Heating was continued an additional 42 h, after which the solvent was evaporated to give a dark oily residue, mainly **29** by NMR. Chromatography gave essentially pure material (93%), which was twice recrystallized from hexane to give pale yellow **29**: mp 106.5–107.5 °C; NMR δ 1.46 (t, 3 H, J = 7 Hz), 3.97 (s, 6 H), 4.07 (q, 2 H, J = 7 Hz), 7.59–7.96 (m, 5 H), 9.78–9.91 (m, 1 H), 13.1 (s, OH). Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.65; H, 5.36.

(g) 10E with AAN 30. This mesitoic acid catalyzed addition was complete within 2.5 h. Chromatography of the residue from vacuum evaporation gave crude product in good yield as a nearly colorless oil. Methoxide/methanol treatment (3.5 h, 22 °C) gave a yellow oil (78%) which was mainly the anticipated product. Chromatography afforded 40% of **30** as a colorless oil: mp, slightly below room temperaturef NMR (300 MHz) δ 1.41 (t, 3 H, J = 7 Hz), 2.09 (d, 1 H, J = 16.5 Hz), 2.82 (dd, 1 H, J = 16.5, 5.1 Hz), 4.03 (q, 2 H, J = 7 Hz), 6.06 (d, 1 H, J = 5.1 Hz), 7.60–7.97 (m, 6 H). MS (CI), calcd for $C_{16}H_{15}O_3$(P + H) m/z 255.1021, found 255.1039.

(h) 8E with AAN 27. The reaction with regioisomer **8E** and AAN was also complete within 2.5 h. The NMR of the crude product suggested that it was largely a single isomer (stereo and regio) of **26**, with pertinent absorptions at δ 1.76 (d, 1 H, J = 13.5 Hz), 3.32 (dd, 1 H, J = 13.5, 5.4 Hz), 3.92 (q, 2 H, J = 7 Hz), and 5.4 (d, 1 H, J = 5.4 Hz). Conversion by methoxide/methanol treatment gave crude **27**: NMR δ 1.43 (t, 3 H, J = 7 Hz), 2.05 (d, 1 H, J = 16.5 Hz), 2.71 (dd, 1 H, J = 16.5, 4.8 Hz), 5.65 (d, 1 H, J = 4.8 Hz), 7.10–8.30 (m, 6 H). This material decomposed on standing in $CDCl_3$ solution overnight and was not further analyzed. The conclusion that no regioisomeric keto ketal is formed is based on the absence of a benzylic proton singlet anticipated for this structure and the good correlation of integrals for absorptions due to **27**.

Acknowledgment. Financial support by the University of California Cancer Research Coordinating Committee is gratefully acknowledged. We thank Dr. U. E. Wiersum (Akzo Research, Arnhem, Holland) for helpful comments, John Fernandez and Jelveh Lameh for carrying out some starting material preparations, and Dr. Hugh Webb and Allan Kerschaw for their assistance in obtaining MS and NMR spectra, respectively. This work was expedited by the very useful correspondence and comparison spectra provided by Prof. D. Wege of the University of Western Australia.

Registry No. **1**, 232-74-6; **4**, 5657-01-2; **5**, 4781-04-8; **6**, 2586-62-1; **7**, 4488-44-2; **8E**, 87262-71-3; **8M**, 87262-72-4; **9E**, 87262-73-5; **9M**, 87262-74-6; **10E**, 87262-75-7; **11E**, 87262-76-8; **11M**, 87262-77-9; **12**, 87262-78-0; **13**, 87262-79-1; **14**, 87262-80-4; *exo*-**16**, 87262-81-5; *endo*-**16**, 87332-56-7; **19**, 87262-82-6; **20**, 87262-83-7; *endo*-**21**, 87262-84-8; **22**, 87262-85-9; **23**, 87262-86-0; **24**, 87262-87-1; **25**, 87262-88-2; **26**, 87262-89-3; **27**, 87262-90-6; **28**, 87262-91-7; **29**, 87262-92-8; **30**, 87262-93-9; DMAD, 762-42-5; AAN, 3061-65-2; MA, 108-31-6; BL, 497-23-4; methyl 2-methyl-1-naphthoate, 56020-58-7; 2-methyl-1-naphthoic acid, 1575-96-8; 2-methyl-1-naphthalenecarbonyl chloride, 10008-12-5; methyl 2-(bromomethyl)-1-naphthoate, 2417-76-7; 2-methylnaphthalene, 91-57-6; 1-bromo-2-(bromomethyl)naphthalene, 37763-43-2; 1-bromo-2-(acetoxymethyl)naphthalene, 87262-94-0; 1-bromo-2-(hydroxymethyl)naphthalene, 76635-70-6; 1-bromo-2-naphthoic acid, 20717-79-7; 1-(bromomethyl)-2-naphthoic acid, 87262-95-1; diethoxycarbenium tetrafluoroborate, 1478-41-7; 3-ethoxy-1,3-dihydrobenzo[*e*]isobenzofuran-3-ium tetrafluoroborate, 87262-97-3; cyclohexene, 110-83-8; dimethoxycarbenium tetrafluoroborate, 18346-68-4.

Ketal Claisen Rearrangements of Simple Aliphatic Ketals[1]

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Received October 4, 1982

The ketal Claisen rearrangement has been studied with eight simple unsymmetrical ketals in order to establish the regioselectivity associated with the transformation. Three different allylic alcohols were examined. Carbon–carbon bond formation on the more highly substituted branch of the parent ketone generally predominated over substitution on the less highly substituted branch. However, additional substituents on the α or β carbons of the ketal lower the selectivity substantially. Extensive β substitution can completely reverse the normal selectivity. The reaction is relatively insensitive to the concentration of the weak acid catalyst. The yields range between 27% and 84%, and the products have been characterized. A model that accounts for the observations is also described.

The Claisen rearrangement is a very general and powerful synthetic tool.[2] The enolate Claisen rearrangement,[3] the ortho ester Claisen rearrangement,[4] and the amide acetal Claisen rearrangement[5] have provided synthetic chemists with convenient methods for exploiting this historically important pathway to γ,δ-unsaturated carbonyl compounds.

Stereochemical studies have also played an important part in this development. The early work of Perrin,[6] Faulkner,[7] and Johnson[8] demonstrated that Claisen rearrangements could be used to generate trans-disubstituted and E-trisubstituted double bonds. Additionally, the olefinic geometries control the relative stereochemistry of

(1) For a preliminary report on aspects of this study, see: Daub, G. William; Sanchez, Michael G.; Cromer, Robbin A.; Gibson, Lester L. *J. Org. Chem.* **1982**, *47*, 743.
(2) (a) Bennett, G. B. *Synthesis* **1977**, 589. Ziegler, Zeigler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.
(3) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.
(4) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.; Faulkner, D. J.; Peterson, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.
(5) Felix, D.; Geschwend-Steen, K.; Wick, A. E.; Eschenmoser, A. *Helv. Chim. Acta* **1969**, *52*, 1030.
(6) Perrin, C. L.; Faulkner, D. J. *Tetrahedron Lett.* **1969**, 2873.
(7) Faulkner, D. J.; Peterson, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 553.
(8) Johnson, W. S. Brocksom, T. J.; Loew, P.; Rich, D. H.; Werthemann, L.; Arnold, R. A.; Li, T.; Faulkner, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 4463.

0022-3263/83/1948-3876$01.50/0

Scheme I

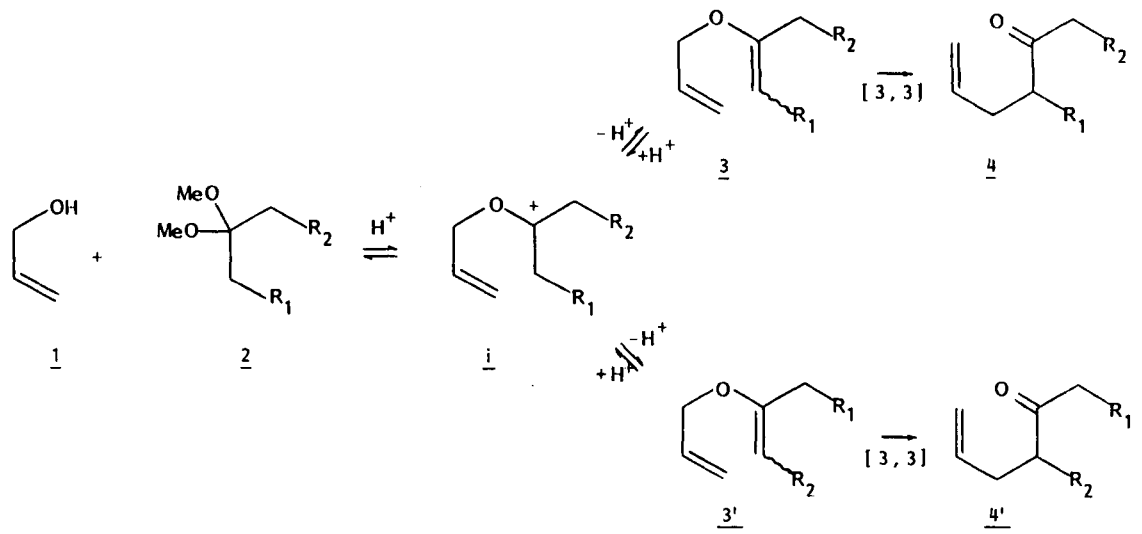
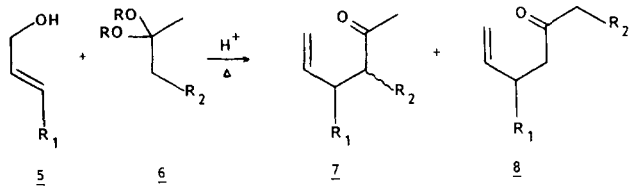


