206. Experiments on the Total Synthesis of Lysolipin I

Part II[1])

Michael Addition of 1,3-Cyclohexanedione to Quinone Acetals[2])

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Summary

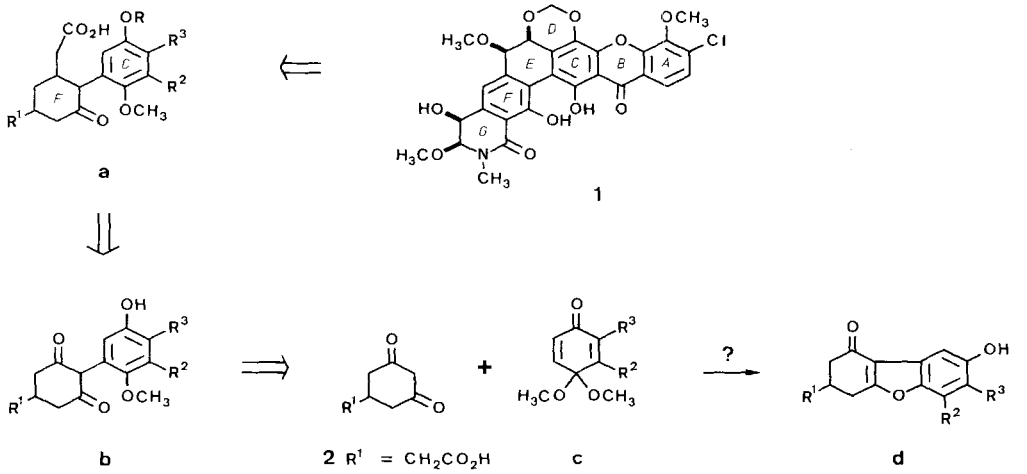
Base-catalyzed reaction of 1,3-cyclohexanedione (**3**) with the quinone monoacetals **4** and **7** leads to the polycyclic products **5** and **8**, respectively, and in the case of **4** to variable amounts of dibenzofuranone **6**. The 2-arylcyclohexanedione **9**, on the other hand, is isolated from the reaction of **3** and bisacetal **11** catalyzed by $ZnCl_2$ *(Scheme 2)*. Treatment of the adduct **8** with $(CH_3O)_2SO_2/K_2CO_3$ results in cleavage of the heterocyclic ring by a *retro-Michael* reaction affording the labile enone **23** which was further transformed to **24** by selective hydrogenation. The 8-acetoxydibenzofuranone **22** is obtainable from **8** by acid treatment and acetylation *(Scheme 4)*. The reactions of the silylenol ethers **27** and **35** with quinone monoacetals were very complex *(Scheme 6)*. The desired arylcyclohexanone derivatives **28** and **36** were formed in very low yields. Under certain conditions (elevated temperature or strong *Lewis* acids as catalysts), single-electron transfer or addition to the ene-acetal rather than to the enone function of the quinone monoacetals became predominant. In connection with this study, the sensitive 2-methoxy-*p*-benzoquinone monoacetals **15** *(Scheme 3)* and **29** *(Scheme 6)* have been prepared and characterized.

1. Introduction. – 2'-Aryl-3'-oxocyclohexylacetic acids of structure **a** are key compounds in our approach [1] to the total synthesis of Lysolipin I (**1**) [2] *(Scheme 1)*. Such 2-arylcyclohexanones have generally been prepared by the addition of an aryllithium or an aryl-*Grignard* reagent to a cyclohexanone (*e.g.* [3]) or a 2-methoxy-2-cyclohexen-1-one [4], followed by more or less tedious transformations of the saturated ring. A retrosynthetic analysis of **a**, however, shows that the precursor **b** might be obtained in a more direct way by *Michael* addition of a 1,3-cyclohexanedione to a quinone or a quinone acetal *(Scheme 1)*. Encouraging reports [5] have demonstrated that, by the use of quinone monoacetals **c**, the regioselectivity of the 1,4-addition can be controlled, and that the major drawback of the addition to quinones, oxidation of the product by

[1]) Part I: [1].

[2]) These results are part of the planned Ph.D. thesis of *U. W.*

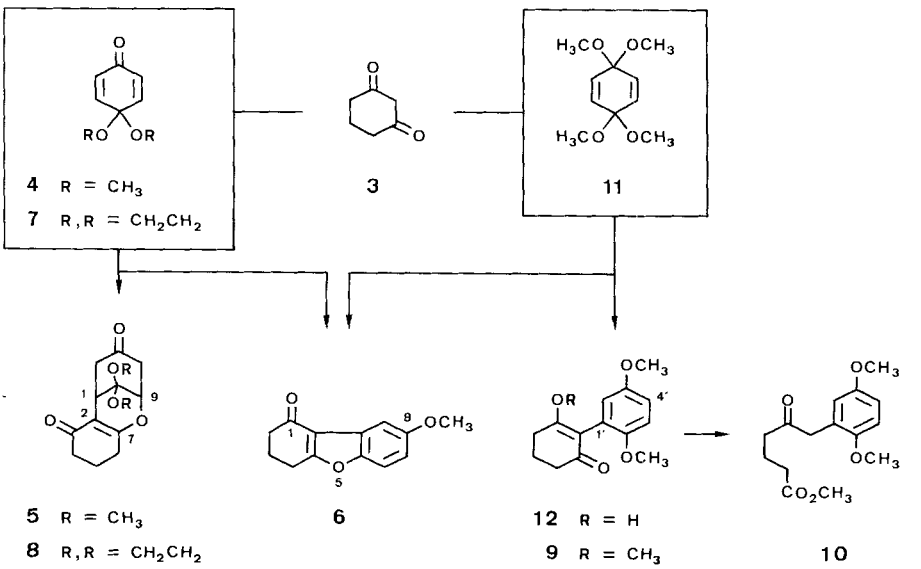
Scheme 1



the starting quinone followed by a second addition, is eliminated. In our special case the acetal protection could also prevent the formation of unwanted tetrahydro-1-dibenzofuranones **d** *(Scheme 1)*. Cyclohexanediones suited for the final synthesis of **1** can then be derived from the acid **2**, which is readily available from 3-oxoglutarate [6].

2. Addition of Dione 3 to *p*-Benzoquinone Mono- and Bisacetals. – Before turning to more complex substrates, the reaction of the parent cyclohexanedione **3** with the acetals of *p*-benzoquinone was studied. Reaction of dimethyl acetal **4** with dione **3** in

Scheme 2



boiling *t*-BuOH catalyzed by *t*-BuOK yielded 65% of the polycyclic product **5**[3]) and 18% of the tetrahydrodibenzofuranone **6**[4]). The analogous process with the ethylene acetal **7** afforded 85% of the adduct **8** as the only isolated product *(Scheme 2)*.

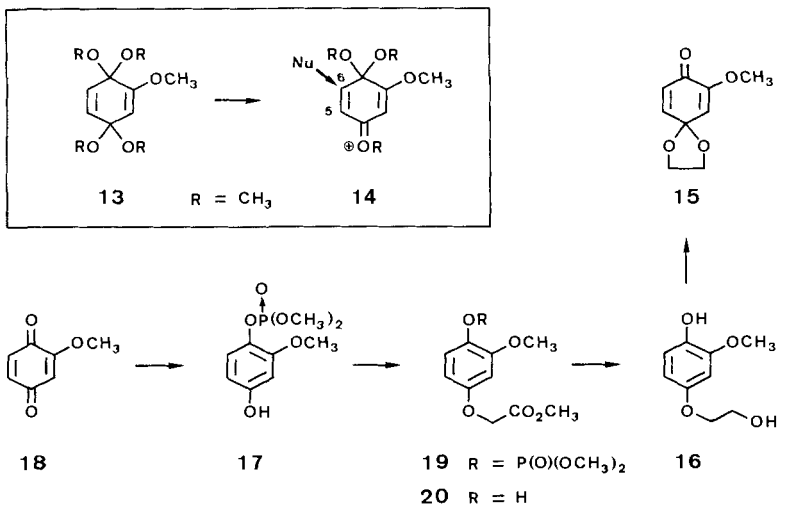
All attempts to isolate 2-aryl-3-methoxy-2-cyclohexenones derived from structures of type **b** *(Scheme 1)* by treatment of the crude mixture with $CH_3SO_3H/CH_3OH/ClCH_2CH_2Cl$ (reflux)[5]) resulted in decomposition of all products except the dibenzofuranone **6**.

More successful was the $ZnCl_2$-catalyzed reaction of **3** with bisacetal **11** according to [8]. *O*-Alkylation ($(CH_3O)_2SO_2/K_2CO_3$) of the crude mixture containing the dione **12** afforded the target compound **9** in 57% yield together with **6** (21%, *Scheme 2*).

