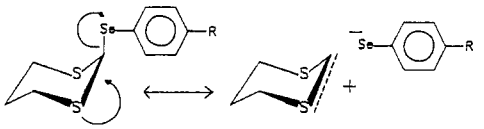
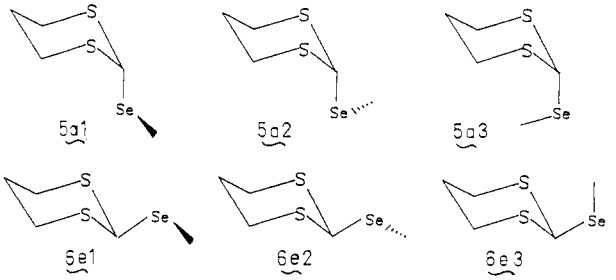
nation to account for the solvent dependence of the equilibria in **1**–**4**. We have already provided[2] evidence for the existence of significant $n_S \rightarrow \sigma^*_{C-Se}$ endo-anomeric interactions [and double-bond no-bond structures (see below)] in the axial conformers of 2-(arylseleno)-1,3-dithianes.



Such polar structures would be more stabilized in acetone than in methylene chloride, resulting in a greater anomeric effect in the former solvent. One also predicts a more negative entropy difference in acetone relative to methylene chloride, owing to imposed order, and this indeed is found to be the case. The results constitute evidence for the dominance of orbital interactions over dipolar interactions in controlling the conformations of 2-(arylseleno)-1,3-dithianes.

Finally, we comment on the entropy differences in the equilibria **1** ⇄ **2** and **3** ⇄ **4**. The rotamers for axial and equatorial 2-(arylseleno)-1,3-dithianes are shown below. Knowledge of the preferred rotamers about the exocyclic bond in acetals and related structures, derived from consideration of the exo-anomeric effect and steric effects,[6a,23,28] leads to the prediction that whereas only $\mathbf{5a}_1$ and $\mathbf{5a}_2$ in the axial isomer will be appreciably populated, all three rotamers in the equatorial isomer might be populated.[29] It is expected, however, that $\mathbf{6e}_1$ and $\mathbf{6e}_2$ will dominate over $\mathbf{6e}_3$. Hence, the equatorial isomer will be favored entropically by a maximum factor of $R \ln {}^3/_2$ (0.81 kcal mol^{-1}) owing to the entropy of mixing. The entropy differences observed for the equilibria in toluene, acetone, and methylene chloride are in excess of this value.



Conclusions

The conformational equilibria of 2-[(4-methoxyphenyl)seleno]-1,3-dithiane and the configurational equilibria of the corresponding 4,6-dimethyl-1,3-dithianes in various solvents have been examined. Plots of ln K vs $1/T$ using data from both types of experiments are linear and yield values for the enthalpy and entropy differences. The equilibrium data in toluene and chloroform are attributed to specific solvation effects. The preferential stabilization, in enthalpy terms, of the axial isomer in acetone vs methylene chloride, and its destabilization, in entropy terms, is interpreted in terms of the dominance of $n_S \rightarrow \sigma^*_{C-Se}$ orbital interactions over dipolar interactions, leading to a polar double-bond no-bond structure.

Acknowledgment. We thank Dr. M. J. Gresser for helpful discussion and the Natural Sciences and Engineering Research Council of Canada for financial support.

(28) Fuchs, B.; Schleifer, L.; Tartakovsky, E. *Nouv. J. Chim.* **1984**, *8*, 275.

(29) The $n_{Se} \rightarrow \sigma^*_{C-S}$ exo-anomeric interactions in 2-(arylseleno)-1,3-dithianes have been discussed previously.[2]

1,4-Dioxene in Organic Synthesis. 6.[1] Substituted 2-Vinyl-1,4-dioxenes: Useful Intermediates for the Synthesis of Highly Functionalized Compounds

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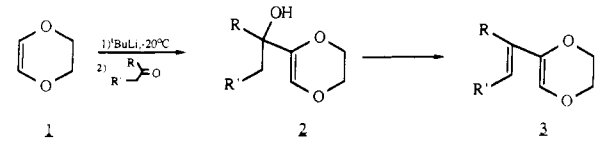
Substituted 2-vinyl-1,4-dioxenes **3**, prepared by dehydration of allylic alcohols **2** with MsCl–Et_3N or $SOCl_2$–Py, undergo a [4 + 2] cycloaddition reaction with various dienophiles. Exposure of **4**, obtained by Diels–Alder reaction with dimethyl acetylenedicarboxylate to DBU followed by acidic hydrolysis affords highly functionalized compounds.

As part of our general interest in synthetic applications of 2,3-dihydro-1,4-dioxin (1,4-dioxene) **1**, we have examined the use of this electron-rich olefin in the formation of carbon–carbon bonds with simultaneous introduction of useful functional groups. Thus, allylic alcohols **2**, easily obtained from 2-lithio-5,6-dihydro-1,4-dioxin and ketones

Scheme I

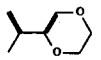
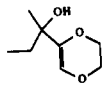
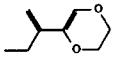
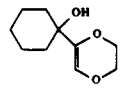
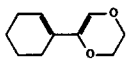
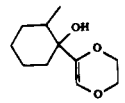
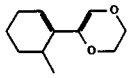
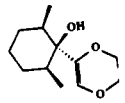
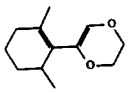
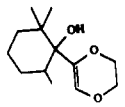
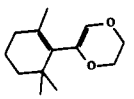


or aldehydes, undergo various transformations leading to α-hydroxymethyl ketones,[2] α,α′-dihydroxy ketones[3] and

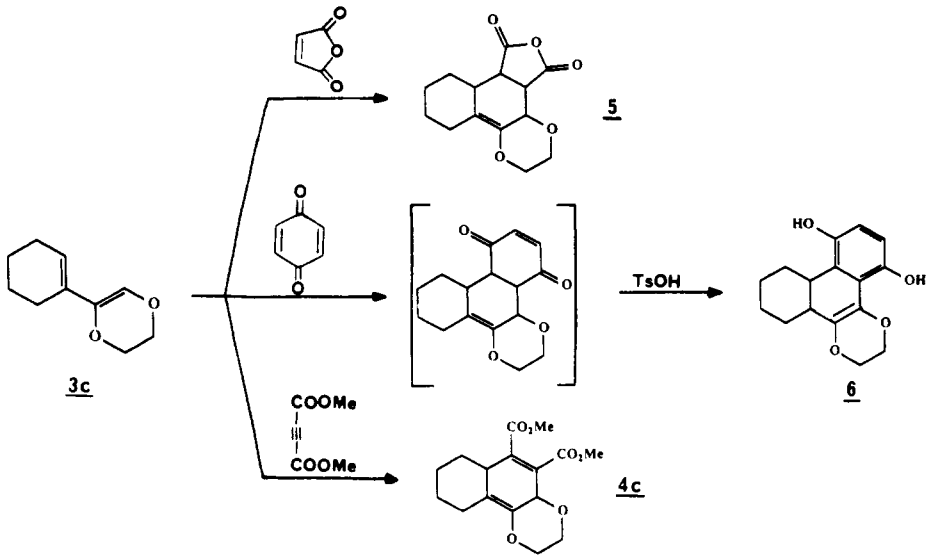
(1) For part 5, see: Bernasseau, J. M.; Bouillot, A.; Fêtizon, M.; Hanna, I.; Rose Maia, E.; Prangé, T. *J. Org. Chem.* **1987**, *52*, 1993.

0022-3263/88/1953-5672$01.50/0

Table I

ketone	allylic alcohol 2		yield, %	diene 3		yield, %
acetone		2a	53		3a	79
butanone		2b	66		3b	72
cyclohexanone		2c	66		3c	89
2-methyl-cyclohexanone		2d	55		3d	62
2,6-dimethylcyclohexanone		2e	63		3e	78
2,2,6-trimethylcyclohexanone		2f	81		3f	93

Scheme II



α-keto thioacetals.[4] We now report the preparation of substituted 2-vinyl-1,4-dioxenes **3** from **2** (Scheme I) and their reactivity with dimethyl acetylenedicarboxylate (DMAD) under Diels–Alder reaction conditions.

