Cycloallenes, 12[◇]

3δ²-Chromene (2,3-Didehydro-2*H*-1-benzopyran): Generation and Interception☆

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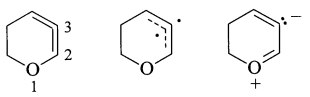
The treatment of 3-bromo-2*H*-chromene (**7**), dissolved in furan, 2-methylfuran, or 2,5-dimethylfuran, with potassium *tert*-butoxide, leads to formation of the epoxybenzo[*c*]chromene derivatives **8**−**11** in yields of 28−59%. Likewise, in styrene solution, *exo*-2-phenylcyclobuta[*b*]chromene **12** is produced (41% yield). With tetrahydrofuran as the solvent, 2-*tert*-butoxy-2*H*-chromene (**13**) is observed as the only product (79% yield). From these results, it is concluded that **7** is converted by β-elimination into the title compound **5**. This reactive intermediate is then intercepted by the furans and styrene in cycloaddition reactions to give compounds **8**−**12**, whereas reaction with KO*t*Bu/HO*t*Bu transforms it to the acetal **13**. The epoxybenzochromenes **8**, **9**, and **11** rearrange on heating at 110°C to give the epoxyxanthene derivatives **16**−**18**.

Six-membered cyclic compounds having an allene subunit as part of the ring are extremely short-lived intermediates.[1][2] Interest in such species has increased following mechanistic studies of the action of enediyne cytostatic agents/antibiotics.[3] Jones and Bergman[4] discussed (and rejected) 1,2,4,5-cyclohexatetraene as a structural alternative to *p*-didehydrobenzene. Furthermore, the formulae of the initial intermediates of the *cis*-enyne cumulene cyclization, leading to six-membered rings, can be drawn not only as diradicals but also as derivatives of 1,2,4-cyclohexatriene (**1**). This is valid for the 1,2,3,5-octatetraen-7-yne that results in the activation of neocarzinostatin[3] and for 1,2,4-heptatrien-6-ynes.[5] Derivatives of **1** are also considered to be the initial products (Diels-Alder adducts) of the reaction of vinylacetylenes with acetylenes.[1][6]

1a **1b** **2**, R = H; **3**, R = Me

A theoretical study predicted the allene structure **1a** to be 2 kcal mol^{-1} more stable than the diradical structure **1b**.[7] The experimentally determined heat of formation confirmed that **1** exists in a form very close in energy to **1b**.[8a] Nevertheless, it is possible to efficiently trap **1**[2a][8b][9] as well as its benzo derivative (**2**)[2a][9] and a dimethyl derivative of the latter, **3**,[10] for which a diradical nature also has to be taken into account, with activated olefins in [2 + 2] and [2 + 4] cycloadditions. Whereas **3** is generated by β-elimination of hydrogen bromide from the corresponding vinyl bromides,[10] dihalocarbene adducts of cyclopentadiene and indene are converted into **1** and **2**, respectively, in Doering-Moore-Skattebøl reactions. An alternative route to **1** is the electrocyclization of hexa-1,3-dien-5-yne.[8]

1-Oxa-2,3-cyclohexadiene (**4**) is produced both by β-elimination from 5-bromo-3,4-dihydro-2*H*-pyran[11][12] and by α-elimination from 6,6-dihalo-2-oxabicyclo[3.1.0]hexanes.[2a][13] Activated olefins,[2a][11][13] potassium *tert*-butoxide,[11b] and enolates[12] are all able to intercept **4**. Generally, nucleophiles attack the central allene carbon atom of six-membered ring allenes. This is true of reactions of potassium *tert*-butoxide with 1,2-cyclohexadiene[1] and **3**,[1][10] of enolates with 1,2-cyclohexadiene,[14] and of butyllithium with 1-oxa-3,4-cyclohexadiene[2a] and 1-phenyl-1-aza-3,4-cyclohexadiene.[2b] However, **4** reacts at positions 2, 3, and 4 with *tert*-butoxide[11b] and may react at position 3[12] and/or position 4[12b] with enolates, depending on the nature of the latter. The involvement of the terminal allene carbon atoms in addition to the central one indicates a polarization of **4** according to formula **4c**, which rationalizes the additions to positions 2 and 4 as the alternative possibilities for attack of a nucleophile on an α,β-unsaturated carbonyl compound.



