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Study of an Unexpected Rearrangement of the α-Phenyl Pyrane Derivatives Prepared via Hetero-Diels−Alder Reaction of Acyclic Vinyl Allenes and Aldehydes

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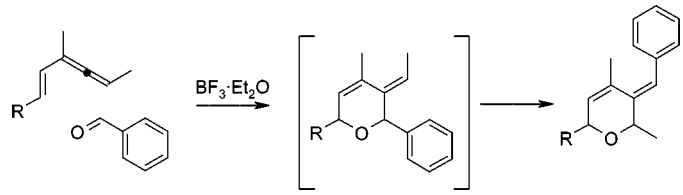
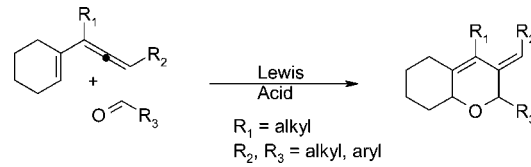


The Lewis acid catalyzed hetero-Diels−Alder reaction between acyclic vinyl allenes and aldehydes as heterodienophiles was studied. This reaction allows for the preparation of pyrane derivatives in good yields, high facial and regioselectivity and moderate *endo*/*exo* ratio. When benzaldehyde was used as the heterodienophile, rearranged products were obtained depending on the reaction conditions. DFT calculations were used to study the rearrangement, concluding that it is a highly selective ionic process, driven by the stability of the rearranged products.

Introduction

Vinylallenes have been used as dienes in Diels−Alder reactions for many years in both the inter- and intramolecular versions of the reaction.[1] The special structural features of the allene moiety introduces interesting differences with the cycloaddition reaction of standard dienes, especially in the regio- and face-selectivity of the reaction.[2] In a study using cyclohexenyl-allenes (semicyclic vinyl allenes), Krause and co-workers[3] concluded that the selectivity in this type of compounds is due to the steric interaction of the incoming dienophile with the substituents on the vinyl allene, following a model first proposed by Reich and co-workers.[4] Theoretical calculations at the ab initio level have also been carried out for the Diels−Alder reaction of vinyl allenes and acrolein,[5] showing that the substitution pattern on the vinyl allene affects the regioselectivity of the process. The same study concluded that the reaction is a concerted asynchronous process. Other theoretical studies indicates that the presence of the allene lowers the activation energy of the reaction when compared to the nonallenic case,[6] making them more reactive than similarly substituted dienes.

SCHEME 1



Recently, we presented our work on the use of semicyclic vinyl allenes as dienes in the hetero-Diels−Alder reaction with aldehydes acting as heterodienophiles.[7] The reaction with imines[8] and the intramolecular version of those reactions[9] were also studied. For the reaction with aldehydes (Scheme 1), it was observed that alkyl-substituted vinyl allenes showed a reactivity similar to that of dienes substituted by strong activating groups (alkoxy or silyloxy).

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(7) Regás, D.; Ruiz, J. M.; Afonso, M. M.; Palenzuela, J. A. *J. Org. Chem.* **2006**, *71*, 9153.
(8) Regás, D.; Afonso, M. M.; Rodríguez, M. L.; Palenzuela, J. A. *J. Org. Chem.* **2003**, *68*, 7845.
(9) (a) Regás, D.; Ruiz, J. M.; Afonso, M. M.; Galindo, A.; Palenzuela, J. A. *Tetrahedron Lett.* **2003**, *44*, 8471. (b) Regás, D.; Afonso, M. M.; Palenzuela, J. A. *Synthesis* **2004**, 757.

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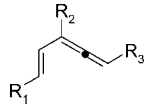
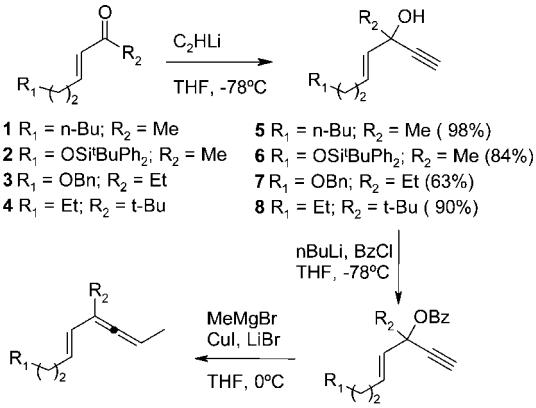


FIGURE 1. General structure of the vinyl allenes used in this work.

SCHEME 2



In the same work, computational studies using Density Functional Theory showed that the reaction with BF_3-complexed aldehydes is a pericyclic, highly asynchronous process that proceeds through a polar transition state.

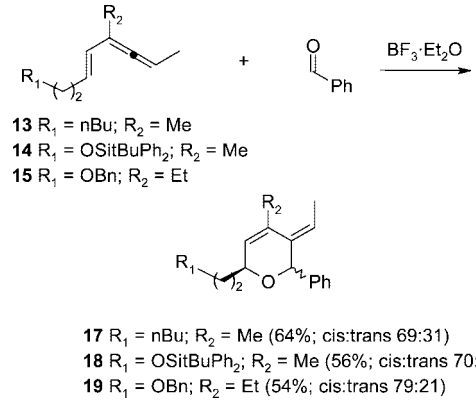
Pursuing our interest in understanding the effect of the allene moiety in pericyclic reactions, we decided to prepare acyclic vinyl allenes with different alkyl groups as substituents on the dienic portion of the molecule and compare their reactivity as dienes in the hetero-Diels−Alder reaction with that of the semicyclic analogs. In this paper, we present the results of that study together with the calculations carried out to explain the unexpected rearrangement observed in some cases during the reaction.

Results and Discussion

Experimental Studies. Figure 1 shows the general structure of the vinyl allenes used in this work. In these acyclic systems, which have been used before in Diels−Alder reactions but not with aldehydes,[3,4,10] the non-allenic double bond lacks one of the substituents existing in the semicyclic ones, and the two remaining substituents on the diene (R_1 and R_2) would act cooperatively as activating groups. The lack of the ring could also result in a more conformationally flexible molecule.

We started by preparing vinyl allenes **13**−**16** according to the synthetic pathway shown in Scheme 2.[11] Starting from the corresponding unsaturated ketones,[12] the propargyl alcohols **5**−**8** were prepared by the addition of lithium acetilyde and then transformed into the benzoates **9**−**12**, which were in turn converted into the vinyl allenes **13**−**16** by the S_N2' addition of the methyl cuprate formed from methyl magnesium bromide and cuprous iodide.[13]

SCHEME 3



When vinyl allene **13** was reacted with benzaldehyde, which was the most reactive aldehyde for the reaction with the semicyclic compounds,[7] under the reaction conditions previously used, that is, addition of 1 equiv of $BF_3 \cdot Et_2O$ to the aldehyde in ethyl ether at 0 °C, after 15 min addition of the vinyl allene and stirring at room temperature for 24 h, a mixture of two compounds was obtained in a 69:31 ratio and moderate yield (64%). The two compounds were identified spectroscopically[14] as the cycloadducts *cis*- and *trans*-**17**, coming respectively from an *endo* (major) and *exo* (minor) approach of the aldehyde to the dienic portion of the vinyl allene, through the less hindered face and with total regioselectivity (Scheme 3).

The reaction of vinyl allenes **14** and **15** with benzaldehyde under the same reaction conditions was similar, yielding 56% of **18** and 54% of **19** in 70:30 and 79:21 *cis*:*trans* mixtures, respectively.

The moderate yields are due mainly to the low stability of the vinyl allenes under the reaction conditions. This behavior is parallel to that of the semicyclic vinyl allenes, showing the same regio- and face-selectivity and similar yields.[7]

When the same reaction was carried out using vinyl allene **16**, substituted by a *tert*-butyl and a methyl group on the allenic portion of the molecule, in a substitution pattern that was not reactive in the semicyclic systems with aldehydes, a mixture of two compounds was again obtained after 72 h. The study of their structure revealed that one of them, which could not be isolated pure, corresponds to the *cis* cycloadduct **20**, but the other compound (**21**) presented some anomalous shifts in the ^{1}H NMR spectrum. Thus, the vinylic proton of the exocyclic double bond, which was expected at around 5 ppm as a quartet, showed up as a singlet at 6.6 ppm, and the proton geminal to both the oxygen and the phenyl group was expected at 5.1 ppm as a singlet but instead appears at 4.5 ppm as a quartet. Those changes indicated that **21** was not the *trans* isomer of **20**. After a complete spectroscopic study it was concluded that the structure of this compound has suffered a rearrangement, with the phenyl group and the vinylic methyl group on the exocyclic double bond exchanging places. Also, the relative stereochemistry of the two positions adjacent to the oxygen was deduced as being *trans* (Scheme 4).

