7-Hydroxymethyl-6-methyl-1-oxa-4-thiaspiro[4.5]dec-6-ene. Exceptionally High Anti to Sulfur Diastereoselectivity under Conditions of Johnson Ortho Ester Claisen Rearrangement Favors Cieplak Mode of Diastereoselection†

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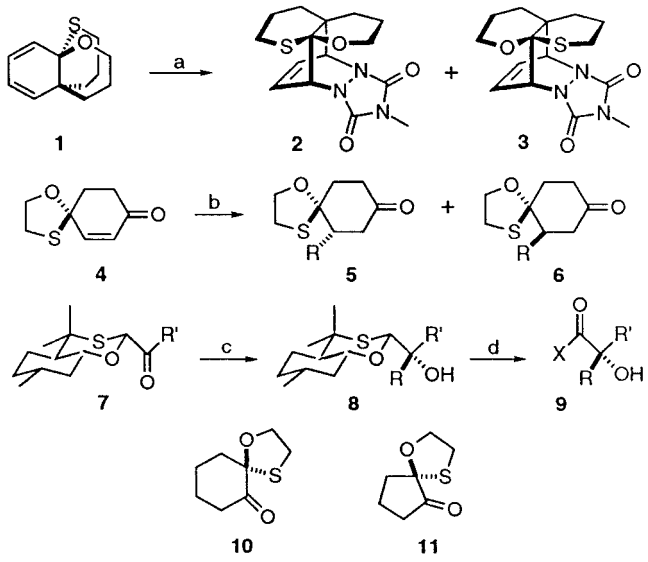
Received August 12, 1998

Introduction

The effect of allylic heteroatoms on diastereofacial selection has been assessed largely under the conditions of Diels−Alder (DA) and nucleophilic additions. In 1,2-diastereoselections, such an addition is reported to be syn to oxygen and anti to sulfur.[1] The study of 1,2-diastereoselection due to an 1-oxa-4-thiaacetal function has received relatively less attention. Paquette et al.[2] have studied the [4.4.4]propellane **1** in addition to *N*-methyltriazolinedione (MTAD) to furnish **2**:**3** = 20:1 (Scheme 1). The reaction had proceeded almost exclusively anti to the sulfur. Sonoda et al.[3] have studied the conjugate addition of Grignard reagents to 1-oxa-4-thiaspiro[4.5]-dec-6-ene-8-one, **4**, and reported anti to sulfur selection ranging from 76 to 96%. The Grignard additions to 2-acyl-1,3-oxathiane **7** proceed to furnish **8** with >95% anti to the sulfur selectivity.[4] This constitutes a method of considerable utility for the enantioselective synthesis of α-hydroxycarbonyl derivatives **9** (X = H, OH). The reaction is reported to follow Cram's chelation model.[5] Very recently, Dimitroff and Fallis[6] have reported high anti to sulfur diastereoselectivity in reactions of nucleophiles with α-keto oxathiolanes **10** and **11**.

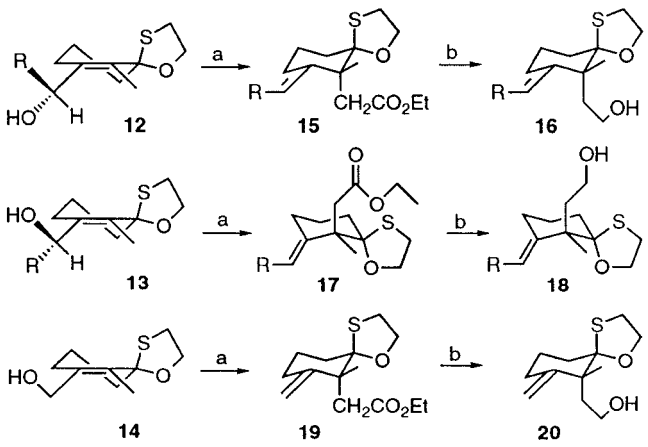
In the above intermolecular reactions, it is difficult to separate the true electronic effects from the cation complexing[7] and electrostatic effects[8] that are envisioned to play significant roles in diastereodeterminations. Since these cation-complexing and electrostatic effects are avoided in [3.3] sigmatropic shift processes, we embarked to study Johnson ortho ester Claisen rearrangement of the carbinols **12**−**14** (R = Me, Ph, Scheme 2). We report herein the results of very high diastereofacial selection that, in the unsubstituted example **14**, favors the Cieplak sense of diastereoselection.[1] Further, the diastereocontrol elements of significance in the substituted species **12** and **13** are the stereochemistry at the carbinol carbon that translates into torsional strain between the vinyl-Me and the carbinol substituent and the stereoelectronic effect that requires an axial bond formation on a preexisting cyclohexene ring.

