A Diels-Alder Cycloaddition and Electrocyclization Sequence as a New [6.5] Annelation Method to Benzene Ring

Eiji WADA, Shuji KANEMASA, and Otohiko TSUGE*
Research Institute of Industrial Science, and Department of Molecular
Science and Technology, Interdisciplinary
Graduate School of Engineering Sciences, Kyushu University, Kasugakoen, Kasuga 816

(Received February 27, 1986)

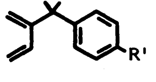
The Diels-Alder reactions of 1-aryl-2-methylene-3-buten-1-ols, readily available from chloroprene and aryl ketones, with olefinic dienophiles and subsequent electrocyclic reactions of the cycloadducts offer a new method of [6.5] annelation to benzene ring. By this way, tetrahydrofluorene skeletons bearing functional groups can be prepared. Stereochemical aspect of this sequence is also discussed.

The Diels-Alder reaction involves the interaction between diene and dienophile forming six-membered ring with an endo double bond. Therefore, two rings annelation including a six-membered ring will be established when another ring-forming reaction is performed across this unsaturated bond. Such sequential ring formation is quite limited,[1] while the double Diels-Alder cycloaddition of cross-conjugated trienes offers an annelation method of this category.[2] It is important that the sequential ring formation is to be initiated by Diels-Alder cycloaddition since this cycloaddition takes place in a highly stereoselective and stereospecific manner. The second ring formation is expected to occur also in a selective way to afford stereochemically defined fused ring systems.[3]

Our method for sequential [6.5] annelation consists of the initial Diels-Alder reactions on 1-aryl-2-methylene-3-buten-1-ols and the subsequent acid-catalized electrocyclic reactions of the cycloadducts. In the Diels-Alder steps, dimethyl maleate, fumarate, and *N*-methylmaleimide are employed as representatives for cis, trans, and cyclic olefinic dienophiles, respectively. It should be emphasized that the present method permits the introduction of several functional groups onto tetrahydrofluorene skeletons.[4]

Results and Discussion

Diene alcohols **1a**—**c** as starting materials in the present [6.5] annelation can be prepared from the reaction of 2-lithio-1,3-butadiene with aryl ketones.[5] Without separation of isomeric allene alcohols as side products, the Diels-Alder reaction with dimethyl maleate (**2**), fumarate (**3**), or *N*-methylmaleimide (**4**) was carried out under reflux in benzene to give the corresponding cycloadducts **5a**—**c**, **6a**—**c**, or **7a**—**c**, in excellent yields (Table 1). These cycloadducts were separated from the unreacted allene alcohols through column chromatography. Then, acid-catalyzed electrocyclic reaction of these cycloadducts was investigated under various conditions.[6]

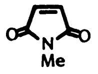


1a-1c

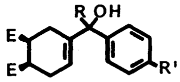
ECH=CHE

2: E=COOMe (cis)

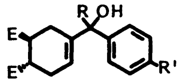
3: E=COOMe (trans)



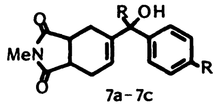
4



5a-5c



6a-6c



7a-7c

a: R=Ph, R'=H; b: R=Me, R'=H; c: R=Me, R'=OMe

The maleate cycloadduct **5a** derived from benzophenone adduct **1a** was found to undergo ready cyclization, in the presence of trifluoroacetic acid (TFA) or zinc chloride, to afford a mixture of two stereoisomeric tetrahydrofluorene derivatives **8a** and **9a** together with a trace amount of diene **10a** (Entries 1—3 in Table 2). Structures of the major product **8a** and the minor one **9a** were assigned to be 3,4a-cis and 3,4a-trans isomers on the basis of coupling constants $J_{3\text{-}4}$, and $J_{4\text{-}4a}$, and also by comparison with their

Table 1. The Diels-Alder Cycloaddition of **1** with **2**—**4**

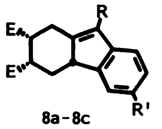
Dienophile (equiv)	Diene	Reaction time/h[a]	Product	Yield/%[b]
2 (2)	**1a**	48	**5a**	82
2 (2)	**1b**	48	**5b**	86
2 (2)	**1c**	48	**5c**	80
3 (2)	**1a**	12	**6a**	86
3 (1.1)	**1b**	16	**6b**	100
3 (1.02)	**1c**	10	**6c**	100
4 (1.2)	**1a**	5	**7a**	86
4 (1)	**1b**	2	**7b**	94
4 (1)	**1c**	5	**7c**	91

a) Under reflux in benzene. b) Isolated yield based on **1**.

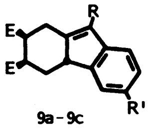
Table 2. Electrocyclic Reaction of Maleate **5** and Fumarate Cycloadducts **6**

Entry	Cyclo-adduct	Reaction conditions[a)]				Total yield/%	Product (isolated yield/%)	3,4a-cis:trans
		Solvent	Catalyst	Temp/°C	Time/h			
1	**5a**	DCM	TFA	−78→0	3	95	**8a** (82), **9a** (11), **10a** (2)	88:12
2		DCM	TFA	rt	8	91	**8a** (83), **9a** (6), **10a** (2)	93: 7
3		DCM	$ZnCl_2$	rt	2.25	91	**8a** (80), **9a** (9), **10a** (2)	90:10
4		BZ	MS	rt	17	93	**8a** (85), **9a** (4), **10a** (4)	95: 5
5	**5b**	DCM	TFA	rt	5 min	89	**8b** (75), **9b** (13), **10b** (1)	85:15
6		THF	6M†-HCl	rt	12	77	**10b** (12), **11** (65)	—
7	**5c**	DCM	TFA	rt	3 min	79	**8c** (68), **9c** (10), **10c** (1)	87:13
8		THF	4M-HCl	rt	24	68	**10c** (14), **12** (54)	—
9	**6a**	DCM	TFA	−78→0	4.5	96	**13a** (41), **14a** (54), **15a** (1)	43:57
10		DCM	TFA	rt	140	74	**13a** (44), **14a** (30)	54:46
11		DCM	$ZnCl_2$	rt	5	93	**13a** (52), **14a** (39), **15a** (2)	57:43
12		BZ	MS	rt	15	93	**13a** (53), **14a** (36), **15a** (4)	60:40
13	**6b**	DCM	TFA	rt	10 min	86	**13b** (56), **14b** (29), **15b** (1)	66:34
14		DCM	TFA[b)]	rt	2	79	**13b** (6), **14b** (4), **16** (69)	—
15		BZ	MS	rt	12	98	**13b** (43), **14b** (33), **16** (22)	56:44
16		THF	3M-HCl	rt	68	52	**16** (52)	—
17	**6c**	DMC	TFA	rt	3 min	69	**13c** (40), **14c** (29)	58:42
18		BZ	MS	rt	40	78	**13c** (21), **14c** (38), **17** (19)	36:64
19		THF	1M-HCl	rt	60	71	**17** (71)	—

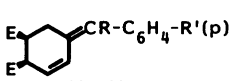
a) Solvent: DCM: dichloromethane; BZ: benzene; THF: tetrahydrofuran. Catalyst: TFA: trifluoroacetic acid; MS: molecular sieves 5A. Unless otherwise stated, the catalyst was used in large excess. b) In the presence of an equimolar amount of TFA. † 1M=1 mol dm^{-3}.



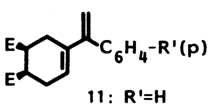
8a-8c



9a-9c



10a-10c



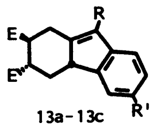
11: R'=H
12: R'=OMe

a: R=Ph, R'=H; b: R=Me, R'=H; c: R=Me, R'=OMe

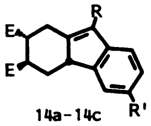
isomers **13a** and **14a** obtained from similar cyclization of fumarate cycloadduct **6a**.⁷⁾ No isomerization between **8a** and **9a** was observed under conditions of the cyclization, indicating that one of two possible conrotatory rotations has predominantly occurred to lead to this high stereoselectivity. This will be discussed later. The highest selectivity in favor for the 3,4a-cis isomer **8a** was obtained (**8a**:**9a**=95:5) when cyclization was carried out in benzene at room temperature in the presence of molecular sieves 5A (Entry 4). Although some examples for the dehydration of tertiary alcohols with molecular sieves are already known,⁸⁾ this example might be the first case in which molecular sieves are utilized in cationic cyclization reactions.

