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[2+3] DIHYDROFURAN ANNULATION VIA VINYLOXIRANATION OF CARBONYL COMPOUNDS

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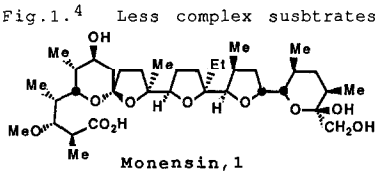
Abstract: Aldehydes were found to undergo facile stereoselective vinyloxiranation with the lithium dienolate of ethyl 2-bromocrotonate (12) at low temperature. The resulting vinyloxiranes were transformed thermolytically to functionalized dihydrofurans. An operational comparison of this heterocyclic annulation is made with its carbocyclic counterpart, the [2+3] cyclopentene annulation, and the potential for a general dihydrofuran synthesis in either a racemic or an asymmetric fashion is addressed.

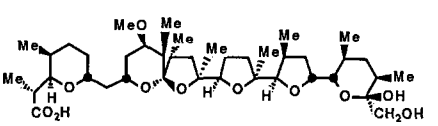
Introduction

The general design of five-membered ring compounds has been the mainstay of our program for some time. A system-oriented approach was implemented for the efficient syntheses of fused cyclopentanoids[2] and annulated pyrrolines[3] by [2+3] or [4+1] annulations. These annulations are based on the additions of ester dienolates equipped with a leaving group at the α-carbon to enones or imines in the former case and on the diene/carbenoid or diene/azide cycloaddition in the latter.

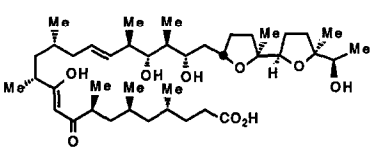
An extension of such annulations to furanoid compounds is desirable, as it opens new access to such targets as monensin (1), nigericin (2), ionomycin (3), and other natural products containing repeating tetrahydrofuran units, Fig.1.[4] Less complex susbtrates containing only two furan nuclei are



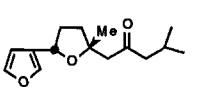
Monensin, 1



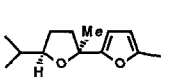
Nigericin, 2



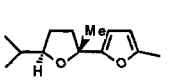
Ionomycin, 3



Ipomeamarone, 4

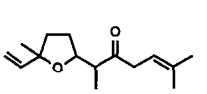


5a

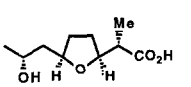


5b

Tobacco norsesquiterpenes



Davanone, 6



Nonactic acid, 7

Figure 1.

ipomeamarone (4)[5] and the norsesquiterpenoids (5) isolated from certain tobacco species.[6] Finally, the 2,5-substitution pattern of the tetrahydrofuran ring inherent in most polyether antibiotics is also found in

the mononuclear systems such as davanone (**6**),[7] and nonactic acid (**7**).[8] This substitution pattern is a direct reflection of the biogenetic "epoxide cascade," a process that has sometimes been mimicked in synthetic approaches to these materials. We noticed that this 2,5-disubstitution could easily be accessed via thermal rearrangement of the appropriate vinyloxirane **8**, Fig. 2.

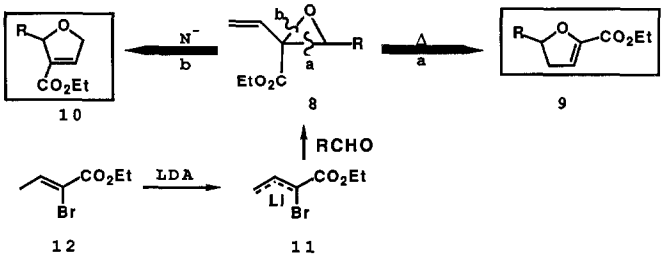


Figure 2.

Several features of this strategy deserve comment in the context of a synthetic design aimed at the polyether antibiotics. First, the acrylate in **9** can be functionalized through reductive alkylation. Second, the ester in **9** can be reduced to generate the aldehyde group in **13** and thus set the stage for the repetition of this process to prepare two connected furanoid units such as **14**, Fig. 3. Third, this iterative process can then be repeated to arrive at the appropriately functionalized polyether segment of the antibiotics mentioned above. The control of stereochemistry during any

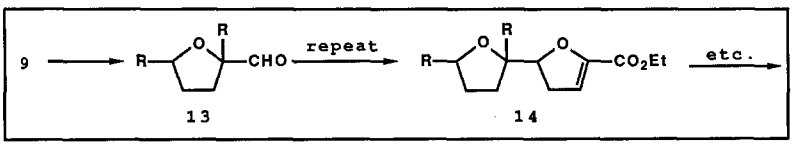


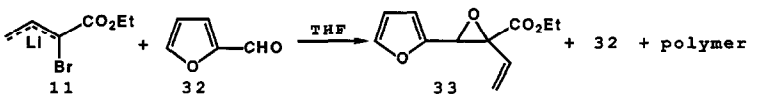
Figure 3.

alkylation step is crucial, as is the eventual asymmetric synthesis of these substrates. The first objective of this methodology is therefore the efficient preparation of the dihydrofurans of type **9** via thermal rearrangement (path **a**, Fig. 2) of appropriate vinyloxiranes of type **8** prepared from the addition of dienolate anion **11** to various carbonyl substrates. The second objective is the investigation of alternative modes of vinyloxirane opening such as path **b**, Fig. 2, brought about by sequential nucleophilic opening of the vinyloxirane in an S_N2' fashion and the intramolecular alkylation of the resulting allylic halides. This process would furnish a 2,3-disubstituted dihydrofuran **10**, whose pattern is also ubiquitous in the furanoid natural products. In this manuscript, we report on the initial findings concerning the feasibility of the [2+3] dihydrofuran annulation and its potential applications to the total synthesis of polyfuranoid natural products.

Results and Discussion

Following a preliminary report on the condensation of lithio-dienolates with carbonyl substrates,[9] we expanded the reaction to include aldehydes and ketones. During these investigations, it became evident that lithio-dienolate **11** was extremely sensitive to anionic polymerization.[10] In retrospect, we also discovered that when the reaction was performed at -78 °C, the yields of vinyloxiranes (and of vinylcyclopropanes also) were erratic because of the above mentioned polymer, whose amounts seemed to be dependent on the temperature, time, and reactant concentration of the reaction. A study was performed with 2-furaldehyde to optimize the yields of the vinyloxiranes. The results are shown in Table 1.