This behavior could be attributed to the fact that, **16** being the least reactive vinyl allene, longer reaction times were needed for the reaction to progress, and thus it was considered

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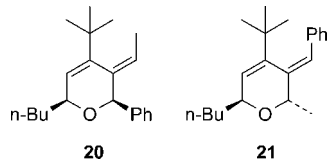
(11) All compounds described in this work were prepared in racemic form.

(12) Compounds **1**−**4** were prepared as described for **3** in Mujica, M. T.; Afonso, M. M.; Galindo, A.; Palenzuela, J. A *Tetrahedron* **1996**, *52*, 2167.

(13) Jansen, A.; Krause, N. *Inorg. Chim. Acta* **2006**, *359*, 1761.

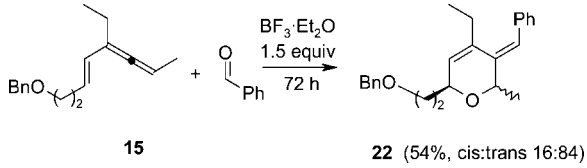
(14) All new compounds were identified by a combination of spectroscopic techniques, including 1D and 2D NMR spectroscopy. The relative stereochemistry was deduced from roesy or goesy experiments.

SCHEME 4



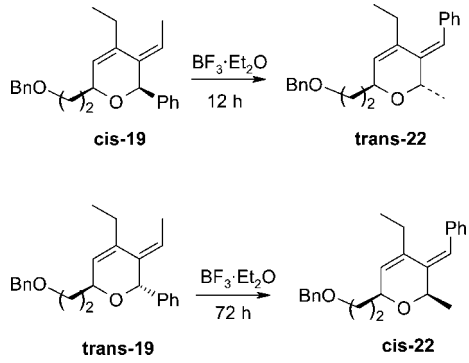
20 **21**

SCHEME 5



15 **22** (54%, cis:trans 16:84)

SCHEME 6



cis-19 **trans-22**

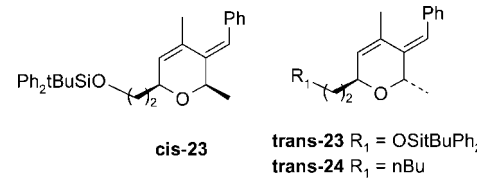
trans-19 **cis-22**

that those somewhat stronger reaction conditions could have facilitated the rearrangement. For that reason, it was decided to repeat the reaction with the other vinyl allenes under forced reaction conditions. This way it was observed, when using **15** as the vinyl allene, benzaldehyde as the heterodienophile, and longer reaction times, that after the two expected cycloadducts were formed, two new compounds started to appear, and their concentration increased in time at the expense of the cycloadducts. Those compounds were isolated, and their structures were studied by NMR spectroscopy. The data obtained was again quite similar to that of the cycloadducts, but with some of the proton NMR signals presenting anomalous shifts similar to those described for compound **21**. After completing the studies, the new compounds were identified as *cis*- and *trans*-**22** (Scheme 5). It is interesting to note that the *cis*:*trans* ratio of the new compounds was inverted with respect to that of the cycloadducts first obtained from the reaction. Thus, at shorter reaction times the *cis*:*trans* ratio of the cycloadducts (***cis*-19** and ***trans*-19**) was 79:21, and when longer reaction times were allowed, the rearranged compounds ***cis*-22** and ***trans*-22** were formed in a 16:84 ratio.

In order to determine the origin of the rearranged products, the cycloaducts *cis*- and *trans*-**19** were subjected independently to a treatment with $BF_3{\cdot}Et_2O$ in ethyl ether. It was found that each cycloadduct was transformed exclusively into one of the new compounds. More specifically, the cycloadduct ***cis*-19** was completely transformed after 12 h into ***trans*-22**, whereas ***trans*-19** was converted into ***cis*-22** in a slower process, completed only after 72 h (Scheme 6). The possibility of equilibrium was ruled out by subjecting the rearranged products to the same reaction conditions without any change being observed.

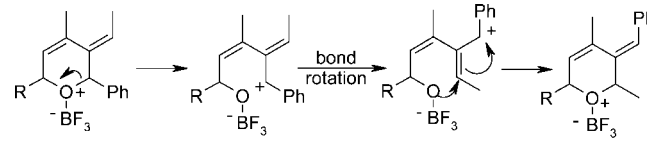
With the cycloadducts ***cis*-18** and ***trans*-18** coming from vinyl allene **14**, the situation was similar, although the rearrangement

SCHEME 7

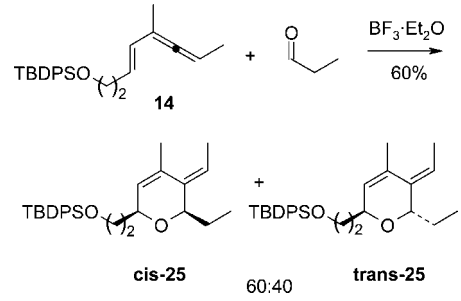


cis-23 **trans-23** R_1 = $OSitBuPh_2$
trans-24 R_1 = nBu

SCHEME 8



SCHEME 9



14 **cis-25** 60:40 **trans-25**

was considerably slower. Thus, only 50% of ***cis*-18** was converted into ***trans*-23** after 4 days, and for ***trans*-18**, 7 days at refluxing CH_2Cl_2 were needed to achieve a similar transformation into ***cis*-23**. Alkyl-substituted ***cis*-17** was more reactive, giving the rearranged ***trans*-24** after 2 days at room temperature in a 69% conversion (Scheme 7).

This behavior was never observed for the semicyclic vinyl allenes, even under stronger reaction conditions.[7]

For the rearrangement to occur, the bond between the oxygen in the cycle and the carbon atom substituted by the phenyl group (the former aldehyde double bond) must be cleaved in a heterolytic fashion and a new bond between the oxygen and the carbon substituted by the methyl group (the former extreme of the allene) must be formed (Scheme 8). Those two steps must proceed rapidly, since the rearrangement seems to be highly stereoselective.

In order to check the importance of the phenyl group in the rearrangement, the reaction of vinyl allene **14** and propionaldehyde was studied. Under the same conditions as before, two compounds were isolated and characterized as the cycloadducts ***cis*-25** and ***trans*-25** obtained in a 60% yield and 60:40 *cis*:*trans* ratio (Scheme 9). Those new compounds were treated with $BF_3{\cdot}Et_2O$ without observing any transformation other than decomposition when the treatment was continued for a long time.

Thus it seems clear that the rearrangement takes place only when the substituents on the cycle (double bond and phenyl group) are able to stabilize the incipient positive charge being formed as the oxygen−carbon bond starts to break, under stronger reaction conditions, usually longer reaction time.[15]

A similar situation, in which a doubly activated oxygen−carbon bond breaks under Lewis acid catalysis, was described by Porco, Schaus, and co-workers when using glycal-derived scaffolds.[16]The outcome of that reaction was different to the one described in this work because of the different arrangement of the reacting groups on the molecule.

Computational Studies. In order to study the mechanism of this rearrangement, computer calculations were undertaken on model compounds **26** (*cis*) and **27** (*trans*), in which the side chain was replaced by a methyl group in order to facilitate the computation, and since the reaction takes place in the presence of $BF_3 \cdot Et_2O$, the effect of this Lewis acid was simulated by including BF_3 coordinated to the oxygen atom in the structures. The method chosen was the density functional theory (DFT)[17] using the MPW1K functional[18] with the 6-31G+(d,p) basis set,[19] which has been shown to give accurate reaction barriers.[20] The use of other more commonly used functionals such as B3LYP did not allow us to locate all stationary points. All calculations were conducted using the Gaussian 03 suite of programs.[21] The solvent (ethyl ether) was simulated by the PCM method.[22] All energies reported include unscaled zero point energy corrections. All stationary points were characterized by a frequency analysis. Due to the cyclohexenic structure of the compounds in study, the possibility of different conformations existing in solution was taken into account, and thus, a full conformational search using molecular mechanics was undertaken.[23] All conformers found were then optimized using DFT calculations, and only two important conformers were found for each of the cycloadduct−BF_3 complexes, the ones in which the phenyl group was pseudoaxial (**26 Ph-ax** and **27 Ph-ax**) being considerably lower in energy than the ones in which that group presented a pseudoequatorial disposition (**26 Ph-eq** and **27 Ph-eq**) (figure 2). This effect must be due to the presence of the Lewis acid, since in the noncomplexed compounds the lower energy isomers present the phenyl group in an pseudoequatorial disposition.

