159. Preparation of Regioselectively Protected Hydroquinones by Phosphorylation of *p*-Benzoquinones with Trialkyl Phosphites[1])

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Summary

The title reaction has been applied to 10 monosubstituted *p*-benzoquinones *(Scheme 2, Table)*. The regioselectivity of the *O*-phosphorylation is influenced by bulky substituents (*t*-butyl and trimethylsilyl) and, electronically, by the methoxy group. The regioselectivity, which is high in nonpolar media (benzene), is lower in polar solvents (CH_2Cl_2 and CH_3CN). The synthetic potential of this transformation, exemplified by the preparation of compounds **29** *(Scheme 3)* and **32** *(Scheme 4)*, is considerably extended by applying milder methods for the phosphate hydrolysis and by using the reagent couple $P(OCH_3)_3$/trimethylsilyl chloride, which gives clean access to *p*-hydroxyphenyl phosphates. *p*-Benzoquinones **4h** and **4i** with strong π-acceptor substituents react in a different way, giving phosphonates. The electronically induced regioselectivity of the *O*- and *C*-phosphorylation is in accordance with the preferences expected for the attack by a nucleophilic phosphorylation agent.

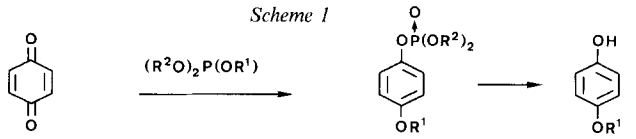
1. Introduction. – An efficient method for the preparation of hydroquinone monoalkyl ethers is the reductive phosphorylation of *p*-benzoquinones by phosphites introduced by *F. Ramirez* and coworkers [1a–c]. *p*-Benzoquinone (**1**), when reacted with trialkyl phosphites **a** in aprotic media, yields 4-alkoxyphenyl phosphates **b** which can be transformed to *p*-alkoxyphenols **c** by alkaline hydrolysis. Phenolic compounds **d** result when the reaction is done in the presence of a proton source (*e.g.* AcOH [2]) or with dialkyl phosphites **e** [3]. 4-(Trimethylsilyloxy)phenyl phosphates **f** are obtained with dialkyl trimethylsilyl phosphites **g** [4] *(Scheme 1)*.

Our interest in this reaction is related to studies of the total synthesis of the antibiotic *Lysolipin I* [5]. The transformation of the quinone **2** [6] to the phosphate **3**, if successful, would be a welcome alternative to other routes for the preparation of 2-arylcyclohexanones related to **3** [6] *(Scheme 1)*. The regioselectivity of the phosphorylation of **2** was hoped to follow the somewhat simple conception that the electron deficient C(1)-carbonyl would be more reactive, giving phosphate **3** as the major product. Since there are no reports supporting this hypothesis[2]), we decided to inves-

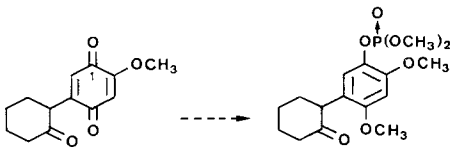
[1]) Part of the planned Ph.D. of *Ch.H.*, ETH No. 7565.

[2]) The only non-symmetrically substituted *p*-quinones studied so far are the complex khellin- and psoralen-quinones [7]. Other examples giving *C*-phosphorylated products are discussed below.

Scheme 1



1 a R^1, R^2 = Alkyl b c
e R^1 = H, R^2 = Alkyl d
g R^1 = TMS, R^2 = Alkyl f

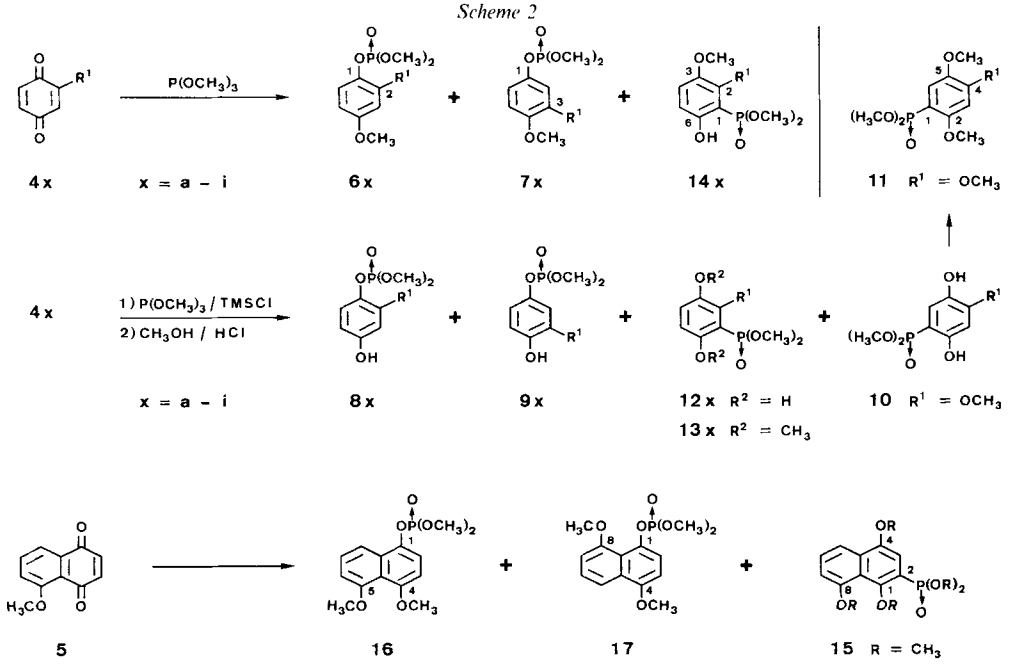


2 3

tigate the regioselectivity of the reductive phosphorylation of monosubstituted *p*-benzoquinones with phosphites.

2. Reaction of Selected *p*-Benzoquinones with Phosphites. – The reductive phosphorylation of *p*-benzoquinones with phosphites was studied with the monosubstituted *p*-benzoquinones **4x** (**x** = **a**–**i**) and with *O*-methyljuglone **5**. The results are assembled in the *Table* and in *Scheme 2*. Since the crucial step of this reaction is the necessarily intermolecular alkyl-group transfer from the P- to the *para*-O-atom (see below, *Discussion*), an improvement of this reaction is conceivable by intercepting the intermediate **h**

Scheme 2



4x x = a – i 6x 7x 14x 11 R^1 = OCH_3

4x 1) $P(OCH_3)_3$ / TMSCl 2) CH_3OH / HCl x = a – i 8x 9x 12x R^2 = H 13x R^2 = CH_3 10 R^1 = OCH_3

5 16 17 15 R = CH_3

Table. *Reaction of* p-*Benzoquinones with Trimethylphosphite*

p-Benzoquinone	Substituent R^1	Reagent	Solvent	4-CH_3O-Phenyl Phosphates		4-OH-Phenyl Phosphates		Phenylphosphonates		
				R^1–C(2)	R^1–C(3)	R^1–C(2)	R^1–C(3)			
4a	OCH_3	$P(OMe)_3$	C_6H_6	**6a** (79%)	**7a** (2.5%)	–	–	–	–	–
		$P(OMe)_3$	CH_3CN	**6a** (51%)	**7a** (9%)	–	–	–	–	–
		$P(OMe)_3$/TMSCl	CH_2Cl_2	–	–	**8a** and **9a** (73%)		**10** (0.6%)	–	–
		$P(OMe)_3$/TMSCl	CH_2Cl_2	**6a** (84%)[a]	**7a** (2.5%)[a]	–	–	–	**11** (13%)[a]	–
4b	CH_3	$P(OMe)_3$	C_6H_6	**6b** (44%)[b]	**7b** (36%)[b]	**8b** (4%)[b]	**9b** (2%)[b]	–	–	–
4c	*t*-Bu	$P(OMe)_3$	C_6H_6	–	**7c** (72%)	–	**9c** (13%)	–	–	–
4d	$Si(Me)_3$	$P(OMe)_3$	C_6H_6	–	**7d** (67%)	–	**9d** (15%)	–	–	–
4e	CH_2OCH_3	$P(OMe)_3$	C_6H_6	**6e** (17%)[b]	7e (50%)[b]	–	–	–	–	–
4f	Br	$P(OMe)_3$	C_6H_6	**6f** (23%)	**7f** (48%)	**8f** (6%)[c]	**9f** (3%)[c]	–	–	–
		$P(OMe)_3$/TMSCl	CH_2Cl_2	–	–	**8f** (40%)[c]	**9f** (40%)[c]	**12f** (14%)	–	–
		$P(OMe)_3$/TMSCl	CH_2Cl_2	**6f** (36%)[a]	**7f** (35%)[a]	–	–	–	–	–
4g	Cl	$P(OMe)_3$	C_6H_6	**6g** (28%)	**7g** (47%)	–	–	–	–	–
4h	$C(O)C_6H_5$	$P(OMe)_3$/TMSCl	CH_2Cl_2	–	–	–	–	**12h** (43%)	–	–
		$P(OMe)_3$/TMSCl	CH_2Cl_2	–	–	–	–	–	**13h** (56%)[a]	–
		$P(OMe)_3$	–	–	–	–	–	**12h**[d]	–	**14h**[d]
4i	CO_2CH_3	$P(OMe)_3$/TMSCl	CH_2Cl_2	–	–	–	–	**12i** (48%)	–	–
		$P(OMe)_3$	C_6H_6	–	–	–	–	**12i** (18%)	**13i** (20%)	**14i** (20%)
5		$P(OMe)_3$/TMSCl	CH_2Cl_2	**16** (21%)[a]	**17** (6.5%)[a]	–	–	–	**15** (59%)[a]	–

[a]) After methylation with $(CH_3O)_2SO_2$.
[b]) Yield calculated using the isomer ratio determined by ^{1}H-NMR or GC.
[c]) Ratio determined by methylation and chromatographic separation.
[d]) Partially separated by CC, combined yield 42%.

(Scheme 7) with a second reagent before the alkyl group is transferred[3]). Possible candidates not catalyzing the *Arbuzov* rearrangement of the phosphite [9] are alkyl sulfates and trialkylsilyl chlorides. While trimethylsilyl chloride (TMSCl) proved to be a very efficient trapping agent, the reaction of phosphonium ion **h** with $(CH_3)_2SO_4$ was found to be of minor importance (see below, *Scheme 3*).

With $P(OCH_3)_3$ the *p*-methoxyphenyl phosphates **6x** (substituent at C(2)) and **7x** (substituent at C(3)) were usually isolated as major products together with the *p*-hydroxyphenyl phosphates **8x** and **9x** which are the main products of the reactions with $P(OCH_3)_3$ in the presence of an excess of TMSCl followed by methanolysis (CH_3OH/acid)[4])[5]).

Methoxy-*p*-benzoquinone **4a** was chosen as the first substrate because of its close relation to quinone **2** *(Scheme 1)*. Treatment of **4a** with $P(OCH_3)_3$ in dry benzene afforded the 2-substituted phenyl phosphate **6a** as the major product (79%) together with traces (2.5%) of the regioisomer **7a**[6])[7]). The reductive phosphorylation of **4a** proceeds therefore with the desired regioselectivity which seems to drop off slightly in CH_3CN[8]). Reaction of **4a** with $P(OCH_3)_3$/TMSCl in CH_2Cl_2 followed by cleavage of the phenyl silyl ether in CH_3OH/HCl gave a mixture of the methoxy-*p*-hydroxyphenyl phosphates **8a** and **9a** (73%) and a small amount of phosphonate **10** (0.6%). The major product **8a** could be isolated by recrystallization. Alkylation of the crude reaction mixture with $(CH_3O)_2SO_2$ gave **6a** (84%), **7a** (2.5%) and phosphonate **11** (13%)[5]).

While almost no regioselectivity was found in the case of methyl-*p*-benzoquinone **4b**[9]), the *t*-butyl- and trimethylsilyl-substituted quinones **4c** and **4d** reacted with exclusive formation of the 3-substituted isomers **7c** and **7d**[10])[11]). The methoxymethyl-substituted quinone **4e** afforded the phosphates **6e** and **7e**[11]) in a 1:3 ratio. Bromo-*p*-benzoquinone (**4f**) gives the *O*-phosphorylated *p*-methoxyphenols **6f** and **7f** in a 1:2 ratio[11]). With $P(OCH_3)_3$/TMSCl 14% of phosphonate **12f**[12]) could be isolated in addition to 80% of a 1:1 mixture of phenols **8f** and **9f** which were analyzed by methylation (→**6f** and **7f**) and chromatographic separation. The reaction of **4f** in CH_2Cl_2 proceeded therefore with lower selectivity than in benzene. In close analogy to the bromo compound **4f**

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[3]) This has, in principal, been achieved previously by either using dialkyl phosphites [3] or trialkyl phosphites and a proton source [2] [8]. The latter method, however, gave poor results when applied to **4a**.

[4]) The same result could, in principle, be obtained by using dialkyl trimethylsilyl phosphites [4] or $P(OTMS)_3$ [10]. However, these reagents are unstable and their preparation is rather tedious [11]. For this reason $P(OCH_3)_3$/TMSCl has already been recommended as a substitute for other transformations [12].

[5]) In some experiments with $P(OCH_3)_3$/TMSCl the isolation and characterization of products is preceded by alkylation with $(CH_3O)_2SO_2$ converting phenols to methyl ethers. Connected with this alkylation were sometimes slightly higher yields, probably due to re-methylation of monoaryl phosphates and arylphosphonic acids, which have been formed by slow dealkylation of the dimethyl esters by TMSCl.

[6]) For the structural assignment see below *(Section 3)*.

[7]) Minor byproducts of this reaction, due in part to moisture [2] [8], are the *p*-hydroxyphenyl phosphates **8a/9a**, 2-methoxyhydroquinone, and polar phosphonates (see below).

[8]) In the case of khellinquinone a change of solvent (benzene to CH_3CN) has been reported to cause a reversal of regioselectivity [7a].

[9]) Structure **6b** was tentatively assigned to the major component of the mixture of **6b/7b**.

[10]) The phenols **9c** and **9d** formed as by-products of the reactions of **4c** and **4d** were converted to **7c** and **7d** by methylation with $(CH_3O)_2SO_2$.

[11]) For the structural assignment see below *(Section 4)*.

[12]) The structure follows from the spectral data (see *Exper. Part*).

the chloro-*p*-benzoquinone (**4g**) afforded **6g** and **7g** in a 1:2 ratio[13]). The quinones **4h** and **4i** with π-acceptor substituents, reacting in a different way with $P(OCH_3)_3$, gave exclusively *C*-phosphorylated products (**12x**, **13x**, and **14x**, *Scheme 2*)[14])[15]). With $P(OCH_3)_3$ alone, a mixture of **12h** and **14h** was obtained in the case of **4h**, a mixture of **12i**, **13i**, and **14i** from **4i**[16]). A much cleaner reaction, affording **12h** and **12i**[16]) as the only products, is obtained by using the reagent couple $P(OCH_3)_3$/TMSCl[17]). Interestingly, *O*-methyljuglone **5** gives the naphthyl phosphonate **15**[12]) as major product (59%) together with the 4,5-dimethoxy-1-naphthyl phosphate (**16**) (21%) and minor amounts of the 4,8-dimethoxy-substituted isomer **17** (6.5%)[11]) *(Scheme 2)*.

