ammonium chloride (20 mL) and ether (20 mL) and was shaken. The organic layer was separated and was extracted with a saturated solution of sodium bicarbonate (3 × 10 mL). The aqueous layer was acidified with 3 M hydrochloric acid and extracted with ether (3 × 30 mL). The combined ether extract was dried and the solvent was removed in vacuo to give 2.60 g (88%) of **12h** as an oil. This material was dissolved in methanol (200 mL) and the solution was stirred for 24 h under one atmosphere of hydrogen with 5% palladium-on-carbon (0.26 g) as catalyst. The suspension was filtered through Celite, and the filtrate was concentrated in vacuo to give 2.4 g (91%) of the saturated acid as an oil. This was dissolved in benzene (200 mL) containing benzoic acid (12 mg), and the solution was refluxed for 24 h under 4Å molecular sieves. After removal of the solvent in vacuo, the residual oil was purified by chromatography (40% ethyl acetate in hexane) to give 1.96 g (85%) of **16**: IR (neat) 1740, 1460, 1380, 1180, 1080 cm^{-1}; NMR ($CDCl_3$) δ 4.34 (m, 1 H), 4.24, 4.22 (2 s, 0.5 H, 0.5 H), 3.52, 3.50, 4.99 (3 s, 1.5 H, 3 H, 1.5 H), 2.7–1.5 (m, 5 H), 1.30, 1.22 (2 d, 1.5 H, 1.5 H), 0.94, 0.92 (2 s, 1.5 H, 1.5 H), 0.84 (s, 3 H); MS, *m/e* 199.133 ($M^+ - OCH_3$) (calcd for $C_{11}H_{19}O_3$ 199.133).

Acknowledgment. Financial support was provided by the National Institutes of Health (Grant No. AI 10964). P.R.J. gratefully acknowledges the Nicholas L. Tartar Fund for a fellowship.

Registry No. 1, 3724-65-0; 1 (lithium dianion), 83439-40-1; 2, 80-59-1; 2 (lithium dianion), 92186-60-2; 3, 111-71-7; 4, 100-52-7; 5, 78-84-2; 6, 18208-39-4; 7, 67-64-1; 8, 120-92-3; 9, 16184-79-5; 10, 87395-22-0; 11a, 56949-93-0; 11a (3,5-dinitrobenzoate), 92186-61-3; 11b, 92186-64-6; 11b (3,5-dinitrobenzoate), 92186-65-7; 11c, 56949-94-1; 11c (3,5-dinitrobenzoate), 92186-68-0; 11d, 92186-70-4; 11d (3,5-dinitrobenzoate), 92186-71-5; 11e, 92186-74-8; 11e (3,5-dinitrobenzoate), 92186-75-9; 11f, 92186-78-2; 11f (3,5-dinitrobenzoate), 92186-79-3; 11g, 92186-82-8; 11g (3,5-dinitrobenzoate), 92186-83-9; 11h, 92186-85-1; 11h (3,5-dinitrobenzoate), 92186-86-2; 11i, 92186-88-4; 11i (3,5-dinitrobenzoate), 92186-89-5; 11j, 92186-92-0; 11j (3,5-dinitrobenzoate), 92186-93-1; 11k, 92186-96-4; 11k (3,5-dinitrobenzoate), 92186-97-5; 11l, 92187-00-3; 11l (3,5-dinitrobenzoate), 92187-01-4; 12a, 92186-62-4; 12a (3,5-dinitrobenzoate), 92186-63-5; 12b, 92186-66-8; 12b (3,5-dinitrobenzoate), 92186-67-9; 12c, 72853-47-5; 12c (3,5-dinitrobenzoate), 92186-69-1; 12d, 92186-72-6; 12d (3,5-dinitrobenzoate), 92186-73-7; 12e, 92186-76-0; 12e (3,5-dinitrobenzoate), 92186-77-1; 12f, 92186-80-6; 12f (3,5-dinitrobenzoate), 92186-81-7; 12g, 92186-84-0; 12g (3,5-dinitrobenzoate), 92219-75-5; 12h, 92187-05-8; 12h (3,5-dinitrobenzoate), 92186-87-3; 12i, 92186-90-8; 12i (3,5-dinitrobenzoate), 92186-91-9; 12j, 92186-94-2; 12j (3,5-dinitrobenzoate), 92186-95-3; 12k, 92186-98-6; 12k (3,5-dinitrobenzoate), 92186-99-7; 12l, 92187-02-5; 12l (3,5-dinitrobenzoate), 92187-03-6; 15, 92187-04-7; trimethyl orthoformate, 149-73-5.

The Synthesis and Selected Chemistry of 6-Alkyl-6-carbalkoxy- and 6-Alkyl-6-(aminocarbonyl)-2,4-cyclohexadien-1-ones and Cyclohexadienone Ketals

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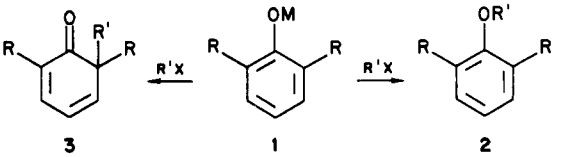
The preparation of several 6-alkyl-6-carbalkoxy-2,4-cyclohexadien-1-ones and corresponding C(1) ketals is described. Birch reduction–alkylation of methyl 2-methoxybenzoates gives 6-alkyl-6-carbomethoxy-1-methoxy-1,4-cyclohexadienes **4a–e** and **5a–d**, and these are converted to bromo ketals **12** and **13**, respectively, by treatment with *N*-bromoacetamide in methanol. Base-catalyzed dehydrobrominations of the bromo ketals produce 2,4-cyclohexadien-1-one dimethyl ketals **15** and **16**; acid-catalyzed ketal hydrolysis gives the title 2,4-cyclohexadienones **17** and **18**. Alternatively, acid-catalyzed enol ether hydrolysis of **4** and **5** gives 2-alkyl-2-carbomethoxy-3-cyclohexen-1-ones **19** and **20**; allylic bromination–dehydrobromination of **19** and **20** (*N*-bromosuccinimide) gives **17** and **18**. Analogous processes with *N,N*-diethylbenzamide derivatives are discussed. Diels–Alder reactions of the 2,4-cyclohexadienones provide a route to bicyclo[2.2.2]oct-5-en-2-ones **29**, from which triplet-sensitized oxa-di-π-methane photorearrangements give tricyclo[3.2.1.$0^{2,8}$]octan-3-ones **30**. The incorporation of optical activity by reduction–alkylation of the *d*-menthol ester of *o*-anisic acid is detailed.

The 2,4-cyclohexadien-1-one ring system embodies a potentially versatile array of functionality in a compact, stereochemically defined environment. Reactions of 2,4-cyclohexadienones include (1) cycloadditions in which the diene unit functions as a two-electron or four-electron component, (2) photochemical rearrangements to diene ketene derivatives and bicyclo[3.1.0]hex-3-en-2-ones, and (3) nucleophilic, electrophilic, and radical additions involving 1,2-, 1,4-, and 1,6-processes. Despite this vast potential for reactivity, 2,4-cyclohexadienones are only occasionally used in multistep organic synthesis. Most likely this situation is a result of an absence of efficient and general methods for the preparation of 2,4-cyclohexadienones.

Carbon alkylation of the alkali metal salts of phenols, **1**, is the most expeditious route to 2,4-cyclohexadienones. Although formation of alkyl aryl ethers, **2**, is favored in



3 **1** **2**

polar or protic solvents, substantial carbon alkylation can occur under nonhomogeneous conditions in hydrocarbon solvents.[1] Only the most reactive alkylation reagents (e.g., methyl iodide, allylic and benzylic halides) are useful under

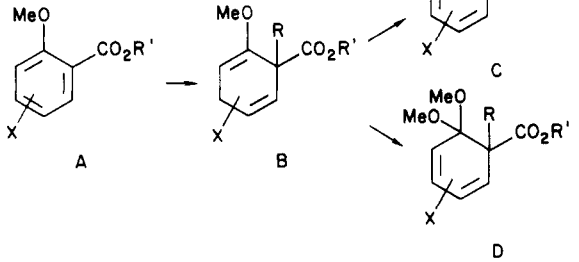
(1) (a) Curtin, D. Y.; Dybvig, D. H. *J. Am. Chem. Soc.* **1962**, *84*, 225. (b) Miller, B. *J. Am. Chem. Soc.* **1965**, *87*, 5115. (c) Miller, B. *J. Org. Chem.* **1970**, *35*, 4262. (d) Schultz, A. G.; Dittami, J. P.; Myong, S. O.; Sha, C.-K. *J. Am. Chem. Soc.* **1983**, *105*, 3273.

0022-3263/84/1949-4429$01.50/0

these conditions, and an even greater strategic limitation is that only symmetrical 2,6-disubstituted phenols are acceptable substrates. Generally, the substituent R in **3** has been restricted to a methyl group.

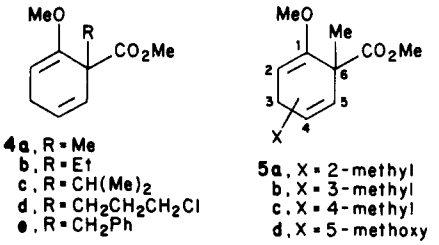
A recently reported intramolecular construction of a 2,4-cyclohexadienone by acid-catalyzed addition of a diazo ketone to the ortho position of a substituted phenol promises to be an important method for preparation of fused and spiro-annelated 2,4-cyclohexadienones.[2] Other specialized methods for 2,4-cyclohexadienone construction involve Claisen rearrangements of propargyl aryl ethers[3] and the high temperature pyrolysis of epoxides derived from fulvene derivatives.[4] The alkylation–oxidation of 2-cyclohexenones[5] and derivatives of cyclohexane-1,3-diones[6] has been reported and phenol[7] and substituted benzene ring[8] oxidations provide 2,4-cyclohexadienones with oxygen substituents at C(6).

In this paper, we describe a versatile, new method for construction of 6-alkyl-6-carbalkoxy(and aminocarbonyl)-2,4-cyclohexadien-1-ones by Birch reduction–alkylation of *o*-methoxybenzoic acid derivatives; e.g., A → B → C.[9] We also report the preparation of the corresponding 2,4-cyclohexadien-1-one dimethyl ketals D. Both C and D are now readily available for detailed synthetic and mechanistic study.[10] Selected Diels–Alder reactions of 2,4-cyclohexadienones and oxa-di-π-methane photorearrangements of several bicyclo[2.2.2]oct-5-en-2-ones also are presented.



Results and Discussion

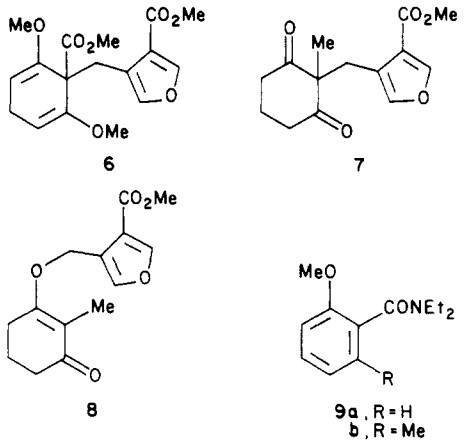
The Birch reduction–alkylation[11] procedure described by Mander and co-workers[11c] was used for the conversion of methyl 2-methoxybenzoate to 6-alkyl-6-carbomethoxy-1-methoxy-1,4-cyclohexadienes **4a–e**. Substrates were



reduced with potassium in NH_3 and THF solution in the presence of *tert*-butyl alcohol. The resulting enolates generally were alkylated in the presence of NH_3. Yields for isolated products were uniformly good with a variety of common alkylation reagents. Entry **4c** demonstrates that hindered alkylation reagents (isopropyl iodide)[12] can be effectively utilized.

A series of 2-, 3-, and 4-methyl-substituted derivatives **5a–c** was prepared from the corresponding anisic ester. The 3-methyl derivative **5b** was obtained as a mixture of diastereoisomers (~1.3:1); methyl 2,6-dimethoxybenzoate provided the 5-methoxy-substituted derivative **5d**.

As part of a program in sesquiterpene lactone synthesis,[13] we prepared **6** from methyl 2,6-dimethoxybenzoate and methyl 4-(bromomethyl)-3-furancarboxylate. In this case, it was necessary to remove the NH_3 prior to addition of the alkylation reagent at −78 °C.[11c] Cyclohexadiene **6**, a masked form of a 1,3-cyclohexanedione, would be difficult to prepare by direct alkylation of the corresponding diketo ester enolate because of competing O-alkylation. This supposition is supported by the alkylation of 2-methyl-1,3-cyclohexanedione with methyl 4-(bromomethyl)-3-furancarboxylate, which produced **7** (56%) and **8** (20%) under the most favorable conditions for C-alkylation.



Benzoic acids used for the preparation of **5a–c** are commercially available. Several methods for synthesis of

(2) (a) Johnson, D. W.; Mander, L. N. *Aust. J. Chem.* **1974**, *27*, 1277. (b) Beames, D. J.; Klose, T. R.; Mander, L. N. *Aust. J. Chem.* **1974**, *27*, 1269. (c) Blair, I. A.; Ellis, A.; Johnson, D. W.; Mander, L. N. *Aust. J. Chem.* **1978**, *31*, 405. (d) This construction is related to a preparation of 2,5-cyclohexadienones by intramolecular phenoxide ion alkylation: Baird, R.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 4238; **1962**, *84*, 788; **1963**, *85*, 567. Masamune, S. *J. Am. Chem. Soc.* **1964**, *86*, 288, 290.

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(5) (a) Fukamiya, N.; Kato, M.; Yoshikoski, A. *J. Chem. Soc., Chem. Commun.* **1976**, 1120. (b) Fukamiya, N.; Kato, M.; Yoshikoski, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1843.

(6) (a) Schultz, A. G.; Sha, C.-K. *J. Org. Chem.* **1980**, *45*, 2040. See ref 1d for experimental detail.

(7) (a) Bubb, W. A.; Sternhell, S. *Tetrahedron Lett.* **1970**, 4499 and references cited therein. (b) Bélanger, A.; Berney, D. J. F.; Borschberg, H.-J.; Brousseau, R.; Doutheau, A.; Durand, R.; Katayama, H.; Lapalme, R.; Leturc, D. M.; Liao, C.-C.; MacLachlan, F. N.; Maffrand, J.-P.; Marazza, F.; Martino, R.; Moreau, C.; Saint-Laurent, L.; Saintonge, R.; Soucy, P.; Ruest, L.; Deslongchampes. P. *Can. J. Chem.* **1979**, *57*, 3348. (c) Büchi, G.; Francisco, M. A.; Philippe, M. *Tetrahedron Lett.* **1983**, *24*, 2531.

(8) Hart, H.; Collins, P. M.; Waring, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1005.

(9) For a preliminary account of this work, see Schultz, A. G.; Dittami, J. P. *Tetrahedron Lett.* **1983**, *24*, 1369.

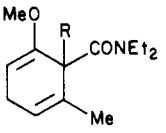
(10) For a review of the chemistry of cyclohexadienones, see: Waring, A. J. In "Advances in Alicyclic Chemistry"; Hart, H., Karabatsos, G. J., Eds.; Academic Press: New York, 1966; Vol. 1, p 129.

