Thermal Ring Annulation of α-Vinylcinnamate Methyl Esters. A Method for the Generation of 3,4-Dihydro-2-naphthoate and 2-Naphthoate Methyl Esters

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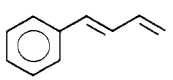
Ring annulation of methyl 2-benzylidene-3-buten-1-oates (methyl α-vinylcinnamates) to generate a series of methyl 3,4-dihydro-2-naphthoates has been accomplished by a thermal reaction. The thermolysis is performed either in the vapor phase at 425 °C or by heating the compound in a high-boiling solvent for an extended period of time. Regiochemistry is entirely predictible with para- and ortho-substituted methyl α-vinylcinnamates generating exclusively 6-substituted and 8-substituted 3,4-dihydro-2-naphthoates, respectively. Meta-substituted α-vinylcinnamates generate a mixture of 5- and 7-substituted 3,4-dihydro-2-naphthoates. 2-Naphthoate methyl esters can also be obtained by including a palladium on carbon catalyst in the liquid-phase version of this thermolysis.

Introduction

As part of our research program, we required laboratory-scale quantities of a series of 6-substituted 3,4-dihydro-2-naphthoate methyl esters including **1b–e**. Two multistep processes for the generation of the 3,4-dihydro-2-naphthoate methyl esters **1a** and **1e** have been published.[1] However, both methods begin with the corresponding α-tetralones, which are generally obtained by a sequential Friedel–Crafts alkylation–acylation with γ-butyrolactone using benzene in the case of **1a** or anisole in the case of **1e**. This Friedel–Crafts process would yield mixtures and undesirable isomers with most other substituted aromatics. Therefore, these approaches did not represent general methods for the regiospecific generation of the desired 6-substituted 3,4-dihydro-2-naphthoates. To our knowledge, there are no other generally applicable approaches to these compounds. Therefore, we sought to find a novel approach to these systems that would be applicable to a wide variety of substituted 3,4-dihydro-2-naphthoates.

As shown in Scheme I, a potentially general approach to the desired dihydronaphthoates **1a–e** would be a thermal ring annulation of para-substituted methyl 2-benzylidene-3-buten-1-oates (**2a–e**), more trivially referred to as α-vinylcinnamates. Fortunately, the required starting α-vinylcinnamates are readily available in stereochemically pure form by using the precedented Perkin condensation of crotonic anhydride with benzaldehydes in the presence of triethylamine[2,3] and subsequent esterification with trimethylorthoformate–methanol.[3]

We were also encouraged by some reports of the thermal cyclization of 1-aryl-1,3-butadienes (**4**) to form simple 1,2-dihydronaphthalenes,[4,5] which are analogous to our desired reaction. However, with the exception of an example containing a methoxy group on the aryl ring, these compounds were devoid of any significant functionality. The effect functionality, especially the olefinic carboxylate, might have on the reaction was unclear. Therefore, we needed to demonstrate that the thermal ring annulation could be extended to include α-vinylcinnamates containing a variety of ring substituents and still yield isomerically pure 3,4-dihydro-2-naphthoates without any accompanying skeletal or functional rearrangement other than the desired ring closure.



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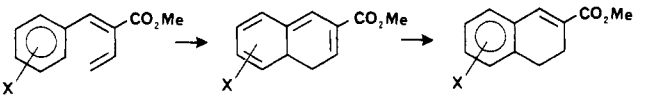
Scheme I. Proposed Route for the Generation of Methyl 3,4-Dihydro-2-naphthoates from Methyl α-Vinylcinnamates



2a, X = H
b, X = *p*-Me
c, X = *p*-Cl
d, X = *p*-CO_2Me
e, X = *p*-OMe
f, X = *o*-OMe
g, X = *m*-OMe

3

1a, X = H
b, X = 6-Me
c, X = 6-Cl
d, X = 6-CO_2Me
e, X = 6-OMe
f, X = 8-OMe
g, X = 5-OMe
h, X = 7-OMe

Results and Discussion

This investigation was initiated by using the literature procedure[2,3] to generate the α-vinylcinnamates **2a–g**, which represent a range of electronic properties and substitution patterns. We then proceeded to demonstrate the feasibility of thermally ring closing these materials to generate the desired 3,4-dihydro-2-naphthanoate methyl esters.