No attempts to extend this transformation to the methoxy-substituted bisacetal **13** were made, since the 4'-methoxy-substituted analogue of **9** *(Scheme 2)* could be obtained by a different route [9]. Furthermore, bisacetal **13** most probably leads to the regio-isomer resulting from attack at C(6), since the carboxonium ion **14** is the thermodynamically favored intermediate formed from **13** *(Scheme 3)*. The desired adduct (**b**, $R^3 = OCH_3$, *Scheme 1*), however, requires bond formation at C(5).

Reaction of the 2-methoxy-substituted monoacetal **15** with dione **3** unfortunately gave an intractable mixture of complex products. Acetal **15** was obtained in low yield (< 10%) by $Tl(NO_3)_3$ oxidation of *β*-hydroxyethyl phenyl ether **16** in $CH_3OH/KHCO_3$

Scheme 3



[3]) Analogous products, formed by a double *Michael* addition to the quinone monoacetal, have been obtained with *β*-ketoesters [5a], *β*-ketoester-derivatives [5b], and with a *Schiff*'s-base derivative of glycine [5c].

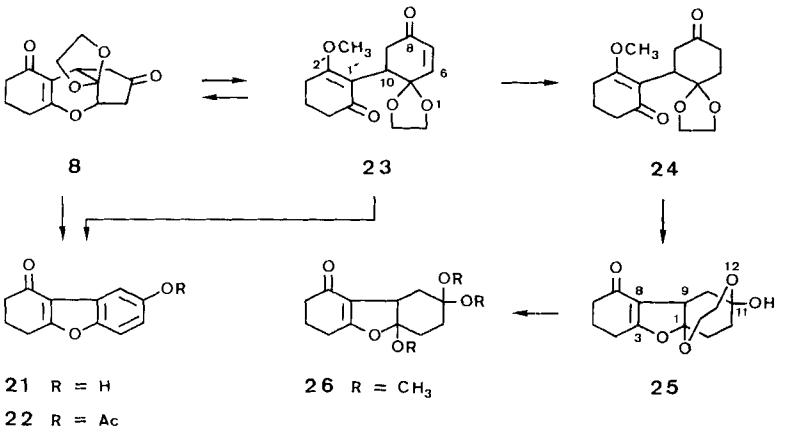
[4]) Inferior results were obtained under the following conditions: EtONa/EtOH (60°), NaH/dioxane (reflux), *t*-BuOK/THF (reflux), or *t*-BuOK/THF/$B(OCH_3)_3$ (reflux).

[5]) Dione **3**, a very polar compound, which is difficult to purify chromatographically on silica gel, can be efficiently *O*-methylated by this method, which has been developed for the esterification of carboxylic acids [7]. However, it was discovered later, that the 2-aryl-substituted derivative **9** is slowly cleaved to the 6-aryl-5-oxohexanoate **10** under these conditions *(Scheme 2)*.

according to [10][6]). Phenol **16** was prepared from phosphate **17** (obtained by reduction of 2-methoxy-*p*-benzoquinone (**18**) with $P(OCH_3)_3$/TMSCl [13]) in *ca.* 75% overall yield by *O*-alkylation with methyl bromoacetate (→**19**), phosphate cleavage (CH_3OH/CsF) affording **20**, and $LiAlH_4$-reduction *(Scheme 3)*.

Next, it was examined whether the polycyclic adduct **8**, obtainable in 85% yield, could be transformed to a 2-arylcyclohexanone related to **9** *(Scheme 2)*. Attempts to hydrolyze the spiroacetal of **8** by treatment with 6N HCl in dioxane resulted in formation of the dibenzofuranone **21** which was isolated in 91% yield as its acetate **22** *(Scheme 4)*. Reaction of **8** with $(CH_3O)_2SO_2/K_2CO_3$ in boiling acetone afforded 94% of the polyfunctional compound **23**, which corresponds to the primary adduct of dione **3** to monoacetal **7** *(Scheme 4)*. Compound **23** was found to be very labile, returning to **8** under very mild conditions[7]), sometimes simply on standing in the refrigerator[8])[9]).

Scheme 4

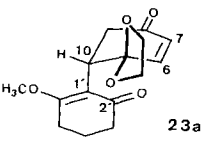


[6]) The same method afforded the corresponding dimethyl acetal from 2,4-dimethoxyphenol in 77% yield. The formation of 2,4-dimethoxyphenol (30%) from the oxidation of **16** implies, that transacetalization with the solvent CH_3OH is a major problem [11]. Since the reaction of **15** with **3** was not successful, no attempts to improve the conversion of **16** to **15** were made. A promising method would be the photochemically mediated oxidation with HgO/I_2 in benzene [12].

[7]) Prolonged exposure to silica gel, silica gel/15% H_2SO_4 in CH_2Cl_2 [14], 2% aq. AcOH in THF, *m*-chloroperbenzoic acid in benzene, dipotassium azodicarboxylate in AcOH, Pd/$BaCO_3$ in AcOEt. Treatment of **23** with $TsOH \cdot H_2O$ in boiling acetone or with CH_3SO_3H in Et_2O at r.t., on the other hand, gave **21** in low yield (no exper. description).

[8]) The dimethyl acetal corresponding to **23** was obtained analogously from adduct **5** (no exper. description). This compound is, however, even more unstable than **23**.

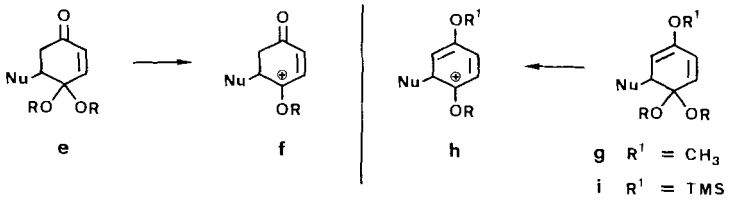
[9]) Models of **23** show that this structure is sterically congested, and that the conformer **23a** with a pseudo-axial methoxycyclohexenone ring could be favored. This would explain the facile intramolecular *Michael* addition (→**8**) by the proximity of the C(2')-keto-O-atom to the C(6)=C(7) bond and the reluctance to aromatize by the equatorial position of H–C(10). The ^{1}H-NMR spectrum (300 MHz) of **23** measured at the probe temp. exhibits line-broadening due to dynamic effects (either rotation around the C(10)–C(1') bond or ring inversion of the spirocyclic moiety). With the exception of the CH_3O-group, this broadening is restricted to the signals of the spirocyclic part. Sharper signals are observed for one of the spiroacetal-H-atoms and for H–C(7). The ^{13}C-NMR spectrum (75 MHz) of **23** exhibiting broad lines at the probe temperature is resolved into the spectra of two conformers (ratio *ca.* 7:3) upon cooling to –20° (see *Exper. Part*).



To explore the synthetic potential of **23**, attempts were made to reduce selectively the C(6)=C(7) bond. The desired spiroacetal **24** could be obtained in high yield by hydrogenation with $Pd/CaCO_3$ in CH_3CN [15][10]). This derivative rearranges under very mild conditions (*e.g.* chromatography on silica gel) to a crystalline derivative with proposed structure **25**, which is transformable to **26** by treatment with CH_3SO_3H/CH_3OH at r.t. *(Scheme 4)*[11]). Attempted epoxidation of **23** with *m*-chloroperbenzoic acid gave **8** and treatment with $H_2O_2/NaOH$ according to [16] led to intractable mixtures[12]).

3. Reaction of Benzoquinone Monoacetals with Silylenol Ethers. – The inaccessability of 2-arylcyclohexane-1,3-diones **b** by 1,4-addition to quinone monoacetals **c** *(Scheme 1)* might be due to the harsh conditions which are required to effect the aromatization of the primary adduct **e**, proceeding *via* an unfavorable carboxonium ion **f** *(Scheme 5)*. The adduct **g**, on the other hand, resulting from the reaction with bisacetal **11** *(Scheme 2)*, is aromatized *via* the less biased intermediate **h** *(Scheme 5)*. Hoping that the primary *Michael* adducts to quinone monoacetals could be trapped as the enolethers **i**, we investigated the reactions with silylenol ethers.