4a **4b** **4c**

In view of the diradical nature of **1**,[8a] the formula **4c**, in addition to **4a** and **4b**, seems to be a plausible representation of **4**. Compared to 1,2-cyclohexadiene, the chirality of which is supported by experiment,[15] the smaller length of the tether across the allene termini and the extension of the allyl to a pentadienyl radical moiety enforce the planar geometry of the allene system of **1**. In **4**, the length of the

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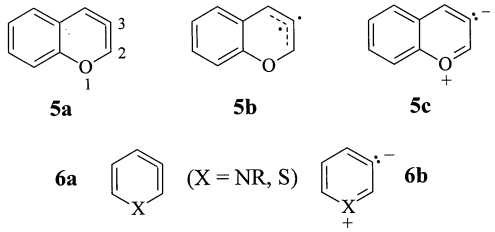
  1434−193X/98/0202−0237 $ 17.50+.50/0

tether, defined as the sum of the lengths of the four bonds (standard bond lengths), is only 5 pm larger than in **1**. Additionally, the participation of a lone electron pair of the oxygen atom, as depicted by formula **4c**, could cause a stabilization similar to the delocalization energy of the π electron in **1b**.

The combination of the specific subunits of **1** or **2** on the one hand, and of **4** on the other, i.e. the replacement of the methylene group in **1** or **2** by an oxygen atom, could further increase the polarity of the resulting species, since the zwitterionic structure should have a particularly low energy owing to its aromatic stabilization. The formulae **5a**−**c** represent the allene, diradical, and ylide character, respectively, of the title compound. We wish to report results that clearly support the intermediacy of **5**, even though it has a shorter tether across the allene system than any derivative of 1,2-cyclohexadiene described heretofore, with the exception of 1,2,4,5-cyclohexatetraene (*p*-didehydrobenzene). Moreover, the outcome of one particular trapping experiment is best rationalized by assuming a strong polarization of **5**, as illustrated by **5c**.

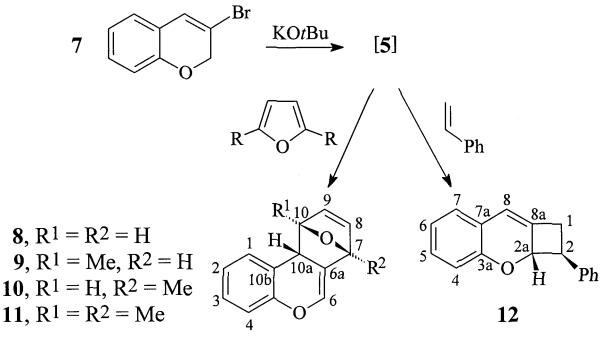


Recently, Shevlin et al.[16] have postulated aza- and thiacyclohexatrienes **6** as intermediates in the reaction cascades that follow the addition of carbon atoms to pyrroles and thiophene, respectively. Based on the observed products and on preliminary calculations, they favour the ylide structure **6b** for the nitrogen derivatives and the allene structure **6a** for the sulfur compound.

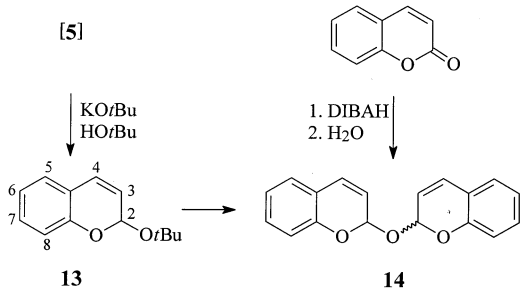
Results and Discussion

Although a phenylchlorocarbene adduct of benzofuran has been described,[17] our attempts to prepare dihalocarbene adducts were unsuccessful, which is why the Doering-Moore-Skattebøl method could not be applied for the generation of **5**. Thus, we utilized 3-bromo-2*H*-chromene (**7**)[18] as a precursor for **5**. Compound **7** was dissolved in furan and the resulting solution was treated at room temperature with potassium *tert*-butoxide, thereby affording the dihydroepoxybenzochromene **8** in 59% yield. Analogously, use of 2-methylfuran and 2,5-dimethylfuran resulted in the formation of **9** and **10** (28%, ratio 2.5:1.0) and of **11** (41%), respectively. Employing styrene as the solvent led to the cyclobutachromene **12** (41%).