Initially, to study the transformation, an AM1[24] semiempirical study of the rearrangement was conducted by stepwise elongation of the C_2-O_1 bond of the two optimized conformers of each cycloadduct. It was observed that, in the four cases, the energy increases steadily as the molecular geometry changed by rotation around the C_3-C_4 bond. At a certain point there is a sharp decrease in the energy as the intermediate structures collapses into the final products (see Supporting Information).

The final products found in this study differ from the starting compounds in either the relative stereochemistry of the substituents at the positions adjacent to the oxygen atom (**28** and **30**) or in the geometry of the exocyclic double bond (**29** and **31**) (Scheme 10). Interestingly, the two lower energy conformers for each cycloadduct give raise to compounds with the experimentally observed stereochemistry, those in which the exocyclic double bond does not change its geometry (**28** and **30**).

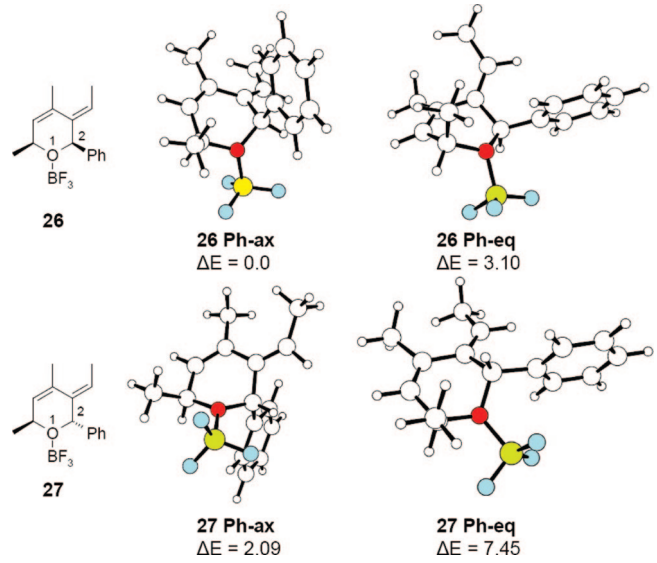
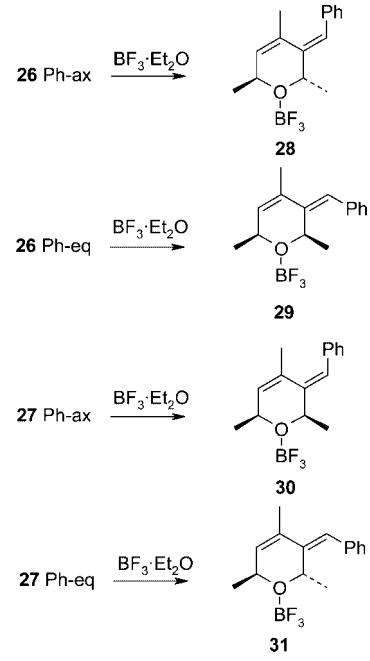


FIGURE 2. Model compounds **26** and **27** and the two lowest energy conformations found for each one. Relative energies are in kcal/mol and were computed at the PCM/MPW1K/6-31+G(d,p) level, using ethyl ether as solvent and including ZPE corrections.

SCHEME 10



(15) Following the reviewers' suggestion, the reaction of vinyl allene **15** and 4-nitrobenzaldehyde was also studied. The electron-withdrawing group should inhibit the rearrangement because the cationic intermediate would not be stabilized by the phenyl group. The reaction yielded the expected cycloadducts in a 88% yield and 83:17 *cis*:*trans* ratio. Those compounds did not suffer the rearrangement under the conditions in which ***cis*-19** and ***trans*-19** were transformed into ***cis*-22** and ***trans*-22**, providing additional support to the proposed mechanism (see Supporting Information for experimental details).

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(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004.
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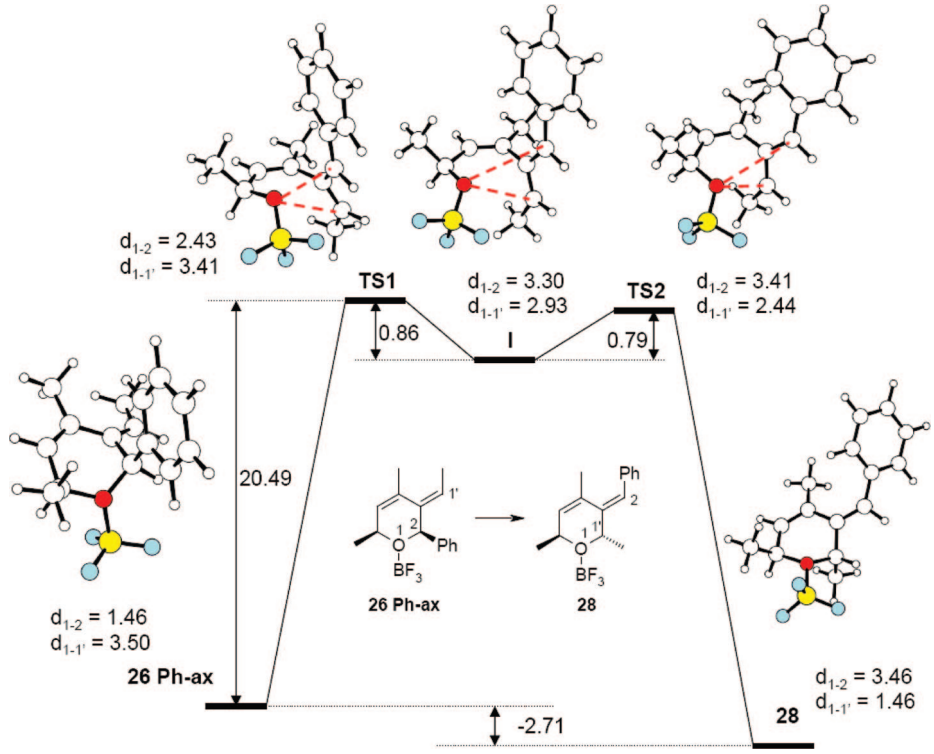

FIGURE 3. Energy profile for the rearrangement of **26 Ph-ax** showing the structures of the stationary points and the relevant distances. Relative energies are in kcal/mol, calculated at the PCM/MPW1K/6-31+G(d,p) level including ZPE corrections. Bond distances are in angstroms.

In order to study in detail the mechanism of the rearrangement, we choose the *cis* cycloadduct **26** in its lower energy conformation, the one in which the phenyl group is pseudoaxial (**26 Ph-ax**), and calculated its reaction profile at the DFT level. This profile is presented in Figure 3 together with the structures of the transition states found and the relevant distances and relative energies.

The geometry of the first transition state (**TS1**) corresponds to the breaking of the C_2-O_1 bond and is located 20.49 kcal/mol higher in energy than the starting compound. The intermediate (**I**) is only 0.86 kcal/mol more stable that **TS1**, and the length of the bonds being broken and formed is quite similar and midway between those of the transition states and of the starting and final compounds. The geometry of the second transition state (**TS2**) corresponds to the formation of the new $C_{1'}-O_1$ bond and is located at a slightly lower energy level than **TS1**. The final product (**28**) is 2.71 kcal/mol more stable than the starting one, due probably to the conjugation of the phenyl ring to the dienic system present in the molecule. The nature of the compounds involved in the reaction was also studied using the second order perturbation analysis of the Fock matrix using NBO calculations.[25] The more relevant interactions are summarized in Figure 4.