Scheme 5



Reaction of monoacetal **4** with β-(trimethylsilyloxy)cyclohexenone **27** catalyzed by 0.1 equiv. of Bu_4NF/molecular sieves (m.s.) [17][13]) at low temperature (−78° – r.t.) gave a low yield (12%) of **6** (no exper. description). The same reactants with 1 equiv. of fluoride afforded, after treatment with $CH_3OH/CH_3SO_3H/ClCH_2CH_2Cl$[5]) and acetylation, 4% of diacetate **28** in addition to 8% of **6**. At elevated temperature (reflux in THF) the amount of **6** could be increased to 50% *(Scheme 6)*. To clarify the reaction path leading to the methylated derivative **6**, silylenol ether **27** was treated under the same conditions with the monosubstituted quinone monoacetals **29**, **30**, **31**, and **32**. *The 2-substituted acetals **29** and **30** are thereby transformed to the 6-substituted 8-methoxydibenzofuranones **33** (30%) and **34** (16%), clearly demonstrating that **27** is added to the ene-acetal and not to the enone function of the quinone monoacetals (Scheme 6)*. The hydroquinone monomethyl ethers corresponding to the monoacetals **29** and **30** are

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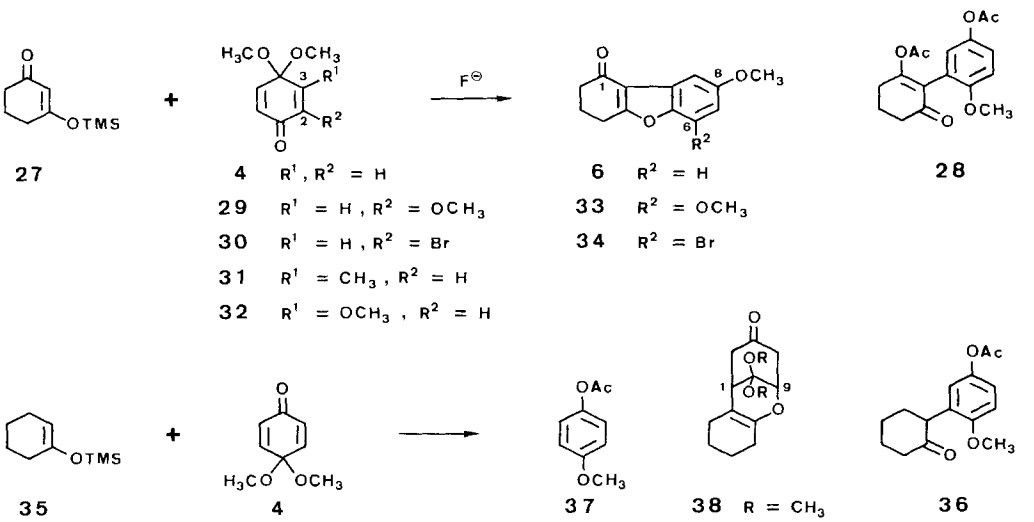
[10]) Other methods for double-bond reduction convert **23** to **8** before hydrogenation[7]). With $Pd/BaSO_4$ (55 psi of H_2) or $((C_6H_5)_3P)RhCl$ hemiacetal **25** was isolated, and 10% Pd/C reduced the methoxycyclohexenone moiety to a cyclohexanone.

[11]) The structures of **25** and **26** are in accordance with the spectroscopic data (see *Exper. Part*). Due to the complexity of the ^{1}H-NMR spectra, an assignment of the rel. configuration of C(9) was not possible.

[12]) Treatment of the diethyl malonate adduct to quinone monoacetal **4** [5a] according to **16** gave 34% of epoxide at 70% conversion (no exper. description).

[13]) Reaction of **4** and **27** catalyzed by $TiCl_4$ [18] or CF_3SO_3TMS [19] led to intractable product mixtures.

Scheme 6



thereby isolated in considerable amounts (27% and 41%, resp.)[14]). Interestingly the 3-substituted monoacetals **31** and **32** are inert to treatment with silylenol ether **27** and fluoride in boiling THF, being recovered in high yield (75–88%, no exper. description)[15]).

Finally, the reaction of quinone monoacetal **4** with the more reactive silylenol ether **35** was investigated under a variety of conditions *(Scheme 6)*. The desired 2-arylcyclohexanone **36** could be isolated in very low yield (4–9%) together with *ca.* 40% of hydroquinone monomethyl ether isolated as acetate **37** from reaction mixtures obtained with an excess of CF_3SO_3TMS/Et_3N [19]. Fluoride catalysis (0.1 equiv. of Bu_4NF, −78° – r.t.) gave complex mixtures containing 6–18% of the tricyclic monoacetal **38**, resulting from a double 1,4-addition to **4**[16]). When quinone monoacetal **4** and enol ether **35** were heated to 200–210° without solvent[17]), hydroquinone monomethyl ether was isolated in quantitative yield as its acetate **37**. A similar result (61% of **37**) was obtained with $TiCl_4$-catalysis [18]. This implies that reactions of quinone acetals initiated by single-electron transfer, so far observed with cuprate and alkyl-lithium reagents [21], can also occur with silylenol ethers[18]).

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[14]) Compound **6** isolated in the base-catalyzed reaction of monoacetal **4** and dione **3** is most probably formed by a similar mechanism.

[15]) Judged by the results of *Coates & MacManus* [5b] and by *Parker et al.* [5c], the monoacetals **31** and **32** are expected to react with dione **3** under base catalysis, giving polycyclic products of type **5** *(Scheme 2)*, which should be further transformable according to *Scheme 4*. Base-catalyzed reaction of **3** with the monoacetals **29** and **30**, on the other hand, is most probably not successful (in analogy to **15**, *Scheme 3*).

[16]) Another complex product (4–10%) originating from 2 equiv. of acetal **4** and 1 equiv. of cyclohexanone (mol. wt. 356) could be isolated. Its complex structure, however, could not be elucidated by routine spectroscopy.

[17]) At elevated temp. *Michael* addition of (2-tetrahydropyranyl)enol ethers to enones has been observed [20].

[18]) While the $TiCl_4$-catalyzed reaction of **4** and **35** proceeds at low temperature, the uncatalyzed process as monitored by ^{1}H-NMR starts not below 180°.

4. Conclusions. – The direct access to 2-arylcyclohexane-1,3-diones and 2-arylcyclohexanones by 1,4-addition to quinone monoacetals failed; the desired products were formed at best in very low yields. It is still possible that these difficulties, which are in part due to steric effects, could be overcome by working at high pressure [22] or by using tris(dimethylamino)sulfonium difluorotrimethylsiliconate as catalyst [23]. More promising is the reaction of **3** with bisacetal **11**, giving the desired product **9** in reasonable yield. Preparatively rewarding is the high yield of the polycyclic compound **8** and its facile transformation to the methyl-enol ether **23** and to the dibenzofuranone **21**, which is thereby obtained in much better yields, than from reactions of *p*-benzoquinone and dione **3** (*cf.* [9]). Since it was recently found that dibenzofuranone derivatives **d** can be efficiently transformed to enol ether derivatives of 2-arylcyclohexane-1,3-diones **b** [9], the synthetic goal depicted in *Scheme 1* could still be attained in an indirect way.

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Experimental Part

General. See [24]. *Purification of Solvents. THF*, distillation from Na/benzophenone; CH_2Cl_2, filtration through Alumina (*Woelm*, basic, activity I); CH_3OH, distillation from $Mg(OCH_3)_2$ formed by the addition of Mg-turnings. *Materials:* The quinone bisacetal **11** was prepared electrolytically [25]. The quinone monoacetals **4**, **7**, and **32** were obtained by regioselective monohydrolysis of the corresponding bisacetals [26], which have been prepared electrolytically [25]. Oxidation of the corresponding hydroquinone monomethyl ethers with $Tl(NO_3)_3/KHCO_3$ in CH_3OH according to [10] afforded the monoacetals **30** and **31**. The silylenol ethers **27** and **35** were obtained according to [27] and [28], respectively. *Bayer-Villiger* oxidation of 2,4-dimethoxybenzaldehyde according to [29] at r.t. (boiling under reflux as described in [29] is not needed) gave, after hydrolysis of the formate, 2,4-dimethoxyphenol.

