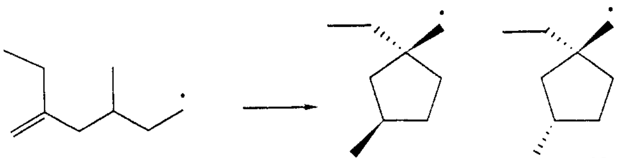
in which the methyl groups are syn. It should be noted that the endo product will also be formed in about 24% yield.



34 35 36

calc 39 71

Conclusions. The model described here is an accurate predictor of regioselectivity and stereoselectivity of alkyl radical cyclization reactions. There are some limitations, as described here. Nevertheless, this model can be used to aid in design of syntheses involving intramolecular radical cyclizations, and the force-field should be extendable to related systems following the techniques described here.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for financial support of this research, the Andrew Mellon Foundation for a Fellowship to D.C.S., Professor Dennis P. Curran for encouragement and helpful comments, and Dr. John Yates and Dr. K. K. Sunil for the Harris versions of the GAUSSIAN 80 and 82 series of programs. We would also like to thank the Harris Corporation for grants of Harris H800 computers at Pittsburgh and UCLA and the National Science Foundation for equipment grants and for supercomputer time used in this research.

Appendix

New MM2 Parameters. Our model can be reproduced with the parameters described here. The incoming radical center is defined as MM2 type 29, while the alkene atom being attacked is type 28. The remaining carbon of the double bond remains type 2. The van der Waals parameters for all carbons are identical with those for any other carbon in MM2 as are stretch-bend an out-of-plane bending of the terminal carbon of the olefin. Our version of MM2 has an atom type equivalence property which allows a user to equivalence two atom types. This enables one to redefine one or two parameters of an atom type without having to duplicate numerous definition cards. For example, to redefine just one C–C bond length in propane, one carbon is defined as type 30, equivalenced to type 1, and then only *one* redefinition card is read in. Otherwise, the parameter list to be read in would be several cards long. The equivalence mechanism, therefore, provides all of these extra definitions internal to the program. The radical center, type 29, is equivalenced to type 1 as is the atom being attacked, type 28. The parameter list, remarkably small, is then as follows:

Torsional Definitions. Fourteen torsional definition cards are read into the program. The first two, types 29-28-2-1 and 29-28-2-5 have $V_1 = V_3 = 0$ and $V_2 = -25.0$. Definitions for rotations about the double bond are as follows (V_1, V_2, and V_3): 5-2-28-5, 0, 0, 0.25; 5-2-28-1, 0, 0.2, 0.2; 1-2-28-5, 0, 0, 0.34; 1-2-28-1, 0.4, 0.03, 0.5. Rotations about the forming bond are as follows: 5-29-28-5, 0, 0, 0.0267; 1-29-28-5, 0, 0, 0.0273; 5-29-28-2, 0, 0, 0.041; 5-29-28-1, 0, 0, 0.065; 1-29-28-2, −0.241, 0.241, 0.399; 1-29-28-1, 1.364, −1.103, 0.339. The remaining parameters are as follows: 5-1-2-28, 0, 0, −0.24; 1-1-2-28, −0.44, 0.24, 0.06.

Bond Stretching and Compression Parameters. The stretching parameters for this model define the forming bond length and the double bond length. Type 29-28 has $l_o = 2.27$ and $K_s = 4.0$, while 28-2 has $l_o = 1.375$ and $K_s = 4.4$.

Angle-Bending Parameters. Seventeen bending parameters are used in our model. The K_B and θ_0 parameters for the radical are as follows: 5-29-5, 0.32, 116.6; 5-29-28, 0.36, 100.5; 5-29-1, 0.36, 116.6; 1-29-1, 0.45, 116.6; 1-29-28, 0.45, 100.5. Bending parameters for angles about the central carbon are as follows: 29-28-5, 0.36, 90.3; 29-28-2, 0.60, 107.0; 5-28-2, 0.36, 120.3; 5-28-5, 0.32, 115.8; 1-28-1, 0.45, 115.8; 29-28-1, 0.45, 90.3; 1-28-2, 0.45, 120.3; 1-28-5, 0.36, 115.8. Finally, angle definitions about the terminal carbon of the double bond are as follows: 28-2-5, 0.36, 121.4; 5-2-5, 0.32, 117.0; 28-2-1, 0.45, 121.4; 5-2-1, 0.36, 117.0. Note: if two double bonds are present in the molecule, care *must* be taken to redefine these last parameters for *only* the double bond involved in the transition state. A complete list is given in Table XII as it appears in an MM2 input.