(11) For key references see: (a) Mander, L. N.; Hamilton, R. J. *Tetrahedron Lett.* **1981**, *22*, 4115. (b) Tami, Y.; Hagiwara, H.; Uda, H. *J. Chem. Soc., Chem. Commun.* **1982**, 502. (c) Hook, J. M.; Mander, L. N.; Woolias, M. *Tetrahedron Lett.* **1982**, *23*, 1095. (d) Hook, J. M.; Mander, L. N.; Urech, R. *Synthesis* **1979**, 374. (e) Hook, J. M.; Mander, L. N. *J. Org. Chem.* **1980**, *45*, 1722. (f) Cossey, A. L.; Gunter, M. J.; Mander, L. N. *Tetrahedron Lett.* **1980**, *21*, 3309. (g) Gunter, M. J.; Mander, L. N. *Aust. J. Chem.* **1981**, *34*, 675. (h) Taber, D. F.; Saleh, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5085. (i) Marshall, J. A.; Wuts, P. G. M. *J. Org. Chem.* **1977**, *42*, 1794.

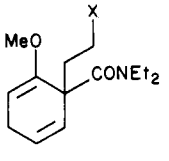
(12) The alkylation of the enolate generated by Birch reduction of *tert*-butyl 2-methoxybenzoate with isopropyl iodide has been reported in ref 11c.

(13) Schultz, A. G.; Motyka, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 5800.

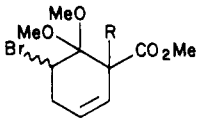
the less readily available 6-methyl-2-methoxybenzoic acid have been reported;[14] however, we desired an efficient, potentially general route to a wide range of 6-alkyl-2-methoxybenzoic acid derivatives. The diethylamide group has been shown to be effective in directing metalation at C(5) in *N,N*-diethyl-2-methoxybenzamide (**9a**).[15] Lithiation of **9a** with *sec*-butyllithium/tetramethylethylenediamine (TMEDA) followed by alkylation with methyl iodide gave the 6-methyl-2-methoxybenzamide **9b**. Reduction of **9b** with potassium in liquid NH_3 and 1 equiv of *tert*-butyl alcohol and alkylation of the resulting amide enolate with methyl iodide gave **10a** in 93% overall yield



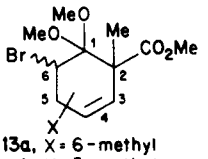
10a, R = Me
b, R = H



11a, X = OAc
b, X = OH



12a, R = Me
b, R = Et
c, R = CH(Me)$_2$
d, R = $CH_2CH_2CH_2Cl$
e, R = CH_2Ph



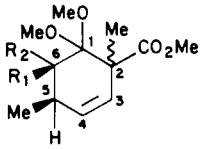
13a, X = 6-methyl
b, X = 5-methyl
c, X = 4-methyl
d, X = 3-methoxy

from **9a**. Alkylation failed with less reactive alkyl halides such as methyl bromoacetate and 2-bromoethyl acetate; 1,4-cyclohexadiene **10b** was isolated on aqueous workup of these alkylation attempts. Cyclohexadiene **11a** was isolated in 95% yield from alkylation of the considerably less hindered amide enolate, derived from Birch reduction of **9a**, with 2-bromoethyl acetate.

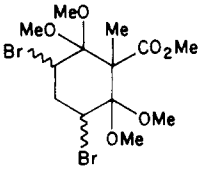
The successful Birch reductions of *N,N*-diethylbenzamides **9a** and **9b** are remarkable in light of literature reports. Reductions of mono N-substituted and unsubstituted benzamides with sodium in liquid NH_3 give 1,4-cyclohexadienes;[16a,b] however, *N,N*-dimethylbenzamide undergoes amide reduction to give benzaldehyde.[16b] The presence of an amide hydrogen atom has been suggested to allow formation of an amide anion which protects the amide group from reduction.[16a] We have found that *N,N*-dimethyl-2-methoxybenzamide undergoes approximately quantitative reductive alkylation (methyl iodide) using either sodium or potassium as reducing agent. Thus, it appears that the ring *o*-methoxy substituent is critical in directing benzene ring rather than amide reduction.

Enol ethers **4a–e** were treated with *N*-bromoacetamide (NBA) in methanol[17] to give bromo ketals **12a–e** in excellent yield. Similarly, **5a–d** were converted into **13a–d**. Bromo ketals were generally obtained as a mixture of diastereoisomers, but in certain cases (e.g., **12a**, **12c**, **13a**, and **13c**), one isomer predominated and was isolated in diastereoisomerically pure form.

Two isomeric bromo ketals were obtained from bromo ketalization of the diastereoisomeric mixture **5b**. Fractional crystallization gave a crystalline compound **13b** (mp 100–104 °C, major isomer) and an oil, **13b′**. Stereochemistry was assigned on the basis of NMR spectral data and chemical reactivity (vide infra).



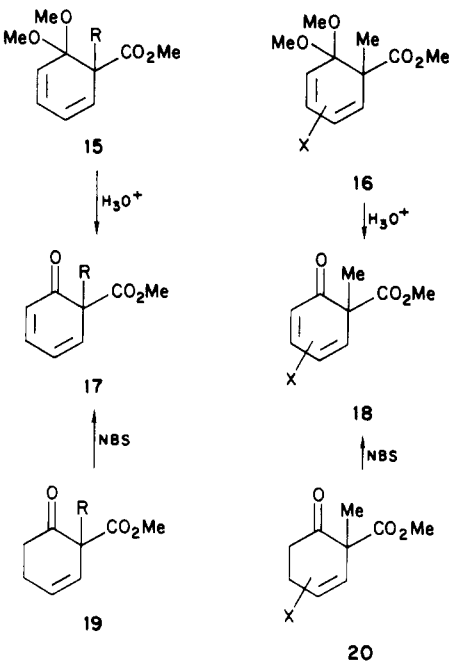
13b, R_1 = Br; R_2 = H_b
b′, R_1 = H_b; R_2 = Br



14

Selective reaction of only one enol ether group occurred on treatment of **5d** with 1 equiv NBA to give **13d** in 93% yield; with 2 equiv NBA the dibromo diketal **14** was obtained in 83% yield. The excellent selectivity must be a result of relative rates of bromo ketalization, reflecting more, 1,3-diaxial interactions in the transition state for the second addition.

Dehydrobrominations of bromo ketals **12a–e** and **13a–d** to give cyclohexadiene ketals **15** and **16**, respectively, were effected by potassium *tert*-butoxide in refluxing *tert*-butyl alcohol or 1,5-diazabicyclo[4.3.0]non-5-ene in refluxing benzene or toluene solutions. Attempts at base-induced



elimination of HBr from **12c** and **12d** resulted in uncharacterized mixtures of products. With the mixture of isomeric bromo ketals **13b** and **13b′**, **13b′** was stable to the elimination reaction conditions while **13b** gave cyclohexadiene **16b**. The assignment of relative configuration at C(5) and C(6) in **13b** (J_{ab} = 3 Hz) and **13b′** (J_{ab} = 10 Hz) is consistent with dehydrobromination by an anti elimination. Configuration at C(2) relative to C(6) in **13b** and **13b′** must be identical, which implies that the ester function in **5b** exerts a considerable stereodirecting effect during bromo ketalization. However, available data do not reveal whether the bromine atom is syn or anti to the ester function.

As expected, cyclohexadiene ketals are generally quite sensitive to acid-catalyzed hydrolysis. Characterization consisted of IR and NMR spectral analysis and hydrolysis

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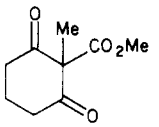
(15) Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34. For amination of the lithiated benzamide, see: Snieckus, V. *Tetrahedron Lett.* **1983**, *24*, 3795.

(16) (a) Kuehne, M. A.; Lambert, B. F. *J. Am. Chem. Soc.* **1959**, *81*, 4278. (b) Dickson, L.; Matuszak, C. A.; Qazi, A. H. *J. Org. Chem.* **1978**, *43*, 1007. (c) Markov, P.; Ivanoff, C. *Tetrahedron Lett.* **1962**, 1139.

(17) Rapoport, H.; Lovell, C. H.; Reist, H. R.; Warren, M. E. *J. Am. Chem. Soc.* **1967**, *89*, 1942.

to the completely characterized 2,4-cyclohexadien-1-ones **17** and **18** by (1) treatment with *p*-toluenesulfonic acid in acetone–water solution or (2) flash chromatography on silica gel. Cyclohexadienones **17a–e** and **18a–d** are stable to storage in a refrigerator for extended periods (weeks to months). They are not as susceptible to Diels–Alder dimerization as are the 6,6-dialkyl analogues.[18,19]

The rather harsh reaction conditions required for elimination of HBr from bromo ketals of type **12** are not compatible with the presence of base-sensitive substituents; e.g., **12d**. A milder process was developed by first converting enol ethers **4a–e** and **5a–d** to cyclohex-3-en-1-ones **19a–e** and **20a–d** by treatment with dilute aqueous acid at room temperature. Selective hydrolysis of one enol ether group in the 2,6-dimethoxy derivative **5d** was performed in moderate yield to give **20d**. Under more forcing conditions, 2-carbomethoxy-2-methyl-1,3-cyclohexanedione (**21**) was obtained in 87% isolated yield.



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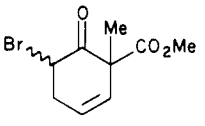
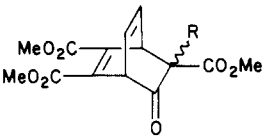


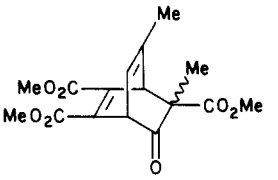
22

Reactions of **19a**, **19b**, **19d**, and **5a–c** with *N*-bromosuccinimide (NBS) in refluxing benzene solution with continuous sun lamp irradiation provided the corresponding 2,4-cyclohexadienone. The formation of 2,4-cyclohexadienone presumably involves allylic bromination to give a β-bromo ketone, from which dehydrobromination occurs under these experimental conditions. Control experiments have demonstrated that α-bromo ketone **22** is not an intermediate in formation of **17a**. In certain cases, β-bromo ketones were detected by ^{1}H NMR spectroscopy; dehydrobromination was completed by addition of an amine base (see Experimental Section).

The Diels–Alder reactivity of 2,4-cyclohexadienones has been reported and there have been applications of this reaction to natural products synthesis.[20,4,5,7b] We are interested in synthetic applications of products obtained from Diels–Alder reactions of 6-alkyl-6-carbalkoxy-2,4-cyclohexadieneones and their ketal derivatives. For this reason, we have examined the reactivity of representative examples of these cyclohexadienones with dimethyl acetylenedicarboxylate (DMAD).[4] Diels–Alder reactions of **17a**, **17e**, and **18c** and DMAD (1.0–1.2 equiv) occur in refluxing benzene solution to give a diastereoisomeric mixture of adducts in approximately quantitative yield. Stereoselectivity is good (9:1 for **24**) to poor (2:1 for **23b**);



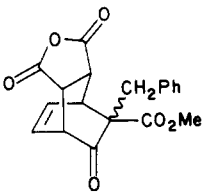
23a, R = Me
b, R = CH_2Ph



24

diastereoisomers could be separated in every case by chromatographic techniques. Control experiments demonstrated that the cycloadducts did not revert to starting material nor did they undergo isomer interconversion under the Diels–Alder reaction conditions. Thus, despite the fact that 6-alkyl-6-carbalkoxy-2,4-cyclohexadienones are not particularly susceptible to Diels–Alder dimerization, they are at least as reactive with DMAD as is 6,6-dimethyl-2,4-cyclohexadien-1-one.[4]

Maleic anhydride reacted with **17e** under more forcing conditions (refluxing toluene, 36 h) to give cycloadduct **25** with only moderate efficiency (41% isolated yield).



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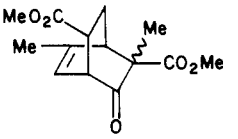

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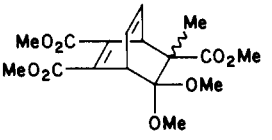
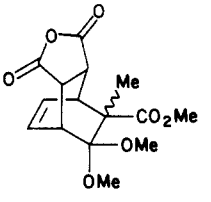


27



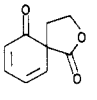
28

Methyl acrylate added in endo fashion to **18c** to give **26** with excellent positional selectivity (only ortho orientation observed), but as a 1:1 mixture of diastereoisomers. Less reactive dienophiles such as 2-cyclopentenone failed to undergo reaction with **18c** and **17e** even with $AlCl_3$ present[21] or under aqueous conditions.[22]

The Diels–Alder reactivity of cyclohexadiene ketal **15a** has been examined. In a relative rate study, a solution of equivalent amounts of **15a**, **17a**, and DMAD in benzene was heated to reflux temperature for 6 h (not enough time to deplete any of the reactants). ^{1}H NMR and VPC analysis of the reaction mixture demonstrated that 2,4-cyclohexadienone **17a** reacted at a rate nine times faster than cyclohexadiene ketal **15a** and that each had produced an ~3:1 mixture of diastereoisomers. Preparative experiments with DMAD gave adduct **27** in 80% isolated yield as an ~3:1 mixture of diastereoisomers that were converted by aqueous acid hydrolysis to the same mixture of diastereoisomers, **23a**, obtained by Diels–Alder reaction

(18) For examples of 2,4-cyclohexadien-1-one dimerizations at room temperature, see: (a) Brown, T. L.; Curtin, D. Y.; Fraser, R. A. *J. Am. Chem. Soc.* **1958**, *80*, 4339. (b) Curtin, D. Y.; Fraser, R. R. *Chem. Ind. (London)* **1957**, 1358.

(19) The enhanced stability of 6-carbomethoxy-2,4-cyclohexadien-1-ones may be dependent on the orientation of the C(6) carbonyl group with respect to the dienone ring. Attempted preparation of i at ~120 °C resulted in formation of dimeric material and very little i; unpublished results of F. Lavieri, RPI Laboratories.



i

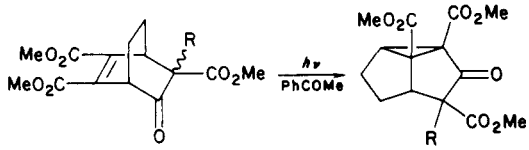
(20) For examples, see: (a) Danishefsky, S.; Dumas, D. *J. Chem. Soc., Chem. Commun.* **1968**, 1287. (b) Holmberg, K.; Kirudd, H.; Westin, G. *Acta Chem. Scand. Ser. B* **1974**, *28*, 913. (c) Stevens, K. E. M.S. Thesis, University of Toronto, 1975. (d) Yates, P.; Stevens, K. E. *Tetrahedron* **1981**, *37*, 4401. (e) Becker, H. D.; Skelton, B.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 1361. (f) Auksi, H.; Yates, P. *Can. J. Chem.* **1981**, *59*, 2510.

(21) Fringuelli, F.; Pizzo, F.; Torticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802.

(22) (a) Breslow, R.; Rideout, D. *J. Am. Chem. Soc.* **1980**, *102*, 7816. (b) Grieco, P. A.; Yoshida, K.; Garner, P. *J. Org. Chem.* **1983**, *48*, 3137.

with **17a**. Cyclohexadiene ketal **15a** also reacted with maleic anhydride to give a single adduct, **28**, but in a disappointing 4.6% yield.