Our first attempt at a thermal ring closure was performed in the liquid phase. A decalin solution of methyl *p*-methyl-α-vinylcinnamate (**2b**) was heated at reflux for 40 h to generate methyl 6-methyl-3,4-dihydro-2-naphthanoate (**1b**). The yield was mediocre (24%), and the major byproducts, as ascertained by GC–MS, were dimeric and consistent with the several available competitive Diels–Alder reaction pathways. (Note that the starting diene and the product dihydronaphthalene are both viable diene acceptors.)

A reasonable method of minimizing the undesirable bimolecular reaction pathways (the Diels–Alder reactions) and favoring the desired unimolecular thermal ring closure was to shift to the vapor phase. The advantage of this approach over the liquid phase can be demonstrated again by using **2b**. This approach gave the desired 3,4-dihydro-2-naphthoate **1b** in 92% yield after the material had

(1) (a) Vebrel, J.; Carrie, R. *Bull. Chim. Soc. Fr., Part II* **1982**, 116. (b) Myrboh, B.; Ila, H.; Junjappa, H. *J. Org. Chem.* **1983**, *48*, 5327. (c) Also see: Holmes, H. L.; Trevor, L. W. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 300.
(2) Kuhn, R.; Ishikawa, S. *Chem. Ber.* **1931**, *64*, 2347.
(3) Kresze, G.; Mavromatis, A. *Tetrahedron* **1978**, *34*, 697.
(4) (a) Volkovitch, P. B.; Conger, J. L.; Castiello, F. A.; Brodie, T. D.; Weber, W. P. *J. Am. Chem. Soc.* **1975**, *97*, 901. (b) Rosen, B. I.; Weber, W. P. *Tetrahedron Lett.* **1977**, 151. (c) Rosen, B. I.; Weber, W. P. *J. Org. Chem.* **1977**, *42*, 47.
(5) Radcliffe, M. M.; Weber, W. P. *J. Org. Chem.* **1977**, *42*, 297.

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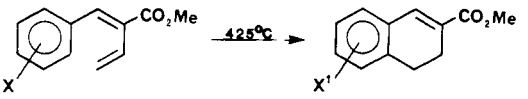
Table I. Vapor-Phase Pyrolysis of α-Vinylcinnamate Esters to 3,4-Dihydro-2-Naphthoate Esters

entry	substrate	substrate substitution	product	product substitution	yield,[a] %
1	**2a**	H	**1a**	H	92
2	**2b**	4-Me	**1b**	6-Me	92
3	**2c**	4-Cl	**1c**	6-Cl	80
4	**2d**	4-CO_2Me	**1d**	6-CO_2Me	56
5	**2e**	4-OMe	**1e**	6-OMe	61
6	**2f**	2-OMe	**1f**	8-OMe	92
7	**2g**	3-OMe	**1g** + **1h**	5-OMe + 7-OMe	61 36

[a] All yields are for isolated materials of >97% purity by GC analysis.

been passed through a quartz-filled hot tube maintained at 425 °C. Most of the yield loss was mechanical, and



there was little or no charring apparent after the reaction is complete. A significant advantage to this approach is that the material obtained directly from the pyrolysis is relatively pure, with the only detectable impurity being the corresponding naphthalene, and was sufficiently pure to be used in most applications. (The naphthalene was about 1–2% of the final product based on GC analysis.)

The reaction appears to be generally applicable and was used to generate a range of functionalized 6-substituted 3,4-dihydro-2-naphthoates in generally good to excellent yields. (The results are summarized in Table I.) In all the cases we examined, there was no detectable migration or loss of the carboxylate or other functional groups originally present in the cinnamate, and, within our analytical limits, the product was free of other olefinic isomers.

The conditions for effecting the ring closure of the α-vinylcinnamates were generally milder (temperatures between 10–60 °C lower), and the annulation generally proceeded in higher yields than is reported for the thermal cyclization of the very simple 1-aryl dienes in the literature.[4,5] In addition, the reaction was complete in a single pass through the tube, whereas the product was generally separated from starting material in the earlier reports. Therefore, it would appear that our initial concerns regarding the effect of the olefinic carboxylate were unfounded, and instead, the carboxylate may be helpful in the ring closure.

