h a 92% yield of 2-octanol is determined by GC. The flask is cooled to room temperature, and the reaction mixture is treated with water (4 mL) and filtered through Celite. The solvent is removed under reduced pressure and the product purified by silica gel column chromatography and distillation [10.5 g, 81% isolated yield, bp 85 °C (18 torr)]. **2-Octanol**: IR (neat, absorptions in cm^{-1}) 3400 (br); ^1H NMR (60 MHz, $CDCl_3$, δ values from internal Me_4Si) 3.8 (m, 1 H), 1.9 (s, 1 H, OH), 1.35 (m, 10 H), 1.2 (t, 3 H), 0.9 (t, 3 H); MS (70 eV, *m/e*, relative intensity) 130 (M^+, traces), 57 (7), 55 (16), 43 (20), 45 (100).

Acknowledgment. This work was supported by the Italian C.N.R. (Progetto Finalizzato Chimica Fine e Secondaria).

Registry No. 1-Decene, 872-05-9; 1-undecene, 821-95-4; (*E*)-2-octene, 13389-42-9; cyclooctene, 931-88-4; 2-methyl-1-heptene, 15870-10-7; 1,8-menthadiene, 138-86-3; allyl benzyl ether, 14593-43-2; cyclohexanone, 108-94-1; 2-octanone, 111-13-7; 2-undecanone, 112-12-9; 4-methyl-2-pentanone, 108-10-1; acetophenone, 98-86-2; 3-pentanone, 96-22-0; 3-heptanone, 106-35-4; 1,4-cyclohexanedione, 637-88-7; 2-methylcyclohexanone, 583-60-8; (+)-camphor, 464-49-3; 5-hexen-2-one, 109-49-9; 2-cyclohexen-1-one, 930-68-7; β-ionone, 79-77-6; 2-propanol, 67-63-0; Ni, 7440-02-0; lithium isopropoxide, 2388-10-5; sodium isopropoxide, 683-60-3; potassium isopropoxide, 6831-82-9.

2,4-Cyclohexadien-1-ones in Organic Synthesis. Intramolecular Diels–Alder Reactivity and the Oxa-di-π-methane Photorearrangement of Diels–Alder Adducts

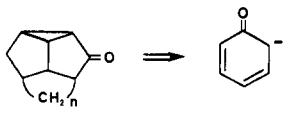
Arthur G. Schultz,* Frank P. Lavieri, and Thomas E. Snead

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Received October 11, 1984

The preparation and intramolecular Diels–Alder reactions of a series of 6-alkenyl-6-(methoxycarbonyl)-2,4-cyclohexadien-1-ones are described. The resulting tricyclic β,γ-enones undergo the oxa-di-π-methane rearrangement to give substrates of potential use in the construction of polyquinane natural products. This methodology provides a means for construction of tetracyclic rings of type A by C-alkylation of the synthetic equivalence of enolate B.

We have reported a general method for the construction of 6-alkyl-6-carbalkoxy-2,4-cyclohexadien-1-ones by Birch reduction–alkylation of *o*-hydroxybenzoic acid derivatives.[1] The chiral auxiliary technique has been used to prepare optically active 2,4-cyclohexadienone derivatives in enantiomerically pure form.[2,3] In this paper, we describe the intramolecular Diels–Alder reactions of 6-alkenyl-6-(methoxycarbonyl)-2,4-cyclohexadien-1-ones. The resulting tricyclic ring systems contain the β,γ-enone functionality and undergo efficient oxa-di-π-methane photorearrangement.[4] These reactions provide a means for construction of tetracyclic rings of type A (demonstrated

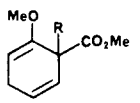


A B

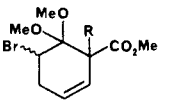
for n = 1, 2, and 3) by a process based on C-alkylation of the synthetic equivalence of enolate B. It is anticipated that this chemistry will be of use in the synthesis of polyquinane natural products.[5]

Results and Discussion

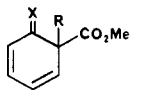
The Birch reduction–alkylation procedure previously described was used to construct 1,4-cyclohexadienes **1a–e** from methyl 2-methoxybenzoate.[1] Reaction of **1a–e** with *N*-bromoacetamide (NBA) in methanol provided bromo ketals **2a–e**.



1a, R=$CH_2CH=CH_2$
b, R=$CH_2CBr=CH_2$
c, R=$CH_2CH_2CH=CH_2$
d, R=$CH_2CH_2CH_2CH=CH_2$
e, R=$CH_2C_6H_4CH=CHCO_2Me$



2

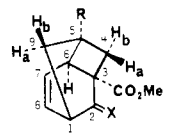


3a-e, X=$(OMe)_2$
f, X=O
R=$CH_2CH_2CH_2CH=CH_2$

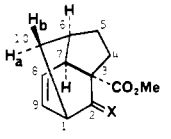
Dehydrobromination was accomplished by heating bromoketals in the presence of an amine in an aromatic solvent. In most cases, the cyclohexadienone ketals were not obtained (e.g., **3a–c, e**), but rather intramolecular Diels–Alder addition occurred to give the bridged adducts directly (e.g., **4a,c**, **5a**, and **7a**). ^1H NMR evidence for the intermediacy of **3a** in the conversion of **2a** to **4a** was provided by heating bromoketal **2a** in *tert*-butyl alcohol in the presence of potassium *tert*-butoxide. In contrast, cyclohexadienone ketal **3d** was obtained in 76% isolated yield from treatment of **2d** with 1,5-diazobicyclo[4.3.0]-non-5-ene (DBN) in refluxing toluene solution (24 h). Tricyclic adduct **6a** could not be obtained from **3d** even at higher reaction temperature (up to ~140 °C). The reluctance of **3d** to undergo Diels–Alder cyclization presumably is a result of unfavorable steric interactions between the developing cyclohexane ring and a ketal methoxyl group. Indeed, **3f**, obtained by ketal hydrolysis of **3d**, underwent smooth cyclization in refluxing toluene solution (7 h) to give **6b** in 95% isolated yield. The remaining

(1) Schultz, A. G.; Ditami, J. P.; Lavieri, F. P.; Salowey, C.; Sundararaman, P.; Szymula, M. B. *J. Org. Chem.* **1984**, *49*, 4429.
(2) Schultz, A. G.; Sundararaman, P. *Tetrahedron Lett.* **1984**, *25*, 4591.
(3) Schultz, A. G.; Puig, S. *J. Org. Chem.* **1985**, *50*, 915.
(4) Photochemically generated tricyclo[3.3.0.$0^{2,8}$]octan-3-ones have been used in polyquinane synthesis: Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820. Demuth, M.; Chandrasekhar, S.; Schaffner, K. *J. Am. Chem. Soc.* **1984**, *106*, 1092.
(5) (a) Paquette, L. A. *Top Curr. Chem.* **1979**, *79*, 41. (b) Trost, B. *Chem. Soc. Rev.* **1982**, *11*, 141.

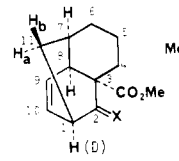
0022-3263/85/1950-3086$01.50/0



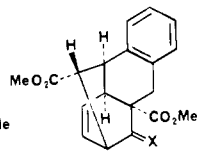
4a, R=H; X=(OMe)$_2$
b, R=H; X=O
c, R=Br; X=(OMe)$_2$
d, R=Br; X=O



5a, X=(OMe)$_2$
b, X=O



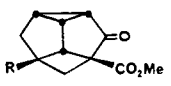
6a, X=(OMe)$_2$
b, X=O



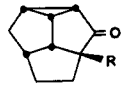
7a, X=(OMe)$_2$
b, X=O

cyclized enones **4b,d**, **5b**, and **7b** were obtained by acid-catalyzed hydrolysis of the corresponding ketal.

