atom make significant contributions to this olefin–metal bonding description. The most dramatic structural changes are in the terminal methylene H coordinates. Ab initio calculations[24] on the free gas-phase structure depict *cis*-butadiene as planar (ϕ = 0.0° and γ = 0.0°) with bond angles H_1–C_1–C_2 = 121.5° and H_2–C_1–C_2 = 121.6°. In contrast, the structure of the Fe complex of butadiene is characterized by very large changes in these parameters: ϕ = 28.1°, γ = 26.6°, with bond angles H_1–C_1–C_2 = 112.1° (Kraitchman analysis) or 117.5° (least-squares analysis) and H_2–C_1–C_2 = 118.6° (Kraitchman analysis) or 117.8° (least-squares analysis). These changes in both the carbon skeleton and the terminal hydrogen coordinates are consistent with a trend in which the terminal sp^2-hybridized carbon atoms of free butadiene acquire more sp^3 character upon complexation with Fe.

The NMR data provide further evidence for these changes in the electronic structure of the olefin. The observed chemical shifts for the terminal methylene protons go from $\delta(H_2)$ = 5.04 and $\delta(H_1)$ = 5.15 ppm in the free butadiene to 0.27 and 1.78 ppm, respectively, in the Fe complex measured in $CDCl_3$. Larger magnitude shifts were observed in benzene solutions, and somewhat smaller shifts were observed in neat solutions. Although the free butadiene values are typical of protons influenced by the diamagnetic deshielding effects of π-electron densities, the corresponding chemical shifts in the Fe complex are more representative of ordinary aliphatic protons.

(24) Bock, C. W.; George, P.; Trachman M. *Theoret. Chim. Acta* **1984**, *64*, 1923.

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Chemoselectivity in the Ruthenium-Catalyzed Redox Isomerization of Allyl Alcohols

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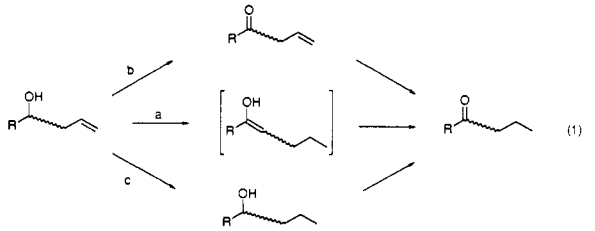
Abstract: Adjustment of oxidation level by internal hydrogen reorganization represents a highly efficient synthetic protocol. Cyclopentadienylbis(triphenylphosphine)ruthenium chloride in the presence of triethylammonium hexafluorophosphate catalyzes the redox isomerization of allyl alcohols to their saturated aldehydes or ketones. High chemoselectivity is observed since simple primary and secondary alcohols and isolated double bonds are not affected by this catalyst. The reaction is sensitive to the degree of substitution on the double bond and requires relatively unhindered olefins. Switching to indenylbis(triphenylphosphine)ruthenium chloride in the presence of triethylammonium hexafluorophosphate significantly expands the scope of the reaction to substrates bearing more substituted olefinic linkages and to cyclic substrates of rings containing eight or more members. The mechanism is probed by deuterium labeling, which shows that the metal catalyzes an intramolecular 1,3-hydrogen shift of the carbinol hydrogen to the terminal olefinic position.

Double-bond isomerizations, a process promoted by many transition metals either via a π-allylmetal intermediate or via a hydrometalation–dehydrometalation, constitute the equivalent of internal reduction–oxidation (redox).[1-10] In those cases where such isomerizations produce olefins possessing hydroxyl groups, irreversible tautomerization can occur to generate ketones to constitute a disproportionation between an alcohol and an olefin (eq 1a). Rearranging the oxidation levels in such a manner



(1)

represents a more atom economical approach to redox chemistry than processes which involve sequential oxidation and reduction (eq 1b) or vice versa (eq 1c). Surprisingly, this conceptually attractive strategy has found little use synthetically. The lack of chemoselectivity may account for this fact. For example, 9-undecen-1-ol isomerizes to decanal in the presence of an iron carbonyl catalyst.[2] While this example shows the potential of moving a double bond over many carbons before capturing it irreversibly by tautomerization of an enol, it highlights the reactivity of all double bonds under the reaction conditions.

Such metal-catalyzed redox reactions of unsaturated alcohols need not occur via double-bond isomerizations. An alternative mechanism envisions interaction of the metal with alcohol to form M–H bonds via β-elimination of a metal alkoxide (or a metal–hydroxyl group complex), which then delivers the hydrogen to the olefin. An analogous process appears to be operating in the isomerization of allylamines to enamines.[10]

(1) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: London, 1981; pp 70–81. Davies, S. G. *Organotransition Metal Chemistry. Applications to Organic Synthesis*; Pergamon Press: Oxford, 1982; pp 266–290.

(2) Fe: Iranpoor, N.; Mottaghinejad, E. *J. Organomet. Chem.* **1992**, *423*, 399. Barborak, J. C.; Herndon, J. W.; Wong, J.-W. *J. Am. Chem. Soc.* **1979**, *101*, 7430. Strauss, J. U.; Ford, P. W. *Tetrahedron Lett.* **1975**, 2917. Cowerd, F. G.; von Rosenberg, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 2157. Damico, R.; Logan, T. J. *J. Org. Chem.* **1967**, *32*, 2356. Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 4591.

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(4) Os: Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313.

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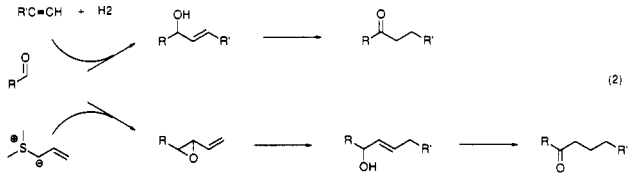
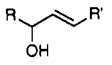
In addition to the efficiency of such strategies, other benefits may accrue from such reactions. Particularly noteworthy are the prospects for diastereo- and enantioselectivity. Disporportionation of allyl alcohols to saturated ketones represents a special case since the same C–H bond is involved regardless of which mechanism operates. Further, simple addition processes provide easy entry to such substrates (eq 2).



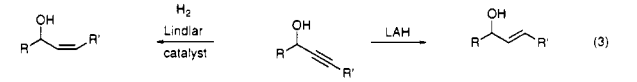
A key to the synthetic utility of such a process is clearly chemoselectivity, i.e., the ability to differentiate an allyl alcohol from either an isolated alcohol or olefin. In conjunction with our studies of ruthenium-catalyzed reactions,[11] we discovered that certain ruthenium complexes catalyze the isomerization of allyl alcohols to saturated ketones. In this article, we record our studies of the chemoselectivity and mechanism of this interesting process.[12]

Synthesis of Substrates

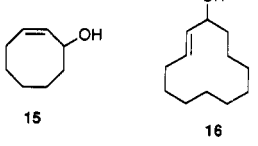
The preparation of substrates **1–14** utilized standard organometallic reactions.



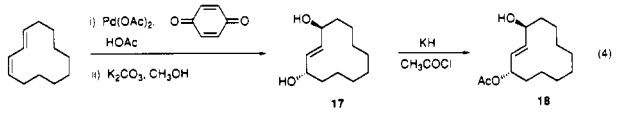
R	R′	R	R′
1 $PhCH_2CH_2$	H	**6** $CH_3CH(OH)(CH_2)_8$	H
2 $CH_3(CH_2)_9CH_2$	H	**7** $CH_2{=}C(CH_3)CH_2CH_2$	n-C_5H_{11}
3 c-C_6H_{11}	H	**8** n-C_4H_9	Ph
4 $CH_2{=}CH(CH_2)_8$	H	**9** $CH_2{=}CHCH(OH)(CH_2)_8$	H
5 $HOCH_2CH_2$-$(CH_2)_8$	H	**10** $CH_2{=}CHCH(OCH_3)$-$(CH_2)_8$	H



R	R′	R	R′
11 $PhCH_2CH_2$	$CH_3(CH_2)_8CH_2$	**12** $PhCH_2CH_2$	$CH_3(CH_2)_8CH_2$
		13 $CH_3CH(OH)(CH_2)_8$	n-C_4H_9
		14 $CH_2{=}CH(CH_2)_8$	n-C_4H_9

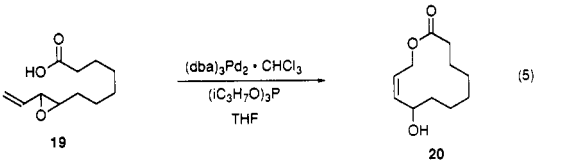


Stereocontrolled reductions of propargyl alcohols (eq 3) serve as a particularly convenient entry to either E or Z olefins. A standard allylic bromination–solvolysis protocol provides the cycloalkenols **15**[13] and **16**.[14] The (E)-enediol **17** arises from the palladium-catalyzed 1,4-dihydroxylation[15] of the known[16] (E,Z)-1,3-cyclododecadiene (eq 4). The diol **17** is obtained as a 9:1 ratio of two

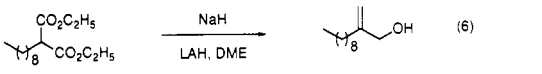


17 18

isomers. That the isomers represent diastereomeric diols rather than E,Z olefinic isomers is discerned by ^1H NMR analysis of the monoacetate **18**, which shows a 15.6 Hz coupling of the vinyl protons in both the major (δ 5.90 and 5.87) and minor (δ 5.70 and 5.55) products. On the basis of analogy, the major diol diastereomer is assigned as depicted. Palladium-catalyzed cycloisomerization of the carboxy vinyl epoxide **19** generates the hydroxydodecenolide **20** (eq 5).[17] LAH reduction of the sodium salt of a monosubstituted malonate is a convenient entry to 2-substituted allyl alcohols (e.g., **21**, eq 6).[18]



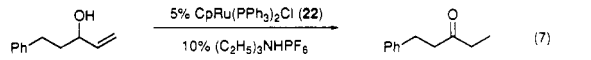
19 20



21

Isomerizations

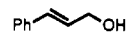
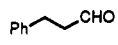
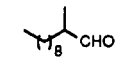
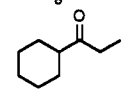
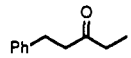
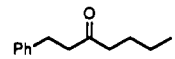
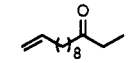
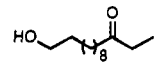
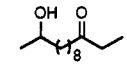
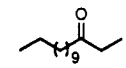
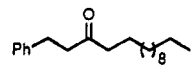
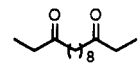
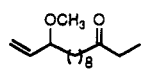
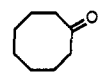
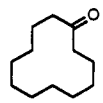
Initial efforts focused on the isomerization of 5-phenyl-1-penten-3-ol to 1-phenyl-3-pentanone[19] (eq 7). Reaction occurs at room temperature in dioxane using cyclopentadienylbis(triphenylphosphine)ruthenium chloride (**22**),[20] but only to the extent of 44% conversion after 7 days. At 60 °C, complete conversion



occurs in 8.5 h to give the ketone in 69% yield. Best results employ 2-butanone at 80 °C (82% yield after 3.5 h) or dioxane at 100 °C (81% yield after 2 h) as solvent. The sensitivity of aldehydes to pH led us to explore the role of the acid cocatalyst in the redox isomerization of 2-(hydroxymethyl)-1-undecene (**21**, Table I, entry 2). In the absence of any cocatalyst, the desired aldehyde, 2-methylundecanal, an important perfumery ingredient,[21] is obtained in only 33% yield. Addition of 10% ammonium or triethylammonium hexafluorophosphate increases the yield to 64% and 68%, respectively. The more neutral pH of the latter led to its selection in our standard protocol. Thus, by adopting the catalyst conditions of eq 7 in dioxane at 100 °C, the results summarized

