3.97 (s, 0.35, CO_2CH_3), 3.61 (s, 0.50, $CHOCH_3$), 8.0–7.3 (m, 4, aromatic H) [lit. NMR ($CDCl_3$): 3-chlorophthalide, δ 7.07 (OCHCl);[1] 3-methoxy-1(3*H*)-isobenzofuranone, δ 6.3 ($OCHOCH_3$), 3.6 ($OCHOCH_3$); methyl 2-formylbenzoate, δ 10.4 (CH=O), 3.9 (CO_2CH_3)].[12] If the reaction was run in methanol as a solvent, only the alkylated product was obtained.

Registry No. **1a**, 6295-21-2; **1b**, 61296-43-3; **2a**, 108-95-2; **2b**, 150-76-5; **2c**, 100-02-7; **2d**, 51-28-5; **2e**, 120-80-9; **4a**, 61133-42-4; **4b**, 87116-18-5; **4c**, 53912-16-6; **4d**, 87116-19-6; **5a**, 18997-19-8; **5b**, 53064-79-2; **6b**, 19820-47-4; **6c**, 4195-17-9; **7a**, 82212-47-3; **7b**, 87116-20-9; **7c**, 87116-21-0; **7d**, 87116-22-1; **1D**, 87116-23-2; CH_3OH, 67-56-1.

o-Quinone Methide Intermediates and Their Role in Coordinated Reactions of Magnesium Phenoxides with α-Branched Aliphatic Aldehydes

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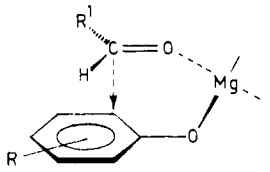
The reactions of (aryloxy)magnesium bromides with α-branched aliphatic aldehydes in apolar solvents have been investigated in order to obtain information on the role of *o*-quinone methide intermediates **8** or **9** in controlling the selectivity of the reactions of phenolic substrates and carbonyl compounds, which usually give a complex mixture of products. These reactions are characterized by high ortho regioselectivity, giving 2,2′-alkylidenebis(phenols) (**3**), 2-alkenylphenols (**4**), and 2,2-dialkyldihydrobenzofurans (**5**), according to the nature of the substituents on the aldehyde and the phenolic substrate. *o*-Quinone methides have been proved to be intermediates in these coordinated reactions by trapping experiments. The observed reaction pathways have been explained with the assumption that the steric bulkiness of the substituents leads the *o*-quinone methides to assume a geometry (**8** or **9**) that determines the subsequent reaction course.

The reactions between phenols and carbonyl compounds or their derivatives in the presence of catalysts usually give a very complex product mixture due to the occurrence of numerous competing pathways.

Recently it has been found that the use of magnesium phenolates in low-polarity media is an efficient control element for these reactions, since it leads to products of high ortho regioselectivity.[1-7] This is achieved through the formation of oriented substrate–reagent complexes (**6**), which have been isolated and studied[8] and which collapse to give ortho attack products.



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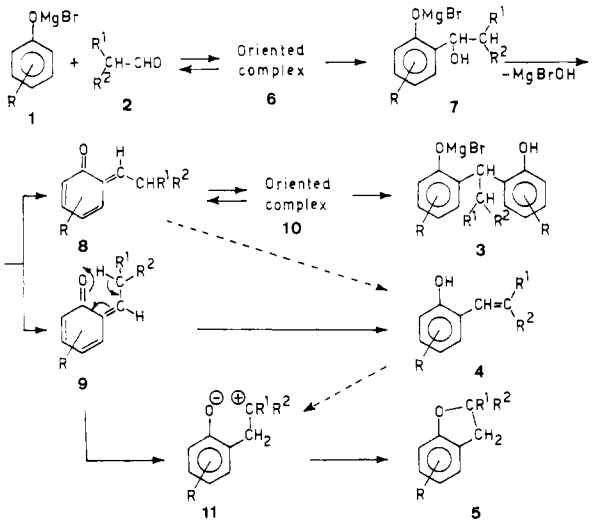
However, several competing processes leading to different products can occur, depending on the particular reagents or reaction conditions employed. Thus, 2,2′-alkylidenebis(phenols) are produced from linear aliphatic aldehydes or their acetals,[1] 2,2′-benzylidenebis(phenols) from aromatic aldehydes,[2] flavenes from certain magnesium phenoxides and cinnamaldehyde,[3] and 2-alkenylphenols from ketals;[4] in the presence of specific magnesium complexing agents, aromatic aldehydes give 2-hydroxybenzophenones,[5] cinnamaldehydes produce 2-hydroxycalchones,[6] and formaldehyde gives salicyl aldehydes[7] in good yields.

