207. Experiments on the Total Synthesis of Lysolipin I

Part III[1])

Preparation and Transformations of Substituted 1,2,3,4-Tetrahydrodibenzofuran-1-ones[2])

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Summary

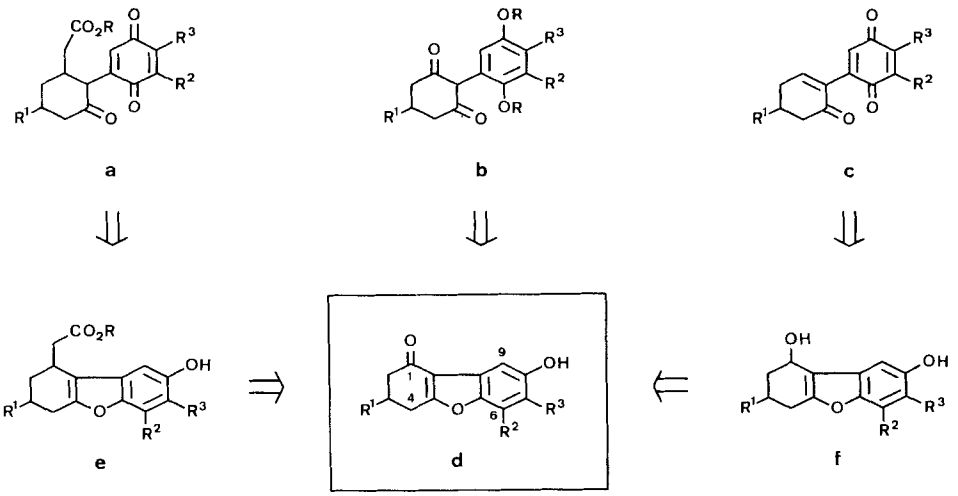
1,2,3,4-Tetrahydrodibenzofuran-1-ones were obtained by *Michael* addition of 1,3-cyclohexadione (**2**) to *o*-benzoquinone (**3**) and to *p*-benzoquinones **8** and **11** *(Scheme 2)*. In addition to the expected 7,8-disubstituted adduct **14**, the $ZnCl_2$-catalyzed reaction of dione **2** with methoxy-*p*-benzoquinone (**11**) afforded a small amount of the 6,8-disubstituted regio-isomer **13** *(Scheme 2)*. The projected cleavage of these dibenzofuranones to 3-methoxy-2-phenyl-2-cyclohexenone **22** could be effected by treatment with NaOH followed by methylation *(Scheme 3)*. Attempted acetalization of such dibenzofuranones resulted in a *retro-Claisen*-type cleavage, giving the benzofuryl-butyrate **16**. Other transformations include reduction of the ketone, of the C(4a)=C(9b) bond, and alkylation with Li-ethoxyacetylide *(Scheme 3)*. Oxidation of 8-hydroxy-7-methoxydibenzofuran derivatives led to *o*-quinones instead of the desired ring cleavage to *p*-quinones *(Scheme 4)*.

1. Introduction. – A retrosynthetic analysis of the complex structure determined for the antibiotic Lysolipin I [3] led to (3'-oxocyclohexyl)acetic acids with a *p*-hydroquinoid substituent at C(2') as starting point for a promising approach to this synthetic problem (*cf.* [1] [4]). Such structural units should readily be available from either the corresponding quinones **a**, cyclohexadiones **b**, or cyclohexenones **c**, which in turn are derivable from 1,2,3,4-tetrahydrodibenzofuran-1-ones **d** by hydrolytic (→**b**) or oxidative (→**a** *via* **e**,→**c** *via* **f**) opening of the furan ring *(Scheme 1)*. 1,2,3,4-Tetrahydrodibenzofuran-1-ones have been prepared by several methods [1] [5] [6], and the projected hydrolytic cleavage of the furan ring (**d**→**b**) was successful with the closely related 3-acyl-2-alkyl-benzofurans [7]. 2-Hydroxydibenzofuran, on the other hand, was cleaved to (2'-hydroxyphenyl)-*p*-benzoquinone by periodate oxidation [8].

[1]) Part II [1].

[2]) Part of these results are included in the Ph. D. thesis of *V. Sch.* [2].

Scheme 1



2. Preparation of Tetrahydrodibenzofuran-1-ones. – The outset of this study was given by the facile access to dibenzofuranone **1**, which is formed from 1,3-cyclohexadione (**2**) and *o*-benzoquinone (**3**), obtained by *in situ* oxidation of catechol (**4**) [5]. Alkylation of **1** with $(CH_3O)_2SO_2/K_2CO_3$ gave the dimethoxy compound **5** in 22% overall yield *(Scheme 2)*[3]. For two reasons we looked for alternative approaches to such dibenzofuranones. *1)* The planned oxidations (**f**→**c**, **e**→**a**, *Scheme 1*) require selectively *O*-protected derivatives of **1** to prevent oxidation to *o*-quinones (partial *O*-methylation of **1** afforded a 1:1-mixture of **6** and **7** [2], *Scheme 2*). *2)* Although the addition to *o*-benzoquinone (**3**) can be extended to 5-substituted 1,3-cyclohexadiones [5], 6-substituted dibenzofuranones of type **d** *(Scheme 1)* are not necessarily available by this method.

Since malonic-acid derivatives and acetoacetates have been found to add readily to *p*-benzoquinones under acid [9] or base [10] catalysis, and since the regioselectivity of these *Michael* additions is well-understood and predictable [11], we decided to investigate the 1,4-addition of cyclohexadione **2** to *p*-benzoquinones.

Reaction of *p*-benzoquinone (**8**) with a twofold excess of **2** in *t*-BuOH/Et_2O (or *t*-BuOH/CH_2Cl_2)[4]) catalyzed by $ZnCl_2$ according to [9a] followed by treatment with $CH_3OH/CH_3SO_3H/ClCH_2CH_2Cl$[5]) and benzylation of the primary product **9** gave the dibenzofuranone **10** in very low yield (10%)[6]). The 7-methoxy-substituted derivative **12** (isolated in 24% yield by acetylation) was obtained analogously from methoxy-*p*-ben-

