Stereoselectivity in the Diels–Alder Reaction of Phenyl- and Oxy-Substituted *o*-Quinodimethanes

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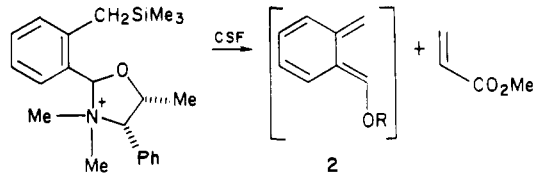
Phenyl-, methoxy-, and acetoxy-substituted *o*-quinodimethanes (*o*-QDM) have been added to dimethyl fumarate and maleate to determine the stereoselectivity of the addition reaction. The *o*-QDM's were generated from the corresponding 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxides, which in turn were prepared via a photochemical reaction of the appropriately substituted *o*-methylbenzaldehyde with SO_2 or from 1,4-dihydro-2,3-benzoxathiin 3-oxides. α-Methoxy-*o*-QDM reacts with fumarate and maleate via an endo transition state giving predominantly *cis*-1-methoxy-2-carbomethoxytetralin. In contrast, α-phenyl-*o*-QDM reacts via an exo transition state giving *trans*-1-phenyl-2-carbomethoxytetralins. Exo addition is also found for (*E*,*E*)-α-phenyl-α′-methoxy-*o*-QDM, thus indicating that the directive effect (endo vs. exo) of a phenyl group dominates over that of a methoxy group.

The stereo- and regioselectivity of the addition of dienophiles to α-substituted *o*-quinodimethanes (*o*-QDM's) is of synthetic interest and has been studied by many groups.[1–6] It has often been deduced that (*E*)-α-hydroxy- and -α-alkoxy-*o*-QDMs of the type **2** react with dienophiles both regio- and stereoselectively via an endo transition state to give the cis-1,2-disubstituted tetralins. An example of the conversion of **1** to **3** has been recently provided by Ito and co-workers.[1]



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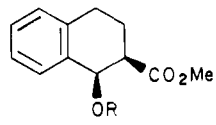

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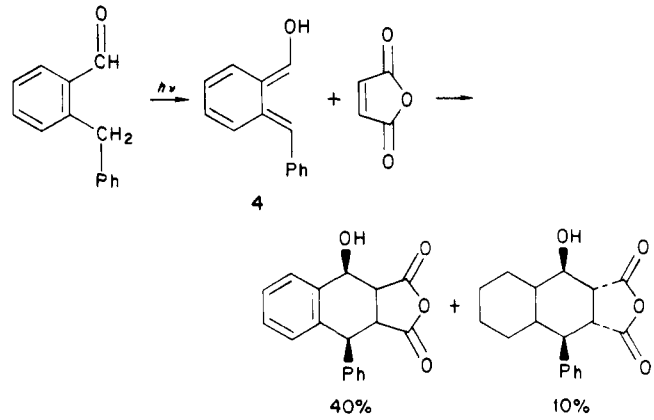
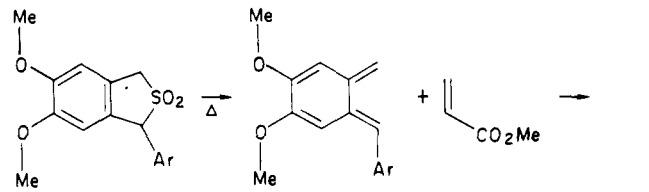
While there is some doubt as to whether alkoxy- and hydroxy-*o*-QDM's of type **2** exist in both *E* and *Z* configurations, it has been concluded by Sammes that only the *E* configuration is involved in Diels–Alder reactions.[3] Pfau and co-workers[2] have studied α-hydroxy-*o*-QDM's prepared photochemically and reached the conclusion that the specificity for endo addition was due to hydrogen bonding between the α-hydroxyl and the substituent group of the dienophile.[2] Inspection of models indicates that the differences in hydrogen bonding for endo vs. exo addition is not remarkable, and in any event it would not explain the tendency for endo addition for alkoxy-*o*-QDM's.[1,6] While hydrogen bonding may play a role in determining the steric course of the additions, it seems more likely that secondary orbital interactions[7,8] and steric repulsions play a more important role. In the presence of phenyl group the preference for endo addition seems less pronounced. Sammes and co-workers found that addition of maleic anhydride to (*E*,*E*)-α-hydroxy-α′-phenyl-*o*-QDM (**4**) gave a 4:1 mixture of endo and exo attack.[9]

Mann and Piper[10] have shown that the α-phenyl sulfone **5** generates an *o*-QDM that adds via an exo transition state to methyl acrylate although they concluded that the



product stereochemistry was a result of thermodynamic control due to reversible addition. With dimethyl maleate



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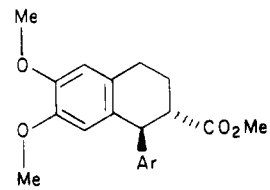

they claimed that the addition was exclusively endo. In this paper we describe our results with α-phenyl-*o*-QDM (**6**), which we find adds both maleate and crotonate in the

† Visiting Professor, 1983–1984: Department of Chemistry, University of Manitoba, Winnipeg, Canada R3T 2N2.