Bicyclo[2.2.2]oct-5-en-2-ones **29a–c** were prepared by platinum-catalyzed hydrogenation of the unconjugated olefinic bond in **23a,b** by the procedure developed by Yates and Stevens[20d] for the preparation of substrates for oxa-di-π-methane photorearrangement to 2,8-dicarbomethoxytricyclo[3.2.1.0^{2,8}]octan-3-ones. The oxa-di-π-methane

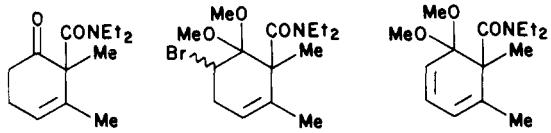


29a, R = Me
b, R = CH_2Ph
c, R = CH_2Ph

30

photorearrangement has great potential for use in natural products synthesis,[23] especially in the area of polyquinane[24] construction. Bicyclooctenones **29a–c** all underwent acetophenone-sensitized photorearrangement to tricyclooctanones **30a–c** in good but unoptimized yields. Significantly, these results demonstrate that the electron-withdrawing carbomethoxy substituent at C(3) of the bicyclooctenone is compatible with the oxa-di-π-methane photorearrangement.[25]

We have examined the possibility of converting benzamide reduction–alkylation products **10a** and **11a** into 2,4-cyclohexadienone derivatives. Enone **31**, bromo ketal **32**, and 2,4-cyclohexadienone ketal **33** all were prepared

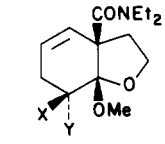


31 **32** **33**

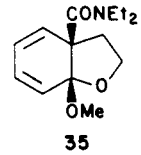
by methods already discussed, but **33** could not be converted to a 2,4-cyclohexadienone by acid-catalyzed ketal hydrolysis. Instead, 2,3-dimethylphenol (~50% yield) and other aromatic products (not fully characterized) were obtained. A similar product distribution was observed for the reaction of enone **31** with NBS. Thus, milder reaction conditions apparently will be required for the isolation of 6-alkyl-6-(aminocarbonyl)-2,4-cyclohexadienones.

Acetate **11a** underwent saponification to give the crystalline alcohol **11b**. With **11b**, we were able to examine an intramolecular bromo ketalization to give fused-ring 2,4-cyclohexadiene ketals, e.g., **35**. Reaction of **11b** with NBA in methanol gave a mixture of bromo ketals **34a** and **34b** in a ratio of 2:1 (62% yield). These diastereoisomers were isolated by high-performance liquid chromatography (HPLC). Interestingly, the distribution of **34a** (18% isolated yield) and **34b** (53%) changed markedly when the bromination was conducted in acetonitrile. Treatment of **11b** with phenylselenenyl chloride[26] produced selenide **34c** in 91% yield. Both **34a** and **34b** were converted to cyclohexadiene **35** in the usual way, and **34c** gave **35** in 96% yield on oxidation–elimination with H_2O_2. In accord with the assignment of stereochemistry in **34a** and **34b**, **34b** underwent complete dehydrobromination in ≤1 h while **34a** required ≥22 h for complete elimination.

Configurational assignments for chiral carbon atoms in **34c** are based on literature precedent.[26] ^{1}H NMR resonances for olefinic protons and the methoxy group in spectra of **34a** and **34c** are nearly identical, suggesting that



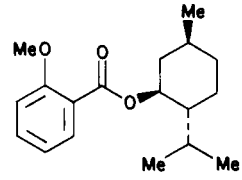
34a, X = Br; Y = H
b, X = H; Y = Br
c, X = SePh; Y = H



35

these compounds have the same relative configuration. Resonances for these protons in spectra of **34b** are markedly different. For this reason, and because both **34a** and **34b** give **35**, **34a** must be the diastereoisomer resulting from syn addition.

We desire methods for the construction of optically active 2,4-cyclohexadienones; consequently, we have examined the Birch reduction–alkylation of the *d*-menthol derived *o*-anisic ester **36**. In accord with literature-based



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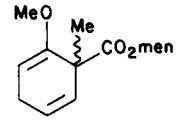
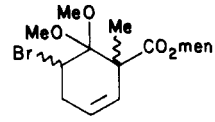
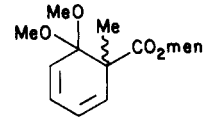


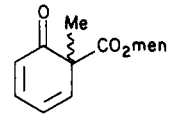
37a,b



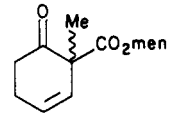
38a
b



39a
b



40a
b



41a,b

expectations,[27] **36** gave a 1:1 mixture of diasteroisomeric cyclohexadienes **37a,b** on alkylation with methyl iodide. The product mixture could not be separated, but was isolated in 83% yield by preparative HPLC. Reaction of **37a,b** with NBA in methanol gave a 1:1 mixture of diastereoisomers which could be separated by fractional crystallization into **38a** (mp 126 °C, 49%) and **38b** (oil, 48%). When the methodology already discussed was used, **38a** and **38b** were converted to 2,4-cyclohexadiene ketals **39a** and **39b**, 2,4-cyclohexadienones **40a** and **40b**, and enones **41a,b**. Individual 2,4-cyclohexadienones **40a** and **40b** contained ~3–4% of the corresponding diastereoisomer (^{1}H NMR integration).

As expected, the CD spectra of **38a** and **38b** exhibited identical curves with opposite signs; λ_{max} (ethanol) 222 nm.

(23) Demuth, M.; Schaffner, K. *Angew, Chem., Int. Ed. Engl.* **1982**, *21*, 820.
(24) (a) Paquette, L. A. *Top. Curr. Chem.* **1979**, *79*, 41. (b) Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141.
(25) Demuth and Schaffner have reported that bicyclo[2.2.2]oct-5-en-2-ones with a carbomethoxy substituent at the bridgehead C(1) position do not undergo the oxa-di-π-methane photorearrangement (ref 23).
(26) (a) Clive, D. L. J.; Chittattu, G.; Curtis, N. J.; Kiel, W. A.; Wong, C. K. *J. Chem. Soc., Chem. Commun.* **1977**, 725. (b) Nicolaou, K. C.; Lysenko, Z. *Tetrahedron Lett.* **1977**, 1257.
(27) For a recent application of *l*-menthol derived esters, in which formation of a C–C bond α to the ester carbonyl group resulted in the production of a 1:1 mixture of disasteroisomers, see: Roberts, R. A.; Schull, V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 2076.
(28) For the preparation of cyclohexadienes **4a**, **4b**, and **5d**, see ref 11c.

Configurational assignments have not been attempted. Menthol esters **39a** and **39b** were found to be resistant to hydrolytic conditions compatible with the ketal function; harsher conditions resulted in decomposition to uncharacterized product mixtures.

Conclusion

We have outlined an efficient method for construction of 6-alkyl-6-carbalkoxy-2,4-cyclohexadien-1-ones and related compounds. Substitution at C(6) is dependent on the highly flexible Birch reduction–alkylation of *o*-anisic esters; substitution at C(2)–C(5) is dependent on the availability of substituted *o*-anisic esters and their compatibility with metal in NH_3 reductions.

This new methodology also provides access to the C(1) carbonyl protected 2,4-cyclohexadienone ketals. The incorporation of optical activity by reduction–alkylation of menthol esters of *o*-anisic acids has been shown to be possible, but this approach necessitates a potentially difficult separation of diastereoisomers. The development of an enantioselective method for synthesis of 2,4-cyclohexadienones is currently under study.

It is anticipated that the chemistry reported in this paper will provide the impetus for an extensive investigation of the chemistry of 2,4-cyclohexadienones. Applications to the area of natural products synthesis will be reported in due course.

Experimental Section

^1H NMR spectra were recorded on Varian T-60 (60 MHz), Varian XL-200 (200 MHz), and Hitachi-Perkin-Elmer R-600 (60 MHz) NMR spectrometers (tetramethylsilane internal standard). ^{13}C NMR spectra were obtained on the Varian XL-200 spectrometer. Infrared spectra were recorded on either a Perkin-Elmer 137b or 298 spectrometer and ultraviolet spectra were recorded on a Perkin-Elmer 552 spectrometer. Mass spectra were obtained on Finnigan OWA-1020 and Hewlett-Packard 5987A GC–MS systems. Preparative HPLC was performed on a Waters Associates preparative LC 500 with Prep Pak 500 silica gel cartridges. Elemental analyses were determined by Spang Microanalytical Laboratories, Eagle Harbor, MI. The 366-nm light source consisted of a water-cooled Hanovia 679A36 450-W mercury arc lamp fitted with Corning color filters 0-52 and 7-54.

Birch Reduction–Alkylation of *o*-Anisic Acid Derivatives. Preparation of 6-Carbomethoxy-6-isopropyl-1-methoxy-1,4-cyclohexadiene (4c). Prepared in 92% yield by the method reported for **4a** and **4b**.[11c] The analytical sample was prepared by Kugelrohr distillation (~80 °C, (0.1 mmHg)) and crystallization from petroleum ether: mp 48–49 °C; ^1H NMR ($CDCl_3$) δ 0.79 (d, 3 H, J = 6.9 Hz), 0.92 (d, 3 H, J = 6.9 Hz), 2.56 (7 line m, 1 H, J = 6.9 Hz), 2.82 (m, 2 H), 3.54 (s, 3 H), 3.70 (s, 3 H), 4.84 (m, 1 H), 5.56 (m, 1 H), 5.98 (m, 1 H); IR (CCl_4) 1720 cm^{-1}; chemical ionization mass spectrum, m/e 211 ($M^+ + 1$).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.34; H, 8.48.

6-Carbomethoxy-6-(3-chloropropyl)-1-methoxy-1,4-cyclohexadiene (4d). A solution of methyl 2-methoxybenzoate (1.0 g, 6 mmol) in dry THF (6 mL) and *tert*-butyl alcohol (0.44 g, 6 mmol) was cooled to −78 °C. Liquid NH_3 (60 mL, predried over sodium amide and then doubly distilled) was added to the reaction mixture. Potassium (0.59 g, 0.015 mol) was added to the stirred solution in small pieces producing a deep blue coloration. Anhydrous lithium iodide (1.8 g, 13 mmol) was added and the reaction was stirred for 1 h at −78 °C. A solution of 1-bromo-3-chloropropane (4.72 g, 30 mmol) in THF (6 mL) was added. The resulting yellow solution was stirred for 1 h at −78 °C and then warmed slowly to room temperature while the NH_3 was removed with a stream of nitrogen. Brine (20 mL) was added and the reaction mixture was extracted with ether (3 × 20 mL). The ether extracts were washed with sodium thiosulfate solution (10%, 2 × 20 mL), water (1 × 20 mL), and brine (2 × 20 mL) and were dried over anhydrous magnesium sulfate. Concentration of the organic extract under reduced pressure afforded an oil (1.5 g, 100%) which crystallized on cooling. HPLC (hexane–ethyl acetate; 15:1) gave **4d** (1.0 g, 67%); crystallization from ethanol: mp 38–39 °C; ^1H NMR ($CDCl_3$) δ 1.6 (m, 2 H), 1.8 (m, 1 H), 2.36 (m, 1 H), 2.86 (br s, 2 H), 3.52 (t, overlapping s at 3.54, 5 H, J = 6 Hz), 3.68 (s, 3 H), 4.9 (br s, 1 H), 5.40 (m, 1 H), 5.95 (m, 1 H); IR (film) 1732, 1688, 1654 cm^{-1}; mass spectrum, m/e (relative intensity) 244 (M^+, 1), 184 (44), 167 (34), 149 (19).

Anal. Calcd for $C_{14}H_{17}ClO_3$: C, 58.89; H, 7.00. Found: C, 58.76; H, 6.83.

6-Benzyl-6-carbomethoxy-1-methoxy-1,4-cyclohexadiene (4e). Prepared in 61% yield as described for **4c**; crystallization from ether: mp 151–152 °C; ^1H NMR ($CDCl_3$) δ 2.35 (m, 1 H), 2.52 (m, 1 H), 3.10 (d, 1 H, J = 13 Hz), 3.34 (d, 1 H, J = 13 Hz), 3.52 (s, 3 H), 3.72 (s, 3 H), 4.65 (t, 1 H, J = 4.0 Hz), 5.60 (m, 2 H), 7.18 (s, 5 H); IR (KBr) 1730, 1690 cm^{-1}; chemical-ionization mass spectrum, m/e 259 ($M^+ + 1$).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.30; H, 6.95.

6-Carbomethoxy-2,6-dimethyl-1-methoxy-1,4-cyclohexadiene (5a). Prepared in 69% yield as described for **4c**; Kugelrohr distillation (~86 °C, (1.8 mmHg)): ^1H NMR ($CDCl_3$) δ 1.42 (s, 3 H), 1.74 (s, 3 H), 2.65 (d, 1 H, J = 20 Hz), 2.82 (d, 1 H, J = 20 Hz), 3.62 (s, 3 H), 3.69 (s, 3 H), 5.48 (m, 1 H), 5.75 (m, 1 H); IR (film) 1730, 1692, 1655 cm^{-1}.

6-Carbomethoxy-3,6-dimethyl-1-methoxy-1,4-cyclohexadiene (5b). Prepared in 80% yield as an ~1.3:1 mixture of diastereoisomers as described for **4c**; flash chromatography (silica gel, hexane–ethyl acetate, 3:1): oil; ^1H NMR ($CDCl_3$) δ 1.06, 1.14 (overlapping d, 3 H, J = 7 Hz), 1.40, 1.41 (two s, 3 H), 2.88–3.12 (m, 1 H), 3.55, 3.56 (two s, 3 H), 3.67, 3.69 (two s, 3 H), 4.70 (br s, 1 H), 5.47 (m, 1 H), 5.73 (m, 1 H); IR (film) 1740, 1680, 1645 cm^{-1}.

6-Carbomethoxy-4,6-dimethyl-1-methoxy-1,4-cyclohexadiene (5c). Prepared in 74% yield as described for **4c**; Kugelrohr distillation (~91 °C, (1.1 mmHg)): ^1H NMR ($CDCl_3$) δ 1.39 (s, 3 H), 1.72 (s, 3 H), 2.75 (br s, 2 H), 3.55 (s, 3 H), 3.68 (s, 3 H), 4.74 (t, 1 H, J = 1 Hz), 5.21 (br s, 1 H); IR (film) 1730, 1690, 1655 cm^{-1}.

6-Carbomethoxy-6-[(4-carbomethoxyfuran-3-yl)-methyl]-1,5-dimethoxy-1,4-cyclohexadiene (6). Prepared in 67% yield by alkylation of the enolate produced by reduction of methyl 1,6-dimethoxybenzoate with methyl 3-(bromomethyl)-furan-4-carboxylate (1 equiv) in THF;[11c] crystallization from hexane (needles): mp 125 °C; ^1H NMR ($CDCl_3$) δ 2.32 (dt, 1 H, J = 20 Hz, J = 2 Hz), 2.70 (dt, 1 H, J = 20 Hz, J = 2 Hz), 3.49 (s, 8 H), 3.73 (s, 3 H), 3.80 (s, 3 H), 4.74 (t, 2 H, J = 2 Hz), 7.51 (s, 1 H), 7.83 (d, 1 H, J = 1 Hz); ^1H NMR (C_6D_6) δ 2.40–2.68 (m, 2 H), 3.20 (s, 6 H), 3.31 (s, 2 H), 3.48 (s, 3 H), 3.51 (s, 3 H), 4.55 (t, 2 H, J = 2 Hz), 7.10 (s, 1 H), 7.80 (d, 1 H, J = 1 Hz); IR (CH_2Cl_2) 1740, 1700, 1665, 1540 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found: C, 60.66; H, 5.90.

