50. Phototransformations of Some 2-Substituted 4*H*-Chromen-4-ones (4-Chromones) Related to the Antitumor Antibiotic Hedamycin[1])

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Dedicated with best wishes to Professor Dr. *Christoph Tamm* on the occasion of this 60th birthday

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Summary

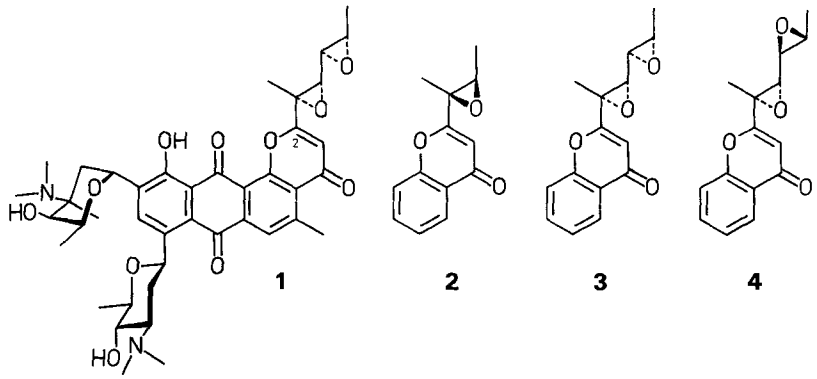
The 2-substituted 4*H*-chromen-4-ones (4-chromones) **2** and **3** have epoxy-substituted side chains at C(2) resembling that of the antibiotic hedamycin (**1**). They were chosen as model compounds and subjected to photolysis either in the presence or in the absence of oxygen. The products obtained were isolated by repeated HPLC., and their structures were determined by spectroscopic methods, mainly ^{1}H- and ^{13}C-NMR. Especially noteworthy are the oxygen dependent formation of the tertiary alcohols **11** and **12** as well as the transformation of the diepoxy-chromone **3** to the allylic alcohols **13** and **14**, the spiro compounds **15** and **16**, and the 2-ethylchromone **19**.

1. Introduction. – Hedamycin (**1**) is an antitumor active antibiotic of the pluramycin type, whose structure was recently determined in our laboratory [1]. It was observed some years ago during the investigation of its biological activity, that solutions of **1** rapidly lost most of their activity when exposed to day-light [2]. These findings prompted us to investigate the role of the diepoxy side chain in this photodeactivation process, since nothing was known about the photochemical behaviour of open chain diepoxides. *Jeger et al.*, however, have studied the photolyses of several epoxy-enones and even of a cyclic diepoxide related to the carotenoids [3].

The simple 2-substituted 4*H*-chromen-4-one (4-chromone) **2** and the more complicated compound **3**, which closely resembles hedamycin, were chosen as models. Both had been synthesized in our laboratory earlier [4] [5]. Thus, these compounds as well as a stereoisomer of **3**, *i.e.* **4**, were subjected to photolysis in the presence or absence of oxygen, the products isolated and their structures determined.

2. Procedure. – Irradiation was effected in the presence or in the absence of oxygen with a 75-W-high-pressure-mercury lamp, which was immersed into the solutions of the compounds. Toluene was

[1]) Part of the planned dissertation of *A. F.*



added to the solvents to filter off any radiation below 280 nm. Thus, only the π,π^*-transitions of the chromone around 300 nm were excited. The resulting activated chromone singlet is known to convert quantitatively to a long-living triplet state by intersystem crossing [6]. Products were separated and their amount determined by HPLC. techniques.

In the first series of irradiations, oxygen was bubbled through the solutions, thus somehow mimicking the standard laboratory conditions under which the photodeactivation of hedamycin was first observed (and where aerial oxygen was present). The second series was carried out in a pure argon atmosphere.

After irradiation and solvent removal, preparative HPLC. on silica gel with hexane/2-propanol was used to separate the products. The fractions thus obtained were further purified by HPLC. on semipreparative silica gel columns, mostly with hexane/CH_3CN/CH_2Cl_2 mixtures. The quantitative product distribution in the different experiments was derived directly from analytical HPLC. elution curves; monitoring was done at 298 nm, corresponding to the mean wavelength of the first two absorption maxima of the 2-substituted chromones. Since different 2-alkyl substituents should not significantly influence the extinction coefficient of this band (*cf.* [4] [5] and *Exper. Part, 2.2*), a correction was only taken into account for 2-acetyl-4-chromone (**7**) (see *Exper. Part, 2.1* and *7*). Chromatography of the photoproduct mixtures on a reversed phase column did not reveal any additional major products.

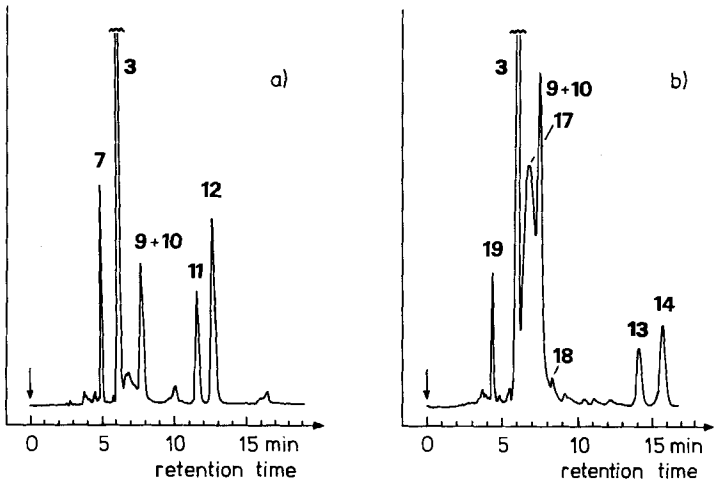


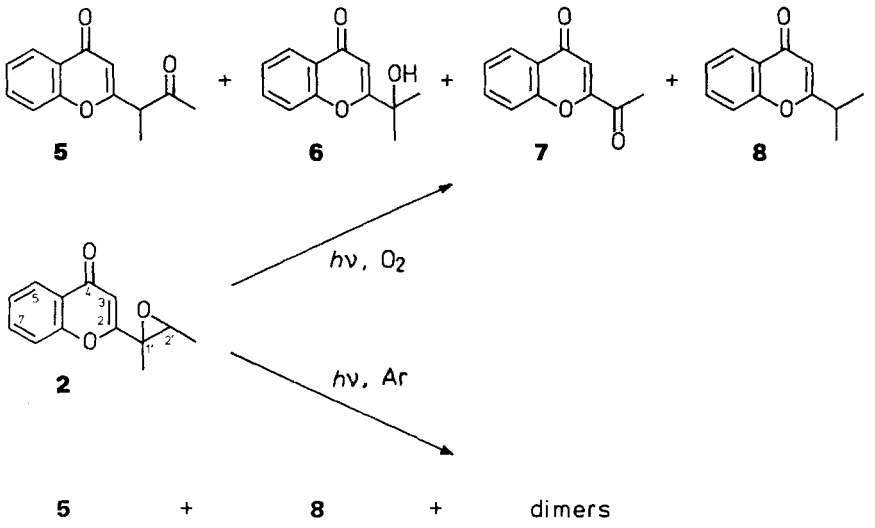
Fig. 1. *HPLC. traces of the product mixtures obtained after irradiation (20 min) of the diepoxychromone 3 in methanol, a) in the presence of oxygen, b) in the absence of oxygen.* Experimental conditions: analytical silica gel column, hexane/CH_3CN/CH_2Cl_2 56:23:21, 1.5 ml/min, monitored at 298 nm.

3. Results and discussion. – The two model compounds **2** and **3** were irradiated for different periods of time and in a variety of solvents. *Tables 1* and *2* summarize the results. They show that quite different products were formed depending on the presence or absence of oxygen (*cf.* also *Fig. 1*). Although the product distribution depends on the solvent, there is no direct correlation with the solvent polarity. Furthermore, it is noteworthy that none of the photoproducts observed needed a proton donor, such as methanol, for its formation.

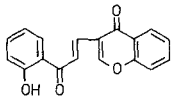
Not all the products formed in the photolyses could be isolated. But even when some minor products were taken into account, the total was mostly quite below 100 percent. A correlation was observed between the amount of products lacking and the appearance and intensity of a yellow coloration of the reaction solution. Dimerization[2]) or polymerization was thougth to be the reason for these observations.

In some photolysis experiments the amounts of dimers or polymers formed were estimated by separating the product mixture on a gel column and quantifying the monomers from the chromatogram trace by means of their UV. absorption (*cf. Table 1*). This supposed dimerization is observed to a greater extent when the photolysis is carried out in the absence of oxygen. Probably the presence of oxygen shortens the lifetime of the chromone triplet state, which is capable of dimerization.