Scheme 1 Literature Examples of 1,2-Diastereoselection Due to Allylically Placed S and O[a]



[a] Reagents: (a) MTAD; (b) (i) cat. $CuBr\cdot SMe_2$, TMSCl, HMPA, −30 °C, (ii) KF; (c) RMgX; (d) $NCS/AgNO_3$ or $HCl/NaClO_3$.

Scheme 2 Johnson Ortho Ester Claisen Rearrangemennt of the Carbinols 12−14 (R = Me, Ph)[a]



[a] R = Me, Ph. Reagents: (a) $MeC(OEt)_3$, toluene, reflux; (b) LAH, Et_2O, 0−20 °C.

† Dedicated to Professor G. Mehta, Director, Indian Institute of Science, Bangalore.

‡ Indian Institute of Technology.

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(1) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.

(2) (a) Paquette, L. A.; Branan, B. M.; Rogers, R. D.; Bond, A. H.; Lange, H.; Gleiter, R. *J. Am. Chem. Soc.* **1995**, *117*, 5992. (b) Paquette, L. A.; Lobben, P. C. *J. Am. Chem. Soc.* **1996**, *118*, 1917.

(3) Sonoda, S.; Houchigai, H.; Asaoka, M.; Takei, H. *Tetrahedron Lett.* **1992**, *33*, 3145.

(4) Wei, J.; Hutchins, R. O. *J. Org. Chem.* **1993**, *58*, 2920 and references therein.

(5) Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748 and references therein.

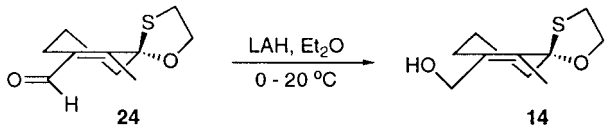
(6) Dimitroff, M.; Fallis, A. G. *Tetrahedron Lett.* **1998**, *39*, 2527.

(7) (a) Yadav, V. K.; Jeyaraj, D. A. *J. Org. Chem.* **1998**, *63*, 3474. (b) Jeyaraj, D. A.; Yadav, V. K. *Tetrahedron Lett.* **1997**, *38*, 6095. (c) Jeyaraj, D. A.; Yadav, A.; Yadav, V. K. *Tetrahedron Lett.* **1997**, *38*, 4483. (d) Fraser, R. R.; Faibish, N. C.; Kong, F.; Bednarski, K. *J. Org. Chem.* **1997**, *62*, 6164. (e) Evans, D. A. *Science* **1988**, *240*, 420. (f) Amstutz, R.; Dunitz, J. D.; Laube, T.; Schweizer, W. B.; Seebach, D. *Chem. Ber.* **1986**, *119*, 434. (g) Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876.

(8) Jeyaraj, D. A.; Yadav, V. K.; Parvez, M.; Gauniyal, H. M. *J. Org. Chem.* **1998**, *63*, 3831.

10.1021/jo981634f CCC: $18.00
Published on Web 03/27/1999

Scheme 3 Synthesis of the Unsubstituted Alcohol 14



Starting Materials

The syntheses of the carbinols **12** and **13** (R = Me, Ph) are reported elsewhere.[8] The aldehyde **24** that has also been reported by us[8] previously was reduced with LAH in Et_2O at 0 °C to furnish the carbinol **14** (Scheme 3) in quantitative yield after chromatographic purification. The stereostructures of the more polar **12** (R = Me, p-methoxybenzoate) and the less polar **13** (R = Ph) have been discerned earlier from single-crystal X-ray diffraction studies.[9] From these and other X-ray structure illucidations, it has been established that in the absence of polar R substituents the carbinols possessing OH function disposed syn to the acetal oxygen are more polar than those that have them anti disposed.