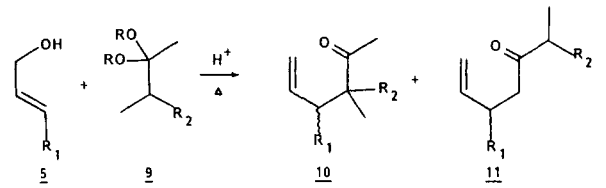
Table I



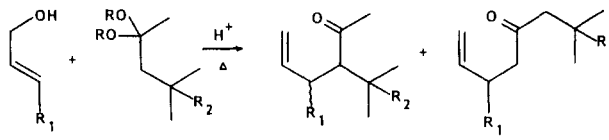
example	method[a]	R_1	R_2	% yield	7/8 ratio[b]
a	A	Ph	Me	63	96:4
b	A	Ph	Et	66	92:8
	B	Ph	Et	47	93:7
c	A	Ph	*i*-Bu	62	96:4
	B	Ph	*i*-Bu	58	95:5
d	A	Pr	Et	28	86:14
	B	Pr	Et	37	86:14
e	A	Pr	*i*-Bu	58	87:13
	B	Pr	*i*-Bu	43	91:9

[a] Method A, 3.0 equiv of ketal; method B, 1.0 equiv of ketal. [b] Reference 19.

Table II



example	method[a]	R_1	R_2	% yield	10/11 ratio[b]
a	A	Ph	Me	73	69:31
b	A	Ph	Et	81	74:26
c	A	Pr	Et	70	73:27



example	method[a]	R_1	R_2	% yield	13/14 ratio[b]
a	A	Ph	H	74	67:33
	B	Ph	H	61	67:33
b	A	Ph	Me	72	0:100
c	A	Pr	H	43	31:69
d	B	Pr	Me	53	0:100

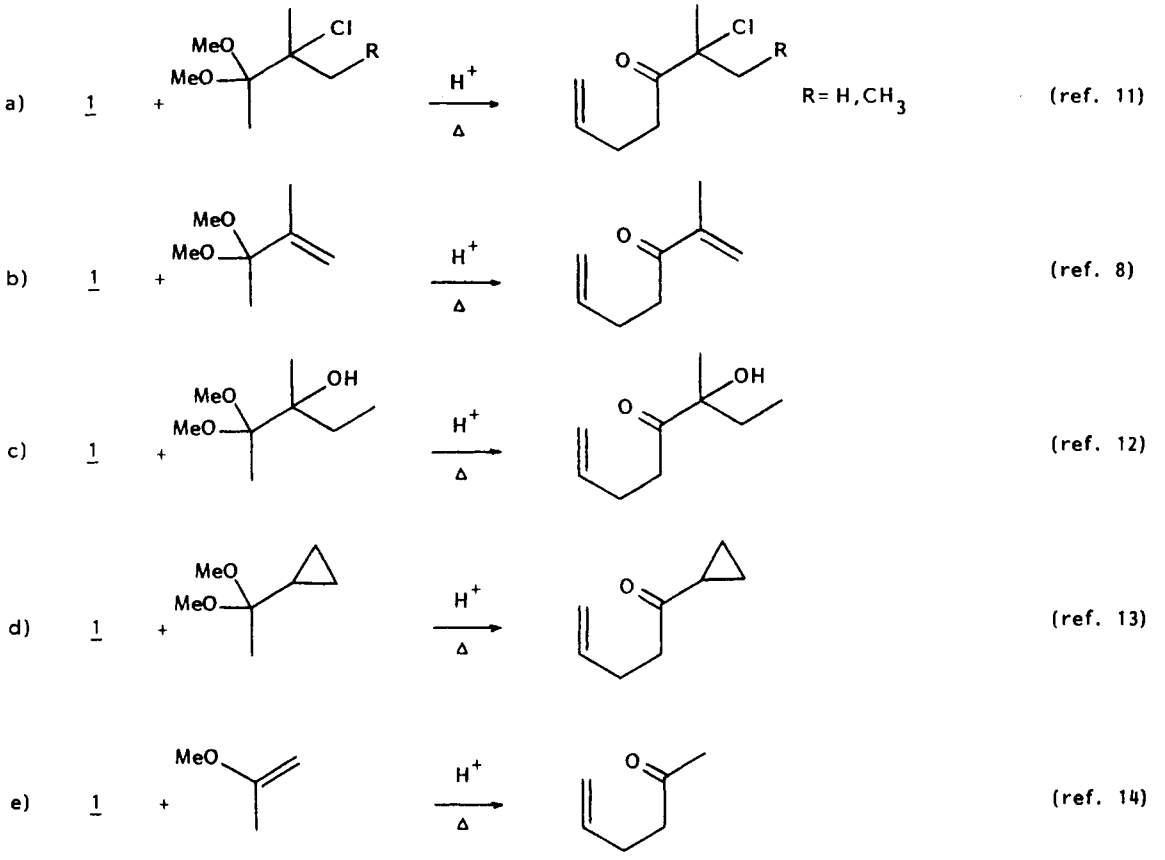
[a] Method A, 3.0 equiv of ketal; method B, 1.0 equiv of ketal. [b] Reference 19.

substituents on the carbon atoms α and β to the new carbonyl group.[9] Ireland, in particular, has exploited this fact in his use of the enolate Claisen rearrangement.[3,10]

The ketal Claisen rearrangement has been developed in only a few specific cases. The work of Johnson and Faulkner[8,11-13] provide the only previous examples of the ketal Claisen rearrangement. The related enol–ether Claisen rearrangement examined by Saucy[14] may also be included in this discussion because it involves a nearly identical reaction pathway. For the more general case, the reaction between an acyclic unsymmetrical ketal (1) and an allylic alcohol (2) can give rise to two isomeric ketonic products. Scheme I details the mechanistic scenario for this process during which the intermediate cation i can be reversibly partitioned along two different pathways. These different paths proceed through isomeric allyl vinyl ethers (3 and 3′) and terminate at isomeric ketones 4 and 4′. The [3,3] sigmatropic rearrangements that lead to 4 and 4′ are virtually irreversible ($K_{eq} \approx 10^6$). This possibility of isomeric reaction products has presumably discouraged others from looking into this method. The ketal Claisen rearrangements reported by Johnson, Faulkner, and Saucy specifically avoid this problem, since one of the two competing paths in each case is blocked[15] (Scheme II). Recent efforts in our laboratory[1] have been designed to answer this regiochemical question, which is inherent in the ketal Claisen rearrangements of simple unsymmetrical ketals.

(9) Hansen, H. J.; Schmid, H. *Tetrahedron* **1974**, *30*, 1959.
(10) (a) Ireland, R. E.; Thaisrivongs, S.; Vanier, N.; Wilcox, C. S. *J. Org. Chem.* **1980**, *45*, 48. (b) Ireland, R. E.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 1155. (c) Ireland, R. E.; Daub, J. P. *J. Org. Chem.* **1981**, *46*, 479.
(11) (a) Werthemann, L.; Johnson, W. S. *Proc. Natl. Acad. Sci. U.S.A.* **1970**, *67*, 1465, 1810. (b) Loew, P.; Johnson, W. S. *J. Am. Chem. Soc.* **1971**, *93*, 3765.
(12) Faulkner, D. J.; Peterson, M. R. *J. Am. Chem. Soc.* **1971**, *93*, 3766.
(13) Johnson, W. S.; Daub, G. W.; Lyle, T. A.; Niwa, M. *J. Am. Chem. Soc.* **1980**, *102*, 7800.
(14) Saucy, G.; Marbet, R. *Helv. Chim. Acta* **1967**, *50*, 2091.
(15) The three examples reported by Johnson and Faulkner (examples a–c, Scheme II) lack hydrogens on one of the adjacent carbon atoms. The other example reported by Johnson (example d, Scheme II) effectively blocks the competing reaction path with a cyclopropyl group, which precludes the formation of an sp^2 carbon atom at one of the α sites. Saucy's enol ether (example e, Scheme II) is symmetrical.