The ketones **5** and **9/10** are typical photorearrangement products of epoxides (*cf.* [9]); in a similar way, **18** would be the rearrangement product of **17**.



[2]) A yellow dimer, **20**, of 4-chromone was obtained by *Schönberg et al.* [7] from a reaction of 4-chromone and sodium ethoxide. On the other hand, the photochemical behaviour of 4-chromone has also been studied [6], and a 'coupling product' [8] was observed, whose structure, however, is not yet published. It might well be compound **20**.



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Formal loss of CO from the starting molecules **2** and **3** leads to a second family of products comprising **8**, and **13**–**18**, respectively. Compounds **8** and **17** might have been formed by loss of CO from the corresponding ketones **5** and **9/10**, respectively; however, when ketone **5** was subjected to photolysis, none of the products shown in *Table 1* was found. But the starting epoxide **2** might generate ketone **5** in some kind of activated form, which then directly yields the decarbonylated product **8**. On the other hand, a probably direct CO-exclusion from epoxides has been observed [10]; in analogy to the photodecarbonylation of ketones [11], one might assume that loss of CO from epoxides will proceed in a solvent cage and be favoured when the radicals formed in the photochemical step are stabilized, a condition met by the radicals formed by fission of one of the oxirane bonds in **2** or **3**.

The photochemical formation of allyl alcohols was reported for β-methyl-α,β-epoxy ketones many years ago [12]; however, there is no analogy to the formation of allyl alcohols **13** and **14** described here. The two spiro compounds **15** and **16** are most certainly formed from the (*Z*)-allyl alcohol **13** by intramolecular addition of the hydroxy group to the chromone double bond (*cf.* [13]).

A comparison of the rates of formation of the ketone **5** and the tertiary alcohol **6** (*cf. Table 1*, exper. in methanol in the presence of oxygen) shows that the concentration of the latter is rather small after short irradiation periods. It still increases when most of the starting material is already consumed. From this the conclusion may be drawn that the alcohol **6** as well as **11/12** need at least two photons for their formation. These compounds might be the products of a reaction of the

Table 1. *Products obtained from photolysis of 2-[(1RS,2SR)-1,2-epoxy-1-methylpropyl]-4H-chromen-4-one* (**2**)

Solvent[a])	Period of irradiation [min]	Starting material **2** recovered[b])	Products[b]) **5**	**6**	**7**	**8**	Dimers and polymers	Sum of polar products
Photolyses under oxygen								
CH_3OH	10	45 ±1[c])	24±0.6	13 ±0.2	1.6±0.1	1.4±0.1	13	
CH_3OH	20	17 ±0.6	30±1.7	24 ±1	2.6±0.2	1.4±0.2	20	
CH_3OH	30	7.3±0.7	33±1.4	29 ±1	3.5±0.5	1.2±0.2	20	2
CH_3CN	30	12	27	7.9	2.7	1.4	60	
CH_2Cl_2	30	8.5	27	14	5.4	1.6	60	
Toluene	30	20	35	20	2.0	1.2		
Photolyses in the absence of oxygen								
CH_3OH	10	42 ±4	25±3	[d])	[d])	3.8±0.3		
CH_3OH	20	10 ±1	21±4	[d])	[d])	5.0±0.3	45	7
CH_3OH	30	2.5±0.2	11±3	[d])	[d])	5.0±0.7		
CH_3CN	20	28	22	[d])	[d])	4.4		
CH_2Cl_2	20	11	19	[d])	[d])	2.8		
Toluene	20	25	35	[d])	[d])	5.5		

[a]) Containing 3.5% *(v/v)* of toluene.

[b]) Yields in percent of the starting material subjected to photolysis (s. *Exper. Part, 7*).

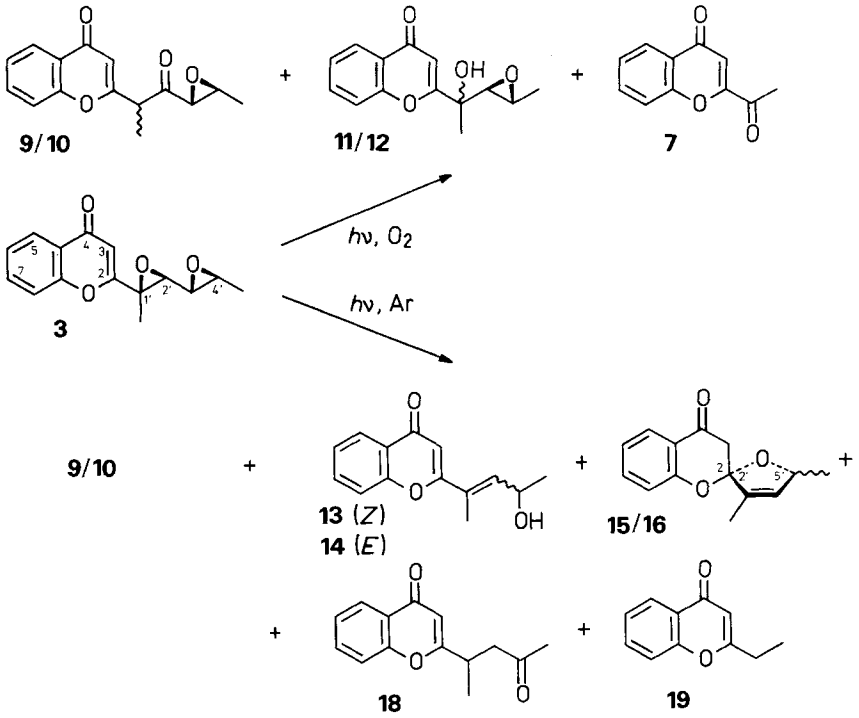
[c]) Values given in this format correspond to the mean from three independent photolyses, and the standard deviation.

[d]) Traces due to incomplete exclusion of oxygen.

Table 2. *Main products obtained from photolysis of 2-[(1*RS, *2*SR, *3*RS, *4*SR*)-1, 2:3, 4-diepoxy-1-methylpentyl]-4*H*-chromen-4-one* (**3**)

Solvent[a])	Period of irradiation [min]	Starting material **3** recovered[b])	Products[b])								
			7	**9/10**	**11**	**12**	**13**	**14**	**18**	**19**	Sum of polar products
Photolyses under oxygen											
CH_3OH	10	54±1[c])	4.6±0.1	12 ±0.7	4.0±0.1	6.9±0.1	[d])	[d])		[d])	
CH_3OH	20	27±0.2	9.0±0.1	10 ±0.6	8.1±0.2	14 ±0.2	[d])	[d])		[d])	7
CH_3OH	30	13±0.1	11 ±0.5	8.3±0.6	10 ±0.2	18 ±0.3	[d])	[d])		[d])	8
CH_3CN	20	16	2.1	3.7	0.9	1.9	[d])	[d])			
CH_2Cl_2	20	34	8.9	5.8	2.9	5.1	[d])	[d])			
Toluene	20	38	3.0	11	4.9	6.6	[d])	[d])		[d])	
Photolyses in the absence of oxygen											
CH_3OH	10	49±4		13 ±2	[e])	[e])	1.2±0.1	2.4±0.5	0.3	0.6±0.1	
CH_3OH	20	20±3		13 ±2	[e])	[e])	2.1±0.2	3.3±0.3	0.8	1.6±0.4	2
CH_3OH	30	9±1		9.6±0.5	[e])	[e])	2.6±1	4.3±1	1.3	2.6±0.5	
CH_3CN	20	14		3.0			1.1	1.9	0	0.5	
CH_2Cl_2	20	28		6.9			8.0	10	2.7	3.4	
Toluene	20	29		10	[e])	[e])	6.6	9.6	1.8	1.5	

[a])[b])[c]) See footnotes [a])[b])[c]) in *Table 1.* [d]) Traces (>0.5%). [e]) Traces due to incomplete exclusion of oxygen.



starting epoxides **2** or **3** with singlet oxygen, formed from $^3O_2$ with any chromone present in the solution acting as a sensitizer. Oxygen must be involved in the primary step during the formation of the alcohols **6**, and **11/12**; if these were only secondary products, the corresponding precursors should be detected in the analogous experiments under argon. The by-product of the reaction seems to be CO_2[3]). To our knowledge, no similar photochemical transformation of epoxides into alcohols has been reported. This is astonishing, since the photochemistry of epoxides has been studied quite often [15].