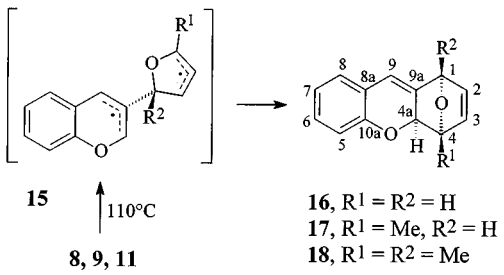
The cycloadducts of **5**, compounds **8**−**12**, are closely related to those of **4**, even with respect to the different positional selectivities of [2 + 4] and [2 + 2] cycloadditions. Possible reasons for this selectivity have been discussed.[2a][11b][13] Other than in the case of **4**,[2a][13] where reaction with styrene gave two diastereomeric products in a



1:1 ratio, the diastereomer of **12** was not observed. Since **12** is most probably more stable than its diastereomer, this result might be taken as an indication of thermodynamic control of the product formation. The styrene adducts of **4** equilibrate readily on heating. For this process, a diradical intermediate has been postulated.[13] Owing to the enhanced strain of **12** and its diastereomer, and the greater stabilization of the common diradical resulting from the cleavage of the C-2−C-2a bond, the equilibration could proceed even under the reaction conditions, thereby resulting in the exclusive formation of **12**. The fact that **12** was found to decompose within hours at room temperature may reflect its easy conversion into the diradical in question.



When the treatment of **7** with potassium *tert*-butoxide was carried out in the absence of a furan or styrene, the acetal **13** was isolated in 79% yield. Probably by reaction with traces of water, **13** readily underwent conversion to the bis(acetals) **14**, which were characterized by comparison with the authentic substance, prepared from coumarin by reduction with diisobutylaluminium hydride.[19] The formation of **13** and **14** in good yields shows that the nucleophilic attack occurred at C-2 of **5** with a high degree of efficiency and selectivity. These results indicate a higher polarity of **5** as compared to **4**, i.e. a greater contribution of **5c** to the ground state of **5** relative to that of **4c** to the ground state of **4**.



On heating in refluxing toluene, the compounds **8**, **9** and **11** underwent a smooth rearrangement to give the dihydroepoxyxanthenes **16**−**18**. This proves that the formation of the substrates from **5** proceeds under kinetic control. As a mechanism for this rearrangement, we considered the Diels-Alder cycloreversion of **8**, **9**, and **11**, regenerating **5** and the corresponding furan, followed by addition of the furan to the formal C-2−C-3 double bond of **5**. However, this possibility could be rejected since thermolysis of **11** in the presence of two equivalents of furan led to the exclusive formation of **18**, and no **16** could be detected. Consequently, we envisage diradicals **15** as being the intermediates, generated by cleavage of the C-10−C-10a bond of the substrates and having ideal stabilization of the single electrons within 1-aryloxy-3-aryl or 1-alkyloxyallyl systems. The rearrangement of **8**, **9** and **11** is reminiscent of the automerization of 5-methylenenorbornene.[20]

Characteristic NMR spectra support the structures proposed for the new compounds. The data for the benzochromenes **8**−**11** and the xanthenes **16**−**18** are collected in Tables 1a, b and 2a, b. We deduce the *exo* position of 10a-H and 4a-H on the 7-oxanorbornene skeleton of **8**−**11** and **16**−**18** from the vicinal couplings of these protons in **8** and **10** [J(10,10a) = 4.0, 4.2 Hz] and **16** [J(4,4a) = 4.3 Hz]. In the case of the other configuration, the fine structure caused by these couplings would not be resolved due to the dihedral angles being close to 90°. The configuration of **12** is based on the observation of two large couplings J(1,2) = 9.5, 8.6 Hz. For the other diastereomer, one would expect

