Preparation of 2*H*-Benzoxetes by Photoinduced [2+2] Cycloaddition of Quinone Methides, Accessible by Dimethyldioxirane (DMD) Oxidation of 2,3-Dimethylbenzofurans

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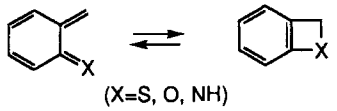
Irradiation ($\lambda > 366$ nm) of the quinone methides **3**, which were formed by valence isomerization of the methyl-, chloro-, and *tert*-butyl-substituted 2,3-dimethylbenzofuran epoxides **2**, afforded the novel 2*H*-benzoxetes **4** by photochemical [2+2] cycloaddition. These strained and highly labile benzoxetes **4** were spectrally (^{1}H and ^{13}C NMR) characterized at subambient temperatures. On prolonged storage (2–3 d) at −20 to −10°C, the benzoxetes **4** reverted to the quinone methides **3** and/or benzofuran epoxides **2**.

The synthetic and mechanistic chemistry of *ortho*-quinoid compounds has received much attention over the last decades[1]. Especially the valence isomerization of these highly conjugated substances has been of current interest. Thus, the 6-methylene-2,4-cyclohexadiene-1-thiones undergo [2+2] cycloaddition to the corresponding strained 2*H*-benzothietes[2] (Scheme 1), which in turn are photochemically or thermally retro-cleaved to the quinoid starting materials.

Scheme 1



(X=S, O, NH)

Sander[3] and Ripoll[4] have recently reported on the thermal and photochemical valence isomerization of 6-methylene-2,4-cyclohexadien-1-imine to 2*H*-benzazete (Scheme 1). The benzoxetes were previously postulated[5] in the thermal isomerization of *ortho*-phenodiquinones; however, an X-ray structure analysis established that instead the corresponding benzoxepines were formed under these conditions[6]. Furthermore, benzazetes[7] and benzoxetes[8] have been claimed as labile intermediates in the [2+2] cycloaddition of arynes with imines and α,β-unsaturated aldehydes to afford phenanthridines and chromenes.

Most recently we demonstrated that photochemically the *ortho*-quinone methides **3**, which are formed by thermal isomerization of the benzofuran epoxides **2**, afford the novel benzoxetes **4** (Scheme 2)[9]. Thus, for the first time such strained valence isomers could be spectrally characterized without recourse to matrix isolation techniques. It was of interest to establish the generality and scope of the photochemical transformation of *ortho*-quinone methides **3** to the respective benzoxetes **4** by examining a variety of substituents (Me, *t*Bu, MeO, Cl) on the benzo ring and their regioisomers. Herein we report our results (Table 1) which reveal that except for the 4-substituted regioisomers, the photochemical transformation **3**→**4** is quite general.

Results and Discussion

The benzofuran epoxides **2a–l** and their valence-isomeric quinone methides **3a–l** were prepared from the corresponding 2,3-dimethylbenzofurans **1a–l** by epoxidation with dimethyldioxirane (DMD)[10] as previously reported[9,11] (Scheme 2). In Table 1 are given the epoxidation conditions and conversions (%) of the benzofurans **1**.

Even in those cases for which the epoxides **2** prevail, the required quinone methides **3** are present in sufficient concentrations for the intended subsequent photochemical experiments as result of their valence isomerization **2**⇌**3**. This was confirmed by UV measurements of the colored acetone solutions of the epoxides **2**, which showed λ_{max} between 385 and 400 nm with tailing to 580 nm. Thus, on irradiation ($\lambda > 366$ nm) the quinone methides **3a,c–e, g–i,k**, derived from the respective benzofuran epoxides **2a,c–e,g–i,k**, photoisomerized at ca. −30°C within 20 h in good yields by [2+2] cycloaddition to the corresponding strained benzoxetes **4a,c–e,g–i,k** (Table 1).

For the 4-substituted benzofuran epoxides **2b,f,l**, no benzoxetes **4b,f,l** were observed even on prolonged irradiation (Table 1). Presumably, steric interactions between the substituents (Me, Cl, tBu) at the 4-position and the methyl group at the planarized benzylic center in the quinone **3b,f,l** are too severe for the respective epoxides **2b,f,l** to open up to the quinone methides **3b,f,l**. Thus, the latter are not produced in sufficient steady state concentrations for the photocyclization to the benzoxetes **4b,f,l** to be effective.