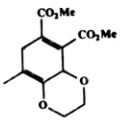
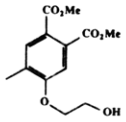
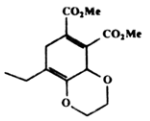
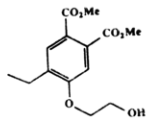
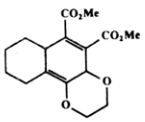
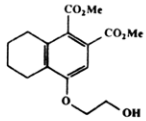
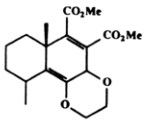
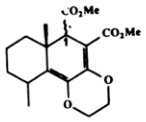
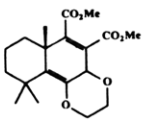
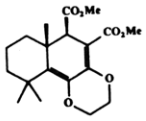
The use of 1,3-dialkoxy-, 1,4-dialkoxy-, and 2,3-dialkoxy-substituted butadienes in the Diels–Alder reaction is well documented and has been an area of great synthetic activity.[5] Thus, if the oxygen atoms are strategically positioned on the diene moiety, the cyclohexene obtained in the cycloaddition step may be conveniently elaborated into functionalized cyclohexanones. We anticipated that dienes **3**, which are equivalent to 1,2-dialkoxybutadienes, might well react with dienophiles to afford Diels–Alder products, which would be amenable toward further elaboration into a range of polyfunctionalized products. Consequently, a series of dienes **3** was prepared and their chemistry investigated.[6]

Results and Discussion

Dehydration of alcohols **2a–e** was smoothly effected with mesyl chloride (4 molar equiv)–triethylamine (8 molar equiv) in dichloromethane providing dienes **3a–e**. Attempts to apply this procedure to the more sterically hindered alcohol **2f** derived from 2,2,6-trimethylcyclohexanone proved unsuccessful. Thionyl chloride in pyridine was found to be more efficient, affording dienes **3d–f** from the corresponding alcohols in good to very good yields (Table I). However, it was found that the recently reported procedure using molecular sieves[7] was the method

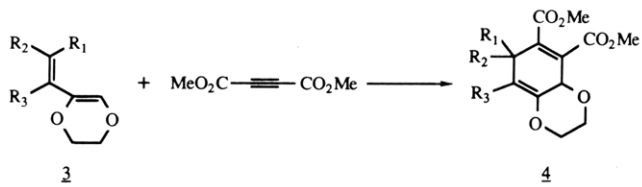
(2) Fétizon, M.; Hanna, I.; Rens, J. *Tetrahedron Lett.* **1985**, *26*, 3453.
(3) Fétizon, M.; Goulaouic, P.; Hanna, I. *Tetrahedron Lett.* **1985**, *26*, 4925.
(4) Fétizon, M.; Goulaouic, P.; Hanna, I. *Synthesis* **1987**, 503.
(5) For a general review on heterosubstituted dienes, see: Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753.
(6) After the completion of this work, it has been reported [4 + 2] cycloadditions of 2-ethenyl-5,6-dihydrodioxin (**3**, R = R′ = H) with tetracyanoethene, diethyl azodicarboxylate, phenyltriazolinedione, and diethyl mesoxalate. Potthoff, B.; Breitmaier, E. *Chem. Ber.* **1986**, *119*, 3204.
(7) Markgrat, J. H.; Greeno, E. W.; Miller, M. D.; Zako, W. J.; *Tetrahedron Lett.* **1983**, *24*, 241.

Table II

diene 3	cycloadduct		yield, %	treatment with DBU		yield, %
3a		4a	75		7	92
3b		4b	95		8	95
3c		4c	84		9	91
3e		4e	78		10a:1β 10b:1α	70[a]
3f		4f	16		11	86

[a] Yield for **10a** after base equilibration (see the Experimental Section).

Scheme III



of choice for the preparation of **3f**. Thus, treatment of a benzene solution of the allylic alcohol **2f** with molecular sieve (4 Å) at room temperature for 4 days gave diene **3f** in quantitative yield. Unexpectedly, attempts to apply this procedure to the dehydration of the other alcohols failed.

It is worthy of note that the dehydration of alcohols **2b** and **2d** either with MsCl–Et_3N or $SOCl_2$–Py afforded almost exclusively the less substituted dienes **3b** and **3d**, respectively.

The substituted 2-vinyl-1,4-dioxenes produced in this manner were subsequently employed in a number of Diels–Alder reactions. Thus **3c** smoothly reacted with maleic anhydride, 1,4-benzoquinone, and dimethyl acetylenedicarboxylate (DMAD) to yield the new heterotri- and -tetracycles **5**, **6**, and **4c** (Scheme II).

With an eye on synthetic applications, we have explored more thoroughly the reactivity of these dienes with DMAD. The cycloaddition of dienes **3** with DMAD would give **4** (Scheme III), which upon isomerization and hydrolysis to remove the dioxane ring should provide highly functionalized bicyclic compounds. These may be valuable intermediates for the synthesis of natural products.

With the less hindered dienes **3a**, **3b**, and **3c**, cycloadditions were carried out with 3 molar equiv of DMAD in refluxing benzene, affording **4a**, **4b**, and **4c**, respectively, in good yields. The reaction with **3e** only occurred at higher temperature (110 °C in sealed tube), leading to the corresponding cycloadduct in 70% yield (Table II). In contrast, the bulkier diene **3f** gave the desired adduct in only 16% yield under drastic conditions (150 °C in sealed ampoule under argon atmosphere for 30 h). This low yield is presumably due to the increased steric requirements for

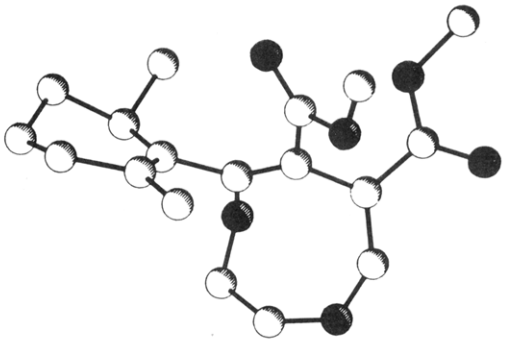


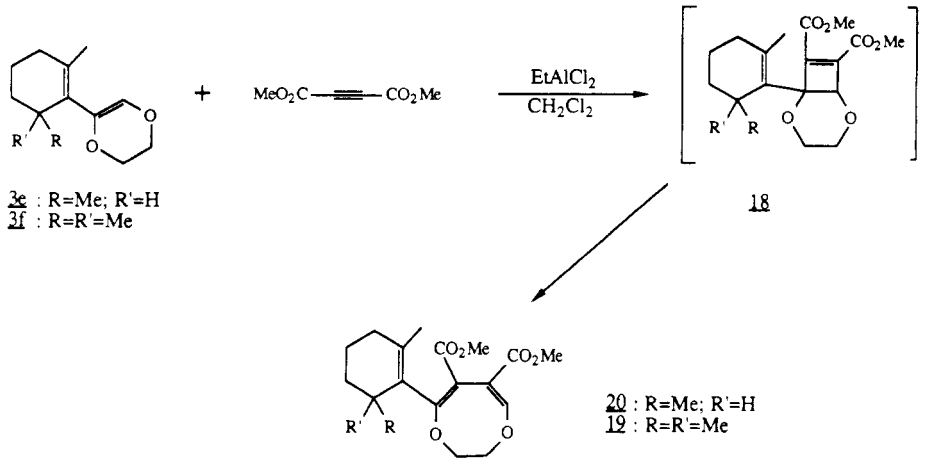
Figure 1. Molecular view of **20**. Black atoms denote oxygens.

the necessary cisoid geometry in the transition state of the Diels–Alder reaction together with the inherent instability of the DMAD at higher temperatures. Attempts made to effect this reaction at room temperature under high pressure (6 kbar) for 24 h failed.