The alcohols **11** and **12** are diastereoisomers. Their ratio depends on the solvent, but not on the duration of irradiation or on the configuration of the starting material. This could be demonstrated by comparing the irradiation of the (1*RS*, 2*SR*, 3*SR*, 4*RS*)-1,2 : 3,4-diepoxy compound **4** with that of the (1*RS*, 2*SR*, 3*RS*, 4*SR*)-isomer **3**. In both cases **11** and **12** were formed in the same ratio.

The pathway leading to 2-acetyl-4-chromone (**7**) is nuclear. However, **7** is definitely not a secondary product of the tertiary alcohol **6**, since irradiation of **6** under oxygen did not lead to **7** or any other product mentioned in *Table 1*. Compounds **6** and **7** might, however, share a common precursor.

The 2-ethylchromone **19** was only isolated from the photolysis of the diepoxy compound **3**; it was not detected among the photoproducts generated from the simpler model **2**.

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[3]) The direct photochemical loss of CO_2 is rare, except with esters (*e.g.* [14]).

The results presented here do not give a direct clue to the nature of the photodeactivation of the antibiotic hedamycin. The photoreactions found are characteristic for the diepoxy side chain only, and not for hedamycin itself, where besides these reactions others may take place involving other parts of the complex molecule. Furthermore, photochemical alteration of the side chain of the antibiotic is not expected to greatly affect the biological activity, since quite a number of highly active compounds of the pluramycin type are known, which just differ in the structure of this side chain at C(2).

4. Structure elucidations (s. *Tables 3* and *4*). – 4.1. *Photoproducts obtained from 2-[1*RS,2SR)-1,2-*Epoxy-1-methylpropyl]-4*H-*chromen-4-one* (**2**) (4*H*-chromen-4-one = 4-chromone). 4.1.1. *2-(1-Methyl-2-oxopropyl)-4*H-*chromen-4-one* (**5**). The two carbonyl absorptions at 1650 and 1725 cm^{-1} observed in the IR. spectrum of **5** indicated that the side chain attached to the still intact 4-chromone nucleus had to contain a ketone function; the elemental analysis ($C_{13}H_{12}O_3$) precluded an ester. The ^{1}H-NMR. spectrum revealed the chromone nucleus, an acetyl CH_3-group and a CH_3CH-fragment. The proposed structure was corroborated by the ^{13}C-NMR. spectrum: the resonances observed at 28.2 and 203.7 ppm are typical for methyl ketones.

4.1.2. *2-(1-Hydroxy-1-methylethyl)-4*H-*chromen-4-one* (**6**). Compound **6** showed IR. bands at 3580 and 3360 cm^{-1} for a hydroxy group and at 1635 cm^{-1} for an intact 4-chromone nucleus. The ^{1}H- and ^{13}C-NMR. spectra confirmed the proposed structure. In the ^{1}H-NMR. spectrum ($(CD_3)_2SO$), a one-proton singlet at 5.69 ppm disappeared upon addition of D_2O to the sample. It had to correspond to a tertiary hydroxy group. A hydroperoxide could be excluded, since the OH-proton of *t*-butylhydroperoxide appears at 11.73 ppm. Furthermore, this spectrum revealed the intact 2-substituted 4-chromone system as well as a six-proton singlet at 1.5 ppm corresponding to two equivalent methyl groups. In the ^{13}C-NMR., the chemical shifts of the aliphatic C-atoms correspond nicely to those found in *α*-cumyl alcohol (72.2 and 31.5 ppm [16]).

4.1.3. *2-Acetyl-4*H-*chromen-4-one* (**7**). The structure of **7** could be derived from its ^{1}H-NMR. spectrum and by comparison with an authentic sample prepared by periodic acid cleavage of **2** in dioxane (identical chromatographic behaviour and ^{1}H-NMR. spectra).

4.1.4. *2-Isopropyl-4*H-*chromen-4-one* (**8**). The ^{1}H-NMR. spectrum of **8** showed only the resonances of an isopropyl group besides the pattern of the H-atoms of the 2-substituted 4-chromone. The chemical shift of H–C(3) corroborated the aliphatic, non-conjugated substitution at the 2-position. The ^{13}C-NMR. and mass spectra were fully consistent with this structure.

4.2. *Photoproducts obtained from 2-[(1*RS,2SR,3RS,4SR)*-1,2:3,4-diepoxy-1-methylpentyl]-4*H-*chromen-4-one* (**3**). 4.2.1. *2-[(3*RS,4SR)*-3,4-Epoxy-1-methyl-2-oxopentyl]-4*H-*chromen-4-ones* (**9/10**). The photoproducts **9/10** were isolated as a 1:1 diastereomeric mixture (NMR.) that could not be separated.

The ^{1}H-NMR. spectrum of **9/10** showed the typical pattern of the 4-chromone protons, the singlet of H–C(3) for each of the two isomers, the pattern of a 1,2-epoxypropyl and of a $CHCH_3$ moiety. The ^{13}C-NMR. signals of the 4-chromone C-atoms of **9/10** were single lines with the exception of those from C(2) and C(3), which gave separate lines for the two isomers ($\Delta\delta = 0.1$ ppm). The chemical shifts again indicated an intact 4-chromone; the value for C(2) pointed to a non-conjugated C(2)-substituent and resembled the one for C(2) in **5**. The side chain C-atoms gave rise to pairs of resonances, each separated by less than 1 ppm. The signals of a 1,2-epoxypropyl moiety, of an aliphatic ketone carbonyl and of C(1′) and CH_3–C(1′) could easily be attributed. The latter two had chemical shifts (46 and 14 ppm) that came very close to those of **5**, especially when the different influences of the CH_3 (in **5**) and the 1,2-epoxypropyl moiety (in **9/10**) were taken into account [17].

Neither in the ^{1}H-NMR. nor in the ^{13}C-NMR. spectra it was possible to allocate definite sets of resonances to each of the two isomers. The IR. spectrum displayed two carbonyl resonances at 1720 and 1640 cm^{-1}, which was consistent with the proposed structures, as was the mass spectrum (M^+ at *m/z* 258 and typical ions documenting the fragmentation of the side chain).

4.2.2. *2-(2*RS,3SR)*-2,3-Epoxy-1-hydroxy-1-methylbutyl]-4*H-*chromen-4-ones* (**11** *and* **12**). The photoproducts **11** and **12** had very similar IR., ^{1}H- and ^{13}C-NMR. spectra suggesting diastereoisomerism. The IR. spectra showed the 4-chromone carbonyl resonance and an OH band. The proposed structures

Table 3. *^{1}H-NMR. data of* **2**, **3**, *and* **5–19**[a])

	H–C(3)	H–C(5)	H–C(6–8)	H–C(1′)	H–C(2′)
2[b])	6.40 (*s*)	8.18 (br. *d*, *J* = 8)	7.8–7.2 (*m*)		3.25 (*qa*, *J* = 6)
3[c])	6.40 (*s*)	8.15 (br. *d*, *J* = 8)	7.8–7.2 (*m*)		3.07 (*d*, *J* = 5)
5	6.31 (*s*)	8.19 (br. *d*, *J* = 8)	7.8–7.3 (*m*)	3.73 (*qa*, *J* = 7)	
6[d])	6.43 (*s*)	8.03 (br. *d*, *J* = 8)	8.0–7.4 (*m*)		1.50 (*s*)
7	6.99 (*s*)	8.22 (br. *d*, *J* = 8)	7.9–7.3 (*m*)		2.65 (*s*)
8	6.19 (*s*)	8.18 (br. *d*, *J* = 8)	7.8–7.3 (*m*)	2.87 (*sept.*, *J* = 7)	1.32 (*d*, *J* = 7)
9[f])	6.27 (*s*)	8.18 (br. *d*, *J* = 8)	7.8–7.3 (*m*)	3.91 (*qa*, *J* = 7)	
10[f])	6.30 (*s*)	8.18 (br. *d*, *J* = 8)	7.8–7.3 (*m*)	3.83 (*qa*, *J* = 7)	
11	6.58 (*s*)	8.21 (br. *d*, *J* = 8)	7.8–7.3 (*m*)		3.14 (*d*, *J* = 2)
12	6.59 (*s*)	8.21 (br. *d*, *J* = 8)	7.7–7.4 (*m*)		3.31 (*d*, *J* = 2)
13	6.32 (*s*)	8.19 (br. *d*, *J* = 8)	7.8–7.2 (*m*)		5.86 (*m*)
14	6.38 (*s*)	8.17 (br. *d*, *J* = 8)	7.8–7.2 (*m*)		6.67 (*d*×*d*, *J* = 8 and 1.3)
15	3.26 and 2.73 (*AB*, *J* = 16)	7.90 (br. *d*, *J* = 8)	7.6–6.9 (*m*)		
16	3.21 and 2.73 (*AB*, *J* = 16)	7.90 (br. *d*, *J* = 8)	7.6–6.9 (*m*)		
17	6.27 (*s*)	8.20 (br. *d*, *J* = 8)	7.8–7.3 (*m*)	2.67 (*qi*, *J* = 7)	2.96 (*m*)
18	6.21 (*s*)	8.19 (br. *d*, *J* = 8)	7.7–7.3 (*m*)	3.32 (*m*)	2.95 (*d*×*d*, *J* = 18 and 6) 2.70 (*d*×*d*, *J* = 18 and 7)
19	6.19 (*s*)	8.18 (br. *d*, *J* = 8)	7.8–7.2 (*m*)	2.68 (*qa*, *J* = 7)	1.32 (*t*, *J* = 7)

[a]) Chemical shifts in ppm downfield from internal TMS (= 0 ppm); coupling constants *J* in Hz; solvent: $CDCl_3$.