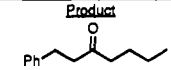
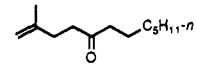
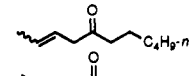
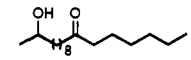
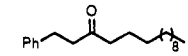
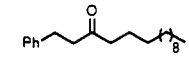
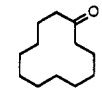
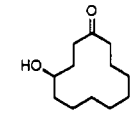
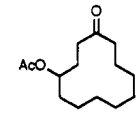
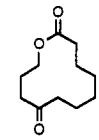
(6) Pt: Clark, H. C.; Kurosawa, H. *Chem. Commun.* **1972**, 150.
(7) Pd: Kraus, M. *Collect. Czech. Chem. Commun.* **1972**, *37*, 460.
(8) Rh and Ru: Lin, Y.; Zhu, X.; Zhou, Y. *J. Organomet. Chem.* **1992**, *429*, 269. Karlen, T.; Ludi, A. *Helv. Chim. Acta* **1992**, *75*, 1604. McGrath, D. V.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3611. Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958. Smadja, W.; Ville, G.; Georgoulis, C. *Chem. Commun.* **1980**, 594. Dedieu, M.; Pascal, Y.-L. *C. R. Acad. Sci. Ser. C.* **1976**, *282*, 65. Strohmeier, W.; Weigelt, L. *J. Organomet. Chem.* **1975**, *86* C17. Sasson, Y.; Rempel, G. L. *Tetrahedron Lett.* **1974**, 4133. Nicholson, J. K.; Shaw, B. L. *Proc. Chem. Soc. London* **1963**, 282.
(9) Cr: Sodeoka, M.; Yamada, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1990**, *112*, 4906. Y: Qian, C.; Zhu, D.; Li, D. *J. Organomet. Chem.* **1992**, *430*, 175.
(10) Cf. allylamine to enamine; Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208. For a recent theoretical treatment, see: Yamakawa, M.; Noyori, R. *Organometallics* **1992**, *11*, 3167.
(11) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579. Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809.
(12) For a preliminary report of a portion of this work, see: Trost, B. M.; Kulawiec, R. J. *Tetrahedron Lett.* **1991**, *32*, 3039.
(13) Cope, A. C.; Kinter, M. R.; Keller, R. T. *J. Am. Chem. Soc.* **1954**, *76*, 2757.
(14) Bartlett, M. F.; Figdor, S. K.; Wiesner, K. *Can. J. Chem.* **1952**, *30*, 291.
(15) Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619.
(16) Cf. Gassman, P. G.; Korn, S. R.; Thummel, R. P. *J. Am. Chem. Soc.* **1974**, *96*, 6948.
(17) Brzezowski, C. M. Ph.D. Thesis, University of Wisconsin—Madison, Madison, WI, 1989, pp 326–7.
(18) Noda, Y.; Kikuchi, M. *Synth. Commun.* **1985**, *15*, 1245.
(19) Schultz, E. M.; Bicking, J. B. *J. Am. Chem. Soc.* **1953**, *75*, 1128.
(20) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.
(21) Wright, R. H. *Am. Perfum. Cosmet.* **1968**, *83*, 43; *Chem. Abstr.* **1969**, *69*, 91487c. Shutikova, L. A.; Voitkerich, S. A.; Cherkaw, V. G.; Masarskŭ, V. E. *Maslo-Zhir. Promst.* **1970**, *36*, 29; *Chem. Abstr.* **1974**, *74*, 12552x. For a recent synthesis, see: Enders, D.; Dyker, H. *Annalen* **1990**, 1107.

Table I. Redox Isomerization Catalyzed by Ruthenium Complex **22** at 100 °C

Entry	Alcohol	Time	Product	Yield
1		8h		90%
2	**21**	3.5h		68%
3	**3**	1.5h		92%
4	**1**	2h		81%
5	**8**	9h		23%[a]
6	**4**	1h		87%
7	**5**	1h		52%
8	**6**	1.5h		90%
9	**2**	2.5h		91%
10	**12**	24h		53% (66%)[b]
11	**9**	1.5h		73%
12	**10**	1h		93
13	**15**	24h		31 (45%)[b]
14	**16**	9h		84%

[a] Dehydration to form 1-phenyl-1,3-heptadiene (67%) was the major process. [b] The yield in parenthesis is based upon recovered starting material.

Table II. Redox Isomerization Catalyzed by Ruthenium Complex **24** in Dioxane at 100 °C

Entry	Alcohol	Time	Product	Yield
1	**8**	2h		83%
2	**7**	3h		82%[a]
3	**14**	8h		77%
4	**13**	10h		69% (84%)[b]
5	**12**	3h		81%
6	**11**	24h		20% (50%)[b,c]
7	**15**	3h		47%[d]
8	**16**	2.5h		87%
9	**17**	4h		35%
10	**18**	3h		86%
11	**20**	6.5h		28%

[a] In addition, a 9% yield of 2-methyl-1,6-dodecadien-5-one is obtained. [b] Yield in parentheses is based upon recovered starting material. [c] In addition, a 13% (33%)[b] yield of 1-phenyl-4-pentadecen-3-one is obtained. [d] Yield determined by gas chromatography using an internal standard.

in Table I are obtained. Entries 1 and 2 of Table I indicate that isomerizations to form aldehydes may proceed well. On the other hand, geraniol fails to isomerize to citronellal.

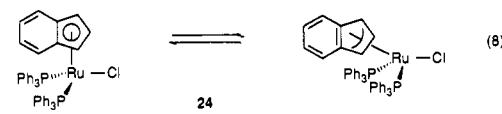
Entries 3–11 of Table I illustrate the extraordinary chemoselectivity of this redox isomerization. Non-allylic primary and secondary alcohols (Table I, entries 7 and 8) are not oxidized. Monosubstituted olefins, which are normally particularly prone to isomerization, do not (Table I, entry 6). Contrasting the diol **9** (Table I, entry 11) and its monomethyl ether **10** (Table I, entry 12) reveals the requirement for a free alcohol in addition to the double bond. The contrast between allyl alcohols **8** (Table I, entry 5) and **12** (Table I, entry 10) indicates that facilitating ionization as in **8** can lead to elimination competing with redox isomerization with sterically more hindered olefinic systems. On the other hand, a multiple redox isomerization (Table I, entry 11) proceeds very well.

The reactivity of cyclic allylic alcohols toward redox isomerization is a function of ring size. A six-membered-ring substrate

23

23 failed. An eight-membered-ring substrate reacts normally, albeit somewhat more slowly (Table I, entry 13). The lower reactivity of the substrates possessing more substituted allylic alcohol units and of cyclic allylic alcohols led us to search for a more active catalyst, but one which would still retain the selectivity.

The enhanced reactivity of indenyl complexes[22] versus their cyclopentadienyl analogues due to the opening of a coordination site by valence tautomerization depicted in eq 8 induced us to examine complex **24**[23] as a catalyst. Gratifyingly, the 23% yield of 1-phenyl-3-heptanone from allyl alcohol **8** increases to 83% while the reaction time for consumption of starting material decreases from 9 to 2 h. Table II summarized the redox isomerizations performed with this new catalyst.



(8)

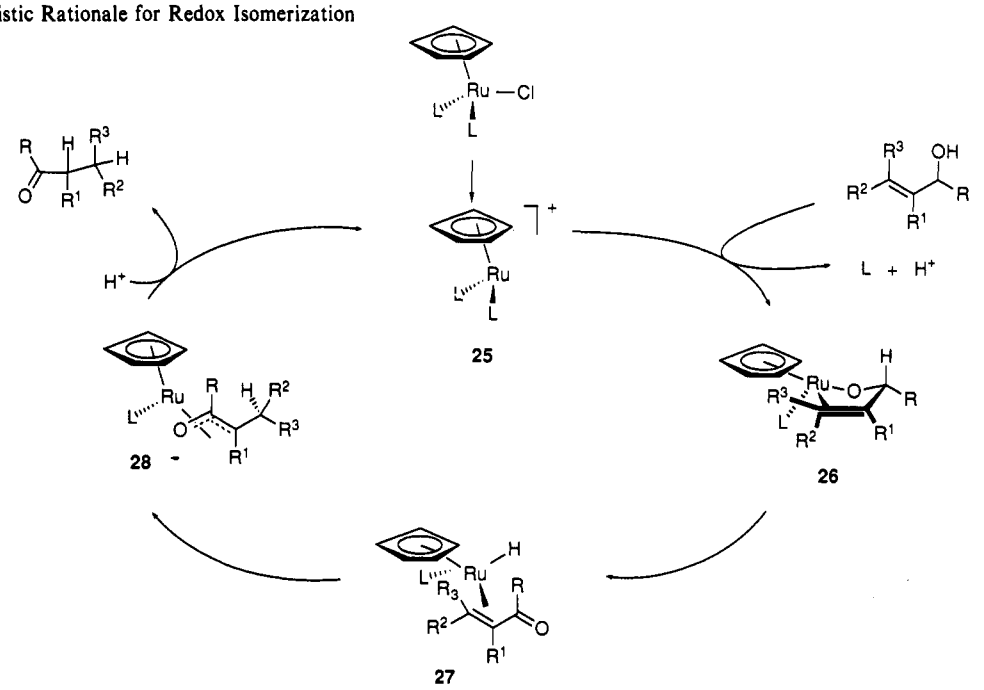
24

The acyclic examples focused on the more heavily substituted olefinic substrates. The above trend is revealed to be general. Redox isomerization of allylic alcohol **12**, which after 24 h still does not go to completion (Table I, entry 10) with complex **22**, provides complete consumption after only 3 h with complex **24** (Table II, entry 5). Significant rate enhancements are also seen

(22) Marder, T. B.; Roe, D. C.; Milstein, D. *Organometallics* **1988**, *7*, 1451. Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384. Bönneman, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. Borrini, A.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Serra, G. *J. Mol. Catal.* **1985**, *30*, 181. Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.

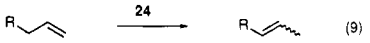
(23) Oro, L. A.; Ciriano, M. A.; Campo, M.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, *289*, 117.

Scheme I. Mechanistic Rationale for Redox Isomerization



with the cyclic substrates (cf. Table I, entries 13 and 14 to Table II, entries 7 and 8).