Additionally, forcefield calculations (Tripos)[12] reveal that the 4-methyl-substituted quinone methide **3b** is disfa-

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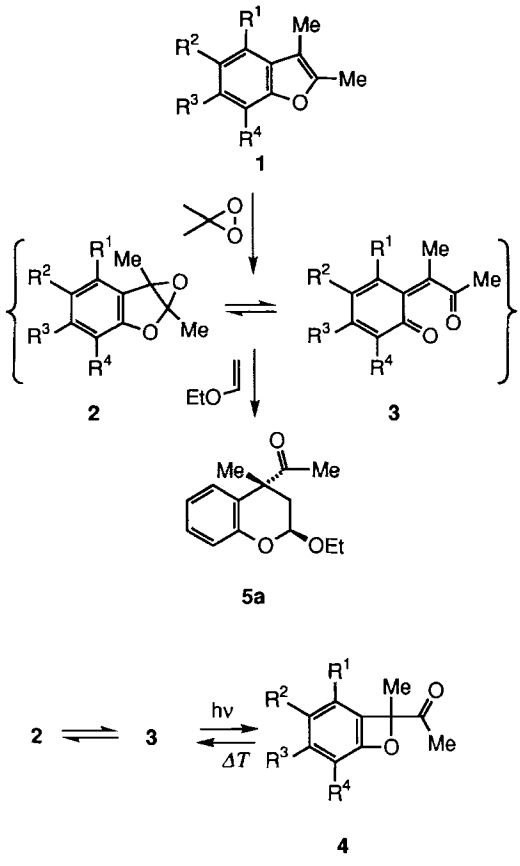
Scheme 2



vored by ca. 5 kcal/mol compared to the 5- and 6-methylderivatives **3c,d**. For the corresponding chloro compounds **3b–h** the destabilization amounts to ca. 3 kcal/mol.

The extremely labile 6-methoxy-substituted quinone methide **3j** gave on irradiation by the Na lamps at −20°C a complex product mixture[5]. Therefore, the photolysis of this derivative was carried out at −78°C with the argon ion laser at 363.8, 351.5, and 333.6 nm; the corresponding benzoxete **4j** was obtained cleanly (Table 1).

The benzoxetes **4** revert at −20°C slowly to the original epoxides **2** and/or quinone methides **3**. Unfortunately, above −20°C, complex reaction mixtures were obtained, which derive from deterioration of the intermediary epoxides[9]. Thus, a kinetic study of the electrocyclic ring-opening **4**→**3**→**2** was precluded. The benzoxetes **4** were characterized spectroscopically (cf. Experimental); particularly characteristic are the ^{13}C-NMR signals of C-2 of the oxete ring δ = 101.9–103.4.

The persistence of the benzoxetes **4** is influenced by the electronic effect of the substituent. While the chloro derivatives **4g–i** persisted for ca. 1 h up to −10°C, the methoxy-substituted oxete **4j** reverted already at −40°C to the quinone methide **3j**. The methyl derivatives **4b–e** possessed intermediate thermal stability. Thus, electron donors (MeO, Me) accelerate the electrocyclic ring-opening, while electron acceptors retard it. Analogous to the electronic effects on the thermal stability of benzofuran epoxides **2**[11], stabilization of the incipient cationic charge at the benzylic center appears to play a role.

To establish that the benzoxetes **4** cleanly revert thermally to the quinone methides **3** and/or benzofuran epoxides **2**, the benzoxete **4a** was treated with an excess of ethyl vinyl ether. The mixture was allowed to warm up to room temperature. Within 7 h the Diels-Alder cycloadduct **5a** (Scheme 2) was formed essentially quantitatively (94%) from the benzoxete **4a**. At least for this unsubstituted case it

Table 1. Epoxidation[a] of the 2,3-dimethylbenzofurans **1** and subsequent photolysis[b] of the resulting epoxides **2** and/or quinone methides **3** to the benzoxetes **4**