2-[(4-Carbomethoxyfuran-3-yl)methyl]-2-methyl-1,3-cyclohexanedione (7). Methyl 3-(bromomethyl)furan-4-carboxylate (0.268 g, 1.2 mmol) was added to a solution of 2-methyl-1,3-cyclohexanedione (0.089 g, 0.71 mmol) and potassium *tert*-butoxide (0.092 g, 0.82 mmol) in *tert*-butyl alcohol (6 mL). The mixture was stirred for 10 min at room temperature and heated to 110 °C for 12 h. After the reaction cooled, water was added and the mixture was extracted with methylene chloride (3 × 20 mL). The organic extracts were combined, dried, and concentrated to give a mixture of **7**, **8**, and starting materials. Flash chromatography (silica gel, hexane–ethyl acetate, 1:1) gave **7** (0.104 g, 56%) as colorless crystals, which were recrystallized from ethanol: mp 77 °C; ^1H NMR ($CDCl_3$) δ 1.19 (s, 3 H), 1.78–2.10 (m, 2 H), 2.52–2.79 (m, 4 H), 3.19 (s, 2 H), 3.75 (s, 3 H), 7.10 (br s, 1 H), 7.83 (d, 1 H, J = 2 Hz); IR (CH_2Cl_2) 1730, 1710 cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.41; H, 6.24.

Enol ether **8** (37.5 mg, 20%): ^1H NMR ($CDCl_3$) δ 1.74 (s, 3 H), 1.99 (q, 2 H, J = 6 Hz), 2.37 (t, 2 H, J = 7 Hz), 2.61 (t, 2 H, J = 2 Hz), 3.85 (s, 3 H), 5.23 (s, 2 H), 7.47 (s, 1 H), 8.02 (s, 1 H); IR (CH_2Cl_2) 1720, 1640, 1620 cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.40; H, 6.29.

***N,N*-Diethyl-2-methoxy-6-methylbenzamide (9b).** With use of the lithiation procedure of Beak and co-workers,[15] a solution of *N,N*-diethyl-*o*-anisamide (**9a**) (535 mg, 2.6 mmol) in dry THF (15 mL) was added to a solution of *sec*-butyllithium (1.3 M in cyclohexane, 2.4 mL, 3.1 mmol) and TMEDA (360 mg, 0.47 mL, 3.1 mmol) in dry THF at −78 °C. After 1 h, methyl iodide (990 mg, 0.44 mL, 7 mmol) was added. After 20 min, the mixture was allowed to warm to room temperature and stirring was continued for 2 h. Water (10 mL) was added and solvent was removed under reduced pressure. An ether solution of the residue was washed with dilute HCl, water, 10% $Na_2S_2O_3$, and brine. The organic layer was dried over anhydrous magnesium sulfate and concentrated to give a pale yellow oil. Kugelrohr distillation (120 °C (0.8 mmHg)) gave **9b** (550 mg, 96%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 3 H, J = 7 Hz), 1.25 (t, 3 H, J = 7 Hz), 2.24 (s, 3 H), 3.15 (q, 2 H, J = 7 Hz), 3.43 (m, 1 H), 3.70 (6 line m, 1 H), 3.79 (s, 3 H), 6.74 (d, 1 H, J = 10 Hz), 6.80 (d, 1 H, J = 8 Hz), 7.20 (t, 1 H, J = 8 Hz); IR ($CHCl_3$) 1630, 1600, 1425 cm^{-1}.

Anal. Calcd for $C_{13}H_{19}O_2N$: C, 70.56; H, 8.65. Found: C, 70.69; H, 8.72.

6-[(*N,N*-Diethylamino)carbonyl]-5,6-dimethyl-1-methoxy-1,4-cyclohexadiene (10a). Liquid NH_3 (50 mL) was added to a solution of **9b** (915 mg, 4.14 mmol) and *tert*-butyl alcohol (307 mg, 4.14 mmol) in THF (5 mL). The mixture was cooled to −78 °C and potassium (404 mg, 0.0104 mol) was added; the resulting blue coloration persisted for ~15 min. A solution of methyl iodide (2.9 g, 1.3 mL, 21 mmol) in THF (5 mL) was added at −78 °C and after 1 h at −78 °C, the NH_3 was removed by a stream of nitrogen. Brine was added and the mixture was extracted with ether. The combined ether extracts were washed with 10% $Na_2S_2O_3$ and brine and dried with anhydrous magnesium sulfate. Removal of solvent gave an oil (980 mg); Kugelrohr distillation gave **10a** (oil, 960 mg, 98%), which slowly solidified on standing in a refrigerator: mp 56–57 °C; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 7 Hz), 1.10 (t, 3 H, J = 7 Hz), 1.47 (s, 3 H), 1.64 (d, 3 H, J = 1.2 Hz), 2.83 (m, 2 H), 3.0–3.4 (m, 2 H), 3.44–3.80 (m, 2 H), 3.52 (s, 3 H), 4.59 (br t, 1 H), 5.44 (br s, 1 H); ^{13}C NMR δ 12.21 (q), 12.97 (q), 18.49 (q), 25.39 (q), 26.05 (t), 40.42 (t), 40.47 (t), 50.90 (s), 54.08 (t), 88.60 (d), 118.99 (d), 135.48 (s), 157.30 (s), 170.78 (s); IR ($CHCl_3$) 1660, 1625 cm^{-1}.

Anal. Calcd for $C_{14}H_{23}O_2N$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.71; H, 9.80; N, 5.82.

Attempted Reduction–Alkylation of 9b with Methyl Bromoacetate or 2-Bromoethyl Acetate. Isolation of 6-[(*N,N*-Diethylamino)carbonyl]-1-methoxy-5-methyl-1,4-cyclohexadiene (10b). Flash chromatography (silica gel, ethyl acetate–hexanes, 2:3) of the crude product mixture gave **10b**: mp 52–54 °C dec; unstable at room temperature; ^{1}H NMR ($CDCl_3$) δ 1.13, 1.19 (two overlapping t, 6 H, J = 7.0 Hz), 1.68 (br s, 3 H), 2.85 (br q, 2 H), 3.25–3.79 (m, 4 H), 3.53 (s, 3 H), 3.96 (t, 1 H, J = 6 Hz), 4.78 (br t, 1 H, J = 2 Hz), 5.62 (br s, 1 H); ^{13}C NMR δ 12.75 (q), 14.21 (q), 21.16 (q), 26.44 (t), 40.94 (q), 41.84 (q), 48.09 (d), 54.09 (q), 91.85 (d), 121.54 (d), 129.75 (s), 152.17 (s), 170.71 (s); IR ($CHCl_3$) 1690, 1630 cm^{-1}; chemical-ionization mass spectrum, m/e (relative intensity) 244 (M^+ + 1, 100), 222 (20), 208 (5.3), 149 (1.8), 123 (5.3).

6-(2-Acetoxyethyl)-6-[(*N,N*-diethylamino)carbonyl]-1-methoxy-1,4-cyclohexadiene (11a). Prepared in 95% yield by alkylation of the enolate produced by reduction of **9a** with 2-bromoethyl acetate (2 equiv) as described for **10a**; flash chromatography (silica gel, ethyl acetate–hexanes, 3:7): oil; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7 Hz), 1.08 (t, 3 H, J = 7 Hz), 2.0 (s, 3 H), 2.0–2.2 (m, 1 H), 2.4–2.6 (m, 1 H), 2.87 (br q, 2 H), 3.1–3.5 (m, 4 H), 3.53 (s, 3 H), 3.97 (m, 2 H), 4.72 (t, 1 H, J = 3.6 Hz), 5.52 (dt, 1 H, J = 10 Hz, J = 1 Hz), 5.85 (dt, 1 H, J = 10 Hz, J = 3.4 Hz); ^{13}C NMR δ 12.38 (q), 13.41 (q), 20.98 (q), 26.51 (t), 35.44 (t), 40.47 (t), 41.05 (t), 49.86 (s), 53.89 (q), 61.81 (t), 91.33 (d), 124.88 (d), 127.96 (d), 154.01 (s), 170.07 (s), 171.07 (s); IR ($CHCl_3$) 1730, 1680, 1630 cm^{-1}.

Bromoketalization of 6-Alkyl-6-carbomethoxy-1-methoxy-1,4-cyclohexadiene Derivatives. Preparation of 6-Bromo-2-carbomethoxy-2-methyl-3-cyclohexen-1-one, Dimethyl Ketal (12a). A solution of **4a** (0.060 g, 0.33 mmol) in methanol (2.6 mL) was cooled to 0 °C, after which a solution of *N*-bromoacetamide (0.054 g, 0.39 mmol) in methanol (1.8 mL) was added. A crystal of *p*-toluenesulfonic acid was added and the reaction mixture was stirred at 0 °C for 30 min. Saturated sodium carbonate (5 mL) was added and the mixture was extracted with methylene chloride. The combined organic layers were washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave **12a** (0.097 g, 100%) as a colorless crystalline solid; the analytical sample was prepared by recrystallization from ethanol: mp 69–71 °C; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 3 H), 2.78 (m, 2 H), 3.48 (s, 3 H), 3.64 (s, 3 H), 3.74 (s, 3 H), 4.94 (m, 1 H), 5.32 (m, 1 H), 5.68 (m, 1 H); IR (film) 1725 cm^{-1}; mass spectrum, m/e (relative intensity) 213 (100), 168 (41), 166 (43).

Anal. Calcd for $C_{11}H_{17}BrO_4$: C, 45.06; H, 5.85. Found: C, 44.90; H, 5.77.

6-Bromo-2-carbomethoxy-2-ethyl-3-cyclohexen-1-one, Dimethyl Ketal (12b). Prepared in 100% yield as described for **12a**; crystalline, 1.5:1 mixture of diastereoisomers (^{1}H NMR analysis). The analytical sample was prepared by recrystallization from hexane: mp 103–104 °C; ^{1}H NMR ($CDCl_3$, mixture of diastereoisomers) δ 0.78–0.94 (overlapping t at 0.86 and 0.89, 3 H, J = 7 Hz), 2.14–2.38 (overlapping q, 2 H, J = 7 Hz), 2.58–2.98 (m, 2 H), 3.42, 3.53, 3.61, 3.66, (four s, 6 H), 3.73 (s, 3 H), 4.38–4.66 (m, at 4.44, t at 4.62, J = 6 Hz, 1 H), 5.77 (br s, 2 H); IR (film) 1725 cm^{-1}; mass spectrum, m/e (relative intensity) 227 (26), 166 (33).

Anal. Calcd for $C_{12}H_{19}BrO_4$: C, 46.92; H, 6.23. Found: C, 46.96; H, 6.15.

6-Bromo-2-carbomethoxy-2-isopropyl-3-cyclohexen-1-one, Dimethyl Ketal (12c). Prepared in 80% yield as described for **12a**; recrystallization from petroleum ether: mp 55–56 °C; ^{1}H NMR ($CDCl_3$) δ 0.82 (d, 3 H, J = 6.7 Hz), 0.98 (d, 3 H, J = 6.7 Hz), 2.53–2.98 (m, 3 H), 3.63 (s, 3 H), 3.65 (s, 3 H), 3.70 (s, 3 H), 4.50 (m, 1 H), 5.58–5.64 (m, 1 H), 5.80–5.89 (m, 1 H); IR (CCl_4) 1720 cm^{-1}; chemical-ionization mass spectrum, m/e 322 (M^+ + 1).

Anal. Calcd for $C_{13}H_{21}BrO_4$: C, 48.61; H, 6.59. Found: C, 48.77; H, 6.71.

6-Bromo-2-carbomethoxy-2-(3-chloropropyl)-3-cyclohexen-1-one, Dimethyl Ketal (12d). Prepared in 92% yield as described for **12a**; HPLC (hexane–ethyl acetate, 9:1); oil; ^{1}H NMR ($CDCl_3$) δ 1.5–2.3 (m, 4 H), 2.77 (m, 2 H), 3.33–3.83 (overlapping peaks at 3.4, 3.47, 3.5, 3.57, 3.63, 3.7, 11 H), 4.23–4.77 (m, 1 H), 5.63 (m, 2 H); IR (film) 1725 cm^{-1}; mass spectrum, m/e (relative intensity) 275 (100), 265 (61), 263 (49).

Anal. Calcd for $C_{13}H_{20}ClBrO_4$: C, 43.90; H, 5.67. Found: C, 43.99; H, 5.44.

2-Benzyl-6-bromo-2-carbomethoxy-3-cyclohexen-1-one, Dimethyl Ketal (12e). Prepared in 98% yield (5.25 g scale) as described for **12a**; 2:1 mixture of diastereoisomers (^{1}H NMR analysis). The analytical sample was prepared by column chromatography (alumina, hexane–ethyl acetate, 4:1): oil; ^{1}H NMR ($CDCl_3$) δ 2.80 (m, 2 H), 3.40 (d, 1 H, J = 12 Hz), 3.50 (d, 1 H, J = 12 Hz), 3.60 (s, 3 H), 3.64 (s, 3 H), 3.68 (s, 3 H), 4.46 (m, 1 H), 5.32 (d, 1 H, J = 10 Hz), 5.66 (m, 1 H), 7.18 (s, 5 H); IR (film) 1730, 1660, 1600 cm^{-1}.

Anal. Calcd for $C_{17}H_{21}O_4Br$: C, 55.30; H, 5.73. Found: C, 55.19; H, 5.75.

6-Bromo-2-carbomethoxy-2,6-dimethyl-3-cyclohexen-1-one, Dimethyl Ketal (13a). Prepared in 92% yield as described for **12a**; flash chromatography (silica gel, hexane–ethyl acetate, 3:1): oil; ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3 H), 1.85 (s, 3 H), 2.61 (dd, 1 H, J = 10 Hz, J = 2 Hz), 2.89 (d, 1 H, J = 10 Hz), 3.59 (s, 3 H), 3.68 (s, 3 H), 3.70 (s, 3 H), 5.52 (m, 2 H); IR (film) 1720, 1655 cm^{-1}.

Anal. Calcd for $C_{12}H_{19}O_4Br$: C, 46.92; H, 6.23. Found: C, 46.95; H, 6.19.

6-Bromo-2-carbomethoxy-2,5-dimethyl-3-cyclohexen-1-one, Dimethyl Ketal (13b and 13b′). Prepared in 91% yield as described for **12a**; ~1.3:1 mixture of diastereoisomers (^{1}H NMR analysis); crystallization from hexane, **13b**: mp 104–105 °C (major isomer); ^{1}H NMR ($CDCl_3$) δ 1.19 (d, 3 H, J = 7 Hz), 1.63 (s, 3 H), 2.79 (m, 1 H), 3.27 (s, 3 H), 3.55 (s, 3 H), 3.69 (s, 3 H), 4.42 (d, 1 H, J = 3 Hz), 5.40 (d, 1 H, J = 12 Hz), 5.48 (dd, 1 H, J = 12 Hz, J = 1 Hz); IR ($CHCl_3$) 1730, 1660 cm^{-1}. The mother liquor contained **13b′**: ^{1}H NMR ($CDCl_3$) δ 1.29 (d, 3 H, J = 7 Hz), 1.47 (s, 3 H), 2.79 (m, 1 H), 3.50 (s, 3 H), 3.63 (s, 3 H), 3.73 (s, 3 H), 4.67 (d, 1 H, J = 10 Hz), 5.20 (d, 1 H, J = 8 Hz), 5.48 (d, 1 H,

J = 8 Hz); IR (film) 1730, 1660 cm^{-1}.

Anal. Calcd for $C_{12}H_{19}O_4Br$: C, 46.92; H, 6.23. Found: C, 46.75; H, 6.23.

6-Bromo-2-carbomethoxy-2,4-dimethyl-3-cyclohexen-1-one, Dimethyl Ketal (13c). Prepared in 78% yield as described for **12a**; Kugelrohr distillation (~120 °C (1.1 mmHg)) and recrystallization of the solidified distillate from hexane: mp 77 °C; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3 H), 1.73 (s, 3 H), 2.64 (m, 2 H), 3.45 (s, 3 H), 3.62 (s, 3 H), 3.71 (s, 3 H), 4.98 (m, 2 H); IR (film) 1730, 1660 cm^{-1}.