Scheme II



Results

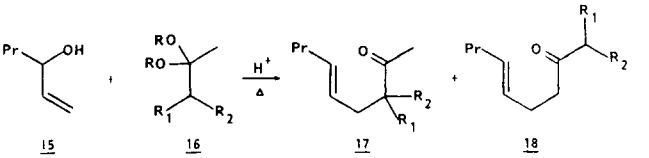
We have examined the ketal Claisen rearrangements of some simple unsymmetrical ketals with three allylic alcohols. Two 3-substituted allylic alcohols [cinnamyl alcohol (**5**, R = C_6H_5) and *trans*-2-hexen-1-ol (**5**, R = $CH_2CH_2CH_3$)] were used in this study. Three types of ketals were used. Group 1 consisted of ketals of 2-alkanones possessing no branching α or β to the carbonyl, group 2 included ketals of 2-alkanones with branching β to the carbonyl, and the ketals in group 3 were ketals of 2-alkanones with one substituent α to the carbonyl group. The ketal and the allylic alcohol were heated to 120 °C in the presence of a catalytic amount (0.15 equiv) of propionic acid for 24 h. Subsequent workup and column chromatography on silica gel afforded the isomeric reaction products. Table I summarizes the results for the reaction between 3-substituted allylic alcohols and type 1 ketals, Table II summarizes the reactions between 3-substituted alcohols and type 2 and 3 ketals, and Table III summarizes the results for 1-substituted allylic alcohols with all types of ketals.

The results in Tables I–III present three significant trends. The more highly substituted ketones (e.g., **7**) predominate over the less highly substituted ketones (e.g., **8**) for type 1 ketals. The second trend is the decrease in regioselectivity observed for type 2 and 3 ketals. In particular, extensive β substitution (Table II, examples b′ and d′; Table III, example e) favors the less highly substituted ketone (e.g. **14**). The last trend is the decrease in regioselectivity as the allylic alcohol is changed from cinnamyl alcohol to *trans*-2-hexen-1-ol to 1-hexen-3-ol.

Discussion

These trends can be accommodated in a reasonably simple model. The intermediate cation (i, Scheme I) is in equilibrium with the isomeric allyl vinyl ethers, which subsequently rearrange to give the observed ketones. This is quite reasonable, since one can show that the rate of protonation of the allyl vinyl ethers is probably 2 orders of magnitude greater than the rate of the [3,3] sigmatropic rearrangement.[16] This fact was experimentally demonstrated in the following way.[17] Authentic allyl vinyl ether **20** was prepared from ester **19** according to established procedures[18] and submitted to the ketal Claisen rear-

Table III



15 16 17 18

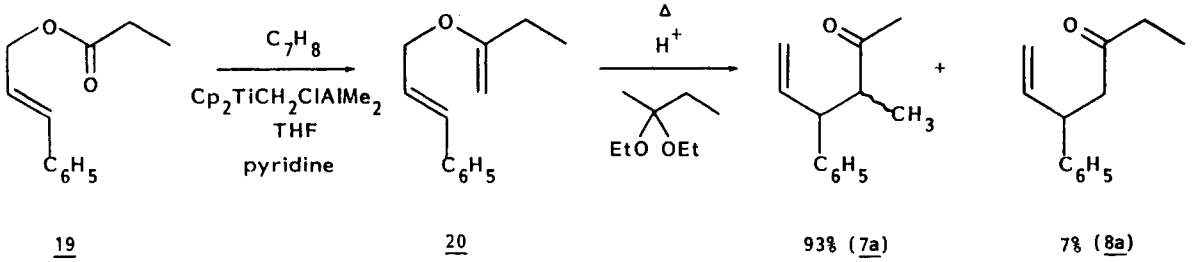
example	method[a]	R_1	R_2	% yield	17/18 ratio[b]
a	A	Et	H	47	50:50
	B	Et	H	40	70:30
b	A	*i*-Bu	H	56	66:34
c	A	Et	Me	61	23:77
	B	Et	Me	42	28:72
d	B	*i*-Pr	H	46	63:37
e	B	*t*-Bu	H	27	7:93

[a] Method A, 3.0 equiv of ketal; method B, 1.0 equiv of ketal. [b] Reference 19.

(16) (a) The work of Salomaa[16b] allows for the approximation of the rate of protonation of the allyl vinyl ether. The rate of protonation has a lower limit of 0.1 [allyl vinyl ether] s^{-1} at 120 °C. The work of Schmid[9] allows for the approximation of the rate of sigmatropic rearrangement of the allyl vinyl ether. This rate has an upper limit of 8.7×10^{-4} [allyl vinyl ether] s^{-1} at 120 °C. (b) Kankaanpera, A.; Salomaa, P.; Juhala, P.; Aaltonen, R.; Mattsen, M. *J. Am. Chem. Soc.* **1973**, *95*, 3618.

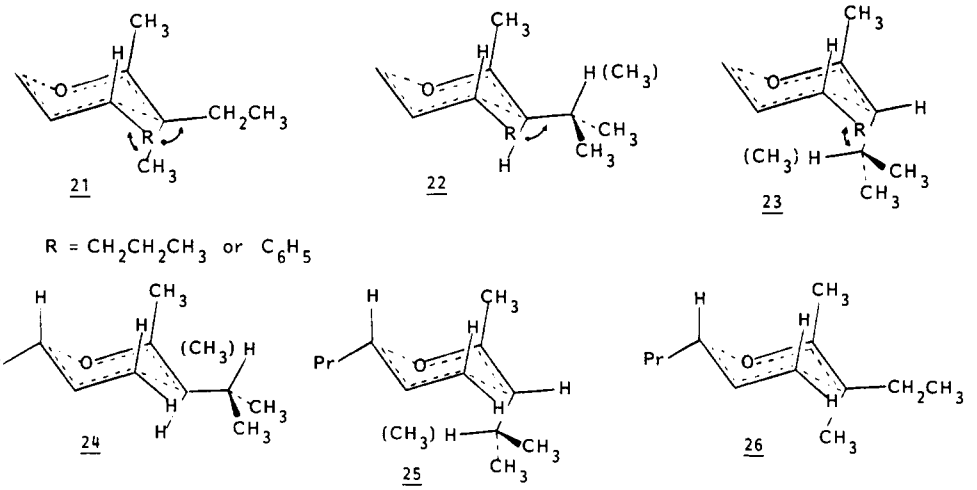
(17) We acknowledge the helpful comments of Professor D. A. Evans, California Institute of Technology, and Professor S. H. Pine, California State University at Los Angeles, in this matter.

Scheme III



19 20

Chart I



21 22 23 24 25 26

rangement conditions (Scheme III). The ratio of ketones **7a** and **8a** obtained in this way (93:7) was identical with the ratio obtained in the simple ketal Claisen (96:4) within experimental uncertainty.[19] The model is also consistent with the fact that both ethyl and methyl ketals work equally well.

Two important features of the reaction mechanism have been established. The intermediate cation and the isomeric allyl vinyl ethers (**3** and **3′**) are in equilibrium, and the allyl vinyl ethers rearrange irreversibly to give ketones **4** and **4′**. Clearly the reaction is described by the Curtin–Hammett principle. Consequently, the product ratio is solely determined by the difference in the free energies of the transition states leading to those products. Any change that increases the difference in the free energies of the transition states increases the regioselectivity, and any change that decreases this difference decreases the regioselectivity. Such changes could include nonbonded interactions in either of the transition states.