Table 4. *^{13}C-NMR. data of* **2**, **3**, **5–12**, **14** *and* **19**[a])

	C(2)	C(3)	C(4)	C(1′)	C(2′)	C(3′)
2[c])	168.3	107.3	178.1	57.6	61.3	13.9
3[d])	166.4	107.6	177.5	57.6	63.6	55.4
5	166.7	110.8	117.9	52.5	203.7	28.2
6	174.1	106.4	179.0	71.3	28.3	
7	155.6	111.5	178.2	192.4	25.9	
8	174.1	107.7	178.5	33.4	20.1	
9[e])	165.9	110.9	177.9	46.0	203.2	54.9*
10[e])	165.8	110.8	177.9	46.9	202.3	55.1*
11	169.7	107.8	178.3	70.6	63.2	51.9
12	170.6	107.9	178.3	70.7	62.5	51.3
14	163.9	108.0	178.9	127.4	139.4	64.9
19	170.6	108.7	177.5	27.4	10.9	

[a]) Chemical shifts given in ppm downfield from internal TMS (= 0 ppm). Assignments with asterisks may be interchanged. Multiplicities were only determined for **19**; resonances of quaternary C-atoms were, however, easily

H–C(3′)	H–C(4′)	H–C(5′)	H_3C–C(1′)	other	
1.46 (*d*, *J* = 6)			1.67 (*s*)		
2.79 (*d* × *d*, *J* = 5 and 2)	3.05 (*qa* × *d*, *J* = 5 and 2)	1.42 (*d*, *J* = 5)	1.81 (*s*)		
2.26 (*s*)			1.51 (*d*, *J* = 7)		
			1.50 (*s*)	5.69 (*s*)[e]	
			1.32 (*d*, *J* = 7)		
3.37 (*d*, *J* = 2)	3.25 (*qa* × *d*, *J* = 5 and 2)	1.42 (*d*, *J* = 5)	1.51 (*d*, *J* = 7)		
3.35 (*d*, *J* = 2)	3.14 (*qa* × *d*, *J* = 5 and 2)	1.35 (*d*, *J* = 5)	1.49 (*d*, *J* = 7)		
3.15 (*qa* × *d*, *J* = 5 and 2)	1.32 (*d*, *J* = 5)		1.73 (*s*)	2.55 (br.)[e]	
3.22 (*qa* × *d*, *J* = 5 and 2)	1.42 (*d*, *J* = 5)		1.61 (*s*)	2.77 (br.)[e]	
4.9 (br. *m*)	1.40 (*d*, *J* = 6)		2.09 (*d*, *J* = 1.5)		
4.81 (*qa* × *d*, *J* = 6 and 8)	1.40 (*d*, *J* = 6)		1.98 (*d*, *J* = 1.2)	2.1 (br.)[e]	
5.87 (*qi*, *J* = 2)		4.95 (*qa* × *qi*, *J* = 6.5 and 2)		1.90 (*t*, *J* = 2)[g]	1.22 (*d*, *J* = 6.5)[h]
5.88 (*qi*, *J* = 2)		4.84 (*qa* × *qi*, *J* = 6.5 and 2)		1.90 (*t*, *J* = 2)[g]	1.25 (*d*, *J* = 6.5)[h]
2.96 (*m*)	1.38 (*d*, *J* = 5.5)		1.40 (*d*, *J* = 7)		
	2.20 (*s*)		1.33 (*d*, *J* = 7)		

[b]) Data from [4]. [c]) Data from [5]. [d]) Solvent: $(CD_3)_2SO$. [e]) OH. [f]) (1:1)-Mixture of **9** and **10**; it is not possible to assign the resonances to the different isomers. [g]) H_3C–C(3′). [h]) H_3C–C(5′).

C(4′)	C(5′)	H_3C–C(1′)	Other C-atoms[b])
		14.0	124.0, 125.8*, 125.3*, 133.7, 118.0, 156.3
51.5	17.1	14.7	123.8, 125.5*, 125.3*, 133.8, 118.0, 156.1
		13.8	123.8, 125.8*, 125.4*, 133.9, 118.0, 156.5
		28.3	123.7, 125.8*, 125.1*, 133.7, 118.0, 156.4
			124.5, 125.9*, 125.7*, 134.8, 118.6, 156.7
		20.1	124.0, 125.8*, 124.9*, 133.4, 117.9, 156.7
59.8*	17.5	14.2	123.8, 125.9*, 125.4*, 133.9, 117.9, 156.4
59.8*	17.4	14.0	123.8, 125.9*, 125.4*, 133.9, 117.9, 156.4
16.9		25.0	124.0, 125.9*, 125.3*, 133.7, 117.9, 156.3
17.0		22.8	123.9, 125.9*, 125.3*, 133.8, 117.9, 156.3
23.1		12.9	123.7, 125.7*, 125.0*, 133.8, 118.0, 156.1
			123.7, 125.3*, 124.8*, 133.3, 117.9, 156.4

detected (low intensity). [b]) Given in the following order: C(4a), C(5), C(6), C(7), C(8), C(8a). [c]) Data from [4]. [d]) Data from [5]. [e]) (1:1)-Mixture of **9** and **10**; it is not possible to assign the resonances to the different isomers.

were fully corroborated by the ^{1}H-NMR., ^{13}C-NMR. and mass spectra. It was not possible, however, to assign the configurations at C(1') of the two diastereoisomers **11** and **12**.

In the ^{1}H-NMR. spectrum ($(CD_3)_2SO$) of **12** the singlet of the OH group appeared at 5.85 ppm (disappeared upon addition of D_2O); this value and that of a singlet methyl resonance were very similar to those of **6**, thus suggesting a close structural relationship. The two oxirane protons gave a complex pattern of higher order splitting at 90 MHz; in a 360-MHz spectrum of a (2:3)-mixture of **11** and **12**, however, separated signals for **12** and almost separated ones for **11** could be obtained and attributed unequivocally to the 1,2-epoxypropyl moiety, their chemical shifts and coupling constants being in good agreement with the ones of the starting material **3**. The NMR. spectra furthermore contained the expected resonances of the 2-substituted 4-chromone part.

4.2.3. *2-[(Z)-3-Hydroxy-1-methyl-1-butenyl]-4*H*-chromen-4-one* (**13**). Only a very small amount of moderately pure photoproduct **13** could be obtained. Its ^{1}H-NMR. spectrum resembled very closely that of **14** (s. below); however, the olefinic proton appeared at 5.86 ppm suggesting that **13** was the (*Z*)-isomer of **14**. The observation that **13** slowly isomerized to **14** confirmed the structure.

4.2.4. *2-[(E)-3-Hydroxy-1-methyl-1-butenyl]-4*H*-chromen-4-one* (**14**). The IR. spectrum of **14** showed the carbonyl absorption of the intact 4-chromone at 1660 cm^{-1} as well as a broad OH band at 3400 cm^{-1}. The ^{1}H-NMR. spectrum ($(CD_3)_2SO$) proved this OH group to be a secondary alcohol. The structure of the substituent at C(2) of the 4-chromone nucleus was again derived from the ^{1}H-NMR. data and spin decoupling experiments.

A methyl group appeared at 1.4 ppm as a doublet ($J = 6$ Hz). It was coupled to the proton (4.81 ppm) attached to the OH-bearing C-atom. This latter was further coupled to an olefinic proton ($J = 8$ Hz, 6.67 ppm), which in turn was split by allylic coupling to a methyl group having its resonance at 1.98 ppm. These data led to the side chain shown in formula **14**. The configuration of the double bond could be derived from the ^{13}C-NMR. spectrum. Assignment of C(1') and C(2') was straightforward, and the resonances of C(3') and C(4') (23.1 ppm) were easily recognized by comparison with 4-methyl-3-penten-2-ol [18]. The chemical shift of 12.9 ppm for CH_3–C(1') is indicative for the (*E*)-configuration of the double bond (*cf. e.g.* [4]).