(1) Ito, Y.; Amino, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1983**, *105*, 1586.
(2) Pfau, M.; Combrisson, S.; Rowe, J. E., Jr.; Heindel, N. D. *Tetrahedron* **1978**, *34*, 3459. Pfau, M.; Rowe, J. E., Jr.; Heindel, N. D. *Tetrahedron* **1978**, *34*, 3469.
(3) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405.
(4) Oppolzer, W. *Synthesis* **1978**, 793.
(5) Kametani, T.; Fukomoto, K. *Acc. Chem. Res.* **1976**, *9*, 319.
(6) Franck, R. W.; John, T. V.; Olejniczak, K. *J. Am. Chem. Soc.* **1982**, *104*, 1106.
(7) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.
(8) Ginsberg, D. *Tetrahedron* **1983**, *39*, 2995.
(9) Arnold, B. J.; Mellows, S. M.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 401.
(10) Mann, J.; Piper, S. E. *J. Chem. Soc., Chem. Commun.* **1982**, 430.

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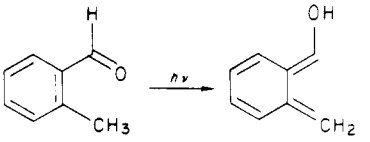
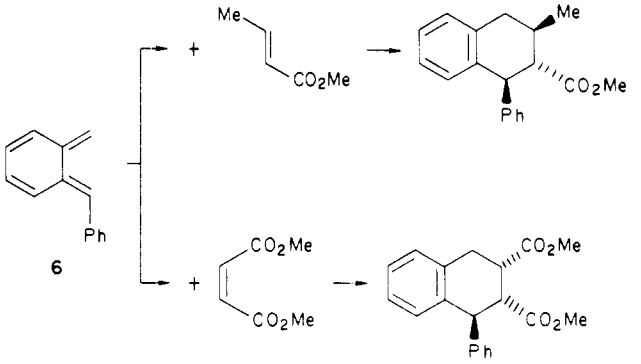
Scheme I

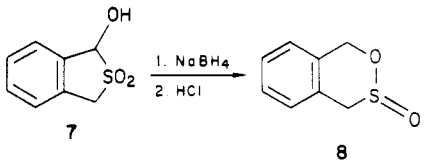


exo manner in contrast to the earlier results of Mann and Piper.[10]



A preliminary report of this part of the work has already been submitted.[11] On the basis of the finding of exo addition of maleate to **6a** we have also investigated the stereoselectivity of addition of dimethyl maleate and fumarate with (*E*,*E*)-α-methoxy-α′-phenyl- and (*E*,*E*)-α-acetoxy-α′-phenyl-*o*-QDM's to determine whether the endo directive effect of the oxy group will outweigh the exo directive effect of the phenyl.

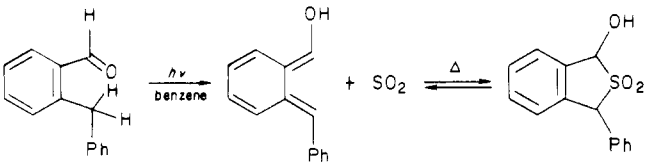
Our current work on *o*-QDM's has been made possible by the discovery of a photochemical route to the *o*-QDM precursors 1-hydroxy-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**7**) and its reduction product 1,4-dihydro-2,3-benzoxathiin 3-oxide (**8**) and their derivatives.[11,12]



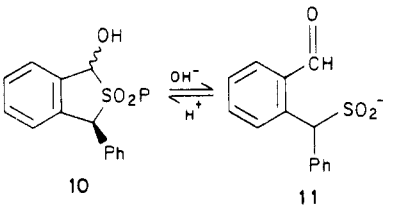
o-QDM Precursors

Although many *o*-QDM precursors are known[1,4,13] they all suffer from the problem that they are difficult to prepare, especially with a variety of substituents. One of the simplest methods for preparing *o*-QDM's involves the photolysis of *o*-methylbenzaldehyde or its derivatives to promote intramolecular H-atom abstraction (Scheme I).[3] While the starting materials are readily available and the reaction is simple, there are problems if the dienophile, added to react with the intermediate α-hydroxy-*o*-QDM, absorbs in the same region of the spectrum as the aldehyde. Further complications arise if the dienophile is photoreactive, such as in the case of the photoisomerization of maleate to fumarate. This latter example is particularly troublesome since fumarate is much more reactive than maleate in Diels–Alder reactions.[14] Due to these limitations we attempted to trap the photoenol with SO_2 (Scheme I) in the hope of using the resulting sulfone or its derivatives to regenerate the *o*-QDM thermally. This methodology proved to be quite effective[12] as illustrated for *o*-benzylbenzaldehyde (**9**) (Scheme II).