On the Regio- and Stereoselectivity of Bu$_4$N[Fe(CO)$_3$NO]-Catalyzed Allylic Alkylation

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Received July 30, 1986

Bu$_4$N[Fe(CO)$_3$NO] has been found to catalyze the alkylation of allylic carbonate with malonate anion. The reaction proceeds with good regioselectivity, the nucleophile attacking predominantly at the carbon where the leaving group was attached. Retention of configuration of the double bond during the course of reaction was observed. Alkylation of methyl (*Z*)-5-carbomethoxy-1-cyclohexen-3-yl carbonate with sodium salt of dimethyl malonate yielded dimethyl ((*Z*)-5-carbomethoxy-1-cyclohexen-3-yl)malonate in a highly stereoselective fashion, and a net retention of configuration at the center undergoing substitution is thus established. On the basis of regio- and stereochemical results, a reaction pathway involving an σ-allyliron complex has been suggested.

Nucleophilic substitution reactions of carbon nucleophiles on allylic esters represents one of the most important carbon–carbon bond-forming reactions promoted or catalyzed by transition-metal complexes. Extensive studies

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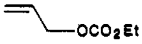
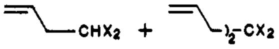
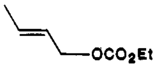
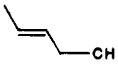
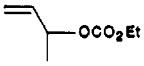
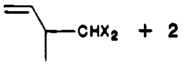
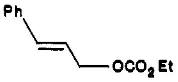
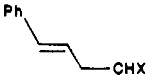
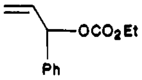
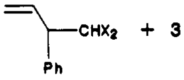
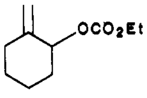
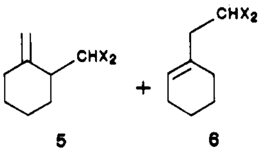
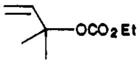
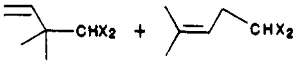
Table I. Regioselectivity of Allylic Alkylation[a]

entry	allylic carbonate	time, h	product[b]	yield,[c] %
1		8	 89:11	76
2		8	 2	76
3		10	 93:7	78
4		10	 3	82
5		12	 75:25	76
6	 4	12	 5 6 64:36	74
7		14	 92:8	78

[a] Reactions were performed with 2 equiv of nucleophile and 25 mol % catalyst in refluxing THF under CO atmosphere. The nucleophile was generated by treating diethyl malonate with sodium hydride in THF. X = CO$_2$Et. [b] The ratio of the regioisomers was determined by GC. [c] Isolated yield.

have been done on the regio- and stereoselectivity of such allylic alkylations and their application in organic synthesis.[1a-e] However, investigations on the use of iron catalysts for allylic alkylation have been rather limited. Ladoulis and Nicholas[2] have reported the coupling of allylic acetate with malonate anion catalyzed by diiron nonacarbonyl with low regio- and stereoselectivity. The alkylation reaction of allylic compounds, (chlorides, formates, and acetates) using sodium tricarbonylnitrosyl ferrate as catalyst has been studied very briefly by Roustan et al.,[3] and good regioselectivity was claimed by the authors. Nevertheless, no further investigations have been made. It occurred to us that this iron-catalyzed allylic alkylation reaction might have potential synthetic utilities if further explorations are made, so we decided to investigate this reaction in more detail, using tetrabutylammonium (tricarbonylnitrosyl)ferrate[4] (Bu$_4$N[Fe(CO)$_3$NO], 1) as the catalyst, which is easier to prepare and less susceptible to air and moisture than the corresponding sodio derivative, making the manipulation much more convenient.