In the initial compound only the conjugation of the two double bonds (donation from the π orbital of one double bond to the π^* of the other) and the strong donation from the oxygen lone pairs to the boron atom of the Lewis acid present values above average, the later one being present in all structures studied. In the first transition state (**TS1**), the incipient positive charge being formed at C_2 is stabilized by

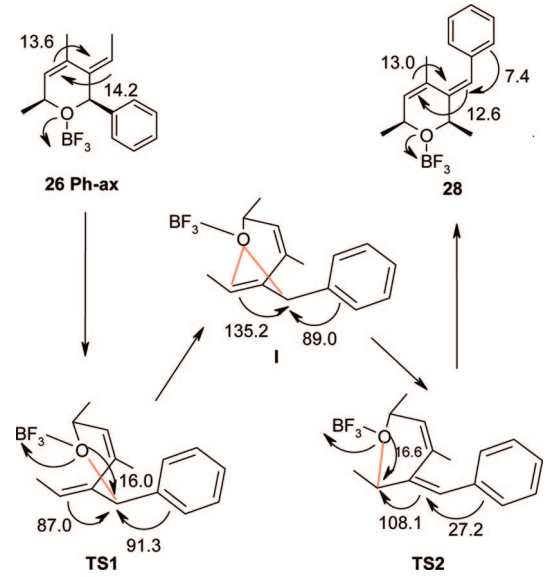

FIGURE 4. More relevant electron donations (in kcal/mol) for each stationary point on the reaction profile, found by a second order perturbation analysis of the Fock matrix using NBO calculations.

donation from the π orbital of the allylic double bond, the π system of the phenyl group, and one lone pair of the oxygen atom. The interaction between the two double bonds diminishes as the C_3-C_4 bond rotates and the π systems become orthogonal. In the intermediate (**I**) the situation is similar, but no donation from the oxygen atom to the cationic center is observed. In the second transition state (**TS2**), the donation now goes from the π system of the phenyl group to the π^* orbital of the allylic double bond and from the π orbital of this double bond to the other end of the allylic system, the $C_{1'}$ carbon to which the oxygen is getting attached. Again, a

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donation from the oxygen atom to the deficient center appears. Finally, in the rearranged product the phenyl group contributes to the conjugation of the dienic system, making this the thermodynamically most stable structure.

This sequence of events explains the importance of the phenyl group (or presumably any group that can stabilize the positive charge) in the rearrangement, since it helps the stabilization not only of the final product but also of the transition states.

Conclusions

In conclusion, we have found that acyclic vinyl allenes can react with aldehydes in the presence of $BF_3 \cdot Et_2O$ in a way similar to the one found for the semicyclic systems used by us previously, yielding pyrane derivatives. When benzaldehyde is used as heterodienophile, the cycloadducts can suffer a selective rearrangement through an ionic mechanism in which the stabilized allylic cation formed by the breaking of the oxygen−carbon bond, induced by the presence of the Lewis acid, rotates and is quickly trapped by the same oxygen atom at the other end of the allylic system. The driving force of the process being the thermodynamic stabilization obtained as a result of the conjugation of the double bonds with the phenyl group. The phenyl group also helps by stabilizing the transition states.

Experimental Section

General Procedure for Preparation of Propargyl Alcohols 5−8. To a solution of acetylene (3 equiv) in THF at −78 °C was added dropwise *n*-BuLi (1.6 M in hexane, 2.5 equiv), and the mixture was stirred for 30 min. Then, a solution of the α,β-unsaturated ketone (1 equiv) in THF was added. The reaction mixture was allowed to warm to room temperature for 2 h. Then it was quenched with aqueous saturated solution of NH_4Cl and extracted with ether. The combined organic extracts were washed with brine, dried (Na_2SO_4), concentrated and purified by column chromatography to give the propargyl alcohols **5**−**8**.

(*E*)-3-Methyl-undec-4-en-1-yn-3-ol (5). Following the general procedure using α,β-unsaturated ketone **1** (1.44 g, 9.33 mmol), the propargyl alcohol **5** was obtained in 98% yield as a colorless oil. IR ($CHCl_3$) 3300, 2900, 2100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.97 (dt, $J = 6.9$, 15.3 Hz, 1H), 5.56 (d, $J = 15.3$ Hz, 1H), 2.54 (s, 1H), 2.23 (brs, 1H), 2.03 (q, $J = 6.9$ Hz, 2H), 1.54 (s, 3H), 1.38−1.26 (m, 8H), 0.86 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ133.4 (d), 131.0 (d), 86.5 (s), 72.5 (d), 67.8 (s), 31.8 (t), 31.6 (t), 30.3 (q), 28.9 (t), 28.8 (t), 22.6 (t), 14.1 (q); HRMS (EI) *m*/*z* calcd for $C_{12}H_{20}O$ 180.1514, found 180.1516.

(*E*)-7-(*tert*-Butyldiphenylsilyloxy)-3-methylhept-4-en-1-yn-3-ol (6). Following the general procedure using 3.25 g of **2** (9.20 mmol), propargyl alcohol **6** was obtained in 84% yield as a colorless oil. IR ($CHCl_3$) 3600, 3400, 2900 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69−7.68 (m, 4H), 7.45−7.26 (m, 6H), 6.04 (dt, $J = 6.9$, 15.4 Hz, 1H), 5.65 (d, $J = 15.4$ Hz, 1H), 3.74 (t, $J = 6.4$ Hz, 2H), 2.55 (s, 1H), 2.33 (q, $J = 6.6$ Hz, 2H), 1.56 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6 (d), 135.4 (d), 133.9 (s), 129.6 (d), 127.6 (d), 86.3 (s), 72.6 (s), 67.8 (s), 63.2 (t), 35.1 (t), 30.2 (q), 26.9 (q), 19.2 (s); MS (EI) *m*/*z* 321 ($M^+ - t$Bu, 10), 303 (6), 229 (17), 199 (100); HRMS (EI) *m*/*z* calcd for $C_{20}H_{21}O_2Si$ ($M^+ - t$Bu) 321.1311, found 321.1262.

(*E*)-7-(Benzyloxy)-3-ethylhept-4-en-1-yn-3-ol (7). Following the general procedure using 1.5 g of **3** (6.88 mmol), propargyl alcohol **7** was obtained in 63% yield as a colorless oil. IR ($CHCl_3$) 3400, 2900, 2100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.26 (m, 5H), 6.03 (dt, $J = 5.2$, 15.4 Hz, 1H), 5.58 (d, $J = 15.4$ Hz, 1H), 4.52 (s, 2H), 3.53 (t, $J = 6.7$ Hz, 2H), 2.57 (s, 1H), 2.40 (q, $J = 6.7$ Hz, 2H), 1.81−1.66 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3 (s), 134.4 (d), 128.4 (d), 128.2 (d), 127.7 (d), 127.6 (d), 85.1 (s), 73.8 (d), 72.8 (t), 71.7 (s), 69.4 (t), 35.4 (t), 32.3 (t), 8.7 (q); MS (EI) *m*/*z* 244 (M^+, 0.52), 226 (24), 197 (40), 171 (26), 91 (100); HRMS (EI) *m*/*z* calcd for $C_{16}H_{20}O_2$ 244.1463, found 244.1457.

(*E*)-3-*tert*-Butylnon-4-en-1-yn-3-ol (8). Following the general procedure using 2.32 g of **4** (13.78 mmol), propargyl alcohol **8** was obtained in 90% yield as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.98 (dt, $J = 6.4$, 15.4 Hz, 1H), 5.60 (d, $J = 15.4$ Hz, 1H), 2.53 (s, 1H), 2.08 (q, $J = 6.4$ Hz, 2H), 1.97 (brs, 1H), 1.40−1.24 (m, 4H), 1.01 (s, 9H), 0.89 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.7 (d), 129.9 (d), 85.3 (s), 76.9 (s), 73.3 (d), 38.4 (s), 31.7 (t), 31.3 (t), 25.0 (q), 22.2 (t), 13.8 (q); MS (EI) *m*/*z* 194 (M^+, 0.5), 179 (8), 137 (63), 81 (100); HRMS (EI) *m*/*z* calcd for $C_{13}H_{22}O$ 194.1670, found 194.1632.

