study, both 2-arylidene-1-indanones (*E*)-**1a–g** and (*Z*)-**1a, c, e** (Scheme 1) and 2-arylidene-1-benzosuberones (*E*)-**4a–g** and (*Z*)-**4a**, **c**, **e** (Scheme 2) have been subjected to alkaline hydrogen peroxide oxidation (method *i*). NMR spectroscopic measurements (*vide infra*) proved that *trans* spiroepoxides **2a–g** and **5a–g** were obtained as sole products in good yields (75–98%) from both isomers. Thus, this simple and efficient procedure can only be used for the preparation of *trans* epoxides



1,2,3	a	b	c	d	e	f	g
R	H	OMe	Me	F	Cl	Br	CN

Scheme 1



Scheme 2

of 2-arylidene-1-indanones and 2-arylidene-1-benzosuberones, as found previously for 2-arylidene-1-tetralones [18].

Dimethyldioxirane (*DMD*, in acetone [19]) proved to be a convenient and powerful oxidant for the epoxidation of electron-poor functionalized olefins. Therefore, substrates (*E*)-**1a–g**, (*Z*)-**1a**, **c**, **e**, (*E*)-**4a–g**, and (*Z*)-**4a**, **c**, **e** were allowed to react with isolated *DMD* (*ca.* 0.1 *M*) at room temperature (*ca.* 25 °C). The progress of the reaction was monitored by thin-layer chromatography (TLC), and fresh batches of *DMD* solution were added in 24 h intervals until complete consumption of the starting materials was achieved. According to NMR spectroscopic investigations, (*E*)-**1a–g** and (*E*)-**4a–g** afforded with *DMD* (3–5 equiv., 72–216 h) *trans*-**2a–g** and *trans*-**5a–g** spiroepoxides in high yields (71–94%) (Table 2) and with complete stereoselectivity. In contrast, the (*Z*)-**1a**, **c**, **e** or (*Z*)-**4a**, **c**, **e** isomers afforded the *cis*-**2a**, **c**, **e** or *cis*-**5a**, **c**, **e** spiroepoxides also with complete stereoselectivity, but only in moderate yields (35–61%, Table 2). As expected for an electrophilic oxidant such as *DMD* longer reaction times were required with increasing electron acceptor character of the substituent *R* [14–16, 18].

In the case of the oxidation of the (*Z*)-2-(4-methylbenzylidene)-1-indanone ((*Z*)-**1c**) with *DMD* 2-(-4-methylbenzylidene)-indane-1,3-dione (**3c**) [20] has also been isolated from the crude reaction mixture as a minor component (5%)

(Scheme 1, Tables 2 and 3), whereas the same oxidation of (*Z*)-2-arylidene-1-benzosuberones (*Z*)-**4c** and (*Z*)-**4e** afforded diones **6c** and **6e** as by-products (7 and 8%) (Scheme 2, Tables 2 and 3). It appears that an oxygen atom insertion into the benzylic C–H bond followed by the oxidation of the intermediary alcohol may take place, as observed previously with other substrates [21]. Such a competing oxidation of the α,β-enones or the intermediary epoxides may explain the moderate yields of the *cis* spiroepoxides obtained from (*Z*) isomers by *DMD* oxidation.

To improve the yield of the *cis*-spiroepoxides obtained from (*Z*)-2-arylidene-1-indanones and (*Z*)-2-arylidene-1-benzosuberones, derivatives (*Z*)-**1a**, **c**, **e** and (*Z*)-**4a**, **c**, **e** have also been oxidized by *m*-chloroperoxybenzoic acid (*m-CPBA*, method *iii*). However, this oxidant afforded a *ca.* 6:1 mixture of the *cis*-**2a**, **c**, **e** and *trans*-**2a**, **c**, **e** (Scheme 1) or *cis*-**5a**, **c**, **e** and *trans*-**5a**, **c**, **e** spiroepoxides (Scheme 2). Obviously, *DMD* is the more convenient oxidant for the complete stereoselective epoxidation of (*Z*)-2-arylidene-1-indanones and (*Z*)-2-arylidene-1-benzosuberones.