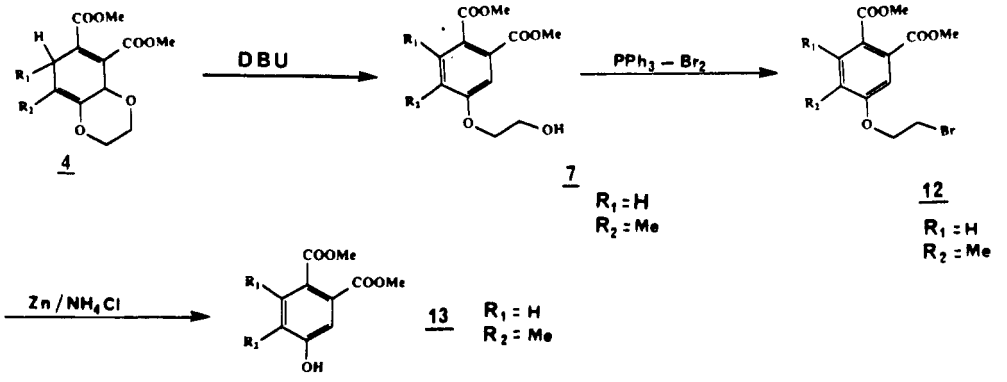
In an effort to promote the Diels–Alder reaction between **3f** and DMAD, we resorted to Lewis acid catalysis. Initial use of boron trifluoride etherate or tin(IV) chloride in methylene chloride at room temperature gave rise to a complex mixture of products. We next turned our attention to alkylaluminum chlorides.[8] Surprisingly, use of 1 equiv of diethylaluminum chloride (Et_2AlCl) or ethylaluminum dichloride ($EtAlCl_2$) in dichloromethane afforded compound **19** in quantitative yield. The structure of this compound was determined from its ^1H and ^{13}C NMR spectra. Specifically, the presence of the trimethylcyclohexene moiety was confirmed by comparison of the spectra of compounds **19** and **3f**. This finding can be rationalized in terms of a regioselective [2 + 2] cycloaddition of acetylenic diester on the carbon–carbon double bond of the dioxene moiety followed by opening of the resulting cyclobutene **18** (Scheme IV). In the same manner, diene **3e** afforded the adduct **20**. In order to

(8) Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, J. C.; Deutsh, E. A.; Cordova, R.; Price, R. T. *Tetrahedron* **1981**, *37*, 3927.

Scheme IV



Scheme V



confirm these unexpected structures, compound **20** was submitted to X-ray diffraction analysis which gave results shown in Figure 1.

X-ray Analysis. Suitable crystals of **20** were prepared by slow evaporation of a $MeOH/CHCl_3$ mixture. They were obtained as thin (0.05 mm) square plates (ca. 0.4 × 0.4 mm) with a tendency to aggregate as twinned crystals. A selected crystal was mounted on a four-circle automatic diffractometer, and 3095 structural factors were measured (see the Experimental Section) up to θ 65°. The system is monoclinic, space group $P2_1/c$ with $Z = 4$ and the following cell parameters: $a = 17.279$ (3) Å, $b = 6.666$ (4) Å, $c = 15.691$ (3) Å, and $\beta = 100.3°$ (1). The resolution of the structure was made by direct method.[9] Most of the atomic positions were located on the E map corresponding to the highest figure of merit. Six missing atoms were obtained after difference Fourier recycling procedure. The refinement of the structure was performed with an isotropic thermal factor, and then with anisotropic factors in a second step. In the last cycle, all the hydrogen atoms were located on Fourier-difference maps. The final agreement factor was $R = 8.3\%$ for 2126 structural factors taken above the 2σ background level and included in the last cycle. A final difference Fourier calculation indicated that the maximum residual peak was below 0.25 $e^-/Å^3$.

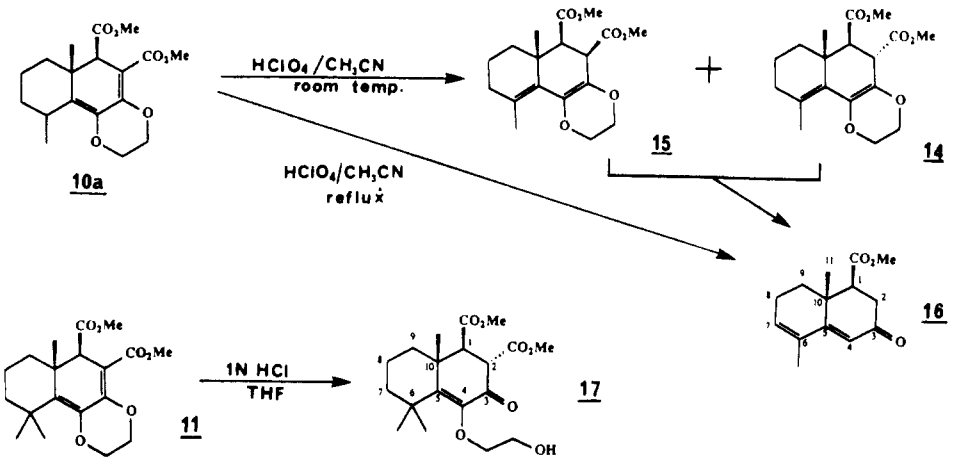
With the cycloadducts in hand, attention was focused on the isomerization of **4** to conjugated diene esters. Unexpectedly, treatment of **4a**, **4b**, and **4c** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing THF[10] afforded aromatic esters **7**, **8**, and **9**, respectively (Table II). The structures of these compounds were determined from their ^1H and ^{13}C NMR spectra (see the Experimental Section). Additional support for these structures was obtained through the cleavage of the phenyl ether into the corresponding phenol. For instance, compound **7** furnished **13** by a two-step conversion: bromination with PPh_3–Br_2 followed by reduction with zinc powder. Attempts to achieve this cleavage with acidic reagents (HCl–HOAc, BBr_3, or BCl_3) failed (Scheme V).

However, when the aromatization was prevented by the replacement of the C-10 hydrogen by a methyl group, isomerization of the carbon–carbon double bond occurred in a straightforward way. Thus, **4f** was treated with DBU in refluxing THF to give the pure isomer **11** in 87% yield. In contrast, treatment of **4e** under the same conditions afforded a mixture of diastereoisomers (**10a** and **10b**), which led after base-catalyzed equilibration (MeONa–MeOH) to the thermodynamically more stable isomer **10a** (Table II). Assignment of the stereostructures **10a**, **10b**, and **11** was mainly based on the analysis of ^1H and ^{13}C NMR spectra and on the fact that the ester group prefers an equatorial orientation. These structures were confirmed by further transformations.

At this stage, we anticipated that conjugated diene esters **10a** and **11**, which are equivalent to dienol ethers, would suffer hydrolysis, leading to the cleavage of the dioxane ring. In fact, treatment of conjugated diene ester **11** with aqueous 1 N HCl in acetone cleanly gave one product, which was assigned structure **17** on the basis of its spectral properties (Scheme VI). Specifically, the ^{13}C NMR spectrum of **17** contains resonances for three quaternary sp^2 carbons (δ 169.5, 171.5, 189.0) in agreement with the conjugated ketone and the esters groups. The ^1H NMR spectrum (200 MHz) shows a pair of doublets (1 H each)

(9) Germain, G.; Main, P.; Woolfson, M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368.
(10) Mori, K.; Watanabe, H. *Tetrahedron* **1986**, *42*, 273.

Scheme VI



centered at δ 3.23 and 3.97 and the 1α and 2β protons, respectively, with a coupling constant of 12 Hz, typical for a trans diaxial arrangement of the protons.

Acidic treatment *at room temperature* of diene **10a** promoted isomerization of double bonds, affording a separable mixture of isomers **14** and **15** in 65:35 ratio (Scheme VI). The spectral properties of these compounds are fully in accord with assigned structures. In particular, the NMR signals for the 1α and 2β protons of the major product **14** appear as two doublets at δ 2.77 and 3.64, respectively, with a coupling constant of 7 Hz, while those of the corresponding protons of **15** show as two broad singlets. Additional support for these assignments was obtained through the epimerization at C-2 of the minor isomer **15** with sodium methoxide in methanol to the thermodynamically more stable **14**.

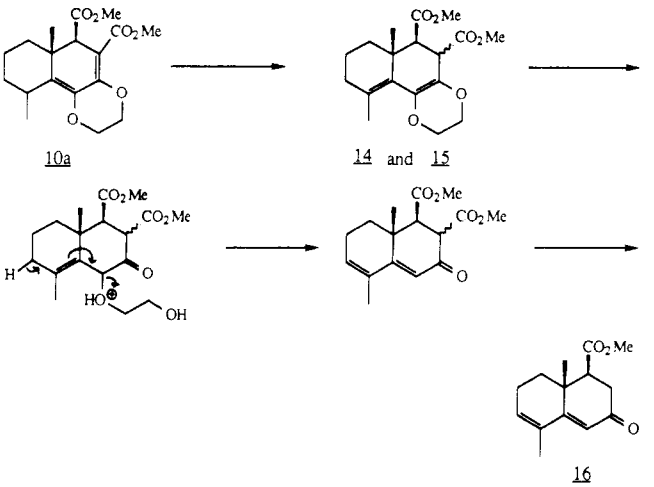
Although various acids (BCl_3, HCl, H_2SO_4, silica gel ...) can isomerize diene **10a** into **14** and **15**, use of perchloric acid in acetonitrile gave best results, the reaction being instantaneous.