General Procedure for Preparation of Benzoates 9−12. To a stirred solution of the propargyl alcohol (**5** − **8**) (1 equiv) in THF (70 mL) at −78 °C under argon was added dropwise *n*-BuLi (1.6 M in hexanes, 1.1 equiv). The reaction mixture was kept at this temperature for 30 min and stirred for a further 5 min at 0 °C. It was then cooled to −78 °C, benzoyl chloride (1.1 equiv) was added, and the reaction mixture was allowed to reach room temperature. The mixture was stirred for 3 h, and saturated aqueous NH_4Cl solution was added. The mixture was then extracted with diethyl ether, and the combined organic layers were washed with a saturated aqueous NaCl solution, dried ($MgSO_4$), concentrated and purified by column chromatography affording the corresponding benzoates (**9** −**12**).

(*E*)-3-Methylundec-4-en-1-yn-3-yl Benzoate (9). Following the general procedure, **5** (1.3 g, 7.21 mmol) was converted into **9** in 78% yield, obtained as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−8.01 (m, 2H), 7.55−7.40 (m, 3H), 6.13 (dt, $J = 6.9$, 15.4 Hz, 1H), 5.74 (d, $J = 15.4$ Hz, 1H), 2.71 (s, 1H), 2.10 (q, $J = 7.2$ Hz, 2H), 1.85 (s, 3H), 1.43−1.27 (m, 8H), 0.87 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (s), 137.0 (s), 133.2 (d), 132.8 (d), 130.8 (s), 130.1 (d), 129.6 (d), 128.2 (d), 82.8 (s), 74.7 (d), 73.9 (s), 31.9 (t), 31.6 (t), 28.9 (q), 28.8 (t), 28.8 (t), 22.6 (t), 14.1 (q); MS (EI) *m*/*z* 284 (M^+, 3), 213 (4), 197 (15), 105 (100); HRMS (EI) *m*/*z* calcd for $C_{19}H_{24}O_2$ 284.1776, found 284.1768

(*E*)-7-(*tert*-Butyldiphenylsilyloxy)-3-methylhept-4-en-1-yn-3-yl Benzoate (10). Following the general procedure, **6** (3.25 g, 8.59 mmol) was converted into **10** in 85% yield, obtained as a colorless oil. IR ($CHCl_3$) 3300, 2900, 1720, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06−8.03 (m, 2H), 7.71−7.69 (m, 4H), 7.57−7.54 (m, 1H), 7.45−7.37 (m, 8H), 6.25 (dt, $J = 6.9$, 15.4 Hz, 1H), 5.87 (d, $J = 15.4$ Hz, 1H), 3.78 (t, $J = 6.3$ Hz, 2H), 2.73 (s, 1H), 2.40 (m, 2H), 1.89 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 (s), 136.0 (d), 134.3 (s), 133.3 (d), 132.5 (d), 131.2 (s), 130.1 (d), 128.7 (d), 128.1 (d), 83.1 (s), 75.3 (d), 74.9 (s), 63.5 (t), 35.7 (t), 29.1 (q), 27.3 (q), 19.6 (s); MS (EI) *m*/*z* 482 (M^+, 0.2), 425 (0.6), 303 (29), 225 (60), 199 (100); HRMS (EI) *m*/*z* calcd for $C_{31}H_{34}O_3Si$ 482.2277, found 482.2269.

(*E*)-7-(Benzyloxy)-3-ethylhept-4-en-1-yn-3-yl Benzoate (11). Following the general procedure, **7** (1.5 g, 6.88 mmol) was converted into **11** in 54% yield as a colorless oil. IR ($CHCl_3$) 3300, 2900, 2100, 1780, 1710, 1600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−8.01 (m, 2H), 7.57−7.53 (m, 1H), 7.44−7.40 (m, 2H), 7.33−7.25 (m, 5H), 6.17 (dt, $J = 6.9$, 15.5 Hz, 1H), 5.70 (d, $J = 15.5$ Hz, 1H), 4.52 (s, 3H), 3.56 (t, $J = 6.8$ Hz, 2H), 2.73 (s, 1H), 2.48−2.42 (m, 2H), 2.21−2.15 (m, 1H), 2.01−1.95 (m, 1H), 1.09 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (s), 138.4 (s), 132.9 (d), 130.9 (d), 130.2 (s), 129.6 (d), 128.3 (d), 127.6 (d), 127.5 (d), 81.3 (s), 78.4 (s), 75.9 (d), 72.9 (t), 69.5 (t), 34.4 (t), 32.5 (t), 8.4 (q); MS (EI) *m*/*z* 348 (M^+, 0.5), 135 (12), 120 (9), 105 (100); HRMS (EI) *m*/*z* calcd for $C_{23}H_{24}O_3$ 348.1725, found 348.1759.

(*E*)-3-*tert*-Butylnon-4-en-1-yn-3-yl Benzoate (12). Following the general procedure, **8** (2.4 g, 12.35 mmol) was converted into **12** in 62% yield as a colorless oil. IR ($CHCl_3$) 3300, 2900, 1725,

1600, 1450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.04−8.02 (m, 2H), 7.57−7.26 (m, 3H), 6.09 (dt, J = 6.8, 15.5 Hz, 1H), 5.50 (d, J = 15.5 Hz, 1H), 2.71 (s, 1H), 2.21 − 2.07 (m, 2H),1.46 − 1.30 (m, 4H), 1.17 (s, 9H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (s), 135.1 (d), 132.7 (d), 131.3 (s), 129.5 (d), 128.3 (d), 126.2 (d), 83.3 (s), 80.7 (s), 76.4 (d), 39.7 (s), 31.8 (t), 31.2 (t), 25.2 (q), 22.2 (t), 13.9 (q); MS (EI) *m/z* 298 (M^+, 3), 242 (4), 193 (30), 105 (100); HRMS (EI) *m/z* calcd for $C_{20}H_{26}O_2$ 298.1933, found 298.1899.

General Procedure for Preparation of Vinyl Allenes 13−16. To a suspension of LiBr (6 equiv) and CuI (6 equiv) in THF at 0 °C under argon was slowly added MeMgBr (6 equiv). After 15 min the corresponding benzoate (**9** − **12**) (1 equiv) in THF was added, and the reaction was allowed to reach room temperature and was stirred for 8 h. After cooling at −20 °C, 50 mL of a saturated aqueous solution of NH_4Cl were added, and the reaction was extracted with diethyl ether, washed with saturated aqueous solutions of $NaHCO_3$ and NaCl, dried over Na_2SO_4, concentrated and purified by column chromatography (*n*-hexane) to give the corresponding vinyl allene (**13**−**16**).

(*E*)-4-Methyl-dodeca-2,3,5-triene (13). Following the general procedure, **9** (1.6 g, 5.62 mmol) was converted into **13** in 53% yield, obtained as a colorless oil. IR ($CHCl_3$) 1940, 1440 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.97 (d, J = 15.6 Hz, 1H), 5.50 (dt, J = 6.9, 15.5 Hz, 1H), 5.16−5.13 (m, 1H), 2.09 (q, J = 6.9 Hz, 2H), 1.72 (s, 3H), 1.65 (d, J = 3.3 Hz, 3H), 1.40−1.26 (m, 8H), 0.89 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8 (s), 129.1 (d), 128.7 (d), 100.5 (s), 84.6 (d), 32.9 (t), 31.9 (t), 29.6 (t), 28.9 (t), 22.6 (t), 15.6 (q), 14.5 (q), 14.0 (q); HRMS (EI) *m/z* calcd for $C_{13}H_{22}$ 178.1721, found 178.1750.

(*E*)-*tert*-Butyl(5-methylocta-3,5,6-trienyloxy)diphenylsilane (14). Following the general procedure, **10** (1.1 g, 2.27 mmol) was converted into **14** in 73% yield, obtained as a colorless oil. IR ($CHCl_3$) 2800, 1940, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.71 (m, 4H), 7.47−7.39 (m, 6H), 6.06 (d, J = 15.7 Hz, 1H), 5.55 (dt, J = 7.8, 15.7 Hz, 1H), 5.18 (brs, 1H), 3.75 (t, J = 6.7 Hz, 2H), 2.41 (q, J = 6.8 Hz, 2H), 1.80 (s, 3H), 1.68 (d, J = 6.7 Hz, 3H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4 (s), 135.4 (d), 134.4 (s), 131.3 (d), 130.0 (d), 128.0 (d), 125.4 (d), 99.7 (s), 85.2 (d), 64.3 (t), 36.6 (t), 27.3 (q), 19.7 (s), 16.0 (q), 15.0 (q); HRMS (EI) *m/z* calcd for $C_{25}H_{32}OSi$ 376.2222, found 376.2256.