The chemoselectivity is somewhat compromised with this more reactive catalyst. While a secondary alcohol remote from the allylic alcohol is compatible (Table II, entry 4), a 2-ene-1,4-diol (Table II, entry 9) provides a modest yield of the γ-hydroxy ketone in contrast to the corresponding monoacetate (Table II, entry 10), which gives an excellent yield of the γ-acetoxy ketone. The propensity for isolated double bonds to isomerize depends upon their steric accessibility. Thus, a 1,1-disubstituted olefin is unaffected (Table II, entry 2), but a monosubstituted olefin is partially isomerized to a 2-substituted alkene without any further migration (Table II, entry 3). This result suggests that an olefin isomerization as in eq 9 may be a synthetically useful process with this catalyst.

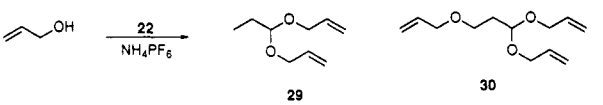


Mechanism

The failure of both isolated olefins and isolated alcohols to react and the chemoselectivity exhibited in the presence of both of these functionalities demonstrate the requirement of an allyl alcohol for reaction. The absolute requirement for a free hydroxyl group (cf. **10** and **18**) and the dramatic rate effect of substituents on the double bond combined with the above suggest that coordination of both entities to ruthenium is necessary. A reasonable mechanistic rationale as depicted in Scheme I emerges.

The facile ionization of ruthenium complexes to the cationic species **25** is well documented.[24] The bis-coordinated allyl alcohol complex **26** accounts for the reactivity observed. Steric hindrance around the double bond imposes a steric barrier to coordination to ruthenium because of the steric demands of the cyclopentadienyl (Cp) and triphenylphosphine ligands.[25] Switching from Cp to indenyl allows the release of some steric strain by permitting this group to move out of the way by reorganizing its complexation from η^5 to η^3. The scheme rationalizes the rate difference between a *Z* and *E* olefin. In a *Z* olefin, R^3 is forced to encounter a severe steric interaction either with the Cp group in **26** or with the triphenylphosphine ligand in the diastereomeric complex where L and Cp are interconverted. This steric effect also contributes to the rate difference between acyclic and cyclic substrates. An alternative explanation envisions β-CH elimination from a simple alkoxide without prior olefin complexation. While we cannot discriminate between invoking olefin coordination in an intermediate as in **26** or in a transition state, application of the concept of Achim's razor leads us to draw this coordination in the intermediate. In the transition state of the CH elimination, the oxygen must move down to rotate the C–H bond toward coplanarity with the π orbital of the olefin.

Another conformational effect may be even more important. The allylic hydrogen must also position itself cis to the ruthenium in the pseudocycle of complex **26** to allow elimination to form the ruthenium hydride **27**.[26] The presence of a coordinated enone is supported by the reaction of neat allyl alcohol with 0.02 mol % **22** and 0.8 mol % ammonium hexafluorophosphate, wherein low but detectable yields of acetals **29** and **30** were obtained. The



latter likely arises by capture of acrolein with excess allyl alcohol. In the case of allyl alcohol **12**, we can detect the presence of the enone corresponding to **27** (see Table II, entry 6). Simultaneous complexation of the olefin of a cyclic substrate requires the plane of the double bond to twist toward orthogonality with respect to the pseudoplane of the ring. Such a geometrical distortion is virtually impossible in rings of seven members or less. On the other hand, such a conformation is accessible in rings of eight members or more.[27] This interpretation completely rationalizes our observations with respect to cyclic substrates wherein a six-membered-ring substrate fails to react, an eight-membered-ring substrate reacts albeit somewhat sluggishly, and a twelve-membered-ring substrate reacts normally. In formulating **27**, we cannot distinguish between olefin and carbonyl group coordination although precedent exists for olefin coordination in an enone.[28] Similarly, the question of a π-oxallyl or a σ-enolate structure (with

(24) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1.

(25) For an example of the effect of these steric barriers in the case of an Fe complex, see: Davies, S. G.; Derome, A. E.; McNally, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2854 and references therein. Also see: Blackburn, B. K.; Davies, S. G.; Sutton, K. H.; Whittaker, M. *Chem. Soc. Rev.* **1988**, *17*, 147.

(26) Cf. Kanemoto, S.; Matsubara, S.; Takai, K.; Oshima, K.; Utimoto, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3607.

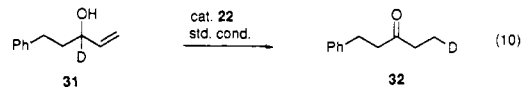
(27) Cf. Vedejs, E.; Gapinski, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 5058 and references therein.

(28) Tanke, R. S.; Crabtree, R. H. *Tetrahedron Lett.* **1988**, *29*, 6737.

the addition of a ligand) for **28** is not mandated by the current data although the π structure, for which precedence does exist, represents the least motion complex.[29]

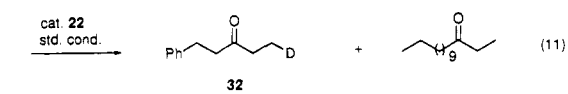
The requirement of a 16-electron configuration for β-hydride elimination in transition metal complexes is generally accepted.[30] In our mechanistic rationale, this elimination step (i.e., **26** and **27**) must be immediately preceded by dissociation of a ligand. The observed influence of alkene substituents on the facility of isomerization argues against dissociation of the olefinic π bond. Given the greater strength of metal–phosphine vs metal–olefin bonds, preferential triphenylphosphine dissociation is also unlikely. Decreasing the hapticity of the cyclopentadienyl ligand from η^5 to either η^3 or η^1 then is required to accommodate this electron count for the β-hydrogen elimination. Such haptotropic shifts in Cp complexes are rare but precedented. For example, carbonyl substitution in $CpRh(CO)_2$ proceeds by an associative mechanism, presumably involving an η^3-cyclopentadienyl ligand.[31] More recently, the complex $(\eta^3\text{-}C_9H_7)Ir(PMe_2Ph)_3$ was prepared[32] and shown by crystallography to have the trihapto idenyl ligand. A monohapto cyclopentadienyl intermediate, analogous to the isolated $(\eta^1\text{-}C_5H_5)Re(CH_3)NO(CO)(PMe_3)_2$,[33] may be involved as well. Thus, the haptotropic shift that may occur in the idenyl-ruthenium complex **24** can be envisioned to facilitate the isomerization reaction in two ways: first, by decreasing steric hindrance at the metal center allowing coordination of more highly substituted olefins and, second, by more easily providing the open coordination site required for β-hydrogen elimination.

Redox isomerization of the monodeuterated substrate **31** probes the CH elimination and readdition processes (**26** → **27** → **28**) (eq 10). Mass spectroscopy established the product **32** to be



31 32 (10)

monodeuterated by a very clean molecular ion peak at 163.1096 (65% of base peak). The location of the deuterium is estalished at the methyl group by ^1H (δ 1.03, tt, J_{HH} = 7.3, J_{HD} = 2.0 Hz), ^2H (δ 1.056, s), and ^{13}C (δ 7.41, t, J_{CD} = 19.41 Hz) NMR spectroscopy. A crossover experiment examines the intramolecularity of this hydrogen shift. Redox isomerization of a 1:1 mixture of the two vinyl carbinols **31** and **2** under standard conditions with catalyst **22** gives the saturated ketones, which are readily separated and analyzed for deuterium content (eq 11). No deuterium is detected in 3-tetradecanone. On the other hand, the isolated 1-phenyl-3-pentanone is fully deuterated in the methyl group as established by comparison to **32** from eq 10. Further support for the existence of **27** derives from the isolation of such an enone as a very minor product in one case (Table II, entry 2).



32 (11)

Discussion

Synthetic efficiency is enhanced if a desired oxidation level can be achieved by internal reorganization rather than sequential reduction–oxidation (or vice versa). Key features of any such methods must be their selectivity and reactivity. The Cp ruthenium complex **22** provides excellent selectivity but at the sacrifice of reactivity that limits the scope of the process. On the other hand, modification of the catalyst to the indenyl complex allows maintenance of most of the selectivity but with a significant expansion of scope.

The different reactivity observed also suggests selectivities that have not yet been explicitly demonstrated in internal competitions. Thus, acyclic allylic alcohols should be able to undergo redox isomerization in the presence of cyclic analogues. An allylic alcohol bearing a terminal vinyl group should react in preference to such a functionality bearing an internal olefin. Clearly, prospects for selective redox isomerization using these catalysts are very bright.

The ability of ruthenium complexes to oxidize alcohols, presumably through a β-hydrogen elimination reaction,[26] and to migrate double bonds through an allylic CH insertion[8] makes the discovery of a catalyst of sufficient attenuation of reactivity such that both types of activation are necessary quite useful. It also suggests that the opportunity for further innovations in catalyst design for modified reactivity is possible.

The synthetic utility derives from the many different ways to synthesize the requisite substrates (vide supra). Special attention should be drawn to the use of vinyl epoxides, which permit an overall sequence as outlined in eq 2. The ready availability of vinyl epoxides and their excellent S_N2' type reactivity with both stabilized[24] and unstabilized[35] nucleophiles impart particular flexibility to this strategy. Further modification of these catalysts, extension of the range and types of substrates, and prospects for asymmetric induction remain exciting challenges.

Experimental Section

General Considerations. All reactions were performed in oven-dried glassware, under an atmosphere of dry nitrogen. Solvents and solutions were transferred by syringe–septum and cannula techniques. Chemicals and solvents which were commercially available were purified by standard procedures prior to use, when necessary. For metal-catalyzed reactions, solvents were deoxygenated by bubbling through a stream of dry nitrogen for 10–20 min prior to syringe transfer. Organic solutions were dried with anhydrous magnesium sulfate, unless otherwise noted. NMR spectra were recorded in $CDCl_3$ (unless otherwise stated), using either a Varian Gemini-300 or EM-400 instrument. IR spectra were recorded on a Nicolet 205 FT instrument as neat films or NaCl plates (unless otherwise stated). Combustion analyses were performed by Robertson Laboratories or by M-H-W Laboratories. High-resolution mass spectra were measured by the Mass Spectrometry Facility of the School of Pharmacy, University of California, San Francisco. Melting points were determined directly after column chromatography, with a Thomas-Hoover capillary apparatus, and are uncorrected.