Table 1a. NMR data of epoxybenzo[*c*]chromene derivatives **8**−**11** in $CDCl_3$: ^{1}H-NMR chemical shifts (δ values); the signal multiplicities and the coupling constants of **8** are representative; the latter were determined to be J(1,2) = 7.5, J(1,3) = 1.7, J(1,10) = 0.4, J(1,10a) = 1.3, J(2,3) = 7.3, J(2,4) = 1.1, J(3,4) = 8.3, J(3,10a) = 0.9, J(6,7) = 0.7, J(6,10) = 0.7, J(6,10a) = 2.6, J(7,8) = 1.8, J(7,10) = 0.7, J(7,10a) = 0.7, J(8,9) = 5.7, J(8,10) = 0.4, J(8,10a) = 0.4, J(9,10) = 1.7, J(10,10a) = 4.0 Hz

Compound	1-H	2-H	3-H	4-H	6-H	7-H	8-H	9-H	10-H	10a-H	CH_3
8[a]	6.97 dtd	7.02 td	7.14 dddd	6.94 dd	6.72 dt	5.31 dq	6.49 ddt	6.06 dd	5.63 br. ddt	3.80 br. t	–
9[b]	7.14	7.04	7.16	6.97	6.68	5.22	6.47	5.96	–	3.47	2.05
10[c]	[d]	[d]	[d]	[d]	6.66	–	6.29	6.04	5.57	3.91	1.72
11	7.12	7.02	7.14	6.95	6.60	–	6.26	5.93	–	3.56	1.67, 2.00

[a] The assignments are based on NOE measurements. – [b] J(8,CH_3) = 0.6 Hz. – [c] J(9,CH_3) = 0.6 Hz. – [d] These signals are superimposed by those of **9**.

Table 1b. NMR data of epoxybenzo[*c*]chromene derivatives **8**−**11** in $CDCl_3$: ^{13}C-NMR chemical shifts [δ values, δ($CDCl_3$) = 77.0]; the assignments of the values in *italics* may be interchanged

Compound	C-1	C-2	C-3	C-4	C-4a	C-6	C-6a	C-7	C-8	C-9	C-10	C-10a	C-10b	CH_3
8[a]	125.2	123.6	127.4	116.0	153.1	134.1	*120.4*	77.6	137.4	130.1	80.4	38.9	*123.9*	–
9	124.2	123.5	127.4	116.2	153.5	*133.7*	*123.4*	77.1	137.8	*133.2*	88.9	43.4	*124.1*	19.8
10	125.3	123.6	127.3	116.0	153.0	134.0	[b]	85.7	140.6	130.8	80.0	41.0	*124.1*	15.2
11	124.4	123.5	127.4	116.3	153.3	134.4	*127.2*	84.9	141.1	133.1	88.2	45.5	*124.2*	15.4, 20.0

[a] The assignments are based on a C,H-COSY spectrum. – [b] This signal was not observed; it was probably superimposed by another line of **10** or by one of **9**.

Table 2a. NMR data of epoxyxanthene derivatives **16**−**18** in $CDCl_3$: ^{1}H-NMR chemical shifts (δ values); the signal multiplicities and the coupling constants of **16** are representative; the latter were determined to be J(1,2) = 1.9, J(1,4) = 0.7, J(1,9) = 0.7, J(2,3) = 5.8, J(3,4) = 1.5, J(4,4a) = 4.3, J(4,9) = 0.7, J(4a,9) = 2.1, J(5,6) = 8.0, J(5.7) = 1.2, J(5,8) = 0.6, J(5,9) = 0.6, J(6,7) = 7.3, J(6,8) = 1.8, J(7,8) = 7.3 Hz