Results and Discussion

In preliminary experiments, we found that allylic carbonates could react with diethyl malonate anion in the presence of a catalytic amount of 1 in refluxing THF, leading to a mixture of monoallylated and diallylated products in a good yield (Table I, entry 1). Allylic acetates and allylic phosphates reacted in a similar fashion but gave lower yields of alkylated products. Dioxane, DME and toluene are poorer solvents than THF. The reaction of various allylic carbonates with diethyl malonate anion was then studied, and the results are summarized in Table I. In each and every case, alkylation occurred predominantly at the carbon atom where the leaving group was attached. Even in the case of a tertiary substrate (entry 7), this generality seems to hold. For entry 6, attack at the carbon where the leaving group was attached was again favored, regardless of the common preference for an endocyclic double bond. These results cannot be explained by the intermediacy of π-allyliron complexes, though Pauson et al.[5] reported that π-allylic dicarbonylnitrosyl complexes have been isolated on reacting allylic halides with sodium tricarbonylnitrosyl ferrate and characterized by IR and ^{1}H NMR spectroscopy; instead, it is likely that σ-allyliron intermediates are involved here.

In an attempt to elucidate whether 1-catalyzed allylic alkylation proceeds via a π-allyl or a σ-allyl intermediate, deuteriated allylic carbonate 7 was reacted with diethyl malonate anion, yielding a mixture of monoallylated

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(1) For reviews and leading references, see the following. (a) Pd catalyzed: Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 8, p 799. Tsuji, J. *J. Organomet. Chem.* **1986**, *300*, 281. (b) Ni: Cuvigny, T.; Julia, M. *J. Organomet. Chem.* **1983**, *250*, C21. (c) Mo: Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543; **1983**, *105*, 3343. (d) W: Trost, B. M.; Hung, M. H. *J. Am. Chem. Soc.* **1983**, *105*, 7757. (e) Rh and Ru: Minami, I.; Shimizu, I.; Tsuji, J. *J. Organomet. Chem.* **1985**, *296*, 269.

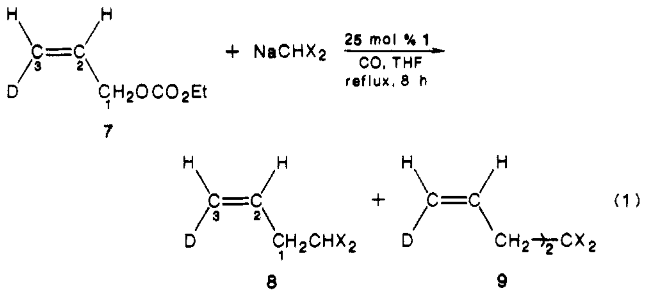
(2) Ladoulis, S. G.; Nicholas, K. M. *J. Organomet. Chem.* **1985**, *285*, C13–C16.

(3) Roustan, J. L. A.; Merour, J. Y.; Houlihan, F. *Tetrahedron Lett.* **1979**, 3721.

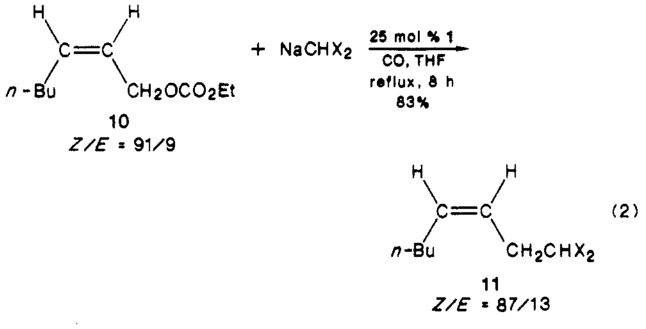
(4) Otsuji, Y.; Ueda, T. In *New Frontier in Organometallic and Inorganic Chemistry*; Science: Beijing, China, **1984**, p 179.