Unexpectedly, when the reaction was carried out with 70% perchloric acid *in refluxing acetonitrile*, only one product was isolated or observed by TLC. Assignment of the structure **16** was established after careful analysis of the spectroscopic data. Thus, instead of the anticipated two methyl ester singlet resonances, the ^1H NMR spectrum of this product shows only one carbomethoxy singlet absorption at δ 3.63. The ^{13}C NMR spectrum displays only 14 carbon resonances, confirming the disappearance of the dioxene moiety. Moreover, the ^1H–^{13}C chemical shift correlation experiment provides additional support for the assignment of the structure **16**, especially for the CH_2 adjacent to the ketone function. On the other hand, the UV spectrum shows the maximum of an intensely absorbing bands at 291 nm in agreement with an heteroannular dienone chromophore (λ_{max}(calcd) = 298 nm).[11]

While it is premature to speculate on the detailed mechanism, conceptually at least the formation of **16** should proceed thorough isomers **14** and **15**. Transformation of these compounds into **16** could be explained by hydrolysis of the enol ether followed by elimination of ethylene glycol and subsequent decarboxylation as shown in Scheme VII.

In summary, substituted 2-vinyl-1,4-dioxenes **3** prepared in a straightforward manner from allylic alcohols **2** undergo [4 + 2] cycloadditions with various dienophiles. We have explored the Diels–Alder reaction of **3** with dimethyl acetylenedicarboxylate as a way of constructing highly functionalized compounds, which may be useful in the synthesis of natural products.

Scheme VII



Experimental Section

General Procedures. Solvents were dried by using standard methods; especially, tetrahydrofuran (THF) and diethyl ether were dried by distillation under nitrogen from sodium benzophenone ketyl. Flash chromatography was performed on 40–63-μm (400–230-mesh) silica gel 60. Melting points were measured with a Reichert apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 399 spectrometer as solutions in CCl_4. ^1H NMR spectra were recorded on a Varian T.60 or a Bruker W.P.200 spectrometers as solutions in $CDCl_3$. ^{13}C NMR were recorded on a Bruker W.P. 200 spectrometer as solutions in $CDCl_3$. Mass spectra were recorded on a R.10-10 NERMAG gamme 1000 spectrometer. UV spectra were recorded on a Shimadzu UV.240 spectrometer. Owing to their relative unstability, allylic alcohols **2** and dienes **3** were not submitted to microanalyses.

X-ray diffraction experiments were performed on a Philips PW 1100 automatic four-circle diffractometer operating with the Cu Kα radiation (λ 1.5418 Å) monochromated by graphite. The orientation matrix of the crystal was calculated from the angular settings of 25 randomly distributed reflections found in the range $10° < \theta > 25°$ and redefined by least-squares procedure. No significant decomposition was found during the data collection and no correction was applied. The reflections were scanned over a 1.2° angle width at a speed of 0.03° s^{-1}, and for each reflection, the background was deduced from two stationary measurements on both sides of the reflection. The intensities were reduced to F structural factors by means of standard Lorentz and polarization

(11) Scott, A. I. *Interpretation of the ultraviolet spectra of natural products*; Pergamon: New York, 1964; p 58.

corrections and considered as observed above the 2σ background level. No absorption correction was applied.

Condensation of 1,4-Dioxane with Ketones. General Procedure. *t*-BuLi (1.7 M/pentane, 12.9 mL, 22 mmol) was added to stirred 1,4-dioxene (1.9 g, 25 mmol, neat) cooled at −40 °C. After the resulting white precipitate was stirred for 2 h at −20 °C, a solution of the corresponding ketone (20 mmol) in THF (20 mL) was added at −40 °C over a period of 15 min. The mixture was stirred at −10 °C for 2 h before adding a solution of ammonium chloride. The mixture was extracted with ether, and the isolated crude material was purified by flash chromatography or distillation.

2-[2-(1,4-Dioxenyl)]-2-propanol (2a): purification by distillation; 53%; bp 72 °C (2 mmHg) [lit.[12] bp 69 °C (1.5 mmHg)]; IR 3610, 1680 cm^{-1}; ^1H NMR (200 MHz) δ 6.14 (s, 1 H), 4.0 (m, 4 H), 2.91 (br s, 1 H), 1.35 (s, 6 H); ^{13}C NMR δ 142.4 (s), 121.5 (d), 69.9 (s), 64.6 (t), 63.9 (t), 27.6 (q).

2-[2-(1,4-Dioxenyl)]-2-butanol (2b): purification by flash chromatography (eluant, ether/pentane, 1/2); 66%; oil; IR 3605, 1680 cm^{-1}; ^1H NMR (200 MHz) δ 6.03 (s, 1 H), 4.0 (m, 4 H), 2.14 (s, 1 H), 1.53 (q, J = 7.4 Hz, 2 H), 1.17 (s, 3 H), 0.76 (t, J = 7.4 Hz, 3 H); ^{13}C NMR δ 140.3 (s), 122.5 (d), 72.7 (s), 64.4 (t), 63.8 (t), 32.5 (t), 24.4 (q), 8.5 (q).

1-[2-(1,4-Dioxenyl)]-1-cyclohexanol (2c): purification by flash chromatography (eluant, ethyl acetate/pentane, 1/4); 66%; oil; IR 3600, 1680, 1450 cm^{-1}; ^1H NMR (60 MHz) δ 6.10 (s, 1 H), 4.0 (m, 4 H), 1.86 (s, 1 H), 1.6 (m, 10 H); ^{13}C NMR δ 141.3 (s), 122.1 (d), 70.7 (s), 64.1 (t), 63.5 (t), 34.4 (t), 25.3 (t), 21.5 (t).

2-Methyl-1-[2-(1,4-dioxenyl)]-1-cyclohexanol (2d): purification by flash chromatography (eluant, ethyl acetate/pentane, 1/8); 55%; oil; IR 3610, 1680, 1160 cm^{-1}; ^1H NMR (200 MHz) δ 6.19 (s, 1 H), 4.0 (m, 4 H), 2.0 (br s, 1 H), 1.5 (m, 9 H), 0.81 (d, J = 6.8 Hz, 3 H); ^{13}C NMR δ 141.4 (s), 122.1 (d), 73.1 (s), 64.1 (t), 63.5 (t), 36.7 (t), 35.5 (d), 29.2 (t), 25.6 (t), 21.0 (t), 15.3 (q).

2,6-Dimethyl-1-[2-(1,4-dioxenyl)]-1-cyclohexanol (2e): purification by flash chromatography (eluant, ethyl acetate/pentane, 1/20); 63%; oil; IR 3620, 1680 cm^{-1}; ^1H NMR (200 MHz) δ 5.97 (s, 1 H), 3.9 (m, 4 H), 1.4 (m, 9 H), 0.68 (d, J = 6.7 Hz, 6 H); ^{13}C NMR δ 138.6 (s), 123.2 (d), 75.7 (s), 64.2 (t), 63.6 (t), 36.7 (d), 29.3 (t), 25.6 (t), 15.6 (q).

2,2,6-Trimethyl-1-[2-(1,4-dioxenyl)]-1-cyclohexanol (2f): purification by flash chromatography (eluant, ethyl acetate/pentane, 1/20), mixture of two diastereoisomers, 81%; oil; IR major + minor: 3610, 1670 cm^{-1}; ^1H NMR (200 MHz) δ (major) 6.17 (s, 1 H), 4.0 (m, 4 H), 1.4 (m, 7 H), 0.98 (s, 3 H), 0.90 (s, 3 H), 0.88 (d, J = 8.4 Hz, 3 H); (minor) 6.12 (s, 1 H), 4.0 (m, 4 H), 1.5 (m, 8 H), 0.93 (s, 3 H), 0.90 (s, 3 H), 0.79 (d, J = 6.7 Hz, 3 H); ^{13}C NMR δ (major) 139.6 (s), 125.0 (d), 78.0 (s), 63.6 (t), 63.5 (t), 37.9 (s), 37.6 (t), 37.3 (d), 31.7 (t), 26.5 (q), 23.1 (q), 16.4 (q).