Compound	1-H	2-H	3-H	4-H	4a-H	5-H	6-H	7-H	8-H	9-H	CH_3
16	5.24 dt	6.82 br. dd	6.32 dd	5.34 ddt	5.11 br. dd	6.77 ddt	7.08 ddd	6.89 td	7.03 br. dd	6.23 br. d	–
17	5.16	6.79	6.12	–	4.74	6.79	7.07	6.88	7.02	6.18	1.83
18	–	6.57	6.11	–	4.80	6.79	7.07	6.88	7.03	6.12	1.67, 1.81

Table 2b. NMR data of epoxyxanthene derivatives **16**−**18** in $CDCl_3$: ^{13}C-NMR chemical shifts [δ values, δ($CDCl_3$) = 77.0]; the assignments of the values in *italics* may be interchanged

Compound	C-1	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-9	C-9a	C-10a	CH_3
16[a]	80.8	139.7	132.3	79.4	75.0	116.1	128.7	122.2	127.4	124.3	114.3	137.9	153.6	–
17	*80.3*	140.1	135.9	87.0	*79.3*	116.1	128.6	122.1	127.3	124.2	113.6	140.4	153.9	17.2
18	*87.5*	143.0	136.6	*86.5*	80.8	116.1	128.5	122.1	127.3	124.2	112.6	144.0	153.7	14.9, 17.3

[a] The assignments are based on a C,H-COSY spectrum.

a value of J(*exo*-1,2) ≈ 2.6 Hz on the basis of experience.[2b][21]

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Experimental Section

Instrumentation: See ref.[22].

(7α,10α,10aα)-10,10a-Dihydro-7,10-epoxy-7H-benzo[c]chromene (**8**): Potassium *tert*-butoxide (5.32 g, 47.5 mmol) was added in small portions to a stirred solution of 3-bromo-2*H*-chromene[18] (**7**, 5.00 g, 23.7 mmol) in freshly distilled furan (32.2 g, 473 mmol) over a period of 30 min at room temperature. The mixture was stirred vigorously for a further 3 h and then treated with water (50 ml). After separation of the layers, the aqueous phase was extracted with diethyl ether (3 × 100 ml). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, petroleum ether/diethyl ether, 20:1 for the first 1.5 l of eluate and 10:1 for a further 1.3 l) to give **8** (2.78 g, 59%) as yellowish crystals, m.p. 72−74°C. − ^{1}H, ^{13}C NMR: Table 1a, b. − $C_{13}H_{10}O_2$ (198.2): calcd. C 78.77, H 5.09; found C 78.42, H 5.07.

(*7α,10α,10aα)-10,10a-Dihydro-10-methyl-* (**9**) *and (7α,10α,10aα)-10,10a-Dihydro-7-methyl-7,10-epoxy-7H-benzo[c]chromene* (**10**): According to the procedure described for the preparation of **8**, from **7** (500 mg, 2.37 mmol) in 2-methylfuran, 139 mg (28%) of a brown solid, m.p. 52°C, was obtained, the NMR spectra of which (Table 1a, b) indicated it to be a 2.5:1.0 mixture of **9** and **10**. − $C_{14}H_{12}O_2$ (212.3): calcd. C 79.22, H 5.70; found C 79.66, H 6.23.

(7α,10α,10aα)-10,10a-Dihydro-7,10-dimethyl-7,10-epoxy-7H-benzo[c]chromene (**11**): According to the procedure described for the preparation of **8**, from **7** (500 mg, 2.37 mmol) in 2,5-dimethylfuran, 218 mg (41%) of **11** was obtained as a yellow oil. − ^{1}H, ^{13}C NMR: Table 1a, b. − $C_{15}H_{14}O_2$ (226.3): calcd. C 79.62, H 6.24; found C 79.66, H 6.23.