3. Synthetic Applications. – The scope of the reductive phosphorylation of *p*-benzoquinones could be considerably extended, if the alkyl substituent introduced at the *para*-O-atom could be chosen independently to the ester groups of the reducing phosphite. However, reaction of methoxy-*p*-benzoquinone (**4a**) with $P(OEt)_3/(CH_3O)_2SO_2$ gave the *p*-ethoxyphenyl compounds **18** (49%) and **19** (12%) as the main products with only *ca.* 5% of the *p*-methoxy compound **20** *(Scheme 3)*[18]). This goal can still be achieved by alkylation of phenol **8a**, which is obtained in high yield by reaction of **4a** with $P(OCH_3)_3$/TMSCl and cleavage of the silyl ether. As an example, the benzyloxy compound **21** was prepared in quantitative yield by treatment of **8a** with $BzBr/K_2CO_3$ *(Scheme 3)*.

Another important problem in connection with our synthetic project *(Scheme 1)* is the removal of the phosphoryl group. It was observed that the usual conditions, reflux in $NaOH/H_2O/ROH$ [1a], gave poor results with the dimethyl phenyl phosphates **6a** and **7a**. This may be due to the sensitivity of electron-rich phenols to oxidation, especially under basic conditions. In addition, it is very likely that the methyl-ester groups of phosphates **6a** and **7a** are cleaved before the phenyl ester, and that the resulting monoaryl phosphates, which are doubly deprotonated in the strongly alkaline medium, are hydrolyzed very slowly [15]. However, a mixture of phosphates **6a** and **7a** was successfully transformed to the acetates **22** (81%) and **23** (3.5%)[19]) by demethylation with trimethylsilyl bromide (TMSBr) [17], hydrolysis of the resulting di(trimethylsilyl) phenyl phosphates **24** and **25** at pH 4 (aq. acetate buffer/dioxane) [15], and acetylation of the resulting phenols **26** and **27**. Analogous treatment of phosphate **21** afforded the

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[13]) The structures of **6g** and **7g** were deduced by comparison of their ^{1}H-NMR spectra with the spectra of **6f** and **7f** (see *Exper. Part*).

[14]) Products of *C*-phosphorylation (without TMSCl complex mixtures of partially *O*-methylated derivatives) are formed in small quantities in all cases (*e.g.* **10** and **11** from **4a**, **12f** from **4f**), but have not been isolated pure and characterized.

[15]) The regioselective *O*-phosphorylation of benzoyl-*p*-benzoquinone (**4h**) with neat $P(OCH_3)_3$, reported in [13], is, however, most probably based on an erroneous structure assignment, since not the slightest trace of such a product could be detected, when this experiment was repeated.

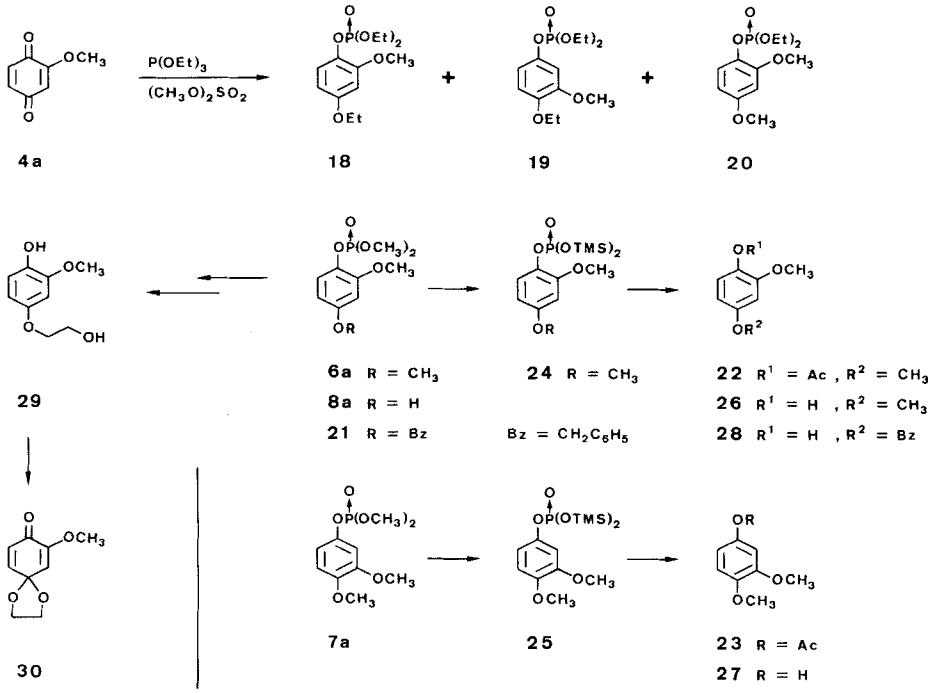
[16]) The structural assignments are based on spectroscopic data. The position of the OH-group in **14h** and **14i** was deduced from the δ-values of the OH-protons (10.36 ppm, **14h**; 10.27 ppm, **14i**) and, in the case of **14i**, from a ^{31}P, ^{1}HO-coupling of *ca.* 1 Hz.

[17]) Phosphonate **14i** was obtained in *ca.* 30% yield from **4i** by treatment with $P(OCH_3)_3$/AcOH [14]. The $P(OCH_3)_3$/TMSCl method with *ca.* 50% yield seems to be superior.

[18]) A full experimental description of these transformations is given in the Ph. D. thesis of *Ch. H.*

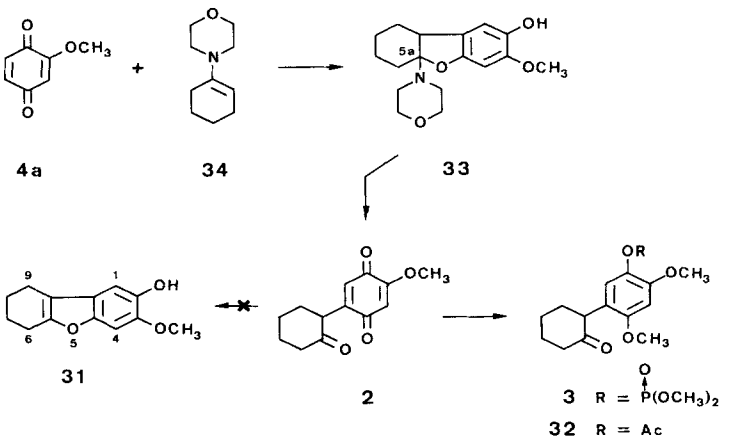
[19]) The structures of **22** and **23**, and therefore also of **6a** and **7a**[6]) were assigned by comparison with authentic samples [16].

Scheme 3



p-benzyloxyphenol **28** in 88% yield *(Scheme 3)*. Phenol **26** was also prepared from pure phosphate **6a** by base-catalyzed transesterification in EtOH. The best result (80% of **26** in 4 days) was obtained with CsF as catalyst [18]. The reaction catalyzed by KF/dicyclohexyl-18-crown-6 [19] was extremely slow (66% of **26** in 49 days), and tetraisopropyl titanate, which is an efficient catalyst for the transesterification of carboxylates [20], was found to be inefficient for the ethanolysis of phenyl phosphate **6a** (13% of **26**, 68% conversion after 1 week at reflux)[18]).

Scheme 4

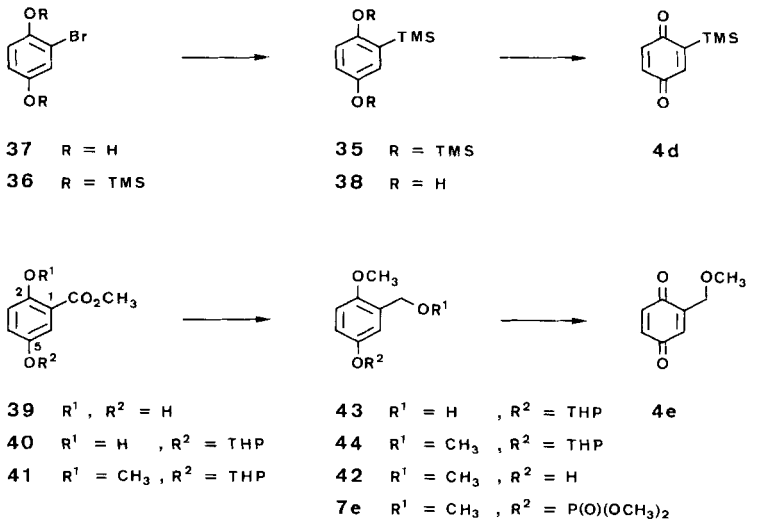


*The reaction of methoxy-*p*-benzoquinone* (**4a**) *with* $P(OCH_3)_3$/*TMSCl, proceeds with high regioselectivity and thus gives access to a variety of selectively O-protected 2-methoxyhydroquinones which are otherwise difficult to prepare*[20]. The facile conversion of phosphate **8a** to the *p*-(2'-hydroxyethoxy)phenol **29** (75% overall yield), the starting material for the preparation of quinone-acetal **30**, illustrates the utility of this approach *(Scheme 3)* [22].

The target compound, 2-arylcyclohexanone **3** *(Scheme 1)*, was finally obtained from quinone **2** in 77% yield by reductive phosphorylation with $P(OCH_3)_3$, without either formation of detectable amounts of the regioisomeric phosphate or, most importantly, of tetrahydrodibenzofurane **31** or derivatives thereof[21]. Phosphate **3** could be converted to the acetate **32** (79% yield) by treatment with TMSBr, hydrolysis at pH 4, and acetylation. The new *p*-benzoquinone **2** was obtained in 84% yield from **4a** by $FeCl_3$-oxidation [23] of the hexahydrodibenzofurane **33**, which results from *Michael* addition of enamine **34** to **4a** according to [24] *(Scheme 4)*.

4. Synthesis of *p*-Benzoquinones 4d and 4e[22]) and Structural Assignment of Products. – The preparation of trimethylsilyl-*p*-benzoquinone (**4d**) [26] could be improved by minor modifications. The protected hydroquinone **35** was obtained from the *O*-trimethylsilyl derivative **36** of 2-bromohydroquinone (**37**) by bromine-lithium exchange and quenching with TMSCl. Mild acidic hydrolysis ($AcOH/H_2O/KF$) in a two-phase system (CH_2Cl_2), containing a phase-transfer catalyst, afforded **38**, which was oxidized with Ag_2O to **4d** *(Scheme 5)*.

Scheme 5



37 R = H
36 R = TMS

35 R = TMS
38 R = H

4d

39 R^1, R^2 = H
40 R^1 = H, R^2 = THP
41 R^1 = CH_3, R^2 = THP

43 R^1 = H, R^2 = THP
44 R^1 = CH_3, R^2 = THP
42 R^1 = CH_3, R^2 = H
7e R^1 = CH_3, R^2 = $P(O)(OCH_3)_2$

4e

(THP = 2-Tetrahydropyranyl)

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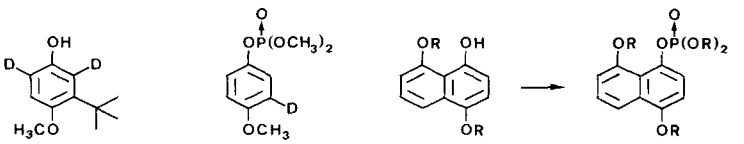
[20]) In some cases the regioselective dealkylation of alkyl aryl ethers [21] may be an alternative.
[21]) The oxidative cleavage of the furane ring of compounds related to **31** has been tried without success [6].
[22]) The other quinones have been prepared by standard or published methods [25] (see *Exper. Part*).

(Methoxymethyl)-*p*-benzoquinone (**4e**) has been prepared previously by oxidation of 2-(methoxymethyl)phenol with *Frémy*'s salt [27]. Our synthesis *(Scheme 5)* has the advantage that it gives access to phosphate **7e**, one of the regioisomers formed in the reaction of **4e** with $P(OCH_3)_3$. Treatment of methyl gentisate **39** with dihydropyrane/pyridinium *p*-toluenesulfonate gave exclusive reaction of the non-chelated OH-group at C(5), affording the monoprotected derivative **40**, which could be transformed to **41** by methylation with CH_3I/K_2CO_3 in 93% overall yield[23]). The *p*-methoxyphenol **42** was obtained in 69% yield from **41** by Li[AlH$_4$]-reduction, methylation of the resulting benzylalcohol **43** ($BuLi/(CH_3O)_2SO_2$), and deprotection of **44** (CH_3OH/CH_3SO_3H). Oxidation of **42** with $Ce(NH_4)_2(NO_3)_6$ (CAN) according to [29] afforded the rather unstable quinone **4e** in 58% yield.

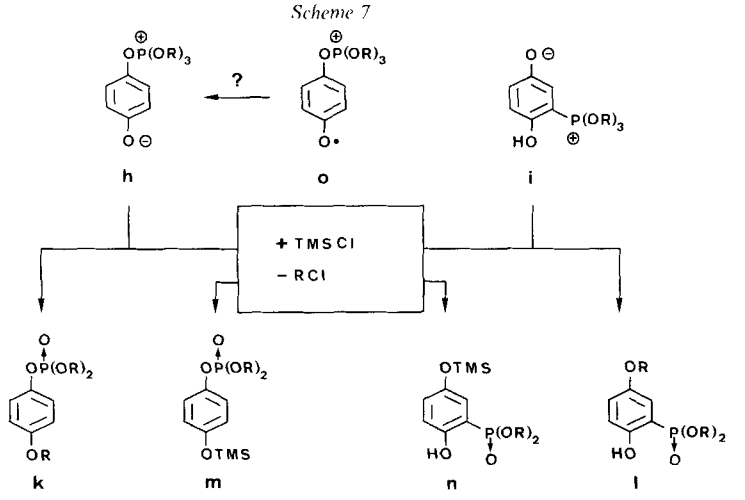
Scheme 6



45 **46** **47** R = CH_3 **17**

The position of the *t*-butyl substituent of **7c** was determined by phosphate hydrolysis and treatment of the resulting phenol with $NaOD/D_2O$ according to [30], giving the deuterated derivative **45** (85% D_2, *Scheme 6*)[18]). The regioisomeric structure (substituent at C(2)) could be ruled out by the incorporation of two D-atoms. Monodeuterated 4-methoxyphenyl phosphate **46** (58% D_1) was obtained by desilylation of **7d** with CF_3CO_2D [31]. The position of the D-atom in **46** (C(3)), and therefore of the trimethylsilyl substituent in **7d** as well, was determined by ^{1}H-NMR[18]). The phosphates **7e** and **17** were identified by phosphorylation of the parent phenols **42** *(Scheme 5)* and **47**,

Scheme 7

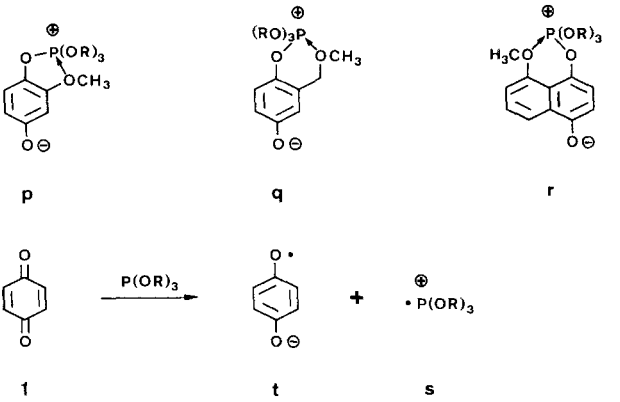


[23]) A preparation of 4-benzyloxysalicylic acid from gentisic acid has been reported without any details [28].

respectively, [29] *(Scheme 6)* with dimethyl chlorophosphate [32][24]). Finally, the structures of the isomeric bromides **6f** and **7f** were determined by phosphate hydrolysis, giving the known [34] 2-bromo-4-methoxyphenol from **6f** and the 3-bromo isomer from **7f**[18]).