Anal. Calcd for $C_{12}H_{19}O_3Br$: C, 46.92; H, 6.23. Found: C, 46.51; H, 6.16.

6-Bromo-2-carbomethoxy-3-methoxy-2-methyl-3-cyclohexen-1-one, Dimethyl Ketal (13d) and Dibromo Diketal 14. Reaction of **5d** with 1 equiv of *N*-bromoacetamide as described for **12a** gave **13d** (93%); recrystallization from hexane: mp 73–75 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3 H), 2.70 (m, 2 H), 3.48 (s, 6 H), 3.62 (s, 3 H), 3.73 (s, 3 H), 4.66 (t, 1 H, J = 4 Hz), 4.85 (t, 1 H, J = 6 Hz); IR (CH_2Cl_2) 1730, 1670 cm^{-1}.

Anal. Calcd for $C_{12}H_{19}O_5Br$: C, 44.59; H, 5.93; Br, 24.73. Found: C, 44.68; H, 5.78; Br, 24.86.

Reaction of **5d** with 2 equiv of *N*-bromoacetamide at 0 °C for 2 h gave dibromo diketal **14** (83%); crystallization from hexane: mp 85–90 °C; ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 3 H), 2.67 (m, 2 H), 3.26 (s, 3 H), 3.31 (s, 3 H), 3.46 (s, 3 H), 3.48 (s, 3 H), 3.67 (s, 3 H), 4.58 (t, 1 H, J = 4 Hz), 5.21 (t, 1 H, J = 4 Hz).

Dehydrobromination of 2-Alkyl-6-bromo-2-carbomethoxy-3-cyclohexen-1-one, Dimethyl Ketal Derivatives. Preparation of 6-Carbomethoxy-6-methyl-2,4-cyclohexadien-1-one, Dimethyl Ketal (15a). A solution of **12a** (0.049 g, 0.17 mmol) and potassium *tert*-butoxide (0.06 g, 0.5 mmol) in *tert*-butyl alcohol (22 mL) was heated at reflux temperature for 20 h. The solvent was evaporated and the residue was extracted with ether (3 × 10 mL). The combined ether extracts were washed with sodium bicarbonate (1 N, 3 × 10 mL), dried, and evaporated to give an oil (0.18 g, 51%): ^{1}H NMR (C_6D_6) 1.28 (s, 3 H), 2.9 (s, 3 H), 3.04 (s, 3 H), 3.18 (s, 3 H), 5.28 (d, 1 H, J = 10 Hz), 5.38 (m, 1 H), 5.54 (m, 1 H), 5.62 (d, 1 H, J = 10 Hz); IR (film) 1725 cm^{-1}. An acceptable elemental analysis could not be obtained presumably as a result of facile hydrolysis of the ketal functionality. 2,4-Cyclohexadienone ketals were characterized by conversion to the 2,4-cyclohexadienones.

6-Carbomethoxy-6-ethyl-2,4-cyclohexadien-1-one, Dimethyl Ketal (15b). Prepared in 43% yield as described for **15a**: oil; ^{1}H NMR (C_6D_6) δ 0.92 (t, 3 H, J = 7 Hz), 1.7–2.5 (m, 2 H), 3.13 (s, 3 H), 3.4 (s, 3 H), 3.5 (s, 3 H), 5.3–6.0 (m, 3 H), 6.1–6.4 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.57, 25.98, 50.26, 50.39, 52.08, 58.97, 100.99, 120.18, 125.79, 126.29, 133.08, 174.29; IR (film) 1730, 1600 cm^{-1}.

6-Benzyl-6-carbomethoxy-2,4-cyclohexadien-1-one, Dimethyl Ketal (15e). Prepared in 92% yield (2.85-g scale) from reaction of **12e** and 1,5-diazabicyclo[4.3.0]non-5-ene in refluxing toluene (12 h), oil. The analytical sample was prepared by flash chromatography (alumina, hexane–ethyl acetate, 8:1): ^{1}H NMR ($CDCl_3$) δ 3.30 (s, 3 H), 3.50 (d, 1 H, J = 10 Hz), 3.55 (s, 3 H), 3.71 (s, 3 H), 3.85 (d, 1 H, J = 10 Hz), 5.50–6.15 (m, 4 H), 7.18 (s, 5 H); IR (film) 1730, 1605 cm^{-1}; chemical-ionization mass spectrum, m/e 289 (M^+ + 1); UV (MeOH) λ_{max} 264 nm (ϵ 4550). An acceptable elemental analysis could not be obtained.

6-Carbomethoxy-2,6-dimethyl-2,4-cyclohexadien-1-one, Dimethyl Ketal (16a). Prepared in 82% yield as described for **15e** (without chromatography): oil; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 3 H), 1.93 (d, 3 H, J = 1 Hz), 3.23 (s, 3 H), 3.28 (s, 3 H), 3.70 (s, 3 H), 5.78 (m, 3 H); IR (film) 1730, 1660, 1600 cm^{-1}.

6-Carbomethoxy-3,6-dimethyl-2,4-cyclohexadien-1-one, Dimethyl Ketal (16b). Prepared by reaction of a mixture of **13b** and **13b′** as described for **15e**. A ^{1}H NMR spectrum of the recovered oil showed that **16b** had cleanly formed at the expense of crystalline **13b**, but **13b′** remained. **16b** was not isolated.

Enol Ether Hydrolysis of 6-Alkyl-6-carbomethoxy-1-methoxy-1,4-cyclohexadiene Derivatives. Preparation of 2-Carbomethoxy-2-methyl-3-cyclohexen-1-one (19a). A solution of **4a** (0.103 g, 0.566 mmol) in methanol (5 mL) and hydrochloric acid (10%, 1 mL) was stirred at room temperature for 1 h. The reaction mixture was neutralized with saturated sodium bicarbonate solution and the methanol was removed under reduced pressure. The residue was extracted with ether (3 × 20 mL). The combined ether extracts were washed with water (2 × 20 mL) and brine (2 × 20 mL) and dried over anhydrous magnesium sulfate. Removal of solvent gave an oil (0.082 g, 86%); HPLC (hexane–ethyl acetate, 15:1) gave **19a** (oil, 0.060 g, 63%): ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 3 H), 2.6 (br s, 4 H), 3.72 (s, 3 H), 5.53–6.2 (m, 2 H); IR (film) 1725 cm^{-1}; mass spectrum, m/e (relative intensity) 168 (M^+, 44), 140 (55), 126 (100).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.01; H, 7.13.

2-Carbomethoxy-2-ethyl-3-cyclohexen-1-one (19b). Prepared in 97% yield as described for **19a**. The analytical sample was prepared by Kugelrohr distillation (75–80 °C (1.5 mmHg)): ^{1}H NMR ($CDCl_3$) δ 0.81 (t, 3 H, J = 7 Hz), 1.84 (m, 1 H), 2.34 (m, 1 H), 2.5 (m, 3 H), 2.72 (m, 1 H), 3.72 (s, 3 H), 5.71 (d, 1 H, J = 10 Hz), 6.16 (m, 1 H); IR (film) 1725 cm^{-1}; mass spectrum, m/e (relative intensity) 182 (M^+, 51), 154 (40), 140 (100).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.84; H, 7.63.

2-Carbomethoxy-2-isopropyl-3-cyclohexen-1-one (19c). Prepared in 79% yield (1.51-g scale) as described for **19a**; Kugelrohr distillation (~76 °C (0.3 mmHg)); ^{1}H NMR ($CDCl_3$) δ 0.84 (d, 3 H, J = 6.8 Hz), 0.90 (d, 3 H, J = 7.0 Hz), 2.30–2.76 (m, 5 H), 3.71 (s, 3 H), 5.78 (dt, 1 H, J = 10 Hz, J = 1.0 Hz), 6.16 (dt, 1 H, J = 9.9 Hz, J = 3.6 Hz); IR (film) 1715, 1735 cm^{-1}; mass spectrum, m/e 196 (M^+).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.37; H, 8.28.

2-Carbomethoxy-2-(3-chloropropyl)-3-cyclohexen-1-one (19d). Prepared in 98% yield as described for **19a**. The analytical sample was prepared by HPLC (hexane–ethyl acetate, 15:1): oil; ^{1}H NMR ($CDCl_3$) δ 1.7 (m, 2 H), 1.92 (m, 1 H), 2.2 (m, 1 H), 2.5 (m, 3 H), 2.76 (m, 1 H), 3.52 (t, 2 H, J = 6 Hz), 3.71 (s, 3 H), 5.7 (d, 1 H, J = 10 Hz), 6.16 (m, 1 H); IR (film) 1725 cm^{-1}; mass spectrum, m/e (relative intensity) 230 (M^+, 4), 202 (7), 198 (9), 188 (22), 125 (81).

Anal. Calcd for $C_{11}H_{15}ClO_3$: C, 57.27; H, 6.55. Found: C, 57.31; H, 6.50.

2-Benzyl-2-carbomethoxy-3-cyclohexen-1-one (19e). Prepared in 98% yield as described for **19a**; flash chromatography (silica gel, hexane–ethyl acetate, 8.5:1) oil: ^{1}H NMR ($CDCl_3$) δ 1.85–2.75 (m, 4 H), 3.22 (d, 1 H, J = 12 Hz), 3.33 (d, 1 H, J = 12 Hz), 3.70 (s, 3 H), 5.60–6.15 (m, 2 H), 7.15 (s, 5 H); IR (film) 1725, 1600 cm^{-1}; UV (MeOH) λ_{max} 220 nm (ϵ 2030) with tailing to 300 nm.

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.83; H, 6.58.

2-Carbomethoxy-2,6-dimethyl-3-cyclohexen-1-one (20a). Prepared in 78% yield by heating a solution of **5a** (43 mg, 0.22 mmol) in benzene (10 mL) with *p*-toluenesulfonic acid monohydrate (83 mg, 0.44 mmol) at reflux temperature for 12 h; flash chromatography (silica gel, hexane–ethyl acetate, 5:1) gave a mixture of diastereoisomers: major isomer (68%) ^{1}H NMR ($CDCl_3$) δ 1.11 (d, 3 H, J = 6.5 Hz), 1.40 (s, 3 H), 2.10–2.18 (m, 1 H), 2.53–2.70 (m, 1 H), 2.95–3.01 (m, 1 H), 3.71 (s, 3 H), 5.70 (dd, 1 H, J = 10 Hz, J = 2 Hz), 5.88 (m, 1 H); minor isomer (32%) ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 3 H, J = 7 Hz), 1.47 (s, 3 H), 2.22–2.38 (m, 1 H), 2.53–2.80 (m, 2 H), 3.69 (s, 3 H), 5.67 (dd, 1 H, J = 8 Hz, J = 3 Hz), 5.87 (m, 1 H); IR ($CHCl_3$) 1735, 1710 cm^{-1} (mixture).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.69; H, 7.81.

2-Carbomethoxy-2,5-dimethyl-3-cyclohexen-1-one (20b). Prepared in 96% yield as described for **19a**: Kugelrohr distillation (~105 °C (1.5 mmHg)); ~1.3:1 mixture of diastereoisomers; ^{1}H NMR ($CDCl_3$) δ 1.08, 1.15 (two d, 3 H, J = 7 Hz), 1.39, 1.42 (two s, 3 H), 2.18–2.83 (m, 3 H), 3.70, 3.72 (two s, 3 H), 5.61–5.96 (m, 2 H); IR (film) 1740, 1715 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.02; H, 7.60.

2-Carbomethoxy-2,4-dimethyl-3-cyclohexen-1-one (20c). Prepared in 95% yield as described for **19a**: ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 3 H), 1.80 (s, 3 H), 2.05–2.82 (m, 4 H), 3.78 (s, 3 H), 5.39 (br s, 1 H); IR (film) 1740, 1720 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.77; H, 7.63.

2-Carbomethoxy-3-methoxy-2-methyl-3-cyclohexen-1-one (20d). A solution of **5d** (50 mg, 0.24 mmol) in anhydrous acetone (0.5 mL) was cooled to 0 °C and *p*-toluenesulfonic acid monohydrate (45 mg, 0.24 mmol) was added. The reaction was carefully monitored by thin-layer chromatography (hexane–ethyl acetate, 3:1). After 15 min, saturated sodium bicarbonate was added and the solution was extracted immediately with ether (2 × 10 mL). The organic extracts were combined, dried over anhydrous magnesium sulfate, and concentrated. The mixture was separated by flash chromatography (silica gel, hexane–ethyl acetate, 3:1) to give diketone **30** (8.5 mg), starting material **5d** (10 mg), and monoketone **20d** (21.5 mg, oil): ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 3 H), 2.32–2.49 (m, 2 H), 2.59 (t, 2 H, J = 4 Hz), 3.57 (s, 3 H), 3.70 (s, 3 H), 4.97 (t, 1 H, J = 2 Hz); IR (film) 1740, 1710, 1660 cm^{-1}.

2-Carbomethoxy-2-methyl-1,3-cyclohexanedione (21). A solution of **5d** (50 mg, 0.24 mmol) in acetone (0.5 mL) and *p*-toluenesulfonic acid monohydrate (44.86 mg, 0.24 mmol) was stirred at room temperature for 0.5 h. Saturated sodium bicarbonate was added and the aqueous mixture was extracted with ether (2 × 10 mL). The organic extracts were combined, dried over anhydrous magnesium sulfate, and concentrated to give a clear oil. The oil was purified by flash chromatography (silica gel, hexane–ethyl acetate, 3:1) to give **21** (38 mg, 87%): ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 3 H), 1.74–2.20 (m, 2 H), 2.54–2.93 (m, 4 H), 3.77 (s, 3 H); IR (film) 1750, 1710 cm^{-1}.

Anal. Calcd for $C_9H_{12}O_4$: C, 58.68; H, 6.57. Found: C, 58.46; H, 6.55.

Reaction of 2-Alkyl-2-carbomethoxy-3-cyclohexen-1-ones with *N*-Bromosuccinimide. Acid-Catalyzed Hydrolysis of 6-Alkyl-6-carbomethoxy-2,4-cyclohexadien-1-one, Dimethyl Ketals. Preparation of 6-Carbomethoxy-6-methyl-2,4-cyclohexadien-1-one (17a). A solution of **19a** (0.224 g, 1.33 mmol) and *N*-bromosuccinimide (0.28 g, 1.6 mmol) in benzene (50 mL) was heated at reflux temperature while irradiated by a sun lamp for 2 h. After cooling to room temperature, the reaction mixture was washed with sodium thiosulfate solution (10%, 2 × 10 mL), water (2 × 10 mL), and brine (2 × 10 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated; HPLC (hexane–ethyl acetate, 9:1) gave an oil (0.149 g, 67%): ^{1}H NMR ($CDCl_3$) δ 1.5 (s, 3 H), 3.72 (s, 3 H), 6.14 (d, 1 H, J = 10 Hz), 6.36 (s, 2 H), 7.12 (m, 1 H); IR (film) 1740, 1660, 1560 cm^{-1}; mass spectrum, m/e (relative intensity) 166 (M^+, 41), 134 (13), 121 (29), 112 (16), 106 (66); UV (MeOH) λ_{max} (ϵ) 302 nm (3800).

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 64.88; H, 6.14.

