The preparation of **21**, described above, was adapted to give [6-^{2}H]-**21** by using D_2/DOAc in the hydrogenation of **18**. The deamination of [6-^{2}H]-**21**·HCl (0.45 g, 2.8 mmole was achieved with sodium nitrite (1.0 g, 14.7 mmol) and perchloric acid in a biphasic system of water (30 mL) and ether (15 mL). Workup as above, followed by HPLC and GC (cf. photolysis of **16**), afforded the major products. ^{2}H NMR: **19** δ 2.36 (47%), 3.68 (53%); **20** δ 2.26 (49%), 4.03 (51%); **29** δ 1.85 (50%), 4.39 (50%). ^{13}C NMR of **29**: δ 37.797 (50%), 37.894 (50%); 48.948 (50%), 49.048 (50%).

Tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane (36). The tosylhydrazone **16** (0.80 mg, 2.7 mmol) and sodium hydride (0.11 g, 2.75 mmol, 60% suspension in paraffin) were stirred in anhydrous THF (20 mL) for 3 h. Pentane (30 mL) was added, and stirring was continued for 2 h. The sodium salt of **16** (0.80 g, 95%) was filtered by suction, washed with pentane, and dried in vacuo. The sodium salt was introduced slowly under vacuum (0.005 mmHg) into a flask which was preheated to 230–250 °C. Volatiles were collected in a receiver cooled with liquid nitrogen. According to GC, the product was 99% pure, and the yield was 88%. The spectra were in agreement with literature data for **36**, obtained from a different source.[22]

For acidolysis, samples (20–25 mg) of **36** were stirred in a sealed vessel with dioxane/H_2SO_4 (70:30). The product ratios **39**:**40** were fairly independent of acidity and conversion: 0.5 N H_2SO_4, 25 °C, 3 days, 8% conversion, 20:80; 0.5 N H_2SO_4, 60 °C, 2 days, 93% conversion, 17:83; 1.0 N H_2SO_4, 25 °C, 3 days, 10% conversion, 19:81; 1.0 N H_2SO_4, 60 °C, 2 days, 100% conversion, 17:83. In a preparative run, **36** (0.23 g, 2.6 mmol) was treated with dioxane/1.0 N H_2SO_4 (7:3, 7 mL) at 60 °C for 3 days. The mixture was diluted with ether and washed with water and saturated $NaHCO_3$ solution. The ether solution was dried ($MgSO_4$) and concentrated by distillation (Vigreux column). The products **39** (17%) and **40** (83%) were separated by HPLC (pentane/ether, 70:30). ^{1}H NMR of **39**: δ 0.89 (dt, endo 6-H, $J_{6n,6x}$ = 11.0 Hz, $J_{1,6n} \simeq J_{6n,7}$ = 1.5 Hz), 1.12 (d, endo 8-H, $J_{8n,8x}$ = 7.2 Hz), 1.22 (dm, exo 3-H, $J_{3n,3x}$ = 14.0 Hz), 1.45 (br dd, exo 6-H, $J_{6n,6x}$ = 11.0 Hz, $J_{5,6x}$ = 7.5 Hz), 1.71 (dd, endo 3-H, $J_{3n,3x}$ = 14.0 Hz, $J_{3n,4}$ = 5.8 Hz), 1.73 (m, exo 8-H), 2.23 (m, 3 H), 2.52 (m, 1 H), 4.20 (br d, 4-H, $J_{3n,4}$ = 5.8 Hz). Comparison of this spectrum with those of **19** and **20** strongly suggests that **39** is tricyclo[3.3.0.0^{2,7}]octan-*exo*-4-ol. ^{1}H NMR of **40**: δ 1.16 (d, endo 4-H, $J_{4n,4x}$ = 9.0 Hz), 1.27 (dm, anti 7-H, $J_{7a,7s}$ = 11.0 Hz), 1.36 (dm, endo 8-H, $J_{8n,8x}$ = 12.5 Hz), 1.57 (m, exo 8-H + OH), 1.79 (dm, syn 7-H, $J_{7a,7s}$ = 11.0 Hz), 2.08 (m, 3-H), 2.16 (m, exo 4-H + 5-H), 2.49 (br s, 1-H), 2.78 (m, 6-H), 3.84 (s, 2-H). These data (400 MHz + COSY) are in agreement with the reported 60-MHz spectrum[21] and confirmed the assignment of **40** as tricyclo[3.2.1.0^{3,6}]octan-*exo*-2-ol.

Coupling Reactions of 4-*tert*-Butyl-*o*-benzoquinone with Olefinic Compounds

Masayuki Takada, Ryuichi Oshima, Yoshio Yamauchi,† Ju Kumanotani,‡ and Manabu Seno*

Institute of Industrial Science, University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo 106, Japan

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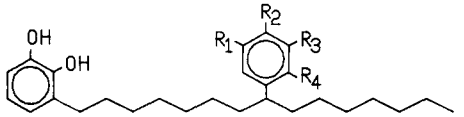
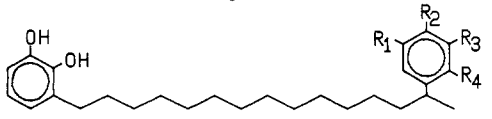
Room-temperature bulk reactions of 4-*tert*-butyl-*o*-benzoquinone (**5**) and four alkenes, 1,4-pentadiene (**6**), methyl sorbate (**7**), methyl linoleate (**8**), and 3-[8′(*Z*),11′(*E*),13′(*Z*)-pentadecatrienyl]veratrole (**9**) have been studied. Reactions with methylene-interrupted olefins **6**, **8**, and **9** afforded C–O and C–C linked 1:1 adducts through dehydrogenation paths, whereas the cycloaddition product **13** was exclusively produced by the reaction with **7**. Comparing the product distribution of these reactions and the orientations predicted by the reactivities of possible reaction species, the hydride ion transfer mechanism has been inferred to dominate in the reaction of **5** and triene **9**. On the other hand, the radical path involving the transfer of a hydrogen atom has been favored for reactions of **6** and **8**.

Quinones and olefins are ubiquitously distributed in biological systems, and reactions between these two classes of substances play significant roles in various stages of biological functions. In the previous paper,[1] we disclosed that physiological oxidation of urushiol in sap of the lac tree, *Rhus vernicifera*, yielded a series of nucleus side chain bound dimers of urushiol, **1** and **2**. It was postulated that

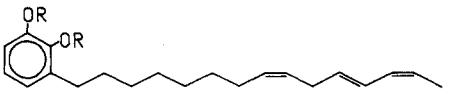


1



2

R_1=R_2=OH, R_3=$C_{15}H_{31}$, R_4=H
R_1=H, R_2=R_3=OH, R_4=$C_{15}H_{31}$
R_1=H, R_2=$C_{15}H_{31}$, R_3=R_4=OH



3 R=H
9 R=CH_3

4 R=$C_{15}H_{31-2n}$ n=1, 2, 3

these dimers were derived through dehydrogenation of the trienyl side chain of the main urushiol congener **3** with urushiol quinone **4** which was produced by laccase-mediated oxidation of urushiol.

Several studies were concerned with dehydrogenation-addition reactions of high-potential quinones with alkenes as hydrogen donors.[2] Diethers were derived from reactions of aryl-substituted olefins with DDQ or *o*-chloranil, and the hydride ion transfer mechanism accounted for features of these reactions.[2b] While some simple olefins undergo dehydrogenation–addition with *o*-chloranil in addition to

† Current address: Japan Spectroscopic Industries Co. Ltd., Ishikawacyo, Hachioji, Tokyo 192, Japan.

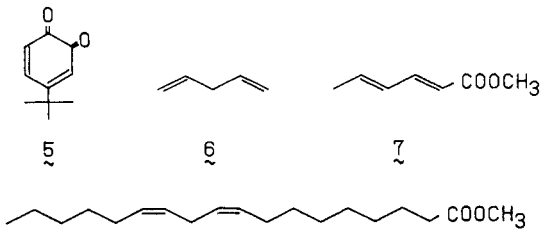
‡ Current address: Ehime University, 3 Bunkyocho, Matsuyama, Ehime 790, Japan.

(1) Oshima, R.; Yamauchi, Y.; Watanabe, C.; Kumanotani, J. *J. Org. Chem.* **1985**, *50*, 2613–2621.