As we anticipated, another feature of this reaction is the ability to direct the ultimate substitution pattern of the product dihydronaphthalene. With para-substituted α-vinylcinnamates, the ring closure yielded exclusively 6-substituted 3,4-dihydro-2-naphthanoates (see entries 1–5 in Table I), while an ortho-substituted α-vinylcinnamate yielded only the 8-substituted 3,4-dihydro-2-naphthanoates (see entry 6 in Table I). Meta substitution led to a mixture of 5- and 7-substituted 3,4-dihydro-1-naphthoates (see entry 7 in Table I).

The interesting feature of the reaction using meta-substituted α-vinylcinnamates is that the 5-substituted isomer predominated. This indicates that the reaction is not sterically controlled as this would have led to a mixture in which the 7-substituted isomer predominated, but instead seems to be electronically controlled. (A similar phenomena was noted by in the earlier literature in which the cyclization of 1-(*m*-methoxyphenyl)-1,3-butadiene was thermally cyclized.[5]) Although this process allows access to these unique compounds, the attainment of a mixture of isomers with meta-substituted systems represents a limitation in the application of this process.

In the course of examining the liquid-phase version of this reaction, we had also found that this process has potential for the direct generation of 2-naphthoates. We were trying to discern whether the proposed Diels–Alder reaction between our starting material **2b** and our product **1b** could be interdicted by dehydrogenation. When the liquid-phase version of the cyclization of **2b** was repeated in the presence of 5% Pd on carbon, methyl 6-methyl-2-naphthoate was obtained in 49% yield. This method could be extended to the generation of the industrially desirable polyester monomer dimethyl 2,6-naphthandioate in 55% yield, by heating the α-vinylcinnamate **2d** at reflux for 5 h in 1-methylnaphthalene (bp 241 °C) in the presence of 5% Pd on carbon.

Summary

Several important advances in the generation of naphthanoid systems are entailed in this report. An excellent method for the ring annulation of α-vinylcinnamate esters to generate 3,4-dihydro-2-naphthoate esters with well-defined substitution patterns has been demonstrated, which entails a thermal ring closure in the vapor phase. The process is especially suited to the generation of 6- and 8-substituted 3,4-dihydro-2-naphthoates, which can be generated from para- and ortho-substituted α-vinylcinnamates, respectively. A mixture of 5- and 7-substituted 3,4-dihydro-2-naphthoates are generated from the meta-substituted α-vinylcinnamates. The ring closure can be extended to permit the direct conversion of α-vinylcinnamates to generate 2-naphthanoates without isolation of the dihydronaphthoate intermediate by including a dehydrogenation catalyst in the liquid-phase version of this process. Other applications of this and related technologies are under active investigation in these laboratories.

Experimental Section

NMR spectra were recorded on a JEOL JMN-GX 400 FT NMR spectrometer, infrared spectra were recorded on a Nicolet 5DX infrared spectrometer, and mass spectra were recorded on a VG Micromass ZAB-2F mass spectrometer. Melting points were recorded on a Fischer-Johns hot stage melting point apparatus and are uncorrected. Elemental analyses were performed in our analytical laboratories. All the methyl 2-benzylidene-3-buten-2-oates (**2a–g**) and their acid precursors were synthesized by the general literature procedures or minor modifications thereof.[2,3] Several of the compounds used do not appear in these references, and their preparation and properties appear below. All necessary chemicals are available from Aldrich Chemical Co., Milwaukee, WI, with the exception of methyl 4-formylbenzoate, which was obtained from Fluka Chemical Co., Hauppauge, NY.

General Procedure A. Synthesis of Methyl 2-Benzylidene-3-buten-1-oates. Synthesis of Methyl 2-(4-Carbomethoxybenzylidene)-3-buten-1-oate (2d). The following procedure for the conversion of methyl 4-formylbenzoate and crotonic anhydride to methyl 2-(4-carbomethoxybenzylidene)-3-buten-1-oate is exemplary of the conversion of benzaldehydes and crotonic anhydride to methyl 2-benzylidene-3-buten-1-oates and is a minor modification of the literature procedure.[2,3]