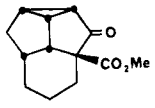
The oxa-di-π-methane photorearrangement was performed by irradiation of an acetone solution of the β,γ-enone in Pyrex glassware in the presence of a triplet sensitizer (acetophenone, 2 equiv). Using these conditions, complete photoconversion required 30–50 h, but isolated yields were good to excellent (e.g., **8a**, 66%; **8b**, 86%; **10**, 89% **11**; 84%). Much shorter reaction time was required when quartz glassware (acetone sensitization) was used in one experiment (**5b** → **9a**, 3 h, 75%).



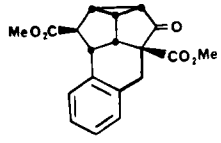
8a, R=H
b, R=Br



9a, R=CO$_2$Me
b, R=CO$_2$H
c, R=H



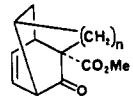
10



11

Tetracycle **9a** is a potential intermediate for triquinacene ring[6] construction. Saponification of the methyl ester group in **9a** gave **9b** and this β-keto acid underwent quantitative decarboxylation in refluxing toluene solution to give ketone **9c**. Thus, the synthetic equivalence of the conversion of B into A is demonstrated.

Orientational Control in the Intramolecular Diels–Alder Reaction. In principle, there are two pathways for Diels–Alder cyclization of **3a–e** and **3f**, one providing the series **4–7** and another resulting in regioisomeric products of type **12**. Literature precedent exists



12

for both modes of intramolecular cycloaddition for the cases in which n = 2 and 3.[7,8] In the work reported here, however, products of type **12** (n = 1–3) were not observed. Structural assignments in the series **4–7** were made by careful consideration of IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data. We now present a brief discussion of the most diagnostic spectroscopic data.

The product resulting from cyclization of **3a** followed by ketal hydrolysis displays ^{13}C NMR resonance at 206.85 ppm. This absorption is typical of a carbonyl group in a six-membered ring but is not compatible with a carbonyl group residing in a five-membered ring (e.g., **12**, n = 1).

^{1}H NMR spectra of **4b** and **4d** display W-coupling between H_{9a} and H_{4b} (J = 3 Hz). Dreiding molecular models indicate that such coupling would be expected for either **4** or **12** (n = 1). H_{9b} appears as the same doublet of doublets in spectra of both **4b** and **4d**. In **4b**, therefore, H_{9b} is coupled to H_{9a} (J = 12 Hz) and H_1 (J = 4 Hz) but not to H_5. An absence of coupling between H_5 and H_{9b} would be expected for structure **4b** because the molecular model shows an ~90° dihedral angle for H_5–C_5–C_9–H_{9b}. A model of **12** (n = 1) suggests that couplings corresponding to $J_{5,9a}$ and $J_{5,9b}$ should be ~2 Hz.

The assignment of structure for **5b** rests firmly on a comparison to ^{1}H NMR spectroscopic data reported for related compounds.[7b] In particular, resonances for H_{10a}, H_{10b}, and H_6 in **5b** are nearly identical with those reported for 5-methylene-1,3,8-trimethyltricyclo[4.3.1.0^{3,7}]-8-decen-2-one and are clearly different than those reported for the type **12** regioisomer 9-methylene-1,3,5-trimethyltricyclo[4.4.0.0^{3,8}]-4-decen-2-one.

Cyclization of **3e** might have been expected to give both **7a** and **12**.[9] However, the product obtained in 54% isolated yield must be **7a** because the observed coupling constant for H_7–H_{11} (J = 4 Hz) is compatible with the dihedral angle for H_7–C_7–C_{11}–H_{11} of ~140° observed in a molecular model of **7a** but not with a dihedral angle of ~90° observed in a model of the corresponding type **12** regioisomer.

^{1}H NMR spectra of **5b** and **6b** are qualitatively similar, however, a definitive assignment of resonances to specific protons, using the literature data[9] as a guide, could not be accomplished. These uncertainties were resolved by spectroscopic studies of **6b** with a deuterium substituent at C_1.[10] Resonances for H_8, H_9, H_{10}, H_1, and H_{11a} were assigned (see Experimental Section), and, significantly, the line shape and multiplicity for H_{11a} in monodeuterated **6b** appeared identical with those for **6b** when H_1 and H_{11a} were decoupled.

Conclusion

The chemistry outlined in this report provides a versatile construction of polyquinanes of type A from *o*-hydroxybenzoic acid precursors. The generality of the Birch reduction–alkylation method[1] coupled with the recent demonstration of a highly enantioselective construction of 2,4-cyclohexadien-1-one derivatives[2] suggests that this methodology should be complementary to the elegant procedures devised by Demuth and Schaffner[4] for poly-

(6) Carceller, E.; Garcia, M. L.; Moyano, A.; Serratosa, F. *J. Chem. Soc., Chem. Commun.* **1984**, *825*.
(7) Greuter, H.; Fráter, Gy.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 526. (b) Greuter, H.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 2382.
(8) (a) Fukamiya, N.; Kato, M.; Yoshikoshi, A. *J. Chem. Soc., Chem. Commun.* **1971**, 1120. (b) Fukamiya, N.; Kato, M.; Yoshikoshi, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1843.
(9) Intramolecular Diels–Alder cyclization of 2,4,6-trimethyl-6-(penta-2,4-dienyl)-2,4-cyclohexadien-1-one is reported to give both 1,3,10-trimethyltricyclo[5.4.0.0^{3,9}]undeca-5,10-dien-2-one and its regioisomer 1,3,9-trimethytricyclo[5.3.1.0^{3,8}]undeca-5,9-dien-2-one.[7a]
(10) Monodeutero-**6b** was prepared by (1) treatment of a solution of **1d** in CH_3OD–DCl to give the α-deuterated ketone, (2) enol ether formation by treatment of the ketone with CH_3OD–D_2SO_4–$HC(OMe)_3$ to give C(2)-deuterated **1d**, and (3) conversion of the enol ether to C(1)-deuterated **6b** (>95% deuterium incorporation as evidenced by GC–MS analysis) by the reported procedure.

quinane natural product synthesis.

Experimental Section

^{1}H 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 5987 A GC–MS systems (methane, chemical ionization gas). Elemental analyses were determined by Spang Microanalytical Laboratories, Eagle Harbor, MI. The light source for all photochemistry was a Hanovia 450-W medium-pressure mercury arc lamp. The lamp was placed in a water-cooled Pyrex immersion well. Reaction vessels containing solutions to be irradiated were attached to the immersion well and were saturated with nitrogen prior to irradiation.

Methyl 2-(Bromomethyl)cinnamate. A rapidly stirred suspension of methyl 2-methylcinnamate[10] (24.31 g, 0.138 mol), *N*-bromosuccinamide (26.7 g, 0.150 mol), and benzoyl peroxide (1.6 g) in carbon tetrachloride (325 mL, distilled from P_2O_5) was heated at reflux for 5 h. After cooling, the mixture was filtered through Celite and the filtrate concentrated to give a pale yellow solid. Recrystallization from 95% ethanol gave methyl 2-bromomethylcinnamate (19.7 g, 63.4%) as fine white needles: mp 83–87 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.84 (s, 3 H), 4.60 (s, 2 H), 6.45 (d, 1 H, J = 16.0 Hz), 7.31–7.45 (m, 3 H), 7.56–7.67 (m, 1 H), 8.07 (d, 1 H, J = 16.0 Hz); IR (KBr) 3100–2800, 1715, 1650, 1420, 1330, 1180 cm^{-1}; mass spectrum, m/e (relative intensity) 256 (M^+, 3.5), 254 (M^+, 3.9), 225 (3.5), 223 (3.9), 175 (44), 161 (43), 142 (89), 131 (7.6), 128 (6.1), 116 (57), 115 (100), 91 (15), 89 (11), 63 (11), 59 (21).

Anal. Calcd for $C_{11}H_{11}BrO_2$: C, 51.79; H, 4.35. Found: C, 51.71; H, 4.44.