Substituted 2-Vinyl-1,4-dioxenes. General Procedure for 2a–c Affording 3a–c. To a stirred solution of **2** (15 mmol) and Et_3N (15 mL, 120 mmol) in dry dichloromethane (50 mL) under argon at 0 °C was added dropwise MsCl (4.0 mL, 60 mmol). After being stirred for 30 min, the mixture was poured into ice and extracted with ether. The isolated crude material was then purified by distillation or flash chromatography.

2-[2-(1,4-Dioxenyl)]-1-propene (3a): purification by distillation; 79%; bp 42–43 °C (4 mmHg); IR 1655, 1620, 1140 cm^{-1}; ^1H NMR (200 MHz) δ 6.20 (s, 1 H), 5.11 (br s, 1 H), 4.68 (br s, 1 H), 4.0 (m, 4 H), 1.72 (br s, 3 H); ^{13}C NMR δ 137.5 (s), 135.3 (s), 125.6 (d), 108.4 (t), 64.2 (t), 64.0 (t), 18.0 (q).

2-[2-(1,4-Dioxenyl)]-1-butene (3b): purification by disillation; 72%; bp 55–56 °C (6 mmHg); IR 1650, 1630, 1150 cm^{-1}; ^1H NMR (200 MHz) δ 6.25 (s, 1 H), 5.14 (s, 1 H), 4.72 (s, 1 H), 4.0 (m, 4 H), 2.56 (q, J = 7.4 Hz, 2 H), 1.04 (t, J = 7.4 Hz, 3 H); ^{13}C NMR δ 141.8 (s), 136.6 (s), 125.3 (d), 106.6 (t), 64.3 (t), 64.1 (t), 24.3 (t), 13.3 (q).

1-[2-(1,4-Dioxenyl)]-1-cyclohexene (3c): purification by flash chromatography (eluant, ethyl acetate/pentane, 5/95); 89%; oil; IR 1655, 1630 cm^{-1}; ^1H NMR (60 MHz) δ 6.13 (s, 1 H), 5.93 (t, J = 3 Hz, 1 H), 4.0 (m, 4 H), 1.7 (m, 6 H).

3-Methyl-2-[2-(1,4-dioxenyl)]-1-cyclohexene (3d). To a stirred solution of **2d** (1.00 g, 5.05 mmol) in pyridine (7 mL) at 0 °C under argon was added dropwise thionyl chloride (0.6 mL, 8.2 mmol). After 15 min, the mixture was poured into concentrated HCl (5 mL)–ice and extracted with ether. The residue was purified by flash chromatography (eluant, ethyl acetate/pentane, 2/98) to give pure **3d** (560 mg, 62%): oil; IR 1650, 1625, 1150 cm^{-1}; ^1H NMR (200 MHz) δ 6.15 (s, 1 H), 5.84 (t, J = 3 Hz, 1 H), 4.0 (m, 4 H), 1.5–2.0 (m, 7 H), 1.08 (d, J = 7.0 Hz, 3 H); ^{13}C NMR δ 136.6 (s), 134.6 (s), 123.5 (d), 120.3 (d), 64.0 (t), 29.8 (t), 26.8 (d), 25.2 (t), 20.3 (q), 17.4 (t).

2,6-Dimethyl-1-[2-(1,4-dioxenyl)]-1-cyclohexene (3e). To a stirred solution of **2e** (1.00 g, 4.72 mmol) in pyridine (7 mL) at 0 °C under argon was added dropwise thionyl chloride (0.5 mL, 6.8 mmol). After 1 h, the mixture was heated at 60 °C for 2 h and, after cooling, was poured into concentrated HCl (5 mL)–ice and extracted with ether. The residue was purified by flash chromatography (eluant, ethyl acetate/pentane, 5/95) to give pure **3e** (720 mg, 78%): oil; IR 1670, 1650, 1150 cm^{-1}; ^1H NMR (60 MHz) δ 5.77 (s, 1 H), 4.0 (m, 4 H), 1.76 (s, 3 H), 1.5 (m, 7 H), 0.97 (d, J = 7 Hz, 3 H); ^{13}C NMR δ 135.6 (s), 133.9 (s), 130.3 (s), 125.4 (d), 64.4 (t), 64.1 (t), 32.1 (t), 31.2 (d), 30.8 (t), 21.2 (q), 20.0 (t), 19.4 (q).

2,6,6-Trimethyl-1-[2-(1,4-dioxenyl)]-1-cyclohexene (3f). To a stirred solution of **2f** (4.40 g, 19.4 mmol) in dry benzene (300 mL) was added 4-Å molecular sieves (30 g). The mixture was then allowed to stand at room temperature for 3 days and then was filtered through Celite. The crude product was purified by flash chromatography (eluant, ethyl acetate/pentane, 5/95) to give the pure **3f** (3.75 g, 93%): oil; IR 1675, 1640, 1140 cm^{-1}; ^1H NMR (60 MHz) δ 5.66 (s, 1 H), 4.0 (m, 4 H), 1.70 (s, 3 H), 1.5 (m, 6 H), 1.00 (s, 6 H).

Diels–Alder Reaction of Dienes 3 with DMAD. General Procedure for 3a–c Affording 4a–c. A solution of **3** (3 mmol) and DMAD (1.28 g, 9 mmol) in dry benzene (8 mL) was stirred and heated under reflux under argon for 0.5–6 h. After cooling, the mixture was concentrated under vacuum and purified by flash chromatography.

3,6-Dihydro-5-methyl-3,4-(ethylenedioxy)-1,2-benzenedicarboxylic acid bis(methyl ester) (4a): (eluant, ether); 75%; mp 108–110 °C (pentane); IR 1735, 1265, 1170 cm^{-1}; ^1H NMR (200 MHz) δ 4.70 (td, J = 7 and 2 Hz, 1 H), 3.9–3.7 (m, 4 H), 3.66 (s, 3 H), 3.62 (s, 3 H), 3.05 (ddd, J = 24, 7, and 2 Hz, 1 H), 2.75 (ddd, J = 24, 7, and 2 Hz, 1 H), 1.56 (s, 3 H); ^{13}C NMR δ 166.8 (s), 166.0 (s), 140.9 (s), 134.7 (s), 131.5 (s), 110.1 (s), 69.0 (d), 68.2 (t), 66.4 (t), 51.9 (q), 32.8 (t), 13.1 (q); MS (EI), m/z (relative intensity) 268 (M^+, 8), 237 (13), 206 (18), 193 (100). Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.44; H, 5.94.

3,6-Dihydro-5-ethyl-3,4-(ethylenedioxy)-1,2-benzenedicarboxylic acid bis(methyl ester) (4b): (eluant, ethyl acetate/pentane, 1/4); 95%; mp 88–89 °C (pentane–ether); IR 1735, 1260, 1170 cm^{-1}; ^1H NMR (200 MHz) δ 4.80 (t, J = 7 Hz, 1 H), 4.0–3.7 (m, 4 H), 3.75 (s, 3 H), 3.71 (s, 3 H), 3.16 (dd, J = 23 and 7 Hz, 1 H), 2.84 (dd, J = 23 and 7 Hz, 1 H), 2.1 (m, 2 H), 0.93 (t, J = 7.5 Hz, 3 H); ^{13}C NMR δ 167.5 (s), 166.5 (s), 140.8 (s), 135.0 (s), 132.0 (s), 116.6 (s), 69.6 (d), 68.9 (t), 66.8 (t), 52.4 (q), 30.7 (t), 20.9 (t), 12.5 (q); MS (EI), m/z (relative intensity) 282 (M^+, 13), 251 (20), 220 (20), 207 (100). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.60; H, 6.36.

