of Agricultural and Life Sciences, Universtiy of Wisconsin, Madison; in part by the funds from U.S. Hatch Project No. 3040, CRGO/USDA Research Grant 84-CRCR-1-1501; and by the University of Wisconsin A.I.D. Title XII strengthening Grant.

Registry No. Acetic acid, 64-19-7; 4-hexen-1-ol acetate, 72237-36-6; 3-hexen-1-ol acetate, 1708-82-3; acetic acid, cyclohexyl ester, 622-45-7; acetic acid, hexyl ester, 142-92-7; butanoic acid, 3-hexenyl ester, 2142-93-0; hexanoic acid, 3-hexenyl ester, 84434-19-5; 2-methyl-4-pentenal, 5187-71-3; 2-hexenal, 505-57-7; 2,2-dimethylhexanal, 996-12-3; 2,6-dimethyl-5-heptenal, 106-72-9; 3-octanone, 106-68-3; 1-methoxy-3-methylene-2-pentanone, 55956-45-1; 2,2,5,5-tetramethyl-3,4-hexanedione, 4388-88-9; diphenylmethanone, 119-61-9; 2,4-hexadien-1-ol, 111-28-4; 3-hexen-1-ol, 544-12-7; 1-hexanol, 111-27-3; 7-octen-4-ol, 53907-72-5; 3-octanol, 589-98-0; 1-nonen-3-ol, 21964-44-3; 3-tetradecene, 36587-78-7; 1-dodecene, 112-41-4; 3,5,5-trimethyl-2-hexene, 26456-76-8; *trans*-ocimene, 27400-72-2; linalool, 78-70-6; methoxybenzene, 100-66-3.

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Synthesis of Methylene-Linked Pyrethroids

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In a simplified approach, new methylene-linked pyrethroid esters and ketones, lacking an ester bridge, are synthesized from (*E*)-(*R,S*)-2,2-dimethyl-3-(2-methylpropenyl)cyclopropane-, (*E*)-(*R,S*)-3-(cyclopentylidenemethyl)-2,2-dimethylcyclopropane-, (*E*)-(*R,S*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-, and (*R,S*)-1-(4-chlorophenyl)-2,2-dimethylethane-1-carboxylic acids and 3-phenoxybenzyl and 5-benzyl-3-furylmethyl halides. The keto esters are prepared via a Meldrum's acid intermediate and classical alkylation of the β-keto ester with a halide. An aqueous, phase transfer (PTA) catalyzed or sodium hydride–1,2-dihydroxypropane decarbethoxylation at 80 °C is used to complete the synthesis. The β-keto esters and subsequent ketones express various biological activities in *Oncopeltus fasciatus* (large milkweed bug), *Tenebrio molitor* (yellow mealworm), and *Spodoptera frugiperda* (fall armyworm).

Pest insects adversely impact on and significantly affect the production and quality of agricultural products (Harein, 1982; Ouye, 1984), and the recent and potential removal of several accepted fumigants and stored product protectants may introduce further critical problems for agriculture (Brady, 1982). Also, because a number of these pests have developed resistance (Elliott et al., 1978; Beard et al., 1985; Bangston et al., 1983; Riskallah, 1983), new, improved, and environmentally safe chemicals are needed

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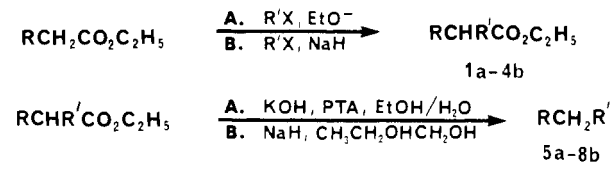


Figure 1. Syntheses of methylene-linked pyrethroids.

for integration into the control effort. Synthetic pyrethroids have historically met these requirements (Elliot and Janes, 1978) and have served as a continuing source for new control chemicals.

In the past these have been largely based on the ester structure, but, about 20 years ago, two pyrethroids were prepared that lacked the ester moiety (Berteau and Casida, 1969; Casida et al., 1969) and these demonstrated similar high activity, when synergized, in test insects (Casida et al., 1969). Since then, two procedures that used α,β-unsaturated ketones (Paul, 1980) have been presented, but more facile methods still are not available and this may account for why these insecticides have gone largely uninvestigated. Now, ketones of various structures can be prepared easily and in good overall yields.

RESULTS AND DISCUSSION

Two significant difficulties existed that prevented a useful and general synthesis of the methylene-linked pyrethroids: (1) a straightforward preparation of the β-keto ester and (2) a high-yield reaction to convert the alkylated β-keto ester directly to the ketone. The synthetic schemes for the preparation of these pyrethroids from β-keto esters offer a straightforward approach such that many other types could be made by these procedures. These goals were met for **1**–**4**, but the Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) route was not as productive for the easy preparation of the β-keto ester **4**. For example, instead of converting the acid chloride to the ketone via a reaction that made use of an organometallic intermediate and then to the keto ester with diethyl carbonate, **1** was synthesized from its acid chloride and Meldrum's acid. The prepared trione can be isolated, but in the scheme used, the crude product was used directly for the next step. Ethanol is used to convert the intermediate to the β-keto ester. Typical yields of the esters are 85% **1**, 82% **2**, 78% **3**, and 51% **4**; **4** was prepared in better yield by condensing the precursor ketone, which was prepared by the less desirable cadmium methyl alkylation (Cason and Rapoport, 1954) of the corresponding acid chloride, with diethyl carbonate. Alkylation of the resultant β-keto esters was completed with use of ethoxide–ethanol or sodium hydride–THF as the medium (Figure 1) and reaction conditions that favored monosubstitution (dilute solutions and slow addition of the halide). All yields are high, and some disubstituted product is formed. These latter products were not fully characterized and were ignored. Product analysis showed that monophenoxybenzyl attachment proceeds in better yields then that of the (benzylfuryl)-methyl addition. With the improvement in the ease of synthesis of the β-keto ester, the last obstacle to overcome involved the conversion of each substituted keto ester to the corresponding ketone. Several literature methods for decarbethoxylation were found to be unsatisfactory (Bailey and Daley, 1964; Lalancette and Lachance, 1970; Brieger and Spencer, 1971; Krapcho, 1973), and, as a consequence, another method was sought to complete the synthesis. In an earlier work, we found that treatment of several simple β-keto esters with a phase-transfer agent (PTA), hexadecyltrimethylammonium bromide, in dilute aqueous alkali afforded ketones in good yields, at lower temperatures (75–80 °C), and in relatively short reaction times (Mills, 1986). This method was used along with another in which the ketones are also produced in similarly good yields, at low reaction temperatures (80 °C) and short reaction times (1–2 h), by treatment with sodium hydride–1,2-dihydroxypropane (Aneja et al., 1983). Figure 1 describes the conversion of the alkylated acetates with the PTA–dilute potassium hydroxide and hydride reagents. Although the yields are not quantitative, they are greatly improved over any that were presented in the very early literature; for example, previous decarbethoxylation of **1a** required reflux in alkali for 24 h, and the resulting yield was only a few percent (Berteau et al., 1969).