Preparation of Substrates. The following substrates were prepared according to literature procedures: 1-cyclohexyl-2-propen-1-ol (**3**),[36] 1-cycloocten-3-ol (**15**),[13] 2-(hydroxymethyl)-1-undecene (**21**),[18] and 8-hydroxy-9-undecen-11-olide (**20**).[17]

5-Phenyl-1-penten-3-ol (1). To a cooled (0 °C) solution of vinylmagnesium bromide (52 mL, 0.75 M, 39.0 mmol) was added 3-phenylpropanal (3.40 g, 25.3 mmol) dropwise over 30 min. The mixture was kept at 0 °C for 30 min and then allowed to warm to ambient temperature over 1 h. The reaction was quenched by addition of ice until effervescence ceased; the suspension was treated with 1 M aqueous sulfuric acid (ca. 20 mL) until homogeneous. The resulting solution was diluted with ether (50 mL); the aqueous layer was separated and washed with ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), evaporated, and subjected to flash chromatography (silica, 1:1 pentane–ether) to yield the product as a yellow oil: 3.01 g (73%); IR ($CDCl_3$) 3355, 3085, 3063, 3027, 2928, 2861, 1644, 1604, 1497, 1454, 1425, 1318 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.319–7.169 (m, 5 H), 5.916 (ddd, J = 17.4, 10.4, 6.1 Hz, 1 H), 5.255 (d, J = 17.4 Hz, 1 H), 5.146 (d, J = 10.4 Hz, 1 H), 4.138 (br quintet, J = 5.9 Hz, 1 H), 2.809–2.642 (m, 2 H), 1.864 (q, J = 7.5 Hz, 2 H), 1.486 (d, J = 4.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.09, 141.28, 128.54, 128.48, 125.92, 114.79, 72.28, 38.32, 31.37; exact mass calcd for $C_{11}H_{14}O$ 162.1045, found 162.1035 (M^+ 29.2).

(29) For an example of a crystallographically characterized η^3-oxaallyl complex, see: Bennett, M. A.; Robertson, G. B.; Watt, R.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1971**, 752.

(30) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley Interscience: New York, 1988; pp 39–42.

(31) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657.

(32) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329.

(33) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154.

(34) Trost, B. M.; Molander, G. *J. Am. Chem. Soc.* **1981**, *103*, 5969. Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575.

(35) For an excellent leading reference, see: Marshall, J. A.; Trometer, J. D.; Blough, B. E.; Crute, T. D. *J. Org. Chem.* **1988**, *53*, 4274. For a review, see: Marshall, J. A. *Chem. Rev.* **1989**, *89*, 1503. Also see: Echavarren, A. M.; Tueting, D. R.; Stille, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 4039.

(36) Aristoff, P. A.; Johnson, P. D.; Harrison, A. W. *J. Am. Chem. Soc.* **1985**, *107*, 7967.

1-Tetradecen-3-ol (2). This compound was prepared as described above using dodecanal (5.0 mL, 22.7 mmol) and vinylmagnesium bromide (25 mL, 1.0 M in THF). Chromatography (silica, 4:1 pentane–ether) gave the product: 3.18 g (76%); R_f = 0.47; IR (film) 3354, 3080, 2924, 2854, 1844, 1645, 1446, 1378, 1318 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.878 (dd, J = 16.9, 10.4, 6.2 Hz, 1 H), 5.227 (d, J = 17.2 Hz, 1 H), 5.110 (d, J = 10.4 Hz, 1 H), 4.103 (br quint, J = 5.8 Hz, 1 H), 1.552 (m, 2 H), 1.451 (d, J = 4.2 Hz, 1 H), 1.260 (br s, 18 H), 0.862 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz δ 141.72, 114.46, 73.21, 37.01, 31.75, 29.40 (5 C), 29.14, 25.13, 22.45, 13.78; exact mass calcd for $C_{14}H_{27}O$ (M^+ – H) 211.2063, found 211.2062 (1.5).

1,12-Tridecadien-3-ol (4). This compound was prepared as described above using 10-undecenal (1.0 mL, 4.81 mmol) and vinylmagnesium bromide (7.4 mL, 1.0 M in THF). Chromatography (silica, 2:1 hexane–EtOAc) gave the product: 810 mg (85%); R_f = 0.63; IR (film) 3353, 3078, 2979, 2928, 2855, 1641, 1465, 1438 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.912–5.762 (m, 2 H), 5.219 (dd, J = 17.2, 1.2 Hz, 1 H), 5.103 (dd, J = 10.4, 1.2 Hz, 1 H), 4.992 (dd, J = 17.2, 1.5 Hz, 1 H), 4.929 (dd, J = 10.2, 1.5 Hz, 1 H), 4.096 (br quint, J = 5.6 Hz, 1 H), 2.038 (q, J = 7.0 Hz, 2 H), 1.522 (m, 2 H), 1.449 (d, J = 4.3 Hz, 1 H), 1.371 (m, 2 H), 1.284 (br s, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.59, 139.21, 114.30, 114.11, 73.01, 36.82, 33.48, 29.24, 29.20, 29.10, 28.79, 28.62, 24.99; exact mass calcd for $C_{13}H_{23}O$ (M^+ – H) 195.1750, found 195.1766 (1.7).

1-Tridecene-3,13-diol (5). (a) 1,1-Dimethoxy-10-undecene. A solution of 10-undecenal (2.00 g, 11.9 mmol) and PPTS (120 mg, 0.478 mmol) in methanol (30 mL) was stirred at room temperature for 17 h. The solution was diluted with ether (30 mL) and treated with $NaHCO_3$ (20 mL, saturated) plus sufficient water to dissolve the salts. The aqueous layer was separated, and the organic layer was washed with brine (2 × 20 mL), dried ($MgSO_4$), and evaporated to give the product: 2.44 g (96%); IR (film) 3077, 2927, 2855, 1641, 1465, 1386 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.818 (ddt, J = 17.1, 10.3, 6.7 Hz, 1 H), 4.993 (d, J = 17.1 Hz, 1 H), 4.935 (d, J = 10.3 Hz, 1 H), 4.363 (t, J = 5.7 Hz, 1 H), 3.317 (s, 6 H), 2.039 (br q, J = 6.7 Hz, 2 H), 1.578 (m, 2 H), 1.289 (br s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.98, 114.00, 104.48, 52.05, 33.40, 32.13, 29.12 (2 C), 29.00, 28.71, 28.56, 24.19.

(b) 1,1-Dimethoxy-11-undecanol. To a cooled (0 °C) solution of 1,1-dimethoxy-10-undecene (1.00 g, 4.67 mmol) in THF (5 mL) was added a solution of BH_3·Me_2S (0.80 mL, 2 M in THF) dropwise over 1 min. The solution was kept at 0 °C for 30 min and then at room temperature for 30 min. After recooling, the mixture was treated with 3 M NaOH (1.6 mL) for 30 min and then H_2O_2 (1.7 mL, 30% aqueous). The mixture was then heated at 60 °C for 1 h, cooled, diluted with ether (20 mL), washed with brine (5 × 10 mL), dried, and evaporated. Flash chromatography (silica, 1:1 hexane–ether) gave 156 mg of starting material (16%, R_f = 0.85) and the product: 786 mg (73% isolated or 86% based on reacted starting material (brsm)); R_f = 0.33; IR (film) 3415, 2927, 2855, 2684, 1465, 1386, 1366 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.365 (t, J = 5.8 Hz, 1 H), 3.644 (q, J = 6.2 Hz, 2 H), 3.318 (s, 6 H), 1.575 (m, 4 H), 1.284 (br s, 15 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 104.51, 62.30, 52.14, 32.36, 32.07, 29.12 (2 C), 29.01 (3 C), 25.36, 24.10; exact mass calcd for $C_{13}H_{28}O_3$ 232.2039, found 232.1971 (0.3).

(c) 11-Hydroxyundecanal. A solution of 1,1-dimethoxy-11-undecanol (500 mg, 2.15 mmol) in THF (2 mL) was treated with H_2SO_4 (0.2 mL, 1 M aqueous) and water (1 mL) and heated at reflux for 4 h. The solution was diluted with ether (20 mL), and the aqueous layer was separated. The organic layer was washed with bicarbonate (5 mL) and brine (5 mL) and dried ($MgSO_4$). Evaporation gave the compound: 390 mg (97%); IR (film) 3375, 2921, 2851, 2728, 1724, 1465 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.777 (t, J = 1.8 Hz, 1 H), 3.647 (q, J = 6.1 Hz, 2 H), 2.426 (dt, J = 1.8, 7.3 Hz, 2 H), 1.653–1.524 (m, 4 H), 1.295 (br s, 12 H), 1.196 (t, J = 5.2 Hz, 1 H).

(d) 1-Tridecene-3,13-diol. A solution of 11-hydroxyundecanal (390 mg, 2.09 mmol) in THF (10 mL) was added to a cooled (0 °C) solution of vinylmagnesium bromide (7 mL, 1.0 M in THF). The suspension was stirred at this temperature for 1 h and then at room temperature for 30 min. The reaction was quenched with $NaHSO_4$ (10 mL, aqueous) and diluted with ether (20 mL). The organic layer was washed with bicarbonate (5 mL) and brine (5 mL) and dried. Flash chromatography on silica (4:1 ether–hexane) gave the product: 250.3 mg (59%); R_f = 0.34; IR (film) 3346, 3079, 2935, 2854, 1645, 1466, 1425, 1371 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.876 (ddd, J = 17.3, 10.3, 6.3 Hz, 1 H), 5.225 (d, J = 17.3 Hz, 1 H), 5.109 (d, J = 10.3 Hz, 1 H), 4.100 (br quint, J = 5.4 Hz, 1 H), 3.645 (q, J = 6.1 Hz, 2 H), 1.589–1.490 (m, 4 H), 1.467 (d, J = 4.2 Hz, 1 H), 1.283 (br s, 15 H); ^{13}C NMR ($CDCl_3$, 100 MHz δ 141.30, 114.36, 73.11, 62.80, 36.94, 32.65, 29.45 (3 C), 29.40, 29.33, 25.66, 25.23; exact mass calcd for $C_{13}H_{26}O_2$ 214.1934, found 214.1926 (0.3).

1-Tridecene-3,12-diol (6). (a) 1,1-Dimethoxy-10-undecanol. 1,1-Dimethoxy-10-undecene (431 mg, 2.01 mmol) was added to a suspension of $Hg(OAc)_2$ (641 mg, 2.10 mmol) in 1:1 THF–H_2O (4 mL); after 2 min, the bright yellow color disappeared, indicating complete reaction. After 30 min, the reaction was treated with NaOH (2 mL, 3 M) and then with a solution of $NaBH_4$ (38.0 mg, 1.01 mmol, in 2 mL of 3 M NaOH). After 30 min, the Hg(0) precipitate was removed by centrifugation, and the THF layer was decanted. The aqueous layer was washed with ether (3 × 3 mL), and the combined organic layers were dried and chromatographed (1:1 hexane–ether; R_f = 0.31) to give the product: 258.3 mg (56%); IR (film) 3341, 2931, 2856, 1464, 1385 cm^{-1}.

(b) 10-Hydroxyundecanal. 1,1-Dimethoxy-10-undecanol (258 mg, 1.12 mmol) was dissolved in THF–H_2O (3 mL + 1 mL) and treated with sulfuric acid (120 μL, 1 M, 0.10 equiv). The resulting bilayer was heated at reflux for 4 h, cooled, diluted with ether (20 mL), and separated; the aqueous layer was washed with ether (3 mL), and the combined organic layers were washed with $NaHCO_3$ and brine (5 mL each) and evaporated to give the pure compound, 190 mg (91%), used directly in the next step: IR (film) 3404, 2928, 2855, 2719, 1725, 1465, 1373 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) 9.76 (t, J = 1.8 Hz, 1 H), 3.786 (m, 1 H), 2.427 (dt, J = 1.8, 7.4 Hz, 2 H), 1.629 (m, 2 H), 1.423 (m, 3 H), 1.302 (br s, 10 H), 1.189 (d, J = 6.2 Hz, 3 H).