The mass spectrum was consistent with the proposed structure.

4.2.5. *Spiro[4-chromanone-2,2'-(3',5'-dimethyl-2',5'-dihydrofurans)]* (**15** *and* **16**). The spectral data for **15** and **16** were almost identical, thus indicating two diastereoisomers. Their ^{1}H-NMR. spectra were consistent with the proposed structures.

In the ^{1}H-NMR. spectrum of **16** (*cf. Fig. 2* and *Tab. 3*) the typical singlet of the 4-chromone H–C(3) at 6–6.5 ppm was absent. Furthermore, the pattern of the aromatic resonances was shifted towards higher field with respect to the 4-chromones; this is typical for 4-chromanones [19]. The *AB* spectrum centered at 3 ppm was attributed to two geminal but otherwise isolated protons. The methyl group at 1.25 ppm (doublet) was coupled ($J = 6.5$ Hz) to a proton at 4.84 ppm. A second methyl group, obviously attached to a double bond, appeared as a narrow triplet at 1.9 ppm. A double resonance experiment showed it to be coupled ($J = 2$ Hz) to an olefinic proton at 5.88 ppm (narrow quintuplet) as well as to the above-mentioned proton at 4.84 ppm ($J = 2$ Hz). This latter proton was further coupled ($J = 2$ Hz) to the olefinic proton. These data led to the structures shown for **15** and **16**. *Dreiding* models showed that the dihedral angle between H–C(4') and H–C(5') was between 50 and 70°, depending on the conformation of the dihydrofuran ring. This led to the rather small coupling constant observed.

The mass spectrum of **16** corroborated the derived structure. It showed a relatively large signal for M^+ at *m/z* 230. In the IR. spectrum, the carbonyl group appeared now at higher wavenumbers (1690 cm^{-1}, typical for phenyl ketones) compared with the 4-chromones. It was not possible to assign the configurations at C(5').

4.2.6. *2-[(2*RS*,3*SR*)-2,3-Epoxy-1-methylbutyl]-4*H*-chromen-4-one* (**17**). According to the IR. absorption at 1650 cm^{-1}, compound **17** contained the intact chromone nucleus. This was confirmed by the usual resonances in the ^{1}H-NMR. spectrum.

Double resonance experiments revealed the signals of two $CHCH_3$ moieties. One of these seemed to belong to a methyl substituted oxirane, as could be seen from the coupling constant ($J = 5.5$ Hz) and the methine chemical shift (2.96 ppm). The other one was coupled to an additional CH (2.96 ppm), which also had to be part of the oxirane moiety. In C_6D_6, separated resonances were observed for the two oxirane protons, each with $J = 2$ Hz.

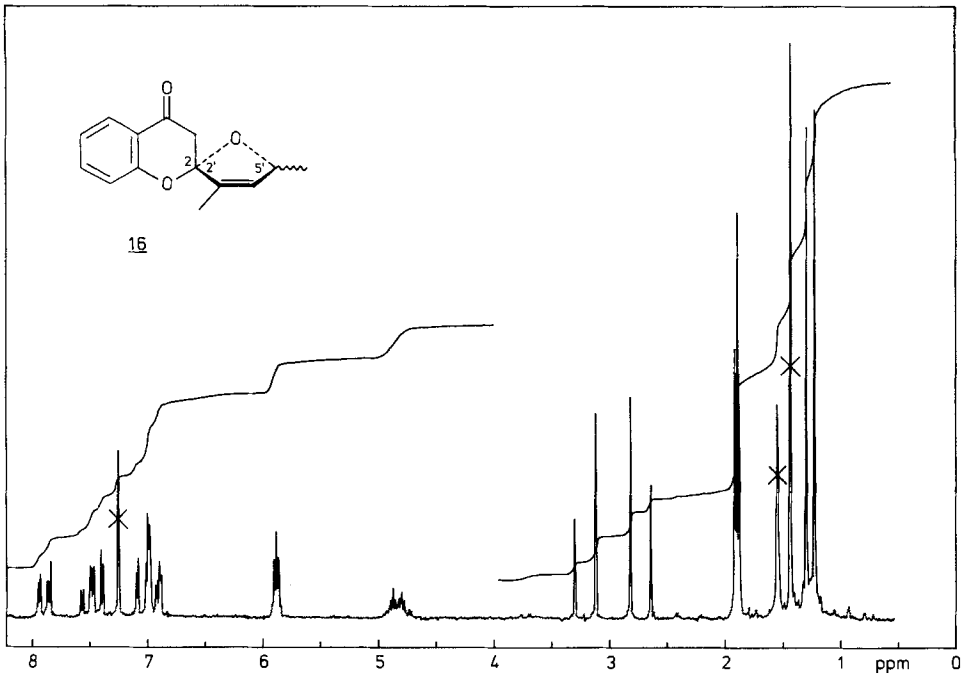

Fig. 2. *90-MHz-^{1}H-NMR. spectrum of the spiro compound **16** in $CDCl_3$.* The crossed peaks correspond to $CHCl_3$ (7.25 ppm), H_2O (1.55 ppm) and an unidentified impurity (1.42 ppm)

Thus, structure **17** seemed reasonable for this photoproduct. The mass spectrum was consistent with this proposal, showing M^+ at *m/z* 230 and a fragmentation pattern closely related to that of **18**.

4.2.7. *2-(1-Methyl-3-oxobutyl)-4*H*-chromen-4-one* (**18**). The IR. spectrum of **18** displayed two carbonyl resonances, belonging to the intact 4-chromone system (1650 cm^{-1}), and, at 1720 cm^{-1}, to an aliphatic ketone. The ^{1}H-NMR. spectrum confirmed structure **18**.

Besides the chromone resonances, a singlet at 2.20 ppm was attributed to an acetyl CH_3 group, and a doublet at 1.33 ppm and a multiplet at 3.32 ppm to a $CHCH_3$ moiety. This latter methine proton was further coupled to a methylene group, which gave rise to an *AB* system centered around 2.8 ppm whose lines were each split into a doublet.

Structure **18** was corroborated by the MS., which showed M^+ at *m/z* 230. The spectrum further contained prominent signals at *m/z* 215, 187, 173, 159, 145 corresponding to successive fragmentation of the side chain, starting from its end.

4.2.8. *2-Ethyl-4*H*-chromen-4-one* (**19**). The ^{1}H-NMR. spectrum of **19** suggested the proposed structure which was confirmed by comparison with an authentic sample synthesized in analogy to [20] (identical IR. and ^{1}H-NMR. spectra, and HPLC. retention times in hexane/tetrahydrofuran 82:18 and hexane/CH_2Cl_2/CH_3CN 75:15:10).

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Experimental Part

1. General remarks. – The apparatus for the photolyses consisted of a 75 W Hg high pressure lamp *TQ 81* (*Quarzlampen GmbH*, Hanau) fitted with a silica cooling jacket. This lamp assembly was immmersed in a 290-ml vessel having a gas inlet with sintered glass disk at the bottom and an opening

at the top, which permitted venting or sample taking. For reactions in the presence of oxygen, a slow stream of technical grade O_2 was bubbled through the reaction solution before and during the irradiation. For irradiations in the absence of oxygen, the solutions were deoxygenated for at least 2 h before as well as during the irradiation by passing 99.998% Ar through it which had been purified by passing it twice through a mixture of 15 ml of 25% pyrogallol solution (*Merck*, for oxygen absorption) and 75 ml of 55% KOH solution, and then through conc. sulfuric acid.