Discussion. – The reductive phosphorylation of monosubstituted *p*-benzoquinones with phosphites was found to proceed with high regioselectivity in the case of methoxy-, t-butyl-, and trimethylsilyl-*p*-benzoquinones (**4a**, **4c**, and **4d**, respectively). Phosphonates, which are usually minor by-products of the other reactions, were formed exclusively with benzoyl- and methoxycarbonyl-*p*-benzoquinone **4h** and **4i**, respectively. Interestingly, *C*-phosphorylation was also the main reaction path of *O*-methyljuglone **5**. These results should help to elucidate the complex mechanism of this reaction [35]. The zwitterionic species **h** and **i** are most likely the immediate precursors of the products, which, in analogy to the *Michaelis-Arbuzov* and the *Perkow* reaction [9] [36], are formed by a nucleophilic dealkylation of the phosphonium ion [1] [35a] [35b]. Intermolecular dealkylation by the phenoxide ion gives **k** and **l**, while interception with TMSCl (or $(CH_3O)_2SO_2$, ROH, H_2O, and AcOH) leads to **m** and **n** *(Scheme 7)*. Alkoxyphosphonium ions are among the most powerful alkylating agents known [37]. This explains the formation of dialkoxy derivatives **13x** and hydroquinones **12x**, by-products of the reaction leading to **14x** *(cf. Scheme 2)*, and the inefficiency of $(CH_3O)_2SO_2$ as trapping agent of **h**. It is, however, rather unlikely that an alkyl radical is transferred from an intermediate radical **o**[25]).

Scheme 8



The regioselective formation of 3-substituted phenyl phosphates (**7c** and **7d**) from *t*-butyl- and trimethylsilyl-*p*-benzoquinones (**4c**) and (**4d**), respectively, is obviously a steric effect of the bulky substituents. The directing effect of the methoxy group, on the other hand, is most probably of electronic nature. In the case of methoxy-*p*-benzoqui-

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[24]) This reagent was prepared by chlorination of $P(OCH_3)_3$ [33].

[25]) Such a step is included in a mechanism proposed by *Boeckestein & Buck* [35c]. If an intermediate **o**, for which some evidence was obtained by ESR [35b] [35c], is involved in the reaction at all, it is most probably reduced to **h** before the dealkylation occurs in order to account for the observed interception by protons, TMSCl, and $(CH_3O)_2SO_2$.

none (**4a**) a possible stabilization of the phosphonium intermediate **p** by the *o*-methoxy substituent could be considered as an explanation for the regioselectivity[26]). This can, however, be ruled out since a similar effect should operate for the intermediates **q** and **r** derived from **4e** and **5**, respectively, and should lead to the preferred formation of **6e** and **17**, the opposite regioselectivity than actually observed *(Scheme 8)*. The preferred formation of **6a** from **4a** and **16** from **5** is therefore due to the conjugation of the methoxy-lone-pairs with either the quinoid or the aromatic nucleus of these systems, and corresponds to the selectivity expected for a nucleophilic phosphorylation agent. These results allow, however, no decision, whether an ionic mechanism with phosphite as attacking species [1a] [39] or a radical mechanism [35] is involved, since a phosphinium radical **s**, generated together with semiquinone **t** in a redox process from **1** and phosphite, could have nucleophilic properties in analogy to carbon-centered radicals substituted with alkoxy groups [40a] *(Scheme 8)*[27]). The phosphonates isolated from the reactions of **4a**, **4f**, **4h**, **4i**, and **5** show that the *C*-phosphorylation of *p*-benzoquinones affords exclusively the regioisomers expected for a nucleophilic 1,4-addition. The reacting nucleophilic species could again be either the phosphite (ionic mechanism) or a phosphinium radical **s** *(Scheme 8)*.

6. Conclusion. – The synthetic potential of the reductive phosphorylation of *p*-benzoquinones could be considerably extended by the introduction of the $P(OCH_3)_3$/TMSCl reagent couple, by application of mild and selective methods for the phosphate hydrolysis, and by finding regio-directing substituent effects. The *t*-butyl and trimethylsilyl substituents which induce a high degree of regioselectivity are of special synthetic value: *t*-butyl as positional protecting group [41] and trimethylsilyl for directing electrophilic aromatic substitutions [42]. Aryl phosphates are furthermore one of the few phenolic derivatives which can react by breaking of the original C–O bond in substitutions by hydrogen [43] or by alkyl groups [44]. *ortho*-Lithiation, on the other hand, gives access to *o*-hydroxyphenyl phosphonates [45].

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Experimental Part

General Remarks. See [46]. *Purification of Solvents and Reagents: benzene*, distillation (Ar) from Na/benzophenone; CH_2Cl_2, filtration through Alumina (*Woelm*, basic, activity I); *TMSCl* and *TMSBr*, distillation from CaH_2; $P(OR)_3$, treatment with Na-wire and distillation. *Materials. p*-Benzoquinones **4b–4d** and **4f–4i** [25] have been prepared by Ag_2O-oxidation of the parent hydroquinones, which are either commercially available, or have been prepared according to published methods. Quinone **4a** was obtained according to [47], **5** according to [29].

1. General Procedures. – 1.1. *Ag_2O-Oxidation of Hydroquinones.* Freshly prepared Ag_2O (60–70 mmol, dried over P_2O_5) was added to the hydroquinone (30 mmol), dissolved in dry benzene (250 ml), containing Na_2CO_3 (5 g). After *ca.* 40 min of reaction (sometimes exothermic, followed by TLC), the salts were removed by

[26]) Intermediate **p** is closely related to the pentavalent P-compounds formed in the reaction of *o*-quinones and α-diketones with phosphites [1] [38].

[27]) A more detailed discussion is given in the thesis of *Ch. H.*, *cf.* also [40b].

filtration *(Celite)*, the filtrate was treated with Na_2CO_3 (3 h), refiltered, and the solvent was removed at reduced pressure. The crude quinone was usually purified by sublimation at h.v. and used immediately after the preparation and purification.

1.2. *Reaction of Quinones with $P(OCH_3)_3$.* To a solution of the quinone in an appropriate solvent $P(OCH_3)_3$ (1.1.–3 equiv. for reactive quinones, 5–10 equiv. for unreactive substrates) was added. After stirring for a given time under exclusion of light at r.t. (Ar), solvent and excess reagent were evaporated (aspirator), the residue was dried at h.v. and purified by chromatography.

1.3. *Reaction of Quinones with $P(OCH_3)_3$/TMSCl Followed by Methanolysis.* A solution of the quinone in CH_2Cl_2 was added to a mixture of $P(OCH_3)_3$ (2–5 equiv.) and TMSCl (10–30 equiv.). After stirring for a given time, volatile materials were removed at reduced pressure. The residue was either treated with CH_3OH/1N aq. HCl (9:1, *v/v*) for 10 min followed by addition of sat. NaCl-solution and extraction with CH_2Cl_2 *(aqueous workup)* or HCl gas was passed for 10 min into a solution of the crude material in CH_3OH. The solvent was evaporated and the residue was freed from HCl by repeated evaporation with CH_3OH (2 ×) and CH_2Cl_2 (1 ×) *(evaporative workup)*. Purification was achieved by chromatography.

2. Reactions with 2-Methoxy-1,4-benzoquinone (4a) [47]. – 2.1. *Treatment of* **4a** *with $P(OCH_3)_3$.* – 2.1.1. *In Benzene.* Quinone **4a** (1.38 g, 10 mmol) in dry benzene (50 ml) was treated with $P(OCH_3)_3$ (1.4 ml, *ca.* 11.5 mmol) for 24 h according to procedure *1.2*. Chromatography (200 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:2) of 843 mg of the crude material (2.676 g) and re-chromatography of mixed fractions (127 mg) afforded 655 mg (79%) of **6a** and 22 mg (2.5%) of **7a**.

Dimethyl 2,4-Dimethoxyphenyl Phosphate (**6a**). An analytical sample was obtained by bulb-to-bulb distillation (140°/h.v.). IR ($CHCl_3$): 3030*w*, 2995*m*, 2955*m*, 2855*w*, 2835*w*, 1609*m*, 1598*m*, 1505*s*, 1455*m*, 1437*m*, 1420*w*, 1314*m*, 1278*s*, 1180*s*, 1158*s*, 1123*m*, 1042*s*, 954*s*, 910*s*, 855*s*, 836*m*, 822*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.74 and 3.81 (2*s*, CH_3O–C(2), CH_3O–C(4)); 3.84 (*d*, *J* = 11, $(CH_3O)_2PO_2$–C(1)); 6.36 (*dd*, *J* = 9 and 3, H–C(5)); 6.50 (*d*, *J* = 3, H–C(3)); 7.15 (*dd*, *J* = 9 and 2, H–C(6)). MS: *262* (100, M^+), 247 (6), 232 (7), 231 (3), 229 (4), 219 (5), 216 (7), 201 (4), 187 (2), 153 (9), 136 (22), 135 (16), 127 (51), 125 (9), 121 (3), 109 (59), 95 (4), 93 (5), 91 (3), 79 (9), 77 (3), 69 (5), 65 (3), 52 (6), 39 (3). Anal. calc. for $C_{10}H_{15}O_6P$ (262.20): C 45.81, H 5.77, P 11.81; found: C 45.85, H 5.97, P 11.84.

Dimethyl 3,4-Dimethoxyphenyl Phosphate (**7a**). IR ($CHCl_3$): 3030*w*, 2995*m*, 2955*s*, 2935*m*, 2855*m*, 2840*m*, 1603*s*, 1502*s*, 1461*s*, 1449*s*, 1440*s*, 1414*w*, 1276*s*, 1261*s*, 1180*s*, 1155*s*, 1123*m*, 1045*s*, 985*s*, 891*s*, 856*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.78 (*d*, *J* = 11, $(CH_3O)_2PO_2$–C(1)); 3.78 and 3.84 (2*s*, CH_3O–C(3), CH_3O–C(4)); 6.70 (*m*, $W_{1/2} \approx 2$, H–C(2), H–C(5), H–C(6)). MS: *262* (100, M^+), 247 (79), 219 (18), 201 (2), 191 (2), 187 (5), 167 (2), 153 (7), 139 (2), 135 (3), 127 (13), 125 (7), 121 (6), 109 (93), 95 (6), 93 (8), 91 (4), 79 (14), 77 (3), 69 (6), 65 (7), 51 (6), 39 (5).

2.1.2. *In CH_3CN.* Quinone **4a** (1.034 g, 7.5 mmol) in CH_3CN (15 ml) was treated with $P(OCH_3)_3$ (2.0 ml, *ca.* 17 mmol) for 30 h according to procedure *1.2*. Chromatography of the crude material (2.01 g) as above afforded 1.006 g (51%) of **6a** and 179 mg (9%) of **7a**.

2.2. *Treatment of* **4a** *with $P(OCH_3)_3$/TMSCl.* – 2.2.1. *Isolation of Dimethyl 4-Hydroxy-2-methoxyphenyl Phosphate* (**8a**). Quinone **4a** (1.387 g, 10.05 mmol) in dry CH_2Cl_2 (20 ml) was treated with $P(OCH_3)_3$ (2 ml, *ca.* 17 mmol, and 0.2 ml, *ca.* 1.7 mmol after 15 h) and TMSCl (13 ml, *ca.* 0.1 mol) for 39 h according to procedure *1.3*. Aqueous workup and flash chromatography (200 g of silica gel, CH_2Cl_2/AcOEt 1:1) yielded 16 mg (0.6%) of phosphonate **10** and 1.838 g (73%) of a mixture of **8a** and **9a**. Isomer **8a** was isolated pure by crystallization (hexane/CH_2Cl_2) and sublimation (80°/h.v.).

8a: m.p. 89.5–91°. IR ($CHCl_3$): 3590*w*, 3550*w*, 3250*m*, 2995*m*, 2955*m*, 2850*w*, 1612*s*, 1600*s*, 1500*s*, 1450*s*, 1433*s*, 1375*m*, 1260*s*, 1154*s*, 1110*s*, 1054*s*, 962*s*, 944*s*, 855*s*, 833*s*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.66 (*s*, CH_3O–C(2)); 3.89 (*d*, *J* = 11, $(CH_3O)_2PO_2$–C(1)); 6.11 (*dd*, *J* = 9 and 3, H–C(5)); 6.27 (*d*, *J* = 3, H–C(3)); 6.84 (*dd*, *J* = 9 and 2, H–C(6)); 7.80 (br., $W_{1/2} \approx 6$, OH). MS (*di.*): 248 (8, M^+), 223 (1), 216 (2), 205 (1), 203 (1), 168 (3), *154* (100), 139 (97), 125 (5), 111 (43), 109 (6), 107 (6), 96 (8), 93 (3), 79 (9), 77 (3), 69 (7), 65 (4), 55 (5), 52 (9). Anal. calc. for $C_9H_{13}O_6P$ (248.17): C 43.56, H 5.26, P 12.48; found: C 43.43, H 5.30, P 12.20.

Dimethyl 2,5-Dihydroxy-4-methoxyphenylphosphonate (**10**): m.p. 126.5–127.5°. IR ($CHCl_3$): 3550*s*, 3200*m*, 2995*m*, 2950*m*, 2910*w*, 2845*m*, 1630*s*, 1589*m*, 1493*s*, 1441*s*, 1377*s*, 1252*s*, 1160*s*, 1076*s*, 1027*s*, 874*m*, 836*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.70 (*d*, *J* = 11, $(CH_3O)_2PO$–C(1)); 3.88 (*s*, CH_3O–C(4)); 5.31 (br., $W_{1/2} \approx 6$, HO–C(5)); 6.43 (*d*, *J* = 6.5, H–C(3)); 6.75 (*d*, *J* = 14, H–C(6)); 9.80 (br., $W_{1/2} \approx 2$, HO–C(2)). MS (*di.*): *248* (100, M^+), 233 (7), 231 (4), 217 (14), 216 (73), 205 (5), 201 (49), 186 (10), 173 (5), 153 (9), 139 (4), 135 (5), 124 (4), 109 (17), 93 (5), 79 (13), 69 (8), 53 (9), 39 (6).

2.2.2. *Methylation of the Reaction Mixture.* Quinone **4a** (1.377 g, 9.97 mmol) was treated as described above with $P(OCH_3)_3$ (2.2 ml) and TMSCl (13 ml) in CH_2Cl_2 (30 ml). Part (496 mg) of the crude material (2.933 g), obtained by evaporative workup (procedure *1.3*) was heated with $(CH_3O)_2SO_2$ (0.4 ml, *ca.* 4 mmol) and K_2CO_3 (2.8 g) in acetone (20 ml) under reflux for 19 h. After removal of solids by filtration and solvent by evaporation, the mixture was worked up with CH_2Cl_2. Chromatography (CH_2Cl_2/AcOEt 1:1) of the crude material (475 mg) and re-chromatography (cyclohexane/CH_2Cl_2/AcOEt 1:1:2) of mixed fractions gave 371 mg (84%) of **6a**, 12 mg (2.5%) of **7a**, and 68 mg (62 mg (13%) after purification by bulb-to-bulb distillation (160°/h.v.)) of **11**.