All synthetic esters and ketones were evaluated by mass spectrometry, and all spectra were examined for selected ions that could be considered representative of each portion of the compound: the acyl and furylmethyl or phenoxybenzyl moieties. In general, each unsubstituted β-keto ester produced a molecular ion and exhibited strong scission α to the cyclopropane ring or to the isopropyl group (**1**–**4**), and chemical ionization confirmed the molecular weight assignments. Fragmentation of the β-keto esters (**1**–**4**) occurs characteristically between the carbonyl carbon and the cyclopropyl ring (m/e 123, 149, 163, 167). Only **2** failed to produce fragments containing the acyl ring plus the carbonyl moiety. Apparently, the latter lack of scission is not uncommon to these compounds and is further demonstrated in the methylene-linked pyrethroids. Fragments arising from cleavage adjacent to the ester group were not observed. Only **1** shows a loss of a carbethoxy fragment in the EI mode, while **3** yields the only ion representative of γ cleavage to the ester function.

Because the alkylated β-keto esters do not survive gas chromatography well, a direct, variably heated insertion probe was used for each analysis (1.5-A current removed the analyte from the probe). The EI spectra of the alkylated keto esters are consistent for the attachment of the alkyl group, and molecular ions confirm the products as monoalkylated β-keto esters. Fragments characteristic of the acyl portion (m/e 123, 149, 163, 167) are present for both the furylmethyl and phenoxybenzyl series, and ions m/e 171 and 183 establish the presence of the (benzylfuryl)methylene and the phenoxybenzyl structures in the respective series. The molecular weight assignments are supported by the appearance of $(M + 1)^{\cdot+}$ ions in each of the individual chemical ionization (methane) spectra. Analyses of the ketone EI patterns again confirm the acyl moieties with fragments at m/e 123/151, 149, 163, and 167 in both the **E** and **F** series. Compounds **5a**, **6a**, **7a**, and **8a** yield fragments representative of (benzylfuryl)methyl and (benzylfuryl)ethyl (m/e 171, 185) and **5a**, **7a**, and **8a** cleaved forming the (benzylfuryl)propionyl ion (m/e 213). Ketones **5a**–**8a** yield ions m/e 183 and 197 characteristic of the phenoxybenzyl ion. The molecular weight assignments garner further support from the chemical ionization data. Confirmation of β-keto ester synthesis, C-alkylation, and subsequent ketone formation is definitively shown by proton magnetic resonance analyses of the synthetic products. ^{1}H NMR data established that the geometry and stereochemistry of all the esters were the same as those of the starting acid. Although the data for the compounds are listed in the Experimental Section, the sample, graphic spectral information presented (Figure 2) is more demonstrative.

All β-keto esters and the subsequent ketones formed by decarbethoxylation generated similar spectral patterns for resonances produced from the vinyl, the β-ketomethine, and the α,β-ketomethylene protons; the alkylation of each

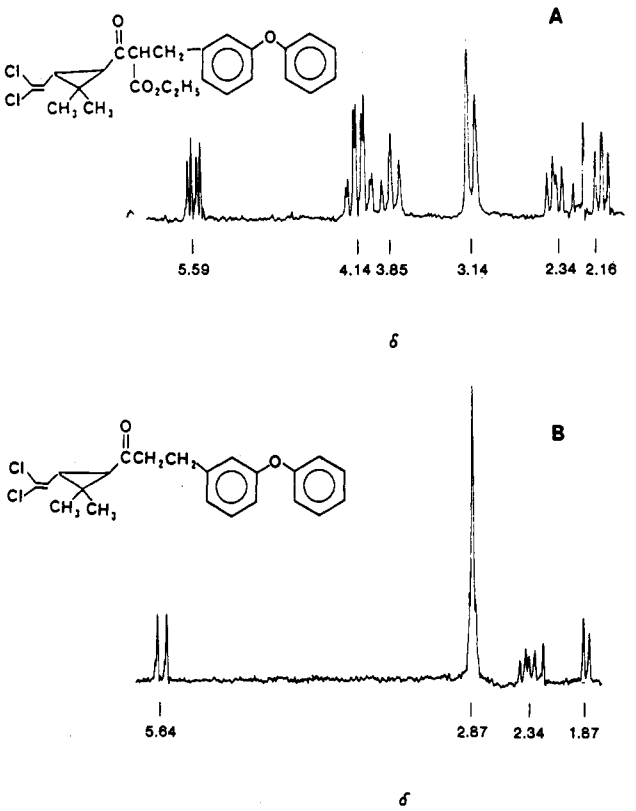


Figure 2. ^{1}H NMR spectra of (*E*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanes.

of the remaining β-keto esters caused a similar change. The vinyl proton resonance (Figure 2A) usually appears as a set of doublets, or a finely split and broadened doublet. Similarly, the ester methylene is changed to a pair of quartets. Both phenomena reflect the production of a new chiral center α to the carbonyl and also conclusively demonstrate carbon–carbon bond formation in the substituted products; the new chiral center (br t) appears at δ 3.85 and the β-methylene at δ 3.14 (d). In most of the β-keto esters (e.g., **1a**, **1b**, **2a**, **2b**) the methine triplet appeared as a defined triplet. In general, the pattern of the cyclopropane protons became more complex as a result of the new chiral center; in the alkyl-substituted vinyl analogues those patterns were complicated further. Following decarbethoxylation, all four mentioned spectral regions (Figure 2B) became simplified; the vinyl appears as a doublet, the ketomethylenes resonate as a broadened singlet or as a distorted triplet ($J \leq 0.5$ Hz), and the specific resonances for the α- and β-cyclopropane protons could be assigned (Figure 2B; δ 1.87 and 2.34, respectively) when not overlapped by other aliphatic resonances (e.g., **2b**, **3b**). ^{1}H NMR spectra for all the other preparations are similar in that the triplet for the ester α-ketomethine and the doublet for the methylene group have similar area shift assignments. These spectra also demonstrate the geometry *E* and stereochemistry *R,S* are retained through the reaction sequence.