exo-2,2a-Dihydro-2-phenyl-1H-cyclobuta[b]chromene (**12**): According to the procedure described for the preparation of **8**, from **7** (500 mg, 2.37 mmol) in styrene, 230 mg (41%) of **12** was obtained as a colourless solid, m.p. 68−71°C, which decomposed at room temperature over a period of several hours. − ^{1}H NMR ($CDCl_3$): δ = 2.87 [dddd, J(1,1) = 14.5, J(1,2) = 9.5, J(1,8) = 2.5, J(1,2a) = 1.6 Hz, 1 H, 1-H_a], 3.30 [dddd, J(1,2) = 8.6, J(1,2a) = 2.7, J(1,8) = 0.9 Hz, 1 H, 1-H_b], 3.79 [td, J(2,2a) = 6.4 Hz, 2-H], 5.15 [dtd, J(2a,8) = 2.5 Hz, 2a-H], 6.17 [≈ tt, J(4,8) = 0.8 Hz, 8-H], 6.84 [ddt, J(4,5) = 7.9, J(4,6) = 1.2, J(4,7) = 0.6 Hz, 4-H], 6.89 [td, J(5,6) = J(6,7) = 7.3 Hz, 6-H], 7.02 [dd, J(5,7) = 1.8 Hz, 7-H], 7.07 (≈ td, 5-H), 7.23−7.43 (m, C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 33.4 (C-1), 48.4 (C-2), 80.0 (C-2a), 113.8 (C-8), 116.1 (C-4), 121.6 (C-6), 123.6 (C-7a), 126.66 (C-*o*), 126.72, 126.8 (C-7, C-*p*), 128.1 (C-5), 128.6 (C-*m*), 134.9 (C-8a), 141.3 (C-*i*). 153.9 (C-3a). − HRMS: calcd. for $C_{17}H_{14}O$ [M^+] 234.1045; found 234.1035.

tert-Butyl 2H-Chromen-2-yl Ether (**13**): Potassium *tert*-butoxide (861 mg, 7.68 mmol) was added in small portions to a stirred solution of **7** (500 mg, 2.37 mmol) in 5 ml of anhydrous tetrahydrofuran over a period of 30 min at room temperature, and stirring was continued for a further 3 h. Then, the vigorously stirred mixture was treated with water and diethyl ether until two layers were formed, which were separated. The aqueous phase was extracted with further diethyl ether (3 × 10 ml). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, to which 20% concentrated aqueous ammonia had been added; petroleum ether/diethyl ether, 50:1) to give **13** (383 mg, 79%) as a colourless solid, m.p. 103−105°C, which decomposed at room temperature over a period of several hours. The NMR spectra displayed the signals of the dichromenyl ethers **14** in addition to those of **13**. − ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, CH_3), 5.77 [dd, J(3,4) = 9.8, J(2,3) = 4.0 Hz, 3-H], 5.94 (d, 2-H), 6.68 (br. d, 4-H), 6.90 [br. d, J(7,8) = 8.0 Hz, 8-H], 6.93 [td, J(5,6) = J(6,7) = 7.3, J(6,8) = 1.2 Hz, 6-H], 7.11 [dd, J(5,7) = 1.5 Hz, 5-H], 7.18 (≈ td, 7-H). − ^{13}C NMR ($CDCl_3$): δ = 28.9 (q) and 75.3 (s) [$OC(CH_3)_3$], 89.6 (d, C-2), 116.6 (d, C-8), 120.8 (s, C-4a), 121.0, 121.1 (2 d, C-4,C-6), 125.8, 127.0, 129.0 (3 d, C-3,C-5,C-7), 151.3 (s, C-8a).