Results and Discussion

All the rearrangements were performed in boiling toluene without any acid catalyst. The use of acid catalysts such as propionic and *p*-toluenesulfonic acids caused decomposition including the cleavage of the acetal function. The more polar carbinol **12** furnished a single ester product **15**. This was reduced to the alcohol **16** as shown. The reaction had proceeded exclusively anti to the sulfur. The stereochemical characterization of **16** (R = Me, Ph) was made possible from a combination of ROESY and 1D NOE spectra; both demonstrated the ring-Me disposed syn to the sulfur as it was found to have good interaction with CH_2S. In the alternate ring conformer, such an interaction must be absent for the large internuclear distance. This assignment was confirmed further from ROESY, NOESY, and 1D NOE studies on **15** (R = Me), which also showed strong interaction of the ring-Me with CH_2S. These spectroscopy-based structural characterizations have been secured firm from the single-crystal X-ray structure of **16** (R = Ph) (Figure 1).

The less polar carbinol **13** rearranged to the single ester **17**. Whereas the stereochemical determination of the corresponding alcohol **18** (R = Me) was secured from a single-crystal X-ray diffraction studies (Figure 2), that of **18** (R = Ph) was discerned from ^{1}H and ^{13}C spectral patterns that were very similar to those for **18** (R = Me) (see below). The rearrangement of **13** had, therefore, proceeded exclusively syn to the sulfur.

Finally, the unsubstituted carbinol **14** rearranged to the single ester **19**. This was reduced to the alcohol **20**. The stereochemical assignment of **20** was made possible from ROESY as well as 1D NOE studies. As in the alcohol **16**, ROESY showed strong interaction between the ring-Me and CH_2S. Further, irradiation of the ring-Me signal resulted in a noticeable enhancement in the CH_2S signal and vice versa. The reaction had, therefore, proceeded exclusively anti to the sulfur.

The stereostructures of the carbinol products **16**, **18**, and **20** (R = Me, Ph) were also supported from definite

(9) Parvez, M.; Jeyaraj, D. A.; Yadav, V. K. *Acta Crystallogr.* **1997**, *C53*, 1961.

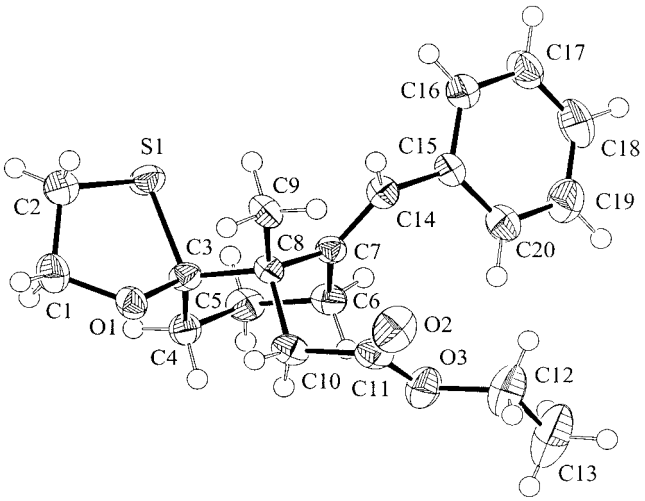


Figure 1. ORTEP plot of the X-ray crystal structure of **16** (R = Ph). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): S1−C3 1.871(4), O1−C3 1.421(4), C7−C14 1.328(5), S1−C3−O1 105.7(3), C6−C7−C14 123.0(4), C7−C14−C15 128.3(4), S1−C3−C8−C7−70.9(4), O1−C3−C8−C7 174.0(3), S1−C3−C8−C10 172.0(3), C4−C3−C8−C9 176.5(3).