All of these competing reactions take place after the first ortho regioselective step has occurred to form salicyl al-

Scheme I



Scheme II

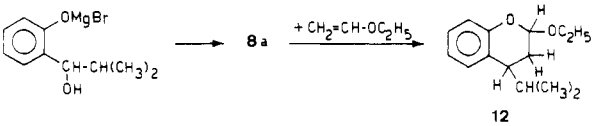


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Table I. Reactions of (Aryloxy)magnesium Bromides with α-Branched Aliphatic Aldehydes[a]

entry	phenol	aldehyde R¹	aldehyde R²	concn, M	recovered phenol, %	product yield,[b] % alkylidene-bis(phenol)	2-alkenyl-phenol	2,3-dihydro-benzofuran
1	C_6H_5OH	CH_3	CH_3	0.13	9	(3a) 70	(4a) 5	(5a) 7
2	4-$CH_3C_6H_4OH$	CH_3	CH_3	0.13	10	(3b) 75		
3	4-$CH_3C_6H_4OH$	C_2H_5	C_2H_5	0.05	38	(3c) 36	(4c) 14	
4	4-$CH_3C_6H_4OH$	C_2H_5	C_2H_5	0.13	11	(3c) 60	(4c) 8	
5	4-*t*-$C_4H_9C_6H_4OH$	CH_3	CH_3	0.05	17	(3d) 30	(4d) 30	(5d) 10
6	4-*t*-$C_4H_9C_6H_4OH$	CH_3	CH_3	0.13	16	(3d) 48	(4d) 17	(5d) 5
7	4-*t*-$C_4H_9C_6H_4OH$	CH_3	CH_3	0.50	12	(3d) 60	(4d) 6	(5d) 8
8	4-*t*-$C_4H_9C_6H_4OH$	C_2H_5	C_2H_5	0.05	35		(4e) 47	
9	4-*t*-$C_4H_9C_6H_4OH$	C_2H_5	C_2H_5	0.13	23	(3e) 27	(4e) 33	
10	4-*t*-$C_4H_9C_6H_4OH$	CH_3	*n*-C_3H_7	0.05	27	(3f) 19	(4f) 41	
11	4-*t*-$C_4H_9C_6H_4OH$	C_2H_5	*n*-C_4H_9	0.05	51	(3g) 2	(4g) 38	
12	2-*t*-$C_4H_9C_6H_4OH$	CH_3	CH_3	0.13	18	(3h) 60		
13	2,5-$(CH_3)_2C_6H_3OH$	CH_3	CH_3	0.13	69		(4i) 28	
14	2-*t*-C_4H_9-5$CH_3C_6H_3OH$	CH_3	CH_3	0.13	52		(4j) 37	
15	2-naphthol	CH_3	CH_3	0.13	19			(5k) 80

[a] In refluxing anhydrous benzene for 24 h. Phenol/aldehyde molar ratio = 1. [b] Calculated on the basis of phenol used. Where the data are not reported, if the product is present, the yield is less than 5%.

cohols (e.g., **7**) and, subsequently, *o*-quinone methides (**8**).

Results and Discussion

Reactions. To obtain further data on the key role of these intermediates,[9] especially in reactions involving ion pairs and their solvation complexes, we have studied the reactions between (aryloxy)magnesium bromides and various α-branched aliphatic aldehydes.

To provide a reference point, the reaction between phenoxymagnesium bromide and 2-methylpropanal was first carried out in refluxing benzene (Scheme I). The major product is 2,2′-(2-methylpropylidene)bis(phenol) (**3a**), the structure of which was established by ^1H NMR analysis (see Table II and ref 1 for signal assigments). Also formed in smaller amounts were 2-(2-methyl-1-propenyl)phenol (**4a**) and 2,3-dihydro-2,2-dimethylbenzofuran (**5a**), whose structure were established by comparison with authentic samples obtained from the corresponding salicyl alcohol **7a**.

That an *o*-quinone methide is a probable intermediate in this reaction was shown by trapping it with ethyl vinyl ether.[10,11] The product (**12** Scheme II) obtained in this fashion was identical (GC/MS) with an authentic sample prepared by the reaction of the monomagnesium salt of the alcohol **7a** with the same ether in refluxing benzene (see ahead for details).