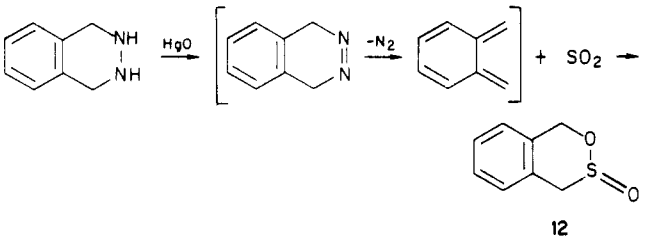
Scheme II



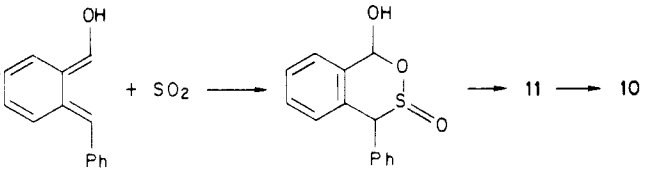
Scheme III



Scheme IV



Scheme V

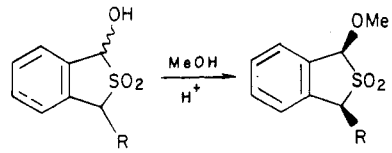


Irradiation of **9** was carried out in benzene containing 10% SO_2 (20 °C) using a Hanovia 450-W medium-pressure lamp and a 1-mm Pyrex filter. When the starting material was consumed, the benzene was evaporated and the sulfone extracted from a methylene chloride solution into 5% aqueous bicarbonate. This extraction is made possible by the fact that the sulfone **10** readily opens in base to the aldehyde–sulfinic acid salt **11** (Scheme III). Reacidification and extraction of the bicarbonate solution gives 40–67% of the hydroxy sulfone **10** as a 1:1 mixture of diastereomers as determined by nuclear magnetic resonance (NMR).

Although the trapping of the *o*-QDM by SO_2 yields the hydroxy sulfone, this may not be a single-step reaction. Durst and Tetreault-Ryan previously showed that trapping of SO_2 by unsubstituted *o*-QDM at ambient temperature yields the cyclic sulfinate ester (sultine) **12** rather than the sulfone (Scheme IV).[15] On the basis of this example, the second step of Scheme III may be better represented by that shown in Scheme V although there is no direct evidence for the intermediate sultine.

The product **10** was converted to the methoxy derivative **13** by refluxing in methylene chloride solution of **10** with an equivalent of CH_3OH in the presence of a catalytic amount of *p*-toluenesulfonic acid.[12] Other alkoxy derivatives of **1** may be prepared in a similar manner. The NMR spectrum of **13** indicates that it is a single isomer which was later assigned the cis configuration on the basis of its cycloaddition reaction with dimethyl fumarate (see

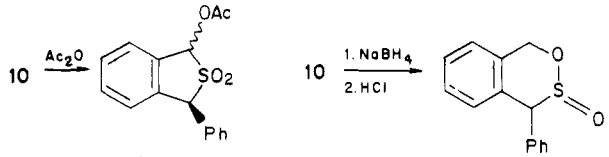
(11) Charlton, J. L.; Durst, T. *Tetrahedron Lett.* **1984**, *25*, 5287.
(12) Charlton, J. L.; Durst, T. *Tetrahedron Lett.* **1984**, *25*, 2663.
(13) Funk, R. L.; Volhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41.
(14) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16.
(15) Durst, T.; Tetreault-Ryan, L. *Tetrahedron Lett.* **1978**, 3253.



7, R = H
10, R = Ph

14, R = H, 46%
13, R = Ph, 92%

below). The methoxy sulfone **14** was prepared by a procedure identical with that used for the preparation of **13**. The acetoxy derivative **15** (cis) and **16** (trans) were prepared by warming the hydroxy sulfone **10** in acetic anhydride and then evaporating the solvent. Unlike the methoxy derivative **13** cis and trans acetates were formed in roughly equal amounts. Their stereochemistry was also determined on the basis of the reaction of the cis acetate **15** with dimethyl fumarate (see below). The sulfone **10**



15, cis
16, trans

17

was converted to the sultine **17** according to our previously reported procedure.[11] The details of this procedure and alternate routes to this and similar sultines will be submitted shortly.[16]

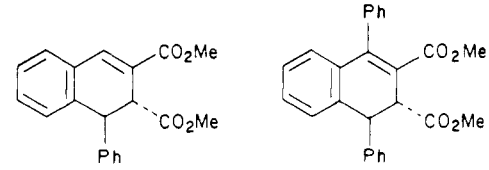
Cycloadditions

The methoxy and acetoxy sulfones **13–16** were all thermalized in the presence of excess dimethyl fumarate and dimethyl maleate as was the sultine **17**. In addition, **17** was thermalized with methyl crotonate. The reaction conditions are summarized in Table I.