The newly prepared pyrethroids (**5a–8b**), each a pair of optical isomers, were tested at the 100 ppm level and relative to *d*-(*E*)-phenothrin, against *Oncopeltus fasiatus* (large milkweed bug, LMB), *Tenebrio molitor* (yellow meal worm, YMW), a stored product pest, and *Spodoptera frugiperda* (fall army worm, FAW), a field pest. Generally, the screen shows these compounds elicit varied activity in the three different insect species and implies that some specificity may be related to certain structures. Prior to this examination (Table I), no data had been reported for

Table I. Insect Bioassay of Methylene-Linked Pyrethroids

	mortality/activity at 100 ppm[a]				
		yellow meal worm		milkweed bug	
compd	fall army worm larvae,[b,c] %	pupae	adult	larvae[d]	adult
1a	0 (66)	0	20	0	0
1b	0 (71)	0	100	0	0
2a	0 (70)	0	100	0	20
2b	0 (70)	0	100	0	20
3a	0 (80)	20	80	40	80
3b	0 (83)	0	70	0	20
4a	0 (75)	0	100	0	0
4b	0 (68)	0	100	0	0
5a	5 (74)	80	100	100	100
5b	30 (49)	20 (0.6)[e]	100	100	100
6a	0 (90)	0	80	0	100
6b	0 (84)	0	100	0	100
7a	80 (68)	100	100	100	100
7b	100 (00)	0	100	100	100
8a	50 (20)	0	70	0	100
8b	10 (10)	100	60	0	80
phenothrin	100 (00)	100	100	100	100

[a] Topical application. [b] First instar, diet application. [c] Relative antifeedent activity (percent of normal growth). [d] Fifth instar. [e] JH rating (scale 0.0–4.0).

the activity of the β-keto esters of any methylene-linked pyrethroid in these insects. Invocation of structure–activity relationships may account for the lack of interest in the earlier evaluation of these compounds. However, as the esters undergo natural decomposition, they then may behave as "proinsecticides" and yield active products. As a consequence, these esters were added to the biological assay to establish their initial activity. All keto esters (**1a–4b**) express no mortality in FAW larvae and no appreciable antifeedent behavior (less than 50% growth). Only ester **3a** showed some activity on the YMW pupae, while **1b–4b** expressed high morbidity and mortality in the adult insect. Again, pyrethroid **3a** showed acceptable toxicity toward the LMB, in both the adult and larval stages.

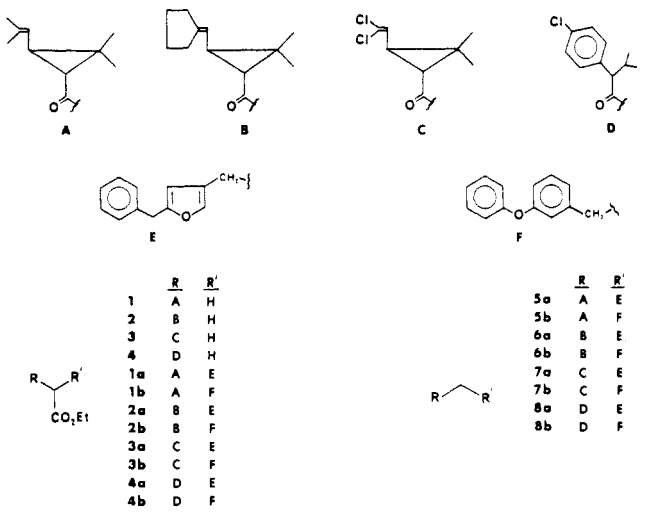
Ketones **7a**, **7b**, and **8a** adversely affected FAW larvae. The pupae of the YMW are very sensitive to ketones **5a**, **7a**, and **8b** while the entire series of ketones (**5a–8b**) produced high kill in the adult. Ketones **5a**, **5b**, **7a**, and **7b** are highly active in larval LMB, while all express high mortality (80–100%) in the adult insect.

In summary, this work documents the following: (1) Additional syntheses are now available for the decarbethoxylation of complex β-keto esters. (2) Methylene-linked pyrethroids can now be readily made and in good yields. (3) The ketones can be expected to exhibit reduced activity relative to the normal pyrethroid esters. (4) Ketone activity is varied in the test insects and appears to be least in the pupal or early larval stages.

EXPERIMENTAL SECTION

General Procedures. ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ or benzene-d_6 with tetramethylsilane as an internal reference from a Varian XL-100 spectrometer. IR spectra were recorded on a Perkin-Elmer Model 299B spectrometer and from chloroform solutions. Mass spectra were obtained from a Extrel Model ELQ-400-2 quadrupole instrument, and a GLC (Hitachi Model 663-30) or a variably heated direct insertion probe (DIP, EI: 70 eV, current program 0–1.5 A/s) was used for sample introduction; methane ($(2.2–2.4) \times 10^{-4}$ Torr) was employed as the reagent gas for chemical ionization spectroscopy. All solvents were ACS grade or better and were distilled from glass.

(*E*)-2,2-Dimethyl-3-(2-methylpropenyl)-, (*E*)-3-(Cyclopentylidenemethyl)-2,2-dimethyl-, and (*E*)-3-(2,2-



Dichlorovinyl)-2,2-dimethyl-1-carboxycyclopropane. Saponification of (*E*)-ethyl chrysanthemate (Shell Oil Co.) yielded the free acid that served as a source for fragment **A**; 50 g of ester in 750 mL of 80% ethanol–water that contained 15% potassium hydroxide by weight was stirred at room temperature for 10 h. The reaction was extracted twice with 100 mL of hexane, acidified with 6 N HCl, and then extracted with 250 mL of methylene chloride. The organic extract was washed twice with water (200 mL) and then dried ($MgSO_4$). After filtration and solvent removal in vacuo, the oil solidified on standing. Recrystallization from methylene chloride–hexane yielded the desired acid, mp 53 °C. Acids employed to generate fragments **B** and **C** were prepared in a similar manner from (*E*)-ethanomethrin (McLaughlin, Gromley, King Co.) and the *E,Z* ethyl ester (Aldrich Chemical Co.), respectively. The ester of the dichlorovinyl ester was saponified as described above, and the resulting *E,Z* acid was separated into each geometrical isomer by stirring the isolate in hexane overnight (1.0 g/10 mL); mp 96–98 °C (Burt et al., 1974). (*R,S*)-2-(4-Chlorophenyl)-3-methylbutanoic acid (structural fragment **D**) was purchased from Frinton Laboratories. ^1H NMR [δ (*J*, Hz)] data follow. Acid **A**: 1.13 (3 H, s, *gem*-methyl), 1.30 (3 H, s, *gem*-methyl), 1.23 and 1.29 (1 H, d set, α-carboxylmethine), 1.71 (3 H, s, vinyl methyl), 2.10 (1 H, br t, β-carboxylmethine), 4.10 (1 H, d, 6, finely split vinyl). **B**: 1.16 (3 H, s, *gem*-methyl), 1.31 (3 H, s, *gem*-methyl), 1.40 (1 H, d, 6, α-carboxylmethine), 1.65 (1 H, m, β-carboxylmethylene), 2.19 (8 H, m, α-cyclopentylmethylene), 5.07 (1 H, d, 7, finely split vinyl). **C**: 1.20 (3 H, s, *gem*-methyl), 1.32 (3 H, s, *gem*-methyl), 1.59 (1 H, d, 6, α-carboxylmethine), 3.27 (1 H, 3.27 q, β-carboxymethine, irr at 1.59 yields a doublet), 5.60 (1 H, d, 7, vinyl). **D**: 0.69 (3 H, d, 6, *gem*-methyl), 1.05 (3 H, d, 6, *gem*-methyl), 2.28 (1 H, m, *gem*-methylmethine), 3.13 (1 H, d, 10, benzylmethine), 7.25 (4 H, q, aromatic).