The following instruments were used for HPLC. analyses: on a preparative scale: *DuPont* liquid chromatograph *830*, fixed wavelength detector (254 nm). Semipreparative and analytical separations: *Spectra Physics* pump and gradient mixer *SP 8700*, variable wavelength detector *SP 8400*, *Hewlett Packard* integrator *3380 A*. Columns: prep.: silica gel, 25×250 mm, *LiChrosorb Si 60*, 7 μm *(DuPont)*; semiprep.: silica gel, 8×250 mm, *LiChrosorb Si 60*, 7 μm (*Knauer AG*, Oberursel, FRG); reversed phase, 8×250 mm, *LiChrosorb RP 18 (Knauer)*; anal.: silica gel, 4.6×250 mm, *LiChrosorb Si 60*, 7 μm *(Knauer)*; reversed phase, 3.9×300 mm μ-*Bondapak C18* (*Waters Ass.*, Milford, USA); gel chromatography: 7.8×300 mm, μ-*Styragel* 100 Å *(Waters)*. Solvents: Acetonitrile *puriss. (Fluka)*, chloroform for chromatography, stabilized with amylene *(Merck)*, hexane for HPLC. (*Fisions*, Loughborough, GB), 2-propanol for HPLC. *(Fisions)*, methanol absolute *(Baker)*, dichloromethane techn. redistilled *(Chem. Fabrik Schweizerhalle)*, tetrahydrofuran for HPLC. freshly distilled from ferrous sulfate *(Fluka)*. – Solvents were removed *in vacuo* at 30–35° using a rotary evaporator. – Melting points were determined on a *Kofler* hot stage and are corrected. – UV./VIS. spectra were measured in 96% ethanol (*Fluka*, 'for UV. spectroscopy') on a *Varian Cary 219* spectrometer. – IR. spectra in $CHCl_3$ or KBr were determined on a *Beckmann IR-8* or a *Perkin-Elmer 125*. – The following instruments served for the recording of NMR. spectra: *Bruker WH 90*, *Bruker WP 200 SY* (Pharmazeutisches Institut der Universität Basel), *Bruker WH 360* (*P. Hug*, *Ciba-Geigy AG*, Basel). – Mass spectra were run either on the *AEI MS 30* of the physikalisch-chemisches Institut (Dr. *J.-P. Stadelmann*) or on a *Varian MAT CH7* at *Ciba-Geigy*, Basel (courtesy Dr. *W. Richter*), or on the GLC./MS. *5995 A* of *Hewlett Packard*, Widen (Dr. *F. Küderli*). FD. mass spectra were kindly measured by Dr. *W. Richter* on a *Varian CH 5-DF*. Elemental analyses were carried out in the analytical laboratory of our Institut *(E. Thommen)*. The skillful help of *K. Aegerter* with some of the IR. and NMR. measurements is gratefully acknowledged.

2. Syntheses. – 2.1. *2-Acetyl-4*H*-chromen-4-one* (**7**) *from* **2**. To a solution of **2** (130 mg, 0.6 mmol) in 20 ml of dioxan *(Fluka, puriss.)*, periodic acid (550 mg, 2.4 mmol, *Fluka, p.a.*) was added, and the suspension obtained was stirred at room temp. for 16 days. The solvent was evaporated and the residue distributed between 30 ml of 2N Na_2CO_3 and 50 ml of CH_2Cl_2. The org. layer was washed successively with 30 ml of water and 30 ml of sat. NaCl-solution, whereas the aq. phase was extracted twice with 50 ml of CH_2Cl_2. The org. extracts were combined, dried over Na_2SO_4, and the solvent was removed. Yellowish crystals were obtained (123 mg) and recrystallized from 1 ml of ethanol to give 70 mg (62%) of **7**. An analytical sample was obtained after recrystallization from toluene/cyclohexane as colourless needles of m.p. 138–139.5° (subl.; [21]: 135–137°, from benzene/petrol ether). – UV. (ethanol): 203 (15400), 235 *S* (12500), 242 (13500), 263 *S* (5130), 306 (5710). – ^{1}H-NMR. (90 MHz, $CDCl_3$): s. *Tab. 3* and [21]. – ^{13}C-NMR. (22.63 MHz, *ca.* 1.4M in $CDCl_3$): s. *Tab. 4*.

$C_{11}H_8O_3$ (188.18) Calc. C 70.21 H 4.29% Found C 69.94 H 4.41%

2.2. *2-Ethyl-4*H*-chromen-4-one* (**19**) was synthesized in analogy to [20]. – UV. (ethanol): 223 (21000), 241 *S* (9100), 262 (7100), 295 (7400), 299 *S* (7200). – ^{1}H-NMR. (*ca.* 4M in $CDCl_3$): s. *Tab. 3*. – ^{13}C-NMR. (*ca.* 4M in $CDCl_3$): s. *Tab. 4*.

$C_{11}H_{10}O_2$ (174.20) Calc. C 75.84 H 5.79% Found C 75.49 H 6.02%

3. Photolysis of 2-[(1*RS*,2*SR*)-1,2-epoxy-1-methylpropyl]-4*H*-chromen-4-one (**2**). – 3.1. *Under oxygen.* A solution of **2** (typically 26 mg, in some cases 100 mg) in 280 ml of abs. methanol and 10 ml of toluene was irradiated in the presence of O_2 (s. *1*) for 30 min (1 h when 100 mg of **2** were used), then the solvents were removed to give the products as a yellow oil. Thereof, 208 mg were separated by prep. HPLC. (6 injections, hexane/2-propanol 94:6, 26 ml/min, 48 bar) into 4 fractions. Fraction 1 contained 4 minor products in small amounts and was not investigated further. Fraction 2 contained mainly **2**. Fraction 3 yielded, after purification on the semiprep. silica gel column (hexane/CH_3CN/CH_2Cl_2 56:23:21, 4 ml/min), 53 mg of *2-(1-hydroxy-1-methylethyl)-4*H*-chromen-4-one* (**6**). Fraction 4 was purified in the same way and gave 46 mg of *2-(1-methyl-2-oxopropyl)-4*H*-chromen-4-one* (**5**).

In a different experiment (carried out by *W. Zaugg*), 707 mg of product mixture were separated by prep. HPLC. as above into 6 fractions. Fraction 1: 69 mg of a mixture of minor products that were not investigated further. Fraction 2: 48 mg, which were rechromatographed on the semiprep. silica gel column (hexane/CH_2Cl_2/CH_3CN 75:18:7, 4 ml/min); *2-isopropyl-4*H*-chromen-4-one* (**8**, 5.5 mg) resulted as a colourless oil. Fraction 3: 102 mg of **2**. Fraction 4: 34 mg, consisting mainly of *2-acetyl-4*H*-chromen-4-one* (**7**). Fraction 5: 104 mg of **6**. Fraction 6: 129 mg of **5**.

3.2. *Under exclusion of oxygen.* As in *3.1*, but in the absence of O_2 (s. *1*), **2** (100 mg, 0.46 mmol) was irradiated for 35 min. Of the crude yellow oil, 765 mg were dissolved in 4.8 ml of 2-propanol and separated by prep. HPLC. (10 injections, hexane/2-propanol 94:6, 22 ml/min) into 5 fractions. Fraction 1: 90 mg of a mixture of minor products, which were not investigated further. Fraction 2: 82 mg of impure **8**, which were further purified on the semiprep. silica gel column (hexane/CH_2Cl_2/CH_3CN 75:18:7, 4 ml/min) to yield 27 mg of **8** as an almost colourless oil. Fraction 3: 146 mg of **2**. Fraction 4: 166 mg of a mixture of **2** and *ca.* 10 minor products, which were not investigated further. Fraction 5: 130 mg of **5**.

Data of **5**. Colourless oil. – IR. ($CHCl_3$): 2990, 1725, 1650, 1600, 1570, 1460, 1380, 1370, 1360, 1310, 1150, 1120, 1070, 930, 910, 870, 850. – ^{1}H-NMR. (90 MHz, *ca.* 0.14M in $CDCl_3$): s. *Tab. 3.* – ^{13}C-NMR. (22.63 MHz, *ca.* 0.42M in $CDCl_3$): s. *Tab. 4.*

$C_{13}H_{12}O_3$ (216.24) Calc. C 72.21 H 5.59% Found C 71.87 H 5,87%

Data of **6**. Colourless needles, m.p. 92–94°. – IR. ($CHCl_3$): 3580, 3360 br., 2990, 2930, 1635, 1605, 1580, 1470, 1390, 1370, 1330, 1290, 1130, 1080, 1050, 1030, 1010, 970, 950, 910, 870, 860. – ^{1}H-NMR. (90 MHz, *ca.* 0.2M in $(CD_3)_2SO$): s. *Tab. 3.* – ^{13}C-NMR. (22.63 MHz, 0.5M in $CDCl_3$): s. *Tab. 4.*

$C_{12}H_{12}O_3$ (204.23) Calc. C 70.58 H 5.92% Found C 70.29 H 5.89%

Data of **7**. See above at *2.1.*

Data of **8**. Colourless oil ([23]: m.p. 43–44°). – IR. ($CHCl_3$): 2970, 2940, 2880, 1640, 1610, 1570, 1480, 1470, 1390, 1380, 1370, 1330, 1070, 950, 880, 870, 850. – ^{1}H-NMR. (90 MHz, 0.2M in $CDCl_3$): s. *Tab. 3.* – ^{13}C-NMR. (22.63 MHz, 0.7M in $CDCl_3$): s. *Tab. 4.* – MS.: 189 (23), 188 (100, M^+), 187 (13), 174 (14), 173 (41), 163 (22), 160 (15), 147 (30), 146 (17), 145 (80), 131 (10), 121 (27), 120 (61), 115 (20), 94 (44), 93 (15), 64 (22), 63 (12).