Birch Reduction–Alkylations of Methyl 2-Methoxybenzoate. 1-Methoxy-6-(methoxycarbonyl)-6-(2-propenyl)-1,4-cyclohexadiene (1a). Ammonia (~250 mL, dried over sodamide for 1 h) was distilled into a mechanically stirred solution of methyl 2-methoxybenzoate (8.32 g, 50.0 mmol), dry *tert*-butyl alcohol (4.9 mL, 52 mmol), and dry THF (50 mL), cooled in a dry ice–acetone bath. Potassium (~4.9 g, 125 mmol) was added until a deep blue color persisted for 15 min. The color was discharged by adding a few drops of 1,3-pentadiene. A solution of allyl bromide (11 mL, 0.127 mol) in dry THF (50 mL) cooled in a dry ice–acetone bath was added. After 15 min, the cooling bath was removed, and ammonia was evaporated by continuous stirring for 5 h. The reaction mixture was poured into brine (200 mL) and extracted with 1:1 ether–methylene chloride (3 × 60 mL). After drying ($MgSO_4$), the combined organic solution was concentrated to a yellow oil, which was purified by Kugelrohr distillation [60–64 °C (0.10 mmHg)] to give **1a** (8.2 g, 79%) as a colorless solid; the analytical sample was obtained by recrystallization from pentane: mp 39–40 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.42–2.56 (m, 1 H), 2.72–2.88 (m, 3 H), 3.54 (s, 3 H), 3.70 (s, 3 H), 4.86 (dd, 1 H, J = 2.0, 2.0 Hz), 4.95–5.06 (m, 2 H), 5.39–5.74 (m, 2 H), 5.92 (m, 1 H); IR ($CHCl_3$) 3080–2800, 1730, 1690, 1655, 1430, 1360, 1230 (br) cm^{-1}; mass spectrum, m/e (relative intensity) 208 (M^+, 35), 167 (64), 166 (19), 149 (27), 135 (45), 123 (48), 121 (59), 109 (37), 108 (100), 91 (30), 77 (25), 59 (20).

An acceptable analysis could not be obtained.

6-(2-Bromo-2-propenyl)-6-(methoxycarbonyl)-1-methoxy-1,4-cyclohexadiene (1b). A solution of methyl 2-methoxybenzoate (2.59 mL, 18.0 mmol) in dry THF (20 mL), *tert*-butyl alcohol (1.69 mL, 18.0 mmol), and ammonia (200 mL) was cooled to −78 °C, and small pieces of potassium (1.42 g) were added. The condenser was replaced by a drying tube, and ammonia was allowed to evaporate (N_2 atmosphere). The reaction was recooled to −78 °C, and 2,3-dibromopropene (1.96 mL, 19.8 mmol) was added. After 1 h, solid NH_4Cl was added, and the cooling bath was removed. Ethyl acetate (100 mL) and saturated NH_4Cl solution (100 mL) were added. The organic phase was washed with NH_4Cl solution (2 × 100 mL), dried over sodium sulfate, and concentrated to give **1b**, as a dark brown oil, that was purified by Kugelrohr distillation [110 °C, (0.8 mmHg)] to give crystalline **1b** (3.88 g, 76%): mp 68–70 °C; ^{1}H NMR ($CDCl_3$) δ 2.86 (m, 3 H), 3.28 (d, 1 H, J = 14 Hz), 3.56 (s, 3 H), 3.71 (s, 3 H), 4.91 (t, 1 H, J = 3 Hz), 5.52 (m, 3 H), 5.96 (dt, 1 H, J = 10 Hz, J = 3 Hz); IR (KBr) 2950, 1730, 1690, 1240 cm^{-1}; chemical-ionization mass spectrum, m/e 288, 287 (M^+ + 1).

Anal. Calcd for $C_{12}H_{15}O_3Br$: C, 50.19; H, 5.27. Found: C, 50.42; H, 5.33.

6-(3-Butenyl)-1-methoxy-6-(methoxycarbonyl)-1,4-cyclohexadiene (1c). Prepared in 76% yield as described for **1a**: Kugelrohr distillation [~75 °C (0.10 mmHg)]; oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.64–2.20 (m, 4 H), 2.78–2.93 (m, 2 H), 3.55 (s, 3 H), 3.69 (s, 3 H), 4.87–5.04 (m, 3 H), 5.37–5.44 (m, 1 H), 5.73–5.96 (m, 2 H); IR ($CHCl_3$) 3100–2780, 1725, 1625, 1450, 1435, 1360, 1220 (br), 1165 cm^{-1}; mass spectrum, m/e (relative intensity) 222 (M^+, 11), 187 (5), 168 (7), 167 (6), 163 (15), 162 (3), 135 (13), 123 (4), 122 (12), 121 (100), 91 (27), 58 (20).

An acceptable analysis could not be obtained.

6-(Methoxycarbonyl)-1-methoxy-6-(4-pentenyl)-1,4-cyclohexadiene (1d). Prepared in 67% yield as described for **1b** with 5-iodo-1-pentene [prepared from the reaction of the corresponding methane sulfonate[11] and sodium iodide (1.1 equiv) in refluxing acetone for 2 h and purified by Kugelrohr distillation (50 °C (15 mmHg))]; **1d** was purified by flash chromatography (silica gel, 7:1 hexane–ethyl acetate): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.20 (m, 2 H), 1.63 (dt, 1 H, J = 4 Hz, J = 12 Hz), 2.0 (m, 3 H), 2.82 (m, 2 H), 3.53 (s, 3 H), 3.66 (s, 3 H) 4.84 (t, 1 H, J = 2 Hz), 4.91 (d, 1 H, J = 9 Hz), 5.02 (br s, 1 H), 5.48 (d, 1 H, J = 10 Hz), 5.7–5.9 (m, 2 H); IR (film) 1730, 1690, 1230 cm^{-1}; chemical-ionization mass spectrum, m/e 237 (M^+ + 1).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.23; H, 8.50.

1-Methoxy-6-(methoxycarbonyl)-6-[2-(2-carbomethoxyvinyl)benzyl]-1,4-cyclohexadiene (1e). Prepared in 56% yield as described for **1b** via the lithium enolate[1] and methyl 2-bromomethylcinnamate: Kugelrohr distillation [~145 °C(0.06 mmHg)]; oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.92–2.12 (m, 1 H), 2.46–2.66 (m, 1 H), 3.22 (d, 1 H, J = 14 Hz), 3.50 (s, 3 H), 3.56 (d, 1 H, J = 14 Hz), 3.76 (s, 3 H), 3.81 (s, 3 H), 4.58–4.67 (m, 1 H), 5.47–5.59 (m, 1 H), 5.68–5.81 (m, 1 H), 6.30 (d, 1 H, J = 16 Hz), 7.08–7.31 (m, 3 H), 7.49–7.60 (m, 1 H), 8.03 (d, 1 H, J = 16 Hz); mass spectrum, m/e (relative intensity) 166 (30), 135 (100), 133 (40), 105 (18), 92 (25), 77 (47), 63 (16), 51 (13); chemical-ionization mass spectrum, m/e (relative intensity) 343 (M^+ + 1, 4), 310 (17), 282 (4), 250 (7), 194 (10), 167 (75), 158 (12), 135 (100).

Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 69.96; H, 6.36.