0022-3263/88/1953-3073$01.50/0

cycloaddition the mechanism of which was attributed to the radical path initiated by the hydrogen atom abstraction from olefins with quinones.[2f,h] *p*-Benzoquinone derivatives couple with cycloheptatriene through dehydrogenation to give C–C adducts with the concomitant occurrence of cycloaddition.[2k] So it has been understood that the mode of quinone dehydrogenation depends on the oxidizing power of quinones, the nature of substrates, and in particular the stability of intermediates derived therefrom.

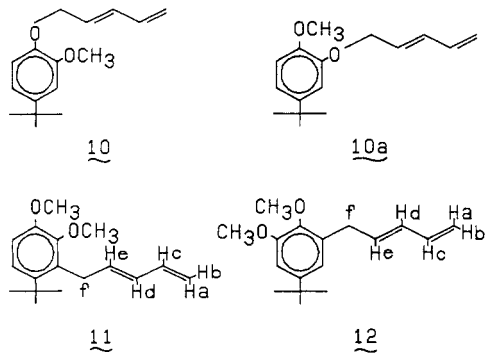
We have attempted to obtain further insight into quinone dehydrogenation of olefinic compounds by examining reactions of several methylene-interrupted alkenes which possibly transform to stable delocalized intermediates after oxidation by quinones. In this paper we report that dehydrogenation–addition takes place at room temperature between 4-*tert*-butyl-*o*-benzoquinone (**5**) and this kind of olefins, i.e., 1,4-pentadiene (**6**), methyl linoleate (**8**), and 3-[8′(*Z*),11′(*E*),13′(*Z*)-pentadecatrienyl]veratrole (**9**), while the reaction of **5** with methyl sorbate (**7**) yields exclusively the Diels–Alder product. The mechanism of former reactions is discussed mainly in view of product distributions.



5 6 7 8

Results

Reaction of 1,4-Pentadiene (6). As the reaction proceeded, quinone **5** was consumed with the simultaneous formation of 1:1 adducts, and the considerable amount of higher molecular weight substances and 4-*tert*-butylcatechol (10%) were produced (Figure 1a). After prolonged reaction, the yield of 1:1 adducts decreased (Table I). The reaction was stopped after 28 h, when the maximum amount of 1:1 products was given (12% based on **5**). At this time, however, 14% of quinone remained unreacted. Adducts were identified as methyl ethers **10–12**.



10 10a 11 12

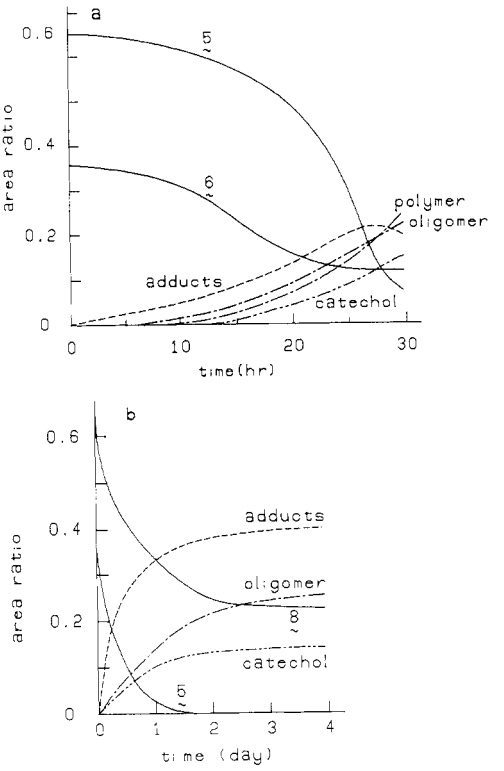
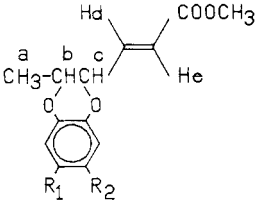


Figure 1. The time course of product distribution in the reaction of (a) 1,4-pentadiene (**6**) and (b) methyl linoleate (**8**) with 4-*tert*-butyl-*o*-benzoquinone (**5**).

The C–O adduct **10** showed a singlet ^{1}H NMR signal due to the methoxyl group at meta to the *tert*-butyl group (δ 3.83) and a doublet of OCH_2 protons (δ 4.53), whereas C–C adducts **11** and **12** exhibited two singlets of two methoxy groups (δ 3.73, 3.80) as well as a doublet from the methylene group linked to the benzene ring (δ 3.63 for **11** and δ 3.36 for **12**); the δ 3.63 peak shifted upfield owing to the steric effect. The substitution patterns of benzene rings and the geometry of double bonds in side chains of adducts **10–12** were explicitly determined from either the IR or the NMR spectra. The product ratio is shown in Table II; only C–C adducts were obtained after a long reaction time.

Reaction of Methyl Sorbate (7). After 3 days, quinone **5** disappeared completely. The methyl ether of cycloaddition product **13** was given in 30% yield; other products were high molecular weight substances and 4-*tert*-butylcatechol. GLC analysis proved that **13** was a 1:1 mixture of two isomers, presumably, with a *tert*-butyl group substituted on 6- or 7-position in the benzene ring.



13 R_1/R_2=H/t-C_4H_9

Reaction of Methyl Linoleate (8). After 3 days, quinone **5** was consumed completely with simultaneous formation of 1:1 adducts together with oligomeric substances and 4-*tert*-butylcatechol (ca. 13%) (Figure 1b). The 1:1 adducts were obtained in 22% yield as methyl ethers, from which C–C adducts **14–17**, C–O adducts **18–21**, and benzodioxins **22** and **23** were separated in the ratio of 62:31:7.

(2) (a) Criegee, R. *Ber.* **1936**, *69*, 2758–2764. (b) Hornor, L.; Metz, H. *Ann.* **1950**, *570*, 89–120. (c) Braude, E. A.; Jackman, L. M.; Linstead, R. P.; Lowe, G. *J. Chem. Soc.* **1960**, 3123–3232. (d) Forster, R.; Horman, I. *J. Chem. Soc. B* **1966**, 1049–1053. (e) Kato, T.; Taniai, M.; Yokoo, K.; Kumanotani, J. *Can. J. Chem.* **1969**, *47*, 2106–2107. (f) Ansell, M. F.; Bignold, A. J. *Chem. Commun.* **1969**, 1096–1097. (g) Becker, H.-D. *J. Org. Chem.* **1969**, *34*, 1203–1210. (h) Ansell, M. F.; Bignold, A. J. *Chem. Commun.* **1970**, 989–990. (i) Kiefer, E. F.; Luts, F. E. *J. Org. Chem.* **1972**, *37*, 1519–1522. (j) Müller, P.; Rocek, J. *J. Am. Chem. Soc.* **1972**, *94*, 2716–2719. (k) Takeshita, H.; Mori, A.; Mametsuka, H. *Chem. Lett.* **1976**, 445–448.

Table I. Yields of 1:1 Adducts and Product Ratios of Reaction between Quinone 5 and Olefins

olefin	feed ratio of 5/olefin	time	yield of 1:1 adducts,[a] %	ratio of C-O/C-C adducts
6	1/3	28 h	12	3/97
	1/3	4 day	8	0/100
	1/4.5	6 day	6	0/100
7	1/1.5	3 day	30	
8	1/1	3 day	22	38/62
9	1/1	24 h	63	82/18

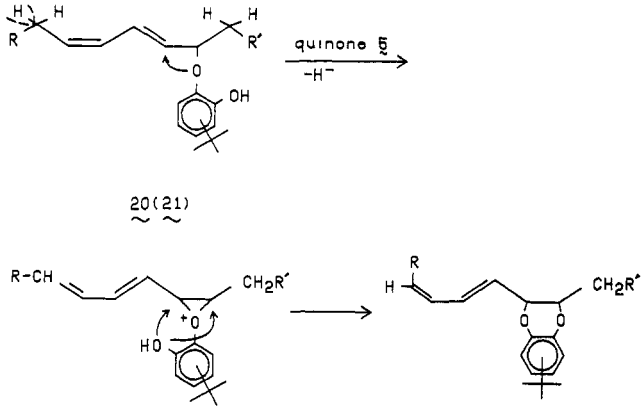
[a] Based on quinone 5.