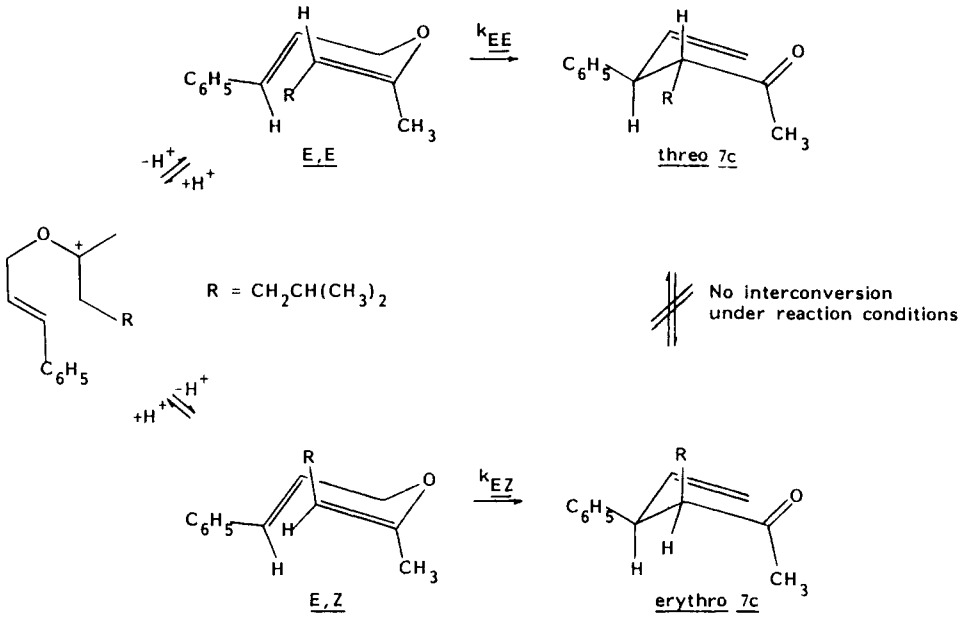
Additional substitution at the α carbon of the ketal lowers the selectivity as seen in Table II (examples a–c) and Table III (example c). The transition state leading to the more highly substituted ketone (e.g., **10**) is destabilized relative to the less highly substituted one (e.g., **11**) by virtue of several nonbonded interactions (see **21**). This presumably reduces the rate of the [3,3] sigmatropic rearrangement for the more highly substituted allyl vinyl ether. The work of Cresson[20] shows that substitution on the allyl terminus slows down the rate of sigmatropic rearrangement. Similarly, substitution of the vinylic terminus might also be expected to retard the rearrangement step. This allows the less highly substituted path to compete more favorably, and the less highly substituted ketone accounts for a larger proportion of the total product.

Additional β substitution of the ketal also decreases the selectivity [see Table II (examples a′–d′) and Table III (examples d, e)]. Unfavorable nonbonded interactions develop in the transition states (**22** and **23**, Chart I), leading to the more highly substituted ketone. In addition, eclipsing interactions along the vinyl double bond destabilize these transition states relative to the transition states that lead to the less highly substituted ketone, which is relatively unaffected by the additional β-methyl groups. These effects result in an increased proportion of the less highly substituted ketone. Excessive β substitution (Table II, examples b′ and d′; Table III, example e) results in the isolation of the less highly substituted ketone as 93–100% of the ketonic products. The selectivity trends for 1-hexen-3-ol are much less clearly defined. Models for these transition states (**24–26**) offer no specific interactions of a magnitude that is meaningful in view of the small energy differences involved between examples.[21] Placement of an additional methyl group on the γ carbon (Table I, examples c and e; Table III, example b) results in no loss of selectivity.

Many of the products in Tables I and II are obtained as a ca. 1:1 mixture of the erythro and threo diastereomers. These are formed from the *E,Z* and *E,E* allyl vinyl ethers, respectively, as shown in Scheme IV. The work of Schmid[9] suggests that the threo isomer should predominate due to the enhanced rate of [3,3] sigmatropic rearrangement of *E,E* isomers over *E,Z* isomers ($k_{E,E}/k_{E,Z}$ = 3). However, Schmid measured these rates for allyl vinyl ethers in which the vinyl group was disubstituted. In the current work the vinyl group is trisubstituted, and the

(18) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.
(19) The product percentages have uncertainties of ±3%.
(20) (a) Cresson, P.; Lecour, L. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1966**, *262*, 1157. (b) Cresson, P.; Bancel, S. *Ibid.* **1968**, *266*, 409.
(21) Any energy effects of less than ~1 kcal/mol cannot be reasonably addressed in these discussions. Temperature controls were not specific enough, and model transition-state interactions have an uncertainty of at least 1 kcal/mol.

Scheme IV

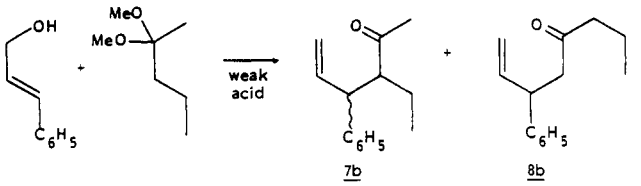


erythro/threo ratios for our examples[22] range from 1.2:1 to 1:1. We have rule out the possibility that acid-catalyzed equilibration of the threo and erythro isomers occurs during the reaction by subjecting a small amount of *erythro*-**7c**[23] to the reaction conditions. No *threo*-**7c** was detected by ^{1}H NMR spectroscopy.[24,25]

The reactions were conducted according to two procedures. Method A involved the use of excess ketal (3.0 equiv), while method B utilized only 1.0 equiv of ketal. From a mechanistic point of view, one would expect the former method to be superior due to the presence of so many preliminary equilibria in the reaction scheme. Indeed, better yields are generally obtained with method A. Method B does prove superior for reactions involving ketals of relatively nonvolatile ketones such as 5-methyl-2-hexanone and other more functionalized ketals.[26] In such cases the excess ketal used in method A is hydrolyzed to the parent ketone during workup, and it complicates the chromatographic separation. The regioselectivity should be relatively independent of the method used. The results in this study support this view to a large extent. One anomalous result appears in Table III (example a), however. The difference between a 70:30 and a 50:50 product ratio is only 0.6 kcal/mol. Such a small energy difference could easily result from small differences in the solvation of the transition states under the two different sets of reaction conditions. Clearly, the two procedures give consistent results for the majority of examples.[21]

The amount and nature of the acid catalyst used in ortho ester Claisen rearrangements has been studied by Raucher.[27] He found that the yield improved as the amount of mesitoic acid was increased from catalytic amounts to 1 equiv. The ketal Claisen rearrangement between cinnamyl alcohol and 2,2-dimethoxypentane was therefore examined in order to determine if a comparable effect was operational. Both propionic and mesitoic acid were examined over a range of concentrations. The results of this study are displayed in Table IV. Clearly there is no such dramatic effect in the present case.

Table IV



acid catalyst	equiv	% yield	7b/8b ratio[a]
propionic	2.0		94:6
propionic	1.5	71	96:4
propionic	1.0	76	96:4
propionic	0.75	70	95:5
propionic	0.50	77	96:4
propionic	0.15	84	88:12
mesitoic	0.75	67	97:3
mesitoic	0.50	78	96:4

[a] See ref 19.

It is evident that there is a decrease in regioselectivity and yield as one proceeds from cinnamyl alcohol to *trans*-2-hexen-1-ol to 1-hexen-3-ol. These changes in the regioselectivity are the result of such small energy effects (<1 kcal/mol) that is is unreasonable to try to account for their origins.[21] The lower yields exhibited by the isomeric hexenols are presumably due to the loss of these somewhat volatile alcohols during the course of the reaction. In addition, the lower molecular weight ketones, some of which contain only 11 or 12 carbons, showed substantial material losses upon isolation.

Conclusions

These results demonstrate that ketal Claisen rearrangements using simple unsymmetrical ketals may exhibit substantial selectivity and proceed in fair to good yields.

(22) The erythro/threo ratios were determined by ^{1}H NMR spectroscopy. The diastereomeric methyl ketone groups displayed different chemical shifts. This was particularly evident for the products derived from cinnamyl alcohol (examples a–c, Table I; example b and a′, Table II) due the strong anisotropic effect of the aromatic ring.

(23) *erythro*-**7c** (<1% threo by ^{1}H NMR) was obtained in selected fractions of the medium-pressure chromatography of **7c**/**8c**.

(24) The detection limits of ^{1}H NMR spectroscopy for the presence of *threo*-**7c** were ±2%.

(25) In order to rigorously demonstrate that equilibration is not occurring, the complementary experiment using *threo*-**7c** should be performed. The inavailability of pure *threo*-**7c** precluded this experiment.

(26) Daub, G. W.; Lunt, S. R. *Tetrahedron Lett.*, in press.

(27) Raucher, S.; Macdonald, J. E.; Lawrence, R. F. *J. Am. Chem. Soc.* 1981, *103*, 2419.