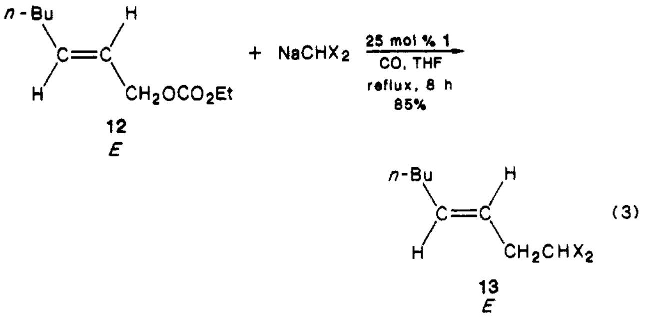
(5) Bruce, R.; Chaudhary, F. M.; Knox, G. R.; Pauson, P. L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1965**, *20B*, 73. See also: Murdoch, H. D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1965**, *20B*, 179.

product 8 and diallylated product 9 (eq 1), which were separated by flash chromatography. At 200 MHz, C_3-H (δ 5.04, d, J = 10.4 Hz) of product 8 was readily discernible. The appearance of a doublet at δ 5.04 indicates unambiguously that the nucleophile exclusively attacks the carbon to which the leaving group is attached and the coupling constant of 10.4 Hz (in comparison to the coupling constant 10.6 Hz of C_3-H in deuteriated allylic carbonate 7) reveals that the *Z* configuration of the double bond was retained. No loss of stereochemistry was observed.



In order to further examine the stereochemical behavior of *Z* and *E* isomeric allylic carbonates during the course of the present iron-catalyzed reaction, allylation of sodium diethyl malonate with (*Z*)-2-heptenyl carbonate (10) (eq 2) and (*E*)-2-heptenyl carbonate (12) (eq 3) were carried out, respectively. In both cases, no substantial isomerization of the double bond was observed, as revealed by comparison of 11 and 13 on capillary GC.

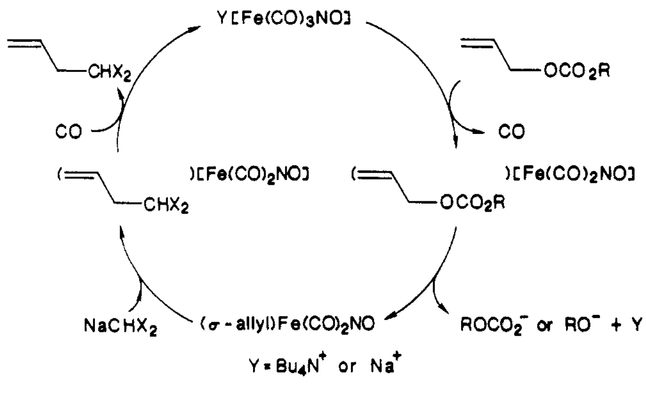




Since it is known that in π-allylpalladium complex mediated allylation reactions, isomerization of the double bond commonly takes place,[6] the observation of retention of configuration of the double bond during the course of iron-catalyzed alkylations of carbonate 10 and 12 further supports the notion that this reaction might not proceed via a π-allyl complex but rather via a σ-allyl complex.

In order to examine the possibility if a slow equilibrium of σ-allyl- and π-allyliron complexes is involved in this iron-catalyzed reaction and the above-mentioned regiochemical outcome stems from the reaction of the σ-allyliron complex with nucleophile is much more rapid than the equilibrium between the σ- and π-allyliron complexes, the following experiment has been carried out: 1-buten-3-yl carbonate was first treated with a stoichiometric amount of 1 in refluxing THF under CO atmosphere for 4 h and then followed by reaction with 2 equiv of the sodium salt of diethyl malonate. The ratio of α- and γ-alkylated product (92/8) was virtually the same as that resulting from the catalytic reaction (93/7) (Table I, entry 3).