The influence of substituents present in the aryl ring of the (aryloxy)magnesium bromide and at the α-carbon of the aliphatic aldehyde was tested by carrying out reactions between 4-methyl-, 2- and 4-*tert*-butyl-, 2,5-dimethyl-, and 2-*tert*-butyl-5-methylphenol with several α-branched aliphatic aldehydes. Also included was the reaction of (2-naphthyloxy)magnesium bromide and 2-methylpropanal. In most of these reactions the amount of phenol that reacted was quite high, and only in runs 11, 13, and 14 (see Table I) was there a significant amount of unreacted starting material. It is in these three cases that the most highly hindered starting materials were used.

Inspection of the product ratios shown in Table I reveals the following features: (a) 2,2′-alkylidenebis(phenols) (**3**) are generally the major product, (b) (4-*tert*-butylphenoxy)magnesium bromide gives more **4** than do the 2-*tert*-butyl and 4-methyl analogues, (c) higher dilution increases the **4**:**3** ratio, (d) alkyl substituents (R^1 and R^2) on the aldehyde have little effect when the aryl substituent is methyl and slightly increase the **4**:**3** ratio when it is *tert*-butyl, (e) the (2,5-dimethylphenoxy)- and (2-*tert*-butyl-5-methylphenoxy)magnesium bromides give **4** as the sole product, and (f) (2-naphthyloxy)magnesium bromide gives **5** as the sole product.

To test the possibility that 2-alkenylphenols (**4**) might be derived by the equilibration of 2,2′-alkylidenebis(phenols) (**3**) in the reaction medium,[12] we treated **3a** with 1–2 mol of EtMgBr in refluxing benzene and showed that it is stable under these conditions. Since it has been reported in the literature that 2,3-dihydrobenzofurans **5** are smoothly cleaved by Grignard reagents in benzene to yield 2-alkenylphenols **4** as the main products,[13] we have also tested the stability of product **5a** in the presence of (aryloxy)magnesium bromides. It was found that no reaction occurs when **5a** is treated in the presence of (aryloxy)magnesium bromides in refluxing benzene for 24 h.

To explain the present results as well as those obtained in earlier studies, we postulate that the 2,2′-alkylidenebis(phenols) **3** are produced via two consecutive ortho-regioselective reactions that occur within "oriented complexes", the first formed from phenol salts and aldehydes and the second formed from the *o*-quinone methide and the phenol salts. The decrease in the yield of **3** with increasing steric bulk of the substituents near the electrophilic center of the *o*-quinone methide **8** and the nucleophilic carbon of the magnesium phenolates is in agreement with the high sensitivity of this type of reaction to steric factors.[14]

In addition to the intermolecular pathway leading to **3**, the *o*-quinone methide also has intramolecular reaction pathways available to it, leading to products such as **4** and **5**.[14,15] The partitioning between the intermolecular and intramolecular pathways, as the data in Table I indicate, is governed both by structural features in the starting

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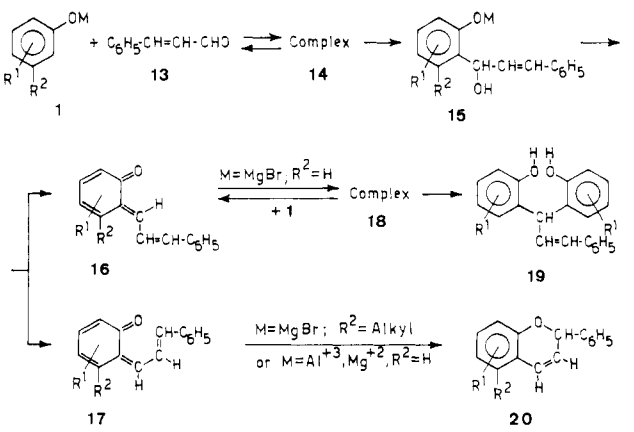
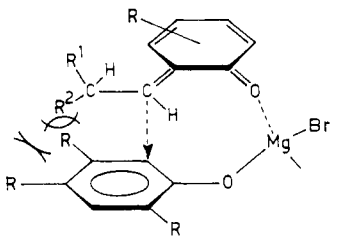
Scheme III



materials and by reaction conditions. Predictably, higher dilution favors the intramolecular pathway that leads to **4** and **5**. The transformation of the *o*-quinone methide to the corresponding 2-alkenylphenol is a keto enol tautomerization, which, if occurring intramolecularly, requires the system to be in a *Z* configuration, which allows the hydrogen on the α-carbon to be proximate to the carbonyl oxygen. It is postulated that steric interference between alkyl group R on the aryl ring and the alkyl groups (R^1 and R^2) on the side chain (from the aldehyde) will tend to favor the *Z* configuration.[15,16]

Thus, in all cases where an alkyl group is present in the 5-position of the starting phenol or when R = *p*-*tert*-butyl and R^1 and R^2 are Et, the only product formed is 2-alkenylphenol (**4**), the result of steric interference hindering the intermolecular reaction to form **3** (as illustrated in **10**) and favoring the intramolecular reaction, via the *Z* configuration, to form **4**.