Other maleate cycloadducts **5b** and **5c** derived from acetophenone adducts **1b** and **1c** similarly cyclized within 5 min at room temperature in the presence of TFA, to give two stereoisomeric tetrahydrofluorenes **8b**+**9b** and **8c**+**9c** (Entries 5 and 7 in Table 2). However, no cyclized product was obtained when **5b** or **5c** was treated with aqueous HCl (Entries 6 and 8). 1-(1-Arylvinyl)cyclohexene **11** or **12** as a major product in this reaction was found to be a kinetically controlled product since **11** or **12** gradually isomerized into 3-methylenecyclohexene **10b** or **10c** under conditions of the dehydration. Although **10b** or **10c** underwent no cyclization, **11** or **12** cyclized on treatment with TFA leading to quantitative yield of **8b**+**9b** or **8c**+**9c**, respectively.⁹⁾

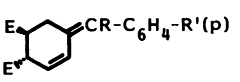
Fumarate cycloadducts **6a**—**c** underwent cyclizations into the corresponding tetrahydrofluorene derivatives **13a**—**c** and **14a**—**c** under similar conditions (Entries 9—19 in Table 2). However, stereoselectivity between **13** and **14** was found extremely low under all the conditions employed for cyclization. This makes a striking contrast with the stereoselective cyclization of maleate cycloadducts **5a**—**c**. Formation of 3-methylenecyclohexenes **15** as side products was not critical, and 1-(1-arylvinyl)cyclohexene **16** or **17** was the only product when acetophenone adduct **6b** or **6c** was treated with aqueous HCl, respectively.



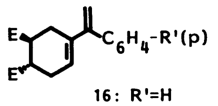
13a-13c



14a-14c



15a-15c



16: R'=H
17: R'=OMe

R=Ph, R'=H; b: R=Me, R'=H; c: R=Me, R'=OMe

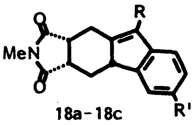
Maleimide cycloadducts **7a**—**c** underwent similar cyclizations in the presence of TFA or molecular sieves

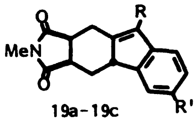
Table 3. Electrocyclic Reaction of Maleimide Cycloadducts **7**

Entry	Cyclo-adduct	Reaction conditions[a]				Total yield/%	Product (isolated yield/%)	3a,4a-cis:trans
		Solvent	Catalyst	Temp/°C	Time/h			
1	**7a**	DCM	TFA	−78→−10	3	93	**18a** (15), **19a** (78)	16:84
2		DCM	TFA	rt	10 min	95	**18a** (29), **19a** (66)	31:69
3		BZ	TFA	rt	20 min	86	**18a** (12), **19a** (74)	14:86
4		BZ	MS	rt	24	97	**18a** (69), **19a** (28)	71:29
5		DCM	MS	rt	20	96	**18a** (51), **19a** (45)	53:47
6	**7b**	DCM	TFA	−78→0	2	75	**18b** (25), **19b** (50)	33:67
7		DCM	TFA	rt	10 min	84	**18b** (36), **19b** (48)	43:57
8		BZ	MS	rt	24	100	**18b** (67), **19b** (17), **20** (16)[b]	80:20
9		DCM	MS	rt	36	100	**18b** (39), **19b** (28), **20** (33)[b]	58:42
10	**7c**	DCM	TFA	rt	5 min	51	**18c** (18), **19c** (33)	35:65
11		BZ	MS	rt	16	100	**18c** (75), **19c** (13), **21** (12)[b]	85:15
12		DCM	MS	rt	16	100	**18c** (59), **19c** (24), **21** (17)[b]	71:29

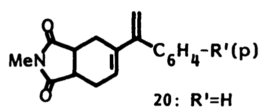
a) Solvent: DCM: dichloromethane; BZ: benzene. Catalyst: TFA: trifluoroacetic acid; MS: molecular sieves 5A. The catalyst was used in large excess in all cases. b) The ratio was determined by GLC.

5A to give two stereoisomeric octahydroindeno[1,2-*f*]isoindoles **18a**—**c** and **19a**—**c** (Table 3). Surprising is that the isomer ratio is very much dependent on the reaction conditions. The reactions in benzene in the presence of molecular sieves 5A preferentially produced 3a,4a-cis isomers **18** (**18**:**19**=71—85:29—15, Entries 4, 8, and 11). On the other hand, the reactions in the presence of TFA favored 3a,4a-trans isomers **19** rather than **18** (**18**:**19**=14—43:86—57, Entries 1—3, 6, 7, and 10). When acetophenone adduct **7b** or **7c** was treated with molecular sieves, noncyclized dehydration product **20** or **21** was formed as a side product, respectively.

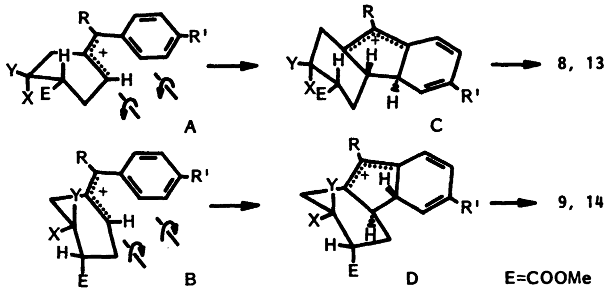

18a-18c


19a-19c

a: R=Ph, R'=H; b: R=Me, R'=H; c: R=Me, R'=OMe

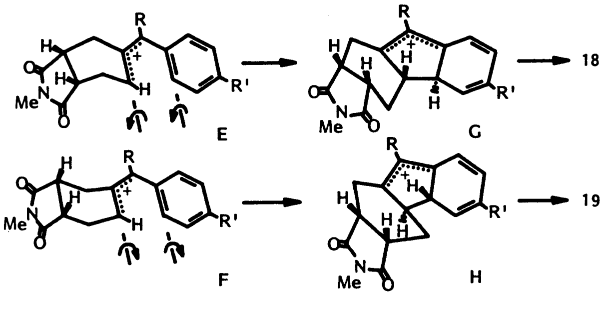

20: R'=H
21: R'=OMe

On the basis of the above results, such difference of stereoselectivity of these electrocyclic reactions may be explained as follows: as it is quite certain that the cyclization involves an aryl-substituted allyl cationic intermediate, the stereochemistry of cyclized products must have been determined at the stage of irreversible cyclization of this cation by either of two possible conrotatory rotations, clockwise and counterclockwise conrotatory rotations. Two half-chair conformations **A** and **B** (X=COOMe, Y=H) are possible for cationic intermediates from the maleate cycloadducts **5**, and they should have almost equal stability. Counterclockwise rotation of **A** leads to 3,4a-cis cyclization product **C**, while clockwise rotation of **B** forms sterically unfavorable 3,4a-trans isomer **D** whose quasi-chair six-membered ring carries an axial ester substituent at the 3-position causing considerable steric repulsion toward axial 4a-H.[10] Consequently, cyclization of **5** has predominantly occurred through counterclockwise rotation of **A** giving **8** as far major product.



On the other hand, stability of two cationic intermediates **A** and **B** (X=H, Y=COOMe) from the fumarate cycloadducts **6** is not identical. Conformer **A** bearing two ester groups at adjacent equatorial positions may be less stable than **B** with two axial ester substituents.[11] The less stable cation **A** undergoes cyclization through a transition state leading to more stable cyclization product **C**, and the more stable cation **B** to less stable product **D**. As a result, stereoselectivity between **13** and **14** was lowered.