3,5,6,7,8,8a-Hexahydro-3,4-(ethylenedioxy)-1,2-naphthalenedicarboxylic acid bis(methyl ester) (4c): (eluant, ethyl acetate/pentane, 1/3); 84%; mp 116–117 °C (pentane–methanol); IR 1735, 1260, 1180 cm^{-1}; ^1H NMR (200 MHz) δ 4.80 (dd, J = 5 and 2 Hz, 1 H), 4.1–3.8 (m, 4 H), 3.80 (s, 6 H), 3.1–2.9 (m, 2 H), 2.3–2.1 (m, 1 H), 1.95–1.8 (m, 2 H), 1.7–1.0 (m, 5 H); ^{13}C NMR δ 167.2 (s), 166.0 (s), 141.2 (s), 139.6 (s), 129.1 (s), 118.3 (s), 69.5 (t), 68.7 (d), 66.5 (t), 51.8 (q), 40.3 (d), 33.7 (t), 26.6 (t), 25.9 (t), 24.5 (t); MS (EI), m/z (relative intensity): 308 ($M^{+\cdot}$, 9), 276 (32), 248 (26), 217 (100). Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.26; H, 6.50.

3,5,6,7,8,8a-Hexahydro-5,8a-dimethyl-3,4-(ethylenedioxy)-1,2-naphthalenedicarboxylic Acid Bis(methyl ester) (4e). A mixture of **3e** (230 mg, 1.18 mmol) and DMAD (0.50 g, 3.54 mmol) was heated under argon in a sealed tube at 110 °C for 30 h. After cooling, the mixture was chromatographed over silica gel (eluant, ethyl acetate/pentane, 1/5) to give pure **4e** (310 mg, 78%): IR 1735, 1250, 1190 cm^{-1}; ^1H NMR (200 MHz) δ 4.63 (d, J = 2 Hz, 1 H), 3.9–3.7 (m, 4 H), 3.64 (s, 6 H), 2.5–2.2 (m, 1

(12) Saylor, R. W.; Sebastian, J. F. *Synth. Commun.* **1982**, 579.

H), 2.0–1.4 (m, 6 H), 1.20 (d, J = 7.5 Hz, 3 H), 1.14 (s, 3 H); ^{13}C NMR δ 168.0 (s), 165.9 (s), 148.8 (s), 141.8 (s), 125.9 (s), 124.6 (s), 69.2 (t), 68.4 (d), 66.5 (t), 51.8 (q), 41.8 (s), 37.3 (t), 36.7 (t), 32.3 (d), 23.5 (q), 21.7 (q), 21.4 (t). Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.58; H, 7.28.

3,5,6,7,8,8a-Hexahydro-5,5,8a-trimethyl-3,4-(ethylenedioxy)-1,2-naphthalenedicarboxylic Acid Bis(methyl ester) (4f). A mixture of **3f** (1.40 g, 6.73 mmol) and DMAD (2.87 g, 20.2 mmol) was heated under argon in a sealed tube at 150 °C for 30 h. After cooling, the mixture was chromatographed over silica gel (eluant, ethyl acetate/pentane, 1/6) to give the starting material **3f** (840 mg, 60%) and the adduct **4f** (380 mg, 16%): IR 1740, 1250 cm^{-1}; ^{1}H NMR (200 MHz) δ 4.58 (s, 1 H), 4.0–3.7 (m, 4 H), 3.74 (s, 3 H), 3.72 (s, 3 H), 1.9–1.4 (m, 6 H), 1.30 (s, 3 H), 1.29 (s, 3 H), 1.20 (s, 3 H); ^{13}C NMR δ 168.3 (s), 165.9 (s), 149.4 (s), 143.9 (s), 127.8 (s), 126.3 (s), 67.5 (d), 67.5 (t), 66.2 (t), 52.1 (q), 40.4 (s), 40.4 (t), 34.7 (s), 33.7 (t), 31.6 (q), 30.3 (q), 28.8 (q), 17.8 (q). Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.05; H, 7.54.

Diels–Alder Reaction of 3c with Maleic Anhydride. Cycloadduct 5. A solution of **3c** (166 mg, 1 mmol) and maleic anhydride (98 mg, 1 mmol) in dry ether (2 mL) was left at 5 °C for 2 days. After removal of ether, the residue was chromatographed over silica gel (eluant, ethyl acetate/pentane, 1/4) to give the pure **5** (150 mg, 54%): mp 110–111 °C (pentane–methanol); IR 1800, 1200 cm^{-1}; ^{1}H NMR (200 MHz) δ 4.23 (br d, J = 8 Hz, 1 H), 4.0–3.8 (m, 4 H), 3.55 (t, J = 8 Hz, 1 H), 3.17 (dd, J = 8 and 5 Hz, 1 H), 2.8–2.7 (m, 1 H), 2.5–1.2 (m, 8 H); ^{13}C NMR δ 170.4 (s), 168.0 (s), 140.8 (s), 117.8 (s), 67.7 (t), 66.4 (t), 65.9 (d), 45.4 (d), 43.5 (d), 32.8 (d), 27.8 (t), 24.6 (t), 23.8 (t), 23.3 (t).

Diels–Alder Reaction of 3c with 1,4-Benzoquinone. Cycloadduct 6. A solution of **3c** (166 mg, 1 mmol) and 1,4-benzoquinone (108 mg, 1 mmol) in dry toluene (3 mL) was stirred and heated under reflux under argon for 2 h. After cooling and removal of toluene under reduced pressure, the residue was diluted in benzene (5 mL), and the mixture was refluxed with p-toluenesulfonic acid (2 mg) for 4 h. After cooling, a solution of sodium bicarbonate was added, and the product was extracted with ether. The isolated crude material was purified by flash chromatography (eluant, ethyl acetate/pentane, 1/4) to give the pure **6** (130 mg, 47%): IR 3625, 3480, 1675, 1470, 1250 cm^{-1}; ^{1}H NMR (60 MHz) δ 7.9 (s, 1 H) (OH), 6.44 (s, 2 H), 5.5 (m, 1 H) (OH), 4.2 (br s, 4 H), 3.1–2.9 (m, 2 H), 2.2 (m, 1 H), 1.7–1.2 (m, 7 H).

Treatment of Adducts 4 with DBU. General Procedure for 4a–c,f Affording 7–9, 11. A solution of **4** (1 mmol) and DBU (5 drops) in dry THF (10 mL) was refluxed under argon for 1–3 h. The mixture was then filtered over silica gel to remove DBU, eluting with ether. The crude was then purified by flash chromatography.

5-Methyl-4-(2-hydroxyethoxy)-1,2-benzenedicarboxylic acid bis(methyl ester) (7): (eluant, ethyl acetate/pentane, 1/1); 92%; mp 58–59 °C (pentane–ether); IR 3620, 1730, 1290 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.49 (s, 1 H), 6.96 (s, 1 H), 4.1–4.0 (m, 2 H), 3.95–3.85 (m, 2 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 2.7 (br s, 1 H), 2.16 (s, 3 H); ^{13}C NMR δ 168.4 (s), 167.4 (s), 158.9 (s), 132.1 (s), 131.5 (d), 129.7 (s), 122.8 (s), 110.6 (d), 69.7 (t), 60.8 (t), 52.4 (q), 52.1 (q), 15.8 (q). Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.49; H, 6.12.

5-Ethyl-4-(2-hydroxyethoxy)-1,2-benzenedicarboxylic acid bis(methyl ester) (8): (eluant, ethyl acetate/pentane, 3/2); 95%; IR 3620, 1730, 1290 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.57 (s, 1 H), 7.05 (s, 1 H), 4.1–4.0 (m, 2 H), 4.0–3.9 (m, 2 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.5 (br s, 1 H), 2.64 (q, J = 7.7 Hz, 2 H), 1.17 (t, J = 7.7 Hz, 3 H); ^{13}C NMR δ 168.4 (s), 167.3 (s), 158.4 (s), 135.2 (s), 131.9 (s), 129.7 (d), 122.6 (s), 110.5 (d), 69.5 (t), 60.5 (t), 52.2 (q), 52.0 (q), 22.6 (t), 13.1 (q). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.79; H, 6.40.

5,6,7,8-Tetrahydro-4-(2-hydroxyethoxy)-1,2-naphthalenedicarboxylic acid bis(methyl ester) (9): (eluant, ethyl acetate/pentane, 3/2); 91%; mp 76–77 °C (pentane–ether); IR 3620, 1735, 1280, 1235 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.17 (s, 1 H), 4.1–4.0 (m, 2 H), 3.95–3.85 (m, 2 H), 3.84 (s, 3 H), 3.80 (s, 3 H), 2.7–2.4 (m, 5 H), 1.8–1.6 (m, 4 H); ^{13}C NMR δ 169.8 (s), 166.1 (s), 156.4 (s), 135.6 (s), 131.8 (s), 128.2 (s), 125.5 (s), 108.6 (d), 69.5 (t), 60.7 (t), 51.9 (q), 26.3 (t), 23.3 (t), 21.9 (t), 21.4 (t). Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.29; H, 6.57.