Table 1. Optimization of vinyloxiranation of 2-furaldehyde

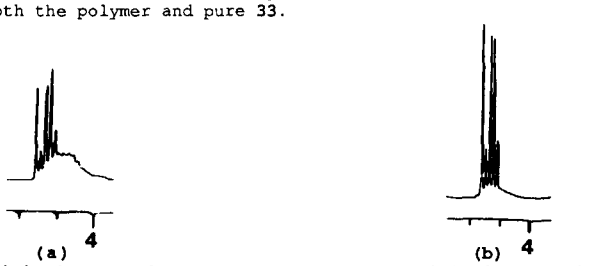


11 32 33

Entry	Mode of addition of 12[1]	32	Conc. of 11	Time, h	Temp., °C	Composition[2] 33 (%)	32 (%)	polymer[2]
1	neat, rt	neat, rt	1.0 M	0.66	-78	48	52	73
2	3 M, THF, -78 °C	neat, rt	1.0 M	1.0	-78 to -45	62	38	56
3	3 M, THF, -90 °C	neat, rt	1.0 M	1.5	-90 to -40	61	39	36
4	0.3 M, THF, -78 °C	neat, rt	0.2 M	1.0	-78 to -40	67	33	43
5	0.3 M, THF, -90 °C	neat, rt	0.2 M	1.5	-90 to -50	87	13	43
6	0.3 M, THF, -90 °C	1.0 M, -90 °C	0.2 M	1.5	-90 to -50	85	15	21
7	0.3 M, THF, -95 °C	1.0 M, -95 °C	0.2 M	2.0	-95 to -45	89	11	18
8	0.3 M, THF, -95 °C	1.0 M, -95 °C	0.2 M	2.0	-95 to rt	unknown		18
9	0.3M, THF, -95°C	1.0 M, -110°C	0.2 M	2.5	-105 to -60	89	11	18

[1] LDA was generated by adding a 2.1 M solution in hexane of n-BuLi to neat diisopropyl amine at 0 °C.

[2] The relative amount of polymer is estimated in % of excess integration of the quartet at δ = 4.1 ppm, corresponding to the methylene of the ethyl ester in both the polymer and pure **33**.



(a) Unoptimized, entry 1 (b) Optimized, entry 9

Figure 4.[3]

[3] The singlet at d=4.17 ppm corresponds to the oxirane H.

The best yields of polymer-free product[10,11] were obtained when the anion was generated at or below -100 °C in THF and the subsequent solution kept at or below -100 °C for 10 to 15 min prior to and throughout the addition of the aldehyde. These optimized conditions were later found applicable to the

vinylcyclopropanation sequences with enones as well.[11] (See Fig. 4 for comparison of NMR spectra.) The isolated yields of the vinyloxiranes are lower than expected due to their decomposition on silica gel. In most cases purification of the crude vinyloxiranes is not necessary and the crude product can be pyrolyzed directly.

Several simple aldehydes were converted to vinyloxiranes by means of this procedure (Table 2).[12] In all cases, only one of the two possible stereoisomers was formed. As the stereocenters contained within the vinyloxiranes were to converge at the sp^2 carbon of the dihydrofuran upon pyrolysis, no attempt was made at this time either to control this process or to provide exact stereochemical assignment. Based on analogies with the aldol-condensation models, the anti adduct of **8** would be expected from the Z dienolate and the *syn*-**8** (syn implies a cis orientation of the vinyl and R groups) should arise from the E species,[13] via transition state **8a** and alkoxyhalide **8b**, Fig. 5. While we do not, at the moment, know the precise composition of dienolate **11**, several observations need to be mentioned. (We use the E/Z convention where the metal takes priority over other groups since it is the alkoxide that determines, by its interaction with solvents or HMPA, the E/Z ratio.)

First, the dienolates are generated from either an E/Z mixture of 2-bromocrotonate **12** or from a distilled **12**, which equilibrated to the E form. Second, the generation of dienolate **11** with or without HMPA had no effect on the stereochemical outcome of the vinyloxiranation. The consistent production of only one isomer, *syn*-**8**, (identified by NOE experiments) seems to suggest either that the reaction proceeds from the E dienolate manifold only or that there is dienolate equilibration through mechanisms other than proton abstraction. The mechanism of dienolate formation from crotonates has been investigated in some detail.[14,15,16] It appears that crotonate-type dienolates prefer form **11a**, as shown by Kende[13], and extrapolation to bromocrotonate **12** could be made based on this analogy, Fig. 5. Rathke[14] and

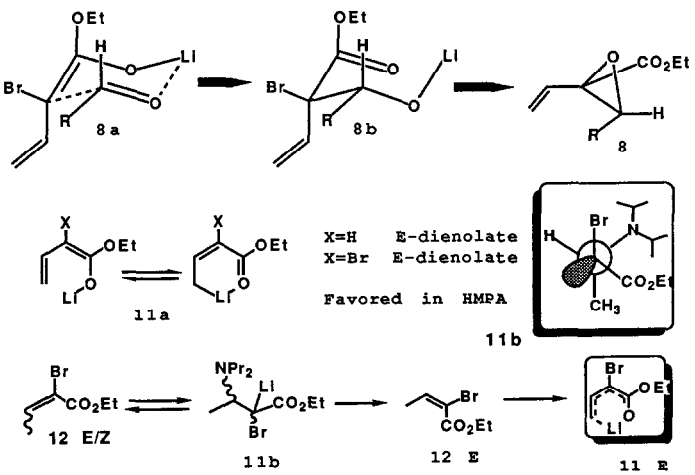


Figure 5.

Schlessinger[15] addressed the dienolate formation of simple crotonates. It seems reasonable to postulate the enolate equilibration via LDA addition-elimination in order to explain the formation of only the E species. Because HMPA is known to favor formation of the Z species in ketone enolates, (i.e., E species of 2-bromocrotonate) and because there was no change in stereochemistry between reactions with HMPA and those without, we could assume that the Z dienolate in its cyclic form **11a** was already present, presumably through equilibration of the E species via LDA-adduct **11b**. What remains to be done are trapping experiments and low-temperature NMR studies in order to prove the stereochemical identity of **11**. A detailed investigation of the stereochemical details of this process will be undertaken as a separate issue. As only one stereoisomer of **8** was obtained, the potential for asymmetric induction during the vinyloxiranation process will be addressed at that time with a chiral auxiliary group approach.