Methyl 4-formylbenzoate (MFB) (12.30 g, 75 mmol) was dissolved in 26 mL of triethylamine. To this mixture was added 14.4 g (9.35 mmol) of crotonic anhydride. The mixture was heated at reflux for 18 h and then added to a solution of 20 g of sodium carbonate in 200 mL of water. The mixture was extracted three times with ethyl acetate (100 mL) and then neutralized with 40 mL of concentrated hydrochloric acid. The resultant mixture of solids and aqueous solution was extracted three times with ethyl acetate (100 mL), and the combined ethyl acetate extracts were dried over anhydrous sodium sulfate and filtered to remove drying agent, and the solvent was removed in vacuo. The product, which is unprecedented in the earlier literature, was purified by chro-

matography to give 6.37 g (37%) of the desired 2-(4-carbomethoxybenzylidene)-3-buten-1-oic acid whose spectral properties and elemental analysis are described below. Mp: 124–127 °C. 400-MHz NMR ($CDCl_3$): δ 3.93 (s, 3 H), 5.53 (d, 1 H, J = 11 Hz), 5.95 (d, 1 H, J = 17 Hz), 6.59 (dd, J = 11, 17 Hz), 7.52 (d, 2 H, J = 9 Hz), 7.73 (s, 1 H), 8.06 (d, 2 H, J = 9 Hz).[6a] IR (KBr): 2600–3600 (s, v br), 1685 (s), 1720 cm^{-1}. MS (50 eV): M^+/e 127, 128, 129, 155, 173, 187, 201, 232. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 66.81; H, 5.16.

The esterification followed the literature procedure[3] and is exemplified by the synthesis of 2-(4-carbomethoxybenzylidene)-3-buten-1-oic acid. To a solution of 14.62 g (0.063 mol) of 2-(4-carbomethoxybenzylidene)-3-buten-1-oic acid in 150 mL of methanol was added 0.62 g of concentrated sulfuric acid and 7 mL of trimethyl orthoformate. The resultant solution was heated at reflux for 12 h and then allowed to cool. To the cooled solution was added 0.66 g of sodium carbonate, and then most of the methanol was removed in vacuo. The residue was dissolved in 250 mL of ethyl acetate and extracted three times with 100 mL of 5% sodium bicarbonate. The combined aqueous layers were neutralized with 10% hydrochloric acid and filtered to give 2.59 g of recovered starting material after drying overnight. The ethyl acetate layer was dried over anhydrous sodium sulfate and filtered, and the ethyl acetate was removed in vacuo. The residue was chromatographed with 5% ethyl acetate in hexane to give 9.98 g (0.0406 mol, 78% yield based on recovered starting material) of the desired methyl 2-(4-carbomethoxybenzylidene)-3-buten-1-oate (**2d**). The characterization of the compound is described below.[6b] Mp: 48–49 °C. 400-MHz NMR ($CDCl_3$): δ 3.86 (s, 3 H), 3.93 (s, 3 H), 5.47 (d, 1 H, J = 12 Hz), 5.86 (d, 1 H, J = 16 Hz), 6.59 (dd, 1 H, J = 12, 16 Hz), 7.47 (d, 2 H, J = 8 Hz), 7.53 (s, 1 H), 8.03 (d, 2 H, J = 8 Hz). IR (KBr): 1283, 1720 cm^{-1}. MS (50 eV): M^+/e 59, 128, 143, 155, 187, 215, 246.

Synthesis of Methyl 2-(2-Methoxybenzylidene)-3-buten-1-oate (2f). Via general procedure A, 20.4 g (0.15 mol) of *o*-methoxybenzaldehyde was converted to 10.44 g (51.2 mmol, 34%) of recrystallized 2-(2-methoxybenzylidene)-3-buten-1-oic acid. Mp: 137–140 °C. 400-MHz NMR ($CDCl_3$): δ 3.87 (s, 3 H), 5.43 (d, 1 H, J = 11 Hz), 5.93 (d, 1 H, J = 17 Hz), 6.59 (dd, 1 H, J = 11, 17 Hz), 6.91 (d, 1 H, J = 9 Hz), 6.96 (t, 1 H, J = 9 Hz), 7.34 (t, 1 H, J = 9 Hz), 7.42 (d, 1 H, J = 9 Hz), 7.95 (s, 1 H). IR (KBr): 1686, 1291, 1255 cm^{-1}. MS (50 eV): M^+/e 115, 129, 144, 159, 204. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.12; H, 6.08.