Dimethyl 2,4,5-Trimethoxyphenylphosphonate (**11**). IR ($CHCl_3$): 3030*w*, 2990*s*, 2950*s*, 2845*m*, 1602*s*, 1583*m*, 1496*s*, 1459*s*, 1436*s*, 1382*s*, 1338*m*, 1313*w*, 1276*s*, 1238*s*, 1085*s*, 1025*s*, 973*w*, 883*w*, 872*w*, 827*s*. ^{1}H-NMR (60 MHz, $CDCl_3$): 3.72 (*d*, *J* = 11, $(CH_3O)_2PO$–C(1)); 3.80, 3.83, and 3.87 (3*s*, CH_3O–C(2), CH_3O–C(4), CH_3O–C(5)); 6.43 (*d*, *J* = 7, H–C(3)); 7.18 (*d*, *J* = 15, H–C(6)). MS: 276 (10, M^+), 262 (7), 261 (5), 247 (5), 243 (5), 229 (5), 219 (5), 215 (4), 209 (5), *168* (100), 153 (91), 140 (10), 139 (9), 125 (49), 110 (55), 109 (21), 107 (10), 95 (19), 93 (14), 91 (9), 87 (11), 84 (37), 79 (27), 77 (14), 71 (12), 69 (22), 65 (11), 60 (17), 57 (16), 55 (12), 51 (13), 45 (17), 43 (44), 41 (27), 39 (12).

2.3. *Dimethyl 4-Benzyloxy-2-methoxyphenyl Phosphate* (**21**). A solution of **8a** (993 mg, 4.0 mmol) and BzBr (0.57 ml, *ca.* 4.8 mmol) in acetone (25 ml) containing K_2CO_3 (6.85 g) was boiled under reflux for 6 h. After evaporation of solvent, the mixture was worked up with CH_2Cl_2. Flash chromatography (80 g of silica gel, hexane/CH_2Cl_2/AcOEt 1:1:1) yielded 1.342 g (99%) of **21**. An analytical sample was obtained by bulb-to-bulb distillation (170°/h.v.). IR ($CHCl_3$): 3030*w*, 2995*m*, 2955*m*, 2915*w*, 2855*w*, 1609*m*, 1598*m*, 1500*s*, 1460*m*, 1447*s*, 1415*w*, 1377*w*, 1275*s*, 1181*s*, 1159*s*, 1123*m*, 1040*s*, 955*s*, 929*s*, 855*s*, 838*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.80 (*s*, CH_3O–C(2)); 3.84 (*d*, *J* = 11, $(CH_3O)_2PO_2$–C(1)); 4.99 (*m*, $W_{1/2} \approx 2$, $C_6H_5CH_2O$–C(4)); 6.42 (*dd*, *J* = 9 and 3, H–C(5)); 6.55 (*d*, *J* = 3, H–C(3)); 7.10 (*d*, *J* = 9, H–C(6)); 7.15–7.5 (*m*, $C_6H_5CH_2O$–C(4)). MS (*di.*): 338 (18, M^+), 247 (7), 244 (1), 219 (1), 127 (2), 109 (19), *91* (100), 79 (3), 65 (6), 63 (1), 51 (1), 39 (2). Anal. calc. for $C_{16}H_{19}O_6P$ (338,29): C 56.81, H 5.66, P 9.16; found: C 56.98, H 5.64, P 9.03.

2.4. *Hydrolysis of the Phosphates* **6a** *and* **7a**. – 2.4.1. *TMSBr and AcOH/AcONa/H_2O-Dioxane.* To a mixture of **6a** and **7a** (369 mg, 1.41 mmol, purified by chromatography) TMSBr (0.6 ml, *ca.* 4.5 mmol) was added (Ar). After stirring for 1 h at r.t., the volatile material was evaporated at reduced pressure. The residue was heated to 100° under reflux for 47 h in a buffer solution, consisting of AcOH (2.6 ml), NaOAc (1.2 g), dioxane (12 ml), and H_2O (*ca.* 8 ml, total volume 20 ml). Workup with Et_2O, treatment of the crude product mixture (194 mg) with Ac_2O/pyridine (2 ml of each) over night, removal of reagents by azeotropic distillation with hexane, and chromatography (30 g of silica gel, hexane/AcOEt 3:2) afforded 225 mg (81%) of **22** and 10 mg (3.5%) of **23**.

2,4-Dimethoxyphenyl Acetate (**22**). IR ($CHCl_3$): 3030*w*, 3000*w*, 2960*m*, 2935*m*, 2915*w*, 2835*m*, 1755*s*, 1609*s*, 1602*s*, 1499*s*, 1453*s*, 1436*s*, 1419*m*, 1366*s*, 1310*s*, 1282*m*, 1258*s*, 1172*s*, 1155*s*, 1118*m*, 1030*s*, 1010*m*, 929*w*, 896*m*, 835*m*, 827*m*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.26 (*s*, CH_3CO_2–C(1)); 3.76 and 3.78 (2*s*, CH_3O–C(2), CH_3O–C(4)); 6.41 (*dd*, *J* = 9 and 3, H–C(5)); 6.52 (*d*, *J* = 3, H–C(3)); 6.91 (*d*, *J* = 9, H–C(6)).

3,4-Dimethoxyphenyl Acetate (**23**). IR ($CHCl_3$): 3030*w*, 3000*w*, 2955*m*, 2930*m*, 2870*w*, 2855*w*, 2835*m*, 1750*s*, 1603*s*, 1500*s*, 1461*s*, 1450*s*, 1439*s*, 1413*m*, 1367*s*, 1332*w*, 1260*s*, 1178*s*, 1148*s*, 1122*s*, 1025*s*, 1014*s*, 955*s*, 912*w*, 892*m*, 835*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.25 (*s*, CH_3CO_2–C(1)); 3.82 and 3.83 (2*s*, CH_3O–C(3), CH_3O–C(4)); 6.5–6.7 (*m*, H–C(2), H–C(6)); 6.82 (*d*, *J* = 9, H–C(5)). MS: 196 (18, M^+), 167 (2), *154* (100), 139 (76), 125 (3), 111 (18), 95 (5), 93 (9), 83 (2), 79 (3), 77 (1), 69 (7), 65 (5), 55 (3), 53 (4), 51 (4), 43 (19), 39 (4).

2.4.2. *CsF/EtOH.* A solution of **6a** (165 mg, 0.63 mmol) and CsF (1.0 g, 6.6 mmol) in EtOH (4 ml) was stirred at r.t., until all **6a** had been consumed (TLC, 90 h). Workup with Et_2O, treatment with Ac_2O/pyridine (*ca.* 1 ml of each) over night, azeotropical removal of reagents (hexane), and chromatography (18 g of silica gel, hexane/AcOEt 3:2) gave 99 mg (80%) of **22**.

2.4.3. *KF/Crown/EtOH.* A solution of **6a** (192 mg, 0.733 mmol), $KF \cdot 2H_2O$ (0.7 g, 7.4 mmol), and dicyclohexyl-18-crown-6 (27.5 mg, 0.074 mmol) in EtOH (5 ml) was stirred at r.t., until no **6a** could be detected by TLC (49 days). Workup, acetylation, and chromatography as described above afforded 96 mg (66%) of **22**.

2.5. *4-Benzyloxy-2-methoxyphenol* (**28**). TMSBr (0.6 ml, *ca.* 4.6 mmol) was added to phosphate **21** (505 mg, 1.494 mmol) under Ar. After stirring for 1 h at r.t., the volatile compounds were evaporated (aspirator), and a buffer solution, consisting of AcOH (2.6 ml), NaOAc (0.6 g), dioxane (12 ml) and H_2O (8 ml), was added. The mixture was heated under reflux (100°) for 64 h and worked up with Et_2O. Bulb-to-bulb distillation (140°/h.v.) followed by flash chromatography (10 g of silica gel, CH_2Cl_2/AcOEt 1:1) afforded 305 mg (88%) of **28**. IR ($CHCl_3$): 3555*s*, 3085*w*, 3065*w*, 3030*w*, 3005*w*, 2965*w*, 2935*w*, 2915*w*, 2865*w*, 2845*w*, 1622*m*, 1610*m*, 1499*s*, 1461*s*, 1448*s*, 1431*m*, 1379*s*, 1286*m*, 1260*s*, 1190*s*, 1155*s*, 1118*s*, 1107*m*, 1079*w*, 1027*s*, 945*w*, 931*w*, 906*w*, 833*m*.

^{1}H-NMR (80 MHz, $CDCl_3$): 3.76 (*s*, CH_3O–C(2)); 4.95 (*m*, $W_{1/2} \approx 2$, $C_6H_5CH_2O$–C(4)); 5.26 (br., $W_{1/2} \approx 2$, HO–C(1)); 6.40 (*dd*, $J = 9$ and 3, H–C(5)); 6.52 (*d*, $J = 3$, H–C(3)); 6.77 (*d*, $J = 9$, H–C(6)); 7.15–7.5 (*m*, $C_6H_5CH_2O$–C(4)). MS: 230 (21, M^+), 139 (7), 111 (3), *91* (100), 79 (2), 65 (9), 51 (3), 39 (3). Anal. calc. for $C_{14}H_{14}O_3$ (230.25): C 73.03, H 6.13; found: C 72.85, H 6.25.

3. Reactions with 2-Methyl-1,4-benzoquinone (4b). – 3.1. *Treatment of* **4b** *with* $P(OCH_3)_3$. Quinone **4b** (984 mg, 8.07 mmol) in dry benzene (30 ml) was reacted with $P(OCH_3)_3$ (1.5 ml and 0.9 ml after 20 h, *ca.* 20 mmol) for 41 h according to procedure *1.2*. Chromatography (110 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:1) of part (1.032 g) of the residue (1.982 g) gave 835 mg (80%) of **6b**/**7b** and 64 mg (6%) of **8b**/**9b**.

Dimethyl 4-Methoxy-2-methyl- and Dimethyl 4-Methoxy-3-methylphenyl Phosphate (**6b**/**7b**). IR ($CHCl_3$): 3030*w*, 2995*m*, 2955*m*, 2910*w*, 2850*m*, 2830*w*, 1605*w*, 1590*w*, 1493*s*, 1462*m*, 1412*w*, 1379*w*, 1275*s*, 1179*m*, 1156*m*, 1118*w*, 1042*s*, 1007*m*, 972*s*, 910*w*, 898*m*, 873*w*, 853*m*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.18 (*m*, $W_{1/2} \approx 2$, 55%) and 2.28 (*m*, $W_{1/2} \approx 2$, 45%) (CH_3); 3.73 and 3.76 (2*s*, CH_3O–C(4)); 3.82 (*d*, $J = 11$, $(CH_3O)_2PO_2$–C(1)); 6.55–6.8 and 6.9–7.25 (2*m*, 3H). MS: *246* (100, M^+), 231 (40), 137 (18), 134 (12), 109 (68), 91 (7), 79 (7), 77 (7).

Dimethyl 4-Hydroxy-2-methyl- and Dimethyl 4-Hydroxy-3-methylphenyl Phosphate (**8b**/**9b**). IR ($CHCl_3$): 3600*w*, 3280*m*, 2995*w*, 2955*m*, 2920*w*, 2855*w*, 1615*w*, 1595*w*, 1493*m*, 1455*m*, 1420*w*, 1380*w*, 1323*w*, 1265*s*, 1182*s*, 1150*m*, 1105*m*, 1060–1045*s*, 1004*m*, 973*s*, 940*m*, 903*m*, 856*m*. ^{1}H-NMR (100 MHz, $CDCl_3$): 2.14 *(major)* and 2.18 *(minor)* (2*m*, $W_{1/2} \approx 2$, CH_3); 3.82 and 3.84 (2*d*, $J = 12$, $(CH_3O)_2PO_2$–C(1)); 4.2–5.2 (br., HO–C(4)); 6.35–6.6 and 6.7–7.0 (2*m*, 3H). MS: *232* (100, M^+), 217 (3), 200 (5), 138 (6), 137 (8), 127 (11), 124 (13), 123 (21), 120 (30), 110 (18), 109 (34), 95 (8), 91 (10), 79 (11), 78 (11), 67 (6), 55 (6).

4. Reactions with 2-(*t*-Butyl)-1,4-benzoquinone (4c). – 4.1. *Treatment of* **4c** *with* $P(OCH_3)_3$. Quinone **4c** (492 mg, 3 mmol) was treated with $P(OCH_3)_3$ (1 ml, *ca.* 8.5 mmol) in dry benzene (20 ml) for 120 h according to procedure *1.2*. Chromatography (200 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 2:2:1) of the crude material gave 625 mg (72%) of **7c** and 112 mg (13%) of **9c**.

*Dimethyl 3-(*t*-Butyl)-4-methoxyphenyl Phosphate* (**7c**). Bulb-to-bulb distillation (150°/h.v.) of **7c** (304 mg) gave an analytical sample (299 mg). IR ($CHCl_3$): 3030*w*, 3000*m*, 2960*s*, 2910*m*, 2870*w*, 2860*w*, 2840*w*, 1605*w*, 1590*w*, 1489*s*, 1458*s*, 1410*m*, 1392*w*, 1361*w*, 1276*s*, 1180*s*, 1140*w*, 1090*m*, 1065*s*, 1045*s*, 982*s*, 892*m*, 882*m*, 856*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.35 (*s*, $(CH_3)_3C$–C(3)); 3.81 (*s*, CH_3O–C(4)); 3.85 (*d*, $J = 11$, $(CH_3O)_2PO_2$–C(1)); 6.79 (*d*, $J = 8.5$, H–C(5)); 7.04 (*ddd*, $J = 8.5$, 3, and 1.5, H–C(6)); 7.09 (*dd*, $J = 3$ and 1, H–C(2)). MS: 288 (33, M^+), *273* (100), 258 (4), 245 (3), 233 (4), 215 (2), 179 (3), 147 (3), 136 (3), 131 (3), 127 (5), 121 (4), 115 (5), 109 (13), 91 (7), 77 (5), 65 (2), 51 (2), 41 (3). Anal. calc. for $C_{13}H_{21}O_5P$ (288.28): C 54.16, H 7.34, P 10.74; found: C 54.25, H 7.52, P 10.66.

*Dimethyl 3-(*t*-Butyl)-4-hydroxyphenyl Phosphate* (**9c**). An analytical sample of **9c** was obtained by sublimation (120°/h.v.), m.p. 133°. IR ($CHCl_3$): 3600*w*, 3300*m*, 3000*m*, 2960*s*, 2915*m*, 2870*w*, 2860*w*, 1610*w*, 1592*w*, 1500*m*, 1485*m*, 1460*m*, 1450*m*, 1419*s*, 1392*w*, 1366*m*, 1326*w*, 1270*s*, 1180*s*, 1133*w*, 1050*s*, 1022*s*, 982*s*, 896*s*, 882*s*, 856*s*, 813*m*. ^{1}H-NMR (80 MHz, $CDCl_3$, *δ-values based on int. $CHCl_3$ = 7.27*): 1.36 (*s*, $(CH_3)_3C$–C(3)); 3.86 (*d*, $J = 11$, $(CH_3O)_2PO_2$–C(1)); 6.53 (*d*, $J = 8.5$, H–C(5)); 6.79 (*ddd*, $J = 8.5$, 3, and *ca.* 1, H–C(6)); 7.00 (*dd*, $J = 3$ and *ca.* 1, H–C(2)); 7.13–7.7 (br., HO–C(4)). MS (*di.*): 274 (27, M^+), *259* (100), 231 (4), 219 (6), 133 (6), 127 (10), 115 (6), 109 (11), 105 (10), 103 (3), 91 (3), 77 (5), 65 (2), 57 (2), 55 (3). Anal. calc. for $C_{12}H_{19}O_5P$ (274.25): C 52.55, H 6.98, P 11.29; found: C 52.64, H 7.02, P 10.69.