To approach dihydrofuran synthesis, vinyloxiranes of type **8** were prepared from dienolate anion **11**, and the modes of their rearrangements examined. Of the two possible bonds that are susceptible to thermolytic cleavage, bond **a** would be expected to undergo scission and generate either biradical **16** or zwitterion **17** (Fig. 6). A review of the literature available on the

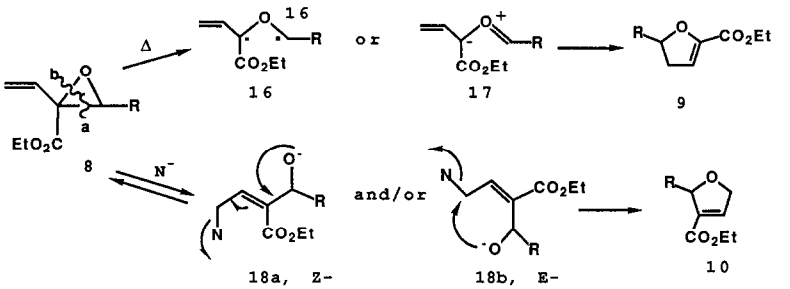


Figure 6.

vinyloxirane rearrangement suggested that zwitterionic intermediates of type **17**[16] may be more likely, although biradical mechanisms have also been postulated.[17] Thermal rearrangements of vinyloxiranes in the context of dihydrofuran preparation have been studied mechanistically,[16,17] as have the rearrangements of oxiranes substituted with a diene system[18], enyne system[19], divinyl systems capable of Cope-type rearrangement,[20] or vinyl-acetylene system in which a Cope-like rearrangement is also possible.[21] Most studies agree on the intermediacy of ylides of type **17** and their electrocyclic closures (4e, 6e or 8e, depending on the extent of conjugation). The diradical cleavage of the C–O bond in oxiranes is favored in those processes that lead to fragmentation,[17b] whereas the ylide mechanism seems better suited to explain the formation of dihydrofurans,[16] vinyldihydrofurans or oxepines,[18,20] and vinylfurans[19] from appropriately substituted precursors. In particular, the kinetics of the Cope-type rearrangements has been studied, and mechanistic distinctions between gas-phase and liquid-phase thermolyses have been made.[17a,20] The rate of racemization for optically active vinyloxiranes has been determined to be faster than the corresponding

dihydrofuran rearrangement.[17b] A retro-ene or [1,5]-homodienyl shift becomes operative in vinyloxiranes bearing a cis relationship between an alkyl and a vinyl group,[16b] in analogy with such processes in alkylvinylcyclopropanes.[22] In one case a carbene intermediate has also been advanced to explain vinylfuran formation from an enyne system.[19a] The kinetics of the Cope-type isomerizations has been studied, and diradical intermediates have been proposed to explain cis/trans isomerization of divinyloxiranes and the resulting distribution between oxepines and vinyldihydrofurans respectively.[20a,b] Only one case of dihydrofuran formation from a vinyloxirane containing an ester group on the vinyl moiety was reported.[16c] In the case of ester substitution at the oxirane portion, as in all of the vinyloxiranes studied here, it was anticipated that zwitterionic intermediates of type **17** would be even more favored, provided the nature of the R group would not override the effect of the carboxylate by preferential stabilization of a radical intermediate. From a purely synthetic viewpoint, the exact nature of the intermediate is not important, as either lead to 2,5-difunctionalized dihydrofurans.

Interesting control of regiochemistry becomes available by examining the nucleophilic opening modes of vinyloxirane **8**. Excluding the normal epoxide opening, and considering only the S_N2' allylic opening, two isomers of allylic alcohols are possible, Fig. 6. The literature suggests that the control of the stereochemistry in these openings is possible[23] with simple alkyl-substituted vinyloxiranes. The presence of the carbethoxy group directly on the oxirane ring introduces new parameters for consideration: electronic control, stable chromophore formation, steric hindrance, etc., in analogy with vinylcyclopropane opening and the known S_N2' alkylation of the resulting allylic systems[24]. Although additions of nucleophiles to systems such as **8** have not been reported, we expected such opening to proceed as shown in Fig. 6. Z Isomer **18a** would be expected to regenerate the starting vinyloxirane system, while E isomer **18b** would undergo ring closure to the 2,3-disubstituted dihydrofuran **10**.

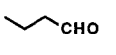
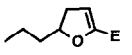
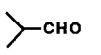
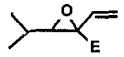
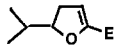
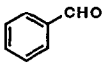
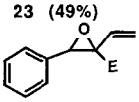
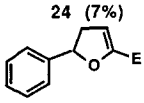
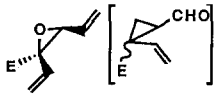
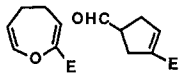
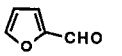
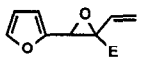
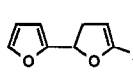
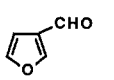
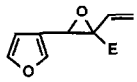
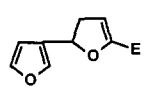
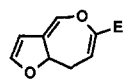
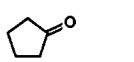
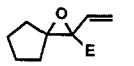
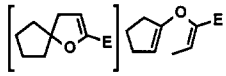
The precise mechanism of the nucleophilic opening of vinyloxiranes, because of its complexity, is being investigated separately.[25] We concentrated our efforts on the thermolytic rearrangements of vinyloxiranes in the context of access to repeating furanoid units that conform to the 2,5-substitution patterns found in such natural products as monensin (**1**), ipomeamarone (**4**), and others, portrayed in Fig. 1. The two substitution patterns (2,5- and 2,3-) are ubiquitously found in nature as a result of biogenesis of furanoid-type natural products.

The vinyloxiranes were evaporated through a horizontally situated Vycor tube in the temperature range of 500-550 °C and, in some cases, excellent yields of dihydrofurans were isolated. The results are shown in Table 2. In most cases, complete conversions to the corresponding dihydrofurans were observed after a single pyrolysis. In the case of vinyloxirane **23**, the recycling of the crude pyrolysate containing unrearranged starting material led to improvement in yield. On the other hand, recycling of the crude pyrolysis mixture containing **20** and **21** did not improve the yield of **21**. The mixtures were purified by flash chromatography on silica.

The rearrangments of oxiranes flanked by two vinyl groups provided insight into some possible control of reaction pathways. For example, oxepine **30** was obtained on pyrolysis of the crude reaction mixture of oxirane **29a** and (presumably) cyclopropane **29b** prepared by vinyloxiranation of acrolein.