1. 2,4,4-Trimethoxy-2,5-cyclohexadien-1-one (29). – To a solution of 2,4-dimethoxyphenol (see above; 87 mg, 0.564 mmol) in dry CH_3OH (6 ml), $KHCO_3$ (617 mg, 6.16 mmol) and, after cooling to −5° (ice/NaCl), a solution of $Tl(NO_3)_3$ (240 mg, 0.62 mmol) in dry CH_3OH (5 ml) were added. After stirring for 22 min, the mixture was added to ice-cooled sat. $NaHCO_3$-soln., filtered *(Celite)*, and worked up with Et_2O (addition of ice). Chromatography (alumina, basic, activity III, CH_2Cl_2) gave 80 mg (77%) of **29**, m.p. 135–136° (Et_2O/hexane). IR ($CHCl_3$): 3035*w*, 3005*m*, 2970*m*, 2940*m*, 2910*w*, 2835*m*, 1686*s*, 1655*s*, 1650*s*, 1625*m*, 1597*m*, 1460*m*, 1443*w*, 1372*m*, 1310*w*, 1255*m*, 1175*m*, 1120*m*, 1085*s*, 1040*m*, 1020*m*, 992*w*, 951*s*, 910*w*, 878*m*, 843*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.37 (*s*, 2 CH_3O–C(4)); 3.70 (*s*, CH_3O–C(2)); 5.69 (*d*, J = 3, H–C(3)); 6.23 (*d*, J = 10, H–C(6)); 6.83 (*dd*, J = 10 and 3, H–C(5)). MS: 184 (26, M^+), 169 (36), 154 (86), *153* (100), 141 (14), 139 (66), 138 (21), 126 (7), 125 (42), 123 (10), 111 (35), 110 (23), 108 (30), 95 (19), 82 (15), 79 (14), 69 (52), 55 (12), 54 (18), 53 (24), 52 (27), 51 (16), 41 (10), 39 (18). Anal. calc. for $C_9H_{12}O_4$ (184.18): C 58.69, H 6.58, O 34.74; found: C 58.69, H 6.57, O 34.90.

2. Preparation of the Cyclic Acetal 15. – 2.1. *Methyl [4-(Dimethylphosphoryloxy)-3-methoxyphenoxy]-acetate* (**19**). A mixture of phosphate **17** [13] (116 mg, 0.458 mmol), $KHCO_3$ (640 mg, 4.64 mmol), and methyl bromoacetate (60 µl, *ca.* 0.6 mmol) in acetone (7 ml) was boiled for 46 h under reflux (Ar). Filtration *(Celite)* and chromatography (15 g of silica gel, CH_2Cl_2/CH_3OH 96:4) of the residue obtained by evaporation of the filtrate afforded 144 mg (96%) of **19**. IR ($CHCl_3$): 3030*w*, 3000*m*, 2955*m*, 2855*w*, 2830*w*, 1756*s*, 1611*m*, 1600*m*, 1505*s*, 1464*m*, 1450*m*, 1436*m*, 1374*w*, 1276*s*, 1182*s*, 1163*s*, 1129*m*, 1112*w*, 1050*s*, 956*s*, 938*m*, 920*m*, 856*s*, 839*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.80 and 3.84 (2*s*, OCH_2COOCH_3, CH_3O–C(3)); 3.86 (*d*, J = 11, $(CH_3O)_2PO_2$–C(4)); 4.59 (*s*, OCH_2COOCH_3); 6.34 (*dd*, J = 9 and 3, H–C(6)); 6.61 (*d*, J = 3, H–C(2)); 7.16 (*dd*, J = 9 and ≈ 1, H–C(5)). MS (*di.*): 320 (70, M^+), 289 (3), 261 (7), 247 (13), 231 (12), 194 (9), 135 (18), 127 (66), *109* (100), 93 (9), 79 (18), 45 (14).

2.2. *Methyl (4-Hydroxy-3-methoxyphenoxy)acetate* (**20**). A solution of **19** (140 mg, 0.438 mmol) and CsF (916 mg, 6 mmol) in CH_3OH (4 ml) was stirred for 68 h at r.t. (Ar). Workup with Et_2O gave 89 mg (96%) of **20**. IR (CCl_4): 3560*m*, 3600–3200*w*, 3005*w*, 2950*m*, 2935*w*, 2845*w*, 1770*s*, 1742*s* (in $CHCl_3$ one band at 1755*s*), 1623*m*, 1612*w*, 1505*s*, 1465*m*, 1451*m*, 1435*m*, 1380*m*, 1352*w*, 1264*m*, 1229*s*, 1200*s*, 1156*s*, 1122*m*, 1106*w*, 1075*m*, 1034*m*, 984*w*, 940*w*, 925*m*, 835*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.78 and 3.83 (2*s*, OCH_2COOCH_3, CH_3O–C(3)); 4.56 (*s*, OCH_2COOCH_3); 5.40 (br., $w_{1/2} \approx 3$, HO–C(4)); 6.33 (*dd*, $J = 9$ and ≈ 3, H–C(6)); 6.58 (*d*, $J \approx 3$, H–C(2)); 6.79 (*d*, $J = 9$, H–C(5)). MS: 212 (83, M^+), 197 (3), 153 (13), *139* (100), 123 (15), 111 (20), 110 (21), 109 (10), 95 (6), 79 (13), 74 (12), 45 (11).

2.3. *4-(2'-Hydroxyethoxy)-2-methoxyphenol* (**16**). A solution of **20** (1.708 g, 8.06 mmol) in dry Et_2O (20 ml) was added dropwise to 1.533 g (40.3 mmol) of $LiAlH_4$ in Et_2O (30 ml). After stirring for 14 h at r.t. (Ar), *Celite* was added and the reaction was quenched by the addition of sat. $(NH_4)_2SO_4$-soln. (dropwise, until the precipitated solids coagulate with the *Celite*). Filtration *(Celite)* and chromatography (100 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:2) of the residue of the filtrate yielded 1.20 g (81%) of **16**, m.p. 65–66° (Et_2O). IR ($CHCl_3$): 3595*m*, 3550*s*, 3600–3200*m*, 3030*w*, 3000*w*, 2960*m*, 2935*m*, 2870*w*, 2845*w*, 1622*m*, 1610*m*, 1502*s*, 1463*m*, 1449*s*, 1431*m*, 1377*s*, 1355*m*, 1300*w*, 1287*w*, 1264*m*, 1190*s*, 1156*s*, 1119*m*, 1106*w*, 1070*m*, 1029*s*, 955*m*, 895*m*, 865*w*, 835*m*, 820*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 2.1–2.6 (br., $HOCH_2CH_2O$–C(4)); 3.82 (*s*, CH_3O–C(2)); 3.6–4.1 (*m*, $HOCH_2CH_2O$–C(4)); 5.2–5.6 (br., HO–C(1)); 6.37 (*dd*, $J = 8$ and 3, H–C(5)); 6.50 (*d*, $J \approx 3$, H–C(3)); 6.80 (*d*, $J = 8$, H–C(6)). MS: 184 (52, M^+), 153 (2), *140* (100), 125 (73), 111 (8), 97 (26), 85 (15), 83 (22), 52 (10), 45 (12).

2.4. *7-Methoxy-1,4-dioxaspiro[4.5]deca-6,9-dien-8-one* (**15**). A solution of $Tl(NO_3)_3$ (600 mg, 1.5 mmol) in dry CH_3OH (5 ml) was added slowly to a ice-cooled solution of **16** (240 mg, 1.302 mmol) in dry CH_3OH (15 ml) containing 1.409 g (14 mmol) of powdered $KHCO_3$ (Ar). After stirring for 1 h at 0°, the reaction was quenched by the addition of ice-cooled sat. $NaHCO_3$-soln. Filtration *(Celite)*, workup with Et_2O and chromatography (20 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 12:8:5) gave 61 mg (30% of 2,4-dimethoxyphenol, 20 mg (8%, 10% based on consumed **16**) of **15**, and 52 mg (21%) of starting material **16**. IR ($CHCl_3$): 3030*w*, 3010*w*, 2960*w*, 2935*w*, 2890*m*, 2845*w*, 1685*s*, 1650*s*, 1623*s*, 1605*w*, 1460*m*, 1455*m*, 1442*w*, 1368*s*, 1246*m*, 1180*m*, 1118*s*, 1085*s*, 1020*s*, 985*w*, 960*s*, 945*s*, 880*w*, 836*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.71 (*s*, CH_3O–C(7)); 4.18 (*s*, 2H–C(2), 2H–C(3)); 5.50 (*d*, $J \approx 3$, H–C(6)); 6.15 (*d*, $J = 10$, H–C(9)); 6.68 (*dd*, $J = 10$ and ≈ 3, H–C(10)). MS: 182 (82, M^+), 167 (8), 154 (53), 152 (12), 151 (10), 139 (59), 126 (20), 122 (52), 113 (24), 109 (34), 98 (45), 95 (53), 94 (16), *79* (100), 69 (59), 66 (14), 64 (14), 53 (29), 51 (55), 50 (22), 43 (12), 39 (26).