(*E*)-((5-Ethylocta-3,5,6-trienyloxy)methyl)benzene (15). Following the general procedure, **11** (1.1 g, 3.15 mmol) was converted into **15** in 50% yield, obtained as a volatile colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.37−7.27 (m, 5H), 6.04 (d, J = 15.8 Hz, 1H), 5.60 (dt, J = 6.9, 16.8 Hz, 1H), 5.30−5.28 (m, 1H), 4.52 (s, 2H), 3.53 (t, J = 6.8 Hz, 2H), 2.44 (q, J = 6.8 Hz, 2H), 2.17−2.08 (m, 2H), 1.69 (d, J = 7.0 Hz, 3H), 1.05 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.2 (s), 138.5 (s), 130.2 (d), 128.3 (d), 127.6 (d), 127.5 (d), 124.2 (d), 106.0 (s), 87.1 (d), 72.89 (t), 70.0 (t), 33.5 (t), 21.6 (t), 14.6 (q), 12.2 (q); MS (EI) *m/z* 242 (M^+, 50), 167 (13), 105 (13), 91 (100); HRMS (EI) *m/z* calcd for $C_{17}H_{22}O$ 242.1670, found 242.1704.

(*E*)-4-*tert*-Butyldeca-2,3,5-triene (16). Following the general procedure, **12** (2.27 g, 7.6 mmol) was converted into **16** in 82% yield, obtained as a volatile colorless oil. IR ($CHCl_3$) 2900, 1945, 1460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.77 (s, 2H), 5.26 (q, J = 7.0 Hz, 1H), 2.10−2.07 (m, 2H), 1.68 (d, J = 6.8 Hz, 3H), 1.38−1.30 (m, 4H), 1.06 (s, 9H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5 (s), 141.4 (s), 132.6 (d), 123.9 (d), 113.1 (s), 87.6 (d), 32.9 (s), 32.7 (t), 31.5 (t), 29.4 (q), 22.2 (t), 14.7 (q), 13.9 (q); MS (EI) *m/z* 193 (M^+ + 1, 92), 192 (M^+, 52), 135 (40), 57 (100); HRMS (EI) *m/z* calcd for $C_{14}H_{24}$ 192.1878, found 192.1821.

General Procedure for Reaction of Vinyl Allenes and Benzaldehyde. To a solution of benzaldehyde (1.1 equiv) in dry ether was added $BF_3 \cdot Et_2O$ (1.1 equiv) at 0 °C under argon. After 15 min the allene (1 equiv) in ether was added, and the reaction was stirred at room temperature for 12−24 h. Then, TEA (2.5 equiv) was added, and the mixture was poured on iced water, extracted with ether, dried over $MgSO_4$ concentrated and purified by column chromatography to give the cycloadducts as a *cis*:*trans* mixture that was separated by HPLC.

***cis*- and *trans*-17.** Using **13** (150 mg, 0.84 mmol) as the vinyl allene and following the general procedure, a 69:31 mixture of *cis* and *trans* **17** was obtained in 64% yield. **(2*R**,6*S**,*E*)-3-Ethylidene-6-hexyl-4-methyl-2-phenyl-3,6-dihydro-2*H*-pyran (*cis*-17)**: pale yellow oil. IR ($CHCl_3$) 2900, 1600, 1450 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.56−7.54 (m, 2H), 7.32−7.19 (m, 3H), 5.50 (s, 1H), 5.11 (s, 1H), 5.02 (m, 1H), 4.43 (brs, 1H), 2.08 (s, 3H), 1.79−1.56 (m, 4H), 1.64 (d, J = 7.5 Hz, 3H), 1.41−1.29 (m, 6H), 0.95 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 141.3 (s), 138.2 (s), 132.4 (s), 130.5 (d), 128.3 (d), 127.9 (d), 127.3 (d), 122.8 (d), 81.3 (d), 75.8 (d), 36.1 (t), 31.9 (t), 29.6 (t), 25.3 (t), 23.3 (q), 22.7 (t), 14.8 (q), 14.0 (q); MS (EI) *m/z* 284 (M^+, 2.9), 269 (2), 208 (12), 193 (14), 189 (12), 105 (100); HRMS (EI) *m/z* calcd for $C_{20}H_{28}O$ 284.2140, found 284.2138. **(2*S**,6*S**,*E*)-3-Ethylidene-6-hexyl-4-methyl-2-phenyl-3,6-dihydro-2*H*-pyran (*trans*-17)**: pale yellow oil. IR ($CHCl_3$) 2900, 1590, 1440 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.61−7.59 (m, 2H), 7.35−7.19 (m, 3H), 5.41 (s, 1H), 5.26 (s, 1H), 5.24 (m, 1H), 4.07 (brs, 1H), 2.07 (s, 3H), 1.80 (d, J = 7.3 Hz, 3H), 1.76−1.72 (m, 1H), 1.67−1.51 (m, 3H), 1.37−1.27 (m, 6H), 0.96 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 141.1 (s), 133.5 (s), 130.6 (d), 130.2 (s), 129.2 (d), 126.6 (d), 123.5 (d), 80.5 (d), 69.6 (d), 35.4 (t), 31.9 (t), 29.4 (t), 25.3 (t), 23.7 (q), 22.7 (t), 14.7 (q), 14.0 (q); MS (EI) *m/z* 284 (M^+, 11), 255 (12), 199 (30), 196 (11), 181 (12), 156 (100); HRMS (EI) *m/z* calcd for $C_{20}H_{28}O$ 284.2140, found 284.2133.

***cis*- and *trans*-18.** Following the general procedure, vinyl allene **14** (150 mg, 0.40 mmol) provided **18** as a 70:30 mixture in 56% yield. ***tert*-Butyl(2-((2*R**,6*S**,*E*)-5-ethylidene-4-methyl-6-phenyl-5,6-dihydro-2*H*-pyran-2-yl)ethoxy)diphenylsilane (*cis*-18)**: pale yellow oil; IR ($CHCl_3$) 2900, 1630, 1585, 1425 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.87−7.83 (m, 4H), 7.49−7.47 (m, 2H), 7.32−7.16 (m, 9H), 5.50 (s, 1H), 5.10 (s, 1H), 4.99 (q, J = 7.4 Hz, 1H), 4.79 (brs, 1H), 4.12 (m, 1H), 3.95 (m, 1H), 2.05−1.97 (m, 2H), 2.03 (s, 3H), 1.59 (d, J = 7.4 Hz, 3H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 141.2 (s), 138.1 (s), 135.8 (d), 134.2 (s), 133.9 (s), 130.6 (d), 129.6 (d), 128.4 (d), 128.0 (d), 127.8 (d), 127.3 (d), 123.0 (d), 81.3 (d), 72.6 (d), 60.2 (t), 38.9 (t), 26.9 (q), 23.4 (q), 19.2 (s), 14.9 (q); MS (EI) *m/z* 482 (M^+, 0.3), 425 (23), 347 (13), 209 (39), 199 (100); HRMS (EI) *m/z* calcd for $C_{32}H_{38}O_2Si$ 482.2641, found 482.2652. ***tert*-Butyl(2-((2*R**,6*R**,*E*)-5-ethylidene-4-methyl-6-phenyl-5,6-dihydro-2*H*-pyran-2-yl)ethoxy)diphenylsilane (*trans*-18)**: IR ($CHCl_3$) 3400, 2900, 1720, 1585, 1460 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.89−7.82 (m, 4H), 7.61−7.59 (m, 2H), 7.34−7.19 (m, 9H), 5.35 (s, 1H), 5.23 (m, 2H), 4.43 (brs, 1H), 4.13 (m, 1H), 3.92 (m, 1H), 2.01 (s, 3H), 1.96−1.90 (m, 2H), 1.77 (d, J = 7.4 Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 140.9 (s), 135.8 (d), 134.2 (s), 133.7 (s), 130.5 (d), 130.3 (s), 129.6 (d), 128.1 (d), 127.8 (d), 123.6 (d), 80.4 (d), 66.9 (d), 60.4 (t), 38.3 (t), 26.9 (q), 23.2 (q), 19.2 (s), 14.7 (q); MS (EI) *m/z* 482 (M^+, 1), 425 (45), 347 (23), 209 (84), 199 (100); HRMS (EI) *m/z* calcd for $C_{32}H_{38}O_2Si$ 482.2641, found 482.2605.