Table II. Ratios of 1:1 Adducts Produced by Reactions between 5 and Olefins

olefin	adduct	ratio (wt %)	isomer	bound[a] position	ratio (wt %)
6	C-O adduct	3	**10**	8-1′	3
	C-C adduct	97	**11**	3-1′	45
			12	6-1′	52
7	Diels-Alder		**13**		
8	C-C adduct	62	**14**	6-13′	16
			15	6-9′	15
			16	6-9′	17
			17	6-13′	14
	C-O adduct	31	**18**	7-13′	10
			19	8-13′	4
			20	7-9′	11
			21	8-9′	6
	benzodioxin	7	**22**	7,8-9′,10′	4
			23	7,8-12′,13′	3
9	C-O adduct	83	**24**	7-8′	6
			25	7-14′	26
			26	8-8′	9
			27	8-14′	42
	C-C adduct	16	**28**	6-8′	2
			29	6-14′	2
			30	5-8′	10
			31	5-14′	2

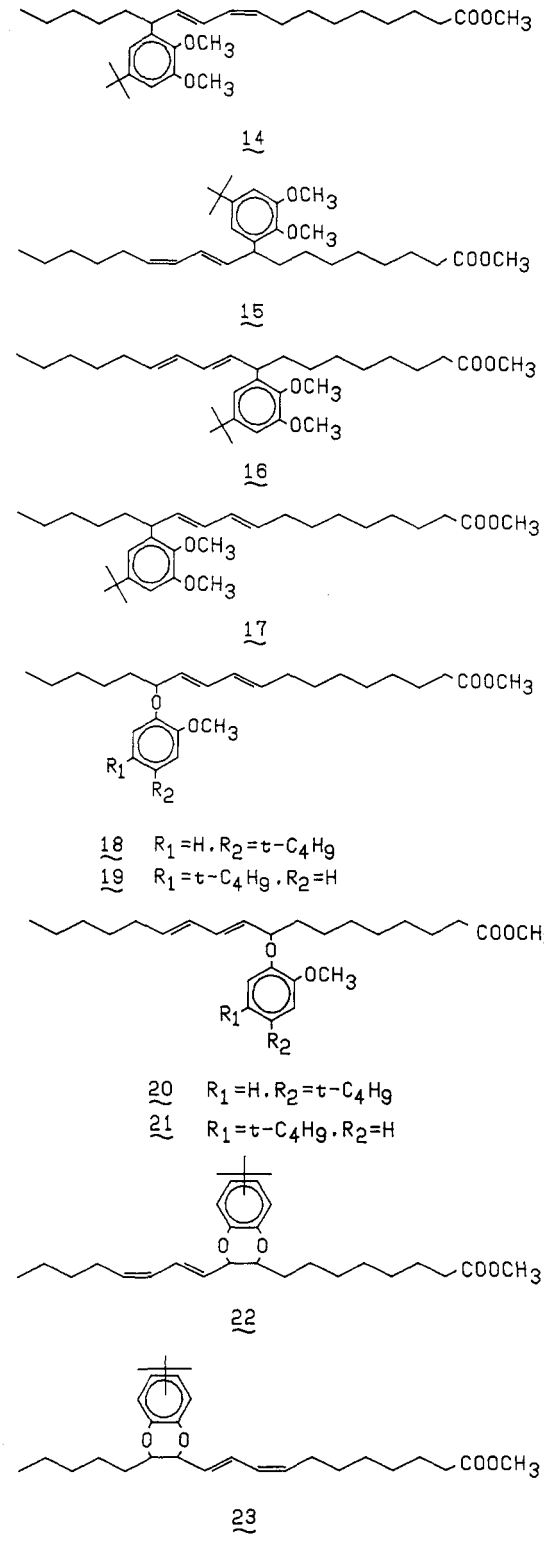
[a] The left side number stands for the position in the nucleus of quinone and that with a prime for that in the olefin position.

Scheme I



22

The C-C adducts **14–17** exhibit an IR band of a 1,2,3,5-tetrasubstituted benzene ring (840 cm^{-1}), and two singlets ^1H NMR signals of methoxy protons (δ 3.72 and 3.83) and a multiplet of C-linked methine proton. Adducts **14** and **15** show IR bands of a conjugated *trans,cis*-diene (980, 940 cm^{-1}), while **16** and **17** show that of a conjugated *trans,trans*-diene (990 cm^{-1}). The positions and geometry of double bonds in these adducts were determined by the consecutive procedure based on partial reduction and reductive ozonolysis of obtained monoenes.[3]



14

15

16

17

18 R_1=H, R_2=t-C_4H_9

19 R_1=t-C_4H_9, R_2=H

20 R_1=H, R_2=t-C_4H_9

21 R_1=t-C_4H_9, R_2=H

22

23

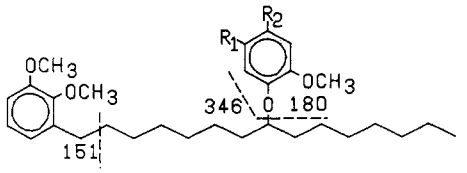
The C-O adducts **18–21** have IR bands assigned to a 1,2,4-trisubstituted benzene ring and a conjugated *trans,trans*-diene and an NMR signal of a multiplet of O-linked methylene protons. In ^1H NMR spectra of **18** and **20**, a singlet of the methoxy group at meta to the *tert*-butyl group (δ 3.78) was recognized, whereas adducts **19** and **21** show a singlet of the methoxy group at para to the *tert*-butyl group (δ 3.76). The positions and stereo-

(3) (a) Yamauchi, Y.; Oshima, R.; Kumanotani, J. *J. Chromatogr.* **1982**, *243*, 71–84. (b) Yamauchi, Y.; Takada, M.; Oshima, R.; Kumanotani, J.; Seno, M. *J. Chromatogr.* **1987**, *408*, 171–180.

chemistry of double bonds were determined as in the cases of C–C adducts.

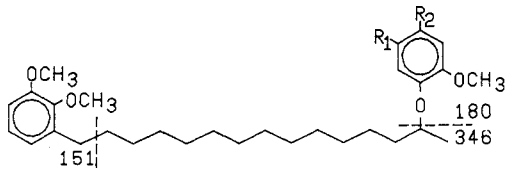
Benzodioxins **22** and **23**, given as minor products, have a 1,2,4-trisubstituted benzene ring (860 and 810 cm^{-1}), a conjugated *cis,trans*-diene (990 and 960 cm^{-1}), and a dioxane ring (1280 cm^{-1}). The positions and stereochemistry of double bonds were elucidated as above. These are not cycloaddition products but probably given by successive dehydrogenation–cyclization of C–O adducts; e.g., the C-9 bound adduct **20** (or **21**) was dehydrogenated by the quinone at C-14 to give the intermediate phenoxonium ion, in which the intramolecular nucleophilic attack occurred to result in the formation of **22** (Scheme I), and vice versa.

Reaction of 3-[8′(*Z*),11′(*E*),13′(*Z*)-pentadecatrienyl]veratrole (9). After 24 h at room temperature, quinone **5** disappeared completely, and 1:1 adducts were obtained in 63% yield along with oligomeric substances (ca. 15%) and 4-*tert*-butylcatechol (8%). They composed a highly complicated mixture and then were resolved after fully hydrogenated, giving methyl ethers of C–O adducts **24–27** and C–C adducts **28–31**; a pair of isomers **25/26** was obtained as a 3:1 mixture and those of **28/29** and **30/31** as 1:1 and 5:1 mixtures, respectively.



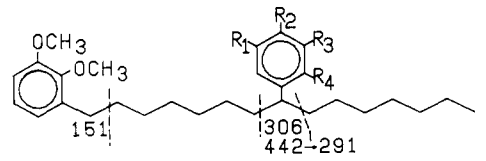
24 R_1=H, R_2=t-C_4H_9

26 R_1=t-C_4H_9, R_2=H



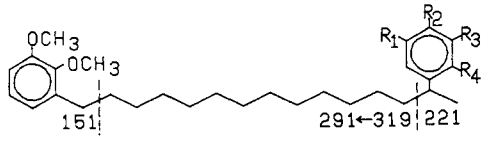
25 R_1=H, R_2=t-C_4H_9

27 R_1=t-C_4H_9, R_2=H



28 R_1=t-C_4H_9, R_2=H, R_3=R_4=OCH_3

30 R_1=R_2=OCH_3, R_3=H, R_4=t-C_4H_9



29 R_1=t-C_4H_9, R_2=H, R_3=R_4=OCH_3

31 R_1=R_2=OCH_3, R_3=H, R_4=t-C_4H_9

The C–O adducts **24–27** contain 1,2,3- (720, 745 cm^{-1}) and 1,2,4-trisubstituted benzene rings (805, 855 cm^{-1}). In their EI-MS diagrams, peaks of primary fragment ions[4] with *m/z* 180 and 346 are prominent. The inspection of the ^1H NMR spectrum reveals that **24** have the methoxy group at meta to the *tert*-butyl group (δ 3.80), the terminal methyl (δ 0.9, triplet), and the methine group linked to O-7 of the quinone nucleus (δ 3.9–4.2). Whereas, adduct **27** has the methoxy group at para to the *tert*-butyl group (δ 3.73), the terminal methyl group (δ 1.10, doublet) which indicates the linkage position being C-14′, as well as the O-linked methine group (δ 4.0–4.3). The NMR spectrum of the 3:1 mixture of isomers **25** and **26** is well interpreted as the superposition of those expected for respective adducts. Neither MS nor NMR data could discriminate the coupling position in the side chain of **24** and **26**; however they were assumed to be C-8, referring to C–C adducts **28** and **30**.