The differentiation of *cis* and *trans* spiroepoxides has been achieved by ^{1}H NMR spectroscopic investigations (Table 2). The characteristic H-3′ singlet signal of the *trans* isomers appears at lower field than that of the *cis* ones [14, 18]. An unambiguous assignment of the *cis* and *trans* isomers was achieved by ID NOE difference measurements. Irradiation of H-3′ resulted in an intensity enhancement of one of the two H-3 protons only in the case of *cis* isomers as a consequence of their spatial proximity. A detailed ^{1}H and ^{13}C NMR spectroscopic study of *trans*-**2** spiroepoxides has already been published [22]; investigations of the remaining epoxides are in progress.

In conclusion, two simple and efficient methods, *viz. Weitz-Scheffer* epoxidation of both (*E*) and (*Z*) isomers and *DMD* epoxidation of the (*E*) isomers of 2-arylidene-1-indanones **1** and 2-arylidene-1-benzosuberones **4**, have been utilized for the stereoselective synthesis of their *trans* epoxides. *cis*-Epoxides are produced stereoselectively by the *DMD* epoxidation of (*Z*)-2-arylidene-1-indanones and (*Z*)-2-arylidene-1-benzosuberones. Neither alkaline hydrogen peroxide nor *m-CPBA* acid are useful for the stereoselective synthesis of the *cis* epoxides **2** and **5**. The former affords the thermodynamically favoured *trans* epoxides, whereas the latter gives *cis-trans* mixtures from the (*Z*) isomers. Thus, this first detailed comparative study of the epoxidation of the (*Z*) isomers of **1** and **4** establishes that the dioxirane oxidation is so far the only method for the stereoselective synthesis of such *cis* epoxides and emphasizes once again its advantages for preparative purposes.

Experimental

All reagents were of commercial grade. Caroate (potassium monoperoxosulfate), the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was used as received as a generous gift from the Peroxid-Chemie GmbH (Munich, Germany). The solvents were purified according to standard literature methods. Chromatography was performed on silica gel 60 (Merck) with hexane/acetone (9:1) or hexane/dichloromethane (1:1) as eluents. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses were performed in-house. IR spectra were measured with a Perkin-Elmer 16 PC instrument for KBr discs. EI mass spectra were run on a VG 7035 spectrometer. ^{1}H NMR spectra were acquired on a Bruker WP 200 SY (200 MHz) spectrometer. Dimethyldioxirane (*ca.* 0.1 *M* acetone solution) was prepared as described in the literature [19] and its peroxide content was determined by iodometric titration. The dimethyldioxirane solutions were stored over molecular sieves (4 Å) at −20 °C. The (*E*) and (*Z*) isomers of **1** and (*E*)-**4a**, **b**, **e**, **g** were synthesized according to known procedures [6, 9, 11].

General Procedure for the Synthesis of (E)-2-Arylidene-1-benzosuberones (**4**)

A mixture of 1-benzosuberone (20.0 mmol), the appropriate aromatic aldehyde (20.0 mmol), KOH (0.660 g, 11.7 mmol), and ethanol (35 ml) was stirred at ambient temperature for 2 h. The precipitated material was removed by filtration, washed with water (3 × 30 ml), and recrystallized from ethanol to afford benzosuberones (*E*)-**4c**, **d**, **f** (Table 1).

General Procedure for the Preparation of (Z)-2-Arylidene-1-benzosuberones (**4**)

The particular (*E*)-2-arylidene-1-benzosuberone (10.0 mmol) was dissolved in benzene (300 ml) and irradiated with a 400 W mercury arc lamp for 2 h. The solvent was removed under reduced pressure (ca. 20 torr), and the residue was submitted to column chromatography on silica gel with hexane/dichloromethane 1:1 as the eluent to give the (*Z*) isomers (*Z*)-**4a**, **c**, **e**.