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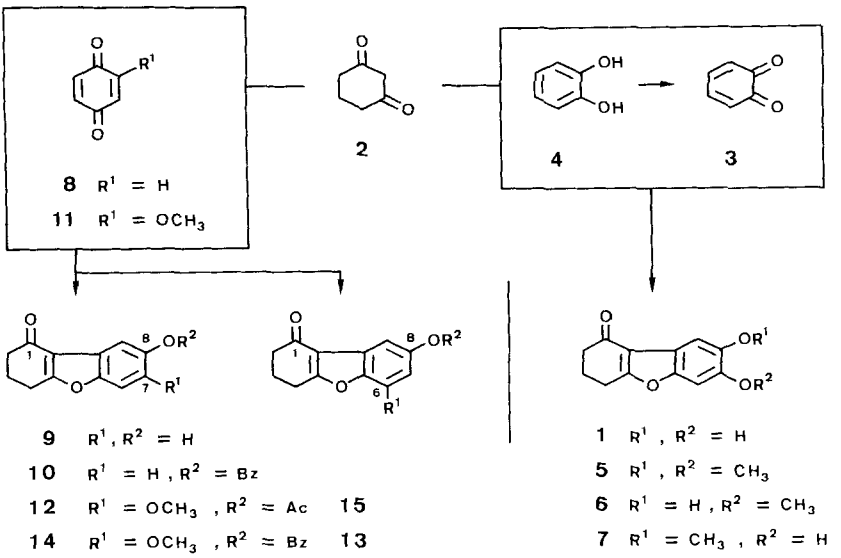
[3]) Much higher yields of **1** (> 90%) have been described in the literature [5b] [5c]. The success of this transformation depends on the rates of oxidation and removal from the reaction medium of the product which is itself sensitive to oxidation.

[4]) In CH_3OH or EtOH etherification of dione **2** by the solvent was a major side-reaction, while in aprotic media (Et_2O, acetone) redox processes were found to predominate.

[5]) Under these conditions [12] excess dione **2** is converted to its methyl-enol ether, which has advantageous properties in chromatographic separations.

[6]) The acetate of dibenzofuranone **9** was obtained much more efficiently (77% yield) by using *p*-benzoquinone monoethylene acetal [1].

Scheme 2



zoquinone (**11**)[7]). Closer examination of the mixture obtained by $ZnCl_2$-catalyzed addition of dione **2** to quinone **11** followed by benzylation led to the detection of the regio-isomer **13**, which was isolated in *ca.* 6% yield in addition to 25% of **14** *(Scheme 2)*[8]).

The unsatisfactory yields of these reactions are in part due to the oxidation of the primary *Michael* adducts (possibly before furan-ring closure) by the starting quinones **8** and **11**, respectively, leading to complex products and the hydroquinone of the starting material. Interestingly, the $TiCl_4$-catalyzed reaction of the silylenol ether derived from **2** with quinone **11** gave a high yield of 2-methoxyhydroquinone [2], indicating a direct redox process between the reactants. Similar observations have been made with quinone monoacetals [1].

3. Transformations of 1,2,3,4-Tetrahydrodibenzofuran-1-ones. – The hydrolytic opening of the furan ring of 1,2,3,4-tetrahydrodibenzofuran-1-ones proved to be more difficult than anticipated. Dimethoxy compound **5** and the analogous compound obtained from dimedone and catechol (**4**) (*cf.* [2] [5]) resisted treatment with 10% aq. KOH in dioxane in the presence of $(CH_3O)_2SO_2$ at reflux temperature, $KOCH_3$ in boiling Et_2O or CH_3OH, followed by addition of $(CH_3O)_2SO_2$, trimethyl orthoformate/CH_3SO_3H in boiling benzene, or CH_3OH/HCl at 70° (*cf.* [2]). Under acetalization conditions (1,2-ethanediol/TsOH·H_2O) ketone **5** was transformed to 4-(2′-benzofuryl)butyrate **16** *(Scheme 3)*. To prepare the 4a,9b-dihydro-derivative **17**, **5** was hydrogenated at 3–5 atm. pressure with 10% Pd/$BaSO_4$ in AcOEt, affording the hexahydrodibenzofuran-1-ols **18** and **19** in a *ca.* 3:1 ratio. Alcohol **18** was also characterized as its

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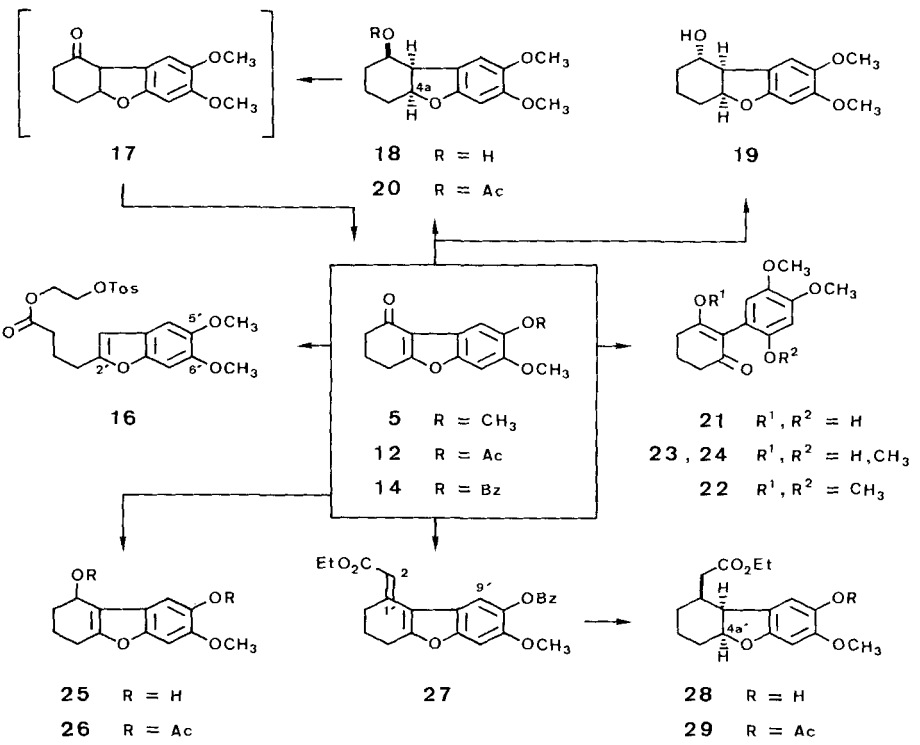
[7]) Benzofuranone **12** was also obtained, albeit in even lower yield, by addition of the morpholino-enamine derived from dione **2** to quinone **11** according to [10c].

[8]) While separation of the acetates **12** and **15** is much more difficult than the separation of the benzyl ethers **13** and **14**, the 8-(2′-tetrahydropyranyloxy) derivatives could also be separated easily by chromatography. Acetate **15** was obtained pure by transformation of the corresponding tetrahydropyranyl ether (*cf.* [2]).