In the IR spectrum of **28/29** are present IR bands of 1,2,3-tri- and 1,2,3,5-tetrasubstituted benzene rings (840, 870 cm^{-1}), while a mixture of **30** and **31** shows peaks due to a 1,2,4,5-tetrasubstituted benzene ring (780, 870 cm^{-1}) besides those of 1,2,3-trisubstituted benzene. In the EI-MS diagram of a mixture of isomers **28/29** are prominent the *m/z* 306 primary fragment (from **28**) together with the *m/z* 249 secondary fragment ion (306 – *tert*-butyl), and the *m/z* 221 primary fragment (from **29**); the ratio of peaks of *m/z* 249 and 221 is ca. 1:3. Also in the MS diagram of 5:1 mixture of isomers **30** and **31**, these fragment ions were observed with the *m/z* 249/221 peak ratio of 3:1. These fragment ions clearly indicate coupling positions in the side chains of C–C adducts. The salient feature of the ^1H NMR spectrum of the 1:1 isomer mixture of **28** and **29** is the simultaneous appearance of the two resonances due to two different terminal methyl groups (a triplet at δ 0.89 from **28** and a doublet at δ 1.1 from **29**) with the same integrated intensities together with the resonance of a proton of the methine group bound to the nucleus (δ 2.9). The spectrum of the 5:1 isomer mixture of **30** and **31** is the superposition of those expected for their structures.

Tables I and II summarize yields and ratios of 1:1 adducts produced by reactions of **5** and olefinic compounds employed in this work, respectively.

Discussion

Reactions between quinone **5** and methylene-interrupted olefins **6**, **8**, and **9** afford 1:1-adducts through dehydrogenation paths. On the other hand, methyl sorbate **7**, which has no active methylene group, reacts with quinone **5** to provide a conventional Diels–Alder product **13**. Then it is conceivable that, for the dehydrogenation–addition of alkenes with quinone **5**, the presence of a bisallylic methylene group is indispensable as an effective hydrogen donor. This may imply that conjugated intermediates derived from olefins are of important role in the rate-determining step of this reaction. No reaction was observed between the quinone **5** and methyl oleate under same conditions as reactions of **6** and **8**, excluding the concerted mechanism comprising the formation of allylic intermediates.

We can summarize the result of quinone dehydrogenation of olefins as follows. (1) The yields of 1:1 dehydrogenation adducts were lower in reactions of dienes, especially **6**, compared with that of triene **9**, which was due to the production of high molecular weight substances. (2) The ratio of C–C and C–O adducts was reversed from the triene case to the diene case; the C–C/C–O products ratio was 18/82 for **9**, 62/38 for **8**, and 97/3 for **6**. (3) Linkage positions in olefins were terminal positions of conjugated systems in possible intermediates, which again indicate the presence of conjugated intermediates. (4) The predominant orientation of C–C adducts were the 5- and 6-posi-

(4) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectroscopy of Organic Compounds*; Holden-Day: San Francisco, 1967.

Scheme II

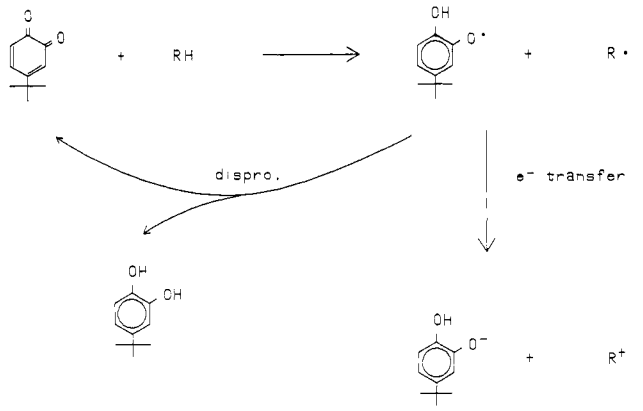
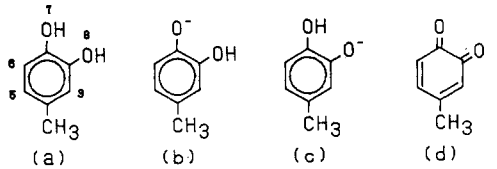


Table III. Frontier Electron Densities ($\times 10^3$) of 4-Methylcatechol and 4-Methyl-*o*-benzoquinone Calculated by an ab Initio Method



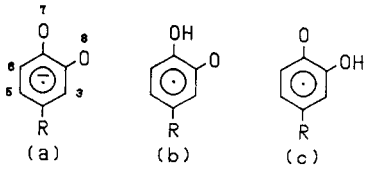
	species	position 3	5	6	7	8
$f^{(E)}$	a	127	222	146	351	261
	b	5	3	255	979	73
	c	240	270	7	85	987
$f^{(R)}$	a	287	321	306	202	156
	b	278	270	369	545	67
	c	368	264	253	74	540
	d	312	202	288	242	277

tions in the quinone nucleus for the triene reaction; however, no C-5-bound product was given in the diene case. For the reaction of **8**, C-3-bound adduct was not produced due to steric hindrance.

The common mechanism of dehydrogenation–addition of quinones and hydrogen donors includes the slow hydride ion transfer, giving the carbenium ion of the hydrogen donor as well as the quinol anion, which then couple to produce addition products.[2c] In some cases, the initial hydride-transfer process proceeds through two successive radical steps; i.e., the quinone abstracts a hydrogen atom to form the semiquinone and the free radical of the donor, and electron transfer occurs to result in the formation of the phenolate and the cation (Scheme II).[5] The free radical itself can be a significant reaction species in some quinone dehydrogenation reactions.[2f,h]

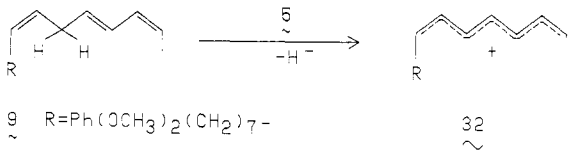
Accordingly, prior to analyzing the product distribution of present reactions, reactivities of possible reaction species were examined. First, molecular orbital calculation was carried out for 4-methylcatechol, its anion, and 4-methyl-*o*-benzoquinone by an ab initio STO-3G method[6]

Table IV. Spin-Density Distribution ($\times 10^3$) in *o*-Benzosemiquinones

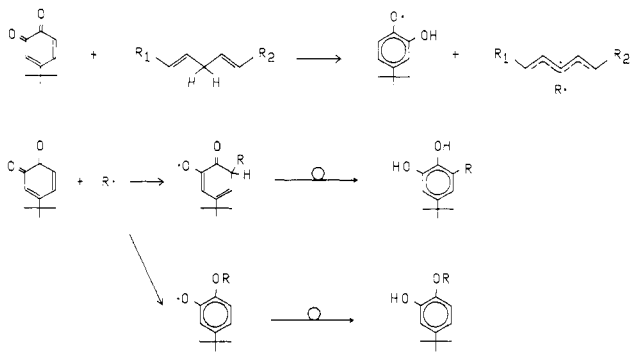


R	form	position 3	5	6	7	ref
H	anion (a)	29	139	29		8a
		26	127	26	164	8b
	neutral (b)	159	332	71		8a
	neutral (c)	71	71	159		8a
CH_3	anion (a)	26	137	52		8c

Scheme III



Scheme IV



as model compounds of 4-*tert*-butylcatechol and its derivatives. Table III summarizes the result of the calculation. On the other hand spin densities (ρ) in *o*-benzosemiquinone and 4-methyl-*o*-benzosemiquinone anions estimated from proton hyperfine splittings[8,9] are listed in Table IV. In the *o*-benzosemiquinone anion radical, the spin density at C-4 (ρ_4) or C-5 (ρ_5) is extremely high as compared with that at C-3 (ρ_3) or C-6 (ρ_6). Methyl substitution at C-4 increases ρ_5 and ρ_6 in the anion radical to a certain extent; however, the low value of ρ_3 is unaltered. Then the order of spin density may be $|\rho_5| \gg |\rho_6| > |\rho_3|$ for either semiquinone or its anion. The spin densities at O-7 (ρ_7) and O-8 (ρ_8) compare with ρ_5 in *o*-benzosemiquinone anion.