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Similar behavior was observed previously in the reaction between magnesium salts of 2,5-dialkylphenols or β-naphthol and cinnamaldehyde, which yielded flavenes (**20**) instead of cinnamilidenebis(phenols) (**19**, Scheme III), which are the usual reaction products with phenols.[3] In these cases (R^2 = H) the complex **18**, which leads to cinnamilidenebis(phenols) (**19**), is destabilized for steric reason and, moreover, a *Z* configuration for the *o*-quinone methide intermediate **17** must be preferred.

Both factors should favor the intramolecular formation of flavenes **20**[17] over products **19** as observed. The fact that good yields of flavenes (**20**) are obtained also in the case of phenols with unsubstituted 5-position when Al^{3+} and Mg^{2+} salts are used[18] seems to be in agreement with this explanation. In this case, in fact, the reactivity of both

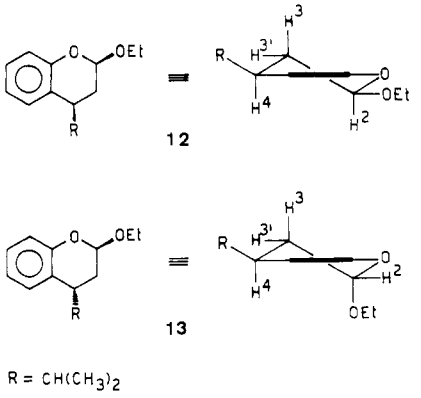

Figure 1.

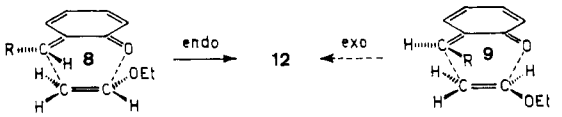

Figure 2.

species in the complex **18** is decreased and the reaction pathway that leads to **20** becomes competitive.

In the reaction conditions employed, generally 2,2′-dialkyldihydrobenzofurans (**5**) are produced from 2-alkenylphenols (**4**). However, with β-naphthol we have no evidence for the formation of the latter compound. In this case, due to the increased stability of the *o*-quinone methide, the [1,5]-H shift to 2-alkenyl-β-naphthol (**4**) seems to be less favored than the [1,2]-H shift, which gives 2,3-dihydrobenzofuran (**5**).

Interestingly, similar results were observed in photochemical studies by Gutsche et al.[14] who obtained in good yields 2,3-dihydrobenzofurans only with substrates that could generate phenyl-stabilized *o*-quinone methides.

Trapping of *o*-Quinone Methides Generated from Alcohols 7. With the aim of supporting our working hypothesis, the stereochemistry of the product obtained by trapping with ethyl vinyl ether the *o*-methide generated from the alcohol **7a** was studied.

Owing to the lack of data on cycloadditions of *o*-quinone methides substituted on the methylene position, the structure of product **12** was studied by 200-MHz ^{1}H NMR, using decoupling experiments for signals assignments (Figure 1). The H-2 resonance was a doublet of doublets with J_{23} = 8.5 Hz and $J_{23'}$ = 2.5 Hz, showing that the OEt group is in an equatorial position, as indicated by the axial–axial coupling constant. The H-4 resonance was a complex signal with J_{34} = 11.2 Hz and $J_{3'4}$ = 6.5 Hz, with a pseudoaxial–axial coupling constant that shows the pseudoequatorial position of isopropyl group. From these data, **12** was verified to be the cis product.[19]

In the cases reported in literature[20] of 2-alkoxy-2,3-dihydrobenzofurans bearing no substituent in the 4-position, the 2-alkoxy group occupies the axial position mainly because of the anomeric effect. In our case, the presence of a bulky group in position 4 of the dihydropyran ring overcomes the anomeric effect and the conformational preference of the system brings the 4-alkyl and 2-ethoxy groups respectively into pseudoequatorial and equatorial position.[19]

From gas chromatographic and NMR data (which show the H-2 at δ 5.28 J_{23} = $J_{23'}$ = 3.1 Hz), the more stable trans

(16) Analogous results have been reported with *o*-quinone dimethanes. See, e.g.: T. Kametani, M. Tsubuki, Y. Kato, H. Nemoto, M. Ihara, and K. Fukomoto, *J. Org. Chem.*, **42**, 2672 (1977).