6-Carbomethoxy-6-ethyl-2,4-cyclohexadien-1-one (17b). Prepared in 53% yield as described for **17a**: HPLC (hexane–ethyl acetate, 9:1), oil; ^{1}H NMR ($CDCl_3$) δ 0.78 (t, 3 H, J = 7 Hz), 2.02 (m, 1 H), 2.1 (m, 1 H). 3.7 (s, 3 H), 6.13 (d, 1 H, J = 10 Hz), 6.4 (m, 2 H), 7.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.13, 30.62, 52.92, 63.28, 123.29, 126.56, 139.78, 141.57, 169.69, 198.43; IR (film) 1730, 1670, 1630, 1560 cm^{-1}; mass spectrum, m/e (relative intensity) 180 (M^+, 10), 148 (15), 121 (55); UV (MeOH) λ_{max} (ϵ) 305 nm (4300).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.45; H, 6.63.

6-Carbomethoxy-6-isopropyl-2,4-cyclohexadien-1-one (17c). A solution of **19c** (25 mg, 0.13 mmol) in CCl_4 (0.9 mL) was cooled to 0 °C. *N*-Bromosuccimide (30 mg, 0.15 mmol) and a few crystals of benzoyl peroxide were added and the mixture was irradiated with a sun lamp, vigorously stirred, and maintained at 0 °C for 1 h. Triethylamine (30 μL, 0.20 mmol) was added and the mixture was stirred at room temperature for ~20 h. Ether was added and the resulting solution was washed with water, sodium thiosulfate, 1 N HCl, and 1 N NaOH. Drying and solvent evaporation gave an oil; Kugelrohr distillation (~60 °C (0.4 mmHg)) gave **17c** (13 mg, 52%): ^{1}H NMR δ 0.83 (d, 3 H, J = 6.8 Hz), 1.02 (d, 3 H, J = 7.0 Hz), 2.81 (7 line m, 1 H, J = 6.9 Hz), 3.70 (s, 3 H), 6.06 (m, 1 H), 6.44 (m, 2 H), 6.98–7.06 (m, 1 H); IR (film) 1665, 1743 cm^{-1}; chemical-ionization mass spectrum, m/e 195 (M^+ + 1). An acceptable elemental analysis for this compound could not be obtained.

6-Carbomethoxy-6-(3-chloropropyl)-2,4-cyclohexadien-1-one (17d). Prepared in 52% yield as described for **17a**: HPLC (hexane–ethyl acetate, 9:1), oil; ^{1}H NMR ($CDCl_3$) δ 1.62 (m, 2 H), 2.14 (m, 1 H), 2.36 (m, 1 H), 3.48 (m, 2 H), 3.69 (s, 3 H), 6.14 (d, 1 H, J = 10 Hz), 6.4 (m, 2 H), 7.12 (m, 1 H); IR (film) 1740, 1670, 1630, 1565 cm^{-1}; mass spectrum, m/e (relative intensity) 228 (M^+, 16), 196 (10), 160 (15), 152 (17); UV (MeOH) λ_{max} (ϵ) 305 nm (3900).

Anal. Calcd for $C_{11}H_{13}ClO_3$: C, 57.77; H, 5.73. Found: 57.75; H, 5.62.

6-Benzyl-6-carbomethoxy-2,4-cyclohexadien-1-one (17e). Prepared in 63% yield as described for **17c**; not stable to vacuum distillation; flash chromatography (silica gel, hexane–ethyl acetate, 7:1); crystallization from hexane: mp 88–89 °C; ^{1}H NMR ($CDCl_3$) δ 3.35 (d, 1 H, J = 12 Hz), 3.55 (d, 1 H, J = 12 Hz), 3.70 (s, 3 H), 5.82–6.40 (m, 4 H), 6.54–7.15 (m, 5 H); IR (film) 1745, 1665, 1630 cm^{-1}; chemical-ionization mass spectrum, m/e 243 (M^+ + 1); UV (MeOH) λ_{max} 308 nm (ϵ 2535) with tailing to 400 nm.

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.47; H, 5.92.

While all ketals **15** underwent acid-catalyzed hydrolysis to 2,4-cyclohexadien-1-ones, the preparation of **17e** by this procedure is representative. A few crystals of *p*-toluenesulfonic acid were added to a solution of **15e** (1.00 g, 3.47 mmol) in acetone–water (4:1, 100 mL). After 12 h at room temperature, the reaction mixture was extracted with hexane (2 × 30 mL). The combined organic extracts were washed with sodium bicarbonate (1 × 50 mL) and brine (1 × 50 mL), dried, and evaporated to give crystalline **17e** (0.44 g, 59%).

6-Carbomethoxy-2,6-dimethyl-2,4-cyclohexadien-1-one (18a). Prepared in 75% yield as described for **17a** and 97% yield by hydrolysis of **16a** as described for **17e**: flash chromatography (silica gel, hexane–ethyl acetate, 3:1), oil; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 3 H), 1.92 (d, 3 H, J = 1 Hz), 3.68 (s, 3 H), 6.18 (m, 2 H), 6.86 (m, 1 H); IR (film) 1740, 1660, 1640, 1580 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 306 nm (1680).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.69. Found: C, 66.43; H, 6.69.

6-Carbomethoxy-3,6-dimethyl-2,4-cyclohexadien-1-one (18b). Prepared in 62% yield as described for **17a**: flash chromatography (silica gel, hexane–ethyl acetate, 3:1), oil; ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 3 H), 2.11 (s, 3 H), 3.69 (s, 3 H), 5.96 (br s, 1 H), 6.23 (AB quartet, 2 H, J = 6 Hz); IR (film) 1750, 1665, 1645 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 308 nm (1940).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.69. Found: C, 66.58; H, 6.65.

6-Carbomethoxy-4,6-dimethyl-2,4-cyclohexadien-1-one (18c). Prepared in 88% yield as described for **17a**; crystallization from ether: mp 81–83 °C; ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 3 H), 1.99 (s, 3 H), 3.68 (s, 3 H), 6.00 (br s, 1 H), 6.12 (d, 1 H, J = 6 Hz), 7.07 (d, 1 H, J = 6 Hz, with weak allylic coupling); IR (CCl_4) 1745, 1675, 1650, 1230 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 312 nm (3680).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.69. Found: C, 66.49; H, 6.59.

6-Carbomethoxy-5-methoxy-6-methyl-2,4-cyclohexadien-1-one (18d). Prepared in 62% overall yield from **13d** by dehydrobromination (as described for **15a**) to give ketal **16d** (not characterized), followed by deketalization during flash chromatography (silica gel, hexane–ethyl acetate, 1:1), oil: ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 3 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 5.40 (d, 1 H, J = 6 Hz), 5.85 (d, 1 H, J = 8 Hz), 7.25 (dd, 1 H, J = 8 Hz, J = 2 Hz); ^{1}H NMR (C_6D_6) δ 1.21 (s, 3 H), 2.95 (s, 3 H), 3.31 (s, 3 H), 4.68 (d, 1 H, J = 6 Hz), 5.82 (d, 1 H, J = 8 Hz), 6.54 (dd, 1 H, J = 8 Hz, J = 6 Hz); IR (CH_2Cl_2) 1750, 1670, 1625, 1540 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 325 nm (7150).

Diels–Alder Reactions of 6-Alkyl-6-carbomethoxy-2,4-cyclohexadien-1-ones. Preparation of 3-Methyl-3,5,6-tricarbomethoxybicyclo[2.2.2]octa-5,7-dien-2-one (23a). A solution of **17a** (0.13 g, 0.78 mmol) and dimethyl acetylenedicarboxylate (0.10 mL, 0.84 mmol) in benzene (1 mL) was heated at reflux temperature for ~20 h. Evaporation of solvent and ^{1}H NMR analysis indicated that **17a** had been consumed and **23a** was present as a 3:1 mixture of diastereoisomers. Flash chromatography (silica gel, hexane–ethyl acetate, 2:1) gave the major isomer (90 mg), mp 97–98 °C and the minor isomer (40 mg), mp 103–104 °C. Major isomer: ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3 H), 3.68 (s, 3 H), 3.81 (s, 3 H), 3.84 (s, 3 H), 4.45 (dd, 1 H, J = 5.9 Hz, J = 1.8 Hz), 4.56 (dd, 1 H, J = 5.8 Hz, J = 1.6 Hz), 6.56–6.77 (m, 2 H); IR (KBr) 1713, 1730 cm^{-1}; chemical-ionization mass spectrum, m/e 309 (M^+ + 1).

Anal. Calcd for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23. Found: C, 58.50; H, 5.17.

Minor isomer: ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 3 H), 3.66 (s, 3 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 4.38 (dd, 1 H, J = 5.4 Hz, J = 2.4 Hz), 4.57 (dd, 1 H, J = 5.6 Hz, J = 1.8 Hz), 6.62 (m, 2 H); IR (KBr) 1715, 1730 cm^{-1}; chemical-ionization mass spectrum, m/e 309 (M^+ + 1).

Anal. Found: C, 58.43; H, 5.16.

3-Benzyl-3,5,6-tricarbomethoxybicyclo[2.2.2]octa-5,7-dien-2-one (23b). Ratio of diastereoisomers = 2:1 from **17e**; flash chromatography (silica gel, hexane–ethyl acetate, 4:1) and crystallization from ether gave the major isomer (37%), mp 151–152 °C, and the minor isomer (19%), mp 107–109 °C. Major isomer: ^{1}H NMR ($CDCl_3$) δ 2.70 (d, 1 H, J = 12 Hz), 3.50 (d, 1 H, J = 12 Hz), 3.62 (s, 3 H), 3.76 (s, 3 H), 3.78 (s, 3 H), 4.36 (dd, 1 H, J = 6 Hz, J = 2 Hz), 4.59 (dd, 1 H, J = 6 Hz, J = 2 Hz), 6.64 (m, 2 H), 7.08 (m, 2 H), 7.50 (m, 3 H); IR (KBr) 1730, 1635 cm^{-1}; chemical-ionization mass spectrum, m/e 385 (M^+ + 1).

Anal. Calcd for $C_{21}H_{20}O_7$: C, 65.62; H, 5.24. Found: C, 65.55; H, 5.44.

Minor isomer: ^{1}H NMR ($CDCl_3$) δ 2.74 (d, 1 H, J = 14 Hz), 3.33 (d, 1 H, J = 14 Hz), 3.47 (s, 3 H), 3.82 (s, 3 H), 3.84 (s, 3 H), 3.58 (m, 2 H), 6.47 (t, 1 H, J = 5 Hz), 6.72 (t, 1 H, J = 5 Hz), 7.12 (m, 2 H), 7.25 (m, 3 H); IR (KBr) 1750, 1720, 1645 cm^{-1}; chemical-ionization mass spectrum, m/e 385 (M^+ + 1).

Anal. Found: C, 65.68; H, 5.43.

3,8-Dimethyl-3,5,6-tricarbomethoxybicyclo[2.2.2]octa-5,7-dien-2-one (24). Ratio of diastereoisomers = 9:1 from **18c** (250 mg); flash chromatography (silica gel, hexane–ethyl acetate, 2:1) and crystallization from hexane gave the major isomer (273 mg), mp 87 °C, and crystallization from hexane–ethyl acetate gave the major isomer (46 mg), mp 91 °C. Major isomer: ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 3 H), 1.98 (d, 3 H, J = 1.5 Hz), 3.69 (s, 3 H), 3.82 (s, 3 H), 3.84 (s, 3 H), 4.15 (d, 1 H, J = 2.2 Hz), 4.40 (d, 1 H, J = 6 Hz), 6.11 (m, 1 H); IR ($CHCl_3$) 1755, 1725, 1650, 1630 cm^{-1}.

Anal. Calcd for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63. Found: C, 59.40; H, 5.66.

Minor isomer: ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 3 H), 2.03 (d, 3 H, J = 1.7 Hz), 3.65 (s, 3 H), 3.80 (s, 3 H), 3.83 (s, 3 H), 4.07 (d, 1 H, J = 2.2 Hz), 4.40 (d, 1 H, J = 6.2 Hz), 6.11 (m, 1 H); IR (film) 1755, 1725, 1650, 1630 cm^{-1}.

Anal. Found: C, 59.73; H, 5.72.

Reaction of 17e with Maleic Anhydride. Preparation of 25. A solution of **17e** (0.094 g, 0.39 mmol) and freshly sublimed maleic anhydride (0.04 g, 0.41 mmol) in anhydrous toluene (1 mL) was heated at reflux temperature for ~36 h. The solvent was evaporated and ^{1}H NMR analysis of the crude product mixture indicated that only one diastereoisomer had formed. Crystallization from ether gave **25** (0.054 g, 41%): mp 151–152 °C; ^{1}H NMR ($CDCl_3$) δ 3.02 (d, 1 H, J = 15 Hz), 3.32 (d, 1 H, J = 15 Hz), 3.4–4.0 (m with overlaping s at 3.76, 7 H), 6.12 (t, 1 H, J = 8 Hz), 6.34 (t, 1 H, J = 8 Hz), 7.05 (m, 2 H), 7.30 (m, 3 H); IR (KBr) 1850, 1770, 1710 cm^{-1}; UV (MeOH) λ_{max} 221 nm (ϵ 2530); chemical-ionization mass spectrum, m/e 341 (M^+ + 1).

Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.74. Found: C, 66.89; H, 4.85.

Reaction of 18c with Methyl Acrylate. Preparation of 26. A solution of **18c** (0.330 g, 1.82 mmol) in methyl acrylate (0.82 mL, ~5 equiv) was heated at reflux temperature for 5 h. Unreacted methyl acrylate was evaporated and ^{1}H NMR analysis indicated that a 1:1 mixture of diastereoisomers of **26** had formed. Flash chromatography (silica gel, hexane–ethyl acetate, 3:1) gave **26** (oil, 0.421 g, 87%, 1:1 mixture of diastereoisomers): ^{1}H NMR ($CDCl_3$) δ 1.33, 1.38 (two s, 3 H), 1.6–2.2 (m with two overlapping s at 1.86 and 1.90, 6 H), 2.86, 3.14 (two m, 1 H), 2.88, 3.48 (two d, 1 H, J = 8 Hz), 3.64, 3.72 (two s, 3 H), 3.66 (s, 3 H), 5.70 (br s, 1 H); IR (film) 1730 cm^{-1}; chemical-ionization mass spectrum, m/e 267 (M^+ + 1).

Reaction of 15a with Dimethyl Acetylenedicarboxylate. Preparation of 27 and Hydrolysis to 23a. Adduct **27** was obtained in 80% yield as a 3:1 mixture of diastereoisomers: ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 3 H), 3.5–3.9 (m, 17 H), 6.00 (dd, 1 H, J = 8 Hz, J = 6 Hz), 6.92 (d, 1 H, J = 8 Hz); IR (film) 1730 (br) cm^{-1}. Hydrolysis (dilute HCl in methanol, 3 days at room temperature) and flash chromatography gave **23a** (80% as the same 3:1 mixture of diastereoisomers obtained from reaction of **17a** and dimethyl acetylenedicarboxylate (^{1}H NMR analysis).

Reaction of 15a with Maleic Anhydride. Preparation of 28. Prepared in 4.6% yield as described for **25** (50 h reaction time); crystallization from ether: mp 191–192 °C; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3 H), 2.66 (dd, 1 H, J = 10 Hz, J = 4 Hz), 3.00 (d, 1 H, J = 10 Hz), 3.4–3.6 (m, with overlapping s at 3.56, 4 H), 3.66 (s, 3 H), 3.74 (s, 3 H), 5.18 (d, 1 H, J = 6 Hz), 5.96 (dd, 1 H, J = 8 Hz, J = 6 Hz), 6.98 (d, 1 H, J = 8 Hz); IR (KBr) 1780, 1740, 1720 cm^{-1}.

Anal. Calcd for $C_{15}H_{18}O_7$: C, 58.06; H, 5.85. Found: C, 57.92; H, 5.90.