4.2. *O-Methylation of* **9c**. A mixture of **9c** (79 mg, 0.288 mmol), $(CH_3O)_2SO_2$ (0.4 ml, *ca.* 3 mmol), and K_2CO_3 (0.4 g) in acetone (20 ml) was boiled under reflux for 80 h. Filtration *(Celite)* and workup with CH_2Cl_2 gave 82 mg (99%) of **7c**.

5. Experiments with 2-Trimethylsilyl-1,4-benzoquinone (4d) [26]. – 5.1. *Synthesis of* **4d**. – 5.1.1. *2,5-Bis(trimethylsilyloxy)phenyl Bromide* (**36**). A mixture of 2-bromo-1,4-hydroquinone (**37**) (1.5 g, 7.93 mmol) and $(TMS)_2NH$ (2.5 ml, 12.8 mmol) was carefully heated and boiled under reflux for 15 h (Ar). Excess reagent was evaporated at reduced pressure (aspirator), and the residue was purified by bulb-to-bulb distillation (90°/h.v.) giving 2.628 g (99%) of **36**. IR ($CHCl_3$): 2955*m*, 2895*w*, 1598*m*, 1554*w*, 1480*s*, 1395*w*, 1252*s*, 1123*w*, 1033*m*, 935*m*, 910*s*, 869*m*, 842*s*. ^{1}H-NMR (80 MHz, $CDCl_3$, *δ-values based on int. $CHCl_3$ = 7.27*): 0.27 and 0.31 (2*s*, $(CH_3)_3SiO$–C(2), $(CH_3)_3SiO$–C(5)); 6.55–6.85 (*m*, H–C(3), H–C(4)); 7.03 (*d*, $J = 3$, H–C(6)). MS: 334 (61, M^+), 332 (57, M^+), 319 (24), 317 (23), 303 (13), 301 (11), 289 (1), 287 (1), 252 (4), 239 (12), 238 (39), 237 (65), 223 (6), 221 (3), 209 (2), 179 (7), 165 (8), 152 (7), 151 (8), 139 (14), 137 (15), 109 (5), 83 (8), *73* (100), 45 (22), 43 (8).

5.1.2. *1,4-Bis(trimethylsilyloxy)-2-trimethylsilylbenzene* (**35**). To a solution of **36** (2.62 g, 7.87 mmol) in dry Et_2O (20 ml) 10 ml of *ca.* 3.2M BuLi in hexane (32 mmol) were added by syringe. After the addition of more Et_2O (15 ml), the mixture was boiled under reflux for 3 h and cooled to r.t. before TMSCl (5 ml, *ca.* 39 mmol)

was added. After stirring for 15 h, the mixture was filtered, the solvent evaporated, and the residue purified by bulb-to-bulb distillation (120°/h.v.) yielding 2.268 g (88%) of **35**. IR ($CHCl_3$): 2955*m*, 2895*w*, 1562*w*, 1556*w*, 1495*w*, 1463*s*, 1382*m*, 1250*s*, 1129*w*, 1066*w*, 950*m*, 914*s*, 890*m*, 840*s*. ^{1}H-NMR (100 MHz, $CDCl_3$, *δ-values based on internal CH_2Cl_2 = 5.33*): 0.27 (*s*, 18H) and 0.32 (*s*, 9H) ($(CH_3)_3SiO$–C(2), $(CH_3)_3SiO$–C(5), $(CH_3)_3Si$–C(1)); 6.5–6.9 (*m*, 3H). MS: 328 (11, M^+), 327 (23, M^+), 326 (73, M^+), 312 (8), 311 (25), 295 (11), 281 (4), 267 (2), 262 (2), 254 (10), 239 (10), 238 (8), 223 (20), 221 (6), 209 (4), 195 (4), 193 (4), 179 (5), 163 (12), 147 (15), 133 (8), 105 (5), 91 (3), *73* (100), 59 (4), 45 (16).

5.1.3. *2-Trimethylsilyl-1,4-benzoquinone* (**4d**). To a solution of **35** (100 mg, 0.306 mmol) in CH_2Cl_2 (1 ml), 0.6 ml of aq. KF/AcOH (1M for each) and a solution of $(Et)_3NBz^+Cl^-$ (7 mg) in H_2O (1 ml) were added. After stirring for 120 h at r.t., the reaction was terminated (TLC, hexane/CH_2Cl_2/AcOEt 2:2:1) and worked up with CH_2Cl_2. The crude *2-trimethylsilyl-1,4-hydroquinone* (**38**) (56 mg) was oxidized with Ag_2O (150 mg, 0.65 mmol) according to the general procedure. Sublimation of part (44 mg) of the crude product (50 mg) (30°/h.v.) afforded 29 mg (58% based on **35**) of **4d**, m.p. 66–67°. IR ($CHCl_3$): 3025–3005*w*, 2960*m*, 2900*w*, 1705*w*, 1660*s*, 1648*s*, 1609*m*, 1575*m*, 1405*w*, 1321*s*, 1275*s*, 1251*s*, 1099*s*, 1006*m*, 921*m*, 845*s*, 640*w*. ^{1}H-NMR (80 MHz, $CDCl_3$, *δ-values based on int. $CHCl_3$ = 7.27*): 0.27 (*s*, $(CH_3)_3Si$–C(2)); 6.7–6.8 (*m*, 2H); 6.85–6.95 (*m*, 1H). MS (*di.*): 180 (1, M^+), *165* (100), 137 (27), 121 (2), 109 (4), 83 (20), 73 (16), 63 (6), 53 (8), 45 (5), 43 (9).

5.2. *Treatment of* **4d** *with $P(OCH_3)_3$.* Quinone **4d** (181 mg, 1.006 mmol) was treated with $P(OCH_3)_3$ (0.4 ml, *ca.* 3.4 mmol) in dry benzene (20 ml) for 6.5 days according to procedure *1.2*. Chromatography (50 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 2:2:1) of the crude material gave 207 mg (67%) of **7d** and 44 mg (15%) of **9d**.

Dimethyl 4-Methoxy-3-trimethylsilylphenyl Phosphate (**7d**). An analytical sample was obtained by bulb-to-bulb distillation (110°/h.v.). IR ($CHCl_3$): 3030*w*, 3000*m*, 2955*s*, 2900*w*, 2855*w*, 2840*w*, 1592*w*, 1581*w*, 1475*s*, 1461*s*, 1440*m*, 1393*s*, 1265*s*, 1243*s*, 1185*s*, 1178*s*, 1138*m*, 1070–1035*s*, 975*s*, 893*m*, 866*s*, 855*s*, 840*s*, 813*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.25 (*s*, $(CH_3)_3Si$–C(3)); 3.78 (*s*, CH_3O–C(4)); 3.86 (*d*, *J* = 11.3, $(CH_3O)_2PO_2$–C(1)); 6.76 (*d*, *J* = 9, H–C(5)); 7.14 (*d*, *J* = 3, *further split*, $W_{½} \approx 2$, H–C(2)); 7.18 (*ddd*, *J* = 9, 3, and 1.5, H–C(6)). MS: 304 (59, M^+), *289* (100), 274 (8), 259 (71), 243 (2), 229 (4), 227 (4), 215 (29), 199 (8), 195 (5), 183 (86), 165 (15), 153 (7), 133 (10), 121 (5), 119 (19), 105 (15), 89 (13), 83 (10), 79 (6), 73 (13), 59 (15). Anal. calc. for $C_{12}H_{21}O_5PSi$ (304.35): C 47.36, H 6.95; found: C 46.93, H 6.98.

Dimethyl 4-Hydroxy-3-trimethylsilylphenyl Phosphate (**9d**). Sublimation (120°/h.v.) gave an analytical sample, m.p. 132°. IR ($CHCl_3$): 3595*w*, 3300*m*, 2990*w*, 2950*m*, 2895*w*, 2850*w*, 1597*w*, 1581*w*, 1482*m*, 1448*m*, 1397*s*, 1347*w*, 1313*m*, 1252*s*, 1137*m*, 1050*s*, 974*s*, 872*s*, 852*s*, 838*s*, 621*w*. ^{1}H-NMR (80 MHz, $CDCl_3$, *δ-values based on int. $CHCl_3$ = 7.27*): 0.30 (*s*, $(CH_3)_3Si$–C(3)); 3.89 (*d*, *J* = 11, $(CH_3O)_2PO_2$–C(1)); 6.2–6.7 (br., HO–C(4)); 6.46 (*d*, *J* = 9, H–C(5)); 6.8–7.15 (*m*, H–C(2), H–C(6)). MS (*di.*): 290 (28, M^+), 276 (16), 275 (45), 274 (99), 213 (16), 185 (56), 183 (15), 167 (14), 166 (17), 165 (29), 155 (17), 151 (17), 150 (14), 137 (29), 135 (17), 125 (14), 123 (28), 121 (18), 119 (16), 111 (16), *109* (100), 107 (24), 105 (93), 97 (31), 95 (27), 93 (25), 91 (70), 89 (31), 85 (32), 83 (56), 81 (28), 79 (49), 77 (40), 75 (99), 73 (55), 71 (45), 69 (48), 61 (45), 57 (76), 55 (56), 45 (65), 43 (74), 41 (46). Anal. calc. for $C_{11}H_{19}O_5PSi$ (290.33): C 45.51, H 6.60; found: C 46.23, H 6.75.

5.3. *O-Methylation of* **9d**. A mixture of **9d** (10 mg, 0.035 mmol), $(CH_3O)_2SO_2$ (25 µl, *ca.* 0.3 mmol), and K_2CO_3 (0.1 g) in acetone (15 ml) was boiled under reflux for 17 h. Filtration *(Celite)*, evaporation of solvent, workup with CH_2Cl_2, and bulb-to-bulb distillation (110°/h.v.) gave 11 mg (quant.) of **7d**.

6. Experiments with 2-Methoxymethyl-1,4-benzoquinone (4e) [27]. – 6.1. *Synthesis of* **4e**. – 6.1.1. *Methyl 5-(2'-Tetrahydropyranyloxy)salicylate* (**40**). A solution of methyl gentisate (**39**) (4.978 g, 29.63 mmol), prepared from gentisic acid, according to [48], dihydropyrane (8.1 ml, *ca.* 89 mmol), and pyridinium *p*-toluenesulfonate (80 mg, 0.32 mmol) in CH_2Cl_2 (80 ml) was stirred for 1 h at r.t. (Ar). Workup with CH_2Cl_2 and flash chromatography (200 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 3:1:1) afforded 7.589 g (quant.) of **40**, m.p. 61–65°. IR (CCl_4): 3415*w*, 3230*m*, 3000*w*, 2945*s*, 2870*m*, 2850*m*, 1725*w*, 1678*s*, 1650*w*, 1612*s*, 1480*s*, 1438*s*, 1386*s*, 1369*m*, 1355*s*, 1332*s*, 1283*s*, 1251*s*, 1200*s*, 1146*m*, 1123*s*, 1110*s*, 1076*s*, 1048*m*, 1037*s*, 1019*s*, 980*s*, 965*s*, 933*m*, 900*s*, 870*m*, 693*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.3–2.2 (*m*, 6H); 3.4–4.1 (*m*, 2H–C(6')); 3.92 (*s*, CH_3O); 5.30 (*m*, $W_{½} \approx 6$, H–C(2')); 6.87 (*d*, *J* = 9, H–C(3)); 7.18 (*dd*, *J* = 9 and 3, H–C(4)); 7.49 (*d*, *J* = 3, H–C(6)); 10.39 (*s*, HO–C(2)). MS: 252 (2, M^+), 221 (2), 168 (95), 153 (2), 137 (80), 136 (94), 111 (2), 108 (70), 85 (99), 84 (86), 83 (41), 80 (47), 69 (18), 67 (36), 57 (50), 56 (40), *55* (100), 54 (34), 53 (38), 52 (37), 51 (20), 43 (45), 41 (60), 39 (35).

6.1.2. *Methyl 2-Methoxy-5-(2'-tetrahydropyranyloxy)benzoate* (**41**). A solution of **40** (7.399 g) and CH_3I (8 ml, *ca.* 0.128 mol) in acetone (150 ml) containing K_2CO_3 (12 g) was boiled under reflux for 7 days. Additional CH_3I (8 ml) had been added after 4 days. After evaporation of reagent and part of the solvent, the mixture was worked up with AcOEt. Flash chromatography (300 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 3:1:1) yielded

7.161 g (93% based on **39**) of **41**. IR ($CHCl_3$): 3025*w*, 2990*w*, 2940*s*, 2870*w*, 2850*w*, 2835*w*, 1718*s*, 1607*w*, 1580*m*, 1489*s*, 1460*s*, 1453*s*, 1433*s*, 1411*m*, 1386*w*, 1355*m*, 1302*s*, 1275*s*, 1178*s*, 1142*m*, 1108*s*, 1073*s*, 1019*s*, 986*s*, 960*s*, 925*w*, 896*s*, 869*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.4–2.2 (*m*, 6H), 3.4–4.2 (*m*, 2H–C(6′)); 3.87 and 3.90 (2*s*, CH_3O–CO–C(1), CH_3O–C(2)); 5.25–5.45 (*m*, H–C(2′)); 6.89 (*d*, $J = 9$, H–C(3)); 7.19 (*dd*, $J = 9$ and 3, H–C(4)); 7.5 (*d*, $J = 3$, H–C(6)). MS: 266 (0.5, M^+), 235 (3), 182 (96), 167 (13), 151 (97), 137 (15), 136 (19), 121 (23), 111 (13), 108 (27), 107 (11), 95 (10), 93 (31), *85* (100), 84 (79), 83 (39), 80 (12), 79 (13), 69 (16), 67 (24), 65 (27), 63 (11), 57 (33), 56 (34), 55 (99), 53 (32), 52 (21), 51 (21), 50 (12), 43 (29), 41 (53), 39 (49).