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(18) G. Sartori, G. Casiraghi, L. Bolzoni, and G. Casnati, *J. Org. Chem.*, **44**, 803 (1979).

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(20) See, e.g., J. Brugidou and H. Christol, *Bull. Soc. Chim. Fr.*, 1974 (1966).

product **13** was verified to be present in the reaction mixture only in 10% compared with **12**.

Assuming a concerted mechanism[21] for the trapping reaction, compound **12** can derive either from an exo attack on the *o*-quinone methide having a *Z* configuration or from an endo attack on the *E* isomer (Figure 2). The second hypothesis seems to be more probable since in analogous concerted reactions of ethyl vinyl ethers with α,β-unsaturated carbonyl compounds, a marked preference for endo attack has been observed.[22]

For support of the previous hypothesis that the *o*-quinone methide derived from 2,5-dimethylphenol reacts in the *Z* configuration (**9**), a trapping experiment with ethyl vinyl ether was performed on the monomagnesium salt of the alcohol **7i** obtained from this phenol. However, the only product observed in this reaction was the 2-alkenylphenol **4i**.

This result agrees with the reported very low reactivity or (*Z*)-α,β-unsaturated ketones with vinyl ethers[23] and with the observed easy elimination process of (*Z*)-*o*-quinone dimethanes.[16]

Conclusions

The results obtained in this study allow us to reach some general conclusion concerning the factors that control the reaction pathways within the complexes formed from magnesium phenoxides and carbonyl compounds. After the first ortho-regiospecific process, which readily occurs through the "oriented complex" **6**, the reaction course is determined by whether or not a second complex (**10**) can form between the *o*-quinone methide **8** and (aryloxy)-magnesium bromide (**1**). The results show that this complex is destabilized when substituents are present in the 5-position of the phenolic nucleus or bulky groups are present on the aldehyde α-carbon or in the para position of the phenol. These factors seem also to favor a *Z* configuration of the *o*-quinone methides **9** which concurs to orient the processes toward the formation of alkenylphenols (**4**), dihydrobenzofurans (**5**), and flavenes (**20**) instead of 2,2′-alkylidenebis(phenols) (**3** and **19**).

Experimental Section

For general directions and analytical instrumentation, see ref 1. All phenols were reagent grade and were used without further purification. Aldehydes were distilled before use and stored under nitrogen. All the reactions were performed under nitrogen.

Reaction of (Aryloxy)magnesium Bromides (1) with 2-Alkylalkanals (2): General Procedure. The diethyl ether solutions of (aryloxy)magnesium bromides were prepared by reaction of equimolar amounts of EtMgBr and the corresponding phenol. After evaporation of the solvent under vacuum, benzene was added (similar results were also obtained in toluene). Then an equimolar amount of aldehyde was added, and the reaction was performed as previously described.[1] GLC analyses were performed on 5% DEGS for phenols, 2-alkenylphenols, and 2,2-dialkyl-2,3-dihydrobenzofurans, 3% SE-30 for 2,2′-alkylidenebis(phenols), and 20% Carbowax 1000 and 20 M for aldehydes. The products were isolated by preparative TLC (hexane/ethyl acetate, 95:5) and were oily or glassy materials with the exceptions of **3a** (mp 112–113 °C), **3b** (mp 149–150 °C), **3c** (mp 135–136 °C), **3h** (mp 113–114 °C), and **5k** (mp 42–43 °C). All products gave

Table II. ^{1}H NMR Spectral Data of Compounds 3–5[a]