General Procedures for the Epoxidation of 2-Arylidene-1-indanones (**1**) *and 2-Arylidene-1-benzosuberones* (**4**)

Method i. A 1 ml (8.82 mmol) sample of a 30% hydrogen peroxide solution was added to a cooled and stirred mixture of the appropriate 2-arylidene-1-indanone (**1**, 1.00 g, 3.34–4.54 mmol) or 2-arylidene-1-benzosuberone (**4**, 1.00 g, 3.05–4.02 mmol) and 2.0 ml (4.0 mmol) of 2 *M* NaOH in methanol (40 ml). Stirring was continued at ambient temperature for 3–24 h, the reaction mixture was diluted with water, and the precipitated material was removed by filtration, washed with water (4 × 20 ml), and dried to obtain the epoxides **2** and **5**.

Method ii. DMD (acetone solution) was added to a cooled and stirred solution of 2-arylidene-1-indanone (*E*)-**1** (0.500 g, 1.67–2.27 mmol) or 2-arylidene-1-benzosuberone (*E*)-**4** (0.500 g, 1.52–

Table 1. New 2-arylidene-1-benzosuberones (**4**)

Product	Yield (%)	mp (°C)	Molecular Formula[a]	IR (KBr) ν(CO)(cm^{-1})	^{1}H NMR ($CDCl_3$/*TMS*) δ(ppm), *J*(Hz)
(*E*)-**4c**	75	107–108	$C_{19}H_{18}O$	1664	2.07 (m, 2 H), 2.39 (s, 3 H), 2.60 (t, 2 H, $J = 6.2$), 2.88 (t, 2 H, $J = 6.2$), 7.19–7.78 (m, 8 H_{arom}), 7.82 (s, 1 H)
(*E*)-**4d**	70	94–95	$C_{18}H_{15}FO$	1662	2.09 (m, 2 H), 2.60 (t, 2 H, $J = 6.0$), 2.89 (t, 2 H, $J = 6.0$), 7.08–7.77 (m, 8 H_{arom}), 7.80 (s, 1 H)
(*E*)-**4f**	69	110–111	$C_{18}H_{15}BrO$	1662	2.05 (m, 2 H), 2.57 (t, 2 H, $J = 6.4$), 2.89 (t, 2 H, $J = 6.4$), 7.18–7.78 (m, 8 H_{arom}), 7.80 (s, 1 H)
(*Z*)-**4a**	60	yellow oil	$C_{18}H_{16}O$	1660	2.09 (m, 2 H), 2.62 (t, 2 H, $J = 6.0$), 2.91 (t, 2 H, $J = 6.0$), 7.15–7.78 (m, 8 H_{arom}), 7.83 (s, 1 H)
(*Z*)-**4c**	63	yellow oil	$C_{19}H_{18}O$	1660	2.10 (m, 2 H), 2.40 (s, 3 H) 2.62 (t, 2 H, $J = 6.2$), 2.92 (t, 2 H, $J = 6.2$), 7.15–7.77 (m, 8 H_{arom}), 7.80 (s, 1 H)
(*Z*)-**4e**	70	yellow oil	$C_{18}H_{15}ClO$	1658	2.07 (m, 2 H), 2.59 (t, 2 H, $J = 6.2$), 2.90 (t, 2 H, $J = 6.2$), 7.17–7.78 (m, 8 H_{arom}), 7.78 (s, 1 H)

[a] Elemental analyses (C, H) were in good agreement with the calculated values

Table 2. Epoxidation of 2-arylidene-1-indanones (**1**) and 2-arylidene-1-benzosuberones (**4**)