Acid Chloride Preparation. Each acid, 100 mM, was treated with thionyl chloride at room temperature or under reflux. Subsequent classical workup produced the desired acid chloride.

5-Benzyl-3-furylmethyl Bromide and 3-Phenoxybenzyl Bromide (Source of Fragments E and F). The halides were prepared by a literature method (Elliott et al., 1967). The isolated product was distilled. Fractions at 0.02 mm and 120–125 °C (90% yield) for the former and 95–104 °C (68% yield) for the later were isolated.

Data: MS, EI [*m/e* (rel intens)] 252 (13), 250 (13), 171 (100), 143 (44), 141 (31), 128 (80), 115 (38), 91 (38), 264 (24)/262 (24), 184 (20), 183 (100), 68 (10), 91 (13); ^1H NMR [δ (*J*, Hz)] 3.90 (2 H, s, benzylmethylene), 4.23 (2 H, s, furylmethylene), 6.02 (1 H, s, furyl), 7.28 (1 H, s, furyl), 7.28 (1 H, aromatic), 3.75 (2 H, s, benzylmethylene), 7.10 (9 H, m, aromatic).

General Methods for the Preparation of 1–4. Meldrum's acid (0.01 M) was dissolved in 75 mL of methylene chloride, and the reaction mixture was placed under nitrogen and brought to 0 °C with an ice bath; pyridine (0.02 M) was then added by means of a dropping funnel. The appropriate acid chloride (0.01 M) was added over a 15–30-min period to the vigorously stirred mixture. After the final addition, the solution was allowed to rise to room temperature and allowed to stand 3–24 h. The reaction was monitored by TLC (silica gel), and development solvents of 3% ethyl acetate and 10% ethyl acetate in hexane were used. Upon termination, the solvent was removed and 75 mL of ether was added (this prevented the formation of stable emulsions). The ether was then washed with 30 mL of 4 N HCl, 2% sodium bicarbonate, and distilled water saturated with sodium chloride. The dried ($MgSO_4$) organic phase was filtered and reduced to a light oil by solvent removal in vacuo. The yields were 85% **1**, 82% **2**, 78% **3**, and 51% **4**.

1: MS, EI/CI [*m/e* (rel intens)] 238 (4), 192 (1), 165 (3), 151 (8), 123 (100), 109 (21), 107 (18), 91 (13), 81 (41), 239 (9), 238 (4), 151 (20), 123 (100); ^1H NMR [δ (*J*, Hz)] 1.16 (3 H, s, *gem*-methyl), 1.32 (3 H, s, *gem*-methyl), 1.20 (3 H, t set, center of ester methyl), 1.72 (6 H, s, vinylmethyl); α-ketocyclopropylmethine hidden under the resonance), 2.10 (1 H, t, irr at 4.92 yields a doublet), 3.41 (2 H, s, a set due to the new chiral center), 4.23 (2 H, q, 6, ester methylene, set of quartets), 4.92 (1 H, br d, 8, vinyl).

2: MS, EI/CI [*m/e* (rel intens)] 264 (9), 194 (47), 183 (28), 172 (10), 161 (17), 151 (11), 150 (11), 149 (81), 135 (86), 134 (43), 265 (12), 245 (1), 219 (11), 183 (14), 135 (100), 107 (8); ^1H NMR [δ (*J*, Hz)] 1.16 (3 H, s, *gem*-methyl), 1.29 (3 H, s, *gem*-methyl), 1.28 (3 H, t, 8, ester methyl), 1.68 (4 H, m, β,β'-cyclopentylmethylene), 2.24 (4 H, m, α,α'-cyclopentylmethylene), 3.36 (2 H, s, methylene), 4.12 (2 H, q, 8, ester methylene), 5.52 (1 H, br d, vinyl).

3: MS, EI/CI [*m/e* (rel intens)] 280 (3), 278 (5), 193 (15), 191 (22), 173 (18), 167 (17), 164 (9), 129 (27), 127 (67), 115 (91), 111 (15), 109 (17), 91 (73), 281 (6), 280 (2), 279 (10), 193 (20), 191 (30), 167 (17), 165 (55), 164 (5), 163 (100), 115 (30); ^1H NMR [δ (*J*, Hz)] 1.20 (3 H, s, *gem*-methyl), 1.24 (3 H, s, *gem*-methyl), 1.29 (3 H, t, 6, ester methyl), 2.02 (1 H, d, 5, α-ketomethine), 2.44 (1 H, q, 5, β-ketomethine, fine splitting), 3.52 (2 H, s, α-ketomethylene), 4.22 (2 H, q, 7, ester methylene), 5.66 (1 H, d, 8, vinyl).

4: MS, EI/CI [*m/e* (rel intens)] 284 (17), 282 (51), 267 (3), 195 (13), 169 (34), 167 (100), 154 (4), 152 (12), 129 (3), 127 (5), 285 (25), 284 (22), 267 (3), 194 (13), 169 (34), 167 (100), 154 (4), 152 (12), 127 (25), 125 (72); ^1H NMR [δ (*J*, Hz)] 0.70 (3 H, d, 9, *gem*-methyl), 1.04 (3 H, d, 9, *gem*-methyl), 1.21 (3 H, t, 6, ester methyl, irr at 4.12 yields a singlet), 2.31 (1 H, m, *gem*-methylmethine), 3.18 (1 H, d, 10, benzylmethine), 3.66 (2 H, s, α-ketomethylene), 4.12 (2 H, q pr, ester methylene); 7.18 (4 H, q, aromatic).