(c) 1-Tridecene-3,12-diol. A solution of vinylmagnesium bromide (3.5 mL, 3.5 mmol, 1 M in THF) was cooled to 0 °C and treated dropwise with a solution of 10-hydroxyundecanal (190 mg, 1.02 mmol) in THF, over 10 min. The suspension was stirred at 0 °C for 30 min and then at room temperature for 1 h. The reaction was quenched with H_2O (3 mL), acidified with sulfuric acid (1 M), diluted with ether (20 mL) and separated; the organic layer was washed with $NaHCO_3$ and brine (5 mL each), dried, and chromatographed (2:1 ethyl acetate–hexane; R_f = 0.60) to give the product: 95.6 mg (44%); IR (film) 3362, 3079, 2968, 2928, 2856, 1644, 1465, 1374, 1318 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) 5.869 (ddd, J = 16.9, 10.4, 6.2 Hz, 1 H), 5.219 (dd, J = 17.2, 1.3 Hz, 1 H), 5.102 (dd, J = 10.4, 1.3 Hz, 1 H), 4.097 (m, 1 H), 3.792 (m, 1 H), 1.544–1.332 (m, 6 H), 1.291 (br s, 12 H), 1.186 (d, J = 6.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 141.57, 114.49, 73.07, 67.96, 39.09, 36.79, 29.36, 29.27 (3 C), 25.48, 25.05, 23.15; exact mass calcd for $C_{13}H_{26}O_2$ (M^+ C_2H_5) 185.1543, found 185.1537.

(*E*)-2-Methyl-1,6-dodecadien-5-ol (7). A cooled (–78 °C) solution of (*E*)-1-bromo-1-heptene[37] (500 mg, 3.07 mmol) in THF (10 mL) was treated with *t*-BuLi (3.8 mL, 6.46 mmol, 2.1 equiv; 1.7 M in pentane); the yellow solution was back-titrated with bromide until the color disappeared, to ensure excess bromide. To this solution was added 4-methyl-4-pentenal[38] (as a 55% by volume mixture with 1,1-diethoxyethane; 0.85 mL, 0.715 g, ca. 3.90 mmol of aldehyde, or 1.3 equiv). The mixture was warmed to room temperature over 3 h and quenched with $NaHSO_4$ (1 mL), and the ether layer was decanted, dried, evaporated, and flash chromatographed (4:1 hexane–ethyl acetate) to give 405.4 mg of the alcohol (72%): R_f = 0.54 (4:1 hexane–ethyl acetate); IR (film) 3355, 3075, 2958, 2929, 2859, 1650, 1455, 1376 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.659 (dt, J = 15.4, 6.6 Hz, 1 H), 5.466 (dd, J = 15.4, 7.1 Hz, 1 H), 4.724 (s, 1 H), 4.711 (s, 1 H), 4.065 (br q, J = 6.3 Hz, 1 H), 2.239–1.988 (m, 4 H), 1.739 (s, 3 H), 1.835–1.256 (cm, 9 H), 0.890 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.54, 132.70, 132.33, 109.89, 72.79, 35.08, 33.64, 32.09 (2 C), 31.31, 28.81, 22.43, 13.96. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 78.88; H, 12.11.

(*E*)-1-Phenyl-1-hepten-3-ol (8). A solution of *n*-butyllithium (5.0 mL, 8.0 mmol, 1.6 M in hexane) was diluted with THF (10 mL), cooled to –78 °C, and treated dropwise with cinnamaldehyde (1.00 mL, 7.94 mmol). The solution was stirred at –78 °C for 30 min, warmed to room temperature, quenched with aqueous $NaHSO_4$, diluted with ether, and separated. The organic layer was washed with $NaHCO_3$ and brine, dried, evaporated, and chromatographed (4:1 hexane–ethyl acetate) to give the product: 1.179 g (78%); R_f = 0.45; IR (film) 3360, 3082, 3060, 3027, 2957, 2931, 2860, 1667, 1620, 1599, 1578, 1494, 1450, 1379, 1332 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.411–7.264 (m, 5 H), 6.575 (d, J = 15.9 Hz, 1 H), 6.229 (dd, J = 15.9, 6.8 Hz, 1 H), 4.282 (br q, J = 6.6 Hz, 1 H), 1.687–1.567 (m, 3 H), 1.456–1.306 (m, 4 H), 0.915 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.89, 132.79, 130.09, 128.58, 127.56, 126.48, 72.81, 36.77, 27.31, 22.32, 13.69; exact mass calcd for $C_{13}H_{18}O$ 190.1358, found 190.1361 (12.4).

1,13-Tetradecadiene-3,12-diol (9). To a suspension of PCC (11.13 g, 51.6 mmol) and Celite (12 g) in CH_2Cl_2 (50 mL) was added 1,10-decanediol (3.00 g, 17.2 mmol). The resulting suspension was stirred for 1 h, diluted with ether (450 mL), filtered, evaporated, and chromatographed (2:1 hexane–ethyl acetate) to yield decanedial: 1.677 g (57%); R_f = 0.61 (2:1 hexane–ethyl acetate); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.768 (t, J = 1.8 Hz, 2 H), 2.429 (dt, J = 1.8, 7.3 Hz, 4 H), 1.626 (m, 4 H), 1.316 (br, 8 H).

(37) Bloch, R.; Benecon, C.; Guibe-Jampel, E. *Tetrahedron Lett.* **1985**, *26*, 1301.

To a solution of vinylmagnesium bromide (30 mL, 30 mmol, 1 M in THF) at 0 °C was added a solution of decanedial (1.677 g, 9.74 mmol) in THF (15 mL) dropwise. The resulting suspension was stirred at 0 °C for 1 h, quenched with saturated aqueous $NaHSO_4$ (15 mL), diluted with water and ether, and separated. The organic layer was washed with $NaHCO_3$ and brine, dried ($MgSO_4$), evaporated, and chromatographed (2:1 hexane–ethyl acetate) to yield the product, 0.849 g (38%), R_f = 0.30 (2:1 hexane–ethyl acetate), which solidified upon standing: mp 34–5 °C; IR (film) 3354, 3078, 2928, 2855, 1644, 1465, 1424, 1320 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.874 (ddd, J = 16.9, 10.4, 6.2 Hz, 2 H), 5.222 (dd, J = 17.2, 1.4 Hz, 2 H), 5.108 (d, J = 10.4 Hz, 2 H), 4.099 (br q, J = 6.3 Hz, 2 H), 1.524 (br, 6 H), 1.294 (br, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.44, 114.28, 72.83, 36.63, 29.15 (2 C), 24.93. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 73.95; H, 11.39.

12-Methoxy-1,13-tetradecadien-3-ol (10). A suspension of pentane-washed NaH (66.8 mg, 2.78 mmol) in THF (10 mL) was treated with a solution of the diol **9** (636 mg, 2.78 mmol) in THF (10 mL) dropwise. The resulting white suspension was stirred at room temperature for 1 h, then treated with freshly distilled iodomethane (175 μL, 2.78 mmol), and stirred for an additional 3 h. The reaction was quenched with aqueous $NaHSO_4$, diluted with ether, and separated. The organic layer was washed with $NaHCO_3$ and brine, dried ($MgSO_4$), evaporated, and chromatographed (4:1 hexane–ethyl acetate) to provide 142.1 mg (21%, 38% brsm) of the desired product (R_f = 0.38) in addition of 49.1 mg (7%) of the dimethyl ether and 283.4 mg (45%) of unreacted starting material: IR (film) 3418, 3078, 2981, 2929, 2856, 1644, 1466, 1422, 1321 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.872 (ddd, J = 17.2, 10.4, 6.3 Hz, 1 H), 5.645 (ddd, J = 16.7, 10.8, 7.8 Hz, 1 H), 5.265–5.085 (m, 4 H), 4.097 (br q, J = 6.3 Hz, 1 H), 3.491 (br q, J = 6.8 Hz, 1 H), 3.271 (s, 3 H), 1.546–1.281 (m, 17 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.57, 139.01, 117.05, 114.42, 83.06, 73.02, 55.88, 36.79, 35.05, 29.21 (2 C), 25.03 (2 C), 24.96 (2 C); exact mass calcd for $C_{15}H_{26}O$ ($M^+ - H_2O$) 222.1985, found 222.1991 (0.6).

(*Z*)-1-Phenyl-4-pentadecen-3-ol (11). (a) 1-Phenyl-4-pentadecyn-3-ol. A solution of 1-dodecyne (0.50 mL, 2.34 mmol) in ether (10 mL) at −78 °C was treated with *n*-butyllithium (1.8 mL, 2.45 mmol, 1.35 M in hexane, 1.05 equiv) dropwise over 10 min. The mixture was stirred at −78 °C for 15 min and then at 0 °C for 45 min. To the resulting suspension was added hydrocinnamaldehyde (323 μL, 2.45 mmol, 1.05 equiv). This solution was stirred at 0 °C for 30 min and then at room temperature for 1 h, quenched with $NaHSO_4$, and diluted with ether (5 mL). The layers were separated, and the organic layer was washed with brine (2 × 5 mL), dried, and chromatographed (3:1 hexane–ether, R_f = 0.33) to give the product: 504 mg (72%); IR (film) 3344, 3086, 3063, 3027, 2926, 2855, 2229, 1604, 1496, 1455, 1378, 1332 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.320–7.173 (m, 5 H), 4.399–4.331 (m, 1 H), 2.792 (t, J = 7.9 Hz, 2 H), 2.224 (dt, J = 1.9, 7.0 Hz, 2 H), 2.039 (m, 2 H), 1.698 (d, J = 5.3 Hz, 1 H), 1.554–1.492 (m, 2 H), 1.264 (br s, 14 H), 0.878 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.71, 128.63, 128.54, 126.03, 86.05, 80.96, 61.95, 39.49, 31.70, 31.29, 29.38, 29.34, 29.12, 28.94, 28.67, 28.47, 22.45, 18.44, 13.85; exact mass calcd for $C_{21}H_{32}O$ 300.2455, found 300.2456 (18.9).

(b) (*Z*)-1-Phenyl-4-pentadecen-3-ol. A hexane (8 mL) suspension of 1-phenyl-4-pentadecyn-3-ol (209 mg, 0.696 mmol), Mn-poisoned Lindlar catalyst, and quinoline (27 μL, 0.228 mmol) was stirred at room temperature under H_2 (1 atm) for 2 days. The suspension was diluted with ether, filtered, washed with HCl (1 M, 3 × 10 mL), $NaHCO_3$ (5 mL), and brine (5 mL), dried, evaporated, filtered through a plug of silica, and evaporated to yield the pure product: 156 mg (74%); R_f = 0.33 (3:1 hexane–ether); IR (film) 3354, 3086, 3063, 3027, 3006, 2925, 2854, 1664, 1496, 1455, 1378, 1303 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.303–7.168 (m, 5 H), 5.549–5.399 (m, 2 H), 4.493–4.431 (m, 1 H), 2.735–2.620 (m, 2 H), 2.073–2.008 (m, 2 H), 1.990–1.885 (m, 1 H), 1.801–1.711 (m, 1 H), 1.382 (d, J = 3.4 Hz, 1 H), 1.358–1.206 (m, 16 H), 0.882 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.89, 132.62, 132.20, 128.32, 128.28, 125.72, 67.06, 38.97, 31.86, 31.66, 29.63, 29.59 (2 C), 29.45, 29.31, 29.25, 27.69, 22.65, 14.09.