compd	ArH[b]	ArCH[c] and ArR	CHR^{1}R^2 or CR^{1}R^2[d]
3a	7.7–6.9 (m, 8 H)	4.20 (d, 1 H)	2.80 (m, 1 H), 0.94 (d, 6 H)
3b	7.05 (bs, 2 H), 6.5–7.0 (m, 4 H)	3.98 (d, 1 H), 2.22 (s, 6 H)	2.4–3.0 (m, 1 H), 0.92 (d, 6 H)
3c	7.20 (bs, 2 H), 6.92 (bd, 2 H), 6.76 (d, 2 H)	4.36 (d, 1 H), 2.27 (s, 6 H)	1.0–2.8 (m, 5 H), 0.88 (t, 6 H)
3d	7.33 (d, 2 H-3), 7.13 (dd, 2 H-5), 6.83 (d, 2 H-6)	4.15 (d, 1 H), 1.26 (s, 18 H)	2.4–3.1 (m, 1 H), 0.95 (d, 6 H)
3e	7.38 (d, 2 H-3), 7.19 (dd, 2 H-5), 6.91 (d, 2 H-6)	4.32 (d, 1 H), 1.27 (s, 18 H)	1.02–2.85 (m, 5 H), 0.93 (t, 6 H)
3f	7.27 (bs, 2 H-3), 6.95 (bd, 2 H-5), 6.65 (d, 2 H-6)	4.14 (d, 1 H), 1.25 (s, 18 H)	0.6–2.8 (m, 11 H)
3g	7.27 (d, 2 H-3), 6.93 (dd, 2 H-5), 6.62 (d, 2 H-6)	4.29 (d, 1 H), 1.27 (s, 18 H)	0.6–2.8 (m, 15 H)
3h	7.4–6.5 (m, 6 H)	4.06 (d, 1 H), 1.36 (s, 18 H)	2.2–2.9 (m, 1 H), 0.98 (d, 6 H)
4a	6.7–7.3 (m, 4 H)	6.10 (bs, 1 H)	1.92 (s, 3 H), 1.67 (s, 3 H)
4c	6.6–7.2 (m, 3 H)	6.12 (bs, 1 H), 2.25 (s, 3 H)	1.5–2.5 (m, 4 H), 1.14 (t, 3 H), 0.96 (t, 3 H)
4d	7.25 (bd, 1 H-5), 7.15 (bs, 1 H-3), 6.88 (d, 1 H-6)	6.25 (bs, 1 H), 1.28 (s, 9 H)	2.00 (bs, 3 H), 1.72 (bs, 3 H)
4e	7.18 (bd, 1 H-5), 7.09 (bs, 1 H-3), 6.82 (d, 1 H-6)	6.11 (bs, 1 H), 1.32 (s, 9 H)	1.5–2.6 (m, 4 H), 1.15 (t, 3 H), 0.98 (t, 3 H)
4f	7.24 (bd, 1 H-5), 7.14 (bs, 1 H-3), 6.88 (d, 1 H-6)	6.22 (bs, 1 H), 1.30 (s, 9 H)	0.7–2.5 (m, 10 H)
4g	7.08 (bd, 1 H-5), 6.97 (bs, 1 H-3), 6.73 (d, 1 H-6)	6.02 (bs, 1 H), 1.28 (s, 9 H)	1.8–2.5 (m, 4 H), 0.6–1.7 (m, 10 H)
4i	6.97 (d, 1 H-5), 6.68 (d, 1 H-4)	5.98 (bs, 1 H), 2.22 (s, 3 H), 2.12 (s, 3 H)	1.96 (bs, 3 H), 1.55 (bs, 3 H)
4j	7.03 (d, 1 H-5), 6.63 (d, 1 H-4)	5.92 (bs, 1 H), 2.09 (s, 3 H), 1.36 (s, 9 H)	1.96 (bs, 3 H), 1.54 (bs, 3 H)
5a	6.5–7.2 (m, 4 H)	2.96 (s, 2 H)	1.43 (s, 6 H)
5d	7.13 (bs, 1 H-3), 7.06 (bd, 1 H-5), 6.47 (d, 1 H-6)	2.95 (s, 2 H), 1.27 (s, 9 H)	1.45 (s, 6 H)
5k	6.9–7.9 (m, 6 H)	3.22 (s, 2 H)	1.52 (s, 6 H)

[a] δ ($CDCl_3$) from Me_4Si. [b] δ_{OH} between 6.9 and 8.0 for compounds **3a–h** and 5.0 and 5.4 for compounds **4a–j**. [c] For compounds **3b–g**, J_o = 9 Hz; J_m = 2 Hz. For compounds **4d–j** and **5d**, J_o = 8 Hz. [d] For compounds **3a–h**, J = 11 Hz. For compounds **3a,b,d,h**, J = 6 Hz; for compounds **3c,e**, J = 7 Hz; for compound **4e**, J = 7.5 Hz.

(21) Preliminary results obtained in our laboratory on the stereochemistry of cycloaddition reactions of methylene-substituted *o*-quinone methides with *E* and *Z* isomers of ethyl propenyl ether seem to support this hypothesis.