1,5,6,7,8,8a-Hexahydro-5,5,8aβ-trimethyl-3,4-(ethylenedioxy)-1β,2-naphthalenedicarboxylic acid bis(methyl ester) (11): (eluant, ethyl acetate/pentane, 1/4); 86%; IR 1740, 1690, 1340 cm^{-1}; ^{1}H NMR (200 MHz) δ 4.3–3.9 (m, 4 H), 3.68 (s, 3 H), 3.66 (s, 3 H), 3.48 (s, 1 H), 1.6–1.3 (m, 6 H), 1.31 (s, 3 H), 1.18 (s, 3 H), 1.17 (s, 3 H); ^{13}C NMR δ 172.5 (s), 166.3 (s), 149.3 (s), 139.0 (s), 134.6 (s), 101.8 (s), 64.8 (t), 62.7 (t), 55.7 (d), 51.0 (q), 50.8 (q), 41.5 (t), 37.9 (t), 37.8 (s), 34.2 (s), 31.3 (q), 27.4 (q), 20.5 (q), 17.7 (t). Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.48; H, 7.59.

1,5,6,7,8,8a-Hexahydro-5,8aβ-dimethyl-3,4-(ethylenedioxy)-1β,2-naphthalenedicarboxylic Acid Bis(methyl ester) (10a) and 1,5,6,7,8,8a-Hexahydro-5,8aβ-dimethyl-3,4-(ethylenedioxy)-1α,2-naphthalenedicarboxylic Acid Bis(methyl ester) (10b). Treatment of **4e** with DBU afforded a mixture of two diastereoisomers **10a** and **10b**. These isomers are separable by flash chromatography; isomer **10b** appeared first and was partially transformed to the more stable isomer **10a** (TLC). However, equilibration with MeONa–MeOH was necessary to obtain pure **10a**. A solution of **4e** (1.00 g, 3 mmol) and DBU (0.5 mL) in dry THF (20 mL) was stirred and heated under reflux under argon for 7 h. The mixture was then filtered over silica gel to remove DBU, eluting with ether. The crude product was dissolved in methanol (10 mL), and a solution of NaOMe in methanol (10 mL) was added dropwise. The mixture was then stirred and heated under reflux under argon for 12 h. After cooling, the mixture was concentrated under vacuum, and water was added. After extraction with ether, the crude material was purified by flash chromatography (eluant, ethyl acetate/pentane, 1/3) to give the pure **10a** (720 mg, 70%).

10a: IR 1735, 1680, 1320 cm^{-1}; ^{1}H NMR (200 MHz) δ 4.3–4.0 (m, 4 H), 3.61 (s, 3 H), 3.52 (s, 3 H), 3.22 (s, 1 H), 2.85–2.7 (m, 1 H), 1.7–1.3 (m, 6 H), 1.12 (s, 3 H), 0.97 (d, J = 7.2 Hz, 3 H); ^{13}C NMR δ 172.5 (s), 166.6 (s), 154.6 (s), 136.4 (s), 131.2 (s), 98.0 (s), 65.8 (t), 63.5 (t), 52.9 (d), 51.2 (q) (2 C), 35.6 (s), 28.4 (t), 27.2 (d), 24.7 (q), 23.7 (t), 20.2 (q), 14.6 (t). Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 63.98; H, 7.07.

10b: IR 1740, 1690, 1340 cm^{-1}; ^{1}H NMR (200 MHz) δ 4.2–3.9 (m, 4 H), 3.54 (s, 3 H), 3.52 (s, 3 H), 3.37 (s, 1 H), 2.8–2.65 (m, 1 H), 1.7–1.3 (m, 6 H), 1.03 (d, J = 7.1 Hz, 3 H), 0.97 (s, 3 H); ^{13}C NMR δ 172.6 (s), 166.6 (s), 150.1 (s), 136.1 (s), 132.1 (s), 100.6 (s), 65.3 (t), 63.5 (t), 55.5 (d), 51.1 (q), 50.9 (q), 36.5 (s), 32.0 (t), 27.9 (d), 25.5 (t), 21.5 (q), 18.9 (q), 15.5 (t).

5-Methyl-4-(2-bromoethoxy)-1,2-benzenedicarboxylic Acid Bis(methyl ester) (12). To a suspension of triphenylphosphine (0.6 g, 2.3 mmol) in acetonitrile (3 mL) cooled in a ice bath was added bromine dropwise until the supernatant solution became slightly yellow. The ice bath was removed, and a solution of **7** (540 mg, 2 mmol) in acetonitrile (3 mL) was added. After the addition, the precipitate dissolved and the solvent was stripped off on a rotatory evaporator. The residue was suspended in ether, and the collected solids were washed five times with ether. The collected ether solution was concentrated, and the residue was purified by flash chromatography (eluant, ethyl acetate/pentane, 1/3) to give the pure **12** (440 mg, 67%): IR 1730, 1290, 1235 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.52 (s, 1 H), 6.95 (s, 1 H), 4.27 (t, J = 6 Hz, 2 H), 3.82 (s, 3 H), 3.80 (s, 3 H), 3.61 (t, J = 6 Hz, 2 H), 2.21 (s, 3 H); ^{13}C NMR δ 167.8 (s), 166.8 (s), 157.9 (s), 131.9 (s), 131.3 (d), 129.6 (s), 123.0 (s), 110.4 (d), 67.8 (t), 52.1 (q), 51.9 (q), 28.8 (t), 15.5 (q).

5-Methyl-4-hydroxy-1,2-benzenedicarboxylic Acid Bis(methyl ester) (13). To a stirred solution of **12** (152 mg, 0.46 mmol) in ethanol (3 mL) was added aqueous ammonium chloride (55 mg in 1 mL of water) and zinc powder (200 mg). The mixture was then stirred and heated under reflux for 1 h. After cooling, the mixture was decanted and filtered over Celite, eluting with ether to give pure **13** (91 mg, 88%): mp 140–141 °C (ether) (lit. mp 147–148 °C,[13] 142–143 °C[14]); ^{1}H NMR (200 MHz) δ 7.55 (s, 1 H), 6.99 (s, 1 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR δ 169.4 (s), 167.9 (s), 157.7 (s), 132.5 (d), 132.3 (s), 127.7 (s), 121.9 (s), 115.0 (s), 52.7 (q), 52.3 (q), 15.6 (q).

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1,2,6,7,8,8a-Hexahydro-5,8aβ-dimethyl-3,4-(ethylenedioxy)-1β,2α-naphthalenedicarboxylic Acid Bis(methyl ester) (14) and 1,2,6,7,8,8a-Hexahydro-5,8aβ-dimethyl-3,4-(ethylenedioxy)-1β,2β-naphthalenedicarboxylic Acid Bis(methyl ester) (15). To a stirred solution of **10** (180 mg, 0.53 mmol) in acetonitrile (15 mL) at 0 °C was added 6 drops of perchloric acid (70% aqueous); after 5 min the mixture was poured into aqueous $NaHCO_3$ and extracted with ether. The residue (mixture of **14** and **15**) was chromatographed (with ethyl acetate/pentane, 1/5, as eluant) to give pure **14** (90 mg) and **15** (48 mg) (**14** + **15**, 76%).

14: mp 116–117 °C (pentane); IR 1755, 1725, 1660, 1630, 1165, 1145 cm^{-1}; ^1H NMR (200 MHz) δ 4.2–3.9 (m, 4 H), 3.63 (d, J = 7.1 Hz, 1 H), 3.63 (s, 3 H), 3.53 (s, 3 H), 2.77 (d, J = 7.1 Hz, 1 H), 2.1–1.9 (m, 2 H), 1.85 (s, 3 H), 1.7–1.1 (m, 4 H), 1.11 (s, 3 H); ^{13}C NMR δ 171.5 (s), 171.2 (s), 133.6 (s), 131.3 (s), 127.0 (s), 124.8 (s), 64.2 (t), 63.5 (t), 53.3 (d), 52.0 (q), 51.2 (q), 44.3 (d), 37.2 (s), 34.7 (t), 34.2 (t), 25.4 (q), 21.8 (q), 18.5 (t); MS (EI), m/z (relative intensity) 336 (M^+, 100), 277 (59).