Esterification of 5.41 g (26.5 mmol) of 2-(2-methoxybenzylidene)-3-buten-1-oic acid as in general procedure A gave 4.46 g (20.5 mmol) of methyl 2-(2-methoxybenzylidene)-3-buten-1-oate (**2f**) along with 0.43 g (2.1 mmol) of starting material. This represents an 84% yield after accounting for recovered starting material. Mp: 34–35 °C. 400-MHz NMR ($CDCl_3$): δ 3.84 (s, 3 H), 3.87 (s, 3 H), 5.39 (d, 1 H, J = 11 Hz), 5.86 (d, 1 H, J = 18 Hz), 6.59 (dd, 1 H, J = 11, 18 Hz), 6.90 (d, 1 H, J = 9 Hz), 6.95 (t, 1 H, J = 9 Hz), 7.32 (t, 1 H, J = 9 Hz), 7.36 (d, 1 H, J = 9 Hz), 7.72 (s, 1 H). IR (CH_2Cl_2 film): 1217, 1250, 1720 cm^{-1}. MS (50 eV): M^+/e 115, 128, 144, 159, 187, 203, 218. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.66; H, 6.50.

Synthesis of Methyl 2-(3-Methoxybenzylidene)-3-buten-1-oate (2g). Via general procedure A, 20.4 g (0.150 mol) of *m*-methoxy benzaldehyde was converted to 5.54 g (27.2 mmol, 18%) of pure 2-(3-methoxybenzylidene)-3-buten-1-oic acid. Mp: 75–76 °C. 400-MHz NMR ($CDCl_3$): δ 3.83 (s, 3 H), 5.50 (d, 1 H, J = 12 Hz), 5.93 (d, 1 H, J = 18 Hz), 6.65 (dd, 1 H, J = 12, 18 Hz), 6.91 (dd, 1 H, J = 3, 9 Hz), 7.00 (d, 1 H, J = 3 Hz), 7.32 (t, 1 H, J = 9 Hz), 7.72 (s, 1 H). IR (KBr): 1688, 1256, 1292 cm^{-1}. MS (50 eV): M^+/e 115, 127, 144, 159, 204. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.46; H, 5.98.

Esterification of 1.92 g (9.41 mmol) of 2-(3-methoxybenzylidene)-3-buten-1-oic acid as in general procedure A gave 1.16 g (5.32 mmol, 57%) of liquid methyl 2-(3-methoxybenzylidene)-3-buten-1-oate (**2g**). 400-MHz NMR ($CDCl_3$): δ 3.82 (s, 3 H), 3.87 (s, 3 H), 5.45 (d, 1 H, J = 11 Hz), 5.85 (d, 1 H, J = 18 Hz), 6.65 (dd, 1 H, J = 11, 18 Hz), 6.88 (d, 1 H, J = 9 Hz), 6.97 (s, 1 H), 7.00 (d, 1 H, J = 9 Hz), 7.30 (t, 1 H, J = 9 Hz), 7.50 (s, 1 H). IR (CH_2Cl_2 film): 1720 cm^{-1}. MS (50 eV): M^+/e 115, 128, 144, 159, 187, 218. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.09; H, 6.44.

General Procedure B. The Vapor Phase Thermal Ring Closure of Methyl 2-Benzylidene-3-buten-1-oates. Pyrolysis of Methyl 2-Benzylidene-3-buten-1-oate (2a). The following example is a general procedure for the vapor-phase cyclization of the methyl 2-benzylidene-3-buten-1-oates to the desired 3,4-dihydro-2-naphthoates.

A quartz tube measuring 14 in. in length (including a pair of 24/40 ground glass joints at each end) and 1 in. in diameter, and possessing indentations at 3 in. from the base was used as a reactor. A quartz wool plug was placed in the reactor in contact with the indentations, and the top of the reactor was fitted with a four-necked reactor head, which was capable of holding a quartz thermocouple well, an inert gas flow inlet, a septum-capped hole (to be used as an inlet for the starting material), and finally, a hole that is large enough to pass in a supply of fine Vycor chips and which can readily be sealed after filling the reactor. (This last requirement is best met by using a fitted ground-glass joint and seal.)