This selectivity may be as high as 25:1 in the most favorable cases. However, alkyl substitution on the α or β carbons of the ketal attenuates this selectivity and may even reverse it in unusual cases.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer 137 sodium chloride spectrophotometer. ^{1}H NMR spectra were determined in $CDCl_3$ by using a Varian EM 360L NMR spectrometer and were reported in parts per million relative to tetramethylsilane. Mass spectrometry was performed on a Finnigan 3200 GC/MS system. Vapor-phase chromatograms were obtained on a Varian Aerograph Series 1200 gas chromatograph fitted with a $^1/_8$ in. × 12 ft 5% SE-30 on Gas-Chrom Z column and a flame-ionization detector. VPC retention times are reported below as follows: VPC retention time, temperature. VPC integrations were determined either manually or on a Hewlett-Packard 3390 integrator and were not corrected for varying detector responses to the isomeric products. Combustion microanalyses were kindly done by Ruby Ju, Department of Chemistry, University of New Mexico. Thin-layer chromatography was performed on precoated TLC sheets, with silica gel as supplied by E. Merck (No. 5575) and a solvent mixture of 7:2:1 of hexane–dichloromethane–acetone. Preparative column chromatography was performed on silica gel (0.063–0.200 mm for gravity columns, 0.040–0.063 mm for medium-pressure columns). All solvents were of reagent grade except hexane, which was washed with H_2SO_4 and saturated $NaHCO_3$ and dried over anhydrous K_2CO_3 before distillation from CaH_2. All ketones were obtained from commercial vendors and distilled before use. Cinnamyl alcohol was obtained from a commercial vendor and recrystallized from ether/hexane (mp 34–35 °C). *trans*-2-Hexen-1-ol and 1-hexen-3-ol were obtained from commercial vendors and used without purification. All of the ketals used in this study were prepared according to the procedure of Johnson.[11a]

General Procedures for Ketal Claisen Rearrangement. Method A. This procedure is a modification of the method of Johnson.[11a] A round-bottomed flask was charged with an allylic alcohol (5.0 mmol), a ketal (15.0 mmol), and propionic acid (4 drops, ~0.8 mmol). The reaction mixture was heated at 120 °C in an oil bath for 24 h with a short-path distillation head to facilitate the removal of the liberated alcohol. The reaction mixture was cooled, diluted with ether, and washed successively with 5% HCl, saturated aqueous $NaHCO_3$, and saturated brine. The organic layer was then dried ($MgSO_4$) and filtered. The volatiles were removed under reduced pressure, and the crude product was submitted to chromatographic analysis (TLC and VPC). The product mixture was separated by column chromatography on silica gel by using either a gravity column (30 g) or a medium-pressure driven column (40 g). A step gradient elution (1–3% ether/hexane, 20-mL fractions) afforded the isomeric ketones. The products were identified and characterized by their spectroscopic properties (IR, ^{1}H NMR, and mass spectra).

Method B. This procedure is identical with method A above, except that the allylic alcohol (10.0 mmol) was allowed to react with only 1 equiv of the ketal (10.0 mmol) and propionic acid (4 drops, ~0.8 mmol). The reaction mixture was worked up and purified as described in method A.

Ketal Claisen Rearrangements of Cinnamyl Alcohol and Various Ketals. 2,2-Diethoxybutane (method A): 63% yield; 96:4 ratio of **7a**/**8a** by VPC.

3-Methyl-4-phenyl-5-hexen-2-one (7a): VPC 6.3 min, 140 °C; IR (ν_{film}^{max}) 3070, 3000, 1725, 1650, 1620, 1500, 1460, 1425, 1360, 1300, 1240, 1070, 1000, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87/1.10 (d/d, 3 H, J = 7 Hz), 1.90/2.18 (s/s, 3 H), 2.95 (m, 1 H), 3.45 (d of d, 1 H, J = 10, 8 Hz), 4.8–5.3 (m, 2 H), 5.6–6.3 (m, 1 H), 7.25 (s, 5 H); mass spectrum, m/e (relative intensity) 188 (M^+), 173, 145, 117 (100), 115, 91. Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.56, H, 8.28.

5-Phenyl-6-hepten-3-one (8a): VPC 7.5 min, 140 °C; IR (ν_{film}^{max}) 3060, 3000, 1720, 1490, 1450, 1180, 1120, 990, 920, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7 Hz), 2.30 (q, 2 H, J = 7 Hz), 2.78 (d, 2 H, J = 7 Hz), 3.90 (q, 1 H, J = 7 Hz), 4.92 (d of t, 1 H, J_d = 16 Hz, J_t = 2 Hz), 4.99 (d of t, 1 H, J_d = 10 Hz, J_t = 2 Hz), 5.6–6.3 (m, 1 H), 7.25 (s, 5 H); mass spectrum, m/e (relative intensity) 188 (M^+), 159, 117 (100), 115, 91.

2,2-Diethoxypentane (method A): 66% yield; 92:8 ratio of **7b**/**8b** by VPC.

3-Ethyl-4-phenyl-5-hexen-2-one (7b): VPC 7.6 min, 175 °C; IR (ν_{film}^{max}) 3050, 2950, 1720, 1640, 1615, 1490, 1425, 1325, 1260, 1210, 1150, 1070, 1020, 1000, 960, 920, 830, 770, 730, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80/0.90 (t/t, 3 H, J = 7 Hz), 1.0–1.8 (m, 2 H), 1.76/2.10 (s/s, 3 H), 2.6–3.0 (m, 1 H), 3.40 (d of d, 1 H, J = 9, 7 Hz), 4.8–5.2 (m, 2 H), 5.6–6.2 (m, 1 H), 7.25 (s, 5 H); mass spectrum, m/e (relative intensity) 202 (M^+), 173, 117 (100), 115, 91. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.91, H, 8.91.

3-Phenyl-1-octen-5-one (8b): VPC 9.2 min, 175 °C; IR (ν_{film}^{max}) 3040, 2900, 1710, 1560, 1470, 1430, 1360, 1120, 990, 910, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3 H, J = 7 Hz), 1.1–1.8 (m, 2 H), 2.25 (t, 2 H, J = 7 Hz), 2.74 (d, 2 H, J = 7 Hz), 3.90 (q, 1 H, J = 7 Hz), 4.93 (d of t, 1 H, J_d = 17 Hz, J_t = 2 Hz), 4.97 (d of t, 1 H, J_d = 10 Hz, J_t = 2 Hz), 5.6–6.2 (m, 1 H), 7.25 (s, 5 H); mass spectrum, m/e (relative intensity) 202 (M^+), 159, 117 (100), 115, 91.

2,2-Dimethoxypentane (method A): 84% yield; 88:12 ratio of **7b**/**8b** by VPC. **Method B**: 47% yield; 93:7 ratio of **7b**/**8b** by VPC.

2,2-Diethoxy-5-methylhexane (method A): 62% yield; 96:4 ratio of **7c**/**8c** by VPC. **Method B**: 58% yield; 95:5 ratio of **7c**/**8c** by VPC. Selected fractions of the chromatography afforded a sample of *erythro*-**7c** (<1% threo by NMR).

3-(2-Methylpropyl)-4-phenyl-5-hexen-2-one (7c): VPC 4.2 min, 180 °C; IR (ν_{film}^{max}) 3000, 2900, 1710, 1450, 1350, 1240, 1150, 990, 925, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.77/0.85 (d/d, 6 H, J = 6 Hz), 1.0–1.8 (m, 3 H), 1.73/2.12 (s/s, 3 H), 2.7–3.2 (m, 1 H), 3.35 (d of d, 1 H, J = 10, 8 Hz), 4.8–5.2 (m, 2 H), 5.6–6.2 (m, 1 H), 7.20 (m, 5 H); mass spectrum, m/e (relative intensity) 230 (M^+), 173, 117 (100), 115, 91. Anal. Calcd for $C_{16}H_{22}O$: C, 83.42; H, 9.63. Found: C, 83.35; H, 9.55.

***erythro*-3-(2-Methylpropyl)-4-phenyl-5-hexen-2-one (*erythro*-7c)**: ^{1}H NMR ($CDCl_3$) δ 0.86 (d, 6 H, J = 5 Hz), 1.2–1.8 (m, 3 H), 1.75 (s, 3 H), 2.7–3.2 (m, 1 H), 3.33 (d of d, 1 H, J = 10, 8 Hz), 5.04 (d of d, 1 H, J = 16, 2 Hz), 5.05 (d of d, 1 H, J = 10, 2 Hz), 5.6–6.2 (m, 1 H), 7.24 (s, 5 H).

8-Methyl-3-phenyl-1-nonen-5-one (8c): VPC 5.6 min, 180 °C; IR (ν_{film}^{max}) 3050, 3000, 1700, 1450, 1340, 1240, 1200, 1160, 990, 910, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.9 (m, 9 H), 2.30 (t, 2 H, J = 6 Hz), 2.85 (d, 2 H, J = 7 Hz), 4.00 (m, 1 H), 4.8–5.2 (m, 2 H), 5.6–6.2 (m, 1 H), 7.26 (s, 5 H); mass spectrum, m/e (relative intensity) 230 (M^+), 159, 121, 117, 115, 99 (100), 91.

2,2-Diethoxy-3-methylbutane (method A): 73% yield; 69:31 ratio of **10a**/**11a** by isolation.