6.1.3. *2-Methoxy-5-(2′-tetrahydropyranyloxy)phenylmethanol* (**43**). A solution of **41** (10.712 g, 40.3 mmol) in dry Et_2O (180 ml) was added dropwise to an ice-cooled mixture of $Li[AlH_4]$ (7.95 g, 209 mmol) in Et_2O (100 ml) (Ar). After boiling under reflux for 1 h, the reaction was cooled (ice) and quenched by the addition of *Celite* (2–3 g) and sat. $(NH_4)_2SO_4$-solution. Boiling under reflux (1 h), filtration *(Celite)*, evaporation of solvent, and flash chromatography (300 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 2:1:1) of the crude material gave 9.179 g (95%) of **43**. Bulb-to-bulb distillation (180°/h.v.) of 480 mg of **43** gave an analytical sample (441 mg). IR ($CHCl_3$): 3595*m*, 3455*w*, 3030*w*, 2990*m*, 2940*s*, 2870*s*, 2850*s*, 2835*m*, 1590*w*, 1490*s*, 1460*s*, 1453*s*, 1440*s*, 1428*s*, 1386*s*, 1355*s*, 1322*m*, 1278*s*, 1178*s*, 1159*s*, 1147*m*, 1122*s*, 1103*s*, 1071*s*, 1020*s*, 982*s*, 958*s*, 936*s*, 904*s*, 885*m*, 870*s*, 845*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.4–2.2 (*m*, 6H); 2.42 (*t*, $J = 6$, $HOCH_2$–C(1)); 3.35–4.2 (*m*, 2H–C(6′)); 3.82 (*s*, CH_3O–C(2)); 4.64 (*d*, $J = 6$, *s after exchanging with* D_2O, $HOCH_2$–C(1)); 5.30 (*m*, $W_{1/2} \approx 6$, H–C(2′)); 6.6–7.1 (*m*, 3H). MS: 154 (68, $M^+ - 84$), 153 (6), 137 (12), 136 (10), 125 (21), 123 (11), 121 (16), 111 (15), 107 (9), 95 (5), 93 (15), *84* (100), 83 (50), 77 (6), 69 (15), 65 (18), 57 (12), 56 (28), 55 (96), 54 (33), 53 (17), 41 (24), 39 (29). Anal. calc. for $C_{13}H_{18}O_4$ (238.27): C 65.53, H 7.61; found: C 65.59, H 7.67.

6.1.4. *2-Methoxymethyl-4-(2′-tetrahydropyranyloxy)anisol* (**44**). To a solution of **43** (1.001 g, 4.21 mmol) in dry THF (100 ml) 6 ml of 1.5M BuLi in hexane (*ca.* 9 mmol) was added at −78° by syringe (Ar). The mixture was warmed to −20° (10 min) and cooled again (−78°). After the addition of $(CH_3O)_2SO_2$ (1.7 ml, *ca.* 18 mmol), the mixture was stirred at r.t. over night. Excess of reagent was quenched with 25% aq. NH_3/H_2O (1:6, v/v) (1 h) and the mixture was worked up with Et_2O. Chromatography (150 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 5:1:1) gave 997 mg (94%) of **44**. ^{1}H-NMR (90 MHz, $CDCl_3$): 1.5–2.2 (*m*, 6H); 3.40 (*s*, CH_3OCH_2–C(2)); 3.3–4.1 (*m*, 2H–C(6′)); 3.75 (*s*, CH_3O–C(1)); 4.45 (*m*, $W_{1/2} \approx 2$, CH_3OCH_2–C(2)); 5.2–5.4 (*m*, H–C(2′)); 6.75 (*d*, $J = 9$, H–C(6)); 6.95 (*dd*, $J = 9$ and 3, H–C(5)); 7.10 (*d*, $J = 3$, H–C(3)).

6.1.5. *4-Methoxy-3-(methoxymethyl)phenol* (**42**). A solution of **44** (895 mg, 3.55 mmol) and CH_3SO_3H (0.2 ml) in CH_3OH (50 ml) was stirred at r.t. for 12 min (Ar). Workup with AcOEt, chromatography (150 g of silica gel, hexane/CH_2Cl_2/AcOEt 4:1:1), and crystallization (CH_2Cl_2/hexane) afforded 463 mg (77%) of **42**, m.p. 70.5–72° (subl., 65°/h.v.). IR ($CHCl_3$): 3600*m*, 3340*m*, 3000*m*, 2935*m*, 2905*m*, 2835*m*, 1600*w*, 1497*s*, 1463*s*, 1453*s*, 1437*s*, 1383*m*, 1370*w*, 1329*w*, 1283*s*, 1267*m*, 1176*s*, 1154*s*, 1121*w*, 1088*s*, 1032*s*, 1000*w*, 958*m*, 905*w*, 872*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.40 (*s*, CH_3OCH_2–C(3)); 3.75 (*s*, CH_3O–C(4)); 4.47 (*m*, $W_{1/2} \approx 2$, CH_3OCH_2–C(3)); 5.2–5.9 (br., HO–C(1)); 6.6–6.9 (*m*, 3H). MS: *168* (100, M^+), 153 (16), 137 (82), 136 (24), 125 (8), 121 (5), 108 (14), 107 (55), 94 (8), 93 (7), 91 (3), 79 (11), 77 (17), 65 (15), 53 (6), 51 (6), 45 (18), 39 (12). Anal. calc. for $C_9H_{12}O_3$ (168.19): C 64.27, H 7.19; found: C 64.25, H 7.21.

6.1.6. *Dimethyl 4-Methoxy-3-(methoxymethyl)phenyl Phosphate* (**7e**). A solution of **42** (34 mg, 0.202 mmol), dimethyl chlorophosphate [32] [33] (0.1 ml, *ca.* 1 mmol), and diisopropylethylamine (0.17 ml, *ca.* 1 mmol) in CH_2Cl_2 (1 ml) was stirred 18 h at r.t. (Ar). Workup with CH_2Cl_2, chromatography (3 g of silica gel, hexane/CH_2Cl_2/AcOEt 1:1:1) of the crude material, and bulb-to-bulb distillation (170°/h.v.) yielded 53 mg (95%) of **7e**. IR ($CHCl_3$): 3040*w*, 2995*m*, 2955*m*, 2855*w*, 2840*w*, 2830*w*, 1595*w*, 1560*w*, 1492*s*, 1461*s*, 1425*m*, 1382*w*, 1366*w*, 1270*s*, 1179*s*, 1156*s*, 1123*w*, 1090*s*, 1040*s*, 986*s*, 900*s*, 885*s*, 855*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.42 (*s*, CH_3OCH_2–C(3)); 3.81 (*s*, CH_3O–C(4)); 3.85 (*d*, $J = 11.3$, $(CH_3O)_2PO_2$–C(1)); 4.46 (*m*, $W_{1/2} \approx 1.5$, CH_3OCH_2–C(3)); 6.79 (*d*, $J = 9$, H–C(5)); 7.12 (*dd*, $J = 9$ and 3, *further split by small couplings*, H–C(6)); 7.22 (*d*, $J = 3$, *further split by small couplings*, H–C(2)). MS: *276* (100, M^+), 261 (44), 245 (94), 244 (14), 233 (15), 229 (7), 215 (37), 187 (6), 151 (43), 150 (12), 135 (22), 127 (26), 121 (13), 120 (10), 119 (13), 109 (60), 93 (8), 91 (13), 79 (10), 77 (10), 65 (9), 45 (21). Anal. calc. for $C_{11}H_{17}O_6P$ (276.14): C 47.83, H 6.20, P 11.21; found: C 47.70, H 6.29, P 11.12.

6.1.7. *2-(Methoxymethyl)-1,4-benzoquinone* (**4e**). To a solution of **42** (258 mg, 1.535 mmol) in CH_3CN (26 ml) a solution of $Ce(NH_4)_2(NO_3)_6$ (1.7 g, 3.1 mmol) in H_2O (10 ml) was added within 12 min. After 5 min the mixture was worked up with CH_2Cl_2. This procedure was repeated, because TLC analysis showed unreacted **42**. Flash chromatography (25 g of *Florisil*, hexane/CH_2Cl_2/AcOEt 4:4:1) gave 136 mg (58%) of **4e**, m.p. 35.5–37.5°. IR ($CHCl_3$): 3030*w*, 2990*w*, 2930*m*, 2880*w*, 2810*m*, 1655*s*, 1614*m*, 1600*m*, 1448*m*, 1405*w*, 1360*w*, 1347*w*, 1325*m*, 1281*s*, 1188*m*, 1133*m*, 1112*m*, 1060*s*, 1002*w*, 967*w*, 908*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.49 (*s*,

CH_3O); 4.31 (*d*, $J \approx 2$, CH_3OCH_2–C(2)); 6.7–6.95 (*m*, 3H). MS: 166 (17, M^+), 152 (32), 151 (17), 137 (34), *124* (100), 109 (38), 95 (20), 94 (17), 82 (12), 81 (30), 77 (6), 69 (8), 67 (10), 66 (13), 65 (20), 55 (17), 54 (22), 53 (24), 45 (29), 39 (37).

6.2. *Treatment of* **4e** *with* $P(OCH_3)_3$. Quinone **4e** (135 mg, 0.888 mmol) was treated with $P(OCH_3)_3$ (1.1 ml, *ca.* 8.9 mmol) in dry benzene (15 ml) for 42 h according to procedure *1.2*. Chromatography (50 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:1) of the crude material (249 mg) gave 165 mg (67%) of a mixture of *dimethyl 4-methoxy-2-(methoxymethyl)- and dimethyl 4-methoxy-3-(methoxymethyl)phenyl phosphate* (**6e** *and* **7e**, respectively), ratio **6e**/**7e** *ca.* 26:74, according to ^{1}H-NMR. Bulb-to-bulb distillation (170°/h.v.) gave an analytically pure sample. IR ($CHCl_3$): 2990*m*, 2950*m*, 2850*w*, 2830*w*, 1593*w*, 1489*s*, 1456*s*, 1425*m*, 1380*w*, 1365*w*, 1270*s*, 1179*s*, 1155*s*, 1035*s*, 985*s*, 967*s*, 898*s*, 885*s*, 853*s*. ^{1}H-NMR (300 MHz, $CDCl_3$, *signals of 2-methoxymethyl isomer* **6e** *only*): 3.42 (*s*, CH_3OCH_2–C(2)); 3.80 (*s*, CH_3O–C(4)); 3.85 (*d*, J = 11.3, $(CH_3O)_2PO_2$–C(1)); 4.54 (*m*, $W_{1/2} \approx 2$, CH_3OCH_2–C(2)); 6.78 (*dd*, J = 9 and 3, H–C(5)); 6.98 (*d*, J = 3, H–C(3)); 7.21 (*dd*, J = 9 and 1, H–C(6)). MS: *276* (100, M^+), 261 (87), 245 (73), 233 (33), 229 (30), 215 (25), 151 (51), 150 (17), 137 (12), 135 (36), 127 (21), 121 (30), 120 (12), 119 (23), 109 (54), 91 (22), 79 (11), 77 (11), 45 (18). Anal. calc. for $C_{11}H_{17}O_6P$ (276.14): C 47.83, H 6.20, P 11.21; found: C 47.69, H 6.24, P 11.04.

7. Experiments with 2-Bromo-1,4-benzoquinone (4f). – 7.1. *Treatment of* **4f** *with* $P(OCH_3)_3$. Quinone **4f** (319 mg, 1.71 mmol) in dry benzene (6 ml) was reacted with $P(OCH_3)_3$ (0.3 ml, *ca.* 2.5 mmol) for 20 h according to procedure *1.2*. Chromatography (60 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:1) of the residue (521 mg) and re-chromatography of mixed fractions (118 mg) gave 124 mg (23%) of **6f**, 254 mg (48%) of **7f**, and 50 mg (9%) of a mixture of **8f** and **9f**, eluted with CH_2Cl_2/AcOEt 1:1. A mixture of **8f**/**9f** (49 mg), $(CH_3O)_2SO_2$ (0.2 ml, *ca.* 1.8 mmol), and K_2CO_3 (0.6 g) in acetone (2 ml) was boiled under reflux for 6 h (Ar). Filtration, workup with CH_2Cl_2, and chromatography (8 g of silica gel, CH_2Cl_2/AcOEt 1:1) gave 21 mg (4%) of **6f** and 11 mg (2%) of **7f**.

Dimethyl 2-Bromo-4-methoxyphenyl Phosphate (**6f**). IR (CCl_4): 3000*w*, 2950*m*, 2910*w*, 2850*w*, 2835*w*, 1597*w*, 1572*w*, 1483*s*, 1460*w*, 1438*m*, 1298*s*, 1280*m*, 1260*m*, 1203*s*, 1180*m*, 1040*s*, 948*s*, 853*s*, 688*w*, 670*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.74 (*s*, CH_3O–C(4)); 3.87 (*d*, J = 11, $(CH_3O)_2PO_2$–C(1)); 6.78 (*dd*, J = 9 and 3, H–C(5)); 7.08 (*dd*, J = 3 and $\approx$ 1, H–C(3)); 7.31 (*dd*, J = 9 and $\approx$ 1.5, H–C(6)). MS: 312 (18, M^+), 310 (18, M^+), 297 (1), 295 (1), 281 (1), 279 (1), *231* (100), 216 (21), 203 (4), 201 (9), 175 (2), 173 (2), 137 (2), 123 (5), 119 (2), 109 (21), 93 (4), 79 (7), 63 (3). Anal. calc. for $C_9H_{12}BrO_5P$ (310.98): C 34.75, H 3.89, P 9.96; found: C 34.60, H 4.00, P 9.31.

Dimethyl 3-Bromo-4-methoxyphenyl Phosphate (**7f**). IR (CCl_4): 3080*w*, 3010*w*, 2955*m*, 2910*w*, 2855*w*, 2840*w*, 1599*w*, 1576*w*, 1486*s*, 1460*m*, 1440*m*, 1400*w*, 1300–1280*s*, 1260*s*, 1198*s*, 1180*s*, 1135*w*, 1070–1040*s*, 960*s*, 874*m*, 852*s*, 676*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.82 (*d*, J = 11, $(CH_3O)_2PO_2$–C(1)); 3.84 (*s*, CH_3O–C(4)); 6.81 (*d*, J = 9, H–C(5)); 7.15 (*ddd*, J = 9, 3, and $\approx$ 2, H–C(6)); 7.40 (*dd*, J = 3 and $\approx$ 1.5, H–C(2)). MS: 312 (84, M^+), 310 (84, M^+), 297 (22), 295 (22), 231 (3), 216 (2), 203 (6), 201 (9), 186 (3), 119 (11), *109* (100), 107 (10), 93 (4), 79 (15), 75 (4), 63 (5), 53 (4), 51 (4), 43 (13). Anal. calc. for $C_9H_{12}BrO_5P$ (310.98): C 34.75, H 3.89, P 9.96; found: C 34.90, H 3.96, P 9.17.

Dimethyl 2-Bromo- and Dimethyl 3-Bromo-4-hydroxyphenyl Phosphate (**8f** and **9f**). IR ($CHCl_3$): 3600*w*, 3520*w*, 3250*m*, 3000*w*, 2960*w*, 2855*w*, 1605*w*, 1590*w*, 1488*m*, 1440*m*, 1330*w*, 1260*m*, 1185*m*, 1052*s*, 960*s*, 883*m*, 860*m*, 813*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.84 and 3.92 (2*d*, J = 12, $(CH_3O)_2PO_2$–C(1)); 6.3–6.6 and 7.4–8.4 (2 br., HO–C(4)); 6.50 (*dd*, J = 9 and 3), 6.7–7.1 (*m*), and 7.28 (*dd*, J = 3 and 1) (3H). MS: 298 (64, M^+), 296 (66, M^+), 266 (4), 264 (4), 262 (3), 231 (17), 217 (34), 202 (12), 201 (8), 189 (11), 186 (15), 184 (14), 159 (4), 155 (3), 123 (15), 113 (14), *109* (100), 105 (31), 95 (9), 93 (6), 91 (8), 79 (28), 77 (13), 63 (8), 62 (9), 53 (12), 51 (13), 47 (8), 43 (7).