In the case of electrocyclization of the maleimide cycloadducts **7**, cationic intermediates **E** and **F** are expected to cyclize into cyclization products **G** and **H**, respectively. During this transformation, conformation of the six-membered ring changes from a folded conformation into an envelope shape.[12] Relative stabilities should be **F**>**E** and **G**>**H**, and this situation resembles to the case of electrocyclization of fumarate cycloadducts **6**. However, difference of stability between **E** and **F** and between **G** and **H** may be relatively smaller.[13] This might be the main reason for the high dependence of stereoselectivity upon reaction conditions. Cyclization under less polar conditions (e.g. use of molecular sieves in benzene) has favored the route going through more stable transition state (**E**→**G**→**18**). On the other hand, cyclization under more polar conditions (e.g. TFA in dichloromethane) has selected the route starting from more stable ionic intermediate (**F**→**H**→**19**).



Thus, the sequence of Diels–Alder reaction and electrocyclization of 1-aryl-2-methylene-3-buten-1-ols works well as a new method of [6.5] annelation. Stereoselectivity in the second electrocyclization step mainly depends upon the structure of dienophiles used in the initial Diels–Alder cycloaddition.

Experimental

General. Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^{1}H-NMR spectra were recorded on a Hitachi R-40 (90 MHz) or a JEOL FX-100 instrument (100 MHz) and ^{13}C-NMR spectra on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were measured with a JEOL JMS-01SG-2 spectrometer at 70 eV of ionization energy. Elemental analyses were performed on a Hitachi 026 CHN micro analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck) or of aluminum oxide 60 F-254 type-E (Merck). Visualization was made with ultraviolet light (254 and 365 nm), iodine, molybdophosphoric acid (5% in ethanol), or *p*-anisaldehyde (5% in ethanol containing 5% of sulfuric acid). For preparative column chromatography, Wakogel C-200, C-300 (Wako), or Kieselgel 60 (230—400 mesh, Merck) was used. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatography (Yanagimoto) with an ionization detector using a glass column (SE-30, 3×2000 mm). Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Materials and Solvents. Benzene and dichloromethane were distilled over sodium wire and calcium hydride, respectively, prior to their use. Zinc chloride was purified by crystallization from anhydrous dioxane and dried over phosphorus pentaoxide under vacuum. 1-Aryl-2-methylene-3-buten-1-ols **1a**—**c** were prepared according to the method previously reported.[5] They are available as mixtures with the corresponding allene alcohols (purity: **1a**: 50%; **1b**: 90%; **1c**: 95%). No separation of **1** from these mixtures is needed, but these mixtures were submitted to the following Diels–Alder cycloadditions. Other solvents such as THF, hexane, and ethyl acetate and olefins **2**—**4** are commercially available, and were used without further purification.

General Procedure for the Diels–Alder Reactions of 1 with 2—4 Leading to 5—7. Diene alcohols **1a**—**c** with the purity shown above and olefins **2**—**4** were heated under reflux in dry benzene (2—5 ml for 1 mmol of **1**) under the conditions listed in Table 1. The crude mixtures were condensed in vacuo and chromatographed over silica gel with hexane-ethyl acetate to give cycloadducts **5**—**7**. The results are summarized in Table 1.

5a: Colorless prisms (ethyl acetate-hexane); mp 113—115 °C; IR (KBr) 3500, 1725, and 1705 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=2.2—2.6 (4H, m, CH$_2$), 2.8—3.2 (3H, m, CH and OH), 3.58, 3.64 (each 3H, s, COOMe), 5.34 (1H, m, 2-H), 7.23, and 7.25 (each 5H, br s, Ph); ^{13}C-NMR (CDCl$_3$) δ=25.71, 26.36 (each t, 3- and 6-C), 39.51, 40.16 (each d, 4- and 5-C), 51.73 (2×C, q, COOMe), 82.49 (s, q-C), 124.64, 127.05, 127.46, 127.58, 127.75 (each d), 140.26, 144.60, 144.95 (each s), and 173.43 (2×C, s, COOMe); MS *m/z* (rel. intensity, %) 363 (M$^+$−17, 23), 362 (87), 303 (25), 302 (72), 244 (23), 243 (80), 183 (23), 165 (55), and 105 (base peak). Found: C, 72.73; H, 6.51%. Calcd for $C_{23}H_{24}O_5$: C, 72.61; H, 6.36%.

5b: (Mixture of two diastereomers): Colorless viscous oil; IR (neat) 3500 and 1725 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=1.61 (3H, s, Me), 2.0—3.1 (7H, m, CH$_2$, CH, and OH), 3.47, 3.49 (each 3H, s, COOMe), 5.86 (1H, m, 2-H), and 7.0—7.5 (5H, m, Ph); ^{13}C-NMR (CDCl$_3$) δ=25.58 (t, CH$_2$), 28.46, 28.80 (each q, Me), 39.52, 39.67, 39.96, 40.15 (each d, CH), 51.61, 51.80 (each q, COOMe), 76.12, 76.51 (each s, q-C), 119.24, 119.49, 125.24, 126.65, 127.92 (each d), 140.73, 140.93, 146.09 (each s), 173.33, 173.48, and 173.68 (each s, COOMe); MS *m/z* (rel. intensity, %) 301 (M$^+$−17, 31), 241 (50), 181 (base peak), and 105 (29). Found: C, 67.80; H, 6.91%. Calcd for $C_{18}H_{12}O_5$: C, 67.91; H, 6.97%.

5c: (Mixture of two diastereomers): Colorless viscous oil; IR (neat) 3500 and 1725 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=1.60 (3H, s, Me), 2.0—3.2 (7H, m, CH$_2$, CH, and OH), 3.51, 3.53, 3.62 (6H, each s, COOMe), 3.74 (3H, s, OMe), 5.85 (1H, m, 2-H), 6.79, and 7.24 (each 2H, br d, Ar); ^{13}C-NMR (CDCl$_3$) δ=25.58 (t, CH$_2$), 28.31, 28.65 (each q, Me), 39.47, 40.01, 40.10 (each d, CH), 51.56, 51.75 (each q, COOMe), 55.11 (q, OMe), 76.12 (s, q-C), 113.20, 119.05, 126.41 (each d), 138.25, 140.93, 158.22 (each s), 173.33, and 173.57 (each s, COOMe); MS *m/z* (rel. intensity, %) 348 (M$^+$, 13), 331 (21), 330 (base peak), 273 (21), 271 (29), 270 (61), 213 (28), 211 (91), 152 (48), and 135 (57). Found: C, 65.22; H, 7.02%. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94%.

6a: Colorless prisms (diethyl ether-hexane); mp 126—128 °C; IR (KBr) 3520, 3480, and 1720 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=2.0—2.6 (4H, m, CH$_2$), 2.7—3.0 (3H, m, CH and OH), 3.57, 3.63 (each 3H, s, COOMe), 5.34 (1H, m, 2-H), 7.22, and 7.26 (each 5H, br s, Ph); ^{13}C-NMR (CDCl$_3$) δ=27.83, 28.00 (each t, 3-and 6-C), 40.86, 41.57 (each d, 4- and 5-C), 51.72 (2×C, q, COOMe), 82.37 (s, q-C), 123.88, 127.17, 127.46, 127.81 (each d), 140.49, 144.48, 144.66 (each s), 174.84, and 175.01 (each s, COOMe); MS *m/z* (rel. intensity, %) 363 (M$^+$−17, 0.3), 302 (34), 243 (43), 183 (55), 165 (71), 155 (25), 105 (61), and 59 (base peak). Found: C, 72.52; H, 6.36%. Calcd for $C_{23}H_{22}O_5$: C, 72.61; H, 6.36%.

6b: (Mixture of two diastereomers): Colorless viscous oil; IR (neat) 3500 and 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.61, 1.62 (3H, each, s, Me), 2.0—3.0 (7H, m, CH_2, CH, and OH), 3.54, 3.61 (6H, each s, COOMe), 5.7—6.0 (1H, m, 2-H), and 7.0—7.5 (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=26.95, 27.53 (each t, CH_2), 28.24, 28.77 (each q, Me), 40.80, 41.33 (each d, CH), 51.67 (2×C, q, COOMe), 75.50, 76.15 (each s, q-C), 118.36, 118.95, 124.88, 124.99, 126.52, 127.81 (each d), 141.02, 145.60, 145.89 (each s), 174.89, and 175.07 (s). Found: C, 68.04; H, 7.07%. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97%.