(22) G. Desimoni, A. Gamba, M. Monticelli, M. Nicola, and G. Tacconi, *J. Am. Chem. Soc.*, **98**, 2947 (1976).

(23) G. Desimoni, G. Colombo, P. P. Righetti, and G. Tacconi, *Tetrahedron*, **29**, 2635 (1973).

satisfactory elemental analyses, and their ^1H NMR spectra are reported in Table II.

If the isolation of 2,2'-alkylidenebis(phenols) (3) was of interest, the crude reaction mixture was submitted to steam distillation, which gave almost pure 3.

Compounds 4f and 4g consisted of mixtures of *E* and *Z* isomers, as shown by analysis on a 5% DEGS GLC column.

Trapping of *o*-Quinone Methide Intermediate 8a. Phenoxymagnesium bromide (2 mmol) was reacted in refluxing benzene (15 mL) with 2-methylpropanal (2 mmol) in the presence of ethyl vinyl ether (2 mmol) for 24 h. After the usual workup, a GS/MS analysis of the reaction mixture showed the presence of a new compound [mass spectrum, *m/e* (relative intensity) 220 (M^+, 19), 177 (100), 149 (30), 133 (29), 121 (10)] identical with the product 12 obtained from the magnesium salt of 7a and ethyl vinyl ether.

Reaction of Magnesium Salt of 7a with Ethyl Vinyl Ether. The alcohol 7a was prepared from 2-hydroxybenzaldehyde and a fourfold molar excess of *i*-PrMgBr. The product was recrystallized from petroleum ether: mp 48–49 °C; mass spectrum, *m/e* (relative intensity) 166 (M^+, 16), 148 (11), 133 (40), 123 (100); ^1H NMR ($CDCl_3$) δ 0.85 and 0.95 (2 d, 6 H), 2.05 (m, 1 H), 3.23 (bs, OH), 4.42 (d, 1 H), 7.0 (m, 4 H), 8.2 (bs, OH). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.45; H, 8.58. 7a was reacted in diethyl ether with an equimolar amount of EtMgBr. After removal of the solvent under vacuum and its replacement by benzene, an equimolar amount of ethyl vinyl ether was added, and the mixture was refluxed for 24 h. GLC analysis (OV 101 column) showed the formation of 4a (45%) and 12 (25%). Product 12 was isolated by preparative TLC (hexane/ethyl acetate, 99:1) as an oil: ^1H NMR (200 MHz, $CDCl_3$) δ 0.70 and 1.04 (2 d, 6 H, $CH^c(CH_3)_2$, J = 7.2 Hz), 1.27 (t, 3 H, $OCH_2{}^{ab}CH_3$, J = 7.2 Hz), 1.78 (m, 1 H, H-3, $J_{33'}$ = 13 Hz, J_{23} = 8.5 Hz, J_{34} = 11.2 Hz), 2.01 (m, 1 H, H-3', $J_{23'}$ = 2.5 Hz, $J_{3'4}$ = 6.5 Hz), 2.43 (m, 1 H, H^c, J_{4c} = 4.6 Hz), 2.94 (m, 1 H, H-4), 3.61 and 4.08 (2 m, 2 H, H^a and H^b, J_{ab} = 11.0 Hz), 5.04 (dd, 1 H, H-2), 6.08 and 7.10 (2 m, 4 H, ArH). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.51; H, 9.06.

Stability of Magnesium Salt of 2,2'-(2-Methylpropylidene)bis(phenol) (3a). Two experiments were performed: the first with the mono and the second one with the bis magnesium salts of 2,2'-(2-methylpropylidene)bis(phenol) (0.13 M), which were obtained as usual through the reaction with EtMgBr. These salts gave only starting material after 24 h of reflux in benzene.

Stability of 2,3-Dihydro-2,2-dimethylbenzofuran (5a) in the Presence of (Aryloxy)magnesium Bromides. This product was allowed to react in benzene (0.13 M) at reflux in the presence of phenoxymagnesium bromide (1:1 molar ratio) and of the more soluble (2,4,6-trimethylphenoxy)magnesium bromide. After 24 h 5a was recovered unchanged.