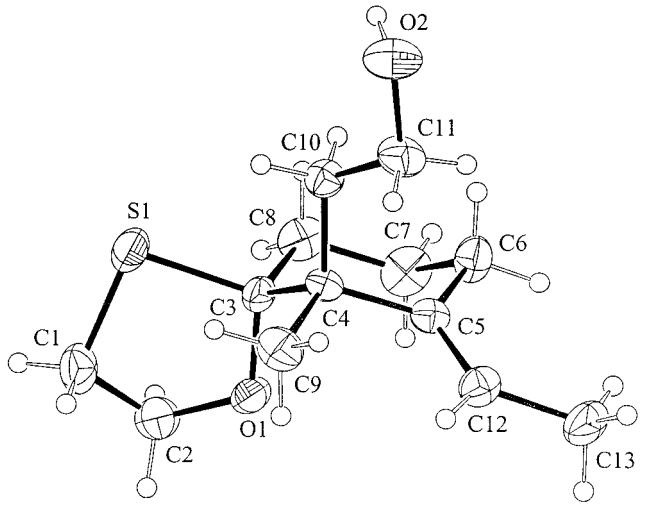


Figure 2. ORTEP plot of the X-ray crystal structure of **18** (R = Me). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): S1−C3 1.863(7), O1−C3 1.418(7), C5−C12 1.317(8),S1−C3−O1 106.2(4), C6−C5−C12 122.6(7), C5−C12−C13 127.8(7), S1−C3−C4−C5 175.6(4), O1−C3−C4−C5 68.2(6), S1−C3−C4−C10 55.9(6), O2−C11−C10−C4 174.8(5).

^{1}H patterns for the ring-*Me* and CH_2OH. An equatorial and syn to the sulfur ring-Me, as in **16**, absorbed almost δ 0.03 downfield compared to the one which was syn to the oxygen, as in **18**. Further, both the CH_2OH protons appeared as a single multiplet when the corresponding carbinol chain was syn to the sulfur, as in **18**, but as two multiplets, back to back, when the said chain was syn to the oxygen, as in **16** and **20**. The ^{13}C spectral features are also of much consequence. An equatorial quaternary Me that was syn to the sulfur, as in **16** and **20**, appeared δ 0.8−0.9 downfield compared to the one that was syn to the oxygen, as in **18**. A definitive ^{13}C assignment for the ring-Me was made from an HMQC experiment on **15** (R = Me). The ^{1}H and ^{13}C absorptions are given in Table 1.

The Claisen rearrangement prefers a reactant-like chair transition structure (TS) over the related boat. In

Table 1. Selected ^{1}H and ^{13}C Chemical Shifts (δ) in the Products 16, 18, and 20

	^{1}H			^{13}C
compd	ring-Me	CH_2OH	CH_2S	ring-Me
16, R = Me	1.226	3.65−3.59 (m) 3.55−3.49 (m)	2.89−2.84 (m)	18.30
18, R = Me	1.200	3.65−3.63 (m)	2.99−2.93 (m) 2.91−2.83 (m)	17.40
16, R = Ph	1.381	3.78−3.72 (m) 3.65−3.60 (m)	2.97−2.93 (m)	18.43
18, R = Ph	1.350	3.70−3.60 (m)	3.03−2.98 (m) 2.96−2.90 (m)	17.67
20	1.276	3.72−3.64 (m) 3.62−3.53 (m)	2.89−2.84 (m)	18.34

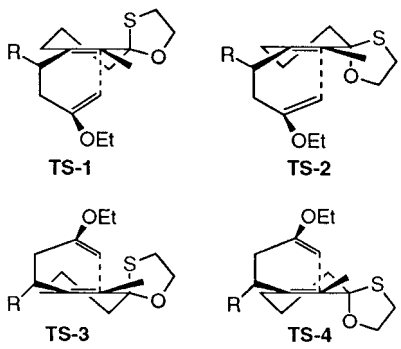


Figure 3. Transition structures for the rearrangement of the carbinols **12**−**14** (R = Me, Ph).

the carbinol precursors, the rotation around the carbinol carbon and the adjacent ring carbon will be restricted for the large steric interactions expected between the ring-Me and either of R and OH. This limits the number of possible transition structures for the more polar **12** to two, namely TS-1 and TS-2 (Figure 3). These two differ from each other only in the conformation of the preexisting cyclohexene ring. The rearrangement through TS-1 will be favored over the alternate TS-2 for the new C−C bond is formed axial in TS-1, and thus, it benefits from stereoelectronic effects.[10] On a similar note, the rearrangement of **13** is favored to proceed through TS-4 and not TS-3 because the new bond formed in TS-4 is axial. This bears very well from the X-ray structure of the so-derived alcohol **18** (R = Me) (Figure 2). The sulfur and oxygen atoms of the acetal occupy, respectively, the equatorial and axial positions and the new carbinol chain the axial position.