After assembly of the head, reactor, and thermal well, the reactor is filled with fine Vycor chips to a height of 20 cm, sealed, and placed in a 12-in. electric furnace so that the entire packed portion of the reactor is centered in the furnace. A flask equipped with a side arm (to be used as a gas outlet) is connected to the bottom of the reactor. An inert gas purge, in this case argon, is established at a level of 100 mL/min. The reactor is then heated to 400–425 °C and maintained at that level for the duration of the reaction. (There is a temperature gradient of as much as 25 °C across the reaction zone.) With use of a syring drive to regulate the rate of addition, 2.12 g (11.3 mmol) of liquid methyl α-vinylcinnamate was added to the reactor via syringe at a rate of 1 mL/h by using the septum-capped inlet. The product, methyl 3,4-dihydro-2-naphthoate, was collected in the bottom flask and weighed 1.94 g (10.3 mmol). This represented a 92% yield, and gas chromatographic analysis revealed the material to be pure. The compound is known in the literature[1,7] and was identified on the basis of its nuclear magnetic resonance spectrum. 400-MHz NMR ($CDCl_3$): δ 2.61 (t, 3 H), 2.86 (t, 3 H), 3.82 (s, 3 H), 7.14–7.26 (m, 5 H), 7.53 (s, 1 H).

Pyrolysis of Methyl 2-(4-Methylbenzylidene)-3-buten-1-oate (2b). Via general procedure B, 5.30 g (26.2 mmol) of liquid methyl 2-(4-methylbenzylidene)-3-buten-1-oate (**2b**) was converted to 4.90 g (24.3 mmol) of pure (>97%) methyl 6-methyl-3,4-dihydro-2-naphthoate (**1b**). (The only detectable impurity is a trace of the methyl 6-methyl-2-naphthoate.) This represents a 92% yield. The compound was characterized on the basis of its spectral characteristics and elemental analysis. Mp: 50–51 °C. 400-MHz NMR ($CDCl_3$): δ 2.35 (s, 3 H), 2.59 (t, 2 H), 2.83 (t, 2 H), 3.71 (s, 3 H), 6.99 (s, 1 H), 7.01 (d, 2 H, J = 9 Hz), 7.09 (d, 2 H, J = 9 Hz), 7.50 (s, 1 H). IR (KBr): 1708, 1278 cm^{-1}. Mass spectrum: (M^+/e) 115, 128, 143, 202. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.95; H, 6.93.

Pyrolysis of Methyl 2-(4-Chlorobenzylidene)-3-buten-1-oate (2c). Via general procedure B, 1.119 g (5.01 mmol) of liquid methyl 2-(4-chlorobenzylidene)-3-buten-1-oate (**2c**) were converted to 0.896 g (4.01 mmol) of methyl 6-chloro-3,4-dihydro-2-naphthoate (**1c**). This represents a yield of 80%. The compound was characterized on the basis of its spectral characteristics and its elemental analysis. Mp: 65–67 °C.[8] 400-MHz NMR ($CDCl_3$): δ 2.60 (t, 2 H), 2.85 (t, 2 H), 3.72 (s, 3 H), 7.11 (d, 1 H, J = 9 Hz), 7.17 (d, 1 H, J = 9 Hz), 7.16 (s, 1 H), 7.48 (s, 1 H). IR (CH_2Cl_2): 1713, 1270 cm^{-1}. MS: (M^+/e) 222. Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98; Cl, 15.92. Found: C, 64.84; H, 4.93; Cl, 15.93.

Pyrolysis of Methyl 2-(4-Carbomethoxybenzylidene)-3-buten-1-oate (2d). Via general procedure B, 0.770 g (3.16 mmol)

(6) (a) The acidic proton was outside the ordinary range of our NMR scan. (b) Although this product was pure by TLC, GC, NMR, and gave a sharp melting point, we were unable to obtain an acceptable elemental analysis.

(7) (a) The compound was a liquid as reported in ref 1a and 7b. Reference 1b reports the material to be a solid with a m.p. of 68 °C. (b) Ito, Y.; Yonezawa, K.; Seegusa, T. *J. Org. Chem.* **1974**, *39*, 2769.