Reaction of Magnesium Salt of 7i with Ethyl Vinyl Ether. The alcohol 7i was prepared from 3,6-dimethyl-2-hydroxybenzaldehyde and a fourfold molar excess of *i*-PrMgBr. The product was recrystallized from petroleum ether: mp 130–131 °C; mass spectrum, *m/e* (relative intensity) 194 (M^+, 19), 176 (21), 161 (54), 151 (100); ^1H NMR ($CDCl_3$) δ 0.75 and 1.10 (2 d, 6 H), 1.95 (m, 1 H), 2.21 (s, 6 H), 2.5 (bs, OH), 4.72 (d, 1 H), 6.49 (d, 1 H), 6.93 (d, 1 H), 8.5 (bs, OH). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.05; H, 9.18. 7i was reacted in diethyl ether with an equimolar amount of EtMgBr. After removal of the solvent under vacuum and its replacement by benzene, an equimolar amount of ethyl vinyl ether was added and the mixture was refluxed for 24 h. GLC analysis (OV 101 column) showed the formation of 4i as the only reaction product.

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Registry No. 1 (R = H), 35770-74-2; 1 (R = 4-CH_3), 36359-92-9; 1 (R = 4-*t*-C_4H_9), 36359-99-6; 1 (R = 2-*t*-C_4H_9), 36359-98-5; 1 (R = 2,5-$(CH_3)_2$), 53863-59-5; 1 (R = 2-*t*-C_4H_9, 5-CH_3), 53863-60-8; 2 ($R^1 = R^2 = CH_3$), 78-84-2; 2 ($R^1 = R^2 = C_2H_5$), 97-96-1; 2 ($R^1 = CH_3$; $R^2 = n$-C_3H_7), 123-15-9; 2 ($R^1 = C_2H_5$; $R^2 = n$-C_4H_9), 123-05-7; 3a, 86847-31-6; 3b, 86847-32-7; 3c, 86847-33-8; 3d, 86847-34-9; 3e, 86862-64-8; 3f, 86847-35-0; 3g, 86847-36-1; 3h, 86847-37-2; 4a, 6395-29-5; 4c, 86847-38-3; 4d, 86847-39-4; 4e, 86847-40-7; (*E*)-4f, 86847-41-8; (*Z*)-4f, 86847-42-9; (*E*)-4g, 86847-43-0; (*Z*)-4g, 86847-44-1; 4i, 86847-45-2; 4j, 86847-46-3; 5a, 6337-33-3; 5d, 86847-47-4; 5k, 86853-50-1; 7a, 86847-48-5; 7a diol, 78131-81-4; 7i, 86847-49-6; 7i diol, 86847-50-9; 12, 86847-51-0; EtMgBr, 925-90-6; *i*-PrBr, 75-26-3; phenol, 108-95-2; 4-methylphenol, 106-44-5; 4-*tert*-butylphenol, 98-54-4; 2-*tert*-butylphenol, 88-18-6; 2,5-dimethylphenol, 95-87-4; 2-*tert*-butyl-5-methylphenol, 88-60-8; 2-naphthol, 1321-67-1; (2-naphthyloxy)magnesium bromide, 36381-65-4; ethyl vinyl ether, 109-92-2; 2-hydroxybenzaldehyde, 90-02-8; 3,6-dimethyl-2-hydroxybenzaldehyde, 1666-04-2.

Transition from Concerted to Stepwise [2 + 4] Cycloaddition Reactions of α,β-Unsaturated Carboxylic Esters

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The stereospecificity of the [2 + 4] cycloaddition reaction of electrophilic α,β-unsaturated esters with *cis*- and *trans*-propenyl ethers and with *trans*-anethole, leading to 3,4-dihydro-2*H*-pyran derivatives, is studied. Reactions with trisubstituted electrophilic olefins are stereospecific and are considered to be concerted, except with methyl 4,4,4-trichloro-2-cyanocrotonate where accompanying cyclobutane formation indicates some stepwise behavior. With tetrasubstituted electrophilic olefins, the reaction products are not stereospecific, and simultaneous cyclobutane formation also indicates stepwise behavior. The reactivity of these olefins is determined by their electronegativity, but the transition from a concerted to a stepwise mechanism appears to be governed by steric hindrance.

The Diels–Alder 1,4-cycloaddition reaction of α,β-unsaturated carbonyl compounds provides an attractive route to 3,4-dihydro-2*H*-pyrans and has been reviewed by Desimoni and Tacconi.[1] The carbonyl compounds include α,β-unsaturated ketones, aldehydes, *N*-acyl imines, etc. More recent reports of similar reactions include the reaction of a vinyl ether with 2-methoxymethylene 1,3-dicarbonyl compounds,[2] cyclic 2-alkylidene 1,3-dicarbonyl compounds,[3] 2-acetyl-2-cyclohexenone,[4] α,β-unsaturated

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