It is noteworthy that the products from all four transition states will possess the exocyclic olefinic bond in the preferred *E* configuration. Why then TS-1 is favored over TS-2 and TS-4 over TS-3? Why did the product **16** not show ring inversion but **18** did? It is obvious that other than the *E* configuration of the olefinic bond in the product, there is another significant control element, namely the stereoelectronic effect. This stereoelectronic effect favors formation of an axial bond on a preexisting six-ring system over that of an equatorial bond construction. The very high diastereoselectivity observed from **12** and **13** may be a consequence of the synergic effects of both these control elements. We provide computational data below to show that the required ring flip is energetically allowed.

(10) (a) Deslongchamps, P. in *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: New York, 1983. (b) Ireland, R. E.; Varney, M. D. *J. Org. Chem.* **1983**, *48*, 1829.

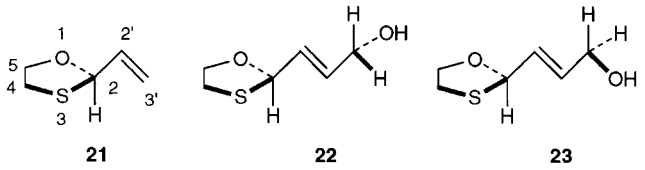


Figure 4. Examples computed to estimate the effect of the 1-oxa-3-thiolane function on the ground-state geometry.

The dihedral angles of S and O with the remote olefinic carbon across the intervening C−C bond in the ground-state geometry of 1-oxa-3-thia-2-vinylcyclopentane (**21**) (Figure 4), i.e., the dihedral angles S3C2C2′C3′ and O1C2C2′C3′, were computed to be 112.07 and 130.62°, respectively, at the HF/6-31G* level of theory.[11] The energy of a rotamer in which these dihedral angles were mutually exchanged in order to mimic and estimate the energy requirement for the above conformational mobility was 0.71 kcal mol^{-1} higher than the conformational minimum. A similar rotamer of 1-oxa-3-thia-2-(2-hydroxymethyl)vinylcyclopentane (**22**) was also 0.71 kcal mol^{-1} higher than the conformational minimum wherein the above dihedral angles were, respectively, 111.98 and 130.80° (111.85 and 130.94°, respectively, at the MP2/631G* level). The additional carbinol function has, therefore, little effect on the conformational profile of 1-oxa-3-thia-2-vinylcyclopentane. The approximate total energy requirement for the said ring flip must, therefore, be the energy required for the flip of one-half chair to the other (5.3 kcal mol^{-1})[12] plus the above 0.71 kcal mol^{-1}. This energy difference is rather small for the boiling temperature of toluene (110 °C), and hence, the flip could occur with much ease. Interestingly, the carbinol conformer **23** that has the carbinol function syn to the acetal sulfur computed only 0.06 kcal mol^{-1} (0.038 kcal mol^{-1} at MP2/6-31G* level) lower than the conformer **22** wherein the same were anti.

The permissible ring flip coupled with the absence of the interaction of R with the ring-Me in **14** may be expected to allow it to rearrange anti to both the sulfur and oxygen with axial C−C bond construction through transition states resembling TS-1 and TS-4, respectively. This amounts to reduced selectivity. In TS-1, the new C−C bond is formed antiperiplanar to the electron-donationg axial C−S bond. The C−O bond, however, will be orthogonal to it by virtue of its near coplanarity with the olefin σ bond. This is in accord with the Cieplak model for diastereoselection that considers electron donation to the incipient σ* orbital from a σ bond on the adjacent carbon.[1] In TS-4, the new C−C bond is formed antiperiplanar to the axial C−O bond and the C−S bond is orthogonal. This is in accord with the Anh−Felkin model that considers electron donation from the incipient bond to an antiperiplanar electron attracting σ bond on the

(11) All the calculations were performed using the program Gaussian 94, Revision C.2. See: Frish, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(12) (a) Anet, F. A. L.; Haq, M. Z. *J. Am. Chem. Soc.* **1965**, *87*, 3147. (b) Jensen, F. R.; Bushweller, C. H. *J. Am. Chem. Soc.* **1969**, *91*, 5774.

adjacent carbon.[13] The molecule **14** may, therefore, be considered to be ingeniously designed to provide a diagnostic composite test of these two models. The rearrangement only anti to the sulfur follows the Cieplak mode of diastereoselection.