Scheme I



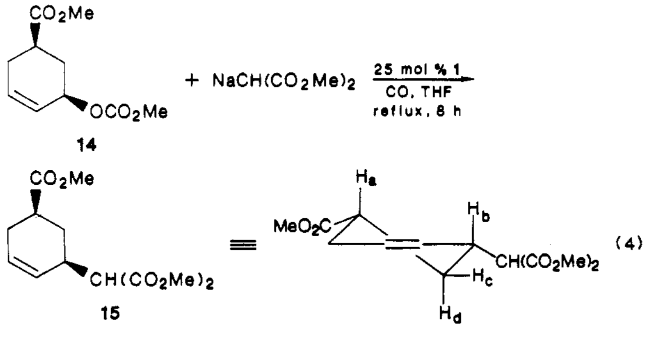
All the above results imply that the 1-mediated reaction, either stoichiometric or catalytic, may possibly proceed via a σ-allyl intermediate and not via a π-allyl intermediate as Roustan et al. have assumed.[3]

It is worthy of mention that 1-catalyzed allylic alkylation does not take place in the absence of carbon monoxide,[7] and this implies that a decomplexation and complexation of CO ligand might be involved in the catalytic cycle. Since $[Fe(CO)_2NO]^-$ formed after the dissociation of one CO ligand from $[Fe(CO)_3NO]^-$ is a 16-electron species, some extent of coordination of the double bond in allylic substrate to the iron atom may take place.

The catalytic cycle may be depicted as shown in Scheme I.

Finally, to determine the stereochemical course of this iron-catalyzed reaction, alkylation of methyl ((*Z*)-5-carbomethoxy-1-cyclohexen-3-yl)carbonate (14), prepared from (*Z*)-3-hydroxy-5-carbomethoxy-1-cyclohexene[6] by treatment with methyl chloroformate in the presence of pyridine, was examined.

Alkylation of 14 (contaminated with 2% of the *E* isomer as revealed by capillary GC) with 2 equiv of sodium salt of dimethyl malonate gave a 75% isolated yield of product 15 (eq 4). At 200 MHz, H_c [δ 2.11 (d of m, J = 12.0 Hz)] and H_d [δ 1.47 (q, J = 12.0 Hz)] were readily discernible. The requisite coupling constants $J_{ad} = J_{bd} = J_{cd}$ = 12.0 Hz indicate that both H_a and H_b are pseudoaxial. Capillary GC of 15 revealed contamination with only 6% of the corresponding *E* isomer, confirming high stereoselectivity. As a consequence, a net retention of configuration



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(6) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(7) Starting allylic carbonate was recovered under this condition.

at the center undergoing substitution is established. Probably, backside displacement of the carbonate from the iron complex results in an initial inversion and then a nucleophilic attack occurs on the face opposite iron with a second inversion at carbon. However, the possibility that the stereoselectivity stems from a result of two consecutive $S_N'2$ reactions could not be excluded.[8]

Studies are currently under way to explore the full scope of this iron-catalyzed reaction and its application in synthesis.

Experimental Section

THF was distilled from sodium benzophenone under a nitrogen atmosphere. Other solvents were routinely dried and distilled under a nitrogen atmosphere before use. ^1H NMR spectra were recorded on an EM-360 or Varian XL-200 spectrometer with Me_4Si as an internal standard. Infrared spectra were taken as liquid films with a Specord 75 spectrometer. Mass spectra were obtained on a Finnigan 4021 GC/MS/DC instrument. Capillary GC was performed on a Hewlett-Packard 5880A gas chromatograph (column: SE-52, 50 m × 0.2 mm).

Materials. 2-Methylene-1-hexanol[9] and (*Z*)-[3-^2H]-allyl alcohol[10] were prepared according to known procedures. (*Z*)- and (*E*)-2-heptenyl alcohols were prepared by using the methods reported in the literature.[11,12]

Preparation of $Bu_4N[Fe(CO)_3NO]$ (1). A solution of $Fe(CO)_5$ (15 mmol) in benzene (5 mL) was added to a mixture of $NaNO_2$ (15 mmol) and Bu_4NBr (15 mmol) in water. The resulting mixture was stirred under N_2 at room temperature for 3 h. The benzene layer was separated, washed with water, and dried over anhydrous Na_2SO_4. After removal of benzene under reduced pressure, $Bu_4N[Fe(CO)_3NO]$ was obtained as yellow crystals in 84% yield, mp 56–56.5 °C, IR (KBr) 1980, 1850 (CO), and 1630 (NO) cm^{-1}, in agreement with that reported by Otsuji and Ueda.[4]