3. Reaction of 1,3-Cyclohexanedione (3) with p-Benzoquinone Acetals. – 3.1. *Reaction with Dimethyl Monoacetal* **4**. A solution of **3** (495 mg, 4.42 mmol), monoacetal **4** (500 mg, 3.24 mmol), and *t*-BuOK (158 mg, 1.4 mmol) in *t*-BuOH (25 ml) was boiled under reflux for 4 d (Ar). Chromatography (100 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:2:2) of the residue, obtained by evaporation, gave 129 mg (18%) of dibenzofurane **6** and 567 mg (65%) of *13,13-dimethoxy-8-oxatricyclo[7.3.1.0^{2,7}]tridec-2(7)-ene-3,11-dione* (**5**). IR ($CHCl_3$): 3030*w*, 2995*m*, 2960*m*, 2945*m*, 2910*w*, 2870*w*, 2835*m*, 1720*s*, 1652*s*, 1620*s*, 1455*m*, 1428*w*, 1412*w*, 1387*s*, 1369*s*, 1357*m*, 1326*w*, 1293*m*, 1280*m*, 1265*m*, 1185*s*, 1148*m*, 1135*m*, 1121*s*, 1100*w*, 1071*s*, 1064*s*, 1038*s*, 1021*s*, 1004*m*, 995*w*, 969*m*, 930*w*, 897*m*, 871*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.85–2.05 (*m*, *5 main peaks*, 2H–C(5)); 2.3–2.4 (*m*, 2H–C(4), 2H–C(6)); 2.44 (*dt*, $J = 16$ and 2.5) and 2.67 (*dd*, $J = 16$ and 4.5) (2H–C(12)); 2.59 (*ddd*, $J = 17$, 2.5, and 2) and 2.80 (*dd*, $J = 17$ and 4.5) (2H–C(10)); 3.29 and 3.39 (2*s*, 2 CH_3O–C(13)); 3.35–3.45 (*m*, H–C(1)); 4.65 (*ddd*, $J = 4.5$, 3.5, and 2, H–C(9)). MS: 266 (50, M^+), 238 (18), 235 (11), 234 (10), 219 (8), 210 (38), 195 (22), 191 (16), 163 (12), 151 (24), *101* (100), 91 (12), 77 (10), 65 (9), 55 (49), 43 (41), 41 (13), 39 (11).

Methoxy-1,2,3,4-tetrahydrodibenzofuran-1-one (**6**). IR ($CHCl_3$): 3030*w*, 2990*w*, 2950*m*, 2885*w*, 2830*m*, 1660*s*, 1615*m*, 1584*s*, 1477*s*, 1455*s*, 1429*s*, 1395*s*, 1355*w*, 1325*w*, 1312*w*, 1271*s*, 1169*s*, 1151*s*, 1133*m*, 1102*w*, 1055*m*, 1040*w*, 1025*m*, 1005*s*, 893*w*, 880*w*, 870*w*, 850*m*, 824*w*, 635*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.1–2.4 (*m*, 2H–C(3)); 2.45–2.65 and 2.85–3.1 (2*m*, *each 3 main peaks*, 2H–C(2), 2H–C(4)); 3.81 (*s*, CH_3O–C(8)); 6.84 (*dd*, $J = 9$ and 3, H–C(7)); 7.30 (*d*, $J = 9$, H–C(6)); 7.49 (*d*, $J = 3$, H–C(9)). MS: *216* (100, M^+), 201 (5), 189 (12), 188 (99), 173 (7), 160 (72), 145 (6), 132 (31), 117 (9), 115 (10), 89 (20), 63 (17), 43 (10). Anal. calc. for $C_{13}H_{12}O_3$ (216.23): C 72.21, H 5.59; found: C 72.23, H 5.58.

3.2. *{8-Oxatricyclo[7.3.1.0^{2,7}]tridec-2(7)-ene-3,11-dione}-13-spiro-2'-{1',3'-dioxolane}* (**8**). A mixture of dione **3** (1.338 g, 11.95 mmol), cyclic monoacetal **7** (1.311 g, 8.63 mmol), and *t*-BuOK (337 mg, 3 mmol) in *t*-BuOH (50 ml) was boiled under reflux for 23 h (Ar). Evaporation (aspirator) and chromatography (200 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:2:2) of the residue gave 1.954 g (85% based on **7**) of **8**, m.p. 156–157° (Et_2O/hexane). UV (EtOH): 261 (11000). IR ($CHCl_3$): 3030*w*, 3000*m*, 2955*m*, 2895*m*, 2840*w*, 1720*s*, 1654*s*,

1620*s*, 1473*w*, 1455*w*, 1429*w*, 1415*w*, 1390*s*, 1375*s*, 1356*w*, 1340*w*, 1325*w*, 1294*w*, 1270*m*, 1187*s*, 1150*m*, 1131*s*, 1092*m*, 1063*s*, 1025*s*, 1005*m*, 987*w*, 971*w*, 949*m*, 930*w*, 906*w*, 873*w*, 858*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.9–2.02 (*m*, *5 main peaks*, 2H–C(5)); 2.3–2.48 (*m*, 2H–C(4), 2H–C(6)); 2.48 (*ddd*, J = 16, 3, and 2.5) and 2.93 (*dd*, J = 16 and 4.5) (2H–C(12)); 2.65 (*dt*, J = 17 and 2.5) and 2.91 (*dd*, J = 17 and 4.5) (2H–C(10)); 3.07–3.14 (*m*, *4 main peaks*, H–C(1)); 4.06–4.2 (*m*, 2H–C(4'), 2H–C(5')); 4.34 (*ddd*, J = 4.5, 3, and 2.5, H–C(9)). ^{13}C-NMR (25 MHz, $CDCl_3$): 20.7 (C(5)); 27.6 and 36.1 (C(4), C(6)); 33.2 (C(1)); 43.2 and 45.8 (C(10), C(12)); 65.4 and 65.6 (C(4'), C(5')); 75.9 (C(9)); 103.2 (C(2)); 113.0 (C(13)); 168.8 (C(7)); 196,1 (C(3)); 206.9 (C(11)). MS: 264 (57, M^+), 236 (17), 209 (10), 208 (46), 164 (18), 163 (11), 136 (15), 108 (11), *99* (100), 77 (7), 57 (34), 56 (16), 55 (55), 43 (31), 42 (14), 41 (31), 39 (15). Anal. calc. for $C_{14}H_{16}O_5$ (264.28): C 63.63, H 6.10, O 30.27; found: C 63.86, H 6.22, O 30.50.

3.3. *Reaction of Dione* **3** *with Bisacetal* **11**. – 3.3.1. *2-(2',5'-Dimethoxyphenyl)-3-methoxy-2-cyclohexen-1-one* (**9**). A solution of $ZnCl_2$ (1.04 g, 7.63 mmol, dried by melting at h.v.) and **3** (3.1 g, 27.64 mmol) in dry dioxane (20 ml) was heated to the boiling point. Solvent was removed continuously by distillation while a solution of bisacetal **11** (2.64 g, 13.18 mmol) in dioxane (5 ml) was added (25 min). Within 2 h, most of the volatile components of the mixture were evaporated at normal pressure, and the residue was worked up with CH_2Cl_2. The crude mixture was treated with $(CH_3O)_2SO_2$ (3.8 ml, *ca.* 39.9 mmol) and powdered K_2CO_3 (23.3 g) in acetone (500 ml) for 24 h (stirring at r.t.). Filtration *(Celite)*, evaporation, and chromatography (200 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:2:2) afforded 602 mg (21% based on **11**) of **6** (see *3.1*), 525 mg (15% based on **3**) of 3-methoxy-2-cyclohexen-1-one, and 1.98 g (57% based on **11**) of **9**, m.p. 92–93° (AcOEt/pentane). IR ($CHCl_3$): 3030*w*, 2995*m*, 2945*s*, 2905*w*, 2870*w*, 2850*w*, 2830*m*, 1645*s*, 1605*s*, 1491*s*, 1457*s*, 1408*m*, 1365*s*, 1355*s*, 1329*w*, 1309*m*, 1289*w*, 1271*s*, 1180*w*, 1170*m*, 1158*m*, 1085*w*, 1080*s*, 1037*s*, 1010*w*, 1000*m*, 960*w*, 935*w*, 916*w*, 908*w*, 883*m*, 855*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.85–2.3 (*m*, 2H–C(5)); 2.3–2.9 (*m*, 2H–C(4), 2H–C(6)); 3.65, 3.71, and 3.75 (3*s*, CH_3O–C(3), CH_3O–C(2'), CH_3O–C(5')); 6.55–6.7 (*m*, 1H) and 6.75–6.95 (*m*, 2H) (H–C(3'), H–C(4'), H–C(6')). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.6 (C(5)); 25.9 and 36.7 (C(4), C(6)); 55.5, 55.9, and 56.4 (3 CH_3O); 112.2, 113.1, and 117.9 (C(3'), C(4'), C(6')); 116.8 and 124.2 (C(2), C(1')); 151.6 and 153.1 (C(2'), C(5')); 173.0 (C(3)); 196.9 (C(1)). MS: 262 (77, M^+), 247 (2), *231* (100), 219 (15), 191 (9), 187 (15), 161 (12), 131 (9), 115 (6), 91 (8), 84 (9), 55 (10). Anal. calc. for $C_{15}H_{18}O_4$ (262.30): C 68.68, H 6.92, O 24.40; found: C 68.55, H 6.99, O 24.78.