(*E*)-1-Phenyl-4-pentadecen-3-ol (12). A suspension of LAH (62 mg, 1.63 mmol) in THF (10 mL) was cooled (0 °C) and treated dropwise with a solution of 1-phenyl-4-pentadecyn-3-ol (200 mg, 0.666 mmol). The suspension was stirred at 0 °C for 30 min and then warmed to room temperature and heated at reflux for 8 h. The mixture was cooled (0 °C), quenched with water and 3 M NaOH (0.5 mL each), dried with $MgSO_4$, filtered through Celite, evaporated, and flash chromatographed (4:1 hexane–ether) to yield the product: 113.7 mg (56%): R_f = 0.24; IR (film) 3351, 3086, 3063, 3027, 2925, 2854, 1671, 1604, 1496, 1455 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.301–7.261 (m, 2 H), 7.208–7.165 (m, 3 H), 5.656 (dt, J = 15.3, 6.7 Hz, 1 H), 5.489 (dd, J = 15.3, 7.1 Hz, 1 H), 4.085–4.060 (m, 1 H), 2.714–2.656 (m, 2 H), 2.032 (q, J = 6.8 Hz, 2 H), 1.893–1.788 (m, 2 H), 1.443 (d, J = 3.7 Hz, 1 H), 1.368 (m, 2 H), 1.258 (br s, 14 H), 0.877 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.97, 132.65, 132.48, 128.37, 128.25, 125.67, 72.35, 38.75, 32.15, 31.85, 31.73, 29.58 (2 C), 29.45, 29.30, 29.14 (2 C), 22.64, 14.07.

(*E*)-5-Heptadecene-7,16-diol (13). A solution of 1-hexyne (0.77 mL, 6.71 mmol) in ether (10 mL) at −78 °C was treated with *n*-BuLi (4.4 mL, 6.17 mmol, 1.39 M in hexane) and warmed to 0 °C over 45 min. A solution of 10-hydroxyundecanal in THF (6 mL) was added, and the resulting suspension was stirred at 0 °C for 1 h, quenched (saturated aqueous $NaHSO_4$), diluted with ether and water (10 mL each), and separated. The aqueous layer was extracted with ether, and the organic layers were washed with $NaHCO_3$ and brine, dried, and flash chromatographed (1:1 hexane–ethyl acetate) to give 274 mg of the compound (38%): R_f = 0.58, IR (film) 3358, 2929, 2856, 2233, 1466, 1375 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.346 (m, 1 H), 3.787 (m, 1 H), 2.212 (dt, J = 1.5, 7.0 Hz, 2 H), 1.643 (m, 2 H), 1.508–1.244 (c, 20 H), 1.189 (d, J = 6.2 Hz, 3 H), 0.911 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 84.98, 81.40, 67.92, 62.36, 39.16, 38.04, 30.64, 29.50, 29.36 (2 C), 29.15, 25.63, 25.09, 23.24, 21.77, 18.22, 13.46.

To a 0 °C suspension of LAH (238 mg, 6.27 mmol) in THF (15 mL) was added a solution of 5-heptadecyn-3-ol (274 mg, 1.02 mmol) in THF (15 mL). The suspension was kept at 0 °C for 30 min, warmed to room temperature, and heated at reflux for 8 h. The mixture was cooled (0 °C), quenched with NaOH (3M) and water (2 mL each), dried, filtered, evaporated, and chromatographed (2:1 hexane–ethyl acetate) to give the enediol (97.3 mg, 36%, R_f = 0.55) and 11,12-heptadecadien-2-ol (95.5 mg, 37%, R_f = 0.53). 5-Heptadecene-7,16-diol: IR (film) 3351, 2927, 2855, 1672, 1466, 1375, 1309 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.632 (dt, J = 15.4, 6.8 Hz, 1 H), 5.446 (ddd, J = 15.4, 7.2, 1.3 Hz, 1 H), 4.033 (q, J = 6.7 Hz, 1 H), 3.785 (m, 1 H), 2.031 (br q, J = 6.7 Hz, 2 H), 1.532–1.261 (c, 22 H), 1.187 (d, J = 6.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.98, 131.97, 73.09, 68.00, 39.24, 37.22, 31.79, 31.27, 29.54, 29.45 (2 C), 25.67, 25.40, 23.35, 22.11, 13.84. 11,12-Heptadecadien-2-ol: IR 3351, 2929, 2855, 1962, 1465, 1376, 1300 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.061 (quintet, J = 4.9 Hz, 2 H), 3.789 (m, 1 H), 1.972 (m, 4 H), 1.457–1.290 (m, 19 H), 1.188 (d, J = 6.2 Hz, 3 H), 0.900 (t, J = 6.7 Hz, 3 H).

(*E*)-5,16-Heptadecadien-7-ol (14). To a solution of 1-hexyne (1.33 mL, 11.55 mmol) in ether (30 mL) at −78 °C was added *n*-BuLi (7.62 mL, 10.59 mmol, 1.39 M in hexane). After stirring for 15 min, the suspension was treated with 10-undecenal (2.00 mL, 9.63 mmol). The mixture was warmed to room temperature over 1.5 h, quenched with saturated $NaHSO_4$ (5 mL), diluted with ether and water (10 mL each), and separated. The organic layer was washed with $NaHCO_3$ and brine, dried, evaporated, and flash chromatographed (4:1 hexane–ethyl acetate) to yield the product: 2.12 g (88%); R_f = 0.58; IR (film) 3359, 3078, 2929, 2856, 2233, 1641, 1466, 1379, 1329 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.816 (ddt, J = 16.9, 10.1, 6.7 Hz, 1 H), 4.994 (dq, J = 17.1, 1.8 Hz, 1 H), 4.931 (dt, J = 10.1, 1.0 Hz, 1 H), 4.347 (br, 1 H), 2.213 (dt, J = 7.0, 1.9 Hz, 2 H), 2.041 (q, J = 7.1 Hz, 2 H), 1.699–1.611 (m, 2 H), 1.560–1.262 (c, 17 H), 0.911 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.03, 114.01, 85.13, 81.34, 62.51, 38.05, 33.70, 30.66, 29.40, 29.29, 29.18, 29.01, 28.82, 25.11, 21.80, 18.25, 13.47.

To a suspension of LAH (380 mg, 10.0 mmol) in THF (30 mL) at 0 °C was added a solution of 16-heptadecen-5-yn-7-ol (1.00 g, 3.99 mmol) in THF (10 mL). The suspension was stirred at 0 °C for 15 min, warmed to room temperature, and then heated at reflux for 8 h. After cooling, the mixture was quenched as described above, dried, filtered, and chromatographed (6:1 hexane–ether) to yield two products: the dienol (762 mg, 75%, R_f = 0.45) and the ene allene (158 mg, 17%, R_f = 0.93). (*E*)-5,16-Heptadecadien-7-ol: IR (film) 3350, 3078, 2927, 2855, 1641, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.819 (ddt, J = 16.9, 10.2, 6.7 Hz, 1 H), 5.638 (dt, J = 15.6, 6.7 Hz, 1 H), 5.449 (ddd, J = 15.4, 7.0, 1.3 Hz, 1 H), 4.992 (dt, J = 17.1, 1.9 Hz, 1 H), 4.932 (dt, J = 10.2, 1.0 Hz, 1 H), 4.035 (q, J = 6.6 Hz, 1 H), 2.069–2.003 (m, 4 H), 1.533–1.211 (m, 19 H), 0.896 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.21, 133.28, 131.92, 114.12, 72.95, 37.06, 33.54, 31.60, 31.10, 29.27 (2 C), 29.15, 28.83, 28.63, 25.19, 21.88, 13.55; exact mass calcd for $C_{17}H_{33}O$ 252.2455, found 252.2453. 1,11,12-Heptadecatriene: IR (film) 3078, 2927, 2855, 1963, 1641, 1465, 1440, 1378, 992, 910, 871 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Mhz) δ 5.821 (ddt, J = 16.9, 10.1, 6.7 Hz, 1 H), 5.064 (quintet, J = 4.7 Hz, 2 H), 5.032–4.908 (m, 2 H), 2.076–1.931 (m, 6 H), 1.383–1.285 (c, 16 H), 0.900 (t, J = 7.1 Hz, 3 H).

(*E,Z*)-Cyclododeca-1,3-diene (16). A solution of (*E*)-2-cyclododecen-1-ol (1.80 g, 9.87 mmol) and PPTS (0.62 g, 2.47 mmol, 25 mol %) in 1,2-dichloroethane (16 mL) was heated at reflux for 42 h. The solution was cooled, diluted with hexane, washed with water, dried, evaporated, and chromatographed (hexane) to give the product:[16] 1.113

(38) Baker, R.; Brimble, M. A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 125.

g (69%): R_f = 0.80; ^{1}H NMR (300 MHz) δ 6.384 (dd, J = 11.0, 15.7 Hz, 1 H), 6.200 (t, J = 10.7 Hz, 1 H), 5.706 (dt, J = 15.9, 4.7 Hz, 1 H), 5.442 (dt, J = 9.6, 8.7 Hz, 1 H), 2.242–2.174 (m, 2 H), 2.138–2.090 (m, 2 H), 1.624–1.188 (m, 12 H).

(*E*)-2-Cyclododecene-1,4-diol (17). To a solution of palladium(II) acetate (82.0 mg, 0.37 mmol) and freshly recrystallized benzoquinone (1.58 g, 14.6 mmol) in acetic acid (25 mL) was added (*E*,*Z*)-cyclododeca-1,3-diene (1.40 mL, 1.243 g, 7.56 mmol) over 4.5 h via a syring pump. After 42 h, TLC showed the diene to be consumed. The mixture was filtered through Celite, diluted with brine (25 mL), and extracted with hexane (4 × 25 mL). The organic layers were washed with water and 3 M aqueous NaOH (3 × 25 mL each), dried, and evaporated. The resulting yellow oil was dissolved in methanol (25 mL), treated with potassium carbonate (2.08 g, 15.1 mmol), and stirred at room temperature overnight. The suspension was then evaporated, and the residue was extracted repeatedly with ethyl acetate and filtered through Celite. The combined extracts were washed with brine, dried, evaporated, and chromatographed (4:1 ethyl acetate–hexane) to give the product: 120.7 mg (8.1%); R_f = 0.34; mp 162–163 °C; IR (film) 3283, 3021, 2924, 2858, 1671, 1458, 1394, 1349, 1261, 1114, 1050, 1012, 979, 934 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.777–5.767 (m, 1.8 H), 5.606–5.586 (m, 0.2 H), 4.36–4.31 (m, 1.8 H), 4.17–4.11 (m, 0.2 H), 1.684 (m, 4 H), 1.418–1.253 (m, 14 H); ^{13}C NMR ($CDCl_3$, 100 MHz, CD_3OD) δ 135.67, 134.05, 74.57, 72.66, 36.08, 35.71, 26.26, 25.71, 25.51, 23.34, 22.72; exact mass calcd for $C_{12}H_{22}O_2$ 198.1621, found 198.1624 (7.1).