Product	*Method i* Time (h)	Yield (%)	*Method ii* Time (h)	Ratio **1** or **4** to *DMD*	Yield (%)	*Method iii* Time (h)	Yield (%)	mp (°C) (MeOH) (Lit. mp)	Molecular Formula[a]	IR (KBr) ν(CO) (cm^{-1})
trans-**2a**	3	91	72	1:2	71	8	9	122–123 (121–122)[2]	$C_{16}H_{12}O_2$	1716
trans-**2b**	3	96	72	1:3	87	–	–	132–133	$C_{17}H_{14}O_3$	1716
trans-**2c**	3	99	72	1:3	94	8	10	116–118	$C_{17}H_{14}O_2$	1716
trans-**2d**	3	84	120	1:3	83	–	–	131–132	$C_{16}H_{11}FO_2$	1716
trans-**2e**	3	97	168	1:3	72	8	9	157–158	$C_{16}H_{11}ClO_2$	1720
trans-**2f**	3	97	168	1:3	76	–	–	158–159	$C_{16}H_{11}BrO_2$	1722
trans-**2g**	–	–	168	1:5	77	–	–	174–175	$C_{17}H_{11}NO_2$	1720
cis-**2a**	–	–	120	1:3	39	8	61	95–96	$C_{16}H_{12}O_2$	1712
cis-**2c**	–	–	96	1:3	35	8	56	161–162	$C_{17}H_{14}O_2$	1716
cis-**2e**	–	–	192	1:5	56	8	63	168–169	$C_{16}H_{11}ClO_2$	1714
3c	–	–	96	1:3	5	–	–	136–137 (133–135)[20]	$C_{17}H_{12}O_2$[b]	1688 1620
trans-**5a**	8	75	168	1:4	83	8	11	77–78	$C_{18}H_{16}O_2$	1676
trans-**5b**	8	77	120	1:3	78	–	–	97–98	$C_{19}H_{18}O_3$	1674
trans-**5c**	8	98	168	1:4	90	8	9	117–118	$C_{19}H_{18}O_2$	1684
trans-**5d**	8	92	192	1:4	79	–	–	96–97	$C_{18}H_{15}FO_2$	1680
trans-**5e**	8	90	192	1:4	79	8	12	100–101	$C_{18}H_{15}ClO_2$	1686
trans-**5f**	8	89	216	1:5	73	–	–	101–102	$C_{18}H_{15}BrO_2$	1684
trans-**5g**	–	–	216	1:5	96	–	–	167–168	$C_{19}H_{15}NO_2$	1684
cis-**5a**	–	–	240	1:7	50	8	59	67–68	$C_{18}H_{16}O_2$	1682
cis-**5c**	–	–	216	1:5	53	8	54	98–99	$C_{19}H_{18}O_2$	1682
cis-**5e**	–	–	336	1:8	61	8	60	85–86	$C_{18}H_{15}ClO_2$	1680
6c	–	–	216	1:4	7	–	–	oil	$C_{19}H_{16}O_3$[b]	1692
6e	–	–	336	1:4	8	–	–	103–104	$C_{18}H_{13}ClO_3$[b]	1690

[a] Elemental analyses (C, H) were in good agreement with the calculated values; [b] EI mass spectra were run on a VG 7035 spectrometer; molecular mass: **3c** (248), **6c** (292), and **6e** (312)

2.01 mmol) in dry CH_2Cl_2 (5.0 ml) and stirred in the dark. Stirring was continued for 24 h, and a new quantity of *DMD* was added. The *DMD* administration was continued in 24 h intervals until complete consumption of the starting material **1** or **4** was achieved. The solvent was evaporated under reduced pressure (*ca.* 25 °C, 20 torr), and the residue was crystallized from methanol to yield the corresponding *trans*-**2a–g** or *trans*-**5a–g** spiroepoxides. The epoxidation of (*Z*)-**1a**, **c**, **e** or (*Z*)-**4a**, **c**, **e** under similar reaction conditions afforded the *cis*-**2a**, **c**, **e** or *cis*-**5a**, **c**, **e** spiroepoxides. The by-products **3c** and **6c**, **e** were isolated from the reaction mixtures of the respective (*Z*)-enones by column chromatography on silica gel with hexane/acetone (9:1) as the eluent.