Alternate β-Keto Ester Preparation of Ethyl (*R,S*)-2-[2-(4-Chlorophenyl)-3-methylbutanoyl]-acetate (4). *A. (R,S)-3-(4-Chlorophenyl)-4-methylpentan-2-one.* Cadmium(II) chloride (1.57 g) mixed in 50 mL of anhydrous ether was added to the Grignard reagent (made from 2.82 g of methyl iodide and 0.415 g of Mg) in 100 mL of anhydrous ether. After careful addition, the mixture was refluxed for 1.5 h. The ether was removed by codistillation with the slow addition of benzene; once all the ether was removed, the total volume of benzene was brought to 50 mL. The reaction was brought to reflux and

removed from the mantle, and the acid chloride (1.50 g), in 50 mL of solvent, was added rapidly; an ice bath was used to maintain the reaction under gentle reflux. After being stirred overnight, the reaction mixture was poured into 300 mL of cold 4 N HCl, and the organic phase was separated and washed once with 10% $NaHCO_3$ and 100 mL of water. The dried ($MgSO_4$) solution was filtered and reduced to a light oil. The oil was added to a preparative, silica gel dry column (1.5 cm × 30 cm) that was developed with 3% ethyl acetate in hexane. Appropriate fractions determined from analytical TLC analysis were combined, and the product was isolated after solvent removal: 0.98 g (74% yield); ^{1}H NMR [δ (J, Hz)] 0.67 (3 H, d, 6, *gem*-methyl), 0.98 (3 H, d, 6, *gem*-methyl), 1.07 (3 H, s, α-ketomethyl), 2.40 (1 H, m, α-ketomethine), 3.31 (2 H, d, 10, β-ketomethine), 7.23 (4 H, q, finely split aromatic); MS, EI [m/e (rel intens)] 212 (3), 210 (14), 195 (4), 169 (24), 168 (12), 167 (72), 151 (13), 139 (13), 127 (32), 125 (100), 111 (20), 97 (27).

B. Ethyl (R,S)-2-[2-(4-Chlorophenyl)-3-methylbutanoyl]acetate (4). Sodium hydride (0.207 g) was carefully added to 50 mL of anhydrous THF that was covered with nitrogen. The above ketone (2.00 g) dissolved in 20 mL of THF was added, and the solution was stirred for 30 min and then brought to reflux. Diethyl carbonate (5.0 g) was added dropwise, and the solution was refluxed for 25 h. The solvent was removed in vacuo, and the residue was taken up in damp ethyl acetate (75 mL). The organic phase was washed once with 0.1 N HCl (25 mL), once with 5% $NaHCO_3$ (25 mL), and with 25 mL of water. The product was isolated and purified as described above; 2.31 g. Mass and nuclear magnetic resonance spectra were identical with those of the product made via the Meldrum's acid route: IR, 1705, 1698 cm^{-1}.

Alkylation Procedures. A. In separate preparations and under protection from moisture, 1 g of compound **1–4** was added to a solution of an equivalent amount of sodium ethoxide in 150 mL of absolute ethanol; each addition was made over a 10-min period. After the reaction was stirred at 50–60 °C for 15 min, an equivalent quantity less 2% of halide, was added in a dropwise manner over 30–45 min. The reaction mixture was allowed to reflux until no further halide was observed by TLC (silica gel/3% ethyl acetate in hexane). Each reaction was processed as above and yielded **1a,b**, **2a,b**, and **3a,b**.

B. Sodium hydride (4.2 mM) was added to 50 mL of anhydrous THF. The mixture was brought to reflux, and an equimolar quantity of the keto ester (**1**, **3**, **4**) in 50 mL of solvent was slowly added over 45 min to the refluxing solution. The remainder of the workup was identical with that in part A, and products **1a,b**, **3a,b**, and **4a,b** were isolated. The following compounds (Figure 1), all colorless oils, were prepared.

(*E*)-1(*R*,*S*)-[3-(5-Benzyl-3-furyl)-2(*R*,*S*)-carbethoxypropionyl]-2,2-dimethyl-3-(2-methylpropenyl)-cyclopropane (1a): MS, EI/CI (m/e (rel intens)] 408 (7), 391 (6), 298 (22), 239 (5), 182 (2), 181 (3), 171 (9), 151 (10), 123 (10), 81 (11)/409 (38), 391 (22), 298 (22), 285 (14), 212 (13), 199 (14), 171 (9), 151 (10), 149 (28), 123 (100), 109 (13), 91 (22); ^{1}H NMR [δ (J, Hz)] 1.09 (3 H, s, *gem*-methyl), 1.13 (3 H, s, *gem*-methyl), 1.20 (3 H, t set, center, ester methyl), 1.84 (1 H, m, α-ketocyclopropylmethine), 2.25 (1 H, m, β-ketocyclopropylmethine), 1.64 (3 H, s, vinyl methyl), 1.69 (3 H, s, vinyl methyl), 2.91 (2 H, d, 7, ester β-methylene, irr at 3.70 collapses to singlet), 3.70 (1 H, t set, ester α-methine), 3.97 (2 H, s, benzylmethylene), 3.60 (2 H, q set, 7, ester methylene), 4.91 (1 H, br d, 8, vinylmethyl), 5.85 (1 H, s, furyl), 7.09 (1 H, s, furyl), 7.22 (5 H, m, aromatic); IR (cm^{-1}) 1740, 1700; yield 78%.

(*E*)-1(*R*,*S*)-[2(*R*,*S*)-Carbethoxy-3-(3-phenoxyphenyl)propionyl]-2,2-dimethyl-3-(2-methylpropenyl)cyclopropane (1b): MS, EI/CI (m/e (rel intens)] 420 (5), 405 (2), 251 (11), 223 (13), 183 (8), 151 (5), 124 (30), 123 (100), 107 (8), 81 (3)/421 (1), 420 (1), 403 (2), 297 (4), 251 (3), 183 (1), 151 (5), 124 (9), 123 (100), 109 (3), 81 (3); ^{1}H NMR [δ (J, Hz)] 1.06 (3 H, s, *gem*-methyl), 1.12 (3 H, s, *gem*-methyl), 1.10 and 1.20 (3 H, t set, ester methyl), 1.60 (3 H, s, vinylmethyl), 1.70 (3 H, s, vinylmethyl), 2.04 (1 H, d, α-vinylcyclopropylmethine), 2.27 (1 H, s, α-ketocyclopropylmethine), 3.16 (2 H, d, 8, ester β-methylene), 3.86 (1 H, set, ester α-methine), 4.12 (2 H, q, 8, ester methylene), 4.88 (1 H, br d, 8, vinyl), 7.10 (9 H, m, aromatic). IR (cm^{-1}) 1740, 1698; yield 85%.