Hydrogenation of 3-Alkyl-3,5,6-tricarbomethoxybicyclo-[2.2.2]octa-5,7-dien-2-ones. Preparation of 3-Methyl-3,5,6-tricarbomethoxybicyclo[2.2.2]oct-5-en-2-one (29a). Prepared from **23a** (major isomer) in 62% yield by the procedure described by Yates and Stevens;[20c,d] crystallization from ether: mp 46–47 °C; ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 3 H), 1.54–2.17 (m, 4 H), 3.44 (m, 1 H), 3.70 (m, 1 H), 3.75 (s, 3 H), 3.80 (s, 3 H), 3.84 (s, 3 H); IR (CCl_4) 1708 cm^{-1}; chemical-ionization mass spectrum, m/e 311 (M^+ + 1).

Anal. Calcd for $C_{15}H_{18}O_7$: C, 58.05; H, 5.86. Found: C, 58.09; H, 5.78.

3-Benzyl-3,5,6-tricarbomethoxybicyclo[2.2.2]oct-5-en-2-ones (29b and 29c). 29b was prepared from **23b** (major isomer) in 80% yield as described for **29a**; crystallization from methanol: mp 170–171 °C; ^{1}H NMR ($CDCl_3$) δ 1.60–2.20 (m, 4 H), 2.80 (d, 1 H, J = 15 Hz), 3.50–3.80 (m with 2 overlapping s at 3.56 and 3.74, 12 H), 7.08 (m, 2 H), 7.26 (m, 3 H); IR (KBr) 1730 (br), 1635 cm^{-1}; UV (MeOH) λ_{max} 238 nm (ϵ 24 600) with tailing to 310 nm; chemical-ionization mass spectrum, m/e 387 (M^+ + 1).

Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.30; H, 5.78.

29c was prepared from **23b** (minor isomer) in 83% yield as described for **29a**; crystallization from methanol: mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.50–2.00 (m, 4 H), 3.06 (d, 1 H, J = 10 Hz), 3.11 (d, 1 H, J = 10 Hz), 3.60–3.74 (m with overlapping s at 3.63, 5 H), 3.78 (s, 3 H), 3.80 (s, 3 H), 7.08 (m, 2 H), 7.24 (m, 3 H); IR (Nujol) 1730 (br) 1640 cm^{-1}; UV (MeOH) λ_{max} 228 nm (ϵ 4800) with tailing to 330 nm; chemical-ionization mass spectrum, m/e 387 (M^+ + 1).

Anal. Found: C, 65.06; H, 5.86.

Photorearrangement of 29a–c. Preparation of 4-Methyl-2,4,8-tricarbomethoxytricyclo[3.2.1.0^{2,8}]octan-3-one (30a). A solution of **29a** (49 mg, 0.16 mmol) in acetophenone (10 mL) was purged with N_2 for 15 min prior to irradiation (Pyrex glassware) with the 366-nm light source for 24 h. Evaporation of acetophenone produced crystalline **30a**; recrystallization from ether (25 mg, 51%): mp 100–101 °C; ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 3 H), 1.59–2.27 (m, 4 H), 3.22–3.28 (m, 2 H), 3.73 (s, 3 H), 3.74 (s, 3 H), 3.76 (s, 3 H); IR (CCl_4) 1713 (br) cm^{-1}; chemical-ionization mass spectrum, m/e 311 (M^+ + 1).

Anal. Calcd for $C_{15}H_{18}O_7$: C, 58.05; H, 5.86. Found: C, 57.95; H, 5.78.

4-Benzyl-2,4,8-tricarbomethoxytricyclo[3.2.1.0^{2,8}]octan-3-ones (30b and 30c). 30b was prepared in 60% yield as described for **30a** (16 h irradiation required); crystallization from ether: mp 130–131 °C; ^{1}H NMR ($CDCl_3$) δ 1.5–2.2 (m, 4 H), 2.30 (d, 1 H, J = 14 Hz), 3.08 (br d, 1 H, J = 6 Hz), 3.52 (d, 1 H, J = 14 Hz), 3.60 (s, 3 H), 3.64 (s, 6 H), 3.82 (br d, 1 H, J = 6 Hz), 7.02 (s, 2 H), 7.18 (m, 3 H); IR (KBr) 1740 cm^{-1}; chemical-ionization mass spectrum, m/e 387 (M^+ + 1).

Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.50; H, 5.63.

30c was prepared in 65% yield as described for **30a** (56 h irradiation required); crystallization from ether: mp 135 °C; ^{1}H NMR ($CDCl_3$) δ 1.5–2.2 (m, 4 H), 3.10 (d, 1 H, J = 14 Hz), 3.18 (br d, 1 H, J = 6 Hz), 3.44 (m, 2 H), 3.64 (s, 3 H), 3.70 (s, 3 H), 3.78 (s, 3 H), 7.20 (m, 5 H); IR ($CHCl_3$) 1730 cm^{-1}; chemical-ionization mass spectrum, m/e 387 (M^+ + 1).

Anal. Found: C, 65.30; H, 5.78.

2-[(*N*,*N*-Diethylamino)carbonyl]-2,3-dimethyl-3-cyclohexen-1-one (31). Prepared in 96% yield as described for **19a**: flash chromatography (silica gel, ethyl acetate–hexanes, 1:9), oil; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7 Hz), 1.12 (t, 3 H, J = 7 Hz), 1.51 (s, 3 H), 1.67 (br s, 3 H), 2.31–2.80 (m, 4 H), 2.80–3.60 (m, 4 H), 5.64 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.26 (q), 12.44

(q), 18.75 (q), 24.44 (t), 24.67 (q), 34.83 (t), 40.13 (t), 41.34 (t), 59.99 (s), 120.49 (d), 137.19 (s), 169.46 (s); IR ($CHCl_3$) 1710, 1620 cm^{-1}.

Anal. Calcd for $C_{13}H_{21}O_2N$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.75; H, 9.40; N, 6.21.

6-Bromo-2-[(*N*,*N*-diethylamino)carbonyl]-2,3-dimethyl-3-cyclohexen-1-one, Dimethyl Ketal (32). Prepared in 98% yield as described for **12a**; crystallization from ether–pentane: mp 190 °C dec; ^1H NMR ($CDCl_3$) δ 1.07 (br t, 6 H, J = 7.0 Hz), 1.71 (s, 3 H), 1.73 (br s, 3 H), 2.50–2.90 (br q, 2 H), 3.25 (s, 3 H), 3.20–3.70 (m, 4 H), 3.40 (s, 3 H), 4.48 (br t, 1 H), 5.41 (br d, 1 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 12.20 (q), 12.80 (q), 20.87 (q), 23.35 (q), 28.56 (t), 32.75 (t), 47.96 (d), 48.79 (q), 51.09 (q), 58.95 (s), 116.77 (d), 139.02 (s), 172.18 (s); IR ($CHCl_3$) 1700, 1610 cm^{-1}.

Anal. Calcd for $C_{15}H_{26}O_3NBr$: C, 51.73; H, 7.53; N, 4.02. Found: C, 51.90; H, 7.50; N, 4.06.

6-[(*N*,*N*-Diethylamino)carbonyl]-5,6-dimethyl-2,4-cyclohexadien-1-one, Dimethyl Ketal (33). Prepared in 98% yield was described for **15a**. The analytical sample was prepared by chromatography on alumina (ethyl acetate–hexanes, 1:9), oil: ^1H NMR ($CDCl_3$) δ 1.14 (t, 6 H, J = 7.0 Hz), 1.28 (s, 3 H), 1.70 (s, 3 H), 3.0–4.8 (m, 4 H), 3.21 (s, 3 H), 3.29 (s, 3 H), 5.57 (m, 2 H), 5.98 (dd, 1 H, J = 8 Hz, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 12.32 (q), 14.46 (q), 19.21 (q), 19.59 (q), 40.46 (t), 43.18 (t), 48.29 (q), 49.65 (q), 58.27 (s), 101.19 (s), 116.54 (d), 125.91 (d), 126.01 (d), 143.23 (s), 172.2 (s); IR ($CHCl_3$) 1620, 1590 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 265 nm (5780).

Anal. Calcd for $C_{15}H_{25}O_3N$: C, 67.38; H, 9.43; N, 5.24. Found: C, 67.45; H, 9.54; N, 5.26.

6-[(*N*,*N*-Diethylamino)carbonyl]-6-(2-hydroxyethyl)-1-methoxy-1,4-cyclohexadiene (11b). A solution of **11a** (1.00 g, 3.39 mmol) in methanol (5 mL) and 1 N NaOH (2 mL) was stirred at room temperature for 15 min. Saturated NH_4Cl (10 mL) was added and the mixture was extracted with ether (3 × 20 mL). The combined ether layers were washed with brine, dried, and evaporated to give crystalline **11b** (763 mg, 89%): mp 67–68 °C; ^1H NMR ($CDCl_3$) δ 1.05 (m, 6 H), 1.68 (m, 1 H), 1.8–2.2 (m, 2 H), 2.34 (m, 1 H), 2.88 (m, 2 H), 3.1–3.5 (m, 5 H, 1 H exchangeable with D_2O), 3.53 (s, 3 H), 3.65 (m, 2 H), 4.66 (t, 1 H, J = 3.6 Hz), 5.71 (dt, 1 H, J_d = 12 Hz, J_t = 2 Hz), 5.87 (dt, 1 H, J_d = 10 Hz, J_t = 2 Hz); IR ($CDCl_3$) 3400, 1680, 1620 cm^{-1}.

Anal. Calcd for $C_{14}H_{23}O_3N$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.32; H, 9.08; N, 5.47.

Reaction of 11b with *N*-Bromoacetamide in Acetonitrile. Reaction conditions were as described for **12a** except that acetonitrile was used as solvent; HPLC (ethyl acetate–hexanes, 1:5) gave **34a** (first fraction, oil, 18%): ^1H NMR ($CDCl_3$) δ 1.14 (t, 6 H, J = 7.5 Hz), 1.93 (m, 1 H), 2.74 (m, 2 H), 3.1 (m, 1 H), 3.2 (m, 2 H), 3.46 (s, 3 H), 3.55 (m, 2 H), 3.90 (m, 1 H), 4.14 (m, 1 H), 4.88 (dd, 1 H, J = 8.7 Hz, J = 7.5 Hz), 5.66 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.09 (q), 13.14 (q), 34.85 (t), 38.15 (t), 41.47 (two overlapping t), 51.98 (q), 52.64 (d), 62.60 (s), 67.72 (t), 106.34 (s), 126.0 (d), 130.26 (d), 169.21 (s); IR ($CHCl_3$) 1620 cm^{-1}; mass spectrum, m/e (relative intensity) 333 (M^+ + 2, 1.75), 331 (1.64), 302 (1.2), 300 (1.1), 253 (9.9), 252 (M^+ – Br, 58).

Anal. Calcd for $C_{14}H_{22}O_3NBr$: C, 50.61; H, 6.75. Found: C, 50.78; H, 6.72.

Further elution gave **34b** (second fraction, mp 63 °C, 53%): ^1H NMR ($CDCl_3$) δ 1.11, 1.14 (two overlapping t, 6 H, J = 7.5 Hz), 1.65 (8 line m, 1 H), 2.74 (m, 2 H), 3.2 (8 line m, 1 H), 3.19 (m, 2 H), 3.34 (s, 3 H), 3.48–3.84 (m, 2 H), 3.96 (m, 1 H), 4.25 (m, 1 H), 4.38 (t, 1 H, J = 6 Hz), 5.70 (dt, 1 H, J_d = 10 Hz, J_t = 4 Hz), 5.99 (td, 1 H, J_d = 10 Hz, J_t = 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 13.56 (q), 13.62 (q), 32.80 (t), 42.20 (3 overlapping t), 51.29 (q), 52.24 (d), 59.16 (s), 67.74 (t), 107.21 (s), 122.67 (d), 132.4 (d), 170.13 (s); IR ($CHCl_3$) 1630 cm^{-1}; mass spectrum, m/e (relative intensity) 333 (M^+ + 2, 3.8), 331 (3.8), 253 (6.5), 252 (M^+ – Br, 42).

Anal. Found: C, 50.69; H, 6.75.

Reaction of **11b** with *N*-bromoacetamide in methanol as described for **12a** gave a 2:1 ratio of **34a** and **34b** in 62% yield (flash chromatography, silica gel, ethyl acetate–methylene chloride, 1:5).

Dehydrobromination of 34a and 34b. In independent experiments, **34a** and **34b** both gave diene **35** (~98%) by the procedure used for preparation of **15e**: crystalline solid; mp 55–56 °C; ^1H NMR ($CDCl_3$) δ 0.99, 1.06 (two overlapping t, 6 H, J = 7.5 Hz), 1.6 (m, 1 H), 2.78 (m, 1 H), 2.88–2.98 (m, 2 H), 3.30 (s, 3 H), 3.48 (m, 3 H), 3.63 (m, 1 H), 5.97 (m, 2 H), 6.20 (m, 2 H); ^1H NMR (C_6D_6) δ 0.80 (t, 3 H, J = 7.5 Hz), 1.09 (t, 3 H, J = 7.5 Hz), 1.49 (8 lime m, 1 H), 2.64, 3.00 (two m, 4 H), 3.20 (s, 3 H), 3.38 (td, 1 H, J_t = 7.4 Hz, J_d = 2 Hz), 3.62 (m, 1 H), 3.85 (m, 1 H), 5.55 (m, 1 H), 5.71 (m, 2 H), 6.10 (dt, 1 H, J_t = 10 Hz, J_d = 1 Hz); IR ($CHCl_3$) 1630, 1580 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 266 (6900).

Anal. Calcd for $C_{14}H_{21}O_3N$: C, 66.90; H, 8.42; N, 5.58. Found: C, 69.70; H, 8.57; N, 5.41.

Reaction of 11b with Phenylselenenyl Chloride in Methylene Chloride. Reaction conditions as described by Clive et al. in the literature[26] gave selenide **34c** (91%): flash chromatography (silica gel, ethyl acetate–methylene chloride, 1:5), oil; ^1H NMR ($CDCl_3$) δ 1.11 (t, 6 H, J = 7 Hz), 1.78 (m, 1 H), 2.48 (m, 2 H), 3.24 (m, 3 H), 3.44 (s, 3 H), 3.57 (m, 2 H), 3.83 (m, 2 H), 4.15 (m, 1 H), 5.71 (br s, 2 H), 7.25 (m, 3 H), 7.64 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.4 (two overlapping q), 31.91 (t), 39.65 (t), 41.42 (two overlapping t), 48.19 (d), 51.47 (q), 61.79 (t), 67.97 (s), 108.42 (s), 125.89 (d), 127.14 (d), 128.80 (d), 130.26 (s), 131.43 (d), 134.40 (d), 169.46 (s); IR ($CHCl_3$) 1630 cm^{-1}.

Anal. Calcd for $C_{20}H_{27}O_3NSe$: C, 58.82; H, 6.67. Found: C, 58.91; H, 6.70.

Selenide **34c** was treated with H_2O_2 (30%) in THF at 0 °C and stirred at room temperature for ~24 h. Chromatography on alumina (CH_2Cl_2) gave crystalline **35** in 96% yield.