Table 3. ^{1}H NMR spectroscopic data of epoxides **2** and **5** and diones **3** and **6**

Product	^{1}H NMR ($CDCl_3$/*TMS*) δ(ppm), *J*(Hz)
trans-**2a**	2.93 (d, 1 H, *J* = 18.0), 3.28 (d, 1 H, *J* = 18.0), 4.50 (s, 1 H), 7.29–8.37 (m, 9 H_{arom})
trans-**2b**	2.93 (d, 1 H, *J* = 17.9), 3.26 (d, 1 H, *J* = 17.9), 3.82 (s, 3 H), 4.42 (s, 1 H), 6.92–7.84 (m, 8 H_{arom})
trans-**2c**	2.38 (s, 3 H), 2.92 (d, 1 H, *J* = 17.8), 3.25 (d, 1 H; *J* = 17.8), 4.43 (s, 1 H), 7.20–7.83 (m, 8 H_{arom})
trans-**2d**	2.90 (d, 1 H, *J* = 18.0), 3.17 (d, 1 H, *J* = 18.0), 4.47 (s, 1 H), 7.07–7.88 (m, 8 H_{arom})
trans-**2e**	2.90 (d, 1 H, *J* = 17.8), 3.25 (d, 1 H, *J* = 17.8), 4.45 (s, 1 H), 7.25–7.88 (m, 8 H_{arom})
trans-**2f**	2.91 (d, 1 H, *J* = 18.0), 3.23 (d, 1 H, *J* = 18.0), 4.45 (s, 1 H), 7.21–7.89 (m,, 8 H_{arom})
trans-**2g**	2.85 (d, 1 H, *J* = 17.9), 3.26 (d, 1 H, *J* = 17.9), 4.52 (s, 1 H), 7.38–7.93 (m, 8 H_{arom})
cis-**2a**	3.50 (br s, 2 H), 4.52 (s, 1 H), 7.23–7.70 (m, 9 H_{arom})
cis-**2c**	2.36 (s, 3 H), 3.49 (br s, 2 H), 4.51 (s, 1 H), 7.16–7.69 (m, 8 H_{arom})
cis-**2e**	3.50 (br s, 2 H), 4.48 (s, 1 H), 7.28–7.70 (m, 8 H_{arom})
3c	2.45 (s, 3 H), 7.32–8.39 (m, 8 H_{arom} + CH)
trans-**5a**	1.26 (m, 1 H), 1.53 (m, 1 H), 1.79 (m, 1 H), 2.02 (m, 1 H), 2.75 (m, 1 H), 2.90 (m, 1 H), 4.39 (s, 1 H), 7.17–7.87 (m, 9 H_{arom})
trans-**5b**	1.31 (m, 1 H), 1.55 (m, 1 H), 1.79 (m, 1 H), 2.04 (m, 1 H), 2.75 (m, 1 H), 2.89 (m, 1 H), 3.81 (s, 3 H), 4.34 (s, 1 H), 6.80–7.82 (m, 8 H_{arom})
trans-**5c**	1.30 (m, 1 H), 1.55 (m, 1 H), 1.80 (m, 1 H), 2.03 (m, 1 H), 2.36 (m, 3 H), 2.76 (m, 1 H), 2.90 (m, 1 H), 4.36 (s, 1 H), 7.14–7.82 (m, 8 H_{arom})
trans-**5d**	1.30 (m, 1 H), 1.59 (m, 1 H), 1.77 (m, 1 H), 2.03 (m, 1 H), 2.79 (m, 1 H), 2.89 (m, 1 H), 4.39 (s, 1 H), 7.04–7.80 (m, 8 H_{arom})
trans-**5e**	1.32 (m, 1 H), 1.59 (m, 1 H), 1.76 (m, 1 H), 2.02 (m, 1 H), 2.81 (m, 1 H), 4.38 (s, 1 H), 7.17–7.80 (m, 8 H_{arom})
trans-**5f**	1.30 (m, 1 H), 1.58 (m, 1 H), 1.75 (m, 1 H), 2.02 ((m, 1 H), 2.79 (m, 1 H), 2.87 (m, 1 H), 4.36 (s, 1 H), 7.16–7.76 (m, 8 H_{arom})
trans-**5g**	1.30 (m, 1 H), 1.64 (m, 1 H), 1.75 (m, 1 H), 2.02 (m, 1 H), 2.88 (m, 2 H), 4.49 (s, 1 H), 7.19–7.75 (m, 8 H_{arom})
cis-**5a**	1.92 (m, 1 H), 1.98 (m, 1 H), 2.28 (m, 1 H), 2.42 (m, 1 H), 3.00 (m, 1 H), 3.13 (m, 1 H), 4.28 (s, 1 H), 7.18–7.59 (m, 9 H_{arom})
cis-**5c**	1.85 (m, 1 H), 1.93 (m, 1 H), 2.21 (m, 1 H), 2.22 (s, 3 H), 2.33 (m, 1 H), 2.93 (m, 1 H), 3.08 (m, 1 H), 4.28 (s, 1 H), 7.03–7.62 (m, 8 H_{arom})
cis-**5e**	1.87 (m, 1 H), 1.96 (m, 1 H), 2.22 (m, 1 H), 2.36 (m, 1 H), 2.96 (m, 1 H), 3.05 (m, 1 H), 4.21 (s, 1 H), 7.16–7.60 (m, 8 H_{arom})
6c	2.25 (s, 3 H), 2.28 (m, 1 H), 2.58 (m, 1 H), 3.07 (m, 1 H), 3.12 (m, 1 H), 4.07 (s, 1 H), 6.90–7.80 (m, 8 H_{arom})
6e	2.24 (m, 1 H), 2.59 (m, 1 H), 3.07 (m, 2 H), 4.04 (s, 1 H), 6.93–7.78 (m, 8 H_{arom})