One may wish to explain the stereochemical outcome of **14** from the differential steric environments of sulfur and oxygen. Since the sulfur has larger bulk than the oxygen, the reaction proceeds anti to the sulfur. However, the observation that the reaction proceeded exclusively anti to the sulfur cannot be understood as a lone consequence of the steric effects arising from it because a rearrangement syn to the sulfur was what occurred exclusively in **13**. One may also tend to envision a proton (from the glass vessel) bound to the two oxygen atoms in the transition state, and hence, the new C−C bond is formed preferably (exclusively in the present case) syn to the acetal oxygen (i.e., anti to the sulfur). This notion, however, can be easily ruled out for (a) the large distance between the two oxygens and (b) the intervention, in space, by the vinyl component that falls between the two oxygens in the transition state resembling TS-1. Further that such a complexation with H^+ did not contribute indeed to the observed diastereoselectivity was proved from a reaction that was conducted in a thoroughly base-treated glassware; the net stereochemical result had not changed.

Conclusion

In conclusion, the stereoelectronic effect is a significant diastereocontrol element in the Johnson ortho ester Claisen rearrangement of species **12**−**14** (R = Me, Ph). The transformation of **14** into **20** exclusively anti to the S is in support of the Cieplak mode of diastereoselection. The Cieplak mode of diastereoselection has previously been supported strongly by Halterman,[14] Johnson and Cieplak,[15] le Noble,[16] Mehta,[17] Meyers,[18] Sato,[19] Takei,[20] and several others. The Anh−Felkin model did not apply.

Experimental Section

The separations of the Johnson ortho ester Claisen rearrangement precursors (the carbinol isomers) were performed on a Chromatotron using silica gel 60 PF_{254} (E. Merck) coated plates. The components were eluted using mixtures of petroleum ether (bp 60−80 °C) and EtOAc.

6-Methyl-1-oxa-4-thiaspiro[4.5]dec-6-ene-7-carbinol (14). A suspension of LAH (0.038 g, 2.0 mmol) in dry Et_2O (5 mL) was cooled to 0 °C. To this was added a solution of 6-methyl-1-oxa-4-thiaspiro[4.5]dec-6-ene-7-carbaldehyde (0.396 g, 2.0 mmol) in Et_2O (5 mL), and the contents were stirred for 30 min. The cooling bath was removed, and the contents were stirred further for 30 min at 20 °C when TLC indicated the reaction was complete. The reaction mixture was cooled back to 0 °C, and water (3−4 drops) was added to decompose the excess LAH. The reaction mixture was diluted with more Et_2O (5 mL), dried in the reaction flask itself with anhydrous Na_2SO_4, and filtered, in that order, to furnish a crude that was filtered through a short column of silica gel to isolate the pure product in quantitative yield: ^{1}H NMR (300 MHz) δ 4.23−4.36 (1H, m), 4.19−4.08 (2H, 2d, J = 12 Hz), 4.11−4.03 (1H, m), 3.18−3.04 (2H, m), 2.19−2.14 (2H, m), 2.12−2.08 (1H, m), 2.01−1.92 (1H, m), 1.91−1.80 (1H, m), 1.80 (3H, t, J = 1.2 Hz), 1.80−1.60 (1H, m). Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.97; H, 8.06. Found: C, 59.75; H, 8.22.

General Procedure for the Johnson Ortho Ester Claisen Rearrangement. A solution of a carbinol (1.0 mmol) and triethyl orthoacetate (0.5 mL) in dry toluene (5 mL) was refluxed under dry nitrogen until the complete disappearance of the carbinol (6−10 h). The solvent and excess triethyl orthoacetate were removed under reduced pressure on a rotovap and the residue filtered through a short column of silica gel to furnish the product ester in near-quantitative yield.