(*E*)-1-Acetoxy-2-cyclododecen-4-ol (18). A suspension of KH (101 mg of a 35% suspension in mineral oil, 0.88 mmol) in THF (3 mL) was cooled to 0 °C and treated dropwise with a solution of (*E*)-2-cyclododecene-1,4-diol (135 mg, 0.68 mmol) in THF (5 mL). The resulting white suspension was stirred at 0 °C for 45 min and then treated with acetyl chloride (63 μL, 0.88 mmol). This mixture was stirred at room temperature for 3 h, quenched with aqueous $NaHSO_4$, diluted with ethyl acetate, and separated. The organic layer was washed with $NaHCO_3$ and brine, dried, evaporated, and chromatographed (2:1 hexane–ethyl acetate) to give the product as a 6:1 mixture of diastereomers: 86.1 mg (53%); R_f = 0.38; IR 3444, 2931, 2862, 1732, 1671, 1464, 1446, 1373 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) major diastereomer, δ 5.903 (dd, J = 15.7, 5.7 Hz, 1 H), 5.866 (ddd, J = 15.6, 6.3, 0.9 Hz, 1 H), 5.339 (ddd, J = 8.1, 6.4, 4.2 Hz, 1 H), 4.345 (q, J = 5.7 Hz, 1 H), 2.061 (s, 3 H), 1.90–1.20 (c, 17 H), minor diastereomer δ 5.701 (dd, J = 15.6, 8.4 Hz, 1 H), 5.549 (dd, J = 15.6, 8.5 Hz, 1 H), 5.227–5.154 (m, 1 H), 4.151–4.078 (m, 1 H), 2.037 (s, 3 H), 1.90–1.20 (m, 17 H); ^{13}C NMR ($CDCl_3$, 75 MHz, asterisk indicates major diastereomer) δ 170.61, 136.96, 135.47*, 130.22, 128.36*, 75.47, 74.02*, 73.56, 73.56, 71.54*, 34.46, 34.14*, 31.70, 31.47*, 24.95*, 24.87, 24.63, 24.42*, 24.21*, 24.16*, 23.94, 21.90, 21.61, 21.35*, 21.20*, 21.09.

General Procedure for Redox Isomerization. The substrate, catalyst (**22** or **24**, 5 mol %), and triethylammonium hexafluorophosphate **33** (10 mol %) were weighed into an oven-dried test tube, which was then sealed with a septum. The tube was deaerated by purging with nitrogen, and the contents were dissolved in dry, deaerated dioxane. The resulting solution was heated at 100 °C under N_2 for the indicated time, until GC or TLC showed the starting material to be consumed. The reaction mixture was then chromatographed on silica, using the solvent mixture indicated, allowing isolation of the products.

1-Phenyl-3-pentanone. Isomerization of 5-phenyl-1-penten-3-ol (**1**, 141.0 mg, 0.870 mmol) with **22** (31.6 mg, 43.5 μmol) and **33** (23.0 mg, 87.0 μmol) in dioxane (0.9 mL) for 2 h at 100 °C gave the product:[19] 113.5 mg (81%); R_f = 0.39 (4:1 hexane–ether); IR (film) 3085, 3064, 3027, 2925, 2854, 1715, 1635, 1604, 1496, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.313–7.176 (m, 5 H), 2.906 (t, J = 7.7 Hz, 2 H), 2.736 (t, J = 7.7 Hz, 2 H), 2.412 (q, J = 7.3 Hz, 2 H), 1.045 (t, J = 7.2 Hz, 3 H).

3-Tetradecanone. Isomerization of 1-tetradecen-3-ol (**2**, 204.2 mg, 0.962 mmol) with **22** (34.9 mg, 48.1 μmol) and **33** (25.4 mg, 96.1 μmol) in dioxane (0.5 mL) for 2.5 h gave the product:[39] 185.1 mg (91%); R_f = 0.55 (19:1 pentane–ether); IR (film) 2929, 2857, 1709, 1463, 1411, 1378, 1361, 1249 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.422 (q, J = 7.3 Hz, 2 H), 2.393 (t, J = 7.4 Hz, 2 H), 1.562 (m, 2 H), 1.256 (br s, 16 H), 1.051 (t, J = 7.3 Hz, 3 H), 0.879 (t, J = 6.7 Hz, 3 H).

1-Cyclohexyl-1-propanone. Isomerization of 1-cyclohexyl-2-propen-1-ol (**3**, 119.1 mg, 0.849 mmol) with **22** (30.8 mg, 42.5 μmol) and **33** (22.4 mg, 84.9 μmol) in dioxane (0.7 mL) for 1.5 h gave the product:[40] 109.2 mg (92%); R_f = 0.52 (19:1 pentane–ether); IR (film) 2977, 2933, 2855, 1712, 1450, 1413, 1375, 1345 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.459 (q, J = 7.3 Hz, 2 H), 2.342 (m, 1 H), 1.844–1.686 (m, 4 H), 1.357–1.212 (m, 6 H), 1.034 (t, J = 7.3 Hz, 3 H).

2-Tridecen-3-one. Isomerization of 1,12-tridecadien-3-ol (**4**, 152.9 mg, 0.779 mmol) with **22** (28.2 mg, 38.8 μmol) and **33** (20.6 mg, 77.9 μmol) in dioxane (0.8 mL) for 1 h gave the product: 132.5 mg (87%); R_f = 0.59 (4:1 hexane–ether); IR (film) 3077, 2977, 2928, 2855, 1716, 1641, 1461, 1415, 1376 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.816 (ddt, J = 17.2, 10.3, 7.1 Hz, 1 H), 4.997 (dd, J = 2.1, 17.2 Hz, 1 H), 4.934 (dd, J = 2.1, 10.3 Hz, 1 H), 2.423 (q, J = 7.3 Hz, 2 H), 2.395 (t, J = 7.5 Hz, 2 H), 2.037 (q, J = 7.1 Hz, 2 H), 1.648–1.522 (m, 2 H), 1.366 (m, 2 H), 1.277 (br s, 8 H), 1.051 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 211.88, 139.24, 114.15, 42.17, 35.57, 33.51, 29.09, 29.03 (2 C), 28.80, 28.67, 23.69, 7.49; exact mass calcd for $C_{13}H_{24}O$ 196.1828, found 196.1825 (10.1).

13-Hydroxytridecan-3-one. Isomerization of 1-tridecene-3,13-diol (**5**, 89.6 mg, 0.418 mmol) with **22** (15.2 mg, 20.9 μmol) and **33** (11.0 mg, 41.8 μmol) in dioxane (0.4 mL) for 1 h gave the product: 46.2 mg (52%); R_f = 0.41 (1:3 hexane–ether); IR 3229, 2974, 2917, 2851, 1706, 1469, 1416, 1376 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.645 (q, J = 6.0 Hz, 2 H), 2.425 (q, J = 7.3 Hz, 2 H), 2.396 (t, J = 7.4 Hz, 2 H), 1.610–1.521 (m, 4 H), 1.274 (br s, 13 H), 1.051 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 212.22, 62.90, 42.23, 35.63, 32.62, 29.28, 29.14 (3 C), 29.05, 25.51, 23.73, 7.54. Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.85; H, 12.23 (MW 214.1934). Found: C, 72.89; H, 12.37 (MW 214.1932 (4.4)).

12-Hydroxytridecan-3-one. Isomerization of 1-tridecene-3,12-diol (**6**, 95.0 mg, 0.443 mmol) with **22** (16.7 mg, 23.1 μmol) and **33** (12.2 mg, 46.2 μmol) in dioxane (0.4 mL) for 1.5 h gave the product: 85.2 mg (90%); R_f = 0.36 (2:1 hexane–ethyl acetate); mp 37–9 °C; IR (film) 3338, 2969, 2920, 2849, 1706, 1461, 1412, 1374 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.785 (m, 1 H), 2.430 (t, J = 7.3 Hz, 2 H), 2.403 (q, J = 7.3 Hz, 2 H), 1.564 (m, 2 H), 1.423 (m, 3 H), 1.285 (br s, 10 H), 1.187 (d, J = 6.2 Hz, 3 H), 1.051 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.30, 68.27, 42.63, 39.54, 36.07, 29.79, 29.63, 29.56, 29.45, 25.96, 24.14, 23.69, 8.07; exact mass calcd for $C_{13}H_{25}O_2$ (M^+ – H) 213.1856, found 213.1855 (2.8). Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.85; H, 12.23. Found: C, 72.89; H, 11.98.

2-Methyl-1-dodecen-5-one. Isomerization of (*E*)-2-methyl-1,6-dodecadien-5-ol (**7**, 101.8 mg, 0.519 mmol) with **24** (21.7 mg, 27.9 μmol) and **33** (14.7 mg, 55.8 μmol) in dioxane (0.6 mL) for 3 h gave the product, 82.7 mg (82%), R_f = 0.67 (9:1 hexane–ethyl acetate), containing a trace (ca. 9%) of (*E*)-2-methyl-1,6-dodecadien-5-one. 2-Methyl-1-dodecen-5-one: IR (film) 3078, 2929, 2857, 1716, 1651, 1457, 1376, 1300 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.729 (s, 1 H), 4.658 (s, 1 H), 2.550 (t, J = 7.6 Hz, 2 H), 2.415 (t, J = 7.4 Hz, 2 H), 2.278 (t, J = 7.4 Hz, 2 H), 1.733 (s, 3 H), 1.574 (m, 2 H), 1.272 (br s, 6 H), 0.879 (t, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.68, 144.52, 110.00, 42.81, 40.83, 31.62, 31.42, 29.16, 29.03, 23.78, 22.57, 14.00; exact mass calcd for $C_{13}H_{24}O$ 196.1828, found 196.1827 (2.1). (*E*)-2-Methyl-1,6-dodecadien-5-one: IR (film) 1677 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.861 (dt, J = 15.9, 6.9 Hz, 1 H), 6.116 (dt, J = 15.9, 1.5 Hz, 1 H).