6c: (Mixture of two diastereomers): Colorless viscous oil; IR (neat) 3500 and 1725 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.62 (3H, s, Me), 1.9—3.0 (7H, m, CH_2, CH, and OH), 3.55, 3.65 (each 3H, s, COOMe), 3.77 (3H, s, OMe), 5.86 (1H, m, 2-H), 6.81, and 7.26 (each 2H, br d, Ar); ^{13}C-NMR ($CDCl_3$) δ=27.30, 27.83 (each t, CH_2), 28.36, 28.94 (each q, Me), 40.98, 41.10, 41.63 (each d, CH), 51.84 (2×C, q, COOMe), 55.19 (q, OMe), 75.62, 76.21 (each s, q-C), 113.43, 118.36, 119.00, 126.35, 126.46, 128.22 (each d), 137.73, 138.09, 141.26, 158.40 (each s), and 175.07 (2×C, s, COOMe). MS *m/z* (rel. intensity, %) 348 (M$^+$, 16), 333 (32), 330 (55), 298 (37), 273 (26), 271 (29), 270 (85), 213 (21), 211 (base peak), 152 (54), 135 (72), and 133 (27). Found: C, 65.41; H, 7.05%. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94%.

7a: Colorless prisms (diethyl ether-hexane); mp 125—126 °C; IR (KBr) 3450, 1770, 1660, and 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.9—2.7 (4H, m, CH_2), 2.86 (3H, s, NMe), 2.96 (2H, m, CH), 5.41 (1H, m, 6-H), and 7.2—7.3 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=24.02 (t, 7-C), 24.85 (q, NMe), 25.39 (t, 4-C), 39.23, 39.96 (each d, 3a- and 7a-C), 81.62 (s, q-C), 124.95, 127.09, 127.09, 127.33, 127.62, 127.87 (each d), 143.90, 144.14, 145.07 (each s), 179.77, and 179.91 (each s, CON); MS *m/z* (rel. intensity, %) 347 (M$^+$, 19), 329 (38), 165 (34), 112 (30), 105 (base peak), 80 (22), 78 (55), and 77 (91). Found: C, 76.08; H, 6.05; N, 4.18%. Calcd for $C_{22}H_{21}NO_3$: C, 76.06; H, 6.09; N, 4.03%.

7b: (Mixture of two diastereomers): Colorless viscous oil; IR (neat) 3420, 1770, and 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.56, 1.58 (3H, each s, Me), 1.8—4.1 (7H, m, CH_2, CH, and OH), 2.79, 2.83 (3H, each s, NMe), 5.96 (1H, m, 6-H), and 7.23 (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=23.63, 23.93, 24.41 (each t, CH_2), 24.66 (q, NMe), 24.85 (t, 4-C), 27.68 (q, Me), 39.37, 39.62, 39.81 (d, CH), 75.87 (s, q-C), 119.49, 119.92, 125.24, 126.94, 128.01 (each d), 144.97, 145.31, 145.55 (each s), 179.27, 179.91, and 180.01 (each s, CON); MS *m/z* (rel. intensity, %) 285 (M$^+$, 5), 270 (19), 79 (36), 78 (30), 77 (69), and 43 (base peak). Found: C, 71.80; H, 6.70; N, 5.07%. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91%.

7c: (Mixture of two diastereomers): Colorless viscous oil; IR (neat) 3450, 1770, and 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.54, 1.56 (3H, each s, Me), 1.8—3.2 (7H, m, CH_2, CH, and OH), 2.82, 2.85 (3H, each 3H, NMe), 3.75 (3H, s, OMe), 5.97 (1H, m, 6-H), 6.78, and 7.19 (each 2H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=23.68, 23.98 (each t, CH_2), 24.46, 24.85 (each q, Me), 24.90 (t, 4-C), 27.48, 27.87 (each q, NMe), 39.37, 39.42, 39.67, 39.86 (each d, CH), 55.21 (q, OMe), 75.29, 75.58 (each s, q-C), 113.35, 113.39, 119.14, 119.73, 126.45, 126.55 (each d), 137.12, 137.66, 145.55, 145.57, 158.42, 158.52 (each s), 179.42, 179.96, and 180.00 (each s, CON); MS *m/z* (rel. intensity, %) 315 (M$^+$, base peak), 300 (91), 272 (31), 192 (65), 151 (80), 135 (25), 121 (53), and 79 (23). Found: C, 68.60; H, 6.67; N, 4.55%. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44%.

General Procedure for the Acid-Catalyzed Electrocyclization of 5—7 Leading to 8—21. The Diels-Alder cycloadducts **5**—**7** were treated with a catalyst such as TFA, $ZnCl_2$, aqeous HCl, and molecular sieves 5A under the conditions shown in Tables 2 and 3. The amounts of catalyst and reaction solvent used for 1 mmol of **5**—**7** are as follows: TFA: 7—15 mmol in 6—10 ml of dichloromethane or benzene; $ZnCl_2$: 1.5—2 g in 10 ml of dichloromethane; aqeous HCl: 5 ml in 5 ml of THF. After the reaction was over, the mixture was poured into ice water and extracted with diethyl ether twice. The combined extracts were washed with aqueous sodium hydrogencarbonate, with water, dried over anhydrous magnesium sulfate, and finally evaporated in vacuo. The residue was subjected to ^{1}H-NMR and GLC analysis to know the ratio of products, and chromatographed over silica gel with ethyl acetate-hexane. All results were summarized in Tables 2 and 3.

8a: Colorless prisms (diethyl ether-hexane); mp 124—125 °C; IR (KBr) 1720 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.67 (1H, q, *J*=13.1 Hz, one of 4-H), 2.61 (1H, dd, *J*=14.8 and 6.0 Hz, one of 1-H), 2.7—3.0 (2H, m, the other of 1- and 4-H), 3.1—3.6 (3H, m, CH), 3.35 (3H, s, 2-COOMe), 3.67 (3H, s, 3-COOMe), and 7.0—7.6 (9H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=28.21, 29.58 (each t, 1- and 4-C), 43.27, 43.52 (each d, 2- and 3-C), 48.78 (d, 4a-C), 51.41, 51.90 (each q, COOMe), 119.88, 122.56, 124.56, 126.65, 127.19, 128.31, 128.79 (each d), 134.50, 137.62, 141.85, 144.92, 146.24 (each s), 172.36, and 173.29 (each s, COOMe); MS *m/z* (rel. intensity, %) 362 (M$^+$, 64), 303 (28), 302 (base peak), 243 (40), 242 (25), 203 (22), 202 (21), and 165 (82). Found: C, 76.36; H, 6.15%. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

8b: Colorless prisms (dichloromethane-hexane); mp 188—189 °C; IR (KBr) 1725 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.39 (1H, dt, *J*=13.1, 13.1, and 12.2 Hz, one of 4-H), 2.01 (3H, t, *J*=1.8 Hz, 9-Me), 2.48 (1H, br dd, *J*=14.0 and 5.5 Hz, one of 1-H), 2.6—3.6 (5H, m, CH_2 and CH), 3.52, 3.68 (each 3H, s, COOMe), and 7.0—7.4 (4H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=9.69 (q, 9-Me), 27.83, 29.71 (each t, 1- and 4-C), 43.50, 43.62 (each d, 2- and 3-C), 48.32 (d, 4a-C), 51.61, 51.84 (each q, COOMe), 118.60, 122.17, 124.17, 126.52 (each d), 131.39, 139.43, 146.19 (each s), 172.43, and 173.43 (each s, COOMe); MS *m/z* (rel. intensity, %) 300 (M$^+$, 21), 240 (88), 182 (22), 181 (base peak), 166 (20), 165 (32), and 141 (26). Found: C, 72.07; H, 6.72%. Calcd for $C_{18}H_{26}O_4$: C, 71.98; H, 6.71%.