Bis(2H-chromen-2-yl) Ethers (**14**): These compounds were obtained according to the procedure described for the preparation of **13**, except that for the flash chromatography (petroleum ether/diethyl ether, 20:1) the SiO_2 was not treated with ammonia. In this way, from **7** (500 mg, 2.37 mmol), 198 mg (60%) of **14** was obtained as colourless crystals, m.p. 163−165°C (ref.[19] 163°C). The ^{1}H-NMR spectrum indicated the presence of both diastereomers of **14**, in the ratio 20:1, as well as a third component, the signals of which had the same intensity as those of the minor isomer **14** and which could have been the hemiacetal corresponding to **14**. − ^{1}H NMR ($CDCl_3$): **14** (major/minor isomer): δ = 5.85/5.76 [dd, J(3,4) = 9.7, J(2,3) = 3.9 Hz, 3-H], 6.10/6.29 (d, 2-H), 6.70/6.69 (br. d, 4-H), 6.90/6.98 [td, J(5,7) = 1.2 Hz, 7-H], 6.95/7.01 [br. d, J(5,6) = 8.2 Hz, 5-H], 7.05/7.12 [dd, J(7,8) = 7.6, J(6,8) = 1.7 Hz, 8-H], 7.18/7.24 [ddd, J(6,7) = 7.3 Hz, 6-H]; third component: δ = 2.95 (d, J = 8.0 Hz, OH), 5.94 [dd, J(3,4) = 9.7, J(2,3) = 3.9 Hz, 3-H], 5.98 (dd, 2-H), 6.72 (br. d, 4-H), the signals of 4-, 5-, 6-, 7- and 8-H were superimposed by those of **14**. − ^{13}C NMR ($CDCl_3$): **14** (major/minor isomer): δ = 90.1/94.5 (d, C-2), 116.5/116.7, 119.5/119.1, 121.8/121.5, 126.9/126.8, 127.1/126.9, 129.4/129.3 (6 d, C-3−8), 120.7/120.2 (s, C-4a), 150.9/151.2 (s, C-8a); third component: δ = 89.6 (C-2), 116.9, 120.9, 121.6, 126.1, 127.0, 129.6 (C-3−8), the signals of C-4a and C-8a were not observed due to their intensities being too low. Wulff and Wolf[19] prepared **14** by the reduction of coumarin with diisobutylaluminium hydride, but characterized the compound only by its m.p. and elemental analysis. To identify the products of our experiment beyond doubt, we repeated this reduction (60% yield, ref.[19] 70%) and obtained a 5:5:1 mixture of the diastereomers **14** and the aforementioned third component, as determined from the NMR spectra.

(1α,4α,4aα)-4,4a-Dihydro-1,4-epoxy-1H-xanthene (**16**): A solution of **8** (50 mg) in toluene (5 ml) was heated under reflux for 3 h. The mixture was then concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, petroleum ether/diethyl ether, 10:1 for the first 100 ml of eluate and 5:1 for a further 100 ml) to give **16** (44 mg, 88%) as a brown, waxy solid. − ^{1}H, ^{13}C NMR: Table 2a, b. − $C_{13}H_{10}O_2$ (198.2): calcd. C 78.77, H 5.09; found C 78.57, H 4.98.

(1α,4α,4aα)-4,4a-Dihydro-4-methyl-1,4-epoxy-1H-xanthene (**17**): A 2.5:1.0 mixture of **9** and **10** was treated according to the procedure described for the rearrangement of **8**. By flash chromatography, **17** (92% yield from **9**) was obtained as brownish-yellow crystals, m.p. 68°C, which probably contained ca. 5% of the isomer having the methyl group at C-1. − ^{1}H, ^{13}C NMR: Table 2a, b. − $C_{14}H_{12}O_2$ (212.3): calcd. C 79.22, H 5.70; found C 79.14, H 5.69.

(*1α,4α,4aα)-4,4a-Dihydro-1,4-dimethyl-1,4-epoxy-1H-xanthene* (**18**) was prepared from **11** according to the procedure described for the rearrangement of **8**: 78% yield, brown oil. − ^{1}H, ^{13}C NMR: Table 2a, b. − HRMS: calcd. for $C_{15}H_{14}O_2$ [M^+] 226.0995; found 226.0993.

Rearrangement of **11** *in the Presence of Furan:* A solution of **11** (65 mg, 0.29 mmol) and furan (39 mg, 0.58 mmol) in C_6D_6 (1 ml) was heated at 110°C in a sealed NMR tube. After 3 h, the NMR spectra indicated the presence of **11** and **18** in a ratio of 1.0:2.3. No **16** was observed.

☆ Dedicated to the memory of Prof. *Wolfgang R. Roth*.

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