Substituent effects on the thermolysis temperatures of the sulfones are notable. While the 1-phenyl sulfone **5** required 200 °C,[10] the 1-methoxy sulfone **14** required only 150 °C and the 1-methoxy-3-phenyl sulfone **13** only 80 °C. The 1-phenyl sultine **17** thermalizes at 80 °C and provides a much milder route to the *o*-QDM than could be achieved by using a corresponding sulfone (cf. **5**). The structures of the adducts **18–27** were deduced from 300-MHz proton NMR spectra (Table II) and/or by conversion to simpler compounds. Configurations and solution conformations were assigned on the assumption that pseudo trans diaxial coupling constants would fall in the range 7–12 Hz and that gauche coupling constants would be 2–5 Hz. The configurations of the adducts are given in Table I and the predominant solution conformations can be found in Table III.

The configuration and conformation of all compounds except for **18** were assignable from the NMR spectra. The configuration for **18** was assumed on the basis of analogy with examples in the literature (see above) and from the fact that dimethyl fumarate also yields the 1,2-cis configuration. In all adducts in which the benzylic phenyl group is equatorial (**22–27**) there is a strong shielding effect on H_8 (cf. **25**), resulting in an upfield shift of 0.2–0.3 ppm for this proton.

Since this shift is not observed in compound **21**, we were able to determine its configuration and solution conformation as shown in Tables I and III and conclude that the adduct is formed by an exo addition of maleate. The structures and configurations of **24**, **25**, and **27** were also confirmed by the fact that they could be induced to eliminate methanol (or acetic acid) to produce the common elimination product **28**. Compound **28** exhibits a $J_{3,4}$ of



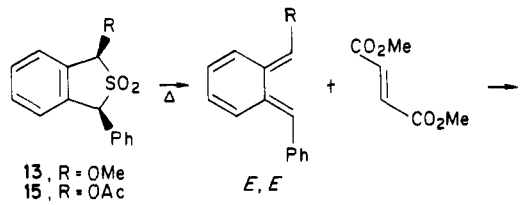
28 29

2.9 Hz in accord with the data of Pfau[2] who finds a $J_{3,4}$ of 4 Hz for the similar compound **29** and 7 Hz for the corresponding cis isomer. Other examples of small trans coupling constants in disubstituted dihydronaphthalenes are recorded in the literature.[17]

Thermolysis of the methoxy sulfone **13** in pure dimethyl fumarate or maleate proceeded by addition and elimination to yield the elimination product **20** for both, in good yield, further establishing the structures of the adducts. The more polar solvent environment presumably promotes the concurrent elimination reaction. The acetoxy adduct **27** was also accompanied by the elimination product **28** even when the thermolysis was carried out in a nonpolar solvent.

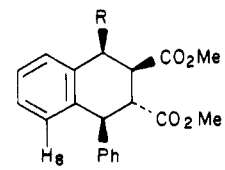
Discussion

As mentioned previously the cis stereochemistries of **13** and **15** were deduced from the stereochemistries of the fumarate adducts **25** and **27**. Both the disrotary extrusion of SO_2 from **13** or **15** and the trapping of the resulting *o*-QDM by fumarate are pericyclic reactions in which the reactant and product stereochemistries are related. Since the phenyl and methoxy substituents are cis in structures **25** and **27**, we can deduce they were also cis in the sulfones **13** and **15** and that the *o*-QDM probably had the *E,E* configuration since the *Z,Z* configuration would be sterically unfavorable.



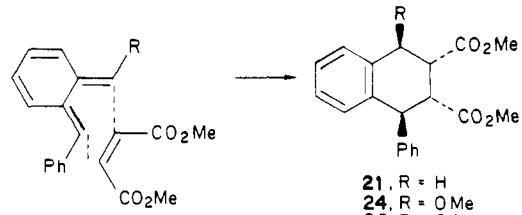
13, R = OMe
15, R = OAc

E, E



25, R = OMe
27, R = OAc

The most important result of this work is the fact that in all cases dimethyl maleate added to all our α-phenyl-*o*-QDM's to yield predominantly the *trans*-1-phenyl-2-carbomethoxytetralins via the exo transition state.