Scheme 3



acetate **20**[9])[10]). Oxidation of **18** with a variety of reagents including DMSO/pyridine·SO_3 [13] gave exclusive formation of **5** with no traces of **17** detectable (*Scheme 3, cf.* [2])[11]).

It was discovered only recently, that a clean hydrolytic cleavage of **5** is possible by treatment with NaOH in aq. EtOH according to [7]. It is quite remarkable, that the 1,3-cyclohexadione moiety is unaffected under these conditions[12]), while the analogous acyclic β-diketones obtained from 3-acyl-2-alkylbenzofurans undergo quantitative *retro-Claisen* reaction [7][13]). Quenching with CH_3I afforded a mixture of the tetramethoxy derivative **22** and partially methylated compounds **23** and **24**. Methylation of **23**

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[9]) Hydrogenation with 5% Pd/C at normal pressure led to extensive hydrogenolysis of the O-function at C(1) (*cf.* [2]).

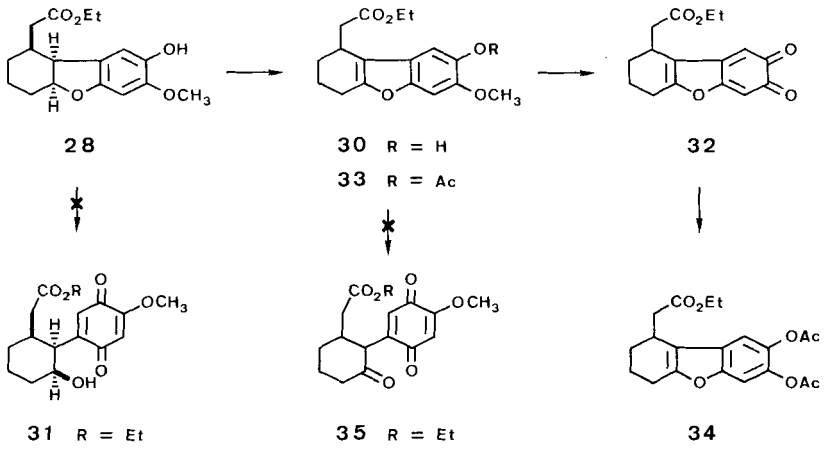
[10]) The structural assignment of the isomers **18** and **19** relies on the assumptions, that the furan double bond is hydrogenated in a *cis*-fashion, and that the main product **18** results from attack *trans* to OH–C(1). Hydrogenation of ketone **17** from the less hindered *exo*-face would also lead to **18**. An unambiguous corroboration of these structures with the aid of the ^{1}H-NMR spectra (300 MHz) was unfortunately thwarted by the rather unusual coupling pattern of **18**/**20** and **19** (see *Exper. Part*).

[11]) Compound **17** might be converted to **5** by autoxidation. Such an oxidation was recently observed in the case of an analogous carbazole derivative [14].

[12]) The ketone cleavage of 1,3-cyclohexadiones requires boiling under reflux in aq. base for 30 h [15].

[13]) Careful acidification and extraction (AcOEt) allows the isolation of the polar crystalline 2-aryl-1,3-cyclohexadione **21**, which is slowly reconverted to **5** (no exp. description).

Scheme 4



and **24** (CH_3I/K_2CO_3/acetone) finally afforded **22** in a combined yield of 67% *(Scheme 3)*[14]). To test the possibility of an oxidative cleavage of the furan ring, the acetate **12** was reduced with $NaBH_4$ to the alcohol **25**, characterized as diacetate **26**. The acetic acid side-chain was introduced by alkylation of **14** with Li-ethoxyacetylide [16] followed by acid treatment, affording the unsaturated ester **27** in high yield[15]). The hexahydro-dibenzofurylacetate **28**, characterized as acetate **29**, was finally obtained from **27** by hydrogenation *(Scheme 3)*[16]).

Unfortunately, the oxidation of **28** with periodic acid according to [19] did not proceed as expected. Instead of ring cleavage, affording the desired *p*-benzoquinone **31**[17]), dehydrogenation to **30** and further oxidation led to the *o*-benzoquinone **32,** as demonstrated by reduction of the crude mixture with dithionite and acetylation, which gave the tetrahydro-dibenzofuranylacetate **33** (10%) and *ca.* 24% of the diacetate **34** *(Scheme 4)*. This result also explains the unavailability of *p*-benzoquinone **35** by oxidation of **30** *(Scheme 4)* and other fruitless attempts at the cleavage of the furan ring of 7-methoxy-8-dibenzofuranol derivatives by oxidation (*e.g.* **25,** *cf.* [2]).

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[14]) In addition to **22**, 10% of starting material **5**, formed in the course of the alkylation of **21**, were isolated. Treatment of **21**[13]) with $(CH_3O)_2SO_2/K_2CO_3$ in boiling acetone gave a 1:1 mixture of **22** and **5** (no exper. description).

[15]) Related 1,2,3,4-tetrahydrodibenzofuran-1-ones have been alkylated successfully with the *Reformatzkii* reagent derived from bromoacetate [6a] [17]. In contrast to 3-ethoxy-2-cyclohexenone [18] such dibenzofuranones have been found to be inert towards the *Wittig-Horner* reagent generated from triethyl phosphonoacetate (*cf.* [2]). The (*E*)-configuration of the C(2)=C(1') bond follows from ^{1}H-NMR measurements. The spatial proximity of H–C(2) and H–C(9') was deduced by a difference-NOE experiment (irradiation at the resonance frequency of H–C(2) gives enhanced sensitivity of H–C(9')).

[16]) The C(2)=C(1') bond is hydrogenated at a faster rate than the furane ring. Under controlled conditions the dihydro derivative **30** *(Scheme 4)* can therefore be isolated (*cf.* [2] [6a]). The relative configuration of **28** relies on similar assumptions as used for the assignment of **18** and **19**[10]). The stereochemical relationship between **18** and **28** was indicated by their ^{1}H-NMR spectra exhibiting similar coupling parameters for the bridgehead H-atoms H–C(4a) (**18**) and H–C(4a') (**28**), respectively.

[17]) Oxidation of the related 2,4-dimethoxyphenol with periodate/AcOH gives 60% of methoxy-*p*-benzoquinone (**11**) [8a].

It is, thus, demonstrated that tetrahydro-dibenzofuranones **d** can be transformed hydrolytically but not by oxidation to 2-aryl-1,3-cyclohexadiones **b** *(Scheme 1)*, which in turn should be transformable to (2'aryl-3'-oxocyclohexyl)acetic acids by routine procedures. Such a derivative, obtained in this special case by an alternative procedure [2] [4], could be cyclized to an octahydro-phenanthrenedione, a key compound of a projected total synthesis of Lysolipin I [4].