	Substituents				Epoxidation					Irradiation			
					Ratio	Temp.	Time	Conv.[c]		Temp.	Time	Conv.[c]	
	R^1	R^2	R^3	R^4	1 : DMD	(°C)	(h)	(%)	Product	(°C)	(h)	(%)	Product
1a	H	H	H	H	1 : 1.1	-40	7	>95	**2a**	-25	21	92	**4a**
1b	Me	H	H	H	1 : 1.2	-35	4	>95	**2b**	-30	48	[d]	-
1c	H	Me	H	H	1 : 1.1	-40	3	>95	**2c**	-30	17	>95	**4c**
1d	H	H	Me	H	1 : 1.2	-50	2	>95	**2d/3d** (31:69)	-35	17	>95	**4d**
1e	H	H	H	Me	1 : 1.2	-45	3	95	**2e**	-25	20	>95	**4e**
1f	Cl	H	H	H	1 : 1.3	-20	8	92	**2f**	-20	48	[d]	-
1g	H	Cl	H	H	1 : 1.4	-20	9	71	**2g**	-20	21	>95	**4g**
1h	H	H	Cl	H	1 : 1.2	-35	6	79	**2h**	-30	19	89	**4h**
1i	H	H	H	Cl	1 : 1.4	-20	10	>95	**2i**	-25	22	>95	**4i**
1j	H	H	OMe	H	1 : 1.1	-60	0.5	>95	**3j**	-78	0.02[e]	82	**4j**
1k	H	tBu	H	H	1 : 1.1	-30	2	>95	**2k**	-30	13	>95	**4k**
1l	tBu	H	tBu	H	1 : 1.3	-45	3	>95	**2l**	-35	48	[d]	-

[a] Dimethyldioxirane, ca. 0.1 M in acetone. – [b] Irradiation with two 250-W Na lamps (λ > 366 nm). – [c] Mass balances >95%; determined by NMR spectroscopy (error ca. ±5%). – [d] No conversion to the corresponding benzoxete **4** was observed. – [e] Irradiation with the 363.8-, 351.1-, and 333.6-nm lines of the argon ion laser.

is thus established that the photochemical electrocyclization **3a**→**4a** reverts thermally.

In summary, irradiation of the quinone methides **3** with visible light generates efficiently the hitherto unknown benzoxetes **4**, which are sufficiently persistent for their spectral characterization at subambient temperature. Only the 4-substituted derivatives resist photocyclization; presumably steric effects prevent valence isomerization of the benzofuran epoxides **2** to the quinone methides **3**, which are required for the photocyclization to the benzoxetes **4**. Thermally, the latter revert cleanly to the quinone methides **3** and/or benzofuran epoxides **2**, as established for the derivative **4a** by [4+2] cycloaddition with ethyl vinyl ether to the benzopyran **5**.

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Experimental

IR: Perkin Elmer 1420. – UV: Hitachi U-3200 spectrophotometer. – ^{1}H and ^{13}C NMR: Bruker AC 200 (200 MHz) and 250 (250 MHz). Carbon multiplicities were established by DEPT experiments. Chemical shifts refer to $SiMe_4$ in $CDCl_3$ or [D_6]acetone. – MS: Varian 8200 Finnigan MAT. – Elemental analyses: Analytical Division of the Institute of Inorganic Chemistry (University of Würzburg). – All solvents were purified by standard methods. Dimethyldioxirane (as acetone solution) was prepared according to ref.[10]. The dimethyldioxirane solutions were stored over molecular sieves at −20°C. – For the irradiations of the quinone methides **3a**–**i**, **k**, **l** two 250-W Na lamps ($\lambda > 366$ nm) and for **3j** a laser (argon ion laser INNOVA-100, Coherent, UV-Optik, λ = 363.8, 351.5, and 333.6 nm) were used. For the photolysis, the samples were placed into a glass Dewar, which was cooled with an ethanol/dry ice bath.

Epoxidation of the 2,3-Dimethylbenzofurans **1** *by Dimethyldioxirane (DMD). General Procedure:* A cooled (−78°C) solution of DMD (1.1 to 1.4 equiv.) in acetone (ca. 0.1 M), was rapidly added to a cooled (−78°C), stirred solution of the benzofurans **1** (0.84–1.00 mmol) in anhydrous CH_2Cl_2 (2 ml) under N_2. Stirring was continued until complete consumption (monitored by TLC) of the benzofurans **1**, while the reaction temp. was allowed to increase to −20°C. The solvent was evaporated (−20°C at 0.01 Torr, 1–2 h) to yield quantitatively the epoxides **2** and/or quinone methides **3** in high purity as established by ^{1}H-NMR spectroscopy.