(*E*)-1(*R*,*S*)-[3-(5-Benzyl-3-furyl)-2(*R*,*S*)-carbethoxypropionyl]-3-(cyclopentylidenemethyl)-2,2-dimethylcyclopropane (2a): MS, EI/CI [m/e (rel intens)] 422 (2), 257 (4), 216 (5), 183 (15), 171 (6), 149 (44), 141 (13), 128 (10), 112 (32), 111 (21), 107 (18), 106 (11), 105 (21), 91 (100), 85 (13), 83 (16), 77 (20)/423 (10), 422 (5), 217 (31), 216 (60), 187 (22), 171 (100), 143 (20), 129 (8), 113 (22); ^{1}H NMR [δ (J, Hz)] 1.14 (3 H, s, *gem*-methyl), 1.24 (3 H, s, *gem*-methyl), 1.26 (3 H, t, 7, ester methyl, set of triplets), 1.64 (5 H, m, β,β'-cyclopentylmethylene/cyclopropylmethine), 2.29 (5 H, m, α,α'-cyclopentylmethylene/cyclopropylmethine), 3.11 (2 H, d, ester β-methylene), 3.55 (2 H, s, benzylmethylene), 3.81 (1 H, t set, ester α-methine), 4.13 (2 H, q, 7, ester methylene), 5.03 (1 H, br d, 6, vinyl), 5.83 (1 H, s, furyl), 7.13 (1 H, s, furyl), 7.27 (5 H, aromatic); IR (cm^{-1}) 1735, 1695; yield 68%.

(*E*)-1(*R*,*S*)-[2(*R*,*S*)-Carbethoxy-3-(3-phenoxyphenyl)propionyl]-3-(cyclopentylidenemethyl)-2,2-dimethylcyclopropane (2b): MS, EI/CI [m/e (rel intens)] 446 (1), 347 (1), 183 (20), 176 (4), 150 (15), 149 (100), 121 (80), 119 (4), 111 (10), 107 (26), 93 (78), 91 (18), 81 (20)/448 (1), 447 (6), 446 (7), 429 (4), 183 (4), 150 (10), 149 (100), 135 (6); ^{1}H NMR [δ (J, Hz)] 1.09 (3 H, s, *gem*-methyl), 1.19 (3 H, s, *gem*-methyl), 1.21 (3 H, t, 6, ester methyl), 1.65 (5 H, m, α-cyclopentyl/allylic cyclopropylmethine), 1.84 (1 H, br m, α-ketocyclopropylmethine), 2.22 (4 H, br m, β-cyclopentylmethylene), 3.14 (2 H, d, 8, ester β-methylene), 3.84 (1 H, t, 7, ester α-methine, finely split, triplet set), 4.12 (2 H, q, ester methylene), 5.04 (1 H, d set, 2, vinyl), 7.12 (9 H, m, aromatic); IR (cm^{-1}) 1740, 1700; yield 92%.

(*E*)-1(*R*,*S*)-[3-(5-Benzyl-3-furyl)-2(*R*,*S*)-carbethoxypropionyl]-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane (3a): MS, EI/CI [m/e (rel intens)] 450 (2), 448 (4), 285 (56), 240 (15), 239 (100), 216 (9), 213 (8), 212 (52), 211 (30), 172 (30), 171 (53), 165 (14), 163 (18), 143 (36), 141 (13), 129 (16), 128 (51), 127 (21), 115 (21), 91 (87)/452 (6), 451 (21), 450 (14), 449 (36), 448 (8), 341 (9), 298 (12), 285 (82), 239 (18), 213 (15), 212 (100); ^{1}H NMR [δ (J, Hz)] 1.07 and 1.15 (3 H, s pr, *gem*-methyl), 1.16 and 1.22 (3 H, s pr, *gem*-methyl), 1.99 (1 H, q, α-ketocyclopropylmethine), 2.50 (1 H, m, β-ketocyclopropylmethine), 2.92 (2 H, d, 8, ester β-methylene), 3.72 (1 H, t set, ester α-methine), 3.88 (2 H, s, benzylmethylene), 4.16 (2) q set, 8, ester methylene), 5.58 (1 H, d, 8, vinyl), 5.81 (1 H, s, furyl), 7.10 (1 H, s, furyl), 7.26 (5 H, aromatic); IR (cm^{-1}) 1740, 1698; yield 80%.

(*E*)-1(*R*,*S*)-[2(*R*,*S*)-Carbethoxy-3-(3-phenoxyphenyl)propionyl]-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane (3b): MS, EI/CI [m/e (rel intens)] 462 (10), 460 (2), 297 (57), 251 (100), 223 (72), 183 (30), 165 (10), 163 (16), 91 (25)/463 (22), 461 (32), 445 (33), 443 (52), 297 (100), 251 (42), 223 (30), 165 (4), 163 (12); ^{1}H NMR

[δ (J, Hz)] 1.05 and 1.09 (3 H, t set, *gem*-methyl), 1.13 and 1.17 (3 H, t set, *gem*-methyl), 1.21 (3 H t, 8, ester methyl), 2.20 (2 H, m, center of cyclopropylmethine), 3.15 (2 H, br d, keto β-methylene), 3.86 (1 H, t set, 8, ester α-methine, irr at δ 3.15 yields a singlet), 4.15 (2 H, q pr, 6, ester methylene), 5.61 (1 H, d pr, 3, vinyl), 7.06 (9 H, m, aromatic); IR (cm^{-1}) 1735, 1698; yield 75%.

2(*R*,*S*)-Carbethoxy-1-(5-benzyl-3-furyl)-4(*R*,*S*)-(4-chlorophenyl)-5-methylhexan-3-one (4a): MS, EI/CI [*m*/*e* (rel intens)] 454 (2), 452 (4), 285 (8), 284 (50), 282 (16), 258 (12), 257 (15), 183 (20), 172 (4), 171 (11), 170 (4), 169 (30), 167 (87), 129 (30), 125 (100)/455 (35), 454 (38), 453 (100), 452 (36), 375 (4), 286 (5), 285 (37), 284 (25), 283 (57), 282 (50), 257 (20), 195 (12), 172 (20), 171 (27), 169 (92), 125 (40); ^1H NMR [δ (J, Hz)] 0.62 (3 H, dd, 12, *gem*-methyl, two sets of doublets), 0.96 (3 H, dd, 12, *gem*-methyl, two sets of doublets), 1.19 (3 H, t, 6, ester methyl), 2.32 (1 H, m, *gem*-methyl methine), 2.82 (2 H, br d, ester β-methylene), 3.06 (2 H, s, benzylmethylene), 3.80 (1 H, s, furyl), 3.34 (1 H, d, 4, α-ketomethine), 3.45 (1 H, t, β-ketomethine, irr at δ 2.82 yields a singlet), 4.11 (2 H, q pr, ester methylene, irr at δ 1.21 yields a singlet), 4.32 (1 H, s, furyl), 7.20 (9 H, m, aromatic); IR (cm^{-1}) 11735, 1700; yield 77%.