This work was supported by *Ciba-Geigy AG*, Basel. We are indebted to the following persons of our analytical department: Prof. *J. Seibl* and Mrs. *L. Golgowsky* (MS), Ms. *B. Brandenberg*, Mr. *F. Fehr* and Mr. *M. Langenauer* (NMR), and Ms. *K. Bleidissel* and Mr. *M. Manser* (elemental analyses).

Experimental Part

General. See [20].

1. Preparation of Tetrahydrodibenzofuran-1-ones. – 1.1. *7,8-Dimethoxy-1,2,3,4-tetrahydrodibenzofuranone* (**5**). A solution of KIO_3 (1.4 g, 6.54 mmol) and $NaOAc \cdot 3H_2O$ (3 g, 22.1 mmol) in H_2O (25 ml) was added dropwise to a solution of 1,3-cyclohexadione (**2**) (1.12 g, 10 mmol), catechol (**4**) (1.1 g, 10 mmol), and $NaOAc \cdot 3H_2O$ (6 g, 44.1 mmol) in H_2O (15 ml) and acetone (3 ml). The precipitated adduct **1** (644 mg) was collected by filtration, dissolved in acetone (30 ml), and treated with $(CH_3O)_2SO_2$ (1.13 ml, *ca.* 12 mmol)/K_2CO_3 (1.8 g) for 5 h under reflux. Workup with AcOEt and crystallization (AcOEt/C_6H_6) afforded 540 mg (22% based on **2** or **4**) of **5**, m.p. 164–164.5°. IR ($CHCl_3$): 3100*w*, 3030*w*, 2960*m*, 2945*m*, 2915*w*, 2878*w*, 2840*w*, 1667*s*, 1627*w*, 1590*m*, 1495*s*, 1474*s*, 1467*s*, 1455*m*, 1442*s*, 1431*m*, 1418*w*, 1396*m*, 1363*m*, 1341*w*, 1320*m*, 1295*s*, 1180*w*, 1160*m*, 1140*m*, 1120*s*, 1060*m*, 1045*m*, 1020*s*, 1008*s*, 953*m*, 875*w*, 868*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.1–2.4 (*m*, 4 main peaks, 2H–C(3)); 2.46–2.66 and 2.85–3.1 (2*m*, *each 3 main peaks*, 2H–C(2), 2H–C(4)); 3.88 and 3.92 (2*s*, CH_3O–C(7), CH_3O–C(8)); 6.99 (*s*, H–C(6)); 7.46 (*s*, H–C(9)). MS(*di.*): *246* (100, M^+), 231 (55), 218 (4), 203 (15), 190 (18), 185 (7), 175 (9), 162 (7), 147 (13), 133 (7), 55 (11). Anal. calc. for $C_{14}H_{14}O_4$ (246.25): C 68.28, H 5.73; found: C 68.27, H 5.82.

1.2. *8-Benzyloxy-1,2,3,4-tetrahydrodibenzofuran-1-one* (**10**). To a solution of dione **2** (6.70 g, 60 mmol) and $ZnCl_2$ (4.08 g, 30 mmol, dried by melting at h.v.) in *t*-BuOH (60 ml), a solution of *p*-benzoquinone (**8**, 3.24 g, 30 mmol) in Et_2O (150 ml) was added within 48 h at 70–80° (Ar). After workup with CH_2Cl_2, the crude material was dissolved in CH_3OH (75 ml), $ClCH_2CH_2Cl$ (150 ml), and CH_3SO_3H(0.5 ml), and this mixture was boiled under reflux for 24 h. Workup with CH_2Cl_2, treatment with BzBr (9.5 ml, *ca.* 80 mmol)/K_2CO_3 (55.2 g) in acetone (200 ml) for 36 h (reflux), workup with CH_2Cl_2, and chromatography (200 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 6:12:1) yielded 867 mg (10% based on **8**) of **10**, m.p. 107–107.5° (AcOEt/cyclohexane). IR ($CHCl_3$): 3085*w*, 3060*w*, 2955*w*, 2885*w*, 2870*w*, 2840*w*, 1662*s*, 1612*m*, 1586*s*, 1495*w*, 1476*s*, 1451*s*, 1430*w*, 1399*s*, 1383*m*, 1355*w*, 1327*w*, 1317*w*, 1273*s*, 1173*s*, 1157*s*, 1135*m*, 1105*w*, 1078*w*, 1058*m*, 1043*w*, 1009*s*, 945*m*, 895*w*, 885*w*, 872*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.1–2.4 (*m*, 2H–C(3)); 2.44–2.66 and 2.80–3.10 (2*m*, *each 3 main signals*, 2H–C(2), 2H–C(4)); 5.08 (*m*, $w_{1/2} \approx 2$, $C_6H_5CH_2O$–C(8)); 6.93 (*dd*, $J = 9$ and 3, H–C(7)); 7.16–7.54 (*m*, H–C(6), $C_6H_5CH_2O$–C(8)); 7.61 (*d*, $J = 3$, H–C(9)). MS(*di.*): 292 (83, M^+), 264 (6), 263 (6), 214 (11), 201 (11), *91* (100), 65 (19).

1.3. *7-Methoxy-1-oxo-1,2,3,4-tetrahydrodibenzofur-8-yl Acetate* (**12**). To a solution of $ZnCl_2$ (1.36 g, 10 mmol, dried by melting at h.v.) and dione **2** (224 mg, 20 mmol) in dry EtOH (10 ml) and dry Et_2O (10 ml), heated in an oil bath of 70° (reflux), a solution of methoxy-*p*-benzoquinone (**11**, [10a]) (922 mg, 6.68 mmol) in EtOH (20 ml) was added within 60 h. Workup with CH_2Cl_2, acetylation (Ac_2O/pyridine), and chromatography (150 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 2:2:1) gave 170 mg (11%) of 2-methoxyphen-1,4-diyl diacetate and 448 mg (24% based on **11**) of **12**, m.p. 160–160.5°. IR ($CHCl_3$): 3035*w*, 2960*w*, 2945*w*, 2895*w*, 2875*w*, 2850*w*, 1760*s*, 1672*s*, 1637*w*, 1592*m*, 1490*s*, 1465*w*, 1453*m*, 1440*s*, 1431*m*, 1416*w*, 1397*w*, 1360*m*, 1354*m*, 1340*w*, 1330*w*, 1319*m*, 1298*s*, 1189*s*, 1175*s*, 1142*s*, 1119*s*, 1057*w*, 1043*w*, 1028*m*, 1006*s*, 957*w*, 920*m*, 887*w*, 882*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.1–2.4 (*m*, 2H–C(3)); 2.29 (*s*, CH_3COO–C(8)); 2.44–2.66 and 2.86–3.1 (2*m*, *each 3 main peaks*, 2H–C(2), 2H–C(4)); 3.83 (*s*, CH_3O–C(7)); 7.05 (*s*, H–C(6)); 7.67 (*s*, H–C(9)). MS(*di.*): 274 (17, M^+), *232* (100), 217 (50), 204 (11), 189 (5), 176 (12), 91 (3), 69 (5), 55 (4), 43 (8). Anal. calc. for $C_{15}H_{14}O_5$ (274.26): C 65.69, H 5.15; found: C 65.52, H 5.34.