3.3.2. *Methyl 6-(2',5'-Dimethoxyphenyl)-5-oxohexanoate* (**10**). A solution of **9** (111 mg, 0.424 mmol) in 5 ml of a mixture of CH_3OH (10 ml), $ClCH_2CH_2Cl$ (20 ml), and CH_3SO_3H (0.1 ml) [7] was boiled under reflux for 23 h. Workup with AcOEt and chromatography (10 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:2:2) gave 30 mg (25%) of **10** and 21 mg (19%) of **9**. IR (CCl_4): 3000*m*, 2950*m*, 2905*m*, 2830*m*, 1740*s*, 1713*s*, 1592*w*, 1500*s*, 1463*m*, 1433*m*, 1370–1360*w*, 1311*m*, 1280*m*, 1265*w*, 1224*s*, 1201*w*, 1193*w*, 1180*m*, 1158*m*, 1128*w*, 1090*w*, 1050*s*, 1029*m*, 935*w*, 880*w*, 855*w*, 710*m*, 702*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.8–2.0 (*m*, *5 main peaks*, 2H–C(3)); 2.25–2.35 and 2.45–2.55 (2*m*, *each 3 main peaks*, 2H–C(2), 2H–C(4)); 3.62 (*s*, 2H–C(6)); 3.64, 3.751, and 3.754 (3*s*, 3 OCH_3); 6.71 (*dd*, $J \approx 2.5$ and 1, H–C(6')); 6.76 (*dd*, J = 9 and 2.5, H–C(4')); 6.79 (*dd*, J = 9 and 1, H–C(3')). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.0 (C(3)); 33.0 and 40.7 (C(2), C(4)); 44.9 (C(6)); 51.5, 55.7, and 55.9 (3 CH_3O); 111.4, 112.7, and 117.4 (C(3'), C(4'), C(6')); 124.6 (C(1')); 151.6 and 153.5 (C(2'), C(5')); 173.6 (C(1)); 207.8 (C(5)). MS: 280 (31, M^+), 249 (14), 207 (5), 151 (60), 137 (10), 136 (7), *129* (100), 121 (60), 108 (10), 101 (97), 97 (10), 91 (24), 77 (17), 65 (15), 59 (55), 55 (26), 51 (7), 41 (10).

4. Transformations of Adduct 8. – 4.1. *1-Oxo-1,2,3,4-tetrahydrodibenzofur-8-yl Acetate* (**22**). A solution of **8** (35.4 mg, 0.134 mmol) in dioxane (4 ml) and 6N aq. HCl (2 ml) was stirred at r.t. for 5 d. Evaporation at reduced pressure, acetylation (Ac_2O/pyridine, 0.5 ml of each, over night), evaporation, and chromatography (10 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:2:2) gave 30 mg (91%) of **22**, m.p. 110–111° (Et_2O/hexane). IR ($CHCl_3$): 3030*w*, 2998*w*, 2955*m*, 2890*w*, 2870*w*, 2835*w*, 1755*s*, 1665*s*, 1622*w*, 1588*s*, 1451*s*, 1429*w*, 1395*s*, 1367*s*, 1325*w*, 1185*m*, 1166*s*, 1141*m*, 1130*m*, 1106*w*, 1055*m*, 1042*w*, 1006*s*, 934*w*, 920*m*, 896*m*, 883*m*, 865*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 2.05–2.45 (*m*, 2H–C(3)); 2.30 (*s*, CH_3COO–C(8)); 2.45–2.75 and 2.9–3.2 (2*m*, 2H–C(2), 2H–C(4)); 7.00 (*dd*, J = 9 and $\approx$ 3, H–C(7)); 7.43 (*d*, J = 9, H–C(6)); 7.74 (*d*, $J \approx 3$, H–C(9)). MS: 244 (8, M^+), *202* (100), 175 (8), 174 (74), 146 (26), 118 (11), 89 (10), 63 (9), 55 (6), 43 (22).

4.2. *10-(2'-Methoxy-6'-oxo-1'-cyclohexenyl)-1,4-dioxaspiro[4.5]dec-6-en-8-one* (**23**). A mixture of **8** (122.7 mg, 0.464 mmol), $(CH_3O)_2SO_2$ (66 µl, *ca.* 0.6 mmol), and powdered K_2CO_3 (383 mg) in acetone (10 ml) was boiled under reflux for 15 h. Filtration *(Celite)*, evaporation, and chromatography (15 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:2:2) yielded 122 mg (94%) of **23**. IR ($CHCl_3$): 3035*w*, 2985*m*, 2945*m*, 2885*m*, 2850*w*, 1675*s*, 1640*s*, 1608*s*, 1456*m*, 1405*w*, 1374*s*, 1345*m*, 1325*w*, 1277*m*, 1256*s*, 1163*s*, 1140*m*, 1120*m*, 1088*m*, 1059*w*, 1038*m*, 1024*m*, 1002*w*, 948*m*, 932*w*, 915*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.9–2.1 (*m*, 2H–C(4')); 2.25–2.5 and

2.5–2.7 (2*m*, 2H–C(3'), 2H–C(5')); 2.6–2.95 (*m*, 2H–C(9)); 3.63 (br., $w_{1/2} \approx 15$, CH_3O–C(2')); ≈ 3.5–4.2 (*m*, 2H–C(2), 2H–C(3), H–C(10)); 6.03 (*d*, *J* = 10, H–C(7)); 6.46 (*d*, *J* = 10, *further broadened*, $w_{1/2} \approx 5$, H–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$, –20°, *multiplicities determined by gated spin-echo techniques, mixture of two conformers, signals of minor conformer (20–30%) in parentheses*): 20.3 (C(4')); 25.6 (25.4), 36.2 (37.6?), and 39.2 (39.6) (C(9), C(3'), C(5')); 36.7 (37.5) (C(10)); 54.4 (55.8) (OCH_3); 64.9 (65.0) and 66.2 (65.9) (C(2), C(3)); 104.8 (105.4) and 115.6 (113.9) (C(5), C(1')); 130.5 (130.0) (C(7)); 146.3 (146.0) (C(6)); 173.9 (175,8) (C(2')); 198.0 (198.2) and 199.0 (199.6) (C(8), C(6')). MS (*di.*): 278 (6, M^+), 164 (2), 250 (1), 236 (5), 208 (2), 151 (2), *126* (100), 103 (5), 99 (11), 98 (53), 55 (11).

4.3. *6-(2'-Methoxy-6'-oxo-1'-cyclohexenyl)-1,4-dioxaspiro[4.5]decan-8-one* (**24**). Freshly prepared enone **23** (49.8 mg, 0.179 mmol) was hydrogenated at normal pressure with 10% $Pd/CaCO_3$ (16 mg) in CH_3CN (5 ml) for 90 min. Filtration *(Celite)* and evaporation at reduced pressure gave 46 mg (91%) of **24**. IR (CCl_4): 2940*s*, 2890*m*, 2847*w*, 2815*w*, 1708*s*, 1655*s*, 1617*s*, 1455*m*, 1442*m*, 1427*w*, 1415*w*, 1403*m*, 1374*s*, 1343*m*, 1332*m*, 1312*w*, 1287*m*, 1268*s*, 1253*s*, 1235*s*, 1210*w*, 1191*m*, 1168*s*, 1140*s*, 1110*s*, 1079*m*, 1029*s*, 980*s*, 945*m*, 930*s*, 920*s*, 860*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.65–1.85 (*m*, 1H); 1.9–2.1 (*m*, 2H–C(4')); 2.17 (*td*, *J* = 13 and 6, 1H); 2.25–2.85 (*m*, 8H); 3.62 (br., $w_{1/2} \approx 5$, CH_3O); 3.7–4.25 (*m*, 2H–C(2), 2H–C(3), H–C(6)). MS (*di.*): 280 (31, M^+), 265 (4), 194 (4), 181 (11), 166 (11), 139 (9), 138 (8), 100 (29), *99* (100), 87 (10), 55 (32), 41 (6).