7.2. *Treatment of* **4f** *with* $P(OCH_3)_3$/*TMSCl*. Quinone **4f** (499 mg, 2.67 mmol) in dry CH_2Cl_2 (3 ml) was treated with a mixture of $P(OCH_3)_3$ (0.6 ml, *ca.* 5 mmol) and TMSCl (2.4 ml, *ca.* 26.5 mmol) for 6 h according to procedure *1.3*. Part (450 mg) of the residue (905 mg) obtained by evaporative workup was chromatographed (50 g of silica gel, CH_2Cl_2/AcOEt 1:1), giving, after re-chromatography of mixed fractions, 56 mg (14%) of **12f** and 314 mg (80%) of a 1:1 mixture (^{1}H-NMR) of **8f** and **9f**. The remaining crude material (442 mg) was dissolved in acetone (2 ml) and treated with $(CH_3O)_2SO_2$ (0.2 ml, *ca.* 4.5 mmol)/K_2CO_3 (620 mg) for 6 h under reflux. Filtration, workup with CH_2Cl_2, and chromatographic separation (silica gel, CH_2Cl_2/AcOEt 1:1) gave 146 mg (36%) of **6f** and 144 mg (35%) of **7f**.

Dimethyl 2-Bromo-3,6-dihydroxyphenylphosphonate (**12f**). IR ($CHCl_3$): 3520*m*, 3600–2400*m*, 3005*w*, 2950*w*, 2850*w*, 1581*m*, 1452*s*, 1316*w*, 1282*w*, 1172*m*, 1135*w*, 1094*m*, 1030*s*, 958*w*, 926*w*, 840*s*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.76 (*d*, J = 12, $(CH_3O)PO_2$–C(1)); 5.42 (*s*, HO–C(3)); 6.88 (*dd*, J = 9 and 6, H–C(5)); 7.16 (*d*, J = 9,

H–C(4)); 10.85 (*d*, $J \approx 1.5$, HO–C(6)). MS: 298 (99, M^+), *296* (100, M^+), 281 (4), 279 (4), 266 (65), 264 (66), 250 (3), 236 (9), 234 (9), 217 (23), 203 (11), 202 (7), 201 (10), 185 (16), 155 (12), 135 (7), 123 (14), 113 (12), 109 (35), 107 (8), 105 (22), 95 (11), 93 (9), 79 (35), 65 (14), 53 (13), 51 (16), 47 (15), 43 (12).

8. Treatment of 2-Chloro-1,4-benzoquinone (4g) with $P(OCH_3)_3$. – Quinone **4g** (513 mg, 3.6 mmol) in dry benzene (50 ml) was treated with $P(OCH_3)_3$ (0.51 ml, *ca.* 3.9 mmol) according to procedure *1.2* for 16 h. The phosphite was added under ice-cooling. Chromatography (silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:1) of the residue and re-chromatography of mixed fractions afforded 277 mg (28%) of **6g** and 451 mg (47%) of **7g**. Bulb-to-bulb distillation (160°/h.v.) afforded analytical samples of **6g** and **7g**.

Dimethyl 2-Chloro-4-methoxyphenyl Phosphate (**6g**). IR ($CHCl_3$): 3005*m*, 2965*m*, 2950*w*, 2910*w*, 2860*w*, 2840*w*, 1605*w*, 1585*w*, 1492*s*, 1463*m*, 1442*m*, 1413*w*, 1285*s*, 1183*s*, 1070*s*, 1051*s*, 1037*s*, 955*s*, 883*s*, 872*s*, 861*s*, 848*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.78 (*s*, CH_3O–C(4)); 3.90 (*d*, J = 11.5, $(CH_3O)_2PO_2$–C(1)); 6.77 (*dd*, J = 9 and 3, H–C(5)); 6.95 (*dd*, J = 3 and 1, H–C(3)); 7.32 (*dd*, J = 9 and 1.5, H–C(6)). MS (*di.*): 268 (10, M^+), 266 (30, M^+), *231* (100), 216 (13), 201 (2), 159 (5), 157 (16), 143 (2), 129 (6), 123 (2), 109 (55), 93 (4), 79 (12), 65 (5), 63 (7). Anal. calc. for $C_9H_{12}O_5ClP$ (266.62): C 40.54, H 4.54, Cl 13.30, P 11.62; found: C 40.73, H 4.72, Cl 13.37, P 11.49.

Dimethyl 3-Chloro-4-methoxyphenyl Phosphate (**7g**). IR ($CHCl_3$): 3005*m*, 2961*m*, 2945*m*, 2905*w*, 2860*w*, 2845*w*, 1602*w*, 1586*w*, 1493*s*, 1462*m*, 1442*m*, 1405*w*, 1282*s*, 1262*s*, 1181*s*, 1140*m*, 1063*s*, 1050*s*, 1030*s*, 970*s*, 878*m*, 860*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.86 (*d*, J = 11.3, $(CH_3O)_2PO_2$–C(1)); 3.88 (*s*, CH_3O–C(4)); 6.88 (*d*, J = 9, H–C(5)); 7.12 (*ddd*, J = 9, 3, and 1.5, H–C(6)); 7.27 (*dd*, J = 3 and 1.5, H–C(2)). MS (*di.*): 268 (23, M^+), 266 (68, M^+), 253 (6), 251 (17), 231 (4), 219 (1), 201 (1), 171 (2), 157 (9), 154 (4), 143 (2), 119 (3), *109* (100), 93 (3), 91 (2), 79 (14), 63 (6), 53 (5), 51 (4), 47 (3). Anal. calc. for $C_9H_{12}O_5ClP$ (266.62): C 40.54, H 4.54, Cl 13.30, P 11.62; found: C 39.79, H 4.47, Cl 13.24, P 11.54.

9. Experiments with 2-Benzoyl-1,4-benzoquinone (4h). – 9.1. *Dimethyl 2-Benzoyl-3,6-dihydroxyphenylphosphonate* (**12h**). Quinone **4h** (448 mg, 2.11 mmol), prepared by Ag_2O oxidation of 2,5-dihydroxy-benzophenone [49], was treated with $P(OCH_3)_3$ (945 mg, 7.6 mmol) and TMSCl (5.5 ml, *ca.* 60 mmol) in CH_2Cl_2 (2 ml) according to procedure *1.3* overnight. Part (400 mg) of the total residue (907 mg), obtained by evaporative workup, was chromatographed (silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:2) giving 131 mg (43%) of **12h**, m.p. 216°. IR (KBr): 2955*w*, 2850*w*, 1660*s*, 1594*m*, 1579*m*, 1482*m*, 1450*m*, 1320*s*, 1270*s*, 1232*s*, 1215*s*, 1175*m*, 1163*w*, 1153*w*, 1140*m*, 1053*s*, 1030*s*, 1012*m*, 942*w*, 926*w*, 863*m*, 830*s*, 793*m*, 776*m*, 727*w*, 709*s*, 685*w*, 672*m*, 615*w*, 588*s*, 550*w*, 485*m*, 410*m*, 380*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.37 (*d*, J = 11, $(CH_3O)_2PO$–C(1)); 6,86 (*dd*, J = 9 and 7, H–C(5)); 7.03 (*d*, J = 9, *further split*, $W_{1/2} \approx 3$, H–C(4)); 7.3–7.8 (*m*, C_6H_5CO–C(2)); 9.1–9.4 (br., HO–C(3)); 9.8–10.2 (br., HO–C(6)). MS (*di.*): 322 (28, M^+), 304 (41), 90 (39), *289* (100), 275 (2), 261 (3), 245 (5), 213 (2), 196 (2), 155 (3), 139 (5), 109 (6), 107 (20), 95 (3), 93 (3), 79 (8), 77 (34), 65 (2), 63 (2), 51 (9).

9.2. *Dimethyl 2-Benzoyl-3,6-dimethoxyphenylphosphonate* (**13h**). Quinone **4h** (442 mg, 2.08 mmol) was treated with $P(OCH_3)_3$ (945 mg) and TMSCl (5.5 ml) according to procedure *1.3*. The crude material, dissolved in acetone (15 ml), was treated with $(CH_3O)_2SO_2$ (0.35 ml, *ca.* 3.7 mmol) and K_2CO_3 (1.75 g) at reflux temp. overnight. The mixture was filtered, and the solvent of the filtrate evaporated. As TLC analysis showed an incomplete conversion, this procedure was repeated (0.3 ml of $(CH_3O)_2SO_2$, 1.7 g of K_2CO_3 in 15 ml of acetone). Chromatography (silica gel, CH_2Cl_2/CH_3OH 24:1) of the crude product (738 mg) gave 409 mg (56%) of **13h**, m.p. 134°. IR ($CHCl_3$): 2990*m*, 2965*m*, 2910*w*, 2850*w*, 2840*w*, 1675*s*, 1596*w*, 1582*m*, 1490*w*, 1460*s*, 1450*m*, 1428*m*, 1315*w*, 1275*s*, 1255*s*, 1212*w*, 1180*w*, 1146*w*, 1045*s*, 964*s*, 925*w*, 890*m*, 827*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.51 and 3.58 (2*d*, J = 11.5, *broadened by dynamic effects, signals coalesce at higher temp.*, $(CH_3O)_2PO$–C(1)); 3.66 and 3.93 (2*s*, CH_3O–C(3), CH_3O–C(6)); 7.02 (*dd*, J = 9 and 7, H–C(5)); 7.13 (*d*, J = 9, H–C(4)); 7.35–7.45 (*m*, 2H), 7.45–7.55 (*m*, 1H), and 7.75–7.83 (*m*, 2H) (C_6H_5CO–C(2)). MS (*di.*): 350 (75, M^+), 335 (4), 332 (17), 319 (38), 318 (53), 317 (25), 303 (42), 289 (12), *273* (100), 258 (7), 243 (17), 241 (8), 215 (8), 185 (7), 139 (7), 127 (6), 109 (8), 105 (99), 93 (11), 91 (8), 77 (73), 53 (6), 41 (12). Anal. calc. for $C_{17}H_{19}O_6P$ (350.31): C 58.29, H 5.47, and P 8.84; found: C 58.00, H 5.43, P 8.67.

9.3. *Treatment of* **4h** *with Neat* $P(OCH_3)_3$. $P(OCH_3)_3$ (6.5 ml, *ca.* 55 mmol) was added to **4h** (452 mg, 2.15 mmol) under N_2 (exothermic). After stirring at r.t. overnight the reagent was evaporated at reduced pressure. Chromatography (silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:2) of the residue (897 mg) and re-chromatography of mixed fractions gave, after elution of minor amounts of non-P-containing products, 65 mg (9%) of **14h** 123 mg (*ca.* 17%) of a mixture of **14h** and **12h** and 113 mg (16%) of **12h**.

Dimethyl 2-Benzoyl-6-hydroxy-3-methoxyphenylphosphonate (**14h**). M.p. 126–128°. IR (KBr): 3040*w*, 2955*w*, 2845*w*, 1675*s*, 1595*m*, 1580*m*, 1463*s*, 1448*m*, 1437*s*, 1398*w*, 1340*w*, 1313*m*, 1302*m*, 1264*s*, 1245*s*, 1200*m*, 1183*w*,

1139*m*, 1062*s*, 1045*s*, 1002*m*, 999*m*, 980*w*, 893*m*, 841*s*, 825*m*, 788*m*, 772*w*, 756*w*, 730*w*, 720*w*,. 705*s*, 686*w*, 669*m*, 640*w*, 613*w*, 590*s*, 568*w*, 490*w*, 443*w*, 424*w*, 412*w*, 370*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.45 (*d*, J = 11, $(CH_3O)_2PO$–C(1)); 3.61 (*s*, CH_3O–C(3)); 7.02 (*dd*, J = 9 and 7, H–C(5)); 7.20 (*dd*, J = 9 and *ca.* 1.5, H–C(4)); 7.35–7.6 (*m*, 3H) and 7.65–7.8 (*m*, 2H) (C_6H_5CO–C(2)); 10.36 (br., $W_{1/2} \approx 3$, HO–C(6)). MS (*di.*): *336* (100, M^+), 321 (7), 305 (13), 304 (58), 289 (89), 274 (27), 259 (18), 245 (4), 243 (6), 227 (4), 211 (4), 164 (4), 155 (7), 139 (11), 127 (5), 109 (12), 105 (46), 93 (9), 91 (4), 79 (9), 77 (50), 65 (5), 63 (4), 51 (11). Anal. calc. for $C_{16}H_{17}O_6P$ (336.29): C 57.15, H 5.10, P 9.21; found: C 56.99, H 5.00, P 9.31.

10. Experiments with 2-(Methoxycarbonyl)-1,4-benzoquinone (4i) [14] [50]. – 10.1. *Dimethyl 3,6-Dihydroxy-2-(methoxycarbonyl)phenylphosphonate* (**12i**). Quinone **4i** (2 g, 12.07 mmol) in dry CH_2Cl_2 (7 ml) was reacted with $P(OCH_3)_3$ (2.52 g, 20.3 mmol) and TMSCl (15.7 ml, *ca.* 170 mmol) overnight according to procedure *1.3*. The addition to the reagents was done with ice-cooling. Chromatography (silica gel, cyclohexane/CH_2Cl_2/AcOEt 1:1:1) of the crude material (2.18 g and 0.362 g, obtained by continuous extraction of the aq. phase with CH_2Cl_2) gave 1.617 g (48%) of **12i**, m.p. 120°. IR ($CHCl_3$): 3600–2300*w*, 2995*w*, 2950*m*, 2920*w*, 2850*m*, 1733*m*, 1676*m*, 1590*w*, 1449*s*, 1360*m*, 1332*m*, 1263*m*, 1185*m*, 1118*m*, 1028*s*, 926*w*, 901*m*, 841*m*. ^{1}H-NMR: see [14]. MS (*di.*): 276 (24, M^+), 245 (20), *244* (100), 243 (3), 216 (14), 212 (3), 186 (33), 173 (2), 171 (3), 160 (5), 122 (5), 109 (8), 108 (13), 95 (5), 94 (11), 93 (7), 79 (13), 65 (7), 53 (7), 51 (5), 47 (5), 39 (2). Anal. calc. for $C_{10}H_{13}O_7P$ (276.18): C 43.49, H 4.74, P 11.21; found: C 43.55, H 4.76, P 11.19.

10.2. *Dimethyl 3,6-Dimethoxy-2-(methoxycarbonyl)phenylphosphonate* (**13i**). A mixture of **12i** (106 mg, 0.384 mmol), $(CH_3O)_2SO_2$ (0.11 ml, *ca.* 1.2 mmol), and K_2CO_3 (0.5 g) in acetone (15 ml) was boiled under reflux over night (Ar). After removal of salts by filtration, and evaporation of solvent (aspirator), the residue was worked up with CH_2Cl_2 giving 108 mg (92%) of **13i**, m.p. 90–92°. IR ($CHCl_3$): 3030*w*, 2990*m*, 2950*m*, 2900*w*, 2850*w*, 2835*m*, 1732*s*, 1583*m*, 1460*s*, 1442*w*, 1428*s*, 1285*s*, 1255*s*, 1160*w*, 1129*m*, 1055–1030*s*, 975*w*, 906*m*, 856*m*, 833*m*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.72 (*d*, J = 12, $(CH_3O)_2PO$–C(1)); 3.76, 3.84, and 3.90 (3*s*, CH_3OCO–C(2), CH_3O–C(3), CH_3O–C(6)); 6.92 (*dd*, J = 9 and 7, H–C(5)); 7.07 (*dd*, J = 9 and $\approx$ 1, H–C(4)). MS (*di.*): 304 (62, M^+), 290 (14), 289 (6), *273* (100), 272 (18), 271 (36), 259 (22), 258 (15), 257 (27), 243 (81), 240 (76), 229 (18), 227 (38), 215 (29), 214 (18), 213 (11), 212 (24), 211 (9), 199 (18), 183 (16), 148 (13), 134 (16), 127 (9), 121 (10), 109 (16), 93 (23), 79 (13), 77 (9), 76 (9), 71 (6), 63 (8), 57 (12), 43 (8).