1.4. *$ZnCl_2$-Catalyzed Addition of Dione* **2** *to Quinone* **11**, *followed by Benzylation.* To a solution of **2** (6.72 g, 60 mmol) and $ZnCl_2$ (4.08 g, 30 mmol, dried by melting at h.v.) in *t*-BuOH (60 ml) a solution of **11** (4.14 g, 30

mmol, freshly sublimed) in CH_2Cl_2 (60 ml) was added within 108 h at 60–70° (exclusion of light, Ar). After heating under reflux for 20 h, part of the solvent was evaporated, and the mixture was worked up with CH_2Cl_2. The crude mixture, dissolved in CH_3OH (75 ml), $ClCH_2CH_2Cl$ (150 ml), and CH_3SO_3H (0.5 ml), was heated under reflux for 16 h. Workup with CH_2Cl_2, treatment with BzBr (9.5 ml, *ca.* 80 mmol)/K_2CO_3 (55.2 g) in acetone (200 ml) for 60 h under reflux, workup with CH_2Cl_2 and several chromatographic separations (silica gel, cyclohexane/CH_2Cl_2/AcOEt 6:12:1) afforded 530 mg (5.5% based on **11**) of **13**, 2.369 g (24.5% based on **11**) of pure **14**, and 114 mg ($\approx$ 1%) of mixed fractions (mainly **14**).

8-Benzyloxy-6-methoxy-1,2,3,4-tetrahydrodibenzofuran-1-one (**13**). M.p. 147–148°. IR ($CHCl_3$): 3030*w*, 2955*m*, 2940*m*, 2885*w*, 2835*w*, 1662*s*, 1640*s*, 1603*s*, 1587*m*, 1488*s*, 1461*m*, 1450*m*, 1440*s*, 1415*w*, 1407*w*, 1380*m*, 1357*w*, 1340*m*, 1315*m*, 1298*s*, 1174*s*, 1150*s*, 1113*w*, 1078*w*, 1055*m*, 1025*m*, 1000*s*, 950*w*, 902*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.06–2.38 (*m*, 2H–C(3)); 2.44–2.66 and 2.86–3.1 (2*m*, *each 3 main signals*, 2H–C(2), 2H–C(4)); 3.81 (*s*, CH_3O–C(6)); 5.07 (*m*, $w_{1/2} \approx 2$, $C_6H_5CH_2O$–C(8)); 6.52 (*d*, $J = 2$, H–C(7)); 7.14–7.56 (*m*, H–C(9), $C_6H_5CH_2O$–C(8)). MS(*di.*): *322* (100, M^+), 245 (19), 244 (25), 231 (5), 203 (7), 91 (95). Anal. calc. for $C_{20}H_{18}O_4$ (322.34): C 74.52, H 5.63; found: C 74.43, H 5.65.

8-Benzyloxy-7-methoxy-1,2,3,4-tetrahydrodibenzofuran-1-one (**14**). M.p. 140–141°. IR ($CHCl_3$): 2940*w*, 2890*w*, 2870*w*, 2840*w*, 1653*s*, 1627*w*, 1586*m*, 1490*s*, 1470*m*, 1460*m*, 1450*s*, 1443*m*, 1394*w*, 1360*m*, 1340*w*, 1316*m*, 1281*s*, 1179*w*, 1155*m*, 1140*m*, 1119*s*, 1055*w*, 1043*w*, 1025*w*, 1007*s*, 954*w*, 913*w*, 885*w*, 877*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.1–2.36 (*m*, 2H–C(3)); 2.44–2.64 and 2.84–3.05 (2*m*, *each 3 main peaks*, 2H–C(2), 2H–C(4)); 3.86 (*s*, CH_3O–C(7)); 5.14 (*m*, $w_{1/2} \approx 2$, $C_6H_5CH_2O$–C(8)); 7.0 (*s*, H–C(6)); 7.56 (*s*, H–C(9)); 7.2–7.6 (*m*, $C_6H_5CH_2O$–C(8)). MS(*di.*): *322* (100, M^+), 279 (1), 231 (97), 203 (20), 91 (67), 55 (15), 43 (5).

2. Transformations of Tetrahydro-1-dibenzofuranones. – 2.1. *2-Tosyloxyethyl 4-(5',6'-Dimethoxy-2'-benzofuryl)butyrate* (**16**). A mixture of dibenzofuranone **5** (60 mg, 0.244 mmol), $TsOH \cdot H_2O$ (91 mg, 0.48 mmol), and 1,2-ethanediol (0.1 ml, *ca.* 1.8 mmol) in toluene (6 ml) was boiled under reflux at a *Dean-Stark* trap for 3 h (Ar). Workup with AcOEt and chromatography (15 g of silica gel, CH_2Cl_2/AcOEt 9:1) gave 58 mg (52%, 62% based on consumed **5**) of **16** and 10 mg (17%) of **5**. IR ($CHCl_3$): 3090*w*, 3030*w*, 2960*m*, 2945*m*, 2915*w*, 2880*w*, 2840*w*, 1738*s*, 1622*w*, 1600*m*, 1484*s*, 1466*s*, 1455*m*, 1440*s*, 1400*w*, 1367*s*, 1320*s*, 1309*m*, 1293*m*, 1176*s*, 1148*s*, 1115*s*, 1097*m*, 1070*w*, 1020*m*, 1006*m*, 935*m*, 887*m*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.8–2.16 (*m*, 2H–C(3)); 2.22–2.44 and 2.6–2.8 (2*m*, *each 3 main peaks*, 2H–C(2), 2H–C(4)); 2.38, (*m*, $w_{1/2} \approx 2$, $CH_3C_6H_4SO_3$–C(2")); 3.86 (*s*, CH_3O–C(5'), CH_3O–C(6')); 3.19 (*m*, $w_{1/2} \approx 2$, 2H–C(1"), 2H–C(2")); 6.28 (*m*, $w_{1/2} \approx 2$, H–C(3')); 6.92 and 6.98 (2*s*, H–C(4'), H–C(7')); 7.20–7.36 and 7.68–7.84 (2*m*, $CH_3C_6H_4SO_3$–C(2")). MS(*di.*): 279 (33), 167 (90), 155 (7), 129 (53), 113 (37), 112 (30), 111 (20), 83 (53), *78* (100), 77 (27), 71 (63), 70 (50), 69 (37), 57 (90), 55 (53), 43 (70), 41 (53).