4. Photolysis of 2-[(1*RS*,2*SR*,3*RS*,4*SR*)-1,2:3,4-diepoxy-1-methylpentyl]-4*H*-chromen-4-one (3). – 4.1. *Under oxygen.* As in *3.1*, **3** (31 mg, 0.12 mmol) was irradiated for 30 min. Of the crude yellowish oil, 72 mg were dissolved in 1 ml of CH_2Cl_2 and separated by prep. HPLC. (2 injections, hexane/2-propanol 94:6, 22 ml/min, 48 bar), into 4 fractions. *Fraction 1:* 31 mg of mainly one product, which was dissolved in 300 µl of CH_2Cl_2 and purified on the semiprep. silica gel column (5 injections, hexane with 15–40% THF, gradient started after elution of the main product, 4 ml/min) to give 3.3 mg of **7** as colourless crystals. *Fraction 2:* 12 mg of **3** as yellowish crystals. *Fraction 3:* 15 mg of material, which were rechromatographed on the semiprep. silica gel column (7 injections, hexane/CH_3CN/CH_2Cl_2 56:23:21, 4 ml/min). Two compounds could be isolated, first 3.3 mg of *2-[(2*RS*,3*SR*)-2,3-epoxy-1-hydroxy-1-methyl]-4*H*-chromen-4-one* (**11**) as oily, almost colourless crystals, and then 6 mg of its diastereoisomer **12** as colourless crystals. *Fraction 4:* 5 mg of brownish oil, a mixture of minor products which were not investigated further.

The *2-[(1*RS*,2*SR*,3*SR*,4*RS*)-1,2:3,4-diepoxy-1-methylpentyl]-4*H*-chromen-4-one* (**4**) was photolyzed in the same way. The same products were obtained in the same ratio as from **3**.

4.2. *Under exclusion of oxygen.* As in *3.1*, but in the absence of O_2 (s. *1*), **3** (31 mg, 0.12 mmol) was irradiated for 20 min. Of the crude yellow oil, 91 mg were dissolved in 1.2 ml of CH_2Cl_2 and separated by prep. HPLC. (2 injections, hexane/2-propanol 94:6, 29 ml/min, 48 bar) into 6 fractions, which all except fraction 3 were mixtures and had to be rechromatographed. *Fraction 1:* 2 mg, which were combined with the corresponding fractions of additional photolysis experiments. Thus, a total of 9 mg was subjected to semiprep. HPLC. on silica gel (hexane/THF 91:9, 4 ml/min) giving first 1.3 mg of *spiro[4-chromanone-2,2'-(3',5'-dimethyl-2',5'-dihydrofuran)]* (**15**) as a nearly colourless amorphous solid, and then 1.4 mg of its diastereoisomer **16** as almost colourless oil. *Fraction 2:* The 18 mg obtained were dissolved in 150 µl of CH_2Cl_2 and injected in 3 portions onto the semiprep. silica gel column, which then was eluted with hexane/THF 9:1 (4 ml/min). After elution of the main product, the column

was washed with hexane/THF 7:3. The yellow oil obtained (1.4 mg) consisted of 80% pure *2-ethyl-4*H-*chromen-4-one* (**19**) according to ^{1}H-NMR. *Fraction 3:* 27 mg of **3**. *Fraction 4:* 10 mg which were dissolved in 200 µl of CH_2Cl_2 and rechromatographed on the semiprep. silica gel column (3 injections, hexane/THF, first 73:27, then 65:35, 4 ml/min) to give 2 portions. The first contained one product, which according to anal. HPLC. was *ca.* 85% pure. Analogous material (6 mg) obtained from additional photolyses were once more purified on the semiprep. silica gel column (3 injections, hexane/CH_2Cl_2/CH_3CN 75:15:10, 4 ml/min) to give 2.3 mg of almost pure *2-[(2*RS,*3*SR*)-2,3-epoxy-1-methylbutyl]-4*H-*chromen-4-one* (**17**) as colourless oil. The second portion consisted of 2.7 mg of **11**/**12**. *Fraction 5:* 9 mg which were dissolved in 200 µl of CH_2Cl_2 and rechromatographed on the semiprep. silica gel column (4 injections, hexane/CH_3CN/CH_2Cl_2 56:23:21, 4 ml/min). A mixture of the diastereoisomeric *2-[(3*RS,*4*SR*)-3,4-epoxy-1-methyl-2-oxopentyl]chromone* (**9** and **10**) was obtained as a yellow oil (4.5 mg). *Fraction 6:* 19 mg which were dissolved in 280 µl of CH_2Cl_2 and separated on the semiprep. silica gel column (4 injections, hexane/CH_3CN/CH_2Cl_2 56:23:21, 4 ml/min). Three compounds were obtained. The first (1 mg) was rechromatographed on the same column (3 injections, hexane/CH_2Cl_2/CH_3CN 64:19:17, 4 ml/min) giving 0.5 mg of *2-(1-methyl-3-oxobutyl)-4*H-*chromen-4-one* (**18**) as a colourless amorphous solid. Of the second compound only 0.5 mg of a yellow oil were eluted. However, 2.4 mg of analogous material obtained from additional photolyses could be purified on the gel column (16 injections, $CHCl_3$, 1 ml/min) to give 0.8 mg of moderately pure *2-[(Z)-3-hydroxy-1-methyl-1-butenyl]-4*H-*chromen-4-one* (**13**) as a yellowish amorphous solid. The third compound (2.5 mg) was the corresponding (*E*)-isomer **14** as brownish crystals.

The diepoxy compound **4** was photolyzed in the same way yielding the same products in the same ratio as from **3**.

Data of the mixture of **9**/**10**. Yellow oil. – IR. ($CHCl_3$): 2990, 2940, 1720, 1640, 1600, 1570, 1460, 1410, 1380, 1330, 1310, 1120, 1060, 1020, 990, 950, 930, 900, 860, 850. – ^{1}H-NMR. (90 MHz, *ca.* 0.1M in $CDCl_3$): s. *Tab. 3.* – ^{13}C-NMR. (22.63 MHz, *ca.* 0.3M in $CDCl_3$): s. *Tab. 4.* – MS.: 259 (10), 258 (46, M^+), 201 (5), 189 (9), 188 (17), 175 (9), 174 (64), 173 (41), 145 (10), 144 (27), 121 (18), 105 (14), 92 (12), 87 (9), 85 (50), 83 (100), 48 (9), 47 (19), 45 (10), 43 (26).

Data of **11**. Colourless crystals from $CHCl_3$/cyclohexane, m.p. 72.5–73.5°. – IR. ($CHCl_3$): 3400, 2980, 1650, 1605, 1570, 1470, 1380, 1370, 1080, 1020, 980, 960, 870. – ^{1}H-NMR. (360 MHz, *ca.* 0.02M in $CDCl_3$): s. *Tab. 3.* – ^{13}C-NMR. (22.63 MHz, 0.25M in $CDCl_3$): s. *Tab. 4.* – MS.: 246 (16, M^+), 189 (72), 147 (72), 121 (25), 92 (16), 65 (12), 63 (11), 43 (100), 39 (12).

Data of **12**. Colourless crystals from cyclohexane, m.p. 135–136°. – IR. ($CHCl_3$): 3450, 2980, 1650, 1610, 1580, 1465, 1380, 1310, 1020, 1000, 980, 840. – ^{1}H-NMR. (360 MHz, *ca.* 0.02M in $CDCl_3$): s. *Tab. 3.* – ^{1}H-NMR. (90 MHz, *ca*, 0.03M in $(CD_3)_2SO$): 8.1–7.4 (*m*, 4 H, 4 arom. H); 6.44 (*s*, 1 H, H–C(3)); 5.85 (*s*, 1 H, HO, exchangeable with D_2O); 3.2–3.0 (*m*, 2 H, H–C(2′), H–C(3′)); 1.45 (*s*, 3 H, H_3C–C(1′)); 1.27 (d, J = 5, 3 H, 3 H–C(4′)). – ^{13}C-NMR. (22.63 MHz, *ca.* 0.3M in $CDCl_3$): s. *Tab. 4.* – MS.: 246 (15, M^+), 190 (12), 189 (100), 147 (50), 121 (17), 92 (9), 44 (30), 43 (63).

