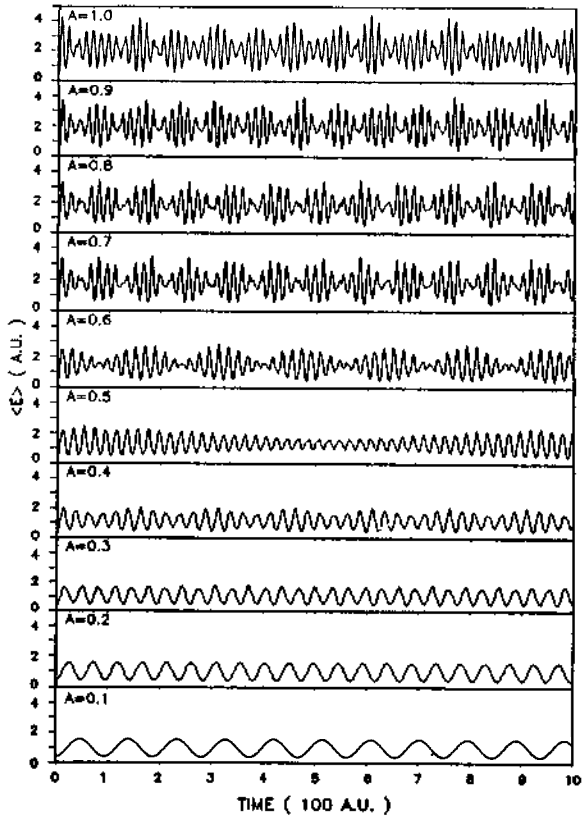

Figure 1. Energy expectation values *vs.* time.

The $\omega = 1.0871$ is taken, that is the resonance frequency of (0–1) transition of quartic oscillator. To see the effect of field strength on the energy absorption, ten cases of A values ringing from 0.1 to 1.0 are studied.

The convergence of calculations as a function of ϵ and N should be studied for A–1.0 which is the most serious case in this illustrative example as shown in Table 1. Taking $N = 8$, one sees that for $\epsilon = 0.05$, at least one significant figure; for $\epsilon = 0.025$, two significant figures are stable by comparing to the results for $\epsilon = 0.0125$ unit $t = 1000$. Next, keeping $\epsilon = 0.05$, and increasing the matrix size by $N = 16, 32$ and so on, the infinite N–limit is studied. For $N = 16$, there are no appreciable truncation errors in the results. Finally, taking the values of $\epsilon = 0.025$ and $N = 16$, one confirms that two significant figures are accurate in the calculation when $t \leq 1000$.

In Figure 1, the numerical results for energy expectation values are displayed. For the cases of weak radiations, *i.e.*, $A = 0.1$ and 0.2, energy absorptions show two-state Rabi oscillation of (0–1) transition with frequency $\omega_R = 0.674A$. When the intensity of radiation is increased, the simple oscillatory behavior disappears but multiple modes of oscillations are intermixed because of the contributions of non-resonant multiphoton transitions.

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Convenient Method for the Preparation of Precursors of Tandem Cope–Claisen Rearrangement

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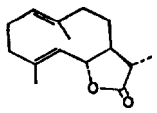
Germacrane sesquiterpenes are of interest not only because of their important role as biogenetic and synthetic precursors to a variety of sesquiterpene lactones but also because of their anti-tumor, cytotoxic, anti-microbial and phytotoxic activity.[1] However, the efforts culminating in the total synthesis[2] of germacrane have been relatively few in number despite the biological importance of the germacrane sesquiterpene lactones. This fact reflects the substantial difficulties in constructing a 10-membered ring with the control of stereochemistry.

We[3] recently reported that the first successful application of the tandem Cope–Claisen rearrangement[4] strategy for the total synthesis of the germacrane sesquiterpene (+)-dihydrocostunolide (**1**). Our investigations to extend the application of this strategy for the synthesis of various germacranolides have necessitated a convenient procedure for the preparation of the requisite precursors **2** and **3**. Since the stereochemical difference between the precursors might be crucial for the success of the tandem Cope–Claisen rearrangement and/or subsequent transformations, our efforts have been focused on the synthesis of each precursor which is completely free of other stereoisomers.

We now wish to report an useful method for the preparation of the precursors **2** and **3**.