Method iii. A sample of (*Z*)-**1a**, **c**, **e** or (*Z*)-**4a**, **c**, **e** (0.500 g, 1.77–2.27 mmol) and *m*-chloroperoxybenzoic acid (0.500 g, 2.90 mmol) were dissolved in benzene (30 ml) and kept at reflux for 8 h; the mixture was stored overnight at room temperature (*ca.* 25 °C). The precipitated *m*-chlorobenzoic acid was removed by filtration and the filtrate was washed with 10% aqueous $NaHCO_3$ (3 × 25 ml) and water (25 ml). The solution was dried over $CaCl_2$, the solvent was evaporated under reduced pressure (*ca.* 25 °C, 20 torr), and the residue was submitted to column chromatography on silica gel with hexane/acetone (9:1) as the eluent to afford *cis*- and *trans*-**2a**, **c**, **e** or *cis*- and *trans*-**5a**, **c**, **e** epoxides.

Acknowledgements

The work in Debrecen and Budapest was sponsored by the *Hungarian National Research Foundation* (Grant Nos. OTKA-1639 and OTKA-T7459), by the *Hungarian Ministry for Culture and Education* (Grant No. 14/94), and by the *European Union* (COST Project D2/0005/94). The work in Würzburg was generously financed by the *Deutsche Forschungsgemeinschaft* (SPP "Peroxidchemie: Mechanistische und Preparative Aspekte des Sauerstofftransfers"). Technical assistance of Mrs. *M. Nagy* is highly appreciated. *C.N.* thanks the *UNIVERSITAS Foundation* of the Hungarian Commercial Bank (Debrecen, Hungary) for a grant and *J.H.* the *J. Varga Foundation* (Budapest, Hungary) for a fellowship.

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Received January 12, 1996. Accepted January 24, 1996