General Procedure for the LAH Reduction of the Johnson Ortho Ester Claisen Products. To an ice-cold solution of the ester (0.01 mmol) in dry ether (2 mL) was added LAH (0.01 mmol) in one portion and the resultant stirred for 20 min. The cooling bath was removed, and the contents were stirred further for 30 min. The excess LAH was destroyed by addition of moist EtOAc, and the contents were diluted with more ether (3 mL). The solid materials were allowed to settle down, and the liquid was decanted. The solids were washed with ether (2 × 3 mL), and the liquid was decanted into the main solution. The resue obtained after solvent removal was filtered through a short bed of silica gel column to afford the alcohol in near quantitative yields.

The ^{1}H and ^{13}C NMR spectral characteristics of **15** (R = Me), **16** and **18** (R = Me, Ph), and **20** and the analytical data on some of these are as given below:

15 (R = Me): ^{1}H NMR (300 MHz) δ 5.39−5.33 (1H, dq, J = 5.6, 1.1 Hz), 4.39−4.35 (1H, m), 4.12−3.97 (3H, m), 2.92−2.88 (3H, m), 2.51 (1H, d, J = 13 Hz), 2.53−2.47 (1H, m), 2.21−2.14 (1H, m), 2.13−2.05 (1H, m), 2.01−1.96 (1H, m), 1.89−1.82 (1H, m), 1.63−1.61 (3H, dd, J = 6.7, 1.0 Hz), 1.49−1.40 (1H, m), 1.37 (3H, s), 1.21−1.17 (3H, t, J = 7.1 Hz); ^{13}C NMR (75 MHz) δ 172.18 (C13), 140.67 (C7), 118.71 (C16), 104.22 (C5), 71.84 (C2), 59.84 (C14), 49.67 (C6), 39.90 (C12), 35.77 (C8), 33.40 (C3), 23.87 (C9), 23.19 (C10), 18.99 (C11), 14.25 (C15), 13.36 (C17).

16 (R = Me): ^{1}H NMR (300 MHz) δ 5.40−5.30 (1H, dq, J = 6.7, 1.1 Hz), 4.42−4.36 (1H, m), 4.08−4.01 (1H, m), 3.65−3.59 (1H, m), 3.55−3.49 (1H, m), 2.89−2.84 (2H, m), 2.53−2.248 (1H, bd), 2.35−2.27 (1H, dt), 2.12−2.04 (1H, m), 2.01−1.84 (4H,m), 1.63−1.61 (3H, dd, J = 6.7, 1.0 Hz), 1.46−1.38 (1H, m), 1.23 (3H, s); ^{13}C NMR (75 MHz) δ 142.72, 117.92, 104.89, 71.73, 60.31, 48.81, 37.41, 35.32, 33.13, 23.90, 23.05, 18.26, 13.30. Anal. Calcd for $C_{13}H_{22}O_2S$: C, 60.51; H, 10.16. Found: C, 60.35; H, 10.30.

16 (R = Ph): ^{1}H NMR (300 MHz) δ 7.34−7.15 (5H, m), 6.42 (1H, s), 4.45−4.00 (1H, m), 4.12−4.08 (1H, m), 3.78−3.72 (1H, m), 3.65−3.60 (1H, m), 2.97−2.93 (2H, m), 2.75−2.67 (1H, bd), 2.42−2.34 (1H, dt), 2.24−1.84 (5H, m), 1.55−1.42 (1H, m), 1.38 (3H, s); ^{13}C NMR (75.5 MHz) δ 145.10, 138.50, 128.97, 128.05, 126.20, 124.58, 104.76, 71.82, 60.19, 49.20, 37.75, 35.20, 33.29, 24.42, 24.12, 18.43. Anal. Calcd for $C_{18}H_{24}O_2S$: C, 71.02; H, 7.95. Found: C, 69.80; H, 8.16.

18 (R = Me): ^{1}H NMR (300 MHz) δ 5.40−5.33 (1H, q, J = 6.9 Hz), 4.40−4.34 (1H, m), 3.95−3.87 (1H, m), 3.63−3.47 (2H, m), 2.99−2.93 (1H, m), 2.91−2.84 (1H, m), 2.59−2.53 (1H, td, J = 14.1, 3.6 Hz), 2.27−2.06 (3H, m), 2.02−1.93 (1H, dt, J = 13, 5.1 Hz), 1.72−1.41 (3H, m), 1.64 (3H, d, J = 6.9 Hz), 1.20 (3H, s); ^{13}C NMR (75 MHz) δ 142.0, 118.1, 103.6, 71.0, 59.9, 52.3, 48.6, 39.4, 36.0, 33.0, 29.7, 23.6, 23.5, 17.4, 13.4. Anal. Calcd for $C_{13}H_{22}O_2S$: C, 60.51; H, 10.16. Found: C, 60.30; H, 10.25.