2(*R*,*S*)-Carbethoxy-4(*R*,*S*)-(4-chlorophenyl)-5-methyl-1-(3-phenoxyphenyl)hexan-3-one (4b): MS, EI/CI [*m*/*e* (rel intens)] 466 (5), 464 (14), 297 (42), 251 (83), 223 (44), 167 (49), 127 (33), 125 (100)/467 (5), 465 (13), 464 (34), 419 (22), 297 (94), 223 (43), 169 (24), 167 (100); ^1H NMR [δ (J, Hz)] 0.60 (3 H, d, 7, *gem*-methyl), 0.93 (3 H, d, 7, *gem*-methyl), 1.10 (3 H, t set, ester methyl), 2.33 (1 H, m, *gem*-methyl methine), 2.98 (2 H, d, 8, ester β-methylene), 3.28 (1 H, d, 10, α-ketomethine), 3.75 (1 H, t set, ester α-methine), 4.12 (2 H, q set, ester methylene), 6.88 (13 H, m, aromatic); IR (cm^{-1}) 1740, 1700; yield 96%.

Decarbethoxylation Procedures. A. A stock solution of reagent was made by dissolving 10% (w/v) hexadecyltrimethylammonium bromide in 10% (w/v) potassium hydroxide in water. The keto ester (1 g) dissolved in a minimum amount of heptane was added to 50 mL of the reagent. the reaction mixture was sonicated at 80 °C and monitored by analytical TLC (usually the reaction was completed at 90 min). The cooled solution was acidified with dilute hydrochloric acid and then extracted twice with 25 mL of ethyl acetate. The combined organic extracts were washed once each with 5% sodium bicarbonate and a saturated sodium chloride solution. After drying ($MgSO_4$), filtration, and removal of the solvent, the isolate was purified by dry-packed silica gel column chromatography that employed ethyl acetate (3–10%) in hexane. Each ketone was a colorless oil or semisolid at −4 °C.

B. A stock reagent of anhydrous 1,2-dihydroxypropane containing 0.5 g of 60% sodium hydride/20 mL was made by heating the mixture for 20 min after the initial exothermic reaction. Upon cooling, 20 mL of the reagent was added to 1 g of the β-keto ester, and the resulting mixture was heated at 80–90 °C under sonication until analytical TLC indicated that the reaction was complete (usually 90 min). The mixture was then poured into acidified ice water that was extracted twice with ether (60-mL total volume). The remainder of the workup followed the one used in procedure A.

(*E*)-1(*R*,*S*)-[3-(5-Benzyl-3-furyl)propionyl]-2,2-dimethyl-3-(2-methylpropenyl)cyclopropane (5a): MS, EI/CI [*m*/*e* (rel intens)] 336 (26), 321 (8), 226 (53), 213 (14), 212 (14), 185 (10), 171 (51), 143 (13), 128 (17), 123 (100)/337 (7), 319 (1), 229 (3), 226 (13), 213 (10), 171 (10), 123 (100); ^1H NMR [δ (J, Hz)] 1.14 (3 H, s, *gem*-methyl), 1.20 (3 H, s, *gem*-methyl), 1.65 (3 H, s, vinylmethyl), 1.68 (3 H, s, vinylmethyl α-ketomethine hidden under resonance), 2.22 (1 H, m, β-ketocyclopropyl methine), 2.68 (4 H, br s, α,β-ketomethylene), 3.40 (2 H, s, benzylmethylene), 4.80 (1 H, br d, 6, vinyl), 5.88 (1 H, s, furyl), 7.10 (1 H, s, furyl), 7.26 (5 H, br s, aromatic); IR (cm^{-1}) 1705; yield 85%.

(*E*)-2,2-Dimethyl-3-(2-methylpropenyl)-1(*R*,*S*)-[3-(3-phenoxyphenyl)propionyl]cyclopropane (5b): MS, EI/CI [*m*/*e* (rel intens)] 348 (8), 333 (4), 293 (2), 225 (39), 197 (29), 184 (13), 183 (61), 124 (63), 123 (100)/350 (25), 349 (100), 331 (4), 291 (11), 184 (13), 183 (42); ^1H NMR [δ (J, Hz)] 1.10 (3 H, s, *gem*-methyl), 1.14 (3 H, s, *gem*-methyl), 1.25 (1 H, d, finely split, 7, α-ketomethine), 2.10 (4 H, m, cyclopentylmethylene), 2.85 (4 H, br s, α,β-ketomethylene), 5.03 (1 H, br d, 8, vinyl), 7.05 (9 H, m, aromatic); IR (cm^{-1}) 1705; yield 87%.

(*E*)-1(*R*,*S*)-[3-(5-Benzyl-3-furyl)propionyl]-3-(cyclopentylidenemethyl)-2,2-dimethylcyclopropane (6a): MS, EI/CI [*m*/*e* (rel intens)] 352 (2), 257 (9), 179 (6), 171 (100), 149 (25), 141 (20), 135 (10), 128 (70), 115 (38), 111 (5), 105 (5), 91 (38)/353 (6), 352 (3), 341 (7), 252 (12), 217 (10), 216 (16), 188 (11), 177 (17), 171 (100), 91 (25); ^1H NMR [δ (J, Hz) 1.12 (3 H, s, *gem*-methyl), 1.20 (3 H, s, *gem*-methyl), 1.64 (6 H, br m, β,β′-cyclopentylmethylene and cyclopropylmethine), 2.22 (4 H, br m, α,α′-cyclopentylmethylene), 2.68 (4 H, br s, α,β-ketomethylene), 3.88 (2 H, s, benzylmethylene), 5.62 (1 H, br d, 6, vinyl, finely split), 5.86 (1 H, s, furyl), 7.12 (1 H, s, furyl), 7.24 (5 H, aromatic); IR (cm^{-1}) 1705; yield 84%.

(*E*)-3-(Cyclopentylidenemethyl)-2,2-dimethyl-1-(*R*,*S*)-[3-(3-phenoxyphenyl)propionyl]cyclopropane (6b): MS, EI/CI [*m*/*e* (rel intens)] 374 (22), 228 (49), 225 (14), 197 (22), 184 (100), 183 (96), 181 (19), 153 (22), 149 (45), 135 (95), 134 (67)/376 (7), 375 (37), 374 (47), 357 (8), 229 (12), 184 (56), 183 (78), 149 (14), 135 (100), 134 (11); ^1H NMR [δ (J, Hz)] 1.05 (3 H, s, *gem*-methyl), 1.09 (3 H, s, *gem*-methyl), 1.63 (4+ H, m, β,β′-cyclopentylmethylene/cyclopropylmethine), 2.24 (4+ H, m, α,α′-cyclopentylmethylene/cyclopropylmethine), 2.84 (4 H, br s, α,β-ketomethylene), 5.02 (1 H, br d, 8, vinyl), 7.10 (9 H, m, aromatic); IR (cm^{-1}) 1705; yield 86%.