According to this information, two reaction paths may conform to the product distribution of the reaction between triene **9** and quinone **5** (Table II): first, the radical coupling of the semiquinone and the heptatrienyl radical derived through the hydrogen atom abstraction of the triene and second, the classical hydride ion transfer mechanism, i.e., electrophilic substitution of 1,7-disubstituted heptatrienyl cation **32** to the catecholate (Scheme III). Both paths are possible as long as the occurrence

(5) Becker, H.-D. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Wiley: London, 1974; pp 335–423.

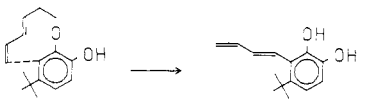
(6) The MO calculation program used was GAUSSIAN 80H (GAUSSIAN 80 HITAC version) in the computer center, University of Tokyo. The molecular coordinates were optimized by the use of MM2, Molecular Mechanics Calculation program Version 2, coded by Dr. E. Osawa; see: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134. For neutral 4-methylcatechol, the next highest occupied and the next lowest unoccupied orbital were in close proximity to the highest occupied and the lowest unoccupied molecular orbitals in energy, and then their contribution was taken into consideration for the estimation of frontier electron densities.[1,7]

(7) (a) Fukui, K.; Yonezawa, T.; Shingu, H. *J. Chem. Phys.* **1952**, *20*, 722–725. (b) Fleming, I. *Frontier Orbital and Organic Chemical Reactions*; Wiley: London, 1976. (c) Fukui, K.; Yonezawa, T.; Nagata, C.; Shingu, H. *J. Chem. Phys.* **1954**, *21*, 1433–1442.

(8) (a) Smith, I. C. P.; Carrington, A. *Mol. Phys.* **1967**, *12*, 439–448. (b) Felix, C.; Sealy, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 1555–1560. (c) Stone, T. J.; Waters, W. A. *J. Chem. Soc.* **1965**, 1488–1494.

(9) McConnell, H. M. *J. Chem. Phys.* **1956**, *24*, 632.

Scheme V



of C-5-bound C–C adducts is concerned (see Tables III and IV). However, the latter mechanism seems more plausible to explain the exclusive formation of C–O adducts. For this ionic reaction route, the reactivity of 4-methylcatechol anion is extremely high at O-7 and O-8 compared with those at C-3, C-5, and C-6 (Table III). The C-3-bound adduct was not formed presumably because of steric hindrance.

On the other hand, as previously mentioned, either the product distribution or the orientation of C–C adducts in reactions of quinone **5** with dienes **6** and **8** were different from that of the triene case to the great extent. The addition of the pentadienyl radical to the quinone may be the adequate reaction mechanism to account for these features. The reactivity of the quinone is predicted to be high at C-3, C-6, and O-8 positions for radical substitution and very low at C-5 position (Table III). Actually, in the reaction of **5** and **8**, the pentadienyl radical was detected by using the spin-trapping technique; the radical may be produced through the hydrogen atom abstraction from the bisallylic position (C-11) of **8** by quinone **5** (Scheme IV).[10] ESR spectra of spin-adducts observed in the reaction of **6** was complicated due to the presence of many types of radical species. The initially formed pentadienyl radical from **6** may be unstable and readily react with other molecules, giving oligomeric substances, which is parallel with the high yield of oligomeric products.

An alternative reaction mechanism is the thermally allowed [3,5] sigmatropic rearrangement[11] of the C–O adduct (Scheme V), which could be given through hydride ion transfer mechanism as in the triene reaction. This mechanism seems to consistent with decrease in the yield of the C–O adduct with the increasing reaction time. However, the production of oligomeric and even polymeric substances in the diene oxidation, especially in the reaction of **6**, favors the radical mechanism. Further, sigmatropic rearrangement usually occurs at high temperatures. Then we conclude that the radical addition is the most plausible path for dehydrogenation–addition of dienes and the quinone.

Also for the reaction of **9**, it is possible to expect the formation of conjugated heptatrienyl radical, since we found the stable spin adduct of a secondary alkyl radical, presumably of the heptatrienyl radical, in the reaction of **5** and 2(*E*),4(*E*),7(*Z*)-butadecatriene.[10] However, in view of the product distribution and the orientation in C–C adduct formation, the two-electron oxidation involving the hydride ion transfer seems more adequate than the radical addition. Further, the amount of oligomeric products is very small and the yield of 1:1 adducts is very high for the triene reaction, and these results add further support for the hydride-transfer mechanism. The reason why the reaction intermediates are different for triene **9** and dienes **6** and **8** is not clear. However, it is worth bearing in mind that the heptatrienyl cation is more stable than the pentadienyl cation, though in a strongly acidic medium.[12]

(10) Takada, M.; Oshima, R.; Tsuchiya, J.; Miyakoshi, T.; Seno, M., unpublished results.
(11) Frater, G.; Schmid, H. *Helv. Chim. Acta* **1970**, *53*, 269–289.
(12) (a) Sorensen, T. S. *J. Am. Chem. Soc.* **1965**, *87*, 5075–5084. (b) Deno, N. C.; Pittman, C. U., Jr.; Turner, J. O. *J. Am. Chem. Soc.* **1965**, *87*, 2153–2157. (c) Olah, G. A.; Pittman, C. U., Jr.; Sorensen, T. S. *J. Am. Chem. Soc.* **1966**, *88*, 2331–2332.

Experimental Section

IR spectra were recorded on a JASCO IRA-1 instrument. ^{1}H NMR spectra were obtained with a Varian EM-390 spectrometer at a resonance frequency of 90 MHz; decoupling experiments were performed to assign each resonance in complicated spectra. EI-MS data were obtained with a Hitachi RMU-3 spectrometer or a Hewlett-Packard 5985B GLC–MS system at the ionization energy of 70 eV.

Gas–liquid chromatography (GLC) was carried out with a Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector on a fused-silica capillary column (ULTRA SE54, 12.5 m × 0.20 mm i.d., thickness of liquid phase = 0.11 μm, Hewlett-Packard) using He as the carrier gas (linear velocity, 40 cm/s) in a split injection mode (split ratio, 100/1). For products of the reaction of **7**, the column temperature was 170 °C, the injection-port temperature was 270 °C, and the detector temperature was 220 °C. For those of **9**, they were set at 310 (for C–O adducts) or 330 (for C–C adducts), 340, and 330 °C, respectively.

The liquid chromatograph was constructed as described in a previous paper.[1] TSK G2000HG columns (60 × 2.2 cm × 2) and Gelko GL A110 and A120 columns (50 × 0.8 cm) were employed for gel-permeation chromatography (GPC) using chloroform as eluent. Columns packed with ODS silica, Develosil ODS-3 (3 μm, 150 × 8 mm i.d.) (column A), Develosil ODS-5 (5 μm, 250 × 8 mm i.d.) (column B), Unisil QC_{18} gel (5 μm, 250 × 8 mm i.d.) (column C), silica gel, Develosil 60-3, (250 × 8 mm i.d.) (column D), and Hitachi 3043Ag gel (10 μm, 10% silver nitrate loading, 250 × 7.6 mm i.d.) (column E) were used for preparative purpose. Analytical liquid chromatography (LC) operation was done on 150 × 4.5 mm i.d. columns packed with the above gels. Column packing was carried out by the slurry method.[13]

1,4-Pentadiene (**6**) and methyl sorbate (**7**) were purchased from Tokyo Kasei Kogyo Ltd., methyl linoleate (**8**) was purchased from Nakarai Chemical Co. Ltd., and all were used without further purification. 3-[8′(*Z*),11′(*E*),13′(*Z*)-Pentadecatrienyl]veratrole (**9**) was isolated from dimethylurushiol according to the method described in the literature.[3] 4-*tert*-Butyl-*o*-benzoquinone (**5**) was prepared from 4-*tert*-butylcatechol by the literature method,[14a] mp 65–66 °C (lit. mp 68 °C,[14b] 67–70 °C[14c]).