8c: Colorless needles (dichloromethane-hexane); mp 182—183 °C; IR (KBr) 1725 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.40 (1H, dt, *J*=13.0, 13.0, and 12.0 Hz, one of 4-H), 1.97 (3H, t, *J*=1.6 Hz, 9-Me), 2.46 (1H, br dd, *J*=14.0 and 5.8 Hz, one of 1-H), 2.3—3.6 (5H, m, CH_2 and CH), 3.30 (1H, dd, *J*=14.0 and 2.3 Hz, the other of 1-H), 3.52, 3.67 (each 3H, s, COOMe), 3.77 (3H, s, OMe), 6.74 (1H, dd, *J*=8.2 and 2.5 Hz, 7-H), 6.95 (1H, d, *J*=2.5 Hz, 5-H), and 7.07 (1H, d, *J*=8.2 Hz, 8-H); ^{13}C-NMR ($CDCl_3$) δ=9.70 (q, 9-Me), 27.78, 29.68 (each t, 1- and 4-C), 43.52 (2×C, d, 2- and 3-C), 48.15 (d, 4a-C), 51.51, 51.75 (each q, COOMe), 55.46 (q, OMe), 109.16, 111.64, 118.75 (each d), 130.79, 137.42, 139.17, 147.84, 157.54 (each s), 172.41, and 173.33 (each s, COOMe); MS *m/z* (rel. intensity, %) 330 (M$^+$, 55), 271 (27), 270 (78), 212 (31), 211 (base peak), 197 (22), 195 (20), 172 (24), 165 (29), 129 (26), and 128 (21). Found: C, 69.21; H, 6.73%. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71%.

9a: Colorless prisms (diethyl ether-hexane); mp 134—136 °C; IR (KBr) 1720 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.32 (1H, dt, *J*=13.0, 13.0, and 4.7 Hz, one of 4-H), 2.25 (1H, ddd, *J*=11.7, 5.8, 4.2 Hz, 2-H), 2.94 (1H, dd, J=13.0 and 11.7 Hz, one of 1-H), 3.13 (1H, ddd, J=13.0, 5.8, and 2.8 Hz, the other of 4-H), 3.02 (1H, dd, J=13.0 and 5.8 Hz, the other of 1-H), 3.32 (1H, dd, J=13.0 and 5.8 Hz, 4a-H), 3.47 (1H, ddd, J=4.7, 4.2, and 2.8 Hz, 3-H), 3.67, 3.78 (each 3H, s, COOMe), and 7.0—7.6 (9H, m, Ar); MS m/z (rel. intensity, %) 362 (M^+, 76), 331 (29), 330 (66), 303 (26), 302 (89), 243 (56), 242 (84), 241 (32), 217 (63), 215 (24), 203 (32), 202 (31), and 165 (base peak). Found: C, 75.98; H, 6.16%. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

9b: Colorless solid; mp 120—122 °C; IR (KBr) 1720 cm^{-1}; ^1H-NMR ($CDCl_3$) δ=1.13 (1H, dt, J=12.7, 12.7, and 4.5 Hz, one of 4-H), 2.03 (3H, t, J=1.6 Hz, 9-Me), 2.40 (1H, ddd, J=12.0, 5.0, and 4.0 Hz, 2-H), 2.6—3.3 (4H, m, CH_2 and CH), 3.40 (1H, m, 4a-H), 3.72, 3.76 (each 3H, s, COOMe), and 6.9—7.4 (4H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=9.89 (q, 9-Me), 24.71 (t, 4-C), 32.70 (t, 1-C), 41.81, 44.83, 45.42 (each d, CH), 51.90 (2×C, q, COOMe), 118.56, 122.22, 124.02, 126.65 (each d), 130.21, 142.04, 145.94, 146.39 (each s), 173.33, and 173.48 (each s, COOMe); MS m/z (rel. intensity, %) 300 (M^+, 13), 240 (37), 182 (26), 181 (base peak), 180 (57), 179 (25), 178 (23), 167 (36), 166 (45), 165 (85), 155 (31), 153 (27), 142 (28), 141 (46), and 115 (30). Found: C, 72.16; H, 6.80%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

9c: This product was not separated in pure form from the mixture with **8c**. ^1H-NMR ($CDCl_3$, only major signals are given): δ=1.15 (1H, dt, J=12.7, 12.7, and 4.7 Hz, one of 4-H), 2.00 (3H, t, J=1.7 Hz, 9-Me), 2.40 (1H, ddd, J=12.0, 4.9, and 4.2 Hz, one of 2-H), 3.71, 3.74, 3.78 (each 3H, s, COOMe and OMe), 6.77 (1H, dd, J=8.2 and 2.5 Hz, 7-H), 6.93 (1H, d, J=2.5 Hz, 5-H), and 7.09 (1H, d, J=8.2 Hz, 8-H); ^{13}C-NMR ($CDCl_3$) δ=9.94 (q, 9-Me), 24.71 (t, 4-C), 32.84 (t, 1-C), 41.86, 44.93, 45.32 (each d, CH), 51.90 (2×C, q, COOMe), 55.55 (q, OMe), 109.35, 111.73, 118.75, 125.67, 129.867 (each d), 139.51, 139.81, 147.65, 157.50 (each s), 173.38, and 173.57 (each s, COOMe); MS m/z 330 (M^+). Found: C, 68.95; H, 6.82%. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71%.

10a—c: These products were not fully characterized because of too poor yields and unsuccessful separation from the major products. Their formation was deduced only on the basis of ^1H-NMR ($CDCl_3$) of crude reaction mixtures and the yields were determined by GLC analysis. **10a**: δ=5.90 (dd, J=10 and 5 Hz, 2-H) and 6.34 (dd, J=10 and 3 Hz, 1-H); **10b**: δ= 2.08 (s, Me), 5.55 (dd, J=10 and 5 Hz, 2-H), and 6.16 (br d, J=10 Hz, 1-H); **10c**: δ=2.06 (s, Me), 5.60 (dd, J=10 and 5 Hz, 2-H), and 6.18 (br d, J=10 Hz, 1-H).

11: Colorless viscous oil; IR (neat) 1730 cm^{-1}; ^1H-NMR ($CDCl_3$) δ=2.2—3.2 (6H, m, CH_2 and CH), 3.67, 3.68 (each 3H, s, COOMe), 5.04, 5.22 (each 1H, s, =CH_2), 5.59 (1H, m, 2-H), and 7.23 (5H, br s, Ph); ^{13}C-NMR ($CDCl_3$) δ=26.37, 27.20 (each t, 3- and 6-C), 39.45, 40.23 (each d, 4- and 5-C), 51.90 (2×C, q, COOMe), 112.40 (t, =CH_2), 126.22, 127.39, 128.12, 128.71 (each d), 135.84, 141.55, 150.78 (each s), and 173.73 (2×C, s, COOMe); MS m/z (rel. intensity, %) 300 (M^+, 51), 269 (24), 240 (base peak), 181 (93), 180 (50), 103 (93), and 42 (20). Found: C, 71.97; H, 6.74%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

12: Colorless viscous oil; IR (neat) 1725 cm^{-1}; ^1H-NMR ($CDCl_3$) δ=2.3—3.2 (6H, m, CH_2 and CH), 3.67, 3.69 (each 3H, s, COOMe), 3.73 (3H, s, OMe), 5.00, 5.14 (each 1H, d, J=1.1 Hz, =CH_2), 5.62 (1H, m, 2-H), 6.81, and 7.13 (each br d, Ar); ^{13}C-NMR ($CDCl_3$) δ=26.30, 27.36 (each t, 3- and 6-C), 39.45, 40.22 (each d, 4- and 5-C), 51.84 (2×C, q, COOMe), 55.19 (q, OMe), 113.37 (t, =CH_2), 113.31, 125.70, 129.52 (each d), 133.63, 135.91, 150.00, 158.92 (each s), and 173.48 (2×C, s, COOMe); MS m/z (rel. intensity, %) 330 (M^+, 23), 270 (29), 211 (46), 210 (22), 133 (45), and 59 (base peak). Found: C, 68.81; H, 6.67%. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71%.