3,3-Dimethyl-4-phenyl-5-hexen-2-one (10a): VPC 6.7 min, 150 °C; IR (ν_{film}^{max}) 3030, 2900, 1710, 1600, 1490, 1460, 1450, 1420, 1360, 1350, 1245, 1110, 1070, 990, 960, 920, 880, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 3 H), 1.13 (s, 3 H), 2.05 (s, 3 H), 3.60 (d, 1 H, J = 9 Hz), 5.06 (d of d, 1 H, J = 16, 2 Hz), 5.12 (d of d, 1 H, J = 10, 2 Hz), 5.9–6.5 (m, 1 H), 7.26 (s, 5 H); mass spectrum; m/e 202 (M^+), 117 (100), 115, 91. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.07; H, 8.78.

2-Methyl-5-phenyl-6-hepten-3-one (11a): VPC 6.7 min, 150 °C; IR (ν_{film}^{max}) 3000, 2900, 1720, 1480, 1450, 1070, 1000, 920, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (d, 3 H, J = 7 Hz), 1.01 (d, 3 H, J = 7 Hz), 2.50 heptet, 1 H, J = 7 Hz), 2.84 (d, 2 H, J = 8 Hz), 3.95 (q, 1 H, J = 7 Hz), 4.97 (d of t, 1 H, J_d = 17 Hz, J_t = 2 Hz), 5.03 (d of t, 1 H, J_d = 10 Hz, J_t = 2 Hz), 5.7–6.2 (m, 1 H), 7.26 (s, 5 H); mass spectrum, m/e (relative intensity) 202 (M^+), 159, 117 (100), 115, 91. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.00; H, 8.93.

2,2-Dimethoxy-3-methylpentane (method A): 81% yield; 74:26 ratio of **10b**/**11b** by isolation.

3-Ethyl-3-methyl-4-phenyl-5-hexen-2-one (10b): VPC 5.7 min, 170 °C; IR (ν_{film}^{max}) 3040, 2950 1700, 1450, 1340, 1120, 995, 920, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.67/0.78 (t/t, 3 h, J = 7 Hz), 1.09/1.17 (s/s, 3 H), 1.1–1.9 (m, 2 H), 1.83/2.10 (s/s, 3 H), 3.60 (d of d, 1 H, J = 10, 7 Hz), 4.8–5.2 (m, 2 H), 5.8–6.2 (m, 1 H), 7.18/7.23 (s/s, 5 H); mass spectrum, m/e (relative intensity) 216 (M^+), 187, 117 (100), 115, 91. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.09; 9.20.

3-Methyl-6-phenyl-7-octen-4-one (11b): VPC 5.7 min, 170 °C; IR (ν_{film}^{max}) 3050, 2950, 1710, 1480, 1440, 1350, 1160, 1060, 990, 910, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7-1.0 (m, 6 H), 1.0–1.7 (m, 2 H), 2.31 (hextet, ^{1}H, J = 7 Hz), 2.80 (d, 2 H, J = 7 Hz), 3.93 (q, 1 H, J = 7 Hz), 4.8–5.2 (m, 2 H), 5.7–6.2 (m, 1 H), 7.23 (s, 5 H); mass spectrum, m/e (relative intensity) 216 (M^+), 159, 117 (100), 115, 91, 85. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.06; H, 8.41.

2,2-Diethoxy-4-methylpentane (method A): 74% yield; 67:33 ratio of **13a′/14a′** by VPC.

3-Isopropyl-4-phenyl-5-hexen-2-one (13a′): VPC 4.5 min, 170 °C; IR (ν_{film}^{max}) 3030, 2950, 1705, 1450, 1350, 1260, 1160, 990, 920, 760, 730, 700; ^{1}H NMR ($CDCl_3$) δ 0.90 (m, 6 H), 1.76/1.95 (s/s, 3 H), 1.9–2.2 (m, 1 H), 2.7–3.1 (m, 1 H), 3.4–3.8 (m, 1 H), 4.8–5.2 (m, 2 H), 5.5–6.2 (m, 1 H), 7.20/7.22 (s/s, 5 H); mass spectrum, m/e (relative intensity) 216 (M^+), 201, 173, 117 (100), 115, 91. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.09; H, 9.19.

3-Phenyl-7-methyl-1-octen-5-one (14a′): VPC 5.2 min, 170 °C; IR (ν_{film}^{max}) 3050, 3000, 1710, 1500, 1450, 1360, 1190, 1150, 1060, 1030, 1000, 910, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (d, 6 H, J = 7 Hz), 1.2–2.0 (m, 1 H), 2.20 (m, 2 H), 2.78 (d, 2 H, J = 7 Hz), 3.91 (q, 1 H, J = 7 Hz), 4.93 (d of t, 1 H, J_d = 16 Hz, J_t = 2 Hz), 5.00 (d of t, 1 H, J_d = 10 Hz, J_t = 2 Hz), 5.6–6.2 (m, 1 H), 7.25 (s, 5 H); mass spectrum, m/e (relative intensity) 216 (M^+), 159, 117, 115, 85 (100). Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.20; H, 9.44.

2,2-Dimethoxy-4-methylpentane (method B): 61% yield; 67:33 ratio of **13a′/14a′** by VPC.

2,2-Dimethoxy-4,4-dimethylpentane (method A): 72% yield of **14b′**.

2,2-Dimethyl-6-phenyl-7-octen-4-one (14b′): VPC 2.3 min, 200 °C; IR (ν_{film}^{max}) 3040, 2930, 1710, 1650, 1610, 1470, 1400, 1360, 1240, 1180, 1070, 1030, 960, 920, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9 H), 2.18 (s, 2 H), 2.75 (d, 2 H, J = 7 Hz), 3.89 (q, 1 H, J = 7 Hz), 4.97 (d of t, 1 H, J_d = 17 Hz, J_t = 2 Hz), 5.04 (d of t, 1 H, J_d = 11 Hz, J_t = 2 Hz), 5.7–6.2 (m, 1 H), 7.23 (s, 5 H); mass spectrum, m/e (relative intensity) 230 (M^+), 159, 117, 115, 99 (100), 91. Anal. Calcd for $C_{16}H_{22}O$: C, 83.42; H, 9.63. Found: C, 83.53; H, 9.64.

Ketal Claisen Rearrangements of *trans*-2-Hexen-1-ol and Various Ketals. 2,2-Dimethoxypentane (methodA): 28% yield; 86:14 ratio of **7d/8d** by VPC. **Method B**: 37% yield; 86:14 ratio of **7d/8d** by VPC.

3-Ethyl-4-propyl-5-hexen-2-one (7d): VPC 3.9 min, 120 °C; IR (ν_{film}^{max}) 3100, 2960, 1710, 1460, 1350, 1170, 995, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6–1.8 (m, 12 H), 1.9–2.6 (m, 5 H) including 2.00/2.03 (s/s, 3 H), 4.7–5.9 (m, 3 H); mass spectrum, m/e (relative intensity) 168 (M^+), 153, 139, 125, 97, 95, 86 (100), 83. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.37; H, 11.85.

3-Propyl-1-octen-5-one (8d): VPC 4.5 min, 120 °C; IR (ν_{film}^{max}) 3100, 2950, 1720, 1460, 1350, 1170, 1000, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6–1.9 (m, 12 H) including 0.87 (t, J = 7 Hz), 2.2–2.7 (m, 5 H), 4.7–5.2 (m, 2 H), 5.3–5.9 (m, 1 H); mass spectrum, m/e (relative intensity) 168 (M^+), 153, 139, 125, 97, 83, 82, 71 (100).

2,2-Diethoxy-5-methylhexane (method A): 58% yield, 91:9 ratio of **7e/8e** by VPC. **Method B**: 43% yield, 91:9 ratio of **7e/8e** by VPC.

3-(2-Methylpropyl)-4-propyl-5-hexen-2-one (7e): VPC 4.4 min, 135 °C; IR (ν_{film}^{max}) 3050, 2950, 1710, 1450, 1360, 1240, 1160, 990, 910; ^{1}H NMR ($CDCl_3$) δ 0.7–1.7 (m, 16 H) including 0.87 (d, J = 6 Hz), 1.9–2.8 (m, 5 H) including 2.07/2.11 (s/s, 3 H), 4.7–5.9 (m, 3 H); mass spectrum, m/e (relative intensity) 196 (M^+), 181, 153, 140, 114, 97 (100), 83. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.40; H, 12.28.

2-Methyl-7-propyl-8-nonen-5-one (8e): VPC 5.8 min, 135 °C; IR (ν_{film}^{max}) 3100, 2970, 1720, 1450, 1370, 1160, 1060, 990, 910, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–1.8 (m, 16 H) including 0.83 (d, J = 5 Hz), 2.2–2.5 (m, 5 H), 4.7–5.1 (m, 2 H), 5.3–5.8 (m, 1 H); mass spectrum m/e (relative intensity) 196 (M^+), 181, 153, 140, 125, 97, 83, 82, 81 (100).