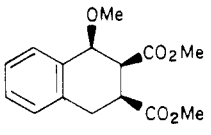
21, R = H
24, R = OMe
26, R = OAc

Methyl crotonate also added to **6** via the exo transition state to give the trans-disubstituted tetralin **23**. From the NMR spectra of the crude adducts, the formation of all adducts, except for **26**, appeared to be at least 90% stereoselective as evidenced by the lack of signals corresponding to other isomers. Adduct **26** was accompanied

(16) Durst, T.; Charlton, *J. Can. J. Chem.*, in press.

(17) Ahmed, R.; Lehrer, M.; Stevenson, R. *Tetrahedron* **1973**, *29*, 3753. Hostettler, F. D.; Seikel, M. K. *Tetrahedron* **1969**, *25*, 2325.

Table I. Cycloadditions. Reactions Conditions and Products



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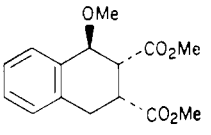

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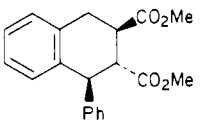

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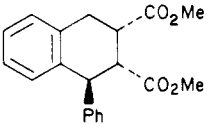

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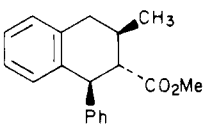


23

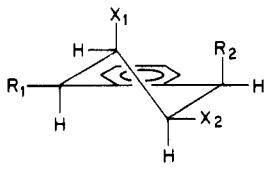
	precursor								
	14	14	17	17	17	13	13	15	15
wt, mg	162	150	107	77	100	188	197	110	96
solv.[a] mL	HCB	HCB	CH	CH	CH	CH	T	X	X
	2	2	10	10	5.5	10	10	10	10
temp, °C	200	150	80	80	80	80	111	138	138
time, h	1	1	5.5	8	7	15	15	15	1
dienophile[a]	M	F	M	F	C	M	F	M	F
product	**18**	**19**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
yield,[b] %	32	38	57	87	60	69	43	39	59[c]

[a] Key: HCB = hexachlorobutadiene; CH = cyclohexane; T = toluene; X = xylene; M = dimethyl maleate; F = dimethyl fumarate; C = methyl crotonate. [b] Isolated yield, after recrystallization or chromotography. [c] Estimated from NMR of crude product, also contained 30% **28**.

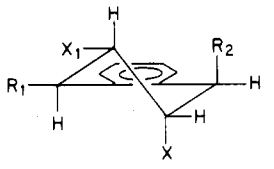
Table II. Chemical Shifts (δ) and Coupling Constants (Hz)

	18	19	21	22	23	24	25	26	27
H_1	3.04	4.63	4.83	4.25	4.36	4.71	4.09	4.77	4.18
H_2	3.36	3.14	3.48	3.1	2.62	3.59	3.61	3.54	3.5
H_3	3.73	3.52	2.97		2.27	3.77	3.30	3.6	3.8
H_{4e}	3.04	3.28	3.19		2.97	4.70	4.70	6.57	6.60
H_{4a}	3.36	2.83		3.3	2.77				
H_8				6.78	6.75	6.94	6.87	6.91	6.80
Ar	7.1	7.15	7.0	7.0	7.0	7.15	7.23	7.1	7.3
	7.3	7.4	7.4	7.4	7.4	7.35		7.4	
OCH_3	3.44	3.28	3.65	3.40	3.52	3.50	3.39	3.66	3.50
OCH_3	3.55	3.75	3.67	3.67		3.54	3.48	3.64	3.73
OCH_3	3.74	3.78				3.62	3.77		
OAc								2.15	2.06
$J_{1,2}$	3.0	3.2	3.0	11.1	10.5	9.0	11.0	7.0	10.0
$J_{2,3}$		11.5	3.6		10.5	4.5	12.1		
$J_{3,4a}$		10.9	11.0		12.0				
$J_{3,4e}$		6.7	6.2		5.0	3.8	2.9	4.9	2.0
$J_{4a,4e}$		16.9	17.5		16.0				

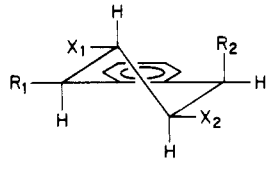
Table III. Conformation of Adducts[a,b]



30



31



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adduct	R_1	R_2	conformation
18	OMe	H	**30**
19	H	OMe	**32**
21	H	Ph	**31**
22	Ph	H	**32**
23	Ph	H	**32**
24	Ph	OMe	**31**
25	Ph	OMe	**32**
26	Ph	OAc	**30**
27	Ph	OAc	**32**

[a] $X_1 = X_2 = CO_2Me$ except for **23**, where $X_1 = CO_2Me$, $X_2 = Me$. [b] While only one enantiomer is shown, a racemate is implied.

by another minor isomer (3:1), which was not isolated but was presumably the all cis endo adduct. Although the isolated yields recorded in Table I are not high, they are not optimized and losses have occurred on isolation. Other products included were *o*-tolualdehyde (from **4**) and *o*-benzylbenzaldehyde (from **14** and **15**) presumably arising from inadvertent hydrolysis of the *o*-QDM's, and the elimination products **20** and **28**.