Table 2[1]

Vinyloxirane-dihydrofuran rearrangement

Carbonyl Substrate	Vinyloxirane (%)[3]	Conditions	Dihydrofuran (%)[3]
		500 °C, .02 mm	
19	20 (47%)		21 (10%)
		500 °C, .02 mm	
22	23 (49%)		24 (7%)
		500 °C, .02 mm	
25	26 (68%)		27 (95%)
		600 °C, .02 mm	
28	29a (52%)[4] 29b		30 (33%)[4], 31 (33%)[4]
28	29a (52%)[4] 29b	400 °C, .02mm	30 (67%)[4] and sm
		500 °C, .02 mm	
32	33 (51%)		34, (49%)
		550 °C, 10^{-4} mm	
35	36 (70%)		37 (75%)
35	36	400 °C, 10^{-4} mm	
			38 (75%)
		495 °C, .02 mm	
39	40 (27%)		41b[2] (17%)[4], 41b[2] (26%)[4]

1. E = CO_2Et
2. Structure determination was based on the spectral data from one irreproducible experiment.
3. Isolated yield.
4. ^{1}H-NMR yield

Similarly, oxirane **36**, containing a second vinyl group as a part of the furan ring, gave **37** and **38**. We investigated these processes in some detail with the hope of controlling the reaction modes, namely the Cope versus dihydrofuran pathways.[26] It proved possible to produce either oxepine **30** or mixtures of oxepine **30** and cyclo-pentene **31** by pyrolysis of the crude mixture of vinyloxirane **29a** and vinylcyclopropane **29b** at different temperatures.

Small amounts (<10%) of the oxepine **30** found in the crude reaction mixtures of acrolein vinyloxiranation suggests that its formation begins to take place at room temperature. These results are somewhat ambiguous, however, and remain to be examined in more detail[26]. For example, if we assume that acrolein gave only the cis vinyloxirane, which would be consistent with the observed stereoselectivity of the vinyloxiranation process, then we cannot explain why only oxepine **30** was isolated on pyrolysis. The literature examples all agree that the cis isomers (which should be isolable) rearrange to oxepines while the trans isomers give mixtures of oxepines and vinyldihydrofurans.[27] The NMR spectrum of the crude divinyloxirane **29** containing signals in the vinyl region suggests the presence of at least two other compounds. Because one of them cannot be the trans oxirane based on the reasoning above, we assume, until further clarification, that the signals correspond to exo/endo vinylcyclopropanes **29b**, which furnish cyclopentene **31** upon pyrolysis. This compound was also produced to the tune of 10% by the pyrolysis of pure oxepine **30**. Such transformations are well precedented but usually require the action of a nucleophile.[28] Analogous reactions have also been reported for divinylaziridines.[29] The exact profile of this reaction will, therefore, be investigated in detail in the near future.

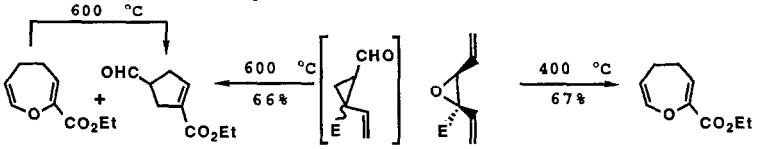


Figure 7.

Similarly, vinyloxirane **36** was pyrolyzed to either **37** or **38** depending on the temperature of thermolysis. Divinyloxiranes in which one vinyl group is a part of an aromatic system are known to furnish annulated oxepines.[30] One example reported in the literature was that of a 2-furylvinyloxirane which gave only the corresponding dihydrofuran at 360 °C.[31] We assume that this rearrangement would have occurred at lower temperature, as in the case of furan **36** and its rearrangement to oxepine **38** at lower temperatures and to dihydrofuran **37** at higher temperature. (See Fig. 8.) It appears that the mode of the rearrangement of various divinyloxiranes can be controlled by

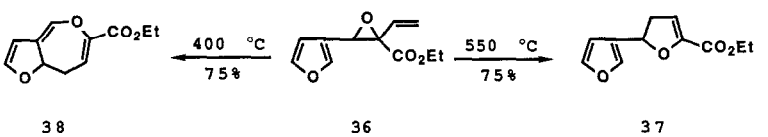


Figure 8.

careful temperature adjustments in the flash-vacuum pyrolyses. These processes suggest the existence of easily controlled equilibria in the vapor phase during pyrolysis. The control of such processes, in direct analogy with the control of 1,5-shift versus diradical cleavage modes of cis alkylvinylcyclopropanes,[22] will become available through precise definition of reaction

times and temperatures. A similar study performed with furans **33** and **36** or any other divinyloxirane will provide valuable insight into the parameters that control their transformations and allow access to fused oxacyclic ring systems.

Finally, only one ketone, cyclopentanone **39**, was found to undergo vinyloxiranation with **11** in poor yields. This result is surprising, especially when such substrates as cyclohexanone, acetophenone, 2-butanone, and others failed to react. We ascribe this lack of reactivity to the enolization of ketones by **11**; however, this explanation is in sharp contrast with the successful vinyloxiranation of cyclopentanone, which is known to prefer enolization during additions of hard nucleophiles to its carbonyl group. A possible solution to this problem lies in the investigation of softer equivalents of **11**, an issue that has been addressed in a preliminary fashion.[9]

Summary

Aldehydes have been shown to yield vinyloxiranes stereoselectively upon condensation with the dienolate of ethyl 2-bromocrotonate. The rearrangement of the vinyloxiranes produced synthetically useful yields of dihydrofurans in an overall [2+3] dihydrofuran annulation sequence. Some insight into the mechanism of vinyloxiranation and the vinyloxirane-dihydrofuran rearrangement became available. The extension of this research will involve detailed investigations of the divinyloxirane rearrangement as the means of access to annulated oxacyclic systems, as well as a study of experimental parameters that dictate control of the various reaction pathways. These and other developments will be reported in the near future. The application of this annulation to the total synthesis of ipomeamarone **4** is in progress. Finally, the elements of asymmetric induction will be addressed by investigating the rigid chiral auxiliary groups in the additions of chiral analog of **11** to aldehydes.

Acknowledgment: The authors are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society (AC-16617), the National Institutes of Health (AI-19749, AI-00564), and the Jeffress Memorial Trust Fund for support of this work. The assistance of Frank Anderson, III, during the early stages of this project is also appreciated.

Experimental Section

All nonhydrolytic reactions were carried out in a nitrogen or argon atmosphere with standard techniques for the exclusion of air and moisture. Glassware used for moisture-sensitive reactions was flame-dried under vacuum. THF, ether, DME, and benzene were distilled from benzophenone ketyl, dichloromethane and toluene from calcium hydride.