2,2-Dimethoxy-3-methylpentane (method A): 70% yield; 73:27 ratio of **10c/11c** by isolation.

3-Ethyl-3-methyl-4-propyl-5-hexen-2-one (10c): VPC 5.2 min, 125 °C; IR (ν_{film}^{max}) 3050, 2900, 1700, 1400, 1360, 1340, 1210, 1160, 990, 910, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6–1.9 (m, 15 H) including 0.97/1.00 (s/s), 1.9–2.5 (m, 4 H) including 2.03/2.07 (s/s, 3 H), 4.7–5.8 (m, 3 H); mass spectrum, m/e (relative intensity) 182 (M^+), 167, 139, 100, 85, 83 (100), 69. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 78.90; H, 11.98.

3-Methyl-6-propyl-7-octen-4-one (11c): VPC 5.2 min, 125 °C; IR (ν_{film}^{max}) 3050, 2950, 1720, 1450, 1360, 1150, 1050, 990, 910; ^{1}H NMR ($CDCl_3$) δ 0.7–1.9 (m, 15 H) including 0.9 (t, J = 7 Hz), 1.05 (d, J = 7 Hz), 2.2–2.9 (m, 4 H), 4.8–5.3 (m, 2 H), 5.3–6.0 (m, 1 H); mass spectrum, m/e (relative intensity) 182 (M^+), 167, 139, 125, 97, 85, 83 (100), 69. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 78.97; H, 12.00.

2,2-Dimethoxy-4-methylpentane (method A): 43% yield; 31:69 ratio of **13c′/14c′** by VPC.

3-Isopropyl-4-propyl-5-hexen-2-one (13c′): VPC 11.3 min, 95 °C; IR (ν_{film}^{max}) 3450, 2930, 1710, 1450, 1350, 1220, 1170, 1000, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–1.8 (m, 14 H), 1.9–2.5 (m, 5 H) including 2.13/2.17 (s/s), 4.7–5.8 (m, 3 H); mass spectrum, m/e (relative intensity) 182 (M^+), 167, 139, 100, 97, 85 (100), 83. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.00; H, 12.08.

2-Methyl-6-propyl-7-octen-4-one (14c′): VPC 13.3 min, 95 °C; IR (ν_{film}^{max}) 3050, 2900, 1710, 1650, 1450, 1350, 1290, 1160, 1050, 990, 910, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–1.1 (m, 9 H), 1.1–1.5 (m, 5 H), 2.0–2.6 (m, 5 H), 4.7–5.2 (m, 2 H), 5.3–5.9 (m, 1 H); mass spectrum, m/e (relative intensity) 182 (M^+), 139, 125, 97, 85 (100). Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.90; H, 12.11.

2,2-Dimethoxy-4,4-dimethylpentane (method B): 53% yield of **14d′**.

2,2-Dimethyl-6-propyl-7-octen-4-one (14d′): VPC 4.9 min, 130 °C; IR (ν_{film}^{max}) 3050, 2950, 1710, 1450, 1350, 1220, 1160, 990, 910, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 7 Hz), 1.00 (s, 9 H), 1.0–1.5 (m, 4 H), 2.2–2.6 (m, 5 H) including 2.26 (s) and 2.33 (d, J = 10 Hz), 4.8–5.1 (m, 2 H), 5.3–5.9 (m, 1 H); mass spectrum; m/e (relative intensity) 196 (M^+), 181, 153, 140, 125, 99 (100), 97, 84, 83, 71. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.75; H, 12.14.

Ketal Claisen Rearrangements of 1-Hexen-3-ol and Various Ketals. 2,2-Dimethoxypentane (method A): 47% yield; 50:50 ratio of **17a/18a** by VPC. **Method B**: 40% yield; 70:30 ratio of **17a/18a** by VPC.

***trans*-3-Ethyl-5-nonen-2-one (17a)**: VPC 4.3 min, 125 °C; IR (ν_{film}^{max}) 3000, 1710, 1450, 1370, 1180, 970, 920, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 6 H, J = 7 Hz), 1.1–1.6 (m, 4 H), 1.7–2.7 (m, 8 H) including 2.06 (s), 5.2–5.5 (m, 2 H); mass spectrum, m/e (relative intensity) 168 (M^+), 140, 139, 125, 86 (100).

***trans*-7-Undecen-4-one (18a)**: VPC 5.4 min, 125 °C; IR (ν_{film}^{max}) 3000, 1720, 1470, 1370, 1140, 1070, 970, 920, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87/0.91 (t/t, 6 H, J = 7 Hz), 1.2–1.7 (m, 4 H), 1.8–2.8 (m, 8 H), 5.3–5.5 (m, 2 H); mass spectrum, m/e (relative intensity) 168 (M^+), 125, 83, 82 (100).

2,2-Diethoxy-5-methylhexane (method A): 56% yield; 66:34 ratio of **17b/18b** by VPC.

***trans*-3-(2-Methylpropyl)-5-nonen-2-one (17b)**: VPC 3.9 min, 150 °C; IR (ν_{film}^{max}) 2900, 1700, 1440, 1330, 1150, 1100, 970, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–1.1 (m, 9 H), 1.1–1.7 (m, 5 H), 1.8–2.8 (m, 8 H) including 2.06 (s), 5.2–5.5 (m, 2 H); mass spectrum, m/e (relative intensity) 196 (M^+), 181, 153, 140, 139, 97 (100). Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.38; H, 12.27.

***trans*-2-Methyl-8-dodecen-5-one (18b)**: VPC 5.3 min, 150 °C; IR (ν_{film}^{max}) 3000, 1720, 1440, 1350, 970, 910, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6–1.1 (m, 9 H) including 0.87 (t, J = 7 Hz) and 0.90 (d, J = 5 Hz), 1.1–1.7 (m, 5 H), 1.7–2.7 (m, 8 H), 5.2–5.5 (m, 2 H); mass spectrum, m/e (relative intensity) 196 (M^+), 181, 167, 140, 125, 99, 83, 82, 81 (100). Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.30; H, 12.17.

2,2-Dimethoxy-3-methylpentane (method A): 61% yield; 23:77 ratio of **17c/18c** by VPC. **Method B**: 42% yield; 28:72 ratio of **17c/18c** by VPC.

***trans*-3-Ethyl-3-methyl-5-nonen-2-one (17c)**: VPC 7.2 min, 120 °C; IR (ν_{film}^{max}) 2950, 1710, 1450, 1350, 1130, 970, 910, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–0.9 (m, 6 H) including 0.77 (t, J = 7 Hz) and 0.87 (t, J = 6 Hz, 1.03 (s, 3 H), 1.1–1.8 (m, 4 H), 1.8–2.3

(m, 7 H) including 2.10 (s), 5.2–5.5 (m, 2 H); mass spectrum, *m/e* (relative intensity) 182 (M^+), 167, 153, 139, 99, 83 (100), 69. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.02; H, 11.91.

***trans*-3-Methyl-7-undecen-4-one (18c)**: VPC 8.3 min, 120 °C; IR (ν_{film}^{max}) 2900, 1700, 1430, 1360, 1060, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–1.1 (m, 9H) including 0.83 (t, J = 7 Hz), 0.97 (t, J = 7 Hz) and 1.06 (d, J = 7 Hz), 1.1–1.7 (m, 4 H), 1.8–2.6 (m, 7 H), 5.2–5.5 (m, 2 H); mass spectrum; *m/e* (relative intensity) 182 (M^+), 125, 97, 85 (100), 83. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.99; H, 11.94.

2,2-Dimethoxy-4-methylpentane (method B): 46% yield; 63:37 ratio of **17d/18d** by VPC.

***trans*-3-Isopropyl-5-nonen-2-one (17d)**: VPC 4.8 min, 130 °C; IR (ν_{film}^{max}) 2900, 1700, 1450, 1340, 1150, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–1.0 (m, 9 H) including 0.83 (t, J = 6 Hz) and 0.90 (d, J = 7 Hz), 1.1–1.6 (m, 3 H), 1.8–2.3 (m, 8 H) including 2.06 (s), 5.2–5.5 (m, 2 H); mass spectrum, *m/e* (relative intensity) 182 (M^+), 139 (100). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.98; H, 12.08.