15: IR 1755, 1720, 1660, 1630, 1160, 1140 cm^{-1}; ^1H NMR (200 MHz) δ 4.14 (s, 4 H), 3.73 (s, 3 H), 3.65 (s, 3 H), 3.33 (br s, 1 H), 2.97 (br s, 1 H), 2.1–1.9 (m, 2 H), 1.88 (s, 3 H), 1.7–1.2 (m, 4 H), 1.17 (s, 3 H); ^{13}C NMR δ 173.2 (s), 172.4 (s), 133.8 (s), 130.5 (s), 127.6 (s), 125.1 (s), 64.4 (t), 63.7 (t), 53.3 (d), 52.2 (q), 51.5 (q), 44.5 (d), 37.0 (s), 34.7 (t), 34.4 (t), 26.5 (q), 22.0 (q), 18.5 (t).

1,2,3,7,8,8a-Hexahydro-5,8aβ-dimethyl-3-oxo-1β-naphthalenecarboxylic Acid Methyl Ester (16). To a stirred solution of **10** (110 mg, 0.30 mmol) in acetonitrile (10 mL) of 0 °C was added 4 drops of perchloric acid (70% aqueous); the mixture was then refluxed for 15 min and after cooling was poured into aqueous $NaHCO_3$ and extracted with ether. The residue was chromatographed (with ethyl acetate/pentane, 1/2, as eluant) to give pure **16** (59 mg, 76%): UV (ethanol) λ_{max} 291 (ε 2.08 × 10^4); IR 1740, 1675, 1630, 1160 cm^{-1}; ^1H NMR (200 MHz) δ 6.0 (m, 1 H), 5.92 (s, 1 H), 3.58 (s, 3 H), 3.85–2.75 (m, 2 H), 2.5 (m, 1 H), 2.4–2.2 (m, 2 H), 1.81 (br s, 3 H), 1.6–1.5 (m, 2 H), 1.23 (s, 3 H); ^{13}C NMR δ 197.0 (s), 173.9 (s), 157.5 (s), 134.6 (d), 131.3 (s), 121.0 (d), 51.7 (q), 51.4 (d), 36.4 (t), 35.8 (s), 32.6 (t), 24.0 (q), 23.2 (t), 19.8 (q).

1,2,3,5,6,7,8,8a-Octahydro-5,5,8aβ-trimethyl-3-oxo-4-(2-hydroxyethoxy)-1β,2α-naphthalenedicarboxylic Acid Bis(methyl ester) (17). To a stirred solution of **11** (40 mg, 0.11 mmol) in acetone (2 mL) was added 10 drops of 1 N HCl; after 3 days the mixture was poured into aqueous $NaHCO_3$ and extracted with ether to give pure **17** (30 mg, 71%): IR 1740, 1680, 1160 cm^{-1}; ^1H NMR (200 MHz) δ 3.98 (d, J = 12 Hz, 1 H), 3.9–3.6 (m, 4 H), 3.72 (s, 3 H), 3.66 (s, 3 H), 3.3 (m, 1 H), 3.23 (d, J = 12 Hz, 1 H), 1.7–1.3 (m, 6 H), 1.32 (s, 3 H), 1.29 (s, 3 H), 1.25 (s, 3 H); ^{13}C NMR δ 189.0 (s), 171.5 (s), 169.5 (s), 160.5 (s), 147.6 (s), 73.0 (t), 62.4 (t), 54.1, 53.4, 52.8, and 52.1 (2 d and 2 q), 39.2 (t), 38.5 (s), 36.3 (s), 35.1 (t), 31.0 (q), 29.2 (q), 22.7 (q), 16.7 (t).

Cycloadduct 19. $EtAlCl_2$ (1.0 M/hexane, 1 mL, 1 mmol) was added to a stirred solution of **3f** (208 mg, 1 mmol) and DMAD (426 mg, 3 mmol) in dry dichloromethane (5 mL) cooled at −50 °C under argon. The mixture was allowed to stand at room temperature for 4 h and then poured into water and extracted with ether. The crude was purified by flash chromatography (eluant, ethyl acetate/pentane, 1/4) to give pure **19** (320 mg, 90%): mp 106–108 °C (methanol); IR 1720, 1620, 1100 cm^{-1}; ^1H NMR (200 MHz) δ 7.48 (s, 1 H), 4.8 (m, 1 H), 4.0–3.8 (m, 2 H), 3.6 (m, 1 H), 3.54 (s, 3 H), 3.53 (s, 3 H), 1.9 (m, 2 H), 1.7–1.2 (m, 4 H), 1.45 (s, 3 H), 1.03 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR δ 168.4 (s), 167.8 (s), 158.2 (s), 157.6 (d), 134.7 (s), 132.8 (s), 121.4 (s), 104.7 (s), 64.6 (t), 60.9 (t), 51.6 (q), 51.5 (q), 39.2 (t), 33.5 (s), 31.9 (t), 29.0 (q), 28.0 (q), 20.8 (q), 18.4 (t). Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.19; H, 7.43.

Cycloadduct 20. $EtAlCl_2$ (1.0 M/hexane, 1 mL, 1 mmol) was added to a stirred solution of **3e** (194 mg) and DMAD (426 mg, 3 mmol) in dry dichloromethane (5 mL) cooled at −50 °C under argon. The mixture was allowed to stand at room temperature for 4 h and then poured into water and extracted with ether. The crude product was purified by flash chromatography (eluant, ethyl acetate/pentane, 1/4) to give pure **20** (290 mg, 84%): mp 74–76 °C (methanol); IR 1720, 1620, 1110 cm^{-1}; ^1H NMR (200 MHz) δ 7.60 (s, 1 H), 4.9 (m, 1 H), 4.1–3.9 (m, 2 H), 3.66 (s, 3 H), 3.65 (s, 3 H), 3.6 (m, 1 H), 2.4 (m, 1 H), 2.0 (m, 2 H), 1.8–1.2 (m, 4 H), 1.60 (s, 3 H), 1.07 (d, J = 7.0 Hz, 3 H); ^{13}C NMR δ 168.3 (s), 167.8 (s), 157.7 (d), 157.1 (s), 135.1 (s), 129.9 (s), 121.4 (s), 103.9 (s), 64.4 (t), 61.4 (t), 51.5 (q), 51.4 (q), 31.9 (t), 30.8 (t), 30.2 (q), 20.5 (d), 19.9 (t), 19.4 (q). Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.07; H, 7.12.

Registry No. **2a**, 83726-24-3; **2b**, 116809-77-9; **2c**, 101823-09-0; **2d**, 116809-78-0; **2e**, 116840-80-3; *cis*-**2f**, 116809-79-1; *trans*-**2f**, 116809-80-4; **3a**, 116809-81-5; **3b**, 116809-82-6; **3c**, 116809-83-7; **3d**, 116809-84-8; **3e**, 116809-85-9; **3f**, 116809-86-0; **4a**, 116809-87-1; **4b**, 116809-88-2; **4c**, 116809-89-3; **4e**, 116809-90-6; **4f**, 116809-91-7; **5**, 116809-92-8; **6**, 116809-93-9; **7**, 116809-94-0; **8**, 116809-95-1; **9**, 116809-96-2; **10a**, 116809-97-3; **11**, 116809-98-4; **12**, 116809-99-5; **13**, 22481-13-6; **14**, 116810-00-5; **15**, 116907-50-7; **16**, 116810-01-6; **17**, 116810-02-7; **19**, 116810-03-8; **20**, 116810-04-9; DMAD, 762-42-5; 1,4-dioxene, 543-75-9; acetone, 67-64-1; butanone, 78-93-3; cyclohexanone, 108-94-1; 2-methyl-cyclohexanone, 583-60-8; 2,6-dimethylcyclohexanone, 766-42-7; 2,2,6-trimethylcyclohexanone, 2408-37-9; maleic anhydride, 108-31-6; 1,4-benzoquinone, 106-51-4.

Supplementary Material Available: Tables of positional parameters, thermal parameters, bond distances, and bond angles for **20** (4 pages). Ordering information is given on any current masthead page.