Data of **13**. Yellowish amorphous solid. – ^{1}H-NMR. (90 MHz, *ca.* 0.008M in $CDCl_3$): s. *Tab. 3.*

Data of **14**. Brownish crystals, m.p. 95–103°. – IR. ($CHCl_3$): 3660, 3590, 3400 br., 3000, 2930, 2880, 1660, 1590, 1570, 1480, 1470, 1400, 1380, 1330, 1130, 1090, 1050, 990, 950, 910, 870, 850. – ^{1}H-NMR. (90 MHz, *ca.* 0.07M in $CDCl_3$): s. *Tab. 3.* (90 MHz, *ca.* 0.009M in $(CD_3)_2SO$): 8.1–7.4 (*m*, 4 H, 4 arom. H); 6.67 (*d*, *J* = 9, 1 H, H–C(2′)); 6.41 (*s*, 1 H, H–C(3)); 5.05 (*d*, *J* = 4, 1 H, HO); 4.7 (*m*, 1 H, H–C(3′)); 1.96 (*s*, 3 H, H_3C–C(1′)); 1.21 (*d*, *J* = 6, 3 H, 3 H–C(4′)). – ^{13}C-NMR. (22.63 MHz, *ca.* 0.2M in $CDCl_3$): s. *Tab. 4.* – MS.: 230 (31, M^+), 188 (17), 187 (36), 121 (100), 120 (11), 110 (44), 109 (75), 105 (19), 96 (11), 95 (45), 93 (11), 92 (14), 67 (15), 65 (19), 64 (12), 63 (11), 56 (11), 42 (47), 41 (76).

Data of **15**. Almost colourless amorphous solid. – IR. ($CHCl_3$): 2980, 2920, 2880, 1820, 1690, 1610, 1580, 1470, 1460, 1400, 1370, 1360, 1340, 1310, 1280, 1120, 1090, 1070, 1020, 1000, 970, 960, 940, 890, 870, 850. – ^{1}H-NMR. (90 MHz, *ca.* 0.01M in $CDCl_3$): s. *Tab. 3.*

Data of **16**. Almost colourless oil. – IR. ($CHCl_3$): 2980, 2940, 1690, 1610, 1580, 1480, 1470, 1400, 1380, 1370, 1360, 1330, 1320, 1280, 1120, 1070, 1030, 1000, 980, 960, 940, 910, 890, 870, 850, 830. – ^{1}H-NMR. (90 MHz, *ca.* 0.01M in $CDCl_3$): s. *Tab. 3* and *Fig. 2.* – MS.: 230 (55, M^+), 187 (31), 185 (14), 121 (100), 120 (10), 110 (50), 109 (77), 96 (12), 95 (61), 93 (11), 92 (20), 67 (16), 65 (21), 64 (13), 63 (14), 43 (39), 41 (24).

Data of **17**. Colourless oil. – IR. ($CHCl_3$): 2980, 2940, 1650, 1610, 1580, 1480, 1470, 1430, 1390, 1380, 1370, 1350, 1330, 1320, 1050, 1030, 1020, 1000, 980, 950, 910, 870, 860. – ^{1}H-NMR. (200 MHz, *ca.* 0.02M in $CDCl_3$): s. *Tab. 3.* – ^{1}H-NMR. (90 MHz, 0.01M in C_6D_6): 8.20 (*m*, 1 H, H–C(5)); 7.1–6.6

(*m*, 3 H, 3 arom. H); 6.19 (*s*, 1 H, H–C(3)); 2.50 (*d*×*d*, *J* = 7 and 2, 1 H, H–C(2')); 2.41 (*qa*×*d*, *J* = 5 and 2, 1 H, H–C(3')); 2.17 (*qi*, *J* = 7, 1 H, H–C(1')); 0.94 (*d*, *J* = 5, 3 H, 3 H–C(4')); 0.84 (*d*, *J* = 7, 3 H, H_3C–C(1')). – MS.: 231 (10), 230 (54, M^+), 201 (11), 189 (12), 188 (21), 187 (60), 186 (21), 174 (21), 173 (38), 162 (22), 158 (20), 147 (10), 146 (10), 145 (43), 131 (10), 121 (100), 120 (41), 117 (12), 115 (17), 110 (11), 109 (28), 105 (13), 95 (12), 93 (15), 92 (43), 89 (10), 77 (12), 69 (21), 65 (19), 64 (19), 63 (18), 53 (11), 43 (34), 41 (12). – FD.-MS.: 230 (M^+).

Data of **18**. Colourless amorphous solid. – IR. ($CHCl_3$): main bands at 3000, 2940, 1720, 1650, 1610, 1580, 1470, 1390, 1000, 950, 915. – ^{1}H-NMR. (200 MHz, *ca.* 0.04M in $CDCl_3$): s. *Tab. 3.* – MS.: 230 (12, M^+), 188 (16), 187 (100), 173 (17), 159 (2), 145 (5), 121 (25), 43 (23). – FD.-MS.: 230 (M^+).

Data of **19**: see above at *2.2.*

5. Photolysis of 5. – As in *3.1* and *3.2*, resp., **5** (25 mg, 0.12 mmol) was irradiated for 30 min. The product mixture was investigated by anal. HPLC. (silica gel, hexane/CH_3CN/CH_2Cl_2 56:23:21 or 82:8:10, 1.5 ml/min). None of the products described above (see *3*) could be detected in the complex mixture (detection limit *ca.* 0.5%). However, appreciable amounts of the starting material **5** were recovered: 75% after irradiation under oxygen and 9% in the absence of oxygen.

6. Photolysis of 6. – As in *3.1*, **6** (17.3 mg, 0.085 mmol) was irradiated for 20 min under oxygen. The product mixture was investigated by anal. HPLC. (silica gel, hexane/CH_3CN/CH_2Cl_2 56:23:21, 1.5 ml/min). Starting material was recovered for 96%. Neither **7** nor any of the other compounds described above (see *3*) was among the products.

7. Determination of the yields of the different photoproducts. – Photolysis experiments were set up as described above, using 0.12 mmol of **2** or **3** (26 and 31 mg, resp.), dissolved in 280 ml of the appropriate solvent (see *Tables 1* and *2*) and 10 ml of toluene. Samples were withdrawn before the irradiation was started and then after appropriate time intervals. The solvent was removed at 40° by blowing N_2 over the liquid surface. Samples which proved thermolabile were lyophilized. The material thus obtained was dissolved in 1 ml of eluent (2 ml for samples withdrawn before irradiation) and the solution used to fill the 20 µl sample loop of the HPLC. apparatus. The chromatogram (silica gel, hexane/CH_3CN/CH_2Cl_2 56:23:21, 1,5 ml/min, *ca.* 40 bar) was monitored at 298 nm. The yields were obtained by dividing the product peak areas by the peak area found for the starting material before irradiation, taking into account the different dilutions. The area of **7** was multiplied by 1.5 to correct for the different extinction coefficients of this compounds and of the 2-alkyl-4*H*-chromen-4-ones. Retention times and capacity factors of a number of photoproducts obtained are compiled in *Table 5* (*cf.* also *Fig. 1*).

Table 5. *Retention times* (t_R) *and capacity factors* (k') *of the main products obtained by photolysis of* **2** *and* **3**[a])

Compound	t_R	k'	Compound	t_R	k'
2	4.5[b])	1.27	**11**	11.3	4.66
5	7.1	2.55	**12**	12.4	5.19
6	13.3	5.67	**13**	14.2	6.10
7	4.8	1.41	**14**	15.7	6.87
8	3.7	0.84	**17**	6.8	2.40
3 and **4**	6.1	2.03	**18**	8.5	3.24
9 and **10**	7.5	2.77	**19**	4.4[b])	1.22

[a]) Anal. SiO_2 column, hexane/CH_3CN/CH_2Cl_2 56:23:21, 1.5 ml/min. [b]) Separation possible with hexane/CH_3CN/CH_2Cl_2 82:8:10.

8. Gel chromatography. – The mixture obtained from the photolysis of **2** was dissolved in $CHCl_3$ and chromatographed on the gel column ($CHCl_3$, 1 ml/min; at 298 nm). The amount of monomeric products was estimated by dividing the sum of the peak areas of all products with retention times longer or equal to that of the starting material, by the peak area found for a sample of starting material, taking into account the different dilutions. The amount of dimeric or polymeric material could then easily be calculated.

9. Reversed-phase chromatography. – The mixtures obtained from the photolyses of **2** and **3** were subjected to reversed-phase HPLC. (H_2O/CH_3CN 9:1 for 1 min, then → 5:5 within 18 min, 1.5 ml/min; at 254 nm). The polar products were eluted within 2.2 min after injection, whereas the elution of the remaining compounds started only 8 min after injection.

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