The preference for exo addition of dimethyl maleate to the phenyl-substituted *o*-QDM's is in contrast to the previously reported addition of maleic anhydride to the photoenol **4**[9] and to the *o*-QDM **6**,[10] both of which give endo adducts. A preliminary study of the addition of maleic anhydride to α-methoxy-α'-phenyl-*o*-QDM also indicates that the addition is primarily endo. The availability of the *o*-QDM precursors described above and the ability to control the stereoselectivity of additions of dienophiles to *o*-QDM's provide a valuable synthetic tool, especially for lignan synthesis, which we are now pursuing.

Experimental Section

Proton magnetic resonance spectra were recorded on a Varian EM360 T-60 or XL300 machine using tetramethylsilane as an internal standard. Infrared spectra were recorded on a Pye-Unicam SP-1000 machine. Mass spectra were obtained from V. G. Analytical Model 7070E double focusing instrument.

***o*-Benzylbenzaldehyde (9).** *o*-Benzylbenzyl alcohol (2 g, 0.01 mol, Aldrich) was dissolved in diethyl ether (20 mL) and then

stirred vigorously with aqueous chromic acid (20 mL of a solution of 5% CrO_3 in 10% aqueous H_2SO_4, 0.01 mol) while cooling in an ice bath. After 20 min the ether was separated, the aqueous layer was extracted with ether, the ether extracts were combined, dried ($MgSO_4$), and evaporated to leave 1.92 g (98%) of aldehyde **9**,[9] which was used without further purification.

1-Hydroxy-3-phenyl-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide (10). Sulfur dioxide (20 mL) was distilled into 200 mL of benzene containing *o*-benzylbenzaldehyde (4.5 g). The solution was irradiated for 22 h, under nitrogen, through a 1-mm Pyrex filter, with a water-jacketed 450-W Hanovia medium-pressure mercury lamp immersed in the solution. The benzene was removed in vacuo and the residue dissolved in methylene chloride and extracted 3 times with 5% aqueous bicarbonate. The extract was acidified to pH 1 (10% HCl), extracted 3 times with methylene chloride, dried ($MgSO_4$), and then evaporated to leave a glassy solid (4.0 g, 67%) as a mixture of cis and trans isomers: ^1H NMR ($CDCl_3$) δ 5.0 (br s, 1 H), 5.43 (s, 0.5 H), 5.59 (s, 0.5 H), 5.71 (s, 0.5 H), 5.78 (s, 0.5 H), 7.1–7.7 (m, 9 H); IR (CH_2Cl_2) 1323, 1194, 1121 cm^{-1}; mass spectrum, *m/e* (relative intensity) 196 (100), 195 (97), 194 (71), 179 (28), 178 (51), 165 (85).

1-Hydroxy-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide (7). Tolualdehyde (2 g, 0.0167 mol, Aldrich) was irradiated with SO_2 in the same manner as for *o*-benzylbenzaldehyde above. The irradiation was stopped after 4 h. The hydroxy sulfone, isolated by extraction of the crude reaction mixture with bicarbonate (1.5 g, 49%), crystallized on standing and could be recrystallized from methylene chloride at −78 °C. The hydroxy sulfone could also be crystallized directly from the crude irradiation mixture using methylene chloride/hexane as solvent (yield 56%): mp 98–100 °C; ^1H NMR ($CDCl_3$) δ 4.16 (br s, 1 H), 4.56 (q, 2 H, J = 15.7 Hz), 5.64 (s, 1 H), 7.55 (m, 3 H), 7.63 (m, 1 H); IR (CH_2Cl_2) 1322, 1200, 1118 cm^{-1}; mass spectrum, *m/e* (relative intensity) 148 (25), 136 (40), 120 (36), 119 (75), 118 (42), 91 (100). Anal. Calcd for $C_8H_8O_3S$: C, 52.00; H, 4.68; S, 17.35. Found: C, 51.91; H, 4.42; S, 17.15.