6-Bromo-2-(methoxycarbonyl)-2-(2-propenyl)-3-cyclohexen-1-one, Dimethyl Ketal (2a). *N*-Bromoacetamide (0.056 g, 3.67 mmol) was added to a solution of enol ether **1a** (0.717 g, 3.44 mmol) in methanol (15 mL) at 0 °C. A few crystals of *p*-toluenesulfonic acid were added, and the reaction was allowed to stand for 1 h. Ether (150 mL) was added, and the resulting organic solution was washed with water (2 × 75 mL) and brine (2 × 75 mL). After drying ($MgSO_4$), the solution was concentrated to give **2a** (1.10 g, 100%) as a cloudy, pale yellow oil (2:1 mixture of diastereomers). This material was sufficiently pure for the next operation. The analytical sample was obtained by Kugelrohr distillation [85–89 °C (0.10 mm Hg)] as a clear pale yellow oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.19–3.08 (m, 4 H), 3.45 (s, 2 H), 3.52 (s, 1 H), 3.62 (s, 2 H), 3.66 (s, 1 H), 3.71 (s, 1 H), 3.73 (s, 2 H), 4.43 (dd, 0.33 H, J = 9 Hz, J = 6 Hz), 4.66 (dd, 0.67 H, J = 7.5 Hz, J = 5.1 Hz), 5.03–5.14 (m, 2 H), 5.50–5.76 (m, 3 H); IR ($CHCl_3$) 3100–2800, 1725, 1460, 1435, 1220 (br) cm^{-1}; mass spectrum, m/e (relative intensity) 289 (96), 287 (100), 257 (17), 255 (17), 239 (65), 229 (19), 227 (14), 207 (26), 149 (12).

Anal. Calcd for $C_{13}H_{19}O_4Br$: C, 48.92; H, 6.00. Found: C, 48.92; H, 5.96.

6-Bromo-2-(2-bromo-2-propenyl)-2-(methoxycarbonyl)-3-cyclohexen-1-one, Dimethyl Ketal (2b). Prepared in 94% yield as described for **2a**; 2:1 mixture of diastereomers (^{1}H NMR analysis). The analytical sample was prepared by flash chro-

(11) Norcross, B. E.; Lansinger, J. M; Martin, R. L. *J. Org. Chem.* **1977**, *42*, 369.

(12) Perrine, T. D. *J. Org. Chem.* **1953**, *18*, 1356.

matography (alumina, 7:1 hexane–ethyl acetate): oil; ^{1}H NMR ($CDCl_3$) δ 2.6–2.9 (m, 4 H), 3.42, 3.52 (2 s, 3 H), 3.60, 3.64 (2 s, 3 H), 3.74, 3.76 (2 s, 3 H), 4.36, 4.65 (2 m, 1 H), 5.53 (br s, 1 H), 5.62 (br s, 1 H), 5.7–5.9 (m, 2 H); IR (film) 2950, 1730, 1680, 1420 cm^{-1}; chemical ionization mass spectrum, m/e 366 (M^+ – 32).

6-Bromo-2-(3-butenyl)-2-(methoxycarbonyl)-3-cyclohexen-1-one, Dimethyl Ketal (2c). Prepared in 100% yield as described for **2a**. The analytical sample was prepared by Kugelrohr distillation [105 °C (0.4 mmHg)]: oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.4–3.0 (m, 6 H), 3.41 (s, 1.8 H), 3.52 (s, 1.2 H), 3.60 (s, 1.8 H), 3.65 (s, 1.2 H), 3.72 (s, 3 H), 4.44 (dd, 0.4 H, J = 10.2 Hz, J = 5.6 Hz), 4.61 (dd, 0.6 H, J = 6.4 Hz, J = 5.8 Hz), 4.9–5.1 (m, 2 H), 5.6–5.9 (m, 3 H); IR ($CHCl_3$) 3100–2800, 1725, 1450, 1435, 1220 (br) cm^{-1}; chemical-ionization mass spectrum, m/e (relative intensity) 303 (22), 301 (25), 271 (45), 269 (46), 254 (20), 253 (100).

Anal. Calcd for $C_{14}H_{21}BrO_4$: C, 50.46; H. 6.35. Found: C, 50.48; H, 6.31.

6-Bromo-2-(methoxycarbonyl)-2-(4-pentenyl)-3-cyclohexen-1-one, Dimethyl Ketal (2d). Prepared in 98% yield as described for **2a**; 5:4 mixture of diastereomers (^{1}H NMR analysis). The analytical sample was prepared by flash chromatography (alumina, 7:1 hexane–ethyl acetate): oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.6 (m, 3 H), 2.0–2.3 (m, 3 H), 2.6–2.9 (m, 2 H), 3.40, 3.52 (2 s, 3 H), 3.59, 3.65 (2 s, 3 H), 3.71, 3.72 (2 s, 3 H), 4.44, 4.60 (2 m, 1 H), 4.95 (d, 1 H, J = 8 Hz), 5.06 (br s, 1 H), 5.70 (m, 3 H); IR (film) 2840, 1730, 1670, 1640, 1430, 1220 (br) cm^{-1}; chemical-ionization mass spectrum, m/e 349, 347 (M^+ + 1).

Anal. Calcd for $C_{15}H_{23}O_4Br$: C, 51.88; H, 6.68. Found: C, 52.09; H, 6.41.

6-Bromo-2-(methoxycarbonyl)-2-[2-(2-carbomethoxyvinyl)benzyl]-3-cyclohexen-1-one, Dimethyl Ketal (2e). Prepared in 100% yield as described for **2a**: 5:2 mixture of diastereomers (^{1}H NMR analysis); oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.70–2.92 (m, 2 H), 3.18–3.86 (m, 14 H), 4.59–4.72 (m, 1 H), 5.10–5.22 and 5.54–5.70 (m, 2 H), 6.30 (d, major isomer, 1 H, J = 16 Hz), 6.34 (d, minor isomer, 1 H, J = 16 Hz), 7.20–7.36 (m, 3 H), 7.54–7.66 (m, 1 H), 8.01 (d, major isomer, 1 H, J = 16 Hz), 8.31 (d, minor isomer, 1 H, J = 16 Hz); IR ($CHCl_3$) 3200–2850, 1730, 1710, 1220 (br) cm^{-1}.

6-(Methoxycarbonyl)-6-(2-propenyl)-2,4-cyclohexadien-1-one, Dimethyl Ketal (3a). A solution of bromoketal **2a** (0.3220 g, 1.01 mmol), potassium *tert*-butoxide (0.250 g, 2.22 mmol), and *tert*-butyl alcohol (75 mL) was heated at reflux for 24 h. The reaction mixture was concentrated to ~20 mL and then diluted with ether (75 mL). The organic solution was washed with water (2 × 75 mL) and brine (1 × 75 mL). After drying ($MgSO_4$), the solution was concentrated to give **3a** (0.200 g, 83%) as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.34–2.48 (m, 1 H), 2.70–2.86 (m, 1 H), 3.27 (s, 3 H), 3.44 (s, 3 H), 3.77 (s, 3 H), 4.98–5.10 (m, 2 H), 5.56–5.78 (m, 2 H), 5.92–6.18 (m, 3 H).

6-(Methoxycarbonyl)-6-(4-pentenyl)-2,4-cyclohexadien-1-one, Dimethyl Ketal (3d). A solution of **2d** (0.754 g, 2.17 mmol) in toluene (20 mL) and 1,5-diazobicyclo[4.3.0]non-5-ene (0.804 mL, 6.50 mmol) was heated at reflux for 24 h. After cooling, the reaction mixture was dissolved in ethyl acetate (100 mL) and washed with water (2 × 100 mL) and brine (1 × 100 mL). The organic layer was dried (Na_2SO_4) and concentrated to give **3d** as a pale yellow oil. Kugelrohr distillation [85 °C (1.0 mmHg)] gave **3d** (0.437 g, 76%); oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.5 (m, 2 H), 1.70 (dt, 1 H, J = 6 Hz, J = 12 Hz), 1.9–2.1 (m, 3 H), 3.24 (s, 3 H), 3.42 (s, 3 H), 3.77 (s, 3 H), 4.91 (d, 1 H, J = 9 Hz), 5.02 (br s, 1 H), 5.58 (d, 1 H, J = 10 Hz), 5.75 (m, 1 H), 5.96 (m, 1 H), 6.11 (m, 2 H); IR (film) 2940, 1720, 1640, 1240 cm^{-1}; chemical-ionization mass spectrum, m/e 267 (M^+ + 1).