13a: Colorless prisms (diethyl ether–hexane); mp 112—113 °C; IR (KBr) 1725 cm^{-1}; ^1H-NMR ($CDCl_3$) δ=1.20 (1H, q, J=12.5 Hz, one of 4-H), 2.48 (1H, t, J=12.3 Hz, one of 1-H), 2.72 (1H, ddd, J=12.3, 9.3, and 3.2 Hz, 2-H), 2.82 (1H, ddd, J=12.5, 5.8, and 2.8 Hz, the other of 4-H), 2.95 (1H, ddd, J=12.5, 9.3, and 2.8 Hz, 3-H), 3.19 (1H, dd, J=12.3 and 3.2 Hz, the other of 1-H), 3.31 (1H, dd, J=12.5 and 5.8 Hz, 4a-H), 3.64, 3.66 (each 3H, s, COOMe), and 7.0—7.6 (9H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=28.75 (t, 4-C), 33.62 (t, 1-C), 44.88, 46.34, 48.39 (each d, CH), 51.90 (2×C, q, COOMe), 119.97, 122.61, 124.65, 126.84, 127.43, 128.55, 128.94 (each d), 134.01, 136.88, 142.43, 144.63, 145.512 (each s), 174.26, and 174.40 (each s, COOMe); MS m/z (rel. intensity, %) 362 (M^+, 15), 302 (20), 243 (46), 242 (42), 241 (25), 215 (36), 204 (22), 203 (47), 202 (47), 166 (22), and 165 (base peak). Found: C, 76.35; H, 6.14%. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

13b: Colorless prisms (diethyl ether–hexane); mp 107—108 °C; IR (KBr) 1720 cm^{-1}; ^1H-NMR ($CDCl_3$) δ=1.00 (1H, q, J=12.5 Hz, one of 4-H), 2.03 (3H, t, J=1.5 Hz, 9-Me), 2.33 (1H, br t, J=12.5 Hz, one of 1-H), 2.4—3.3 (5H, m, CH_2 and CH), 3.66, 3.71 (each 3H, s, COOMe), and 7.0—7.4 (4H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=9.65 (q, 9-Me), 28.06 (t, 4-C), 33.36 (t, 1-C), 44.77, 46.00, 47.77 (each d, CH), 51.77 (2×C, q, COOMe), 118.65, 122.18, 124.30, 126.77 (each d), 130.77, 140.25, 145.36, 146.07 (each s), 174.54, and 174.77 (each s, COOMe); MS m/z (rel. intensity, %) 300 (M^+, 13), 240 (34), 182 (20), 181 (63), 180 (37), 167 (28), 166 (30), 165 (47), 142 (24), 141 (48), 115 (26), and 59 (base peak). Found: C, 72.13; H, 6.75%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

13c: Colorless prisms (diethyl ether–hexane); mp 112—114 °C; IR (KBr) 1725 cm^{-1}; ^1H-NMR ($CDCl_3$) δ=1.02 (1H, q, J=12.5 Hz, one of 4-H), 2.00 (3H, q, J=1.6 Hz, 9-Me), 2.30 (1H, br t, J=12.5 Hz, one of 1-H), 2.4—3.2 (5H, m, CH_2 and CH), 3.66, 3.70 (each 3H, s, COOMe), 3.77 (3H, s, COOMe), 6.77 (1H, dd, J=8.3 and 2.4 Hz, 7-H), 6.91 (1H, d, J=2.4 Hz, 5-H), and 7.21 (1H, d, J=8.3 Hz, 8-H); ^{13}C-NMR ($CDCl_3$) δ=10.00 (q, 9-Me), 28.35 (t, 4-C), 33.77, (t, 1-C), 45.06, 46.36, 47.94 (each d CH), 52.00 (2×C, q, COOMe), 55.59 (q, OMe), 109.60, 112.01, 119.19 (each d), 130.60, 138.30, 139.42, 147.36, 158.01 (each s), 174.89, and 175.07 (each s, COOMe); MS m/z (rel. intensity, %) 330 (M^+, 73), 271 (28), 270 (87), 212 (31), 211 (base peak), 210 (26), 195 (28), 185 (31), 172 (27), 165 (23), 129 (31), and 128 (24). Found: C, 69.04; H, 6.73%. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71%.

14a: Colorless prisms (diethyl ether–hexane); mp 130—132 °C; IR (KBr) 1725 cm^{-1}; ^1H-NMR ($CDCl_3$) δ=1.44 (1H, dt, J=13.0, 13.0, and 4.4 Hz, one of 4-H), 2.71 (1H, dd, J=14.8 and 5.8 Hz, one of 1-H), 2.9—3.5 (5H, m, CH_2 and CH), 3.39, 3.79 (each 3H, s, COOMe), and 7.0—7.6 (9H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=25.14 (t, 4-C), 29.92 (t, 1-C), 40.93, 42.69 (each d, 2- and 3-C), 45.95 (d, 4a-C), 51.56, 52.04 (each q, COOMe), 119.78, 122.46, 124.17, 126.45, 127.00, 128.16, 128.74 (each d), 134.54, 136.88, 142.53, 144.92, 146.63 (each s), 172.90, and 173.72 (each s, COOMe); MS m/z (rel. intensity, %) 362 (M^+, 53), 302 (66), 243 (49), 242 (63), 241 (24), 215 (26), 203 (27), 202 (31), and 165 (base peak). Found:

C, 76.22; H, 6.12%. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

14b: Colorless viscous oil; IR (neat) 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.19 (1H, dt, J=13.0, 13.0, and 4.7 Hz, one of 4-H), 2.03 (3H, t, J=1.6 Hz, 9-Me), 2.4—3.6 (5H, m, CH_2 and CH), 2.56 (1H, br dd, J=14.0 and 5.8 Hz, one of 1-H), 3.55, 3.77 (each 3H, s, COOMe), and 7.0—7.4 (4H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=9.59 (q, 9-Me), 24.65 (t, 4-C), 30.18, (t, 1-C), 41.12, 42.83 (each d, 2- and 3-C), 45.53 (d, 4a-C), 51.83, 52.12 (each q, COOMe), 118.65, 122.30, 124.01, 126.54 (each d), 130.89, 140.60, 146.48, 146.83 (each s), 173.25, and 174.13 (each s, COOMe); MS *m/z* (rel. intensity, %) 300 (M$^+$, 34), 240 (55), 182 (22), 181 (base peak), 180 (49), 167 (24), 166 (37), 165 (65), 142 (22), 141 (36), 115 (22), and 59 (35). Found: C, 72.16; H, 6.83%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

14c: Colorless prisms (diethyl ether-hexane); mp 107—108 °C; IR (KBr) 1720 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.21 (1H, dt, J=13.0, 13.0, and 4.7 Hz, one of 4-H), 2.00 (3H, t, J=1.6 Hz, 9-Me), 2.34 (1H, br dd, J=14.5 and 5.4 Hz, one of 1-H), 2.4—3.5 (5H, m, CH_2 and CH), 3.57, 3.77, 3.79 (each 3H, s, COOMe and OMe), 6.79 (1H, dd, J=8.2 and 2.4 Hz, 7-H), 6.95 (1H, d, J=2.4 Hz, 5-H), and 7.09 (1H, d, J=8.2 Hz, 8-H); ^{13}C-NMR ($CDCl_3$) δ=9.80 (q, 9-Me), 24.83 (t, 4-C), 30.47 (t, 1-C), 41.27, 43.03, 45.62 (each d, CH), 51.90, 52.19 (each q, COOMe), 55.60 (q, OMe), 109.38, 111.67, 118.83 (each d), 130.28, 138.26, 139.50, 148.48, 157.51 (each s), 173.19, and 173.95 (each s COOMe); MS *m/z* (rel. intensity, %) 330 (M$^+$, base peak), 271 (29), 270 (96), 211 (76), 210 (22), 195 (21), and 185 (32). Found: C, 69.30; H, 6.74%. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71%.