(8) The literature describes a preparation of this compound, but the authors were unsure of the purity of the compound or which isomer was present. See ref 7b.

of methyl 2-(4-carbomethoxybenzylidene)-3-buten-1-oate (**2d**) (as a solution in 1.5 g of methyl acetate) was converted to 0.440 g (1.80 mmol) of methyl 6-carbomethoxy-3,4-dihydro-2-naphthoate (**1d**). This represents a 56% yield. The compound is known in the literature,[9] and the compound was characterized on the basis of a comparison of its NMR spectrum and melting point. 400-MHz NMR ($CDCl_3$): δ 2.65 (t, 2 H), 2.92 (t, 2 H), 3.84 (s, 3 H), 3.92 (s, 3 H), 7.23 (d, 1 H, J = 9 Hz), 7.53 (s, 1 H), 7.85 (s, 1 H), 7.87 (d, 1 H, J = 9 Hz). Mp: 121–123 °C (lit. mp 126 °C).

Pyrolysis of Methyl 2-(4-Methoxybenzylidene)-3-buten-1-oate (2e). Via general procedure B, 1.96 g (8.99 mmol) of liquid methyl 2-(4-methoxybenzylidene)-3-buten-1-oate (**2e**) was converted to 1.20 g (5.56 mmol) of methyl 6-methoxy-3,4-dihydro-2-naphthanoate (**1e**). This represents a 61% yield. The compound is known in the literature[1b] and was characterized on the basis of a comparison of its NMR spectrum and melting point with the literature. 400-MHz NMR ($CDCl_3$) δ 2.60 (t, 2 H), 2.85 (t, 2 H), 3.80 (s, 3 H), 3.82 (s, 3 H), 6.72 (s, 1 H), 6.73 (d, 1 H, J = 9 Hz), 7.13 (d, 1 H, J = 9 Hz), 7.49 (s, 1 H). Mp: 46–47 °C (lit.[1b] mp 50–51 °C).

Pyrolysis of Methyl 2-(2-Methoxybenzylidene)-3-buten-1-oate (2f). Via general procedure B, 1.99 g (9.21 mmol) of methyl 2-(2-methoxybenzylidene)-3-buten-1-oate (**2f**) (added as a solution in 3.06 of methyl acetate) was converted to 1.84 g (8.52 mmol) of methyl 8-methoxy-3,4-dihydro-2-naphthoate (**1f**). This represents a 92% yield. The liquid product was identified on the basis of its spectral properties and elemental analysis. 400-MHz NMR ($CDCl_3$) δ 2.57 (t, 2 H), 2.82 (t, 2 H), 3.81 (s, 3 H), 3.85 (s, 3 H), 6.73 (d, 1 H, J = 9 Hz), 6.77 (d, 1 H, J = 9 Hz), 7.20 (t, 1 H, J = 9 Hz), 7.95 (s, 1 H). IR (CH_2Cl_2): 1707 cm^{-1}. MS (50 eV): M^+/e 115, 144, 159, 187, 203, 218. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.88; H, 6.42.

Pyrolysis of Methyl 2-(3-Methoxybenzylidene)-3-buten-1-oate (2g). Via general procedure B, 0.950 g (4.40 mmol) of methyl 2-(3-methoxybenzylidene)-3-buten-1-oate (**2g**) was cyclized to a mixture of two distinguishable methoxy-substituted 3,4-dihydro-2-naphthoate esters, which were separated by medium-pressure liquid chromatography (5% ethyl acetate in hexane) to give 0.580 g (2.69 mmol) of methyl 5-methoxy-3,4-dihydro-2-naphthanoate (**1g**) and 0.340 g (1.58 mmol) of methyl 7-methoxy-3,4-dihydro-2-naphthanoate (**1h**). This represents a 61% and a 36% yield, respectively. The compounds were identified on the basis of their spectral properties and elemental analyses, which are listed below.

Methyl 5-Methoxy-3,4-dihydro-2-naphthoate (1g). Mp: 54–56 °C. 400-MHz NMR ($CDCl_3$): δ 2.59 (t, 2 H), 2.87 (t, 2 H), 3.81 (s, 3 H), 3.84 (s, 3 H), 6.84 (d, 1 H, J = 9 Hz), 6.85 (d, 1 H, J = 9 Hz), 7.17 (t, 1 H, J = 9 Hz), 7.49 (s, 1 H). IR (CH_2Cl_2): 1707 cm^{-1}. MS (50 eV): M^+/e 115, 144, 159, 187, 203, 218. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.71; H, 6.47.