Reaction of 1,4-Pentadiene. A clear mixture of 1,4-pentadiene (1.65 g, 24 mmol) and **5** (1.32 g, 8.1 mmol) was allowed to stand at room temperature under N_2 for 28 h in the dark, during which the reaction was followed by analytical GPC. The excess 1,4-pentadiene was removed under reduced pressure below 50 °C. The residue was subjected to preparative GPC, and a fraction of 1:1 reaction products was collected: yield 12%. It was then methylated with dimethyl sulfate in dry acetone in the presence of K_2CO_3 at 60 °C for 5 h to yield 127 mg of product. It was resolved by reversed-phase liquid chromatography (RPLC) (column A; eluent, CH_3CN/H_2O, 8/2 (v/v); flow rate, 2.4 mL/min) and liquid–solid chromatography (LSC) (column D; eluent, *n*-hexane/ethyl acetate, 97.5/2.5 (v/v); flow rate, 2.0 mL/min), giving adducts **10** (2 mg), **11** (29 mg), and **12** (34 mg).

1-[2′(*E*),4′-Pentadienyloxy]-2-methoxy-4-*tert*-butylbenzene (10): IR (neat) 2980, 2920, 2870, 1610, 1590, 1520, 1460, 1415, 1365, 1270, 1250, 1220, 1180, 1150, 1040, 1005, 960, 905, 860, 805 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 7.07–6.71 (m, 3 H, Ar), 6.62–5.72 (m, 3 H, CH=C), 5.37–5.00 (m, 2 H, CH_2=C), 4.53 (d, 2 H, CH_2O, J = 4.5 Hz), 3.83 (s, 3 H, OCH_3), 1.28 (s, 9 H, *tert*-butyl). The retention time was 6.8 min on RPLC and 7.3 min on LSC.

3-[2′(*E*),4′-Pentadienyl]-4-*tert*-butylveratrole (11): IR (neat) 2980, 2920, 2870, 2840, 1650, 1600, 1490, 1410, 1365, 1330, 1270, 1220, 1090, 1040, 1020, 1005, 950, 895, 800, 710 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 6.85 and 6.75 (AB q, 2 H, Ar, J_{AB} = 8.9 Hz), 6.28 (dt, 1 H, H_c), 5.99 (dd, 1 H, H_d), 5.82 (dt, 1 H, H_e), 5.00 (dd, 1 H, H_b), 4.87 (dd, 1 H, H_a), 3.80 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.63 (d, 2 H, CH_{2f}, 1.37 (s, 9 H, *tert*-butyl), $J_{a,d}$ = 1.2 Hz, $J_{a,c}$ = 9.7 Hz, $J_{b,c}$ = 15.0 Hz, $J_{b,d}$ = 1.4 Hz, $J_{c,d}$ = 9.7 Hz, $J_{d,e}$ = 19.0 Hz, $J_{e,f}$ = 4.5 Hz; EI-MS, m/z (relative intensity) 260 (16,

(13) Yamauchi, Y.; Kumanotani, J. *J. Chromatogr.* **1981**, *210*, 512–515.
(14) (a) Goldschmidt, S.; Graff, F. *Ber.* **1928**, *61*, 1858–1869. (b) Teuber, H. J.; Straiger, G. *Ber.* **1955**, *88*, 802–827. (c) Buben, I.; Pospíšil, J. *Collect. Czech. Chem. Commun.* **1969**, *34*, 1991–2001.

M^+), 204 (100), 203 (44), 189 (53), 173 (23), 156 (42), 115 (58), 91 (32). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.84; H, 9.40. The retention time was 9.7 min on RPLC and 5.1 min on LSC.

6-[2′(*E*),4′-Pentadienyl]-4-*tert*-butylveratrole (12): IR (neat) 2980, 2920, 2870, 2840, 1650, 1600, 1590, 1495, 1465, 1410, 1360, 1310, 1290, 1250, 1220, 1120, 1090, 1010, 950, 925, 895, 845, 810, 770 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.68 (br s, 2 H), 6.31 (dt, 1 H, H_c), 6.04 (dd, 1 H, H_d), 5.76 (dt, 1 H, H_e), 5.05 (dd, 1 H, H_b), 4.91 (dd, 1 H, H_a), 3.83 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.36 (d, 2 H, CH_2), 1.28 (s, 9 H, *tert*-butyl), $J_{a,d}$ = 1.2 Hz, $J_{a,c}$ = 9.5 Hz, $J_{b,c}$ = 15.0 Hz, $J_{c,d}$ = 9.2 Hz, $J_{b,d}$ = 1.4 Hz, $J_{d,e}$ = 15.0 Hz, $J_{e,f}$ = 6.2 Hz; EI-MS, *m/z* (relative intensity) 260 (61, M^+), 245 (100), 203 (22), 18 9 (27), 173 (30), 140 (46), 115 (41), 91 (61). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 77.99; H, 9.42. The retention time was 9.7 min on RPLC and 5.6 min on LSC.

Reaction of Methyl Sorbate. A clear mixture of methyl sorbate (3.02 g, 24 mmol) and **5** (2.62 g, 16 mmol) was allowed to stand at room temperature under N_2 for 3 days in the dark. The reaction mixture was subjected to preparative GPC to collect a fraction of 1:1 adducts (75 mg 30% based on **5**). It contained exclusively the Diels–Alder adduct **13**, which was purified by LSC (column D; eluent, *n*-hexane/ethyl acetate, 96/4 (v/v)) and RPLC (column A; eluent, CH_3CN/H_2O, 9/1 (v/v)).

***trans*-2-[3′-Methoxy-3′-oxo-1′(*E*)-propenyl]-3-methyl-6(and 7)-*tert*-butyl-2,3-dihydro-1,4-benzodioxin (13)**: mp 72–73 °C; IR (KBr) 2970, 2920, 2870, 1725, 1660, 1590, 1520, 1505, 1310, 1280, 1200, 1170, 1090, 1020, 980, 930, 865, 815, 710 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.99 (dd, 1 H, CH_d), 6.99–6.73 (m, 3 H, Ar), 6.30 (d, 1 H, CH_e), 4.37 (dd, 1 H, CH_c), 3.88 (dq, 1 H, CH_b), 3.73 (s, 3 H, $COOCH_3$), 1.42 (d, 3 H, CH_{3a}), 1.25 (s, 9 H, *tert*-butyl), $J_{a,b}$ = 7.8 Hz, $J_{b,c}$ = 6.5 Hz, $J_{c,d}$ = 5.8 Hz, $J_{d,e}$ = 13.5 Hz; EI-MS, *m/z* (relative intensity) 290 (56, M^+), 275 (100), 259 (9), 108 (35), 93 (48), 91 (24), 67 (46). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.78; H, 7.89. GLC showed that this is a 1:1 mixture of isomers with a *tert*-butyl group attached at the 6- and 7-positions.

Reaction of Methyl Linoleate. A homogeneous mixture of methyl linoleate (0.95 g, 3.23 mmol) and **5** (0.53 g, 3.23 mmol) was allowed to stand at room temperature under N_2 for 3 days in the dark. It was methylated as described above and subjected to preparative GPC, and a fraction of 1:1 adducts was collected (320 mg, 22% based on **5**). It was resolved by RPLC (column B; eluent, CH_3CN/H_2O, 9/1 (v/v); flow rate, 2.0 mL/min) and LSC (column D; eluent, *n*-hexane/ethyl acetate, 97/3 (v/v); flow rate, 2.0 mL/min). From the second fraction of the RPLC, C–C adducts **14** and **15** (33 mg) and, from the third fraction **16** and **17** (30 mg) were obtained, respectively. They were separated by preparative LSC. C–O adducts **18–21** (28 mg) and benzodioxins **22** and **23** (10 mg) were obtained from the first fraction of RPLC, which were separated by LSC. The detail of this separation procedure is described elsewhere[3b] along with the following structural studies. Structures of these 1:1 adducts were determined by using a consecutive procedure based on partial reduction and reductive ozonolysis of formed monoenoic compounds.[3b] That is, each product was reduced with hydrazine to give monoolefinic compounds, which were separated by RPLC and analyzed by IR to elucidate the configuration. They were submitted to ozonolysis followed by derivatization of the resulting aldehydes into (2,4-dinitrophenyl)hydrazones.[3a] They were identified by RPLC comparing chromatograms of standard (2,4-dinitrophenyl)-hydrazones (DNP-hydrazones) of several normal alkanals; methyl 9-oxononanoate and methyl 12-oxododecanoate derived from methyl linoleate were also used as standards.