18 (R = Ph): ^{1}H NMR (300 MHz) δ 7.32−7.15 (5H, m), 6.38 (1H, s), 4.42−4.38 (1H, m), 3.97−3.93 (1H, m), 3.74−3.62 (2H,

(13) (a) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. (b) Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61.

(14) (a) Halterman, R. L.; McEvoy, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 6690. (b) Halterman, R. L.; McEvoy, M. A. *Tetrahedron Lett.* **1992**, *33*, 753.

(15) (a) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447. (b) Johnson, C. R.; Cieplak, A. S. *J. Am. Chem. Soc.* **1987**, *109*, 5875. See also: (c) Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876.

(16) (a) Cheung, C. K.; Tseng, L. T.; Lin, M.-H.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598. (b) Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5874.

(17) (a) Mehta, G.; Khan, F. A. *J. Am. Chem. Soc.* **1990**, *112*, 6140. (b) Mehta, G.; Khan, F. A. *J. Chem. Soc., Chem. Commun.* **1991**, 18. (c) Mehta, G.; Khan, F. A.; Ganguly, B.; Chandrasekhar, J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2275. (d) Ganguly, B.; Chandrasekhar, J.; Khan, F. A.; Mehta, G. *J. Org. Chem.* **1993**, *58*, 1734.

(18) Meyers, A. I.; Romine, J. L.; Fleming, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 7245. However, for a contradiction by Meyers himself, see: Meyers, A. I.; Wallace, R. H. *J. Org. Chem.* **1989**, *54*, 2509.

(19) Sato, T.; Kido, M.; Otera, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2254.

(20) Sonoda, S.; Houchigai, H.; Asaoka, M.; Takei, H. *Tetrahedron Lett.* **1992**, *33*, 3145.

m), 3.03−2.98 (1H, m), 2.96−2.90 (1H, m), 2.79−2.74 (1H, bd), 2.38−2.32 (1H, m), 2.28−2.05 (3H, m), 1.85−1.78 (1H, m), 1.72−1.57 (3H, m), 1.35 (3H, s); ^{13}C NMR (75 MHz) δ 144.9, 138.5, 129.1, 128.0, 126.1, 124.8, 103.7, 71.0, 59.76, 49.0, 39.7, 35.9, 33.2, 25.0, 24.0, 17.7. Anal. Calcd for $C_{18}H_{24}O_2S$: C, 71.02; H, 7.95. Found: C, 69.85; H, 8.14.

20: ^{1}H NMR (400 MHz) δ 4.86 (1H, s), 4.80 (1H, s), 4.43−4.38 (1H, m), 4.06−4.02 (1H, m), 3.72−3.64 (1H, m), 3.62−3.54 (1H, m), 2.89−2.84 (2H, m), 2.39−2.28 (2H, m), 2.20−2.14 (1H, bd), 2.10−1.87 (4H, m), 1.60−1.48 (1H, m), 1.28 (3H, s); ^{13}C NMR (75 MHz) δ 152.6, 110.1, 104.4, 71.8, 60.2, 48.6, 37.3, 35.2, 33.3, 31.5, 24.4, 18.3.

Acknowledgment. The authors thank CSIR, Government of India, for financial assistance and the Computer Centre staff of IIT Kanpur for the generous allocation of computer time on the Silicon Graphics series of mini supercomputers.

Supporting Information Available: Copies of ^{1}H NMR spectra of **15** (R = Me), **16** (R = Me, Ph), **18** (R = Me, Ph), and **20**, ^{13}C NMR spectra of **15** (R = Me), **16** (R = Me, Ph), **18** (R = Me, Ph), and **20**, COSY and ROESY of **15** (R = Me), **16** (R = Me, Ph), **18** (R = Ph), and **20**, NOESY and TOCSY of **15** (R = Me), and HMQC of **15** (R = Me). This material is available free of charge via the Internet at http://pubs.acs.org.

JO981634F