Methyl 7-Methoxy-3,4-dihydro-2-naphthoate (1h).[1b] 400-MHz NMR ($CDCl_3$): δ 2.59 (t, 2 H), 2.80 (t, 2 H), 3.80 (s, 3 H), 3.82 (s, 3 H), 6.77 (d, 1 H, J = 1 Hz), 6.80 (dd, 1 H, J = 1, 9 Hz), 7.07 (d, 1 H, J = 9 Hz), 7.49 (s, 1 H). IR (CH_2Cl_2 film): 1710 cm^{-1}. MS (50 eV): M^+/e 115, 144, 159, 187, 203, 218. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.53; H, 6.52 (liquid).

Liquid-Phase Pyrolysis of Methyl 2-(4-Methylbenzylidene)-3-buten-1-oate (2b). With a 100-mL round-bottom flask as a reaction vessel, a solution of 0.530 g (2.62 mmol) of methyl 2-(4-methylbenzylidene)-3-buten-1-oate (**2b**) in 53 mL of decalin was heated at reflux for 40 h. Most of the decalin was removed by distillation, and the residue was separated by chromatography with 3% ethyl acetate in hexane as eluent. This procedure yielded 0.130 g (0.64 mmol) of pure methyl 6-methyl-3,4-dihydro-2-naphthanoate (**1b**). This corresponds to yield of 24%. The product was identical with that obtained in the vapor-phase reaction described above.

General Procedure C. Synthesis of 2-Naphthoates. Synthesis of Methyl 6-Methyl-2-naphthanoate from Methyl 2-(4-Methylbenzylidene)-3-buten-1-oate (2b). The following procedure is exemplary of the procedure for the single-vessel cyclization–dehydrogenation of methyl 2-benzylidene-3-buten-1-oates **2** to generate methyl 2-naphthanoates.

With use of a 100-mL round-bottomed flask as a reaction vessel, a solution of 0.533 g of methyl 2-(4-methylbenzylidene)-3-buten-1-oate (**2b**) in 53 mL of decalin containing 0.103 g of 5% Pd on carbon was heated at reflux for 40 h under a slow, continuous stream of an inert gas (argon). The product was isolated by adding the solution to a chromatography column and eluting with 3% ethyl acetate in hexane. The yield was 0.257 g (49%) of pure methyl 6-methyl-2-naphthanoate (mp 121–123 °C; lit. mp 123.5–124.5 °C.).[10,11]

Synthesis of Dimethyl 2,6-Naphthalenedicarboxylate. Via general procedure C, with the exception that 1-methylnaphthalene at reflux for 5 h was used in place of decalin at reflux for 40 h, 0.855 g of methyl 2-(4-carbomethoxybenzylidene)-3-buten-1-oate (**2d**) was cyclized and dehydrogenated by 0.250 g of 5% Pd on carbon to give 0.470 g (55%) of pure dimethyl 2,6-naphthalenedicarboxylate by using the following isolation method.

At the end of the reaction, the mixture was allowed to cool slightly and was then filtered to remove catalyst. The solvent was removed by distribution under vacuum, and the residue was redissolved in 10 mL of ethyl acetate. The ethyl acetate initially dissolved all the residue, and then crystals began to form, giving 0.365 g of pure dimethyl 2,6-naphthalenedicarboxylate. Chromatography yielded another 0.105 g of the desired product for a combined yield of 0.470 g (55%) of pure dimethyl 2,6-naphthalenedicarboxylic acid. (mp 193–193.5 °C; lit. mp 188–190 °C).[11,12]

(9) Dinulescu, I. G.; Geirgescu, E. G.; Stanescu, L.; Avram, M. *Tetrahedron Suppl. 1* **1981**, *37*, 55.

(10) Adcock, W.; Wells, P. R. *Aust. J. Chem.* **1965**, *18*, 1351.

(11) Identified on the basis of its spectral properties and comparison with the properties reported in the literature.

(12) Available from Aldrich Chemical Co., Milwaukee, WI.