***cis*-1-Methoxy-3-phenyl-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide (13).** The hydroxy phenyl sulfone **10** (200 mg, 0.0077 mol) and *p*-toluenesulfonic acid (10 mg) were refluxed in dry methanol (25 mL) for 35 min. The solution was evaporated to near dryness at 30 °C, diluted with 5% aqueous bicarbonate, and extracted with CH_2Cl_2. The organic extracts were dried ($MgSO_4$) and evaporated to leave 186 mg (88%), which by NMR proved to be a mixture of **12** and *o*-benzylbenzaldehyde. Recrystallization from methanol gave 96 mg (46%) of colorless crystals: ^1H NMR ($CDCl_3$) δ 3.83 (s, 3 H), 5.27 (s, 1 H), 5.35 (s, 1 H), 7.27 (m, 9 H); IR (CH_2Cl_2) 1321, 1203, 1137 cm^{-1}.

1-Methoxy-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide (14). The 1-hydroxy-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (100 mg) was treated with *p*-toluenesulfonic acid and methanol as described above for the preparation of **13**. The solution was refluxed for 1 h and worked up to yield 98.4 mg (92%) of **14**: mp 57–58 °C; ^1H NMR ($CDCl_3$) δ 3.8 (s, 3 H), 4.3 (q, 2 H), 5.27 (s, 1 H), 7.4 (m, 4 H); IR (CH_2Cl_2) 1315, 1119, 1172 cm^{-1}; mass spectrum, *m/e* (relative intensity) 134 (90), 120 (37), 119 (98), 91 (100), 64 (43). Anal. Calcd for $C_9H_{10}SO_3$: C, 54.53; H, 5.08. Found: C, 54.67; H, 5.02.

***cis*- and *trans*-1-Acetoxy-3-phenyl-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxides (15 and 16).** The acetates were prepared from the hydroxy sulfone **10** by adding it (200 mg) to excess acetic anhydride (20 mL), warming the mixture to 55 °C for 2 h, and then evaporating it at 20 °C under high vacuum to give the acetates **15**/**16** (40/60 mixture) in 100% yield. The cis isomer **15** could be crystallized from the mixture with benzene/hexane as solvent. **15**: ^1H NMR ($CDCl_3$) δ 2.22 (s, 3 H), 5.48 (s, 1 H), 6.73 (s, 1 H), 7.2–7.6 (m, 9 H); IR (CH_2Cl_2) 1767, 1333, 1206 cm^{-1}; mass spectrum, *m/e* (relative intensity) 238 (0.7), 196 (33), 195 (45), 179 (21), 178 (100). Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.61. Found: C, 63.34; H, 4.35; S, 10.83. The trans isomer **16** was isolated by chromatography on silica gel using ethyl acetate/hexane (1:7) as eluant. **16**: ^1H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 5.63 (s, 1 H), 6.78 (s, 1 H), 7.12 (m, 1 H), 7.3–7.65 (m, 8 H); IR (CH_2Cl_2) 1765, 1340, 1205 cm^{-1}; mass spectrum, *m/e* (relative intensity) 238 (3), 196 (41), 195 (53), 179 (21), 178 (100), 165 (29), 152 (10). Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.61. Found: C, 63.36; H, 4.30; S, 10.72.

Cycloaddition Reactions. The conditions for the formation and trapping of *o*-quinodimethanes are given in Table I. Excess dienophile was removed at 100 °C under high vacuum. Hexachlorobutadiene (HCB) was removed by applying the product to a silica gel column with hexane and eluting with hexane until the HCB was removed. The adducts were then eluted with ethyl acetate/hexane. Adducts **21**, **22**, **24**, and **26** were obtained by crystallizing the crude reaction mixture from ethanol. The remaining adducts were obtained by flash chromatography (1:5 ethyl acetate/hexane). IR and mass spectral and elemental analysis data for selected adducts are given below.