6-(Methoxycarbonyl)-6-(4-pentenyl)-2,4-cyclohexadien-1-one (3f). To a solution of ketal **3d** (0.223 g, 0.837 mmol) in acetone–water (25 mL, 4:1) was added a few crystals of *p*-toluenesulfonic acid. After 22 h at room temperature, the reaction mixture was dissolved in ethyl acetate (100 mL) and was washed with water (1 × 100 mL) and brine (1 × 100 mL). The organic extract was dried over sodium sulfate and concentrated to give **3f**. Flash chromatography (silica gel, 7:1 hexane–ethyl acetate) gave **3f** (0.150 g, 82% yield) as a clear oil: ^{1}H NMR ($CDCl_3$) 1.1–1.3 (m, 2 H), 2.00 (m, 3 H), 2.26 (dt, 1 H, J = 5 Hz, J = 12 Hz), 3.67 (s, 3 H), 4.95 (d, 1 H, J = 8 Hz), 5.00 (br s, 1 H), 5.70 (m, 1 H), 6.10 (d, 1 H, J = 10 Hz), 6.29 (d, 1 H, J = 9 Hz), 6.40 (m, 1 H), 7. 06 (dd, 1 H, J = 6 Hz, J = 9 Hz); IR (film) 2950, 1730, 1660, 1630, 1560, 1240 (br) cm^{-1}; chemical-ionization mass spectrum, m/e 221 (M^+ + 1).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.63; H, 7.44.

3-(Methoxycarbonyl)tricyclo[5.3.1.0^{3,8}]undec-9-en-2-one (6b). A solution of **3f** (0.161 g, 0.731 mmol) in dry toluene (10 mL) was heated at reflux for 7 h. Evaporation of solvent and Kugelrohr distillation [85 °C (0.5 mmHg)] gave **6b** (0.153 g, 95%) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.3–1.7 (m, 6 H), 1.76 (dt, 1 H, $J_{11a,11b}$ = 12 Hz, $J_{11a,7}$ = 12 Hz, $J_{11a,1}$ = 3 Hz), 2.04 (m, 1 H), 2.23 (br d, 1 H, J = 12 Hz), 2.91 (dd, 1 H , $J_{8,9}$ = 6 Hz, $J_{8,7}$ = 4 Hz), 3.18 (m, 1 H, $J_{1,10}$ = 6 Hz, $J_{1,11a}$ = 3 Hz, $J_{1,11b}$ = 3 Hz), 3.62 (s, 3 H), 6.24 (t, 1 H, $J_{10,1}$ = 6 Hz, $J_{10,9}$ = 6 Hz), 6.55 (t, 1 H, $J_{9,10}$ = 6 Hz, $J_{9,8}$ = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 16.6, 28.8, 29.2, 29.8, 32.2, 43.3, 48.8, 52.4, 56.5, 128.6, 137.3, 171.8, 209.6; IR (film) 2940 1720, 1430, 1230 cm^{-1}; chemical-ionization mass spectrum, m/e 221 (M^+ + 1).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.91; H, 7.25.

Dehydrobromination and Intramolecular Diels–Alder Reactions of 2-Alkenyl-6-bromo-2-(methoxycarbonyl)-3-cyclohexen-1-one, Dimethyl Ketal Derivatives. 3-(Methoxycarbonyl)tricyclo[3.3.1.0^{3,6}]non-7-en-2-one, Dimethyl Ketal (4a). A solution of bromoketal **2a** (10.21 g, 32.0 mmol) and 1,5-diazabicyclo[4.3.0]non-5-ene (9.9 mL, 80 mmol) in dry toluene (35 mL) was heated at reflux for 42 h. After cooling, the reaction mixture was poured into ether (75 mL) and was washed with water (2 × 50 mL) and brine (1 × 50 mL). After drying ($MgSO_4$), the solution was concentrated; Kugelrohr distillation [80–85 °C (0.10 mmHg)] gave **4a** as a colorless solid (4.75 g, 62%): recrystallization from pentane (3.60 g, 47%, mp 78–79.5 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.02–1.13 (m, 1 H), 1.84 (d, 1 H, J = 9.4 Hz), 1.93 (dd, 1 H, J = 12 Hz, J = 4 Hz), 2.05 (m, 1 H), 2.15–2.25 (m, 1 H), 3.02–3.10 (m, 1 H), 3.18 (s, 3 H), 3.25–3.36 (m, 1 H) 3.29 (s, 3 H), 3.66 (s, 3 H), 6.15–6.23 (m, 1 H), 6.51–6.60 (m, 1 H); IR ($CHCl_3$) 2820–3080, 1720, 1435, 1280 cm^{-1}; chemical-ionization mass spectrum, m/e (relative intensity) 239 (M^+ + 1, 7), 207 (100).

Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.47; H, 7.52.

5-Bromo-3-(methoxycarbonyl)tricyclo[3.3.1.0^{3,6}]non-7-en-2-one, Dimethyl Ketal (4c). Prepared in 69% yield as described for **4a** (refluxing xylenes, 24 h); flash chromatography (silica gel, 7:1 hexane–ethyl acetate) gave **4c** as an oil: ^{1}H NMR ($CDCl_3$) δ 1.56 (br d, 1 H, J = 12 Hz), 2.50 (dd, 1 H, J = 12 Hz, J = 4 Hz), 2.60 (d, 1 H, J = 10 Hz), 2.73 (dd, 1 H, J = 10 Hz, J = 2 Hz), 2.98 (br s, 1 H), 3.15 (s, 3 H), 3.28 (s, 3 H), 3.70 (m with overlapping s at 3.68, 7 h), 6.17 (t, 1 H, J = 6 Hz), 6.66 (t, 1 H, J = 6 Hz); IR (film) 2950, 1730, 1430 cm^{-1}; chemical-ionization mass spectrum, m/e 317, 319 (M^+ + 1).

3-(Methoxycarbonyl)tricyclo[4.3.1.0^{3,7}]dec-8-en-2-one, Dimethyl Ketal (5a). Prepared in 83% yield as described for **4a**: Kugelrohr distillation [~85 °C (09.15 mmHg)]; oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.29–2.00 (m, 6 H), 2.16–2.34 (m, 1 H), 2.64–2.81 (m, 2 H), 3.18 (s, 3 H), 3.41 (s, 3 H), 3.64 (s, 3 H), 6.24 (m, 1 H), 6.35 (m, 1 H); IR ($CDCl_3$) 3100–2800, 1720, 1430, 1300, 1280, 1220 (br) cm^{-1}; chemical-ionization mass spectrum, m/e (relative intensity) 253 (M^+ + 1, 8), 251 (6), 249 (2), 221 (100).

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.53; H, 7.91.

3,11-Bis(methoxycarbonyl)-5,6-benzotricyclo[5.3.1.0^{3,8}]-undec-9-en-2-one, Diemthyl Ketal (7a). Prepared in 54% yield as described for **4a**, recrystallized from methanol: mp 173–175 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.66–2.74 (m, 1 H), 2.78–2.86 (m, 1 H), 3.01 (d, 1 H, J = 19 Hz), 3.18–3.31 (m, 2 H), 3.26 (s, 3 H), 3.47 (s, 3 H), 3.59 (d, 1 H, J = 19 Hz), 3.70 (s, 6 H), 6.06–6.17 (m, 1 H), 6.73–6.86 (m, 1 H), 7.11–7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 33.8, 38.9, 39.3, 40.2, 48.2, 50.9, 51.4, 51.8, 52.0, 55.7, 106.2, 124.6, 125.9, 126.5, 127.7, 127.9, 133.5, 137.6, 139.9, 174.6, 174.7; IR ($CHCl_3$) 3100–2800, 1730, 1710, 1480, 1430, 1270, 1210 (br) cm^{-1}; mass spectrum, m/e (relative intensity) 372 (21, M^+), 340 (54), 313 (26), 276 (24), 249 (26), 205 (100), 185 (89), 178 (54), 167 (56), 165 (47), 152 (22), 115 (36), 75 (27), 59 (31).