Preparation of Ethyl Allylic Carbonates. General Procedure. To a cooled (0 °C) and stirred solution of allylic alcohol (10 mmol) and dry pyridine (20 mmol) in dry ether (10 mL) was added ethyl chloroformate (10 mmol) dropwise over 10 min. The mixture was stirred at room temperature (for secondary and tertiary alcohols at reflux temperature) for 3–24 h, and then dilute hydrochloric acid was added. After extraction with ether, the organic layer was washed with brine and dried over Na_2SO_4. Following evaporation of the solvent, the carbonate was isolated either by distillation or column chromatography.

Ethyl 1-methylenecyclohexan-2-yl carbonate (4): ^1H NMR (CCl_4) δ 1.30 (t, J = 6 Hz, 3 H), 1.30–2.40 (m, 8 H), 4.05 (q, J = 6 Hz, 2 H), 4.06–5.00 (m, 3 H); IR (neat) 1750, 1660 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.22; H, 8.70. Found: C, 65.31; H, 8.97.

Ethyl (*Z*)-[3-^2H]propen-1-yl carbonate (7): ^1H NMR (CCl_4) δ 1.33 (t, J = 7 Hz, 3 H), 4.15 (q, J = 7 Hz, 2 H), 4.55 (d, J = 6 Hz, 2 H), 5.20 (d, J = 11 Hz, 1 H), 5.65–6.20 (m, 1 H); IR (neat) 1750 cm^{-1}; MS, *m/e* 132 (M^+ + 1), 59, 42 (base).

Ethyl (*Z*)-2-heptenyl carbonate (10): ^1H NMR (CCl_4) δ 0.80–1.40 (m, 10 H), 2.00–2.20 (m, 2 H), 4.10 (q, J = 8 Hz, 2 H), 4.68 (d, J = 7 Hz, 2 H), 5.48–5.80 (m, 2 H); IR (neat) 1700 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.48; H, 9.74. Found: C, 64.42; H, 9.91.

Ethyl (*E*)-2-heptenyl carbonate (12): ^1H NMR (CCl_4) δ 0.90–1.50 (m, 10 H), 1.80–2.25 (m, 2 H), 4.10 (q, J = 7 Hz, 2 H), 4.40 (d, J = 6 Hz, 2 H), 5.40–5.80 (m, 2 H); IR (neat) 1700, 980 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.48; H, 9.74. Found: C, 64.25; H, 9.86.

Methyl (*Z*)-5-carbomethoxy-1-cyclohexen-3-yl carbonate (14): ^1H NMR (200 MHz, $CDCl_3$) δ 1.85 (t of d, J = 12.5, 9.3 Hz, 1 H), 2.40 (m, 4 H), 3.72 (s, 3 H); 3.80 (s, 3 H), 5.28 (m, 1 H), 5.73 (m, 1 H), 5.92 (m, 1 H); IR (neat) 1760, 1742 cm^{-1}; MS, *m/e*, 214 (M^+), 154, 139, 79 (base), 59.

Alkylation of Allylic Carbonates with Sodium Salt of Diethyl Malonate Catalyzed by 1. General Procedure. In a 25-mL flask was placed NaH (2 mmol) and THF (10 mL) under CO atmosphere, then diethyl malonate (2 mmol) in THF (10 mL) was added dropwise and stirred for 10 min.

Allylic carbonate (1 mmol) in THF (10 mL) was added to a 50-mL flask containing **1** (0.25 mmol) and THF (10 mL) under CO atmosphere. After the mixture was stirred for 10 min, the sodium salt of diethyl malonate prepared was transferred to this flask, and the resulting mixture was stirred at reflux for 8 to 14 h under CO. Ether was added, and the mixture was washed with brine. The organic layer was separated, and a saturated ether solution of I_2 was added to it until the brown color did not fade for at least 1 h so as to decompose the iron catalyst, making the subsequent workup simpler.[13] Then, 1 N aqueous solution of $Na_2S_2O_3$ was added to remove excess I_2. The organic layer was then dried over Na_2SO_4. The product was isolated by column chromatography.