Analytical TLC was performed on silica gel 60F-254 plates. Flash chromatography was performed on Kieselgel 60 (EM Reagents, 230-400 mesh). Mass spectra were recorded on a DuPont 20-491 or a Varian MAT-112 instrument (low resolution) or on a double focusing DuPont 21-110C or VGT instruments (exact mass). Infrared spectra were recorded on neat samples (NaCl plates) on a Perkin-Elmer 283B or 710B spectrometer. Proton NMR spectra were obtained on a Bruker WP-270 instrument. Proton chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane as an internal reference (0.0 ppm). Carbon NMR spectra were recorded on Bruker WP-270 or NR-80 instruments. Carbon chemical shifts are reported in ppm relative to the center line of the $CDCl_3$ triplet (77.0 ppm) and the multiplicity is indicated by CH_3, CH_2, CH, C (INEPT experiments).

General Procedure for Vinyloxiranation. To a stirred solution of lithium diisopropylamide (5.2 mmol), prepared from diisopropylamine (0.73 mL) and n-butyllithium (2.09 mL, 2.5 M in hexane), in 8 mL of THF and 1.0 mL of HMPA at -110 °C, was added a solution of ethyl 2-bromocrotonate (0.965 g; 5.0 mmol) in 17 mL of THF, cooled to -105 °C, over a period of 25 min, while maintaining the temperature of the reaction at or below -100 °C . After the addition was complete, the reaction mixture was stirred for 15 min and then treated with a solution of the appropriate aldehyde (5.0 mmol) in 7 mL of THF cooled to -105 °C. This addition took 5 min and was also done at a rate that kept the temperature of the reaction at or below -100 °C. Stirring was continued between -100 and -110 °C for 0.5 h and at -78 °C for 1 h. The reaction mixture was then warmed to -50 °C over 0.5 h, then diluted with saturated NH_4Cl solution and ether. The ether layer was washed with 3N HCl (1 x 15 mL), water (4 x 15 mL), and brine and then dried over Na_2SO_4. Removal of the solvent in vacuo gave the crude vinyloxirane.

r-3-Propyl-2-trans-carbethoxy-2-ethenyloxirane (20). Butyraldehyde (0.44 mL) gave 940 mg of a clear yellow liquid which by GC contained 56% of the desired oxirane. The crude material was filtered through 20 g of silica gel (10% deactivated with H_2O) with hexane/ether (95:5) as eluant to give **20** (523 mg, 83% pure by GC). An analytical sample was obtaned by flash chromatography (silica gel, 10% deactivated with H_2O) with hexane/ethyl acetate (95:5) as eluant. R_f=0.47 (10% ethyl acetate, 90% hexane); **IR** (neat) 2930, 1750, 1732, 1300, 1250, 1075 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 0.89 (t, 3H, J=7.1 Hz), 1.25 (t, 3H, J=7.0 Hz), 1.37-1.49 (m, 4H), 3.22 (t, 1H, J=5.8 Hz), 4.20 (q, 2H, J=7.0 Hz), 5.30 (dd, 1H, J_1=17.1, J_2=1.8 Hz), 5.35 (dd, 1H, J_1=10.8, J_2=1.8 Hz), 6.26 (dd, 2H, J_1=17.1, J_2=10.8 Hz); **^{13}C-NMR** ($CDCl_3$) δ 13.1 (CH_3), 13.5 (CH_3), 18.6 (CH_2, double intensity), 27.9 (CH_2), 60.2 (C), 60.9 (CH_2), 63.9 (CH), 118.3

(CH_2), 128.2 (CH), 169.1 (C); **Mass Spectrum** (CI, m/e (rel. int.)) 185 (80, M^++1), 167 (22), 157 (15), 139 (100), 115 (41), 111 (86), 101 (47), 83 (30). **Calcd. for** $C_{10}H_{17}O_3$: 185.1177. **Found:** 185.1177.

r-3-Isopropyl-2-trans-carbethoxy-2-ethenyloxirane (23). Isobutyraldehyde (0.46 mL) gave 710 mg of a clear yellow liquid, which by GC contained 78% of the desired oxirane. The residue was filtered through 20 g of silica gel (10% deactivated with H_2O) with hexane/ether (95:5) as eluant to give **23** (540 mg, 83% pure by GC). An analytical sample of **23** was obtained by flash chromatography (silica gel, 10% deactivated with H_2O) with hexane/ethyl acetate (95:5) as eluant. R_f= 0.50 (20% ethyl acetate, 80% hexane); **IR** (neat) 2960, 1750, 1730, 1244, 1033 cm^{-1}; ^{1}**H-NMR** ($CDCl_3$) δ 0.87 (d, 3H, J=8.1 Hz), 1.03 (d, 3H, J=7.1 Hz), 1.24 (t, 3H, J=7.1 Hz), 1.41-1.57 (m, 1H), 2.89 (d, 1H, J=9.2 Hz), 4.17 (q, 2H, J=7.0 Hz), 5.27-5.33 (m, 2H), 6.25-6.39 (m, 1H); ^{13}**C-NMR** ($CDCl_3$) δ 14.0 (CH_3), 17.9 (CH_3), 19.4 (CH_3), 25.9 (CH), 61.1 (C), 61.5 (CH_2), 70.1 (C), 118.8 (CH_2), 128.3 (CH), 169.6 (C); **Mass Spectrum** (CI, m/e (rel. int.)) 185 (M^++1, 83), 169 (63), 157 (14), 139 (98), 129 (25), 123 (19), 111 (55).

Calcd for $C_{10}H_{16}O_3$: 184.1019 **Found:** 184.1103.

r-3-Phenyl-2-trans-carbethoxy-2-ethenyloxirane (26). Benzaldehyde (0.51 mL) afforded 1.03 g of a clear yellow liquid which was 95% pure by GC. The residue was filtered through 20 g of silica gel (10% deactivated with H_2O), with hexane/ether (9:1) as eluant to give pure **26** (736 mg, 68%). R_f=0.57 (20% ethyl acetate, 80% hexane); **IR** (neat) 1745, 1730, 1258, 1140, 1040, cm^{-1}; ^{1}**H-NMR** ($CDCl_3$) δ 1.32 (t, 3H, J=7.1 Hz), 4.29 (qd, 2H, J_1=7.1, J_2=0.7 Hz), 4.43 (s, 1H), 5.20 (dd, 1H, J_1=10.4, J_2=1.5 Hz), 5.41 (dd, 1H, J_1=17.3, J_2=1.5 Hz), 5.91 (dd, 1H, J_1=17.3, J_2=10.4 Hz), 7.24 (m, 5H); ^{13}**C-NMR** ($CDCl_3$) δ 13.6 (CH_3), 61.3 (CH_2), 62.5 (C), 63.8 (CH), 119.9 (CH_2), 126.6 (CH, double intensity), 126.9 (CH), 127.4 (CH, double intensity), 127.7 (CH), 132.4 (C), 168.4 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 162 (12), 145 (19), 135 (100), 117 (29), 107 (65), 79 (25), 55 (78).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47; **Found:** C, 71.36; H, 6.26.