2.2. *Hydrogenation of* **5**. A solution of **5** (432 mg, 175 mmol) in AcOEt (70 ml) was hydrogenated at 3–5 atm. *(Parr-Shaker)* with 30 mg of 10% Pd/$BaSO_4$ for 6 h. The catalyst was removed by filtration. Chromatography (50 g of silica gel, cyclohexane/AcOEt 1:1) of the residue yielded 53 mg (*ca.* 12%) of impure **5** and 307 mg (70%) of a mixture of **18** and **19**. Part (154 mg) of this mixture was separated by crystallization (CH_2Cl_2/hexane) and chromatography of the mother liquor (silica gel, hexane/CH_2Cl_2/AcOEt 1:1:1) into 103 mg (67%) of **18**, 22 mg (14%) of **19**, and 18 mg (*ca.* 12%) of a 9:1 mixture of **19** and **18**.

(1R,4aS*,9bR*)-7,8-Dimethoxy-1,2,3,4,4a,9b-hexahydrodibenzofuran-1-ol* (**18**): m.p. 148–149° (CH_2Cl_2/hexane). IR ($CHCl_3$): 3615*w*, 3580*w*, 3035*w*, 2940*s*, 2915*m*, 2875*m*, 2840*w*, 1618*m*, 1493*s*, 1467*s*, 1455*s*, 1444*s*, 1417*w*, 1327*w*, 1360*m*, 1341*m*, 1328*w*, 1300*m*, 1292*m*, 1272*w*, 1177*s*, 1166*s*, 1112*s*, 1101*m*, 1060*m*, 1030*m*, 1000*m*, 978*m*, 927*w*, 906*w*, 897*w*, 887*w*, 875*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.2–2.1 (*m*, 2H–C(2), 2H–C(3), 2H–C(4), HO–C(1)); 3.41 (*dd*, $J = 8$ and 5, H–C(9b)); 3.80 (*s*, CH_3O–C(7), CH_3O–C(8)); 3.9–4.2 (*m*, H–C(1)); 4.6–4.9 (*m*, H–C(4a)); 6.47 (*m*, $w_{1/2} \approx 1$) and 6.93 (*m*, $w_{1/2} \approx 2$) (H–C(6), H–C(9)). MS(*di.*): *250* (100, M^+), 235 (13), 217 (11), 191 (65), 167 (12), 166 (14), 43 (15).

(1R,4aS*,9bR*)-7,8-Dimethoxy-1,2,3,4,4a,9b-hexahydrodibenzofur-1-yl Acetate* (**20**). Acetylation of **18** (23 mg) with Ac_2O/pyridine gave 27 mg (98%) of **20**, purified by chromatography (silica gel, hexane/CH_2Cl_2/Et_2O 2:2:1). IR ($CHCl_3$): 3030*w*, 2995*w*, 2940*m*, 2865*w*, 2830*w*, 1722*s*, 1613*m*, 1490*s*, 1461*m*, 1450*m*, 1440*m*, 1412*w*, 1375*w*, 1367*m*, 1360*m*, 1340*w*, 1325*w*, 1300*w*, 1185*s*, 1172*m*, 1161*m*, 1144*m*, 1120*w*, 1110*m*, 1098*m*, 1063*m*, 1050*w*, 1030*m*, 990*m*, 972*m*, 934*w*, 917*w*, 908*w*, 892*w*, 969*w*, 850*m*, 822*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.39–1.53 (*m*, 1H); 1.55–1.95 (*m*, 5H); 1.91 (*s*, CH_3COO–C(1)); 3.62 (*dd*, $J = 8$ and 5,5 H–C(9b)); 3.82 and 3.83 (2*s*, CH_3O–C(7), CH_3O–C(8)); 4.80 (*dt*, $J = 8$ and 5.5, H–C(4a)); 5.25 (*ddd*, $J = 8.5$, 5.5, and 4, H–C(1)); 6.46 (*s*, H–C(6)); 6.87 (*d*, $J \approx 0.7$, H–C(9)). MS(*di.*): *292* (100, M^+), 277 (3), 249 (10), 233 (10), 232 (55), 217 (30), 205 (17), 204 (50), 191 (63), 178 (10), 167 (13), 151 (12), 73 (27), 61 (34), 45 (74), 43 (67).

(1S,4aS*,9bR*)-7,8-Dimethoxy-1,2,3,4,4a,9b-hexahydrodibenzofuran-1-ol* (**19**). M.p. 116–117° (CH_2Cl_2/hexane). IR ($CHCl_3$): 3600*w*, 3550–3300*w*, 3030*w*, 2995*w*, 2935*m*, 2865*w*, 2830*w*, 1614*m*, 1489*s*, 1460*m*, 1450*m*, 1440*m*, 1413*w*, 1364*w*, 1336*w*, 1298*w*, 1183*s*, 1161*s*, 1108*s*, 1080*w*, 1045*w*, 1035*w*, 995*m*, 972*m*, 882*m*, 865*w*, 850*m*, 825*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.25–1.4 (*m*, 1H); 1.5–1.9 (*m*, 4H); ≈ 1.75 (br., *exchangeable with* D_2O, HO–C(1)); 2.05–2.2 (*m*, 1H); 2.80 (*dd*, *J* = 8 and 6.5, H–C(9b)); 3.47 (*m*, *after exchange with* D_2O, *ddd*, *J* = 10.5, 8, and 4, H–C(1)); 3.827 and 3.833 (2*s*, CH_3O–C(7), CH_3O–C(8)); 4.73 (*dt*, *J* ≈ 6.5 and 3.5, *further broadened by small couplings*, H–C (4a)); 6.49 and 6.93 (2*s*, H–C(6), H–C(9)). MS(*di.*): *250* (100, M^+), 235 (9), 232 (1), 217 (7), 191 (58), 163 (7), 147 (6), 91 (5), 77 (7), 69 (9).