5-tert-Butyl-2,3-dihydro-2,3-dimethyl-2,3-epoxybenzofuran (**2k**) was obtained quantitatively from 159 mg (0.788 mmol) of benzofuran **1k** and 11 ml (0.924 mmol) of DMD (0.084 M) by following the above procedure at −30°C for 3 h. – ^{1}H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.28 (s, 9H), 1.76 (s, 3H), 1.84 (s, 3H), 6.84 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 1.9 Hz, 1H), 7.61 (dd, J = 8.5/1.9 Hz, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 11.9 (q), 14.1 (q), 31.6 (q), 34.8 (s), 67.2 (s), 95.3 (s), 110.6 (d), 121.6 (d), 127.0 (d), 130.4 (s), 144.1 (s), 158.9 (s).

4,6-Di-tert-butyl-2,3-dihydro-2,3-dimethyl-2,3-epoxybenzofuran (**2l**) was obtained quantitatively from 100 mg (0.388 mmol) of benzofuran **1l** and 5 ml (0.500 mmol) of DMD (0.01 M) by following the above procedure at −45°C for 3 h. – ^{1}H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.30 (s, 9H), 1.50 (s, 9H), 1.89 (s, 3H), 1.99 (s, 3H), 6.87 (d, J = 1.7 Hz, 1H), 7.06 (d, J = 1.7 Hz, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 14.6 (q), 19.6 (q), 31.0 (q), 31.5 (q), 34.9 (s), 35.3 (s), 66.5 (s), 94.4 (s), 106.8 (d), 116.2 (d), 123.3 (s), 149.3 (s), 152.6 (s), 160.8 (s).

Irradiation ($\lambda > 366$ nm) of the Epoxides **2** *and their Valence-Isomeric Quinone Methides* **3**. *General Procedure:* Compounds **2** and **3**, which were prepared as above or as previously reported[9,11], were irradiated in 5–10 ml of acetone at −35 to −20°C in a 20-ml test tube or in $CDCl_3$ in an NMR tube by two 250-W sodium lamps until the solution became colorless (11–22 h). After solvent removal at −20°C/0.1 Torr, the product was examined by NMR spectroscopy at −55 to −30°C. For the photolysis of the extremely labile quinone methide **3j**, a laser was used as light source.

2-Acetyl-2-methyl-2H-benzoxete (**4a**) was obtained in 92% yield from epoxidation of 50.0 mg (0.340 mmol) of **1a** with 4 ml (0.400 mmol) of DMD (0.1 M) at −40°C for 7 h and subsequent irradiation at −25°C for 21 h by following the above procedure. – ^{1}H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.90 (s, 3H), 2.31 (s, 3H), 6.73–6.76 (m, 1H), 6.86–6.93 (m, 1H), 7.08–7.11 (m, 1H), 7.22–7.30 (m, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 20.3 (q), 25.2 (q), 103.2 (s), 107.7 (d), 120.7 (d), 121.0 (d), 130.0 (d), 132.7 (s), 164.7 (s), 206.8 (s).

Benzofuran epoxide **2b**, which was obtained from the epoxidation of 50.0 mg (0.310 mmol) of **1b** with 3.5 ml (0.350 mmol) of DMD (0.01 M) at −35°C for 4 h, showed on irradiation at −30°C for 48 h no conversion to the corresponding benzoxete **4b**.

2-Acetyl-2,4-dimethyl-2H-benzoxete (**4c**) was obtained quantitatively from the epoxidation of 50.0 mg (0.310 mmol) of **1c** with 3.5 ml (0.350 mmol) of DMD (0.1 M) at −40°C for 3 h and subsequent irradiation at −30°C for 17 h by following the above procedure. – ^{1}H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.88 (s, 3H), 2.29 (s, 3H), 2.30 (s, 3H), 6.63 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 0.7 Hz, 1H), 7.06 (dd, J = 8.0/0.7 Hz, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 20.0 (q), 21.5 (q), 24.7 (q), 102.1 (s), 107.0 (d), 121.4 (d), 129.8 (d), 130.0 (s), 132.6 (s), 162.2 (s), 206.5 (s).