Methyl 13-(2′,3′-dimethoxy-5′-*tert*-butylphenyl)-9(*Z*),11-(*E*)-octadecadienoate (14): IR (neat) 2940, 2860, 1725, 1590, 1485, 1465, 1360, 1270, 1170, 1080, 980, 940, 840 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.67 (br s, 2 H, Ar), 6.20–5.19 (m, 4 H, CH=), 3.83 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.61 (s, 3 H, $COOCH_3$), 1.34–1.28 (m, 29 H, CH_2 and *tert*-butyl), 0.87 (t, 3 H, terminal CH_3, *J* = 6.0 Hz); EI-MS, *m/z* 490 (saturated M^+). Retention time was 34 min on RPLC and 19.6 min on LSC. Two monoolefinic components given by partial reduction were separated by column E; the front fraction exhibited an IR band due to a trans double bond (960 cm^{-1}), whereas the rear one showed no recognizable IR band in the range 900–1000 cm^{-1}, indicating that it has a cis double bond. After reductive ozonolysis followed by conversion into DNP-hydrazones, the front fraction showed in RPLC peaks ascribed to those of 11-methoxy-11-oxoundecanal, and the rear fraction gave those of 9-methoxy-9-oxononanal together with their aromatic fragments. This established the structure of **14**.

Methyl 9-(2′,3′-dimethoxy-5′-*tert*-butylphenyl)-10(*E*),12-(*Z*)-octadecadienoate (15): IR (neat) 2940, 2860, 1725, 1590, 1485, 1465, 1360, 1270, 1170, 1080, 980, 940, 840 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.67 (br s, 2 H, Ar), 6.21–5.20 (m, 4 H, CH=), 3.83 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.61 (s, 3 H, $COOCH_3$), 1.34–1.28 (m, 29 H, CH_2 and *tert*-butyl), 0.87 (t, 3 H, terminal CH_3, *J* = 6.0 Hz); EI-MS, *m/z* 490 (saturated M^+). Retention time was 34 min on RPLC and 20.6 min on LSC. The cis monoene derived by partial reduction afforded DNP-hydrazone of hexanal and the trans component that of octanal, respectively.

Methyl 9-(2′,3′-dimethoxy-5′-*tert*-butylphenyl)-10(*E*),12-(*E*)-octadecadienoate (16): IR (neat) 2920, 2850, 1720, 1580, 1490, 1465, 1360, 1270, 1170, 1080, 990, 840 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.67 (br s 2 H, Ar), 6.20–5.19 (m, 4 H, CH=), 3.83 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.60 (s, 3 H, $COOCH_3$), 1.36–1.28 (m, 29 H, CH_2 and *tert*-butyl), 0.87 (t, 3 H, terminal CH_3, *J* = 6.0 Hz); EI-MS, *m/z* 490 (saturated M^+). Retention time was 37 min on RPLC and 19.6 min on LSC. Partial reduction gave trans monoenes, from which DNP-hydrazones of hexanal and octanal were derived along with their aromatic fragments.

Methyl 13-(2′,3′-dimethoxy-5′-*tert*-butylphenyl)-9(*E*),11-(*E*)-octadecadienoate (17): IR (neat) 2920, 2850, 1720, 1580, 1490, 1465, 1360, 1270, 1170, 1080, 990, 840 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.67 (br s 2 H, Ar), 6.21–5.19 (m, 4 H, CH=), 3.83 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.60 (s, 3 H, $COOCH_3$), 1.36–1.28 (m, 29 H, CH_2 and *tert*-butyl), 0.87 (t, 3 H, terminal CH_3, *J* = 6.0 Hz); EI-MS, *m/z* 490 (saturated M^+). Retention time was 37 min on RPLC and 22.8 min on LSC. Trans monoenes derived by partial reduction afforded DNP-hydrazones of 9-methoxy-9-oxononanal and 11-methoxy-11-oxoundecanal together with their aromatic fragments.

Methyl 13-(2′-methoxy-4′-*tert*-butylphenoxy)-9(*E*),11-(*E*)-octadecadienoate (18): IR (neat) 2980, 2920, 2870, 1730, 1590, 1520, 1480, 1360, 1180, 1090, 990, 860, 810 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.73 (br s, 3 H, Ar), 6.20–5.19 (m, 4 H, CH=), 4.68–4.21 (m, 1 H, PhOCH), 3.78 (s, 3 H, OCH_3), 3.60 (s, 3 H, $COOCH_3$), 2.13 (t, 2 H, CH_2COO, *J* = 7.0 Hz), 1.29–1.27 (m, 29 H, CH_2 and *tert*-butyl), 0.86 (t, 3 H, terminal CH_3, *J* = 6.0 Hz). Retention time was 28 min on RPLC and 17 min on LSC. Hydrazine reduction yielded only a trans monoene component, which gave DNP-hydrazones of 9-methoxy-9-oxononanal and 11-methoxy-11-oxoundecanal along with their aromatic fragments.

Methyl 13-(2′-methoxy-5′-*tert*-butylphenoxy)-9(*E*),11-(*E*)-octadecadienoate (19): IR (neat) 2980, 2920, 2870, 1730, 1590, 1520, 1480, 1360, 1180, 1090, 990, 860, 810 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.73 (br s, 3 H, Ar), 6.22–5.19 (m, 4 H, CH=), 4.64–4.19 (m, 1 H, PhOCH), 3.76 (s, 3 H, OCH_3), 3.59 (s, 3 H, $COOCH_3$), 2.18 (t, 2 H, CH_2COO, *J* = 7.0 Hz), 1.26–1.24 (m, 29 H, CH_2 and *tert*-butyl), 0.86 (t, 3 H, terminal CH_3, *J* = 6.0 Hz). Retention time was 28 min on RPLC and 19 min on LSC. The partial reduction followed by reductive ozonolysis gave the similar result as in the case of **18**.

Methyl 9-(2′-methoxy-4′-*tert*-butylphenoxy)-10(*E*),12-(*E*)-octadecadienoate (20): IR (neat) 2980, 2920, 2870, 1730, 1590, 1520, 1480, 1360, 1180, 1090, 990, 860, 810 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.73 (br s, 3 H, Ar), 6.20–5.19 (m, 4 H, CH=), 4.68–4.21 (m, 1 H, PhOCH), 3.78 (s, 3 H, OCH_3), 3.60 (s, 3 H, $COOCH_3$), 2.13 (t, 2 H, CH_2COO, *J* = 7.0 Hz), 1.33–1.27 (m, 29 H, CH_2 and *tert*-butyl), 0.86 (t, 3 H, terminal CH_3, *J* = 6.0 Hz). Retention time was 28 min on RPLC and 20.7 min on LSC. A trans monoene component yielded by partial reduction gave DNP-hydrazones of hexanal and octanal along with their fragments.

Methyl 9-(2′-methoxy-5′-*tert*-butylphenoxy)-10(*E*),12-(*E*)-octadecadienoate (21): IR (neat) 2980, 2920, 2870, 1730, 1590, 1520, 1480, 1360, 1180, 1090, 990, 860, 810 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.70 (m, 3 H, Ar), 6.22–5.19 (m, 4 H, CH=), 4.64–4.19 (m, 1 H, PhOCH), 3.76 (s, 3 H, OCH_3), 3.59 (s, 3 H, $COOCH_3$), 2.13 (t, 2 H, CH_2COO, *J* = 7.0 Hz), 1.32–1.23 (m, 29 H, CH_2 and *tert*-butyl), 0.84 (t, 3 H, terminal CH_3, *J* = 6.0 Hz).

Retention time was 28 min on RPLC and 24 min on LSC. The similar result was given as in the case of **20** by partial reduction and reductive ozonolysis of the obtained monoene component.

2-[1′(*E*),3′(*Z*)-Octadienyl]-3-(8′-methoxy-8′-oxooctyl)-6(or 7)-*tert*-butyl-2,3-dihydro-1,4-benzodioxin (22): IR (neat) 2970, 2920, 2870, 1590, 1505, 1280, 1170, 1090, 1020, 990, 960, 860, 805 cm^{-1}. Retention time was 24 min on RPLC and 8.7 min on LSC. Partial reduction gave trans and cis monoene components. From the trans component DNP-hydrazones of heptanal and its fragment were derived, whereas those of pentanal and the aromatic fragment were derived from the cis monoene.