2.3. *3-Methoxy-2-(2',4',5'-trimethoxyphenyl)-2-cyclohexen-1-one* (**22**). A mixture of **5** (118 mg, 0.482 mmol) and 4 ml of a solution of NaOH (6 g) in H_2O (10 ml) and EtOH (50 ml) was boiled under reflux for 4 h (Ar). After the addition of CH_3I (1 ml and 1 ml after 14 h, 5.56 g, *ca.* 32 mmol), the solution was warmed in an oil bath (50°) for 18 h (Ar). Workup with AcOEt gave 71 mg of products (mainly **5** and **22**) from the org. phases and 93 mg of **23**/**24** from extraction (AcOEt) of the acidified aq. phases. The partially methylated material (93 mg of **23**/**24**) was treated with CH_3I (1 ml, 2.28 g, *ca.* 16 mmol)/K_2CO_3 (1.5 g) in acetone (5 ml) for 39 h under reflux (50°, Ar). Workup with AcOEt and chromatography (15 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 2:5:3 +5% CH_3OH) of the combined crude products (155 mg) gave 12 mg (10%, after re-chromatography, silica gel, CH_2Cl_2/AcOEt 10:1) of **5** and 95 mg (67%, 74% based on consumed **5**) of **22**; m.p. 116–117° (CH_2Cl_2/hexane). IR ($CHCl_3$): 3030*w*, 2995*m*, 2940*m*, 2910*w*, 1845*w*, 2830*w*, 1642*s*, 1599*s*, 1505*s*, 1459*s*, 1432*w*, 1390*m*, 1362*m*, 1353*s*, 1325*w*, 1293*m*, 1275*w*, 1253*m*, 1162*m*, 1129*m*, 1079*m*, 1032*s*, 1000*w*, 950*w*, 856*m*, 838*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.85–2.3 (*m*, 2H–C(5)); 2.3–2.85 (*m*, 2H–C(4), 2H–C(6)); 3.64, 3.70, 3.79, and 3.85 (4*s*, 4 OCH_3); 6.54 (*s*, H–C(3'), H–C(6')). MS (*di.*): *292* (100, M^+), 277 (28), 261 (26), 249 (17), 246 (7), 191 (9), 175 (5), 163 (5), 161 (5), 147 (5), 131 (6), 115 (6), 103 (10), 91 (10), 77 (11), 69 (17), 55 (24). Anal. calc. for $C_{16}H_{20}O_5$ (292.32): C 65.74, H 6.90; found: C 65.63, H 6.84.

2.4. *Reduction of* **12** *with* $NaBH_4$. To a solution of **12** (229 mg, 0.835 mmol) in CH_3OH (50 ml) a solution of $NaBH_4$ (635 mg, 16.7 mmol) in H_2O (4 ml) was added in portions. After stirring for 2 h at r.t., the mixture was worked up with AcOEt giving 190 mg (97%) of crude *7-methoxy-1,2,3,4-tetrahydrodibenzofuran-1,8-diol* (**25**): IR ($CHCl_3$): 3600*w*, 3545*m*, 2945*m*, 2870*w*, 2845*w*, 1628*m*, 1598*w*, 1476*s*, 1460*m*, 1440*s*, 1370*s*, 1358*m*, 1335*m*, 1315*m*, 1272*m*, 1255*m*, 1190*m*, 1161*w*, 1137*s*, 1121*m*, 1056*w*, 1023*w*, 981*w*, 961*w*, 954*w*, 930*w*, 893*w*, 884*m*, 860*m*, 823*w*.

7-Methoxy-1,2,3,4-tetrahydrodibenzofuran-1,8-diyl Diacetate (**26**). Crude **25** (106 mg) was acetylated with Ac_2O/pyridine (0.75 ml of each) giving 142 mg (95% based on **12**) of **26**. IR ($CHCl_3$): 3035*w*, 2955*m*, 2945*m*, 2875*w*, 2850*w*, 1757*s*, 1722*s*, 1630*m*, 1592*w*, 1488*s*, 1452*m*, 1438*m*, 1372*s*, 1350*w*, 1330*m*, 1316*m*, 1275*m*, 1263*s*, 1180*m*, 1160*m*, 1146*s*, 1120*m*, 1078*w*, 1053*w*, 1027*m*, 1014*m*, 977*w*, 962*m*, 950*w*, 941*w*, 920*m*, 904*m*, 892*w*, 870*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.84–2.12 (*m*, 2H–C(2), 2H–C(3)); 2.03 (*s*, CH_3COO–C(1)); 2.29 (*s*, CH_3COO–C(8)); 2.58–2.84 (*m*, 2H–C(4)); 3.80 (*s*, CH_3O–C(7)); 6.00–6.16 (*m*, H–C(1)); 7.00 and 7.19 (2*s*, H–C(6), H–C(9)). MS (*di.*): 318 (33, M^+), 276 (34), 259 (14), 258 (16), *234* (100), 217 (40), 216 (77), 201 (34), 43 (48).

2.5. *Ethyl (8'-Benzyloxy-7'-methoxy-1',2',3',4'-tetrahydrodibenzofuran-1'-ylidene)acetate* (**27**). To a suspension of $LiNH_2$ in NH_3 (liq.), prepared by $FeCl_3$-catalyzed reaction of Li (658 mg, 93 mgAt) with NH_3 (*ca.* 20 ml, distilled from Na), 2-bromovinylethylether (7.753 g, 51.4 mmol) was added at −78°. After stirring for 1 h at −78°, dry THF (100 ml) was added and most of the NH_3 was evaporated. This reagent solution was cooled to −78°, and **14** (1.5 g, 4.66 mmol) dissolved in THF (10 ml) was slowly added. After stirring for 15 min at −78°, the mixture was warmed to r.t., quenched by the careful addition of sat. $(NH_4)_2SO_4$-soln., acidified (2N HCl) and worked up with AcOEt. Flash chromatography (100 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 12:24:1) afforded 1.374 g (75%, 87% based on consumed **14**) of **27** and 214 mg (14%) of starting mat. **14**. M.p. 138–139°. IR ($CHCl_3$): 3095*w*, 3060*w*, 3035*w*, 2985*w*, 2940*m*, 2905*w*, 2875*w*, 2842*w*, 1695*s*, 1620*s*, 1488*s*, 1451*s*, 1373*w*, 1348*s*, 1296*s*, 1253*w*, 1167*s*, 1120*s*, 1030*m*, 1010*m*, 960*w*, 943*w*, 879*w*, 864*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.36 (*t*, *J* = 7, CH_3CH_2O–C(1)); 2.01 (*quint.*, *J* ≈ 6.5, 2H–C(3')); 2.83 (*t*, *J* ≈ 6.5, 2H–C(4')); 3.13–3.22 (*m*, *3 main peaks*, 2H–C(2')); 3.91 (*s*, CH_3O–C(7')); 4.23 (*q*, CH_3CH_2O–C(1)); 5.18 (*s*, $C_6H_5CH_2O$–C(8)); 6.10 (*m*, $w_{1/2}$ ≈ 4, H–C(2)); 7.02 (*s*, H–C(6')); 7.25–7.42 (*m*, 3H) and 7.48–7.55 (*m*, *2 main peaks*, H-*ortho*) ($C_6H_5CH_2O$–C(8')); 7.29 (*s*, H–C(9')). MS (*di.*): 392 (59, M^+), 347 (8), 302 (21), *301* (100), 273 (7), 257 (19), 227 (14), 200 (9), 199 (11), 171 (9), 128 (9), 115 (7), 91 (46). Anal. calc. for $C_{24}H_{24}O_5$ (392.43): C 73.45, H 6.16; found C 73.49, H 6.33.