Vinyloxiranation of acrolein: Vinyloxiranation of acrolein (0.73 mL) gave 620 mg of a clear yellow liquid. The crude material was filtered through silica gel with hexane/ether (70:30) as eluant to give a mixture of what we believe to be **29a** and **29b** (440 mg). The ^{1}**H-NMR** spectrum of the crude mixture had the following features: δ ($CDCl_3$) 1.25 (m), 1.40 (m), 1.70 (m), 2.05 (m), 2.25 (m), 2.45 (m), 3.35 (m), 3.70 (m), 4.15 (m), 4.80-5.60 (overlapping peaks), 6.10-6.50 (overlapping peaks), 9.00 (d), 9.28 (d).

3-(2'-Furyl)-2-carbethoxy-2-ethenyloxirane (33). 2-Furaldehyde (0.41 mL) gave 1.04 g of 9:1 a mixture of **33** and starting material. The residue was filtered through silica gel (10% deactivated with H_2O) with hexane/ether (95:5) as eluant to give pure **33** (527 mg, 51%). R_f=0.34 (10% ethyl acetate, 90% hexane); **IR** (neat) 3010, 1735, 1255 cm^{-1}; ^{1}**H-NMR** ($CDCl_3$) δ 1.31 (t, 3H,

J=7.1 Hz), 4.26 (qd, 2H J_1=7.1, J_2=1.2 Hz), 4.33 (s, 1H), 5.37 (dd, 1H, J_1=10.9, J_2=1.5 Hz), 5.50 (dd, 1H, J_1=17.4, J_2=1.5 Hz), 6.13 (dd, 1H, J_1=17.4, J_2=10.9 Hz) 6.26 (d, 1H, J=3.1, Hz), 6.32 (dd, 1H, J_1=3.1, J_2=1.9 Hz), 7.37 (dd, 1H, J_1=1.9, J_2=0.8 Hz); **^{13}C-NMR** ($CDCl_3$) δ 14.1 (CH_3), 58.8 (CH), 62.1 (CH_2), 62.9 (C), 110.1 (CH), 110.4 (CH), 120.4 (CH_2), 127.3 (CH), 143.3 (CH), 147.3 (C), 168.4 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 208 (30, M^+), 162 (15), 134 (65), 107 (100), 79 (50).

Calcd. for $C_{11}H_{12}O_4$: 208.0736. **Found:** 208.0737.

3-(3'-Furyl)-2-carbethoxy-2-ethenyloxirane (36). 3-Furaldehyde (0.43 mL) gave 1.04 g of a 6:1 mixture of **36** and starting material, respectively. The residue was filtered through silica gel (10% deactivated with H_2O) with hexane/ether (95:5) as eluant to give pure **36** (730 mg, 70%). R_f=0.44 (20% ethyl acetate, 80% hexane); **IR** (neat) 3145, 3080, 1775, 1640, 1595, 1045, 1025, cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.31 (t, 3H, J=7.2 Hz), 4.22 (s, 1H), 4.26 (qd, 2H J_1=7.1, J_2=1.5 Hz), 5.37 (dd, 1H, J_1=10.8, J_2=1.5 Hz), 5.45 (dd, 1H, J_1=17.2, J_2=1.5 Hz), 6.09 (dd, 1H, J_1=17.2, J_2=10.8 Hz) 6.32 (m, 1H), 7.32 (m, 1H), 7.37 (m, 1H); **^{13}C-NMR** ($CDCl_3$) δ 13.7 (CH_3), 58.4 (CH), 61.5 (CH_2), 62.4 (C), 109.4 (CH), 118.3 (C), 119.8 (CH_2), 127.5 (CH), 141.6 (CH), 142.6 (CH), 168.6 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 208 (3, M^+), 125 (100), 107 (28), 97 (55), 55 (59).

Calcd. for $C_{11}H_{12}O_4$: 208.0736. **Found:** 208.0744.

2-Carbethoxy-2-ethenyl-1-oxaspiro[2.4]heptane (40). Cyclopentanone (0.44 mL) afforded 900 mg of a clear yellow liquid which by GC contained 30% of **40.** The crude was filtered through silica gel(10% deactivated with H_2O) with hexane/ether (95:5) as eluant to give of **40** (353 mg, 75% pure by GC). An analytical sample of **40** was obtained by flash chromatography (silica gel, 10% deactivated with H_2O) with hexane/ethyl acetate (80:20) as eluant. R_f=0.36 (10% ethyl acetate, 90% hexane); **IR** (neat) 2930, 1725, 1240 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.28 (t, 3H, J=7.1 Hz), 1.5-1.9 (m, 8H), 4.23 (m, 2H), 5.33 (m, 2H), 6.19 (dd, 1H, J_1=17.3, J_2=10.9 Hz); **^{13}C-NMR** ($CDCl_3$) δ 14.0 (CH_3), 24.6 (CH_2), 25.2 (CH_2), 29.6 (CH_2), 30.4 (CH_2), 61.0 (CH_2), 65.4 (C), 76.1 (C), 117.8 (CH_2), 130.8 (CH), 168.6 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 196 (M^+, 0.3), 123 (11), 113 (61), 85 (51), 67 (24), 55 (100).

Calcd for $C_{11}H_{16}O_3$: 196.1099. **Found:** 196.10711.

Anal Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. **Found:** C, 65.96; H, 8.30.

General Procedure for Pyrolysis of Vinyloxiranes. A sample of the vinyl oxirane was evaporated at the specified temperature (0.02 mm) through a horizontally situated Vycor tube (41 cm, 5 mm i.d.) heated to 500 °C. The pyrolysate was condensed in a liquid-nitrogen-cooled trap. The apparatus was washed with CH_2Cl_2 and the solvent evaporated to give the crude oxolene.