Anal. Calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.56; H, 6.43.

3-(Methoxycarbonyl)tricyclo[3.3.1.0^{3,6}]non-7-en-2-one (4b). A solution of ketal **4a** (1.17 g, 4.91 mmol) and *p*-toluenesulfonic

acid (0.960 g, 5.05 mmol) in benzene (60 mL) was heated at reflux for 1 h. After cooling, the solution was diluted with ether (60 mL) and washed with saturated $NaHCO_3$ solution (2 × 50 mL) and brine (1 × 50 mL). After drying ($MgSO_4$), the solution was concentrated to give **4b** (0.921 g, 98%) as a colorless solid; mp 64–66 °C; recrystallization from ethyl acetate–hexane (0.808 g, 86%, mp 66–67 °C): ^1H NMR ($CDCl_3$, 200 MHz) δ 1.39–1.50 (m, 1 H, $J_{9a,9b}$ = 12 Hz, $J_{9a,5}$ = 6 Hz, $J_{9a,1}$ = 0.5 Hz, $J_{9a,4b}$ = 3 Hz), 1.75 (d, 1 H, $J_{4a,4b}$ = 10 Hz), 2.11 (dd, 1 H, $J_{9b,9a}$ = 12 Hz, $J_{9b,1}$ = 4 Hz), 2.55 (q, 1 H, $J_{5,6}$ = 6 Hz, $J_{5,9a}$ = 6 Hz, $J_{5,4b}$ = 6 Hz), 2.67–2.77 (m, 1 H, $J_{4b,4a}$ = 10 Hz, $J_{4b,9a}$ = 3 Hz, $J_{4b,5}$ = 6 Hz), 3.48 (m, 1 H, $J_{6,7}$ = 6 Hz, $J_{6,8}$ = 1 Hz, $J_{6,5}$ = 6 Hz), 3.58 (m, 1 H, $J_{1,8}$ = 6 Hz, $J_{1,9b}$ = 4 Hz, $Jj_{1,9a}$ = 0.5 Hz), 3.70 (s, 3 H), 6.27–6.34 (t, 1 H, $J_{7,8}$ = 6 Hz, $J_{7,6}$ = 6 Hz), 6.55–6.64 (dt, 1 H, $J_{8,7}$ = 6 Hz, $J_{8,1}$ = 6 Hz, $J_{8,6}$ = 1 Hz); IR (KBr) 2990, 2930, 1710 (br), 1610, 1440 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 29.65, 32.86, 36.30, 43.89, 49.18, 52.10, 56.70, 131.54, 135.52, 170.02, 206.85; UV (methanol) λ_{max} (ϵ) 291 (187), 205 nm (3440).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.81; H, 6.28.

5-Bromo-3-(methoxycarbonyl)tricyclo[3.3.1.0^{3,6}]non-7-en-2-one (4d). Prepared in 94% yield as described for **4b**; Kugelrohr distillation [90 °C (2 mmHg)] and crystallization: mp 114–116 °C; ^1H NMR ($CDCl_3$) δ 1.89 (dd, 1 H, $J_{9a,4b}$ = 3 Hz, $J_{9a,9b}$ = 12 Hz), 2.53 (d, 1 H, $J_{4a,4b}$ = 10 Hz), 2.64 (dd, 1 H, $J_{9b,9a}$ = 12 Hz, $J_{9b,1}$ = 4 Hz), 3.19 (dd, 1 H, $J_{4b,4a}$ = 10 Hz, $J_{4b,9a}$ = 3 Hz), 3.38 (dd, 1 H, $J_{1,8}$ = 6 Hz, $J_{1,9b}$ = 4 Hz), 3.72 (s, 3 H), 3.86 (dd, 1 H, $J_{6,7}$ = 6 Hz, $J_{6,8}$ = 1 Hz), 6.39 (t, 1 H, $J_{7,8}$ = 6 Hz, $J_{7,6}$ = 6 Hz), 6.72 (dt, 1 H, $J_{8,7}$ = 6 Hz, $J_{8,1}$ = 6 Hz, $J_{8,6}$ = 1 Hz); IR (KBr) 2940, 1730 (br), 1430 cm^{-1}; chemical-ionization mass spectrum, m/e 271, 273 (M^+ + 1).

Anal. Calcd for $C_{11}H_{11}O_3Br$: C, 48.73; H, 4.09. Found: C, 48.91; H, 4.26.

3-(Methoxycarbonyl)tricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (5b). Prepared in 90% yield as described for **4b**: Kugelrohr distillation [~85 °C (0.3 mm Hg)]; oil; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.43 (m, 1 H, $J_{10b,10a}$ = 12 Hz, $J_{10b,1}$ = 3 Hz, $J_{10b,6}$ = 2 Hz), 1.62 (m, 1 H), 1.73 (m, 1 H, $J_{10a,10b}$ = 12 Hz, $J_{10a,6}$ = 10 Hz, $J_{10a,1}$ = 3 Hz), 1.9–2.1 (m, 2 H), 2.28 (m, 1 H), 2.50 (m, 1 H), 3.12 (m, 1 H, $J_{7,8}$ = 6 Hz, $J_{7,6}$ = 2 Hz, $J_{7,9}$ = 1 Hz), 3.20 (m, 1 H, $J_{1,10a}$ = 3 Hz, $J_{1,10b}$ = 3 Hz, $J_{1,9}$ = 6 Hz), 3.68 (s, 3 H), 6.32 (dt, 1 H, $J_{9,1}$ = 6 Hz, $J_{9,8}$ = 6 Hz, $J_{9,7}$ = 1 Hz), 6.41 (t, 1 H, $J_{8,7}$ = 6 Hz, $J_{8,9}$ = 6 Hz); ^{13}C NMR δ 31.3, 31.4, 32.7, 34.1, 47.4, 48.2, 52.4, 60.9, 128.5, 132.6, 171.0, 208.5; IR ($CHCl_3$) 2950, 1720 (br), 1430, 1275, 1240 (br) cm^{-1}; chemical-ionization mass spectrum, m/e (relative intensity) 207 (M^+ + 1, 93), 193 (2.1), 177 (2), 176 (11), 175 (100); UV (methanol) λ_{max} (ϵ) 205 (3710), 294 nm (214).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.73; H, 6.86.

3,11-Bis(methoxycarbonyl)-5,6-benzotricyclo[5.3.1.0^{3,8}]-undec-9-en-2-one (7b). Prepared in 100% yield as described for **4b**: flash chromatography (silica gel, 7:1 hexane–ethyl acetate); oil; ^1H NMR ($CDCl_3$) δ 2.66 (dd, 1 H, $J_{11,7}$ = 4 Hz, $J_{11,1}$ = 2 Hz), 3.26 (d, 1 H, J = 16 Hz), 3.40 (dd, 1 H, $J_{8,9}$ = 6 Hz, $J_{8,7}$ = 2 Hz), 3.56 (d, 1 H, J= 16 Hz), 3.66 (m, 2 H), 3.74 (s, 3 H), 3.78 (s, 3 H), 6.34 (t, 1 H, $J_{10,1}$ = 6 Hz, $J_{10,9}$ = 6 Hz), 6.74 (t, 1 H, $J_{9,8}$ = 6 Hz, $J_{9,10}$ = 6 Hz), 7.1–7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 29.8, 37.6, 39.6, 49.4, 52.6, 52.9, 53.6, 54.9, 127.0, 127.2, 127.3, 128.9, 129.0, 130.7, 136.7, 138.4, 171.1, 172.2, 207.3; IR (film) 2970, 1720, 1430 cm^{-1}; chemical-ionization mass spectrum, m/e 327 (M^+ + 1).

Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 69.89; H, 5.50.