2.6. *Hydrogenation of* **27**. A solution of **27** (207 mg, 0.528 mmol) in dry EtOH was hydrogenated at normal pressure with 5% Pd/C (*ca.* 5 mg). After 15 h of reaction, TLC analysis (cyclohexane/CH_2Cl_2/AcOEt 6:12:1) showed, that only partial hydrogenation had occurred. Addition of more 5% Pd/C (*ca.* 10 mg) was followed by

stirring under H_2 for 36 h. Removal of catalyst by filtration *(Celite)* and evaporation of solvent afforded 142 mg of crude **28**, 74 mg of which was acetylated (Ac_2O/pyridine). Chromatography (8 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 6:12:1) gave 2.5 mg (*ca.* 2.5%) of **33** and 51 mg (53%) of **29**.

Ethyl [(1'S,4a'S*,9b'R*)-8'-Acetoxy-7'-methoxy-1',2',3',4',4a',9b'-hexahydrodibenzofuran-1'-yl]acetate* (**29**). IR ($CHCl_3$): 3030*w*, 2980*m*, 2940*s*, 2860*w*, 2835*w*, 1755*s*, 1724*s*, 1625*s*, 1600*w*, 1493*s*, 1466*m*, 1450*s*, 1422*m*, 1370*s*, 1347*m*, 1327*m*, 1313*m*, 1300*m*, 1266*m*, 1180*s*, 1169*s*, 1112*m*, 1097*m*, 1060*m*, 1045*m*, 1025*m*, 1018*m*, 1003*m*, 980*m*, 920*m*, 885*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.24 (*t*, $J = 7$, CH_3CH_2O); 1.06–1.96 and 2.14–2.52 (2*m*, 9H); 2.24 (*s*, CH_3COO–C(8')); 3.49 (*dd*, $J \approx 8$ and 4, H–C(9b')); 3.73 (*s*, CH_3O–C(7')); 4.12 (*q*, $J = 7$, CH_3CH_2O); 4.90 (*dt*, $J \approx 8$ and 4, H–C(4a')); 6.42 (*s*, H–C(6')); 6.86 (*m*, $w_{1/2} \approx 3$, H–C(9')). MS: 348 (15, M^+), 307 (20), *306* (100), 261 (10), 260 (8), 218 (23), 217 (9), 177 (23), 43 (10).

Ethyl (8'-Acetoxy-7'-methoxy-1',2',3',4'-tetrahydrodibenzofuran-1'-yl)acetate (**33**). IR ($CHCl_3$): 3035*w*, 2930*m*, 2860*w*, 2840*w*, 1755*s*, 1723*s*, 1625*w*, 1480*m*, 1447*m*, 1435*m*, 1368*m*, 1335*m*, 1325*m*, 1316*m*, 1276*m*, 1260*m*, 1165*s*, 1140*s*, 1115*m*, 1095*w*, 1067*w*, 1021*m*, 960*w*, 916*m*, 902*w*, 890*w*, 865*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.23 (*t*, $J = 7$, CH_3CH_2O); 1.5–2.1 (*m*, 2H–C(2'), 2H–C(3')); 2.28 (*s*, CH_3COO–C(8')); 2.35 (*dd*, $J = 13$ and 10) and 2.81 (*dd*, $J = 13$ and 5) (2H–C(2)); 2.55–2.80 (*m*, 2H–C(4')); 3.2–3.5 (*m*, H–C(1')); 3.80 (*s*, CH_3O–C(7')); 4.13 (*q*, $J = 7$, CH_3CH_2O); 7.00 and 7.08 (2*s*, H–C(6'), H–C(9')). MS: 346 (35, M^+), *304* (100), 259 (11), 217 (50), 216 (35), 205 (12), 201 (8), 91 (9), 85 (34), 55 (14), 43 (21).

2.7. Oxidation of **28** *with* HIO_4. To a solution of $HIO_4 \cdot 2H_2O$ (60 mg, 0.263 mmol) in H_2O (2.5 ml), a solution of crude **28** (68 mg, 0.222 mmol) in CH_3CN (10 ml) was added at 0°. After 1 min the orange colored mixture was worked up with Et_2O. The residue of the org. layers (65 mg) was dissolved in CH_2Cl_2 and shaken with an aq. solution of NaS_2O_4. Workup with CH_2Cl_2, acetylation (Ac_2O/pyridine), and chromatography (13 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 6:12:1) of the crude mixture (83 mg) gave 8 mg (10%) of **33** and 20 mg (*ca.* 24%) of impure *ethyl (7',8'-diacetoxy-1',2',3',4'-tetrahydrodibenzofuran-1-yl)acetate* (**34**). IR ($CHCl_3$): 3030*w*, 2980*m*, 2935*m*, 2865*w*, 2845*w*, 1767*s*, 1725*s*, 1623*w*, 1493*w*, 1472*s*, 1448*s*, 1435*m*, 1370*s*, 1345*m*, 1326*m*, 1306*m*, 1285*m*, 1165*s*, 1129*s*, 1107*s*, 1080*m*, 1069*m*, 1030*m*, 1010*m*, 970*w*, 940*w*, 920*m*, 903*m*, 893*m*, 865*w*. ^{1}H-NMR (90 MHz, $CDCl_3$): 1.23 (*t*, $J = 7$, CH_3CH_2O); 1.3–2.1 (*m*, 2H–C(2'), 2H–C(3')); 2.27 (*s*, CH_3COO–C(7'), CH_3COO–C(8')); 2.35 (*dd*, $J = 15$ and 10) and 2.80 (*dd*, $J = 15$ and 5) (2H–C(2)); 2.5–2.8 (*m*, 2H–C(4')); 3.1–3.55 (*m*, H–C(1')); 4.13 (*q*, CH_3CH_2O); 7.24 (*m*, $w_{1/2} \approx 2$, H–C(6'), H–C(9')).

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