Diethyl (1-methylene-2-cyclohexanyl)malonate (5): ^1H NMR (CCl_4) δ 1.25 (t, J = 7 Hz, 3 H), 1.29 (t, J = 7 Hz, 3 H), 1.40–1.70 (m, 6 H), 2.30–2.40 (m, 2 H), 2.70 (m, 1 H), 3.47 (d, J = 11 Hz, 1 H), 3.70 (q, J = 7 Hz, 2 H), 3.90 (q, J = 7 Hz, 2 H), 4.55 (m, 2 H); IR (neat) 1760, 1740, 1655 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.30; H, 8.90.

Diethyl (1-cyclohexenylmethyl)malonate (6): ^1H NMR (CCl_4) δ 1.21 (t, J = 7 Hz, 6 H), 1.40–2.15 (m, 8 H), 2.40 (d, J = 8 Hz, 2 H), 3.30 (t, J = 8 Hz, 1 H), 4.05 (q, J = 7 Hz, 4 H) 5.35 (m, 1 H); IR (neat) 1750, 1730 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.28; H, 8.65.

Diethyl (*Z*)-[1-^2H]propen-3-ylmalonate (8): ^1H NMR (CCl_4) δ 1.30 (t, J = 8 Hz, 6 H), 2.68 (t, J = 8 Hz, 2 H), 3.46 (t, J = 7 Hz, 1 H) 4.25 (q, J = 7 Hz, 4 H), 5.04 (d, J = 10.4 Hz, 1 H), 5.74–5.90 (m, 1 H); IR (neat) 1750 cm^{-1}; MS, *m/e* 202 (M^+ + 1) (base), 156, 128, 110, 99, 83, 55.

Diethyl di-(*Z*)-[1-^2H]propen-3-ylmalonate (9): ^1H NMR (CCl_4) δ 1.20 (t, J = 7 Hz, 6 H), 2.53 (d, J = 8 Hz, 4 H), 4.10 (q, J = 7 Hz, 4 H), 5.00 (d, J = 10.5 Hz, 2 H), 5.30–5.80 (m, 2 H); IR (neat) 1740, 1620 cm^{-1}; MS, *m/e* 243 (M^+ + 1), 200, 154 (base), 126, 95, 81, 42.

Diethyl (*Z*)-2-heptenylmalonate (11): ^1H NMR (CCl_4) δ 0.80–1.40 (m, 13 H), 1.70–2.10 (m, 2 H), 2.30–2.60 (m, 2 H), 3.15 (t of d, J = 7 Hz, 1 H), 4.10 (q, J = 7 Hz, 4 H), 5.20–5.50 (m, 2 H); IR (neat) 1740 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.43. Found: C, 65.83; H, 9.29.

Diethyl (*E*)-2-heptenylmalonate (13): ^1H NMR (CCl_4) δ 0.80–1.40 (m, 13 H), 1.70–2.10 (m, 2 H), 2.30–2.60 (m, 2 H), 3.15 (t of d, J = 7 Hz, 1 H), 4.10 (q, J = 7 Hz, 4 H), 5.20–5.50 (m, 2 H); IR (neat) 1740, 970 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.43. Found: C, 65.76; H, 9.30.

Dimethyl ((*Z*)-5-carbomethoxycyclohexen-3-yl)malonate (15): ^1H NMR (200 MHz, $CDCl_3$) δ 1.47 (q, J = 12.0 Hz, 1 H), 2.11 (d of m, J = 12.0 Hz, 1 H), 2.17–2.34 (m, 2 H), 2.64 (m, 1 H), 3.01 (m, 1 H), 3.29 (d, J = 8.6 Hz, 1 H), 3.69 (s, 3 H), 3.75 (s, 6 H), 5.54 (d of m, J = 10.0 Hz, 1 H), 5.78 (m, 1 H); IR (neat) 1760, 1742 cm^{-1}; MS, *m/e* 270 (M^+), 239, 210, 178, 139.

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(13) An alternate way is to pass a stream of air through the reaction mixture, but I_2 is more efficient.