10.3. *Treatment of* **4i** *with* $P(OCH_3)_3$. Quinone **4i** (810 mg, 4.88 mmol) in dry benzene (25 ml) was treated with $P(OCH_3)_3$ (7 ml, *ca.* 59 mmol) overnight according to procedure *1.2*. Part (500 mg) of the crude mixture (1.49 g) was separated by chromatography (silica gel). Elution with cyclohexane/CH_2Cl_2/AcOEt 1:1:1 and re-chromatography of mixed fractions gave 88 mg (18%) of **14i**, 25 mg (*ca.* 5%) of a mixture of **14i** and **12i**, and 68 mg (15%) of **12i**. Elution with CH_2Cl_2/AcOEt 1:1 and re-chromatography afforded 101 mg (20%) of **13i**.

Dimethyl 6-Hydroxy-3-methoxy-2-(methoxycarbonyl)phenylphosphonate (**14i**). M.p. 95–98°. IR ($CHCl_3$): 3600–2400*m*, 3000*w*, 2950*w*, 2920*w*, 2845*w*, 1734*s*, 1605*w*, 1583*w*, 1462*s*, 1431*m*, 1315*m*, 1242*s*, 1120*s*, 1029*s*, 995*m*, 920*w*, 865*m*, 842*w*, 822*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 3.72 (*d*, J = 12, $(CH_3O)_2PO$–C(1)); 3.76 and 3.86 (2*s*, CH_3OCO–C(2), CH_3O–C(3)); 7.06 (*dd*, J = 9 and 6, H–C(5)); 7.13 (*dd*, J = 9 and $\approx$ 1, H–C(4)); 10.27 (*d*, $J \approx 1$, HO–C(6)). MS (*di.*): 290 (45, M^+), 275 (1), 259 (36), *258* (100), 243 (92), 229 (4), 228 (3), 215 (6), 201 (4), 196 (7), 185 (5), 164 (16), 137 (5), 127 (4), 109 (7), 108 (10), 93 (25), 79 (12), 65 (6), 63 (5).

11. Experiments with 5-Methoxy-1,4-naphthoquinone (5) [29]. – 11.1. *Dimethyl 4,8-Dimethoxy-1-naphthyl Phosphate* (**17**). Naphthol **48** [29] (21.5 mg, 0.105 mmol) was treated with dimethyl chlorophosphate [32] [33] (0.2 ml, 2 mmol) and diisopropylethylamine (0.09 ml, *ca.* 0.5 mmol) in CH_2Cl_2 for 20 h at r.t. (Ar). Chromatography (silica gel, CH_2Cl_2/AcOEt 1:1) gave 28 mg (85%) of **17**, m.p. 110–111°. IR ($CHCl_3$): 3030*w*, 2995*m*, 2955*m*, 2940*w*, 2910*w*, 2855*w*, 2835*w*, 1624*w*, 1600*s*, 1510*m*, 1462*m*, 1449*m*, 1409*s*, 1380*s*, 1369*m*, 1326*w*, 1268*s*, 1248*s*, 1147*w*, 1075–1035*s*, 1006*m*, 917*m*, 904*m*, 854*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.85 (*d*, J = 11, $(CH_3O)_2PO_2$–C(1)); 3.95 (*s*, CH_3O–C(4), CH_3O–C(8)); 6.69 (*d*, $J \approx 9$) and 6.90 (*d*, $J \approx 8$) (H–C(3), H–C(7)); 7.26 (*dd*, J = 8 and 3, H–C(2)); 7.39 (*t*, $J \approx 9$, H–C(6)); 7.85 (*d*, $J \approx 9$, H–C(5)). MS (*di.*): 312 (7, M^+), 297 (4), 203 (3), 186 (5), 185 (3), 171 (12), 158 (10), 145 (5), 143 (8), 139 (3), 130 (7), 127 (16), 115 (19), *109* (100), 102 (7), 93 (3), 91 (3), 89 (4), 79 (7). Anal. calc. for $C_{14}H_{17}O_6P$ (312.26): C 53.85, H 5.49, P 9.92; found: C 53.66, H 5.47, P 9.72.

11.2. *Treatment of* **5** *with* $P(OCH_3)_3$/*TMSCl*. Quinone **5** (195 mg, 1.036 mmol) in CH_2Cl_2 (15 ml) was treated with $P(OCH_3)_3$ (0.7 ml, *ca.* 6 mmol) and TMSCl (2.4 ml, *ca.* 19 mmol) for 14 days according to procedure *1.3*. Methylation of the residue, obtained by evaporative workup, with $(CH_3O)_2SO_2$ (0.7 ml, *ca.* 7.3 mmol) and K_2CO_3 (9.2 g) in acetone (20 ml) as above and chromatography (silica gel, CH_2Cl_2/AcOEt 1:1) gave 22 mg (6.5%) of **17**, 69 mg (21%) of **16** and 208 mg (200 mg (59%) after re-chromatography, silica gel, CH_2Cl_2/CH_3OH 97:3) of **15**.

Dimethyl 4,5-Dimethoxy-1-naphthyl Phosphate (**16**). IR ($CHCl_3$): 3030*w*, 2995*m*, 2910*w*, 2855*w*, 2835*w*, 1621*w*, 1599*m*, 1583*s*, 1510*w*, 1505*w*, 1461*m*, 1455*m*, 1447*m*, 1408*s*, 1383*s*, 1360*w*, 1328*w*, 1270*s*, 1165*w*, 1155*w*, 1110*m*, 1065–1030*s*, 983*s*, 942*s*, 912*w*, 853*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.87 (*d*, J = 11, $(CH_3O)_2PO_2$–C(1)); 3.94 and 3.97 (2*s*, CH_3O–C(4), CH_3O–C(5)); 6.75 (*d*, J = 8.5, H–C(3)); 6.91 (*d*, J = 8.5, *further split*, $W_{1/2} \approx 2$, H–C(6)); 7.38 (*dd*, J = 8.5 and 1.5, H–C(2)); 7.44 (*t*, J = 8.5, H–C(7)); 7.71 (*dd*, J = 8.5 and 1, H–C(8)). MS: 312 (46, M^+), 297 (3), 269 (2), 203 (7), 188 (4), 176 (13), 175 (12), 171 (34), 143 (10), 141 (10), 131 (8), 130 (7), 129 (9), 127 (10), 117 (10), 115 (27), 109 (57), 104 (10), 97 (15), 91 (60), 85 (12), 83 (18), 81 (18), 80 (35), 79 (22), 77 (15), 76 (10), 71 (20), 69 (29), 67 (16), 65 (14), 57 (38), 55 (41), 54 (22), 51 (12), *43* (100), 41 (61).

Dimethyl 1,4,8-Trimethoxy-2-naphthylphosphonate (**15**). IR ($CHCl_3$): 3080*w*, 3040*w*, 2990*m*, 2950*m*, 2940*m*, 2910*w*, 2850*w*, 2840*w*, 1613*m*, 1591*m*, 1569*s*, 1500*w*, 1455*m*, 1447*m*, 1425*w*, 1407*s*, 1346*s*, 1265*s*, 1106*m*, 1072*s*, 1030*s*, 976*m*, 885*w*, 863*m*, 830*m*, 812*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.86 (*d*, J = 11, $(CH_3O)_2PO$–C(2)); 3.91, 4.00, and 4.01 (3*s*, CH_3O–C(1), CH_3O–C(4), CH_3O–C(8)); 6.96 (*d*, J = 8, *further split*, $W_{1/2} \approx 2$, H–C(7)); 7.14 (*d*, J = 14, H–C(3)); 7.49 (*t*, $J \approx 8$, H–C(6)); 7.89 (*dd*, $J \approx 8$ and 1.5, H–C(5)). MS: 326 (11, M^+), 311 (4), 297 (5), 279 (4), 216 (4), 185 (5), 141 (4), 129 (3), 115 (5), 97 (6), 92 (25), 91 (47), 87 (11), 85 (66), *83* (100), 79 (6), 78 (10), 77 (6), 71 (10), 69 (11), 65 (8), 57 (19), 55 (14), 47 (24), 43 (24), 41 (22).

12. Synthesis of 2-Arylcyclohexanone 32. – 12.1. *2-Methoxy-5-(2'-oxocyclohexyl)-1,4-benzoquinone* (**2**). To a solution of 1-morpholinocyclohexene (**34**) (636 mg, 3.81 mmol) in dry CH_2Cl_2 (7 ml) a solution of quinone **4a** (477 mg, 3.46 mmol) in dry CH_2Cl_2 (*ca.* 10 ml) was added within 11 h at 0° (Ar). After stirring at r.t. for 6 h, the solvent was evaporated, and the dried (h.v.) residue *(2-hydroxy-3-methoxy-5a-morpholino-5a,6,7,8,9,9a-hexahydro-dibenzofurane* (**33**) was dissolved in 75% aq. CH_3OH (10 ml). Addition of $FeCl_3$ (1.34 g, 8.27 mmol) dissolved in H_2O (40 ml), followed by stirring at r.t. for 30 min (exclusion of light), workup with CH_2Cl_2, and chromatography (*Florisil*, CH_2Cl_2/AcOEt 9:1) gave 680 mg (84% based on **4a**, 76% based on **34**) of **2**, m.p. 115° (decomp.). IR ($CHCl_3$): 2940*m*, 2905*w*, 2865*w*, 2850*w*, 1711*s*, 1677*s*, 1655*s*, 1650*s*, 1608*s*, 1490*w*, 1460*m*, 1450*m*, 1367*m*, 1337*m*, 1313*m*, 1300*m*, 1282*w*, 1178*s*, 1122*m*, 1070*w*, 1022*w*, 999*m*, 960*w*, 937*w*, 895*m*, 860*m*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.5–2.3 (*m*, 6H); 2.3–2.6 (*m*, 2H–C(3')); 3.6–3.9 (*m*, H–C(1')); 3.78 (*s*, CH_3O–C(2)); 5.92 (*s*, H–C(3)); 6.44 (*d*, $J \approx 1$, H–C(6)). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 25.1 (C(5')); 27.6 (C(4')); 31.8 (C(6')); 42.2 (C(3')); 50.0 (C(1')); 56.3 (CH_3O–C(2)); 107.7 (C(3)); 131.4 (C(6)); 147.9 (C(5)); 158.5 (C(2)); 181.9 (C(4)); 186.3 (C(1)); 208.1 (C(2')). MS (*di.*): 236 (79), 234 (67, M^+), 208 (46), 206 (79), 191 (23), 179 (21), 178 (29), 177 (93), 165 (50), 163 (27), 153 (46), 147 (58), 135 (25), 123 (56), 91 (25), 79 (21), 77 (23), *69* (100).

12.2. *Dimethyl 2,4-Dimethoxy-5-(2'-oxocyclohexyl)phenyl Phosphate* (**3**). Quinone **2** (574 mg, 2.45 mmol) in dry CH_2Cl_2 (13 ml) was treated with $P(OCH_3)_3$ (0.65 ml, *ca.* 5.6 mmol) for 20 h according to procedure *1.2*. Chromatography (190 g of silica gel, CH_2Cl_2/AcOEt 1:1) of the residue (994 mg, dried at h.v.) afforded 682 mg (77%) of **3**, m.p. 94.5–96.5° (CH_2Cl_2/hexane). IR ($CHCl_3$): 3035*w*, 3005*s*, 2960*s*, 2945*s*, 2890*w*, 2860*m*, 2845*m*, 1710*s*, 1615*m*, 1600*w*, 1510*s*, 1463*s*, 1454*s*, 1439*s*, 1404*m*, 1325*s*, 1280*s*, 1178*s*, 1125*m*, 1050*s*, 970*s*, 945*s*, 932*s*, 888*w*, 856*s*, 835*w*, 815*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.5–2.4 (*m*, 6H); 2.35–2.6 (*m*, 2H–C(3')); 3.72, 3.77, 3.84, and 3.88 (2*s*, and *d*, $J \approx 12$, $(CH_3O)_2PO_2$–C(1), CH_3O–C(2), CH_3O–C(4)); *ca.* 3.75 (*m, hidden by the CH_3O-signals*, H–C(1')); 6.49 (*m*, $W_{1/2} \approx 2$, H–C(3)); 6.98 (*d*, $J \approx 1.5$, H–C(6)). MS (*di.*): 358 (83, M^+), *330* (100), 315 (5), 314 (4), 301 (7), 289 (4), 288 (8), 275 (24), 262 (4), 261 (4), 255 (3), 254 (3), 245 (5), 226 (5), 205 (14), 189 (9), 175 (53), 161 (7), 151 (3), 147 (6), 145 (7), 138 (7), 127 (13), 109 (18), 93 (3), 91 (5), 79 (4), 77 (4), 69 (3). Anal. calc. for $C_{16}H_{23}O_7P$ (358.32): C 53.63, H 6.47, P 8.64; found: C 53.68, H 6.48, P 8.60.

12.3. *2,4 Dimethoxy-5-(2'-oxocyclohexyl)phenyl Acetate* (**32**). To phosphate **3** (169 mg 0.472 mmol) TMSBr (0.4 ml, *ca.* 3 mmol) was added (Ar). After stirring at r.t. for 1 h, the volatile components were evaporated (aspirator), and a buffer solution, consisting of AcOH (2.6 g), NaOAc (0.6 g), dioxane (12 ml), and H_2O (*ca.* 8 ml, total volume 20 ml), was added to the residue. Heating to 100° under reflux for 47 h, workup with AcOEt, acetylation (1.2 ml of Ac_2O/pyridine, overnight, azeotropical removal of reagents (hexane)), and chromatography (15 g of silica gel, cyclohexane/CH_2Cl_2/AcOEt 2:2:1) yielded 110 mg (79%) of **32**, m.p. 103.5–105° (CH_2Cl_2/hexane). IR ($CHCl_3$): 3035*w*, 3005*m*, 2940*s*, 2890*w*, 2865*m*, 2840*m*, 1757*s*, 1710*s*, 1619*s*, 1597*w*, 1510*s*, 1462*s*, 1453*s*, 1438*s*, 1408*m*, 1370*s*, 1322*s*, 1300*m*, 1275*w*, 1186*s*, 1175*s*, 1122*s*, 1067*w*, 1037*s*, 965*w*, 940*w*, 915*s*, 883*w*, 856*w*, 818*w*. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.5–2.4 (*m*, 6H); 2.23 (*s*, CH_3CO_2–C(1)); 2.3–2.6 (*m*, 2H–C(3')); 3.73 and 3.78 (2*s*, CH_3O–C(2), CH_3O–C(4)); 3.6–3.9 (*m*, H–C(1')); 6.49 (*s*, H–C(3)); 6.74 (*s*, H–C(6)). MS (*di.*): 292 (17, M^+), *250* (100), 222 (66), 207 (5), 205 (5), 193 (9), 180 (6), 167 (11), 161 (20), 151 (3), 147 (4), 137 (7), 133 (6), 107 (2), 91 (5), 77 (3), 69 (5), 55 (2), 43 (9). Anal. calc. for $C_{16}H_{20}O_5$ (292.32): C 65.74, H 6.90; found: C 65.49, H 6.96.

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