4.4. *11-Hydroxy-2,12,15-trioxatetracyclo[9.4.2.0^{1,9}.0^{3,8}]heptadec-3(8)-en-7-one* (**25**). Crude **23**, freshly prepared from **8** (103 mg, 0.39 mmol) as described in *4.2*, was dissolved in benzene/EtOH (10 ml of each) and hydrogenated at normal pressure with $((C_6H_5)_3P)_3RhCl$ (96 mg) for 20 h. Evaporation and chromatography (10 g of silica gel, CH_2Cl_2/CH_3OH 96:4) gave 82 mg (78% based on **8**) of **25**, m.p. 177–178° ($CHCl_3$/hexane). UV (EtOH): 263 (14600). IR ($CHCl_3$): 3580*m*, 3500–3200*w*, 2997*m*, 2950*m*, 2890*m*, 1640*s*, 1610*s*, 1441*m*, 1429*m*, 1387*s*, 1369*m*, 1352*m*, 1332*m*, 1315*w*, 1300*m*, 1270*w*, 1163*s*, 1131*s*, 1113*s*, 1063*m*, 1032*m*, 1015*s*, 1001*w*, 968*s*, 946*m*, 935*s*, 903*m*, 866*w*, 855*w*, 835*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.45–1.65 (*m*, 2H); 1.75–1.25 (*m*, 5H); 2.2–2.6 (*m*, 4H); 2.34 (*dd*, *J* = 12.5 and 3, H–C(10)); 3.22 (*m*, $w_{1/2} \approx 7$, H–C(9)); 3.29 (br., $w_{1/2} \approx 2$, *exchangeable with D_2O*, HO–C(11)); 3.85–4.0 (*m*, 2H), 4.0–4.13 (*m*, 1H), and 4.13–4.3 (*m*, 1H) (2H–C(13), 2H–C(14)). ^{13}C-NMR (75 MHz, $CDCl_3$, *: *assignment interchangeable*): 21.0 (C(5)); 28.6 and 36.4* (C(4), C(6)); 28.6, 32.9 and 36.5* (C(10), C(16), C(17)); 32.6 (C(9)); 64.1 and 64.7 (C(13), C(14)); 101.2 (C(8)); 109.8 and 112.6 (C(1), C(11)); 173.4 (C(3)); 196.9 (C(7)). MS (*di.*): 266 (66, M^+), 248 (1), 221 (7), 167 (6), 162 (9), 142 (27), 137 (14), 113 (6), 100 (47), *99* (100), 87 (31), 86 (65), 55 (28), 43 (12), 42 (15).

4.5. *5a,8,8-Trimethoxy-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1-one* (**26**). A solution of **25** (10.8 mg, 0.041 mmol) and CH_3SO_3H (10 µl) in CH_3OH (2 ml) was stirred at r.t. for 16 h. The reaction was quenched with sat. $NaHCO_3$-soln. and worked up with Et_2O. Chromatography (10 g of silica gel, CH_2Cl_2/CH_3OH 96:4) gave 10.5 mg (*ca.* 90%) of **26**. IR (CCl_4): 2940*s*, 2890*m*, 2850*w*, 2835*m*, 1655*s* (in $CHCl_3$: 1645*s*), 1615*s* (in $CHCl_3$: 1608*s*), 1451*m*, 1435*w*, 1429*m*, 1383*s*, 1370*s*, 1353*w*, 1340*w*, 1330*m*, 1291*m*, 1285*m*, 1266*w*, 1247*m*, 1220*w*, 1185*s*, 1170*s*, 1150*s*, 1118*s*, 1063*s*, 1046*s*, 1010*m*, 980*m*, 950*m*, 930*s*, 900*m*, 865*w*, 854*w*, 828*s*, 707*w*, 620*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.38–1.55 (*m*, 1H); 1.68–1.9 (*m*, 3H); 1.9–2.1 (*m*, 3H); 2.08 (*dd*, *J* = 12.5 and 3, H–C(9)); 2.2–2.37 (*m*, 1H); 2.37–2.57 (*m*, 3H); 3.22, 3.23, and 3.36 (3*s*, 3 CH_3O); 3.46 (*m*, $w_{1/2} \approx 8$, H–C(9a)). ^{13}C-NMR (25 MHz, $CDCl_3$): 21.0 (C(3)); 25.7, 28.6, 28.9, 34.0, and 36.8 (C(2), C(4), C(6), C(7), C(9)); 31.4 (C(9a)); 47.9, 48.7, and 49.9 (3 CH_3O); 102.2, 103.6, and 113.1 (C(5a), C(8), C(9b)); 172.9 (C(4a)); 195.8 (C(1)). MS (*di.*): 282 (4, M^+), 251 (23), 250 (43), 235 (14), 219 (26), *181* (100), 162 (8), 153 (11), 138 (8), 101 (16), 89 (21), 88 (94), 58 (24), 55 (20), 43 (20).

5. Reactions of 3-(Trimethylsilyloxy)-2-cyclohexen-1-one (27) with Quinone Monoacetals. – 5.1. *Reaction with Monoacetal* **4**. – 5.1.1. *Reaction at r.t. in the Presence of Molecular Sieves (m.s.).* A suspension of m.s. 4 Å (2 g) in a solution of $(Bu)_4N^+F^- \cdot 3H_2O$ (662 mg, 2.1 mmol) in dry THF (5 ml) was kept at r.t. for 20 h. After the addition of **27** (387 mg, 2.1 mmol) and **4** (308 mg, 2 mmol) dissolved in THF (2 ml), the mixture was stirred at r.t. for 5 d. The residue obtained by filtration *(Celite)* and evaporation was heated with 5 ml of a mixture of CH_3OH (10 ml), 1,2-dichloroethane (20 ml) and CH_3SO_3H (0.1 ml) [7] for 20 h under reflux. Evaporation, acetylation (Ac_2O/pyridine over night), evaporation, and chromatography (100 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:2:2) yielded 35 mg (8%) of **6** (see *3.1*) and 29 mg (4.5%) of *2-(5'-acetoxy-2'-methoxyphenyl)-3-oxo-1-cyclohexenyl acetate* (**28**). IR ($CHCl_3$): 3040*w*, 2995*w*, 2955*m*, 2873*w*, 2835*w*, 1757*s*, 1675*s*, 1647*m*, 1604*w*, 1583*w*, 1490*m*, 1465*w*, 1455*w*, 1415*w*, 1368*m*, 1354*m*, 1290*w*, 1268*m*, 1178*s*, 1156*s*, 1057*w*, 1034*m*, 1000*s*, 980*w*, 911*m*, 891*w*, 872*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.95 and 2.11 (2*s*, 2 CH_3COO); 2.0–2.35 (*m*, 2H–C(5)); 2.45–2.9 (*m*, 2H–C(4), 2H–C(6)); 3.72 (*s*, CH_3O–C(2')); 6.58 (*d*, *J* = 3, H–C(6')); 6.83 (*dd*, *J* = 9 and 3, H–C(4')); 7.04 (*d*, *J* = 9, H–C(3')). ^{13}C-NMR (25 MHz, $CDCl_3$): 20.8 and 21.0 (C(5), 2 CH_3COO); 29.0 and 37.4 (C(4), C(6)); 55.6 (CH_3O); 114.7 and 115.8 (C(3'), C(4')); 123.1 (C(6')); 125.3 and 126.1 (C(2), C(1')); 141.9

(C(5')); 156.7 (C(2')); 166.2, 167.7, and 169.3 (C(1), 2 CH_3COO); 196.8 (C(3)). MS: 318 (6, M^+), 276 (5), 258 (4), 235 (13), 234 (85), 217 (26), *216* (100), 192 (19), 174 (32), 161 (18), 137 (8), 91 (5), 55 (6), 43 (20).

5.1.2. *Reaction in Boiling THF.* To a solution of $(Bu)_4N^+F^- \cdot 3H_2O$ (26 mg, 0.09 mmol) and **27** (187 mg, 1.014 mmol) in dry THF (2 ml) a solution of **4** (125 mg, 0.81 mmol) in THF (10 ml) was added. After boiling under reflux for 97 h, the solvent was evaporated at reduced pressure, and the residue was boiled under reflux for 43 h in 8 ml of a mixture of CH_3OH (10 ml), $ClCH_2CH_2Cl$ (20 ml) and CH_3SO_3H (0.1 ml) [7]. Chromatography (35 g of silica gel, CH_2Cl_2/CH_3OH 96:4) of the crude material obtained by evaporation gave 88 mg (50% based on **4**) of **6** (see *3.1*).