***cis*- and *trans*-19.** Following the general procedure, after 24 h, vinyl allene **15** (80 mg, 0.33 mmol) provided **19** as a 79:21 *cis*:*trans* mixture in a 54% yield. **(2*R**,6*S**,*E*)-6-(2-(Benzyloxy)ethyl)-4-ethyl-3-ethylidene-2-phenyl-3,6-dihydro-2*H*-pyran (*cis*-19)**: ^1H NMR (400 MHz, C_6D_6) δ 7.52−7.47 (m, 2H), 7.36−7.16 (m, 8H), 5.58 (s, 1H), 5.11 (s, 1H), 5.03 (q, J = 7.0 Hz, 1H), 4.70 (brs, 1H), 4.36 (s, 2H), 3.80−3.74 (m, 1H), 3.69−3.64 (m, 1H), 2.48−2.41 (m, 1H), 2.37−2.30 (m, 1H), 2.10−2.08 (m, 2H), 1.59 (d, J = 7.2 Hz, 3H), 1.08 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 141.3 (s), 139.2 (s), 138.7 (s), 137.2 (s), 128.4 (d), 128.3 (d), 128.2 (d), 128.0 (d), 127.8 (d), 127.5 (d), 127.4 (d), 127.2 (d), 122.3 (d), 81.5 (d), 73.2 (d), 72.7 (t), 66.8 (t), 36.5 (t), 28.4 (t), 14.8 (q), 13.2 (q); MS (EI) *m/z* 348 (M^+, 0.8), 319 (3), 257 (14),

195 (100); HRMS (EI) *m/z* calcd for $C_{24}H_{28}O_2$ 348.2089, found 348.2143. **(2*S**,6*S**,*E*)-6-(2-(Benzyloxy)ethyl)-4-ethyl-3-ethylidene-2-phenyl-3,6-dihydro-2*H*-pyran (*trans*-19)**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.61−7.59 (m, 2H), 7.38−7.19 (m, 8H), 5.37 (s, 1H), 5.31 (s, 1H), 5.24 (q, J = 7.2 Hz, 1H), 4.41 (brs, 2H), 3.82−3.76 (m, 1H), 3.66−3.62 (m, 1H), 2.53−2.47 (m, 1H), 2.33−2.27 (m, 1H), 2.02 (q, J = 5.7 Hz, 2H), 1.75 (d, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 140.9 (s), 139.3 (s), 136.1 (s), 132.8 (s), 128.5 (d), 128.2 (d), 128.0 (d), 127.8 (d), 127.5 (d), 127.2 (d), 123.3 (d), 80.8 (d), 72.8 (t), 67.5 (d), 66.8 (t), 35.8 (t), 28.5 (t), 14.8 (q), 13.2 (q); HRMS (EI) *m/z* calcd for $C_{24}H_{28}O_2$ 348.2089, found 348.2091.

Reaction of Vinyl Allene 16 and Benzaldehyde. Following the general procedure, using 1.5 equiv of $BF_3\cdot Et_2O$ and after 72 h, vinyl allene **16** (154 mg, 0.8 mmol) gave 59% yield of a 52:48 mixture of cycloadduct **20**, which could not be isolated pure, and rearranged product **21**. **(2*R**,6*S**,*E*)-4-*tert*-Butyl-6-butyl-3-ethylidene-2-phenyl-3,6-dihydro-2*H*-pyran (20)**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.51−7.49 (m, 2H), 7.29−7.16 (m, 3H), 6.01 (d, J = 3.6 Hz, 1H), 5.51 (s, 1H), 5.47 (q, J = 7.1 Hz, 1H), 4.02 (m, 1H), 1.98−1.95 (m, 1H), 1.80−1.75 (m, 2H), 1.65 (d, J = 7.1 Hz, 3H), 1.47−1.42 (m, 3H), 0.97 (s, 9H), 0.95−0.91 (m, 3H). **(2*R**,6*R**,*E*)-3-Benzylidene-6-butyl-4-*tert*-butyl-2-methyl-3,6-dihydro-2*H*-pyran (21)**: IR ($CHCl_3$) 3300, 2900, 1595, 1460, 1360 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 7.39−7.10 (m, 5H), 6.52 (s, 1H), 5.87 (d, J = 3.8 Hz, 1H), 4.41 (q, J = 6.2 Hz, 1H), 4.35 (m, 1H), 1.81−1.60 (m, 4H), 1.44 (d, J = 6.1 Hz, 3H), 1.44−1.39 (m, 2H), 1.06 (s, 9H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 147.8 (s), 140.0 (s), 139.4 (s), 129.5 (d), 129.2 (d), 128.1 (d), 127.1 (d), 124.8 (d), 75.4 (d), 72.1 (d), 35.6 (t), 31.5 (q), 28.0 (t), 23.0 (t), 18.2 (q), 14.1 (q); MS (EI) *m/z* 298 (M$^+$, 10), 241 (12), 184 (25); HRMS (EI) *m/z* calcd for $C_{21}H_{30}O$ 298.2296, found 298.2176.

Reaction of Vinyl Allene 15 and Benzaldehyde under Forced Reaction Conditions. Following the general procedure using vinyl allene **15** (80 mg, 0.33 mmol), with 1.5 equiv of $BF_3\cdot Et_2O$ and after 72 h, the rearranged compounds **22** were obtained in 54% yield as a 16:84 *cis*:*trans* mixture. **(2*S**,6*R**,*E*)-3-Benzylidene-6-(2-(benzyloxy)ethyl)-4-ethyl-2-methyl-3,6-dihydro-2*H*-pyran (*cis*-22)**: colorless oil; ^{1}H NMR (400 MHz, C_6D_6) δ 7.41−7.10 (m, 10H), 6.52 (s, 1H), 5.57 (s, 1H), 4.63 (brs, 1H), 4.45 (s, 2H), 4.20 (q, J = 6.2 Hz, 1H), 3.82−3.78 (m, 1H), 3.73−3.67 (m, 1H), 2.14−2.00 (m, 3H), 1.48 (d, J = 6.2 Hz, 3H), 1.15−1.11 (m, 1H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 139.3 (s), 139.0 (s), 138.7 (s), 138.4 (s), 129.8 (d), 128.8 (d), 127.9 (d), 127.6 (d), 126.8 (d), 122.4 (d), 73.6 (d), 73.0 (d), 72.8 (t), 66.7 (t), 36.7 (t), 26.8 (t), 18.5 (q), 13.1 (q); HRMS (EI) *m/z* calcd for $C_{24}H_{28}O_2$ 348.2089, found 348.2073. **(2*R**,6*R**,*E*)-3-Benzylidene-6-(2-(benzyloxy)ethyl)-4-ethyl-2-methyl-3,6-dihydro-2*H*-pyran (*trans*-22)**: colorless oil; ^{1}H NMR (400 MHz, C_6D_6) δ 7.42−7.09 (m, 10H), 6.34 (s, 1H), 5.50 (s, 1H), 4.61 (brs, 1H), 4.49 (q, J = 6.5 Hz, 1H), 4.47 (s, 2H), 3.83−3.77 (m, 1H), 3.72−3.67 (m, 1H), 2.15−1.96 (m, 4H), 1.40 (d, J = 6.5 Hz, 3H), 0.80 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 Mz, C_6D_6) δ 139.3 (s), 138.7 (s), 137.4 (s), 135.8 (s), 129.2 (d), 129.1 (d), 128.3 (d), 128.0 (d), 127.8 (d), 127.3 (d), 126.8 (d), 124.1 (d), 74.2 (d), 72.6 (t), 67.9 (d), 66.9 (t), 36.0 (t), 26.8 (t), 18.0 (q), 13.1 (q); MS (EI) *m/z* 348 (M$^+$, 0.6), 257 (10), 91 (100); HRMS (EI) *m/z* calcd for $C_{24}H_{28}O_2$ 348.2089, found 348.2086.