4-(Methoxycarbonyl)tetracyclo[4.2.1.0^{2,8}.0^{4,9}]nonan-3-one (8a). A solution of **4b** (93.8 mg, 0.488 mmol) in acetophenone (10 mL) was irradiated through Pyrex glassware for 48 h. Acetophenone was removed by evaporation at reduced pressure; Kugelrohr distillation [62–64 °C (0.40 mmHg)] gave **8a** (61.7 mg, 66%) as a colorless oil, crystallization from ethyl acetate–pentane (38.5 mg, 41%, mp 93–98 °C). The analytical sample was obtained by recrystallization from ethyl acetate–pentane: mp 106–108 °C; ^1H NMR ($CDCl_3$, 200 MHz) 1.40–1.46 (m, 1 H), 1.96–2.05 (m, 1 H), 2.26–2.36 (m, 2 H), 2.45–2.67 (m, 2 H), 2.68–2.78 (m, 1 H), 2.89–3.03 (m, 1 H), 3.52–3.62 (m, 1 H), 3.74 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 29.33, 35.88, 36.60, 37.64, 38.75, 41.02, 51.04, 52.33, 60.76, 170.46, 212.56; IR ($CHCl_3$) 3160–2820, 1735, 1710, 1500, 1420, 1205 (br) cm^{-1}; mass spectrum m/e (relative intensity) 192 (M^+, 13), 161 (17), 160 (22), 132 (32), 131 (23), 114 (52), 105 (87), 104 (32), 103 (28), 91 (20), 86 (59), 79 (100), 78 (46), 77 (74), 68 (17), 65 (11).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.82; H, 6.14.

6-Bromo-4-(methoxycarbonyl)tetracyclo[4.2.1.0^{2,8}.0^{4,9}]nonan-3-one (8b). A solution of **4d** (0.096 g, 0.354 mmol) in acetone (10 mL) and acetophenone (0.083 mL) was irradiated through Pyrex glassware for 48 h. The reaction mixture was concentrated and chromatographed (alumina, 2:1 hexane–ethyl acetate) to give **8b** (83 mg, 86% yield) as a colorless crystalline solid. The analytical sample was obtained by recrystallization from ether: mp 124.5–125.0 °C; ^1H NMR ($CDCl_3$) δ 2.3 (m, 3 H), 2.74 (d, 1 H, J = 16 Hz), 2.91 (dd, 1 H, J = 6 Hz, J = 6 Hz), 2.99 (d, 1 H, J = 12 Hz), 3.12 (dd, 1 H, J = 16 Hz, J = 4 Hz), 3.76 (s, 3 H), 3.82 (d, 1 H, J = 6 Hz); IR (KBr) 2920, 1730, 1440 cm^{-1}; chemical-ionization mass spectrum, m/e 271, 273 (M^+ + 1).

Anal. Calcd for $C_{11}H_{11}O_3Br$: C, 48.73; H, 4.09. Found: C, 48.56; H, 4.15.

4-(Methoxycarbonyl)tetracyclo[5.2.1.0^{2,9}.0^{4,10}]decan-3-one (9a). A solution of **5b** (2.94 g, 14.3 mmol) in acetone (300 mL) was degassed with argon prior to irradiation through quartz glassware for 3 h. The solvent was removed under reduced pressure to give **9a** (2.62 g, 89%) as a yellow oil. The analytical sample was obtained by Kugelrohr distillation [75 °C (0.33 mmHg), 2.21 g, 75%]: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.10–2.44 (m, 8 H), 2.78 (dd, 1 H, J = 11 Hz, J = 5 Hz), 2.94–3.12 (m, 1 H), 3.29 (dd, 1 H, J = 6 Hz, J = 6 Hz), 3.74 (s, 3 H); ^{13}C NMR δ 29.6, 30.5, 32.1, 33.8, 35.1, 40.6, 52.4, 52.5, 57.7, 70.0, 171.9, 213.0; iR ($CHCl_3$) 3050–2850, 1735, 1715, 1310, 1205 cm^{-1}; chemical-ionization mass spectrum, m/e (relative intensity) 207 (M^+ + 1, 100).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.62; H, 7.06.

4-(Methoxycarbonyl)tetracyclo[6.2.1.0^{2,10}.0^{4,11}]undecan-3-one (10). Prepared from **6b** in 89% yield by 30 h of irradiation as described for **8b**: flash chromatography (alumina, 3:1 hexane–ethyl acetate); oil; ^1H NMR ($CDCl_3$) δ 1.2–1.6 (m, 6 H), 1.9–2.0 (m, 3 H), 2.26 (br d, 1 H, J = 12 Hz), 2.70 (m, 2 H), 3.01 (t, 1 H, J = 6 Hz), 3.70 (s, 3 H); IR (film) 2930, 1720 (br), 1430 cm^{-1}; chemical-ionization mass spectrum, m/e 221 (M^+ + 1).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.83; H, 7.31.

4,9-Bis(methoxycarbonyl)-6,7-benzotetracyclo-[6.2.1.0^{2,10}.0^{4,11}]undecan-3-one (11). Prepared from **7b** in 84% yield by 50 h of irradiation as described for **8b**: flash chromatography (alumina, 7:1 hexane–ethyl acetate); oil; ^1H NMR ($CDCl_3$), δ 2.30 (m, 2 H), 2.56 (d, 1 H, J = 8 Hz), 3.14 (ddd, 1 H, J = 8 Hz, J = 8 Hz, J = 2 Hz), 3.38 (m, 3 H), 3.74 (s, 3 H), 3.78 (s, 3 H), 4.04 (dd, 1 H, J = 8 Hz, J = 8 Hz), 7.0–7.2 (m, 4 H); IR (film) 2970, 1720 (br), 1480, 1250 (br) cm^{-1}; chemical-ionization mass spectrum, m/e 327 (M^+ + 1).

Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found, 69.96; H, 5.24.

3-Oxotetracyclo[5.2.1^{2,9}.0^{4,10}]decane-4-carboxylic Acid (9b). Potassium hydroxide (0.6632 g, 11.8 mmol) was added to a solution of **9a** (1.48 g, 7.18 mmol) in methanol (7 mL). After 34 h at room temperature, the solvent was removed under reduced pressure, and the residue was partitioned between ether (25 mL) and 3 N NaOH (35 mL). The organic solution was extracted with 3 N NaOH (25 mL). The combined aqueous solution was acidified with cold concentrated HCl and extracted with ether (3 × 40 mL). The combined organic solution was washed with brine (25 mL), dried ($MgSO_4$), and concentrated to give **9b** (1.21 g, 88%) as a yellow solid. This material was sufficiently pure for the next operation; the analytical sample was prepared by recrystallization from ethyl acetate–hexane: mp 134–135 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.34–1.45 (m, 1 H), 1.62–1.76 (m, 2 H), 1.99–2.42 (m, 5 H), 2.80–2.86 (m, 1 H), 2.97–3.13 (m, 1 H), 3.37–3.42 (m, 1 H), 9.00 (br s, 1 H); IR ($CHCl_3$) 3300–2800, 1725, 1700, 1510, 1420 cm^{-1}; mass spectrum, m/e (relative intensity) 192 (M^+, 19), 191 (26), 174 (28), 148 (27), 146 (26), 119 (39), 105 (27), 104 (48), 91 (100).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.88; H, 6.22.

Tetracyclo[5.2.1^{2,9}.0^{4,10}]decan-3-one (9c). A solution of keto acid **9b** (0.380 g, 1.97 mmol) in dry toluene (5 mL) was heated at reflux for 5 h and evaporated to give **9c** (0.289 g, 99%) as a light yellow oil. Kugelrohr distillation [67–70 °C (0.20 mmHg)]

gave **9c** (0.277 g, 95%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.22–1.33 (m, 1 H), 1.45–1.71 (m, 2 H), 1.81–1.99 (m, 4 H), 2.18–2.34 (m, 1 H), 2.58–2.75 (m, 2 H), 2.86–3.12 (m, 2 H); ^{13}C NMR ($CDCl_3$) 25.21, 30.86, 32.26, 33.19, 33.39, 39.91, 51.22, 52.25, 54.72, 219.84; mass spectrum, *m/e* (relative intensity) 148 (M^+, 22), 120 (22), 105 (22), 104 (60), 92 (71), 91 (100).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.12; H, 8.07.