(*E*)-1(*R*,*S*)-[3-(5-Benzyl-3-furyl)propionyl]-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane (7a): MS, EI/CI [*m*/*e* (rel intens)] 378 (7), 376 (3), 361 (6), 226 (10), 213 (60), 185 (21), 172 (31), 171 (100), 165 (11), 163 (15), 143 (13)/379 (37), 378 (27), 377 (47), 376 (23), 213 (100), 199 (10), 185 (15), 172 (9), 171 (15), 165 (9), 163 (16); ^1H NMR [δ (J, Hz)] 1.17 (3 H, s, *gem*-methyl), 1.22 (3 H, s, *gem*-methyl), 1.85 (1 H, d, 5, α-ketocyclopropylmethine), 2.30 (1 H, m, β-cyclopropylmethine), 2.70 (4 H, br s, α,β-ketomethylene), 3.90 (2 H, s, benzylmethylene), 5.61 (1 H, s, 7, vinyl), 5.86 (1 H, s, furyl), 7.09 (1 H, s, furyl), 7.25 (5 H, br s, aromatic); IR (cm^{-1}) 1715; yield 74%.

(*E*)-3-(2,2-Dichlorovinyl)-2,2-dimethyl-1(*R*,*S*)-[3-(3-phenoxyphenyl)propionyl]cyclopropane (7b): MS, EI/CI [*m*/*e* (rel intens)] 388 (1), 226 (14), 225 (100), 197 (96), 184 (11), 183 (86), 129 (3), 127 (5)/391 (24), 389 (42), 353 (9), 226 (13), 225 (100), 197 (22), 183 (33), 165 (6), 164 (5), 91 (38); ^1H NMR [δ (J, Hz)] 1.12 (3 H, s, *gem*-methyl), 1.19 (3 H, s, *gem*-methyl), 1.86 (1 H, d, 6, α-ketomethine), 2.36 (1 H, m, 6, β-ketomethine, d with irr at δ 5.61), 2.85 (4 H, br s, α,β-methylene), 5.61 (1 H, d, 8, vinyl), 7.09 (9 H, m, aromatic); IR (cm^{-1}) 1715; yield 71%.

(*R*,*S*)-1-(5-Benzyl-3-furyl)-4-(4-chlorophenyl)-5-methylhexan-3-one (8a): MS, EI/CI [*m*/*e* (rel intens)] 382 (1), 380 (6), 213 (100), 197 (5), 195 (15), 185 (3), 169 (38), 167 (90), 127 (14), 125 (52), 174 (15), 171 (28), 89 (21), 87 (8)/385 (3), 384 (1), 383 (16), 382 (4), 213 (100), 171 (35),

169 (26), 167 (75), 127 (15), 125 (60), 87 (2); ^{1}H NMR [δ (J, Hz)] 0.54 (3 H, d, 6, *gem*-methyl), 0.96 (3 H, d, 6, *gem*-methyl), 2.03 (2 H, s, benzylmethylene), 2.35 (1 H, m, *gem*-methylmethine, irr at δ 2.35 collapses *gem*-methyl to a singlet), 2.65 (4 H, br s, α,β-ketomethylene), 3.26 (1 H, d pr, 10, benzylmethine, irr at δ 2.35 yields singlet pr), 5.71 (1 H, s, furyl), 6.95 (1 H, s, furyl), 7.20 (4 H, q, finely split, aromatic); IR (cm^{-1}) 1710; yield 85%.

(*R*,*S*)-4-(4-Chlorophenyl)-5-methyl-1-(3-phenoxyphenyl)hexan-3-one (8b): MS, EI/CI [m/e (rel intens)] 394 (2), 392 (5), 226 (17), 225 (100), 198 (10), 197 (49), 184 (12), 183 (83), 127 (23), 126 (12), 125 (69), 115 (18), 103 (12), 91 (35), 77 (29)/395 (16), 394 (15), 393 (50), 392 (10), 271 (18), 225 (28), 211 (12), 209 (16), 183 (11), 153 (100), 77 (60); ^{1}H NMR [δ (J, Hz)] 0.62 (3 H, d, 6, *gem*-methyl), 0.92 (3 H, d, 6, *gem*-methyl), 2.41 (1 H, m, α-*gem*-methylmethine), 2.81 (4 H, br m, α,β-ketomethylene), 3.25 (1 H, d, 10, α-ketomethine), 7.01 (13 H, m, aromatic); yield 78%.

Insect Bioassays. Each test compound was dissolved in acetone/DMSO (1:1, v/v) to produce a formulation concentration of 100 μg/μL. Topical application was performed with a 1-μL calibrated glass micropipet, and 1 μL of the formulation was applied ventrally on the last three abdominal segments of each of five adults, male and female (large milkweed bug adult and 5th instar, yellow meal worm adult and pupae). Mortality and morbidity were recorded after 72 h.

Feed additive tests on the fall army worm were performed with the same formulation as described above. Each 100 g of standard hot diet containing 100 μL of the formulation was poured into one 1-oz. cup and allowed to cool. First instar larvae were weighed and mortality or antifeedant activity was noted after 7 days. The mode of action may be by ingestion, contact, or vapor.

Registry No. (±)-**1a**, 118713-94-3; (±)-**1b**, 118760-37-5; (±)-**2a**, 118760-38-6; (±)-**2b**, 118760-39-7; (±)-**3a**, 118760-40-0; (±)-**3b**, 118713-95-4; **4a**, 113674-26-3; **4b**, 118713-96-5; (±)-**5a**, 118713-97-6; (±)-**5b**, 118713-98-7; (±)-**6a**, 118713-99-8; (±)-**6b**, 118714-00-4; (±)-**7a**, 118714-01-5; (±)-**7b**, 118714-02-6; (±)-**8a**, 118714-03-7; (±)-**8b**, 118714-04-8; (±)-A-OEt, 15543-65-4; (±)-A-OH, 705-16-8; (±)-A-Cl, 34909-52-9; (±)-B-OH, 22521-75-1; (±)-B-Cl, 22451-97-4; (±)-C-OEt, 63142-57-4; (±)-(*Z*)-C-OEt, 63142-56-3; (±)-C-OH, 55701-07-0; (±)-(*Z*)-C-OH, 55701-06-9; (±)-C-Cl, 66182-41-0; (±)-D-OH, 55291-27-5; (±)-D-Cl, 69979-37-9; (±)-D-Me, 118713-93-2; E, 51632-16-7; F, 33486-18-9; (±)-1, 118713-89-6; (±)-2, 118713-90-9; (±)-3, 118713-91-0; (±)-4, 118713-92-1; (±)-(*E*)-ethanomethrin, 26769-72-2; Meldrum's acid, 2033-24-1.

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