15a: Colorless prisms (diethyl ether-hexane); mp 120—121 °C; IR (KBr) 1725 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.50 (1H, dd, J=14.5 and 11.0 Hz, one of 5-H), 2.85 (1H, dd, J=14.5 and 4.0 Hz, the other of 5-H), 3.08 (1H, ddd, J=11.0, 9.0, and 4.0 Hz, 4-H), 3.61, 3.69 (each 3H, s, COOMe), 3.6—3.8 (1H, m, 3-H), 5.79 (1H, dd, J=10.1 and 3.1 Hz, 2-H), 6.33 (1H, dd, J=10.1 and 2.9 Hz, 1-H), and 7.0—7.5 (9H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=30.53 (t, 5-C), 42.24, 44.65 (each d, 3- and 4-C), 52.06, 52.30 (each q, COOMe), 124.89, 127.30, 128.01, 128.18, 129.24, 129.54, 130.25, 130.95 (each d), 140.83, 141.54, 141.66 (each s), 173.12, and 174.77 (each s, COOMe); MS *m/z* (rel. intensity, %) 362 (M$^+$, 5), 243 (base peak), 165 (72), and 59 (31). Found: C, 76.36; H, 6.15%. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

16: Colorless viscous oil; IR (neat) 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.0—3.3 (6H, m, CH_2 and CH), 3.66, 3.67 (each 3H, s, COOMe), 5.05, 5.19 (each 1H, br s, =CH_2), 5.60 (1H, m, 2-H), and 7.24 (5H, br s, Ph); ^{13}C-NMR ($CDCl_3$) δ=28.36, 29.06 (each t, 3- and 6-C), 40.86, 41.57 (each d, 4- and 5-C), 51.72 (2×C, q, COOMe), 112.25 (t, =CH_2), 125.64, 127.11, 127.81, 128.28 (each d), 135.33, 140.91, 149.83 (each s), and 174.84 (2×C, s, COOMe); MS *m/z* (rel. intensity, %) 300 (M$^+$, 19), 269 (20), 268 (27), 240 (65), 182 (23), 181 (base peak), 180 (53), 165 (26), 103 (84), and 77 (26). Found: C, 72.07; H, 6.78%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

17: Colorless viscous oil; IR (neat) 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.1—3.1 (6H, m, CH_2 and CH), 3.67, 3.68 (each 3H, s, COOMe), 3.77 (3H, s, OMe), 5.01, 5.11 (each 1H, s, =CH_2), 5.62 (1H, m, 2-H), 6.82, and 7.14 (each 2H, br d, Ar); ^{13}C-NMR ($CDCl_3$) δ=28.35, 29.30 (each t, 3- and 6-C), 40.89, 41.65 (each d, 4- and 5-C), 51.83 (2×C, q, COOMe), 55.12 (q, OMe), 111.66 (t, =CH_2), 113.42, 125.48, 129.54 (each d), 133.42, 135.89, 149.60, 159.01 (each s), and 175.19 (2×C, s, COOMe); MS *m/z* (rel. intensity, %) 330 (M$^+$, 25), 270 (63), 212 (23), 211 (base peak), 210 (49), 195 (20), 165 (26), 133 (91), 115 (20), 103 (36), and 77 (29). Found: C, 68.54; H, 6.75%. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71%.

18a: Colorless prisms (diethyl ether-hexane); mp 202—204 °C; IR (KBr) 1770 and 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.33 (1H, dt, J=14.6, 14.6, and 6.7 Hz, one of 4-H), 2.62 (1H, dd, J=14.8 and 6.5 Hz, one of 10-H), 2.8—3.4 (4H, m, CH_2 and CH), 3.04 (3H, s, NMe), 3.29 (1H, dd, J=14.8 and 7.5 Hz, the other of 10-H), and 7.6—7.0 (9H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=24.95 (q, NMe), 25.83 (t, 4-C), 27.78 (t, 10-C), 40.28, 40.48 (each d, 3a- and 10a-C), 45.56 (d, 4a-C), 120.31, 123.19, 124.90, 127.15, 127.73, 128.80, 128.91 (each d), 134.23, 137.25, 141.55, 144.87, 146.43 (each s), 179.05, and 179.73 (each s, CON); MS *m/z* (rel. intensity, %) 329 (M$^+$, base peak), 218 (37), 217 (54), 202 (23), and 165 (25). Found: C, 80.28; H, 5.83; N, 4.46%. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25%.

18b: Colorless needles (diethyl ether-hexane); mp 64—67 °C; IR (KBr) 1765 and 1685 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.73 (1H, dt, J=12.8, 12.8, and 11.2 Hz, one of 4-H), 2.04 (3H, t, J=1.7 Hz, 9-Me), 2.3—3.3 (5H, m, CH_2 and CH), 2.81 (3H, s, NMe), 3.46 (1H, br d, J=15.2 Hz, one of 10-H), and 7.0—7.4 (4H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=9.99 (q, 9-Me), 21.00 (t, 4-C), 24.56 (q, NMe), 32.75 (t, 10-C), 40.64, 41.27 (each d, 3a- and 10a-C), 46.05 (d, 4a-C), 118.75, 122.36, 124.36, 126.89 (each d), 131.77, 138.98, 145.70, 146.0 (each s), 178.25, and 179.03 (each s, CON); MS *m/z* (rel. intensity, %) 267 (M$^+$, base peak), 181 (32), 167 (50), 166 (39), 165 (71), 156 (78), 155 (81), 153 (21), 152 (40), 141 (68), 115 (45), and 58 (23). HRMS Found: *m/z* 267.1256. Calcd for $C_{18}H_{19}NO_3$: M, 267.1257.

18c: Colorless prisms (diethyl ether-hexane); mp 143—145 °C; IR (KBr) 1770 and 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.80 (1H, dt, J=12.7, 12.7, and 11.2 Hz, one of 4-H), 2.04 (3H, t, J=1.7 Hz, 9-Me), 2.4—3.3 (5H, m, CH_2 and CH), 2.90 (3H, s, NMe), 3.48 (1H, br d, J=15.6 Hz, one of 10-H), 3.79 (3H, s, OMe), 6.80 (1H, dd, J=8.2 and 2.3 Hz, 7-H), 6.93 (1H, d, J=2.3 Hz, 5-H), and 7.13 (1H, d, J=8.2 Hz, 8-H); MS *m/z* (rel. intensity, %) 297 (M$^+$, 98), 186 (27), and 185 (base peak). Found: C, 73.19; H, 6.48; N, 4.91%. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71%.

19a: Colorless plates (diethyl ether-hexane); mp 180—181 °C; IR (KBr) 1760 and 1675 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.92 (1H, dt, J=12.6, 12.6, and 11.2 Hz, one of 4-H), 2.65 (1H, dd, J=15.5 and 8.2 Hz, one of 10-H), 2.5—3.4 (5H, m, CH_2 and CH), 2.83 (3H, s, NMe), 3.60 (1H, d, J=15.5 Hz, the other of 10-H), and 7.0—7.6 (9H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=21.48 (t, 4-C), 24.61 (q, NMe), 32.86 (t, 10-C), 40.72, 41.55 (each d, 3a- and 10a-C), 46.63 (d, 4a-C), 120.31, 122.95, 124.90, 127.20, 127.64, 128.76, 129.00 (each d), 134.08, 137.64, 141.16, 145.02, 145.90 (each s), 178.17, and 179.05 (each s, CON); MS *m/z* (rel. intensity, %) 329 (M$^+$, 44), 243 (21), 217 (32), 215 (29), 202 (30), 167 (29), 166 (42), and 165 (base peak). Found: C, 80.26; H, 5.86; N, 4.43%. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25%.

19b: Colorless prisms (diethyl ether-hexane); mp 92—94 °C; IR (KBr) 1770 and 1685 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.22 (1H, dt, J=15.0, 15.0, and 6.8 Hz, one of 4-H), 2.03 (3H, t, J=1.8 Hz, 9-Me), 2.67 (1H, br d, J=12.9 Hz, one of 10-H), 2.7—3.4 (5H, m, CH_2 and CH), 3.05 (3H, s, NMe), and 7.0—7.6 (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=10.09 (q, 9-Me), 24.95 (q, NMe), 24.95 (t, 4-C), 27.68 (t, 10-C), 40.10, 40.54 (each d, 3a-and 10a-C), 44.98 (d, 4a-C), 118.71, 122.56, 124.36, 126.89 (each d), 131.37, 138.98, 145.94, 146.09 (each s), 179.03, and 179.77 (each s, CON); MS *m/z* (rel. intensity, %) 267 (M^+, base peak), 181 (22), 167 (62), 166 (22), 165 (48), 156 (76), 155 (80), 153 (20), 141 (37), 116 (20), and 113 (27). Found: C, 76.19; H, 6.42; N, 5.27%. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24%.