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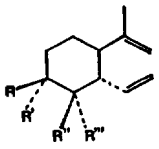
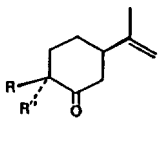
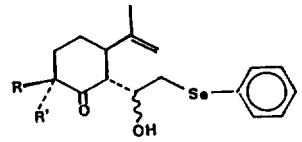


2a R,R',R'',R''' = H,Me,H,OH
2b R,R',R'',R''' = Me,H,H,OH
3a R,R',R'',R''' = H,Me,OH,H
3b R,R',R'',R''' = Me,H,OH,H



4a R,R' = H,Me
4b R,R' = Me,H



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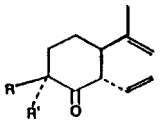

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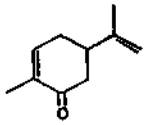
Scheme 1

As shown in Scheme 1, Kowalski's method[5] was successfully employed for the vinylation of (+)-dihydrocarvone which is commercially available as a mixture of **4a** and **4b**. The ketone **4a** was isolated from this mixture by flash chromatography[6], and treatment of **4a** with LDA followed by kinetic aldol condensation with (phenylseleno)acetaldehyde at −78 °C gave the selenide **5a**. The crude β-hydroxyselenide **5a** was treated with mesyl chloride and triethylamine to afford **6a**.[7] Although a complete separation of **6a** was not effected by flash chromatography, a brief purification of the crude elimination product was helpful for better results. Reduction of **6a** with L-Selectride[8] at −78 °C followed by an oxidative workup produced exclusively the divinyl axial alcohol **2a** in overall 44% yield from **4a**. Similarly, treatment of the ketone **6b** with L-Selectride afforded predominantly the equatorial alcohol **3b** in overall 41% yield from **4b**. ^{1}H NMR of **3b** showed a doublet of doublets (J = 10.3, 4.8 Hz) at δ3.40 characteristic of a proton on the hydroxyl carbon. The opposite stereoselectivity (**3b**:**2b** = 98:2) of L-Selectride for reduction of **6b** is especially noteworthy as compared with that obtained from **6a**. The axially positioned methyl group in **6b** is believed to prevent the incoming bulky L-Selectride from attacking the keone from the same side of methyl group.

On the other hand, reduction of the ketone **6a** with lithium tri-tert-butoxyaluminohydride at 0 °C gave an 80:20 mixture of **3a**:**2a** and a subsequent purification by flash chromatography provided the divinyl equatorial alcohol **3a** in overall 31% yield from **4a**. The formation of the equatorial alcohol **3a** is confirmed by spectral data [^{1}H NMR δ2.86 (t, J = 10.2 Hz)]. Interestingly, reaction of **6b** with lithium tri-tert-butoxyaluminohydride at 0 °C provided an 85:15 mixture of **3b** and **2b**, which could not be resolved effectively by flash chromatography.

An alternate route has been examined for the synthesis of the divinyl equatorial alcohol **3a** as shown in Scheme 2. Treatment of (R)-carvone (**7**) with LDA followed by alkylation with methyl bromoacetate produced **8** in 75% yield. The enone **8** was reduced with *K*-Selectride[9] and the reaction was quenched with trifluoroacetic acid to provide **9** in 77% yield. Reduction of the ketone **9** with lithium tri-tert-butoxy-



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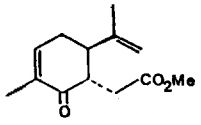

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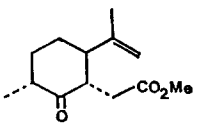

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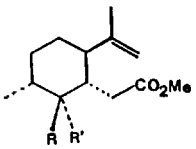
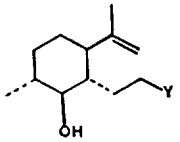
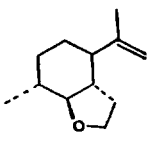


10a R,R' = OH,H
10b R,R' = H,OH



11 Y = OH
12 Y = SeAr



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Scheme 2

aluminohydride provided the equatorial alcohol **10a** in 76% yield as a colorless liquid. It is interesting to note that **10a** is quite stable relative with **10b** which is readily cyclized to give a lactone.[4a] Conversion of **10a** into the diol **11** was accomplished witH LAH in 97% yield. Reaction of **11** with *o*-nitrophenylselenocyanate in the presence of tributylphosphine[10] gave the selenide **12** in 63% yield and the cyclic ether **13** in 35% yield. Oxidation of **12** with H_2O_2 provided **3a** and **13** in 37% and 30% yield, respectively. The formation of the by-product **13** was the serious problem in the last two steps. At this stage, the reasons for greater tendency of the equatorial intermediates to form the cyclic ether **13** remain unclear.

In summary, depending on the reducing reagent employed, the procedure via the β-hydroxyselenide **5** gives either the divinyl equatorial alcohol **3** or the axial alcohol **2a**. This procedure provides an easy, reproducible and stereoselective method for the syntheses of the divinyl alcohols **2a**, **3a** and **3b** which are important precursors in the study of tandem Cope-Claisen rearrangement.

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