General Procedure for Rearrangement of Cycloadducts. To a solution of the cycloadduct (1 equiv) in ether at 0 °C was added $BF_3\cdot Et_2O$ (1.0−2.5 equiv). The reaction mixture was allowed to warm to room temperature and was stirred until TLC showed no further transformation. Then TEA was added, and the solvent was removed. Column chromatography afforded the pure compounds.

Rearrangement of *cis*-17. Following the general procedure, ***cis*-17** (68 mg, 0.24 mmol), using 1.1 equiv of $BF_3\cdot Et_2O$ and after 2 d, afforded 14 mg of starting material and ***trans*-24** (47 mg, 0.165 mmol, 69%) as a yellow oil. **(2*R**,6*R**,*E*)-3-Benzylidene-6-(2-(benzyloxy)ethyl)-2,4-dimethyl-3,6-dihydro-2*H*-pyran (*trans*-24)**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.24−7.11 (m, 5H), 6.36 (s, 1H), 5.45 (s, 1H), 4.55 (q, J = 6.5 Hz, 1H), 4.35 (brs, 1H), 1.79−1.63 (m, 5H), 1.66 (s, 3H), 1.45 (d, J = 6.5 Hz, 3H), 1.42−1.37 (m, 5H), 0.97 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz C_6D_6) δ 138.9 (s), 138.8 (s), 131.4 (d), 129.2 (d), 127.4 (d), 126.6 (d), 124.3 (d), 73.7 (d), 70.0 (d), 35.5 (t), 32.0 (t), 29.6 (t), 25.6 (t), 22.8 (t), 22.1 (q), 18.4 (q), 14.0 (q); MS (FAB) *m/z* 284 (M$^+$, 0.9), 200 (54), 186 (39), 171 (64), 157 (32), 129 (49), 105 (100); HRMS (EI) *m/z* calcd for $C_{20}H_{28}O$ 284.2140, found 284.2145.

Rearrangement of *cis*-18. Following the general procedure, ***cis*-18** (50 mg, 0.10 mmol), using 2.5 equiv of $BF_3\cdot Et_2O$ and after 4 d, afforded 20 mg of starting material and ***trans*-23** (25 mg, 0.05 mmol, 50%) as a yellow oil: **(2-((2*R**,6*R**,*E*)-5-Benzylidene-4,6-dimethyl-5,6-dihydro-2*H*-pyran-2-yl)ethoxy-(*tert*-butyl)diphenylsilane (*trans*-23)**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.88−7.85 (m, 4H), 7.32−7.06 (m, 6H), 6.30 (s, 1H), 5.38 (s, 1H), 4.65 (brs, 1H), 4.28 (q, J = 6.4 Hz, 1H), 4.11 (m, 1H), 3.95 (m, 1H), 1.96 (m, 2H), 1.52 (s, 3H), 1.39 (d, J = 6.4 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR (75 MHz C_6D_6) δ 138.8 (s), 138.6 (s), 135.8 (d), 135.7 (d), 134.2 (s), 134.1 (s), 131.3 (d), 129.6 (d), 129.3 (d), 129.2 (d), 126.6 (d), 124.3 (d), 73.3 (d), 67.1 (d), 60.6 (t), 38.2 (t), 26.9 (q), 22.1 (q), 19.2 (s), 18.3 (q); MS (EI) *m/z* 482 (M$^+$, 0.2), 425 (10), 247 (23), 199 (100); HRMS (EI) *m/z* calcd for $C_{32}H_{38}O_2Si$ 482.2641, found 482.2638.

Rearrangement of *trans*-18. To a solution of ***trans*-18** (50 mg, 0.1 mmol) in CH_2Cl_2 at 0 °C was added $BF_3\cdot Et_2O$ (2.5 equiv). The reaction mixture was refluxed for 7 d, then TEA was added, and the solvent was removed. Column chromatography afforded 20 mg of starting material and ***cis*-23** (25 mg, 0.05 mmol, 50% yield) as a yellow oil; **(2-((2*R**,6*S**,*E*)-5-Benzylidene-4,6-dimethyl-5,6-dihydro-2*H*-pyran-2-yl)ethoxy(*tert*-butyl)diphenylsilane (*cis*-23)**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.95−7.83 (m, 4H), 7.34−7.18 (m, 6H), 6.54 (s, 1H), 5.46 (s, 1H), 4.66 (brs, 1H), 4.18 (m, 2H), 4.00 (m, 1H), 2.01 (m, 2H), 1.63 (s, 3H), 1.46 (d, J = 6.4 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 139.6 (s), 139.3 (s), 135.7 (d), 134.3 (s), 134.2 (s), 132.2 (d), 131.9 (d), 129.6 (d), 129.3 (d), 126.7 (d), 122.9 (d), 73.1 (d), 72.5 (d), 60.4 (t), 39.2 (t), 26.9 (q), 22.0 (q), 19.3 (s), 18.4 (q).

Reaction of Vinyl Allene 14 and Propionaldehyde. Following the general procedure, vinyl allene **14** (150 mg, 0.40 mmol), propionaldehyde (0.44 mmol), and $BF_3\cdot Et_2O$ (1.1 equiv), after 24 h, provided compounds ***cis*-25** (63 mg, 0.14 mmol) and ***trans*-25** (41 mg, 0.096 mmol) in a 60:40 ratio, and 60% yield. ***tert*-Butyl(2-((2*R**,6*S**,*E*)-6-ethyl-5-ethylidene-4-methyl-5,6-dihydro-2*H*-pyran-2-yl)ethoxy)diphenylsilane (*cis*-25)**: IR ($CHCl_3$) 3500, 2900, 1700, 1460, 1420 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 7.90−7.86 (m, 4H), 7.32−7.30 (m, 6H), 5.44 (s, 1H), 5.37 (q, J = 7.3 Hz, 1H), 4.57 (brs, 1H), 4.11 (m, 1H), 3.96 (m, 1H), 3.89 (m, 1H), 2.00 (s, 3H), 1.96 (q, J = 6.2 Hz, 2H), 1.79 − 1.70 (m, 2H), 1.76 (d, J = 7.3 Hz, 3H), 1.27 (s, 9H), 1.13 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 136.8 (s), 135.8 (d), 134.2 (s), 132.4 (s), 130.4 (d), 129.7 (d), 127.8 (d), 118.2 (d), 78.6 (d), 72.1 (d), 60.6 (t), 39.2 (t), 26.9 (q), 25.7 (t), 23.2 (q), 19.2 (s), 14.9 (q), 10.4 (q); MS (EI) *m/z* 434 (M$^+$, 0.1), 377 (15), 299 (12), 199 (100), 178 (97), 161 (94); HRMS (EI) *m/z* calcd for $C_{28}H_{38}O_2Si$ 434.2641, found 434.2603. ***tert*-Butyl(2-((2*R**,6*R**,*E*)-6-ethyl-5-ethylidene-4-methyl-5,6-dihydro-2*H*-pyran-2-yl)ethoxy)diphenylsilane (*trans*-25)**: IR ($CHCl_3$) 3300, 2900, 1720, 1585, 1460, 1420 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.92−7.87 (m, 4H), 7.33−7.25 (m, 6H), 5.37 (s, 1H), 5.17 (q, J = 7.3 Hz, 1H), 4.59 (brs, 1H), 4.18−4.08 (m, 2H), 4.01−3.94 (m, 1H), 1.98 (s, 3H), 1.95−1.83 (m, 3H), 1.74 (d, J = 7.3 Hz, 3H), 1.62−1.53 (m, 1H), 1.28 (s, 9H), 1.05 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 135.9 (s), 135.8 (d)

134.2 (s), 134.2 (s), 129.6 (d), 127.8 (d), 127.4 (d), 120.4 (d), 80.9 (d), 66.0 (d), 60.6 (t), 38.7 (t), 26.9 (q), 25.3 (t), 23.3 (q), 19.2 (s), 14.6 (q), 10.7 (q); MS (EI) *m*/*z* 434 (M^+, 0.7), 377 (13), 299 (10), 199 (97), 178 (85), 161 (100); HRMS (EI) *m*/*z* calcd for $C_{28}H_{38}O_2Si$ 434.2641, found 434.2628.

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Supporting Information Available: General methods, NMR spectra for all new compounds and tables including total energies and Cartesian coordinates for all stationary points discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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