19c: Colorless needles (diethyl ether–hexane); mp 149—151 °C; IR (KBr) 1765 and 1685 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.22 (1H, ddd, J=16.0, 14.0, and 6.5 Hz, one of 4-H), 1.3—3.4 (6H, m, CH_2 and CH), 2.00 (3H, t, J=1.6 Hz, 9-Me), 3.05 (3H, s, NMe), 3.79 (3H, s, OMe), 6.79 (1H, dd, J=8.2 and 2.3 Hz, 7-H), 6.92 (1H, d, J=2.3 Hz, 5-H), and 7.10 (1H, d, J=8.2 Hz, 8-H); ^{13}C-NMR ($CDCl_3$) δ=10.14 (q, 9-Me), 24.99 (q, NMe), 24.99 (t, 4-C), 27.78 (10-C), 40.20, 40.59 (each d, 3a- and 10a-C), 44.88 (d, 4a-C), 55.50 (q, OMe), 109.40, 112.13, 119.00 (each d), 130.84, 136.59, 139.12, 147.70, 157.64 (each s), 179.03, and 179.77 (each s, CON). Found: C, 72.97; H, 6.47; N, 4.92%. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71%.

20: Colorless viscous oil; IR (neat) 1775 and 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.0—3.3 (6H, m, CH_2 and CH), 2.94 (3H, s, NMe), 5.08, 5.26 (each 1H, s, =CH_2), 5.70 (1H, m, 6-H), and 7.0—7.4 (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=24.61 (t, 4- or 7-C), 24.90 (q, NMe), 25.63 (t, 4- or 7-C), 38.94, 39.76 (each d, 3a- and 7a-C), 113.15 (t, =CH_2), 126.36, 127.43, 127.96, 128.35 (each d), 139.51, 140.59 (each s), 179.47, and 179.86 (each s, CON); MS *m/z* (rel. intensity, %) 267 (M^+, base peak), 181 (28), 167 (40), 165 (33), 156 (73), 155 (62), 141 (34), 128 (21), 115 (26), 112 (27), 103 (59), 78 (25), and 77 (67). Found: C, 76.28; H, 6.62; N, 5.20%. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24%.

21: Colorless needles (diethyl ether–hexane); mp 102—103 °C; IR (KBr) 1765 and 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.1—3.2 (6H, m, CH_2 and CH), 2.96 (3H, s, NMe), 3.77 (3H, s, OMe), 5.05, 5.17 (each s, =CH_2), 5.74 (1H, m, 6-H), 6.89, and 7.06 (each 2H, br d, Ar); ^{13}C-NMR ($CDCl_3$) δ= 24.51 (t, 4- or 7-C), 24.80 (q, NMe), 25.78 (t, 4- or 7-C), 38.84, 39.67 (each d, 3a- and 7a-C), 55.07 (q, OMe), 112.13 (t, =CH_2), 113.25, 125.92, 129.28 (each d), 132.84, 139.70, 148.62, 158.91 (each s), 179.38, and 179.77 (each s, CON); MS *m/z* (rel. intensity, %) 297 (M^+, base peak), 186 (21), 185 (50), and 133 (22). Found: C, 72.85; H, 6.55; N, 4.88%. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71%.

References

1) B. M. Trost and M. Shimizu, *J. Am. Chem. Soc.*, **104**, 4299 (1982); T. Minami, Y. Taniguchi, and I. Hirao, *J. Chem. Soc., Chem. Commun.*, **1984**, 1046.

2) O. Tsuge, E. Wada, S. Kanemasa, and H. Sakoh, *Bull. Chem. Soc. Jpn.*, **57**, 3221 (1984); O. Tsuge, S. Kanemasa, H. Sakoh, and E. Wada, *ibid.*, **57**, 3234 (1984); S. Kanemasa, H. Sakoh, E. Wada, and O. Tsuge, *ibid.*, **58**, 3312 (1985); S. Kanemasa, H. Sakoh, E. Wada, and O. Tsuge, *ibid.*, **59**, 1869 (1986).

3) Recent reviews on Diels–Alder reactions: W. Oppolzer, *Angew. Chem. Int. Ed. Engl.*, **16**, 10 (1977); W. Oppolzer, *Synthesis*, **1978**, 793; G. Brieger and J. N. Bennett, *Chem. Rev.*, **80**, 63 (1980); T. Wagner-Jauregg, *Synthesis*, **1980**, 165; J. Sauer and R. Sustmann, *Angew. Chem. Int. Ed. Engl.*, **19**, 779 (1980); S. Danishefsky, *Acc. Chem. Res.*, **14**, 400 (1981); M. Petrzilka and J. I. Grayson, *Synthesis*, **1981**, 753; D. L. Boger, *Tetrahedron*, **39**, 2869 (1983).

4) Although some electrocyclic reactions on 1-aryl-2-propen-1-ols and diarylmethanols are known (Ref. 6), there have been reported only a few extensions to the functionalized systems (S. K. Dasgupta, R. Dasgupta, S. R. Ghosh, and U. R. Ghatak, *J. Chem. Soc., Chem. Commun.*, **1969**, 498; F. A. Neugebauer and W. R. Groh, *Chem. Ber.*, **107**, 1903 (1974)).

5) E. Wada, S. Kanemasa, I. Fujiwara, and O. Tsuge, *Bull. Chem. Soc. Jpn.*, **58**, 1942 (1985).

6) C. U. Pittman, Jr., and W. G. Miller, *J. Am. Chem. Soc.*, **95**, 2947 (1973); W. G. Miller and C. U. Pittman, Jr., *J. Org. Chem.*, **39**, 1955 (1974); L. M. Tolbert, *ibid.*, **44**, 4584 (1979).

7) The axial hydrogen at the 4-position of **8a** is antiparallel to both 3-H and 4a-H so that it couples with them with large coupling constants of 13.1 Hz, while the corresponding hydrogen of **9a** which is cis and trans to 3-H and 4a-H, respectively, couples with them with coupling constants of 4.7 and 13.0 Hz.

8) O. Makabe, Y. Murai, and S. Fukatsu, *Heterocycles*, **13**, 239 (1979); H. Narkgraf, E. W. Greeno, M. D. Miller, and W. J. Zaks, *Tetrahedron Lett.*, **24**, 241 (1983); O. Tsuge, E. Wada, S. Kanemasa, and H. Sakoh, *Chem. Lett.*, **1984**, 469 and 709.

9) Protonation of **11** or **12** leads to the cationic intermediate which is the same to that involved in the electrocyclization of **5** forming **8** and **9**.

10) Both clockwise rotation of **A** and counterclockwise rotation of **B** lead to boat conformations, therefore these rotations were excluded.

11) It is known that, in 4,5-disubstituted cyclohexene series, 4,5-diequatorial conformer is always more stable than 4,5-diaxial isomer (N. S. Zefirov, V. N. Chekulaeva, and A. I. Belozerov, *Tetrahedron*, **25**, 1997 (1969)). However, the conformer **B** with two axial ester groups is expected to be more stable than the conformer **A** with two equatorial esters because only the axial esters can interact with the cationic centers stabilizing these centers. As a similar interaction, see G. P. Kugatova-Shemyakina and G. M. Nikolaev, *Tetrahedron*, **23**, 2987 (1967).

12) The envelope conformation can be replaced by another name, twisted half-chair conformation.

13) As the six-membered ring of **H** takes twisted half-chair conformation, the 1,3-steric repulsion between 3a-carbonyl and 4a-H is insignificant. Accordingly, the energy difference between **G** and **H** should be smaller that between **C** and **D** (X=H, Y=COOMe).