***trans*-2-Methyl-7-undecen-4-one (18d)**: VPC 5.7 min, 130 °C; IR (ν_{film}^{max}) 3000, 1710, 1460, 1390, 1370, 1300, 1170, 1150, 1070, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–1.0 (m, 9 H) including 0.83 (t, J = 7 Hz) and 0.90 (d, J = 6 Hz), 1.0–1.6 (m, 3 H), 1.7–2.6 (m, 8 H), 5.2–5.5 (m, 2 H); mass spectrum, *m/e* (relative intensity) 182 (M^+), 140, 139, 125, 85 (100). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.94; H, 12.10.

2,2-Dimethoxy-4,4-dimethylpentane (method B): 27% yield; 7:93 ratio of **17e/18e** by VPC.

***trans*-3-*tert*-Butyl-5-nonen-2-one (17e)**: VPC 4.6 min, 140 °C; IR (ν_{film}^{max}) 3000, 1710, 1450, 1360, 1200, 1030, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 12 H) including 0.96 (s), 1.1–1.7 (m, 2 H), 1.8–2.5 (m, 8 H) including 2.10 (s), 5.2–5.5 (m, 2 H); mass spectrum; *m/e* (relative intensity) 196 (M^+), 181, 139 (100), 97.

***trans*-2,2-Dimethyl-7-undecen-4-one (18e)**: VPC 5.2 min, 140 °C; IR (ν_{film}^{max}) 2950, 1710, 1440, 1340, 1220, 1070, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 12 H) including 0.83 (t, J = 7 Hz) and 1.00 (s), 1.1–1.6 (m, 2 H), 1.7–2.6 (m, 8 H), 5.2–5.5 (m, 2 H); mass spectrum, *m/e* (relative intensity) 196 (M^+), 140, 125, 99 (100), 83, 82, 71. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.51, H, 12.20.

Study on the Effect of Acid Catalyst. The reaction between cinnamyl alcohol and 2,2-dimethoxypentane in the presence of a weak acid catalyst was examined by using propionic acid and 2,4,6-trimethylbenzoic acid. The reactions were performed according to the procedure described in method A except that the amount of acid catalyst was varied. The yields and product ratios were determined as described above.

Preparation and Reaction of Authentic 2-(*trans*-Cinnamyloxy)-1-butene. *trans*-Cinnamyl Propionate (19). Propionic anhydride (20.0 mmol, 2 equiv) was added to an ice cold solution of *trans*-cinnamyl alcohol (10.0 mmol) in pyridine (10 mL) over a 5-min period. The ice bath was removed, and the reaction mixture was allowed to stir at 25 °C for 24 h. The reaction mixture was quenched with water (2.0 mL), allowed to stir an additional 20 min, and diluted with ether (50 mL). The organic layer was washed with saturated $NaHCO_3$ (2×), saturated $CuSO_4$ (5×), and brine (1×). The resulting solution was dried ($MgSO_4$) and filtered. The volatiles were removed under reduced pressure, and the crude product was evaporatively distilled (0.2 mmHg, 160 °C) to give cinnamyl propionate (64% yield).

***trans*-Cinnamyl propionate (19)**: IR (ν_{film}^{max}) 3000, 1750, 1600, 1500, 1450, 1400, 1350, 1200, 1070, 1010, 970, 890, 850, 810, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 7 Hz), 2.40 (q, 2 H, J = 7 Hz), 4.75 (d, 2 H, J = 6 Hz), 6.23 (d of t, 1 H, J_d = 16 Hz, J_t = 6 Hz), 6.70 (d, 1 H, J = 16 Hz), 7.33 (s, 5 H).

2-(*trans*-Cinnamyloxy)-1-butene (20). The following reaction was conducted according to the method of Pine.[18] A solution of *trans*-cinnamyl propionate (1.8 mmol) in a mixture of anhydrous toluene (3.0 mL), anhydrous THF (1.0 mL), and anhydrous pyridine (18 μL) was degassed under reduced pressure and cooled to −40 °C under an atmosphere of dry nitrogen. A solution of $Cp_2TiCH_2AlClMe_2$[28] (2.4 mmol, 1.33 equiv) in anhydrous, O_2-free toluene was added via syringe to the chilled ester solution over a 5-min period. The reaction mixture was stirred at -40 °C for 30 min and allowed to warm to 25 °C over a 2-h period. The reaction was quenched by the dropwise addition of 0.7 mL of 15% aqueous NaOH solution to the chilled (−10 °C) reaction mixture. The reaction mixture was allowed to warm to 25 °C, and gas evolution occurred. The reaction mixture was diluted with ether, dried (Na_2SO_4), and filtered through a Celite pad. The volatiles were removed under reduced pressure, the residues were triturated with hexane, and the insoluble inorganic salts were removed by filtration. Thin-layer chromatographic analysis (solvent A) of the organic layer revealed the presence of the desired product (R_f 0.67) along with a small amount of *trans*-cinnamyl propionate (R_f 0.58) and some inorganic salts. The yellow solution was rapidly filtered through a plug of neutral alumina (5 g) to remove the inorganic salts, and the resulting colorless solution was evaporated under reduced pressure to give the crude 2-(*trans*-cinnamyloxy)-1-butene (**20**): 40% yield (contaminated with 15% toluene by NMR); IR (ν_{film}^{max}) 3050, 3000, 1640, 1600, 1490, 1450, 1350, 1320, 1270, 1240, 1090, 1020, 960, 940, 910, 800, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (t, 3 H, J = 7 Hz), 2.07 (q, 2 H, J = 7 Hz), 3.90 (s, 2 H), 4.36 (d, 2 H, J = 5 Hz), 6.30 (d of t, 1 H, J_d = 16 Hz, J_t = 5 Hz), 6.70 (d, 1 H, J = 16 Hz), 7.33 (s, 5 H).

Reaction of 2-(*trans*-Cinnamyloxy)-2-butene under Claisen Conditions. 2-(*trans*-Cinnamyloxy)-2-butene (0.72 mmol) and 2,2-diethoxybutane were allowed to react according to the procedure described in method A. Gas chromatographic analysis of the crude product at 140 °C revealed the presence of two new compounds (τ = 6.3 min and τ = 7.5 min) in a ratio of 93:7, respectively. These two materials were shown to be identical with authentic 3-methyl-4-phenyl-5-hexen-2-one [R_f 0.54 (solvent A), τ = 6.3 min (140 °C)] and 5-phenyl-6-hepten-3-one [R_f 0.60 (solvent A), τ = 7.5 min (140 °C)], respectively, by thin-layer and gas chromatographic analysis.

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Registry No. (*E*)-**5** (R_1 = Ph), 4407-36-7; (*E*)-**5** (R_1 = Pr), 928-95-0; **6** (R = Et; R_2 = Me), 52752-16-6; **6** (R = Et; R_2 = Et), 80359-80-4; **6** (R = Me; R_2 = Et), 55904-98-8; **6** (R = Et; R_2 = CH_2CHMe_2), 80359-82-6; **7a** (isomer 1), 32252-97-4; **7a** (isomer 2), 32096-07-4; **7b** (isomer 1), 80359-84-8; **7b** (isomer 2), 80359-84-8; **7c** (isomer 1), 87012-57-5; **7c** (isomer 2), 80359-88-2; **7d** (isomer 1), 87039-19-8; **7d** (isomer 2), 87012-58-6; **7e** (isomer 1), 87012-59-7; **7e** (isomer 2), 87012-60-0; **8a**, 80359-92-8; **8b**, 80359-93-9; **8c**, 80359-95-1; **8d**, 87012-61-1; **8e**, 87012-62-2; **9** (R = Et; R_2 = Me), 80359-83-7; **9** (R = Me; R_2 = Et), 72409-06-4; **10a**, 80359-89-3; **10b** (isomer 1), 80359-90-6; **10b** (isomer 2), 80359-91-7; **10c** (isomer 1), 87012-63-3; **10c** (isomer 2), 87012-64-4; **11a**, 80359-96-2; **11b**, 80359-97-3; **11c**, 87039-20-1; **12** (R = Et; R_2 = H), 80359-81-5; **12** (R = Me; R_2 = H), 1112-78-3; **12** (R = Me; R_2 = Me), 72409-07-5; **13a** (isomer 1), 80359-87-1; **13a** (isomer 2), 80359-86-0; **13c** (isomer 1), 87012-65-5; **13c** (isomer 2), 87012-66-6; **14a**, 70245-09-9; **14b**, 80359-94-0; **14c**, 87012-67-7; **14d**, 87012-68-8; **15**, 4798-44-1; **17a**, 87012-69-9; **17b**, 87012-70-2; **17c**, 87012-71-3; **17d**, 87012-72-4; **17e**, 87012-73-5; **18a**, 87012-74-6; **18b**, 87012-75-7; **18c**, 87012-76-8; **18d**, 87012-77-9; **18e**, 87012-78-0; **19**, 78761-38-3; **20**, 87012-79-1; propionic anhydride, 123-62-6.

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