5-n-Propyl-2-carbethoxy-2-oxolene (21). Pyrolysis of **20** (117 mg, 0.63 mmol), evaporated at 40 °C, afforded a mixture of **21** and **20** (1:1.5 respectively by GC). The crude material was chromatographed on 9 g of silica

gel with hexane:ether (95:5) as eluant to give pure **21** (12 mg, 10%). R_f=0.52 (30% ether; 70% hexane); **IR** (neat) 2950, 1735, 1630, 1310, 1120 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 0.92 (t, 3H, J=7.2 Hz), 1.29 (t, 3H, J=7.2 Hz), 1.25-1.63 (m, 3H), 1.71-1.86 (m, 1H), 2.41 (ddd, 1H, J_1=17.2, J_2=8.6, J_3=3.0 Hz), 2.8 (ddd, 1H, J_1=17.2, J_2=10.2, J_3=3.0 Hz), 4.23 (q, 2H, J=7.2 Hz), 4.64-4.75 (m, 1H), 5.85 (t, 1H, J=3.0 Hz); **^{13}C-NMR** ($CDCl_3$) δ 13.9 (CH_3), 14.2 (CH_3), 18.3 (CH_2), 35.8 (CH_2), 38.1 (CH_2), 60.9 (CH_2), 82.9 (CH), 110.2 (CH), 148.2 (C), 160.5 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 184 (M^+, 12), 149 (72), 99 (53), 82 (21), 69 (42), 55 (100).

Calcd. for $C_{10}H_{16}O_3$: 184.1099 **Found:** 184.1116.

5-Isopropyl-2-carbethoxy-2-oxolene (24). Pyrolysis of **23** (155 mg, 0.84 mmol), evaporated at 45 °C, afforded a mixture of **24** and starting material. After repyrolyzing the crude material two more times, 80 mg of a yellow liquid was obtained. A pure sample of the **24** (11 mg, 7%) was obtained by preparative TLC (Whatman PKGF, silica gel, 500 μ, 20 x 20 cm; 2% ethyl acetate, 98% hexane; three elutions). R_f=0.35 (10% ethyl acetate, 90% hexane); **IR** (neat) 2920, 1735, 1630, 1257 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 0.89 (d, 3H, J=6.8 Hz), 0.95 (d, 3H, J=6.8 Hz), 1.29 (t, 3H, J=7.1 Hz), 1.87-1.99 (m, 1H), 2.48 (ddd, 1H, J_1=17.4, J_2=9.3, J_3=3.0 Hz), 2.71 (ddd, 1H, J_1=17.4, J_2=9.3, J_3=3.0 Hz), 4.23 (q, 2H, J=7.3 Hz), 4.45 (ddd, 1H, J_1=10.2, J_2=9.4, J_3=6.4 Hz), 5.83 (t, 1H, J=3.0 Hz); **^{13}C-NMR** ($CDCl_3$) δ 11.6 (CH_3), 14.2 (CH_3), 17.1 (CH_3), 32.8 (double intensity, CH_2, CH), 60.9 (CH_2), 87.9 (CH), 110.3 (CH), 148.4 (C), 160.5 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 184 (M^+, 3.7), 171 (3.3), 157 (5.3), 149 (39), 81 (43), 69 (100), 55 (51).

Calcd. for $C_{10}H_{16}O_3$: 184.1099. **Found:** 184.1105.

5-Phenyl-2-carbethoxy-2-oxolene (27). Pyrolysis of **26** (100 mg, 5 mmol), evaporated at 50 °C, afforded pure **27** (95 mg, 95%). R_f=0.42 (10% ethyl acetate, 90% hexane); **IR** (neat) 1735, 1730, 1637, 1257, 1230, 1120 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.31 (t, 3H, J=7.3 Hz), 2.77 (ddd, 1H, J_1=17.5, J_2=8.8, J_3=3.0 Hz), 3.21 (ddd, 1H, J_1=17.5, J_2=10.8, J_3=3.0 Hz), 4.28 (q, 2H, J=7.3 Hz), 5.67 (dd, 1H, J_1=10.8, J_2=8.8, Hz), 5.96 (t, 1H, J=3.0 Hz), 7.30 (m, 5H); **^{13}C-NMR** ($CDCl_3$) δ 14.0 (CH_3), 38.6 (CH_2), 60.8 (CH_2), 83.4 (CH), 110.0 (CH), 125.5 (CH), 127.7 (CH), 128.3 (CH), 141.6 (C), 148.0 (C), 159.9 (C); **Mass Spectrum** (70 eV, m/e (rel.int.)) 218 (M^+, 79), 160 (27), 145 (96), 127 (52), 117 (100), 105 (41), 91 (31), 77 (42).

Anal Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. **Found:** C, 70.33; H, 6.55.

2-Carbethoxy-2,6-oxepine (30). Pyrolysis (400 °C, 10^{-4} mm) of the mixture of **29a** and **29b** (70 mg) afforded a mixture of **30** and starting material (63% and 37% by NMR). R_f=0.49 (70% hexane, 30% ether), **IR** (neat) 3050, 2980, 2940, 1722, 1650, 1255, 1125 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.26 (t, 3H, J=7.2 Hz), 2.27 (m, 2H), 2.42 (m, 2H), 4.19 (q, 2H, J=7.2 Hz), 4.88 (dt, 1H, J_1=7.4, J_2=5.6 Hz), 6.26 (d, 1H, J=7.4 Hz), 6.42 (t, 1H, J=6.5 Hz); **^{13}C-NMR** ($CDCl_3$) δ 14.1 (CH_3), 25.2 (CH_2), 26.2 (CH_2), 61.2 (CH_2), 109.4 (CH), 119.5 (CH), 142.3 (CH), 144.8 (C), 163.1 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 168 (M^+, 40), 95 (51), 85 (61), 67 (70), 55 (100).

Calcd for $C_9H_{12}O_3$: 168.0786. **Found:** 168.0801.

Ethyl 4-formyl-cyclopent-1-ene (31). Pyrolysis (600 °C, 0.02 mm) of the mixture of **29a** and **29b** (33 mg) afforded a 1:1 mixture of **30** and **31**, 66% (^{1}H-NMR yield). For **31**: R_f=0.17 (30% ether, 70% hexane); **IR** (neat) 3030, 2980, 2760, 1745, 1725, 1650 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.26 (t, 1H, J=7.1 Hz), 2.61-2.79 (m, 1H), 2.80-2.98 (m, 3H), 3.13-3.23 (m, 1H), 4.17 (q, 2H, J=7.1 Hz) 6.66 (m, 1H), 9.66 (d, 1H, J=1.4 Hz); **^{13}C-NMR** ($CDCl_3$) δ 14.18 (CH_3), 31.8 (CH_2), 33.1 (CH_2), 48.8 (CH), 60.3 (CH_2), 140.9 (CH), 143.0 (C), 164.5 (C), 201.5 (CH); **Mass Spectrum** (70 eV, m/e (rel. int.)) 168 (M^+, 2), 161 (40), 133 (70), 105 (85), 79 (88), 77 (89), 67 (97), 55 (100).
Calcd for $C_{10}H_{12}O_4$: 196.0735. **Found:** 196.672.