2-Pentyl-3-[11′-methoxy-11′-oxoundeca-1′(*E*),3′(*Z*)-dienyl]-6(or 7)-*tert*-butyl-2,3-dihydro-1,4-benzodioxin (23): IR (neat) 2970, 2920, 2870, 1730, 1590, 1505, 1280, 1170, 1090, 1020, 990, 960, 860, 805 cm^{-1}. Retention time was 24 min on RPLC and 9.5 min on LSC. The similar analysis was implemented as for **22**. DNP-hydrazones of 10-methoxy-10-oxodecanal and its fragment were identified from the trans monoene given by partial hydrogenation and those of 8-methoxy-8-oxooctanol and its fragment from the cis monoene.

Reaction of 3-[8′(*Z*),11′(*E*),13′(*Z*)-Pentadecatrienyl]veratrole. A homogeneous mixture of veratrole **9** (0.778 g, 2.3 mmol) and **5** (0.375 g, 2.3 mmol) was allowed to stand at room temperature under N_2 for 24 h in the dark. The methylated reaction mixture was subjected to preparative GPC, and a fraction of 1:1 adducts was collected in 63% yield. It was hydrogenated with hydrazine hydrate in ethanol at 40 °C for 98 h to yield 400 mg of product. It was separated by RPLC (column A; eluent, CH_3CN/CH_2Cl_2, 9/1 (v/v); flow rate, 2.0 mL/min) and LSC (column D; eluent, hexane/ethyl acetate, 97.5/2.5 (v/v); flow rate, 2.0 mL/min).

3-[8-(2′-Methoxy-4′-*tert*-butylphenoxy)pentadecyl]veratrole (24): IR (neat) 2940, 2860, 1600, 1580, 1520, 1480, 1460, 1360, 1265, 1220, 1180, 1140, 1090, 1040, 1010, 970, 910, 855, 805, 780, 745, 720 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.80–6.57 (m, 6 H, Ar), 4.21–3.90 (m, 1 H, PhOCH), 3.78 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 2.52 (t, 2 H, $PhCH_2$, J = 6.8 Hz), 1.28 (br, 33 H, CH_2 and *tert*-butyl), 0.90 (t, 3 H, CH_3, J = 6.5 Hz); EI-MS, m/z (relative intensity) 526 (2.6, M^+), 346 (22), 180 (72), 165 (100), 151 (34), 136 (42), 121 (11). Anal. Calcd for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 77.37; H, 10.56. Retention time was 16.0 min on RPLC and 8.0 min on LSC. GLC retention time was 3.94 s.

3-[14-(2′-Methoxy-4′-*tert*-butylphenoxy)pentadecyl]veratrole (25) and 3-[18-(2′-methoxy-5′-*tert*-butylphenoxy)-pentadecyl]veratrole (26) (3:1 mixture): IR (neat) 2940, 2860, 1600, 1580, 1520, 1480, 1460, 1360, 1265, 1220, 1180, 1145, 1090, 1040, 1010, 940, 905, 855, 805, 780, 745, 720 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.89–6.54 (m, 6 H, Ar), 4.34–4.02 (m, 1 H, PhOCH), 3.77 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 2.53 (t, 2 H, $PhCH_2$, J = 6.9 Hz), 1.23 (m, 33 H, CH_2 and *tert*-butyl); EI-MS, m/z (relative intensity) 526 (2.8, M^+), 346 (27), 180 (84), 165 (100), 151 (24), 136 (30), 121 (8). Anal. Calcd for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 77.54; H, 10.57. Retention time was 15.7 min on RPLC and 9.5 min on LSC. GLC retention time was 3.66 s and 5.34 s, respectively.

3-[14-(2′-Methoxy-5′-*tert*-butylphenoxy)pentadecyl]veratrole (27): IR (neat) 2940, 2850, 1600, 1580, 1480, 1460, 1360, 1265, 1220, 1180, 1145, 1090, 1010, 960, 885, 855, 805, 780, 745, 720 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.88–6.52 (m, 6 H, Ar), 4.30–4.02 (m, 1 H, PhOCH), 3.76 (s, 3 H, OCH_3), 3.73 (s, 6 H, OCH_3), 2.53 (t, 2 H, $PhCH_2$, J = 6.8 Hz), 1.26 (br s, 33 H, CH_2 and *tert*-butyl), 1.09 (d, 3 H, CH_3, J = 7.0 Hz); EI-MS, m/z (relative intensity) 526 (5, M^+), 346 (19), 180 (59), 165 (100), 151 (80), 136 (74), 121 (19). Anal. Calcd for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 77.49; H, 10.54. Retention time was 15.7 min on RPLC and 10.3 min on LSC. GLC retention time was 5.04 s.

3-[8-(1′,2′-Dimethoxy-5′-*tert*-butylphenyl)pentadecyl]veratrole (28) and 3-[14-(1′,2′-dimethoxy-5′-*tert*-butylphenyl)pentadecyl]veratrole (29) (1:1 mixture): IR (neat) 2920, 2850, 1580, 1485, 1465, 1360, 1310, 1270, 1210, 1170, 1120, 1080, 1010, 920, 870, 840, 805, 780, 745, 720 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.85–6.48 (m, 5 H, Ar), 3.80 (br s, 6 H, OCH_3) 3.72 (s, 6 H, OCH_3), 3.04–2.78 (m, 1 H, PhCH), 2.53 (t, 2 H, $PhCH_2$, J = 6.8 Hz), 1.53–1.24 (m, 33 H, CH_2 and *tert*-butyl), 1.10 (d, 1.5 H, CH_3, J = 7.0 Hz), 0.89 (t, 1.5 H, CH_3, J = 6.5 Hz); EI-MS, m/z (relative intensity) 540 (43, M^+), 306 (1), 249 (6.6), 221 (20.5), 207 (19), 191 (19), 151 (76), 136 (58), 91 (30), 57 (100). Retention time was 19 min on RPLC and 13.2 min on LSC. GLC retention time was 2.33 s and 3.19 s, respectively.

4-[8-(1′,2′-Dimethoxy-5′-*tert*-butylphenyl)pentadecyl]veratrole (30) and 4-[14-(1′,2′-dimethoxy-5′-*tert*-butylphenyl)pentadecyl]veratrole (31) (5:1 mixture): IR (neat) 2940, 2860, 1585, 1485, 1465, 1360, 1310, 1270, 1220, 1170, 1085, 1010, 920, 870, 840, 805, 780, 745, 720 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 6.86–6.50 (m, 5 H, Ar), 3.79 (br s, 6 H, OCH_3), 3.70 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.04–2.78 (m, 1 H, PhCH), 2.50 (t, 2 H, $PhCH_2$, J = 6.8 Hz), 1.40–1.22 (m, 33 H, CH_2 and *tert*-butyl), 1.10 (d, 0.5 H, CH_3, J = 6.3 Hz), 0.85 (t, 0.85 H, CH_3, J = 6.3 Hz); EI-MS, m/z (relative intensity) 540 (46 M^+), 306 (2.7), 249 (17), 221 (5.5), 207 (30), 192 (17), 151 (100), 136 (59), 91 (25), 57 (45). Anal. Calcd for $C_{35}H_{56}O_4$: C, 77.73; H, 10.45. Found: C, 77.65; H, 10.62. Retention time was 19 min on RPLC and 13.8 min on LSC. GLC retention time was 2.28 s and 3.13 s, respectively.

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Registry No. **5**, 1129-21-1; **6**, 591-93-5; **7**, 689-89-4; **8**, 112-63-0; **9**, 83532-40-5; **10**, 114582-87-5; **11**, 114582-88-6; **12**, 114582-89-7; **13** (R_1 = H, R_2 = *t*-C_4H_9), 114582-90-0; **13** (R_1 = *t*-C_4H_9, R_2 = H), 114583-06-1; **14**, 114582-91-1; **15**, 114582-92-2; **16**, 114582-93-3; **17**, 114582-94-4; **18**, 114582-95-5; **19**, 114582-96-6; **20**, 114595-18-5; **21**, 114582-97-7; **22**, 114583-07-2; **23**, 114595-19-6; **24**, 114582-98-8; **25**, 114582-99-9; **26**, 114583-00-5; **27**, 114583-01-6; **28**, 114583-02-7; **29**, 114583-03-8; **30**, 114583-04-9; **31**, 114583-05-0; 4-methylcatechol, 452-86-8; 4-methyl-1,2-benzenediol,1-ion(1−), 80132-22-5; 4-methyl-1,2-benzenediol,2-ion(1−), 114691-53-1; 4-methyl-*o*-benzoquinone, 3131-54-2.