2-Acetyl-2,5-dimethyl-2H-benzoxete (**4d**) was obtained quantitatively from the epoxidation of 100 mg (0.620 mmol) of **1d** with 7 ml (0.700 mmol) of DMD (0.1 M) at −50°C for 2 h and subsequent irradiation at −35°C for 17 h by following the above procedure. – ^{1}H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.88 (s, 3H), 2.20 (s, 3H), 2.26 (s, 3H), 6.59–6.74 (m, 2H), 6.97 (d, J = 7.5 Hz, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 20.0 (q), 22.5 (q), 24.7 (q), 102.4 (s), 108.2 (d), 120.3 (d), 122.7 (d), 129.4 (s),140.4 (s), 164.6 (s), 206.5 (s).

2-Acetyl-2,6-dimethyl-2H-benzoxete (**4e**) was obtained nearly quantitatively from the epoxidation of 50.0 mg (0.310 mmol) of **1e** with 3.5 ml (0.350 mmol) of DMD (0.1 M) at −45°C for 3 h and subsequent irradiation at −25°C for 20 h by following the above procedure. – ^{1}H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.89 (s, 3H), 2.21 (s, 3H), 2.30 (s, 3H), 6.77–7.08 (m, 3H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 13.1 (q), 20.4 (q), 25.1 (q), 102.1 (s), 117.8 (s), 118.5 (d), 121.0 (d), 131.5 (d), 132.1 (s), 162.8 (s), 206.7 (s).

Benzofuran epoxide **2f**, which was obtained from the epoxidation of 100 mg (0.560 mmol) of **1f** with 8 ml (0.800 mmol) of DMD (0.01 M) at −20°C for 8 h, showed on irradiation at −20°C for 48 h no conversion to the corresponding benzoxete **4f**.

2-Acetyl-4-chloro-2-methyl-2H-benzoxete (**4g**) was obtained in 71% yield (based on consumed benzofuran **1g**) from the epoxidation of 50.0 mg (0.280 mmol) of **1g** with 3 ml (0.300 mmol) of DMD (0.1 M) at −20°C for 9 h and subsequent irradiation at −20°C for 21 h by following the above procedure. – ^{1}H NMR (200

MHz, $CDCl_3$, −35°C): δ = 1.87 (s, 3H), 2.29 (s, 3H), 6.67 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 1.4 Hz, 1H), 7.22 (dd, *J* = 8.3/1.4 Hz, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 19.9 (q), 24.8 (q), 101.9 (s), 108.7 (d), 121.4 (d), 125.3 (s), 129.9 (d), 133.3 (s), 162.4 (s), 205.5 (s).

2-Acetyl-5-chloro-2-methyl-2H-benzoxete (**4h**) was obtained in 68% yield (based on consumed benzofuran **1h**) from the epoxidation of 50.0 mg (0.280 mmol) of **1h** with 3 ml (0.300 mmol) of DMD (0.1 M) at −35°C for 6 h and subsequent irradiation at −30°C for 19 h by following the above procedure. – ^1H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.86 (s, 3H), 2.27 (s, 3H), 6.67 (d, *J* = 0.7 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 7.02 (dd, *J* = 7.6/0.7 Hz, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 20.0 (q), 24.9 (q), 102.8 (s), 108.6 (d), 120.4 (d), 121.7 (d), 130.5 (s), 134.9 (s), 164.1 (s), 205.8 (s).

2-Acetyl-6-chloro-2-methyl-2H-benzoxete (**4i**) was obtained quantitatively from the epoxidation of 50.0 mg (0.280 mmol) of **1i** with 5 ml (0.500 mmol) of DMD (0.1 M) at −20°C for 10 h and subsequent irradiation at −25°C for 22 h by following the above procedure. – ^1H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.91 (s, 3H), 2.32 (s, 3H), 6.81 (dd, *J* = 7.1/7.1 Hz, 1H), 6.85 (dd, *J* = 7.1/0.7 Hz, 1H), 7.02 (dd, *J* = 7.1/0.7 Hz, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 20.1 (q), 25.0 (q), 103.4 (s), 110.7 (s), 119.3 (d), 122.1 (d), 130.0 (d), 133.4 (s), 159.1 (s), 205.4 (s).