Preparation of the *d*-Menthol Ester of *o*-Anisic Acid 36. A solution of *d*-menthol (312 mg, 2 mmol), triethylamine (202 mg, 2 mmol), and *o*-anisoyl chloride (342 mg, 2 mmol) in methylene chloride (1 mL) was heated at reflux temperature for 12 h. Methylene chloride was added and the resulting solution was washed with 10% HCl and brine, dried, evaporated, and chromatographed (silica gel, hexanes–methylene chloride, 3:7) to give an oil, which slowly solidified on standing (536 mg, 96%, mp 42 °C): ^1H NMR ($CDCl_3$) δ 0.81 (d, 3 H, J = 7 Hz), 0.93 (d, 6 H, J = 7 Hz), 1.11 (m, 3 H), 1.54 (m, 2 H), 1.72 (m, 2 H), 2.12 (m, 2 H), 3.89 (s, 3 H), 4.92 (dt, 1 H, J_t = 10 Hz, J_d = 4 Hz), 6.98 (m, 2 H), 7.45 (m, 1 H), 7.74 (m, 1 H); IR ($CHCl_3$) 1700 cm^{-1}; chemical-ionization mass spectrum, m/e 291 (M^+ + 1).

Birch Reduction–Alkylation of *d*-Menthol Ester 36. Preparation of 36a,b. Prepared in 83% yield as a 1:1 mixture of distereoisomers as described for **4c**: flash chromatography (silica gel, ethyl acetate–methylene chloride, 1:49), oil; ^1H NMR ($CDCl_3$) δ 0.72 (d, 3 H, J = 7.0 Hz), 0.87 (two overlapping d, 6 H, J = 7.0 Hz), 1.0 (m, 3 H), 1.40 (s, 3 H), 1.42 (m, 1 H), 1.64 (m, 3 H), 1.9 (m, 2 H), 2.83 (m, 2 H), 3.50, 3.54 (two s, 1:1, 3 H), 4.66 (dt, 1 H, J_t = 10 Hz, J_d = 4 Hz), 4.74 (m, 1 H), 5.49 (dt, 1 H, J_d = 10 Hz, J_t = 2.2 Hz), 5.78 (dt, 1 H, J_d = 9.8 Hz, J_t = 3.4 Hz); IR ($CHCl_3$) 1730, 1680 cm^{-1}; chemical-ionization mass spectrum, m/e 307 (M^+ + 1).

Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 73.91; H, 9.27.

Bromoketalization of 36a,b. Preparation of 38a and 38b. Prepared as described for **12a**: crystallization from hexane gave **38a** (49%), mp 126 °C; ^1H NMR ($CDCl_3$) δ 0.74 (d, 3 H, J = 7 Hz), 0.90 (t, 6 H, J = 7 Hz), 1.00 (m, 2 H), 1.40 (m, 2 H), 1.48 (s, 3 H), 1.65 (m, 3 H), 1.97 (m, 2 H), 2.74 (m, 2 H), 3.45 (s, 3 H), 3.62 (s, 3 H), 4.70 (dt, 1 H, J_t = 10 Hz, J_d = 6 Hz), 5.00 (dd, 1 H, J = 6.2 Hz, J = 6.0 Hz), 5.27 (dt, 1 H, J_d = 10 Hz, J_t = 2.0 Hz), 5.63 (dt, 1 H, J_d = 10 Hz, J_t = 4 Hz); ^{13}C NMR ($CDCl_3$) δ 16.09 (q), 20.83 (q), 21.18 (q), 22.02 (q), 23.26 (t), 26.00 (d), 31.42 (d), 34.21 (t), 34.99 (t), 40.36 (t), 46.96 (d), 50.59 (d), 51.62 (q), 51.74 (q), 57.32 (s), 75.40 (d), 98.10 (s), 124.58 (d), 131.90 (d), 172.19 (s); IR ($CHCl_3$) 1720 cm^{-1}.

Anal. Calcd for $C_{20}H_{33}O_4Br$: C, 57.55; H, 7.97. Found: C, 57.73; H, 7.88.

Concentration of the mother liquor and flash chromatography (silica gel, ethyl acetate–methylene chloride, 1:49) gave **38b** (48%, oil): ^1H NMR ($CDCl_3$) δ 0.75 (d, 3 H, J = 7.0 Hz), 0.91 (d, 6 H, J = 6.6 Hz), 1.00 (m, 2 H), 1.40 (m, 2 H), 1.49 (s, 3 H), 1.65 (m, 3 H), 1.97 (m, 2 H), 2.72 (m, 2 H), 3.43 (s, 3 H), 3.62 (s, 3 H), 4.71 (dt, 1 H, J_t = 10 Hz, J_d = 6 Hz), 5.01 (dd, 1 H, J = 6.2 Hz, J = 6.0 Hz), 5.27 (dt, 1 H, J_d = 10 Hz, J_t = 2.0 Hz), 5.65 (dt, 1 H, J_d = 10 Hz, J_t = 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ 15.91 (q), 20.89 (q), 21.10 (q), 22.02 (q), 23.09 (t), 25.90 (d), 31.40 (d), 34.23 (t), 34.72 (t), 40.43 (t), 47.01 (d), 50.31 (d), 51.46 (q), 52.70 (q), 57.40 (s), 75.43 (d), 98.15 (s), 124.57 (d), 132.10 (d), 172.32 (s); IR ($CHCl_3$) 1720 cm^{-1}.

Anal. Found: C, 57.60; H, 7.98.

CD measurements: **38a** and **38b** exhibited identical maxima with opposite sign at λ_{max} 222 nm (EtOH).

Dehydrobromination of 38a and 38b. Preparation of 39a and 39b. Prepared as described for **15c**; **39a**: chromatography (alumina, hexane–methylene chloride, 1:1), oil, 95%; ^{1}H NMR ($CDCl_3$) δ 0.74 (d, 3 H, J = 7.8 Hz), 0.90 (t, 6 H, J = 7.2 Hz), 1.08 (m, 2 H), 1.34 (s, 3 H), 1.4 (m, 2 H), 1.65 (m, 3 H), 1.97 (m, 2 H), 3.28 (s, 3 H), 3.37 (s, 3 H), 4.73 (dt, 1 H, J_t = 10 Hz, J_d = 4.4 Hz), 5.63 (d, 1 H, J = 10 Hz), 5.87 (br d, 2 H, J = 2.4 Hz), 6.08 (8 line m, 1 H); ^{1}H NMR (C_6D_6) δ 0.79 (d, 3 H, J = 6.2 Hz), 0.88 (t, 6 H, J = 7.2 Hz), 1.08 (m, 2 H), 1.47 (m, 4 H), 1.60 (s, 3 H), 2.20 (m, 3 H), 3.20 (s, 3 H), 3.30 (s, 3 H), 4.95 (dt, 1 H, J_t = 12 Hz, J_d = 4.2 Hz), 5.53 (dt, 1 H, J_d = 10 Hz, J_t = 1.2 Hz), 5.62 (m, 1 H), 5.78 (m, 1 H), 5.98 (dt, 1 H, J_d = 8 Hz, J_t = 2 Hz) (indicated the presence of ≤4% of diastereoisomer **39b**); IR ($CHCl_3$) 1725, 1670 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 260 nm (3270); chemical-ionization mass spectrum, m/e 337 (M^+ + 1).

Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.39; H, 9.59. Found: C, 71.31; H, 9.62.

39b: oil, 85%; ^{1}H NMR ($CDCl_3$) δ 0.74 (d, 3 H, J = 7 Hz), 0.90 (m, 6 H), 1.08 (m, 2 H), 1.34 (s, 3 H), 1.40 (m, 2 H), 1.65 (m, 3 H), 1.97 (m, 2 H), 3.25 (s, 3 H), 3.34 (s, 3 H), 4.75 (dt, 1 H, J_t = 10 Hz, J_d = 4 Hz), 5.64 (d, 1 H, J = 10 Hz), 5.85 (m, 2 H), 6.06 (8 line m, 1 H); ^{1}H NMR (C_6D_6) δ 0.72 (d, 3 H, J = 6.4 Hz), 0.9 (two overlapping d, 6 H, J = 3.5 Hz), 1.08 (m, 2 H), 1.46 (m, 4 H), 1.61 (s, 3 H), 2.0–2.2 (m, 3 H), 3.16 (s, 3 H), 3.36 (s, 3 H), 4.93 (dt, 1 H, J_t = 10 Hz, J_d = 4 Hz), 5.55 (dt, 1 H, J_d = 10 Hz, J_t = 1.2 Hz), 5.63 (m, 1 H), 5.7, (m, 1 H), 5.88 (dt, 1 H, J_d = 8 Hz, J_t = 2 Hz) (indicated the presence of ≤3% **39a**); IR ($CHCl_3$) 1725, 1670 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 260 nm (3300); chemical-ionization mass spectrum, m/e 337 (M^+ + 1).

Anal. Found: C, 71.49; H, 9.66.

Ketal Hydrolysis of 39a and 39b. Preparation of 2,4-Cyclohexadien-1-ones 40a and 40b. Prepared in 98% yield as described for the conversion of **16a** into **18a**; **40a**: chromatography (alumina, methylene chloride), oil; ^{1}H NMR ($CDCl_3$) δ 0.73 (d, 3 H, J = 6.8 Hz), 0.86 (two overlapping d, 6 H, J = 7.2 Hz), 0.95 (m, 1 H), 1.26 (m, 3 H), 1.49 (s, 3 H), 1.6 (m, 4 H), 1.92 (m, 1 H), 4.58 (td, 1 H, J_t = 10 Hz, J_d = 4 Hz), 6.14 (br d, 1 H, J = 10 Hz), 6.31 (m, 3 H), 7.05 (8 line m, 1 H); IR ($CHCl_3$) 1730, 1665 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 302 nm (4170); mass spectrum, m/e (relative intensity) 290 (M^+, 1.6), 193 (1.4), 152 (18), 134 (16), 108 (18).

Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.44; H, 9.03. Found: C, 74.33; H, 9.12.

40b: oil, 92%; ^{1}H NMR ($CDCl_3$) δ 0.72 (d, 3 H, J = 7.0 Hz), 0.86 (two overlapping d, 6 H, J = 7.2 Hz), 0.95 (m, 1 H), 1.26 (m, 3 H), 1.49 (s, 3 H), 1.60 (m, 4 H), 1.92 (m, 1 H), 4.64 (dt, 1 H, J_d = 4.0 Hz, J_t = 10 Hz), 6.10 (br d, 1 H, J = 10 Hz), 6.30 (m, 2 H), 7.04 (8 line m, 1 H); IR ($CHCl_3$) 1730, 1665, 1630 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 302 nm (4180); mass spectrum, m/e (relative intensity) 290 (M^+, 14), 152 (95), 134 (100).

Anal. Found: C, 74.35; H, 8.92.

Enol Ether Hydrolysis of 36a,b. Preparation of 41a,b. Prepared in 90% yield as described for **19a**; flash chromatography (silica gel, hexanes–methylene chloride, 1:4), oil, 1:1 mixture of **41a** and **41b**. This mixture was converted to a 1:1 mixture of **40a,b** (90%) as described for the conversion of **19c** to **17c**. Spectral and analytical data for **41a,b**: ^{1}H NMR ($CDCl_3$) δ 0.73 (d, 3 H, J = 7 Hz), 0.89 (m, 6 H), 0.95 (m, 2 H), 1.3 (m, 1 H), 1.39 (s, 3 H), 1.4–2.0 (m, 7 H), 2.52 (m, 2 H), 2.70 (m, 1 H), 4.66 (td, 1 H, J_t = 10 Hz, J_d = 4 Hz), 5.69 (br d, 1 H, J = 10 Hz), 5.97 (dt, 1 H, J_d = 10 Hz, J_t = 3.4 Hz); IR ($CHCl_3$) 1730, 1710 cm^{-1}.

Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 74.05; H, 9.73.

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Registry No. **4a**, 21173-69-3; **4b**, 82478-12-4; **4c**, 92242-74-5; **4d**, 86990-71-8; **4e**, 92242-75-6; methyl 4-(bromomethyl)furan-3-carboxylate, 92242-76-7; *cis*-**5b**, 92242-77-8; *trans*-**5b**, 92242-78-9; **5c**, 92242-79-0; **5d**, 82478-17-9; **6**, 92242-80-3; **7**, 92242-81-4; **8**, 92242-82-5; **9a**, 51674-10-3; **9b**, 88430-97-1; **10a**, 92242-83-6; **10b**, 92242-84-7; **11a**, 92242-85-8; **11b**, 92269-49-3; **12a**, 86990-72-9; *cis*-**12b**, 92242-86-9; *trans*-**12b**, 92242-87-0; **12c**, 92242-88-1; *cis*-**12d**, 92242-89-2; *trans*-**12d**, 92242-90-5; *cis*-**12e**, 92242-91-6; *trans*-**12e**, 92242-92-7; **13a**, 92242-93-8; **13b**, 92242-94-9; **13c**, 92242-95-0; *cis*-**13d**, 92242-96-1; *trans*-**13d**, 92242-97-2; **14**, 92242-98-3; **15a**, 86990-75-2; **15b**, 86990-76-3; **15c**, 92242-99-4; **15d**, 92243-00-0; **15e**, 92243-01-1; **16a**, 92243-02-2; **16b**, 92243-03-3; **16c**, 92243-04-4; **16d**, 92243-05-5; **17a**, 70588-24-8; **17b**, 86990-77-4; **17c**, 92243-06-6; **17d**, 86990-79-6; **17e**, 92243-07-7; **18a**, 92243-08-8; **18b**, 92243-09-9; **18c**, 92243-10-2; **18d**, 92243-11-3; **19a**, 63548-79-8; **19b**, 86990-78-5; **19c**, 92243-12-4; **19d**, 87067-85-4; **19e**, 92243-13-5; **20a**, 92243-14-6; **20b**, 92243-15-7; **20c**, 92243-16-8; **20d**, 92243-17-9; **21**, 92243-18-0; **23a** (isomer 1), 92243-19-1; **23a** (isomer 2), 92343-37-8; **23b** (isomer 1), 92243-20-4; **23b** (isomer 2), 92343-38-9; **24** (isomer 1), 92243-21-5; **24** (isomer 2), 92343-39-0; **25** (isomer 1), 92243-22-6; **25** (isomer 2), 92343-40-3; **26** (isomer 1), 92243-23-7; **26** (isomer 2), 92343-41-4; **27** (isomer 1), 92243-24-8; **27** (isomer 2), 92343-42-5; **28** (isomer 1), 92243-25-9; **28** (isomer 2), 92343-43-6; **29a**, 92243-26-0; **29b** (isomer 1), 92243-27-1; **29b** (isomer 2), 92343-44-7; **30a**, 92243-28-2; **30b** (isomer 1), 92243-29-3; **30b** (isomer 2), 92343-45-8; **31**, 92243-30-6; **32**, 92243-31-7; **33**, 92243-32-8; **34a**, 92243-33-9; **34b**, 92243-34-0; **34c**, 92243-35-1; **35**, 92243-36-2; **36**, 92243-37-3; **37** (isomer 1), 92243-38-4; **37** (isomer 2), 92243-39-5; **38**, 92243-40-8; **39** (isomer 1), 92243-41-9; **39** (isomer 2), 92243-42-0; **40** (isomer 1), 92269-41-5; **40** (isomer 2), 92243-43-1; **41** (isomer 1), 92243-44-2; **41** (isomer 2), 92243-45-3; DMAD, 762-42-5; 2-$MeOC_6H_4CO_2Me$, 606-45-1; 2,6-$(MeO)_2C_6H_3CO_2Me$, 2065-27-2; $BrCH_2CO_2Me$, 96-32-2; $AcO(CH_2)_2Br$, 927-68-4; AcNHBr, 79-15-2; CH_2=$CHCO_2Me$, 96-33-3; methyl 4-(bromomethyl)furan-3-carboxylate, 92243-46-4; 2-methyl-1,3-cyclohexanedione, 1193-55-1; maleic anhydride, 108-31-6; 2-cyclopentenone, 930-30-3.