5-(2'-Furyl)-2-carbethoxy-2-oxolene (34). Pyrolysis of **33** (98 mg, 0.47 mmol, 71% pure by GC), evaporated at 45 °C, afforded 86.5 mg of a yellow oil. The crude product was purified by chromotography (silica gel, hexane/ethyl acetate, 95:5, 90:10, 85:15) to give pure **34** (48 mg, 49%). R_f=0.17 (10% ethyl acetate, 90% hexane); **IR** (neat) 3110, 2975, 1720, 1630 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.29 (t, 3H, J=7.1 Hz), 3.05 (dd, 1H, J_1=3.0, J_2=1.0 Hz), 3.08 (d, 1H, J=3.0 Hz), 4.24 (qd, 2H, J_1=7.1, J_2=2.2 Hz), 5.65 (t, 1H, J=9.9 Hz), 5.98 (t, 1H, J=3.0 Hz), 6.33 (dd, 1H, J_1=3.2, J_2=1.9 Hz), 6.37 (d, 1H, J=3.2 Hz), 7.4 (m, 1H); **^{13}C-NMR** ($CDCl_3$) δ 13.9 (CH_3), 34.4 (CH_2), 60.8 (CH_2), 76.5 (CH), 108.3 (CH), 110.1 (CH, double intensity), 142.8 (CH), 147.5 (C), 152.3 (C), 159.7 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 208 (9, M^+), 134 (13), 107 (28), 86 (67), 84 (100).
Calcd. for $C_{11}H_{12}O_4$: 208.0736. **Found:** 208.0729.
Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. **Found:** C, 55.36; H, 5.55.

5-(3'-Furyl)-2-carbethoxy-2-oxolene (37). Pyrolysis (550 °C, 10^{-4} mm) of **36** (1.19g, 5.7 mmol), evaporated at 180 °C, gave 1.07 g of a yellow oil. The crude oxolene was filtered through 5 g of silica gel with methylene chloride as eluant to give **37** (1.07 g, 83% pure). An analytical sample of **37** was obtained by flash chromatography (silica gel) with hexane/ether (9:1) as eluant. R_f=0.33 (30% ether, 70% hexane); **IR** (neat) 3200, 3025, 1740, 1625, 1130, 1040 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.28 (t, 3H, J=7.0 Hz), 2.76 (ddd, 1H, J_1=17.3, J_2=8.6, J_3=3.0 Hz), 3.10 (ddd, 1H, J_1=17.3, J_2=10.4, J_3=3.0 Hz), 4.23 (qd, 2H, J_1=7.0, J_2=1.3 Hz), 5.63 (dd, 1H, J_1=10.4, J_2=8.6 Hz), 5.95 (t, 1H, J=3.0 Hz), 6.42 (m, 1H), 7.37 (m, 1H), 7.43 (m, 1H); **^{13}C-NMR** ($CDCl_3$) δ 14.3 (CH_3), 37.4 (CH_2), 61.2 (CH_2), 77.0 (CH), 108.7 (CH), 110.2 (CH), 126.1 (C), 139.9 (CH), 143.8 (CH), 148.3 (C), 160.3 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 208 (M^+, 8), 123 (32), 107 (55), 95 (84), 79 (93), 67 (100), 55(62).
Calcd for $C_{11}H_{12}O_4$: 208.0736. **Found:** 208.0772.

2-Carbethoxy-[5,6,b]-4,5-dihydrofurano-2,6-oxepine (38). Pyrolysis (400 °C, 10^{-4} mm) of **36** gave a mixture of **38** and starting material (7.3:1). Separation by flash chromatography (silica gel, hexane/ether 9:1) yielded pure **38** as a white crystaline solid (375 mg, 75%). **m.p.** 58.5 - 60.5 °C; R_f=0.50 (30% ether, 70% hexane); **IR** (neat) 3030, 2960, 1744, 1665, 1592, 1272, 1180 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.27 (t, 3H, J=7.1 Hz), 2.40 (ddd, 1H, J_1=15.3, J_2=9.2,

J_3=3.0 Hz), 2.98 (ddd, 1H, J_1=15.9, J_2=9.3, J_3=3.4 Hz), 4.21 (q, 2H, J=7.1 Hz), 5.10 (dt, 1H, J_1=10.0, J_2=3.4 Hz), 5.44 (d, 1H, J=3.0 Hz), 6.18 (dd, 1H, J_1=9.2, J_2=3.4 Hz), 6.45 (dd, 1H, J_1=10.0, J_2=3.0 Hz), 6.46 (s, 1H); **^{13}C-NMR** ($CDCl_3$) δ 14.1 (CH_3), 33.0 (CH_2), 61.5 (CH_2), 79.5 (CH), 101.7 (CH), 109.4 (CH), 120.2 (C), 128.6 (CH), 143.7 (C), 149.2 (CH), 162.9 (C); **Mass Spectrum** (70 eV, m/e (rel. int.)) 208 (M^+, 13), 135 (51), 125 (85), 107 (85), 79 (100), 55 (95).

Calcd for $C_{11}H_{12}O_4$: 208.0736. **Found:** 208.0701.

Ethyl 2-(cyclopent-1-enyloxy)but-2-enoate (41b). Pyrolysis (495 °C, .02 mm) of **40** (60 mg) afforded **41b** (in low yield) and starting material. R_f=0.63 (15% ethyl acetate, 85% hexane); **IR** (neat) 2928, 2875, 1725, 1645, 1255 cm^{-1}; **^{1}H-NMR** ($CDCl_3$) δ 1.25 (t, 3H, J=7.1 Hz), 1.71 (d, 3H), 1.81-1.95 (m, 2H), 2.19-2.30 (m, 2H), 2.40-2.50 (m, 2H), 4.19 (q, 2H, J=7.1 Hz), 4.41 (m, 1H), 6.45 (q, 1H, 6.9 Hz); **^{13}C-NMR** ($CDCl_3$) δ 11 (CH_3), 14 (CH_3), 21.5 (CH_2), 28 (CH_2), 31 (CH_2), 61 (CH_2), 98 (CH), 125 (CH), 143 (C), 167 (C), 168 (C).

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1 Recipient of the Research Career Development Award, NIH (AI-00564), 1984-1989.

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