2-Acetyl-4-tert-butyl-2-methyl-2H-benzoxete (**4k**) was obtained quantitatively from the epoxidation of 159 mg (0.788 mmol) of **1k** with 11 ml (0.924 mmol) of DMD (0.084 M) at −30°C for 2 h and subsequent irradiation at −30°C for 13 h by following the above procedure. – ^1H NMR (200 MHz, $CDCl_3$, −35°C): δ = 1.25 (s, 9H), 1.87 (s, 3H), 2.29 (s, 3H), 6.63 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 1.5 Hz, 1H), 7.28 (dd, *J* = 8.1/1.5 Hz, 1H). – ^{13}C NMR (50 MHz, $CDCl_3$, −35°C): δ = 20.0 (q), 24.7 (q), 31.5 (q), 34.6 (s), 102.3 (s), 106.3 (d), 117.8 (d), 126.2 (d), 132.1 (s), 143.5 (s), 161.9 (s), 206.7 (s).

Benzofuran epoxide **2l**, which was obtained from the epoxidation of 100 mg (0.388 mmol) of **1l** with 5 ml (0.500 mmol) of DMD (0.01 M) at −45°C for 3 h, showed on irradiation at −35°C for 48 h no conversion to the corresponding benzoxete **4l**.

2-Acetyl-5-methoxy-2-methyl-2H-benzoxete (**4j**) was obtained in 82% yield from the epoxidation of 90.0 mg (0.500 mmol) of **1j** with 10 ml (0.700 mmol) of DMD (0.056 M) at −60°C for 30 min and subsequent irradiation at −78°C for 1.2 min with the 363.8-, 351.5-, and 333.6-nm lines of the argon ion laser. – ^1H NMR (200 MHz, [D_6]acetone, −55°C): δ = 1.77 (s, 3H), 2.19 (s, 3H), 3.76 (s, 3H), 6.39 (dd, *J* = 7.9/1.7 Hz, 1H), 6.51 (d, *J* = 1.7 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H). – ^{13}C NMR (50 MHz, [D_6]acetone, −55°C): δ = 20.1 (q), 24.5 (q), 55.5 (q), 95.4 (d), 102.7 (s), 106.3 (d), 122.2 (d), 131.2 (s), 162.4 (s), 166.0 (s), 205.6 (s).

4-Acetyl-2-ethoxy-3,4-dihydro-4-methyl-2H-benzopyran (**5a**): To a solution of 225 mg (1.37 mmol) of epoxide **2a** in 2 ml of dry acetone was added 1 ml of ethyl vinyl ether (large excess) at −30°C. The reaction mixture was stirred at this temp. for 4 d, the solution was allowed to warm up to room temp. and the solvent evaporated (20°C at 15 Torr). The residue was purified by column chromatography (silica gel, Et_2O/pentane, 1:1) to afford 307 mg (94%) of **5a** as a colorless oil. Analogously, benzoxete **4a** (20.0 mg, 0.123 mmol) and 0.5 ml of ethyl vinyl ether afforded at room temp. for 7 h in $CDCl_3$ the benzopyran **5a**. – IR (CCl_4): $\tilde{\nu}$ = 3010 cm^{-1}, 2980, 2950, 1730, 1570, 1255, 1230, 1170, 1020, 995, 640. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.04 (t, *J* = 7.1 Hz, 3H), 1.41 (s, 3H), 1.58 (dd, *J* = 5.8/13.7 Hz, 1H), 1.81 (s, 3H), 2.44 (dd, *J* = 4.0/13.7 Hz, 1H), 3.37–3.85 (m, 2H), 5.16 (dd, *J* = 4.0/5.8 Hz, 1H), 6.73–7.09 (m, 4H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.7 (q), 24.0 (q), 25.2 (q), 36.9 (t), 48.0 (s), 63.5 (t), 97.7 (d), 117.5 (d), 121.2 (d), 126.1 (s), 126.6 (d), 128.2 (d), 151.4 (s), 209.3 (s). – MS (70 eV), *m/z* (%): 234 (17) [M^+], 191 (61) [$M^+ - COCH_3$], 147 (80), 146 (30), 145 (100), 131 (12), 115 (13), 91 (17), 43 (18). – $C_{14}H_{18}O_3$ (234.3): calcd. C 71.77, H 7.74; found C 71.86, H 7.75.

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