18: mp 75–78 °C; IR (CH_2Cl_2) 1735 cm^{-1}; mass spectrum, *m/e* (relative intensity) 263 (21), 231 (22), 218 (34), 187 (52), 159 (100), 143 (49). **19**: IR (CH_2Cl_2) 1738 cm^{-1}; mass spectrum, *m/e* (relative intensity) 246 (11), 214 (18), 203 (17), 187 (100), 186 (63), 159 (66). **21**: mp 109.5–111.5 °C; IR (CH_2Cl_2) 1736 cm^{-1}; mass spectrum, *m/e* (relative intensity) 324 (4), 293 (4), 264 (46), 206 (19), 205 (100). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.33; H, 5.94. **22**: mp 106–108 °C; IR (CH_2Cl_2) 1736 cm^{-1}; mass spectrum, *m/e* (relative intensity) 324 (7), 293 (4), 264 (49), 206 (19), 205 (100), 204 (22). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.98; H, 6.12. **23**: mp 100–101 °C; IR (CH_2Cl_2) 1722 cm^{-1}; mass spectrum, *m/e* (relative intensity) 280 (29), 221 (23), 220 (100), 205 (52), 179 (25). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.55; H, 7.19. **24**: mp 119–121 °C; IR (CH_2Cl_2) 1747 cm^{-1}; mass spectrum, *m/e* (relative intensity) 339 (22), 323 (29), 322 (100), 294 (58), 263 (51), 262 (70). **25**: IR (CH_2Cl_2) 1735 cm^{-1}; mass spectrum, *m/e* (relative intensity) 339 (1), 322 (7), 264 (19), 262 (100), 235 (15), 231 (70), 219 (14), 204 (31), 204 (26). **26**: mp 139–140 °C; IR (CH_2Cl_2) 1742 cm^{-1}; mass spectrum, *m/e* (relative intensity) 339 (42), 322 (100), 294 (71), 263 (52), 262 (62), 231 (74), 204 (73), 203 (59). **27**: IR (CH_2Cl_2) 1745 cm^{-1}; mass spectrum, *m/e* (relative intensity) 322 (7), 263 (56), 262 (100), 231 (54), 204 (23), 203 (18).

Elimination of Methanol from 24 and 25. Formation of 28. The adduct **24** (129 mg) or **25** (179 mg) and toluenesulfonic acid (25 mg) were refluxed in toluene (20 mL) for 5 and 15 h, respectively. The solution was diluted with methylene chloride, washed with 5% aqueous bicarbonate, dried ($MgSO_4$), and evaporated to dryness. Recrystallization from ethanol gave crystalline **28**: 56 mg (49%) from **24** and 65 mg (40%) from **25**. NMR investigation of the crude product before crystallization confirmed that **28** was the exclusive product: mp 121 °C; ^1H NMR ($CDCl_3$) δ 3.59 (s, 3 H), 3.73 (s, 3 H), 4.05 (d, 1 H, J = 2.8 Hz), 4.73 (d, 1 H, J = 2.8 Hz), 6.9–7.3 (m, 9 H), 7.70 (s, 1 H); IR (CH_2Cl_2) 1710, 1732 cm^{-1}; mass spectrum, *m/e* (relative intensity) 322 (5), 263 (51), 262 (100), 231 (40), 204 (46), 203 (36), 202 (31); exact mass calcd for $C_{20}H_{18}O_4$ 322.1205, found 322.1206.

Elimination of Acetic Acid from 26. The adduct **26** (26 mg) and toluenesulfonic acid (5 mg) were refluxed in toluene (5 mL) and worked up as described above for the elimination of methanol from **24** and **25** to give **28** (15 mg, 68%).

Elimination Product 20. Methoxy sulfone **14** was heated in pure dimethyl maleate (64 mg in 1 g at 200 °C) and dimethyl fumarate (51 mg in 0.75 g at 150 °C) for 1 h. Each reaction was worked up by evaporating the ester at 100 °C under high vacuum and isolating the elimination product **20** by chromatography on silica gel (1:5 ethyl acetate/hexane): ^1H NMR ($CDCl_3$) δ 3.14 (dd, 1 H, J = 8.0, 16.1 Hz), 3.36 (dd, 1 H, J = 3.4, 16.1 Hz), 3.61 (s, 3 H), 3.84 (s, 3 H), 3.88 (dd, 1 H, J = 3.4, 8.0 Hz), 7.2–7.35 (m, 4 H), 7.67 (s, 1 H); IR (CH_2Cl_2) 1711, 1732 cm^{-1}; mass spectrum, *m/e* (relative intensity) 246 (13), 187 (78), 186 (45), 155 (45), 143 (44), 128 (100); exact mass calcd for $C_{14}H_{14}O_4$ 246.0892, found 246.0871.

Registry No. (±)-**7**, 98678-32-1; **9**, 32832-95-4; (±)-*trans*-**10**, 98678-31-0; (±)-*cis*-**10**, 98678-47-8; (±)-**13**, 98678-33-2; (±)-**14**, 98678-34-3; (±)-**15**, 98678-35-4; (±)-**16**, 98678-36-5; (±)-**17**, 98678-44-5; (±)-**18**, 98678-37-6; (±)-**19**, 98678-38-7; (±)-**20**, 98678-46-7; (±)-**21**, 98678-39-8; (±)-**22**, 98678-40-1; (±)-**23**, 98678-41-2; (±)-**24**, 98678-42-3; (±)-**25**, 98757-18-7; (±)-**26**, 98678-43-4; (±)-**27**, 98719-13-2; (±)-**28**, 98678-45-6; M, 624-48-6; F, 624-49-7; C, 623-43-8; 2-$PhCH_2C_6H_4CH_2OH$, 1586-00-1; *o*-MeC_6H_4CHO, 529-20-4.