Acknowledgment. This work was supported by the National Institutes of Health (GM 26568). NMR spectra were recorded on a Varian XL-200 instrument purchased with funds provided, in part, by a National Science Foundation Department Instrumentation grant. Mass spectra were obtained on a Hewlett-Packard 5987 GC–MS system purchased with funds provided by the National Science Foundation and Grant 1 510 RR01677 awarded by the National Institutes of Health-BRS Shared Instrument Program.

Registry No. **1a**, 97253-90-2; **1b**, 97253-91-3; **1c**, 91029-50-4; **1d**, 91036-26-9; **1e**, 97253-92-4; *cis*-**2a**, 97254-14-3; *trans*-**2a**, 97253-93-5; *cis*-**2b**, 97254-15-4; *trans*-**2b**, 97253-94-6; **2c**, 97253-95-7; *cts*-**2d**, 97254-16-5; *trans*-**2d**, 97253-96-8; *cis*-**2e**, 97254-17-6; *trans*-**2e**, 97253-97-9; **3a**, 97253-98-0; **3d**, 97253-99-1; **3f**, 97254-00-7; **4a**, 97254-02-9; **4b**, 97277-65-1; **4c**, 97254-03-0; **4d**, 97254-05-2; **5a**, 97254-04-1; **5b**, 94225-53-3; **6b**, 97254-01-8; **7a**, 97277-64-0; **7b**, 97254-06-3; **8a**, 97254-07-4; **8b**, 97254-08-5; **9a**, 97254-09-6; **9b**, 97254-12-1; **9c**, 97254-13-2; **10**, 97254-10-9; **11**, 97254-11-0; 2-MeC_6H_4CH=$CHCO_2Me$, 70625-38-6; 2-$(BrCH_2)C_6H_4CH$=$CHCO_2Me$, 70625-62-6; 2-$MeOC_6H_4CO_2Me$, 606-45-1; $BrCH_2C$-H=CH_2, 106-95-6; CH_2=$C(Br)CH_2Br$, 513-31-5; $I(CH_2)_3CH$=C-H_2, 7766-48-5.

Synthesis of Unsymmetrical Biphenyls by Reaction of Nitroarenes with Phenols

G. Patrick Stahly

Research and Development Department, Ethyl Corporation, Baton Rouge, Louisiana 70821

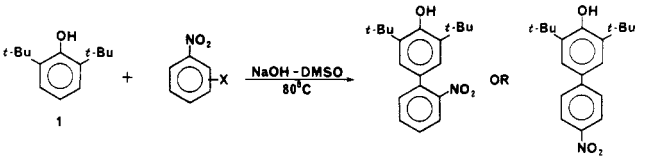
Received December 11, 1984

The anion of 2,6-di-*tert*-butylphenol (**1**) behaves as a carbon nucleophile toward nitroarenes bearing leaving groups ortho or para to the nitro group, affording biphenyls by conventional S_NAr processes. However, **1** reacts with *m*-dinitrobenzene (**2**), *o*-nitrobenzonitrile, or *m*-nitrobenzonitrile to give biphenyls by formal displacements of nitroarene hydrogen atoms. This oxidative coupling process also occurs between unhindered phenols, even phenol itself, and compound **2**. Mechanistic features of the oxidative coupling reaction are discussed.

A variety of methods exist for the preparation of biphenyls.[1] In some cases unsymmetrical biphenyls have been synthesized by nucleophilic aromatic substitution reactions involving electron-rich arenes and halonitroarenes.[2] There are also reports of aryl–aryl bond formation by formal nucleophilic aromatic substitution for hydrogen.[3]

Reactions in which an aromatic hydrogen atom is replaced are well documented for nitroarenes and a variety of nucleophiles.[4] They occur via intermediate Meisenheimer complexes which decompose in various ways. Nucleophiles bearing leaving groups at the nucleophilic center give rise to complexes which undergo subsequent elimination.[5] With simpler nucleophiles oxidation of the intermediate complex may occur spontaneously[6] or by addition of an oxidant.[7] Presumably the nitroarene itself functions as the oxidant in the former cases, usually af-

Table I. Nucleophilic Aromatic Substitution Reactions



X	time, h[a]	product	yield, %[b]
2-F	18	3	97
2-Cl	24	3	71
2-Br	4	3	79
2-I	2	3	63[c]
2-NO_2	17	3	64
2-SO_2Ph	20	3	68
3-Cl		no reaction	
3-SO_2Ph		complex product mixture	
4-NO_2	3	4	77
4-SO_2Ph	30	4	69

[a] Reaction times not optimized. [b] Based on weight of crude material from PTLC. [c] A mixture of **3** and unreacted *o*-iodobenzene (22%) was recovered.

(1) (a) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327. (b) Miller, R. B.; Dugar, S. *Organometallics* **1984**, *3*, 1261.

(2) (a) Wright, J.; Jorgensen, E. C. *J. Org. Chem.* **1968**, *33*, 1245. (b) Moore, G. G. I. U.S. Patent 4 172 151, 1979. (c) Effenberger, F.; Agster, W.; Fischer, P.; Jogun, K. H.; Stefowski, E. D.; Kollmannsberger-von Nell, G. *J. Org. Chem.* **1983**, *48*, 4649.

(3) (a) Björklund, C.; Nilsson, M.; Wennerström, O., *Acta Chem. Scand.* **1970**, *24*, 3599. (b) Wennerström, O., *Acta Chem. Scand.* **1971**, *25*, 2341. (c) Moberg, C.; Wennerström, O. *Acta Chem. Scand.* **1971**, *25*, 2871. (d) Russkikh, S. A.; Konstantinova, A. V.; Fokin, E. P. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk* **1983**, *137*. (e) Halle, J. C.; Pouet, M. J.; Simonnin, M. P.; Terrier, F. *Tetrahedron Lett.* **1985**, *26*, 1307.

(4) (a) deBoer, Th. J.; Dirkx, I. P. In "Chemistry of the Nitro and Nitroso Groups"; Feuer, H., Ed.; Interscience Pub.: New York, 1969; Part 1, p 487. (b) Chupakhin, O. N.; Postovskii, I. Ya. *Usp. Khim.* **1976**, *45*, 908.

(5) (a) Makosza, M.; Goliński, J.; Baran, J. *J. Org. Chem.* **1984**, *49*, 1488 and references cited therein. (b) Stahly, G. P.; Stahly, B. C.; Lilje, K. C., *J. Org. Chem.* **1984**, *49*, 578.

(6) (a) Neresheimer, H.; Ruppel, W., U.S. Patent 2 080 057, 1937. (b) King, T. J.; Newall, C. E. *J. Chem. Soc.* **1962**, 367. (c) Foster, R.; Mackie, R. K. *Tetrahedron* **1962**, *18*, 1131. (d) Landolt, R. G.; Snyder, H. R. *J. Org. Chem.* **1968**, *33*, 403. (e) Makosza, M.; Jagusztyn-Grochowska, M.; Ludwikow, M.; Jawdosiuk, M. *Tetrahedron* **1974**, *30*, 3723. (f) Onys'ko, P. P.; Gololobov, Yu. G. *Zh. Obshch. Khim.* **1979**, *49*, 39. (g) Konieczny, M. T.; Ledochowski, A. *Pol. J. Chem.* **1980**, *54*, 2233. (h) Hamana, M.; Iwasaki, G.; Saeki, S. *Heterocycles* **1982**, *17*, 177. (i) Iwasaki, G.; Hamana, M.; Saeki, S. *ibid* **1982**, *19*, 163.

0022-3263/85/1950-3091$01.50/0