5.2. *Reaction with the 2-Methoxysubstituted Monoacetal* **29**. A solution of **29** (351 mg, 1.905 mmol), **27** (374 mg, 2.03 mmol) and $(Bu)_4N^+F^- \cdot 3H_2O$ (64 mg, 0.2 mmol) in 12 ml of dry THF was boiled under reflux for 5 d. After evaporation of solvent (aspirator) the residue was treated with 7 ml of a mixture of CH_3OH (10 ml), $ClCH_2CH_2Cl$ (20 ml) and CH_3SO_3H (0.1 ml) [7] for 24 h under reflux. Evaporation and chromatography (60 g of silica gel, Et_2O/hexane 2:1) gave 80 mg (27%) of 2,4-dimethoxyphenol and 142 mg (30%) of *6,8-dimethoxy-1,2,3,4-tetrahydrodibenzofuran-1-one* (**33**): m.p. 154–155° (Et_2O/hexane). IR ($CHCl_3$): 3030*w*, 3000*w*, 2960*m*, 2835*w*, 1665*s*, 1625*s*, 1604*s*, 1590*m*, 1492*s*, 1462*w*, 1453*m*, 1445*w*, 1432*m*, 1405*w*, 1360*w*, 1345*m*, 1318*m*, 1301*s*, 1186*w*, 1176*s*, 1153*s*, 1116*w*, 1059*m*, 1040*m*, 1020*w*, 1005*s*, 935*w*, 903*w*, 885*w*, 824*m*, 610*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 2.1–2.45 (*m*, 2H–C(3)); 2.45–2.75 and 2.85–3.3 (2*m*, 2H–C(2), 2H–C(4)); 3.75 and 3.97 (2*s*, CH_3O–C(6), CH_3O–C(8)); 6.44 and 7.08 (2*d*, $J \approx 2.5$, H–C(7), H–C(9)). MS: *246* (100, M^+), 231 (4), 218 (54), 203 (7), 190 (36), 161 (7), 147 (12), 119 (9), 115 (7), 104 (5), 91 (7), 89 (7), 69 (9), 63 (8), 55 (6). Anal. calc. for $C_{14}H_{14}O_4$ (246.26): C 68.28, H 5.73; found: C 68.38, H 5.82.

5.3. *Reaction with the 2-Bromosubstituted Monoacetal* **30**. A solution of **30** (343 mg, 1.47 mmol), **27** (330 mg, 1.79 mmol), and $(Bu)_4N^+F^- \cdot 3H_2O$ (100 mg, 0.3 mmol) in dry THF (8 ml) was boiled under reflux for 7 d (Ar). The residue obtained by evaporation was treated with 10 ml of a mixture of CH_3OH (10 ml) $ClCH_2CH_2Cl$ (20 ml) and CH_3SO_3H (0.1 ml) [7] for 24 h under reflux. Evaporation and chromatography (50 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:2:2) gave 122 mg (41%) of 2-bromo-4-methoxyphenol and 71 mg (16%) of *6-bromo-8-methoxy-1,2,3,4-tetrahydrodibenzofuran-1-one* (**34**): m.p. 154–155° (Et_2O/hexane). IR ($CHCl_3$): 3090*w*, 3030*w*, 3000*m*, 2960*m*, 2930*m*, 2870*w*, 2855*w*, 2840*m*, 1670*s*, 1612*m*, 1590*s*, 1481*s*, 1454*m*, 1443*m*, 1426*s*, 1393*m*, 1358*w*, 1342*w*, 1330*w*, 1316*w*, 1280*m*, 1262*w*, 1178*s*, 1169*s*, 1145*w*, 1125*s*, 1056*m*, 1033*s*, 1019*s*, 1002*s*, 904*w*, 885*w*, 965*m*, 850*m*, 644*w*. ^{1}N-NMR (80 MHz, $CDCl_3$): 2.05–2.45 (*m*, 2H–C(3)); 2.45–2.75 and 2.9–3.2 (2*m*, 2H–C(2), 2H–C(4)); 3.85 (*s*, CH_3O–C(8)); 7.06 and 7.45 (2*d*, $J \approx 3$, H–C(7), H–C(9)). MS (*di.*): 296 (99, M^+), *294* (100, M^+), 281 (3), 279 (3), 268 (78), 266 (78), 252 (7), 250 (19), 240 (46), 238 (46), 224 (6), 222 (17), 212 (5), 210 (5), 200 (8), 194 (11), 169 (6), 167 (6), 159 (24), 116 (12), 115 (11), 88 (10), 63 (12).

6. Reaction of 1-(Trimethylsilyloxy)cyclohexene (35) with Monoacetal 4. – 6.1. *Reaction Catalyzed by CF_3SO_3TMS.* A solution of **4** (597 mg, 3.87 mmol) and **35** (0.97 ml, *ca.* 5 mmol) in dry CH_2Cl_2 (4 ml) was added to a cooled (−78°) solution of CF_3SO_3TMS (2.8 ml, *ca.* 15 mmol) and Et_3N (2.3 ml, *ca.* 16 mmol) in CH_2Cl_2 (13 ml). After stirring for 19 h at r.t., the reaction was quenched by the addition to 1M aq. HCl and worked up with CH_2Cl_2. The residue of the org. phases was treated over night with Ac_2O/pyridine (*ca.* 2 ml of each). Evaporation and chromatography (100 g of silica gel, hexane/acetone 3:1) gave 270 mg (42%) of 4-methoxyphenyl acetate (**37**) and 99 mg (9%) of *4-methoxy-3-(2'-oxocyclohexyl)phenyl acetate* (**36**): IR ($CHCl_3$): 3030*w*, 2995*m*, 2935*s*, 2860*m*, 2830*m*, 1750*s*, 1708*s*, 1610*w*, 1491*s*, 1460*m*, 1445*m*, 1439*w*, 1420*m*, 1367*s*, 1335*w*, 1317*m*, 1298*w*, 1275*w*, 1190*s*, 1174*s*, 1153*m*, 1124*m*, 1063*m*, 1031*s*, 1011*m*, 950*m*, 930*m*, 899*m*, 886*m*, 868*w*, 835*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.5–2.4 (*m*, 6H); 2.25 (*s*, CH_3COO–C(1)); 2.3–2.7 (*m*, 2H–C(3')); 3.75 (*s*, CH_3O–C(4)); 3.6–4.15 (*m*, H–C(1')); 6.81 (*d*, $J = 9$, H–C(5)); 6.85 (*d*, $J \approx 3$, H–C(2)); 6.98 (*dd*, $J = 9$ and ≈ 3, H–C(6)). MS: 262 (8, M^+), *220* (100), 192 (21), 176 (28), 163 (24), 161 (13), 150 (10), 137 (15), 135 (8), 123 (10), 107 (18), 91 (12), 77 (12), 43 (21).

6.2. *Reaction Catalyzed by F^-.* A solution of monoacetal **4** (284 mg, 1.843 mmol) and **35** (313 mg, 1.82 mmol) in 2 ml of dry THF was added to a cooled (−78°) solution of $(Bu)_4N^+F^- \cdot 3H_2O$ (51 mg, 0.19 mmol) in THF (10 ml). After stirring for 6 h at −78° and for 14 h at r.t., the mixture was worked up with CH_2Cl_2. Chromatography (20 g of silica gel, hexane/acetone 3:1) gave 87 mg (18% based on **4**) of *13,13-dimethoxy-8-oxatricyclo[7.3.1.0^{2,7}]tridec-2(7)-en-11-one* (**38**): m.p. 102–103° (Et_2O/hexane). IR (CCl_4): 2990*m*, 2960*s*, 2938*s*, 2860*m*, 2835*s*, 1718*s*, 1692*s*, 1450*m*, 1442*m*, 1414*w*, 1395*m*, 1363*m*, 1322*w*, 1284*m*, 1218*m*, 1196*s*, 1180*w*, 1173*w*, 1149*s*, 1132*w*, 1109*s*, 1065*s*, 1046*m*, 1013*m*, 997*m*, 964*m*, 915*w*, 903*w*, 880*m*, 690*m*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.3–1.8 (*m*, 2H–C(4), 2H–C(5)); 1.75–2.2 (*m*, 2H–C(3), 2H–C(6)); 2.2–2.85 (*m*, H–C(1), 2H–C(10), 2H–C(12)); 3.30 and 3.31 (2*s*, $2CH_3O$–C(13)); 4.41 (*dt*, $J \approx 4.5$ and 3, H–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.7 and 22.8 (C(4), C(5)); 26.5 and 26.8 (C(3), C(6)); 37.8 (C(1)); 41.2 and 45.3 (C(10), C(12)); 48.2 and 48.8

(2 CH_3O); 70.6 (C(9)); 97.0 and 105.0 (C(2), C(13)); 144.3 (C(7)); 206.9 (C(11)). MS (*di.*): 252 (48, M^+), 221 (7), 220 (7), 181 (9), 165 (14), 135 (17), *101* (100), 91 (10), 79 (8), 77 (7), 67 (8), 55 (32), 41 (13). Anal. calc. for $C_{14}H_{20}O_4$ (252.31): C 66.65, H 7.99, O 25.36; found: C 66.65, H 7.93, O 25.22.

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