1-Phenyl-3-heptanone. Method A. Isomerization of (*E*)-1-phenyl-1-hepten-3-ol (**8**, 108.6 mg, 0.571 mmol) with **23** (20.7 mg, 28.5 μmol) and **33** (15.1 mg, 57.2 μmol) in dioxane (0.7 mL) for 9 h gave the product, 25.1 mg (23%), R_f = 0.38 (19:1 hexane–ether), and a 1.7:1 mixture of dienes using from dehydration: 66.3 mg (67%); R_f = 0.61 (19:1 hexane–ether); IR (film) 3087, 3064, 3028, 2958, 2933, 2873, 1947, 1873, 1805, 1715, 1604, 1496, 1454, 1410, 1371 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.311–7.263 (m, 2 H), 7.214–7.174 (m, 3 H), 2.897 (t, J = 7.4 Hz, 2 H), 2.728 (t, J = 7.4 Hz, 2 H), 2.386 (t, J = 7.5 Hz, 2 H), 1.543 (quint, J = 7.6 Hz, 2 H), 1.348–1.224 (m, 2 H), 0.886 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 210.65, 141.32, 128.54, 128.39, 126.12, 43.99, 42.51, 29.51, 25.59, 22.01, 13.49. The dienes were identified by ^{1}H NMR ($CDCl_3$, 300 MHz): major product (*E*,*E*) δ 6.765 (dd, J = 15.7, 10.4 Hz, 1 H), 6.444 (d, J = 15.7 Hz, 1 H), 6.27–6.13 (m, 1 H), 5.832 (dt, J = 15.1, 7.0 Hz, 1 H), 2.127 (q, J = 7.2 Hz, 2 H); minor product (*E*,*Z*) δ 7.075 (dd, J = 16.6, 11.1 Hz, 1 H), 6.529 (d, J = 15.8 Hz, 1 H), 6.27–6.13 (m, 1 H), 5.541 (dt, J = 10.7, 7.7 Hz, 1 H), 2.274 (dq, J = 1.4, 7.5 Hz, 2 H).

Method B. Isomerization of **8** (114.5 mg, 0.602 mmol) with **24** (23.4 mg, 30.1 μmol) and **33** (15.9 mg, 60.2 μmol) in dioxane (0.8 mL) for 2 h gave the product: 95 mg (83%); R_f = 0.38 (19:1 hexane–ether).

3,12-Tetradecanedione. Isomerization of 1,13-tetradecadiene-3,12-diol (**9**, 80.6 mg, 0.353 mmol) with **22** (12.8 mg, 17.6 μmol) and **33** (9.3 mg, 35.2 μmol) in dioxane (0.4 mL) for 1.5 h gave the product:[42] 58.7 mg (73%); R_f = 0.31 (8:1 hexane–ethyl acetate); IR (film) 2973, 2931, 2915, 2850, 1710, 1461, 1420, 1376 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ

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2.421 (q, J = 7.3 Hz, 4 H), 2.391 (t, J = 7.4 Hz, 4 H), 1.559 (m, 4 H), 1.272 (br s, 8 H), 1.049 (t, J = 7.4 Hz, 6 H).

12-Methoxy-13-tetradecen-3-one. Isomerization of 12-methoxy-1,13-tetradecadien-3-ol (**10**, 65.1 mg, 0.269 mmol) with **22** (9.8 mg, 13.4 μmol) and **33** (7.1 mg, 26.9 μmol) in dioxane (0.3 mL) for 1 h gave the product: 60.6 mg (93%); R_f = 0.49 (6:1 hexane–ethyl acetate); IR (film) 3078, 2979, 2931, 2856, 2820, 1716, 1643, 1461, 1419, 1376 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.643 (ddd, J = 16.7, 10.8, 7.8 Hz, 1 H), 5.210–5.145 (m, 2 H), 3.489 (q, J = 6.8 Hz, 1 H), 3.271 (s, 3 H), 2.420 (q, J = 7.3 Hz, 2 H), 2.390 (t, J = 7.4 Hz, 2 H), 1.605–1.460 (m, 4 H), 1.272 (br, 10 H), 1.050 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 212.35, 139.03, 117.03, 83.02, 55.96, 42.22, 35.61, 35.11, 29.27, 29.13, 29.09, 29.00, 24.98, 23.66, 7.51. Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.91; H, 11.66.

1-Phenyl-3-pentadecanone. Method A. Isomerization of (*Z*)-1-phenyl-4-pentadecen-3-ol (**11**, 64.6 mg, 0.213 mmol) with **24** (8.3 mg, 10.7 μmol) and **33** (5.6 mg, 21.3 μmol) in dioxane (0.5 mL) for 24 h gave 21.0 mg of a mixture (R_f = 0.69–0.62, 5:1 hexane–ethyl acetate) of 1-phenyl-3-pentadecanone (20%) and (*E*)-1-phenyl-4-pentadecen-3-one (13%, product ratio by ^{1}H NMR integration). In addition, 39.0 mg (60%) of starting material (R_f = 0.15, 5:1 hexane–ethyl acetate) was recovered. The α,β-unsaturated ketone (*E*)-1-phenyl-4-pentadecen-3-one was identified in the mixture by ^{1}H NMR [($CDCl_3$, 300 MHz) δ 6.821 (dt, J = 15.9, 6.9 Hz), 6.088 (d, J = 15.9 Hz)] and by IR [(film) 1676 cm^{-1}].

Method B. Isomerization of (*E*)-1-phenyl-4-pentadecen-3-ol (**12**, 45.7 mg, 0.151 mmol) with **22** (5.5 mg, 7.6 μmol) and **33** (4.0 mg, 15.1 μmol) in dioxane (0.2 mL) for 24 h gave the product [mp 32–33 °C, 24.0 mg (53%, 66% based on recovered starting material), R_f = 0.55 (9:1 hexane–ethyl acetate)] and unreacted starting material [9.3 mg (20%), R_f = 0.26 (9:1 hexane–ethyl acetate)]: IR (film) 3086, 3064, 3028, 2926, 2854, 1716, 1604, 1494, 1455, 1409, 1371, 1090, 1031 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.307–7.172 (m, 5 H), 2.896 (t, J = 7.6 Hz, 2 H), 2.723 (t, J = 7.4 Hz, 2 H), 2.374 (t, J = 7.5 Hz, 2 H), 1.547 (m, 2 H), 1.248 (br s, 18 H), 0.880 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.35, 141.15, 128.42, 128.27, 126.01, 44.20, 43.03, 31.88, 29.75, 29.61 (2 C), 29.57, 29.43, 29.36, 29.32, 29.18, 23.77, 22.66, 14.09. Anal. Calcd for $C_{21}H_{24}O$: C, 83.38; H, 11.33. Found: C, 83.38; H, 10.51.

Method C. Isomerization of **12** (61.2 mg, 0.202 mmol) with **24** (7.9 mg, 10.1 μmol) and **33** (5.3 mg, 20.2 μmol) in dioxane (0.4 mL) for 3 h gave the product: 49.4 mg (81%); R_f = 0.55 (9:1 hexane–ethyl acetate). The compound was characterized as described above.

2-Hydroxy-11-heptadecanone. Isomerization of 5-heptadecene-7,16-diol (**13**, 40.1 mg, 0.148 mmol) with **24** (5.8 mg, 7.4 μmol) and **33** (3.9 mg, 14.8 μmol) in dioxane (0.18 mL) for 10 h gave 7.4 mg (18%) of unreacted starting material and the product: 27.5 mg (69%, 84% brsm); R_f = 0.56 (2:1 hexane–ethyl acetate); mp 50–51 °C; IR (film) 3320, 3235, 2956, 2922, 2845, 1703, 1497, 1463, 1412, 1373, 1132, 1023, 927, 848 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.791 (m, 1 H), 2.385 (t, J = 7.5 Hz, 4 H), 1.538 (m, 4 H), 1.451–1.229 (c, 19 H), 1.186 (d, J = 6.2 Hz, 3 H), 0.880 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.75, 68.10, 42.79, 42.75, 39.29, 31.57, 29.52, 29.37, 29.30, 29.19, 28.90, 25.69, 23.81 (2 C), 23.45, 22.46, 13.99; exact mass calcd for $C_{17}H_{34}O_2$ 270.2560, found 270.2544 (3.0%).

16-Heptadecen-7-one and (*E*,*Z*)-15-Heptadecen-7-one. Isomerization of 5,16-heptadecadien-7-ol (**14**, 148.2 mg, 0.587 mmol) with **24** (22.8 mg, 29.4 μmol) and **33** (15.5 mg, 58.7 μmol) in dioxane (0.5 mL) for 8 h gave a mixture of the products, 113.4 mg (77%), R_f = 0.43 (15:1 hexane–ether), consisting of a ca. 3.5:1 ratio of internal:terminal olefins. 16-Heptadecen-7-one: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.833 (ddt, J = 16.9, 10.2, 6.8 Hz, 1 H), 5.013 (d of m, J = 17.1 Hz, 1 H), 4.954 (d of m, J = 10.2 Hz, 1 H). (*E*,*Z*)-15-Heptadecen-7-one: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.48–5.38 (m, 2 H). In addition, the mixture showed the following resonances arising from both compounds: IR (film) 3014, 2929, 2856, 1716, 1641, 1465, 1411, 1375, 965 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.406 (t, J = 7.4 Hz, 4 H), 2.067–1.964 (m, 2 H), 1.670–1.611 (m, 2 H), 1.587–1.326 (m, 4 H), 1.295 (br s, 16 H), 0.902 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 211.53, 139.05, 131.47, 130.66, 124.50, 123.56, 114.04, 42.72, 33.71, 32.49, 31.56, 29.46, 29.41, 29.30, 29.23, 29.16, 29.00, 28.87, 28.82, 26.70, 23.77, 22.43, 17.83, 13.95; exact mass calcd for $C_{17}H_{32}O$ 252.2455, found 252.2453.

Cyclooctanone. Method A. Isomerization of 2-cycloocten-1-ol (**15**, 152.5 mg, 1.21 mmol) with **22** (43.9 mg, 60.4 μmol) and **33** (31.9 mg, 121 μmol) in dioxane (0.9 mL) for 24 h gave, after chromatographic separation (R_f = 0.36, 4:1 pentane–ether), 47.0 mg of product (31%, 45% brsm) plus 33% unreacted starting material.

Method B. Isomerization of **15** (46.6 mg, 0.369 mmol) with **24** (14.3 mg, 18.4 μmol) and **33** (9.8 mg, 37.1 μmol) in dioxane (0.5 mL) for 3 h gave the product in a 47% yield, by GC integration vs tridecane internal standard.

Cyclododecanone. Method A. Isomerization of 2-cyclododecen-1-ol (**16**, 104.3 mg, 0.572 mmol) in **22** (20.8 mg, 28.6 μmol) and **33** (15.1 mg, 57.2 μmol) in dioxane (0.7 mL) for 9 h gave the product, 87.4 mg (84%), R_f = 0.54 (4:1 hexane–ether).

Method B. Isomerization of **16** (110.4 mg, 0.606 mmol) with **24** (23.5 mg, 30.3 μmol) and **33** (16.0 mg, 60.6 μmol) in dioxane (0.6 mL) for 2.5 h gave the product, 95.5 mg (87%), R_f = 0.55 (4:1 hexane–ether).

4-Hydroxycyclododecanone. Isomerization of (*E*)-2-cyclododecene-1,4-diol (**17**, 91.5 mg, 0.461 mmol) with **24** (17.9 mg, 23.1 μmol) and **33** (12.2 mg, 46.1 μmol) in dioxane (0.6 mL) for 4 h gave the product: 32.2 mg (35%); R_f = 0.25 (2:1 hexane–ether); IR (film) 3450, 2933, 2862, 1709, 1467, 1443, 1363 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.63 (br, 1 H), 2.761–2.712 (m, 2 H), 2.351–2.292 (m, 1 H), 2.224–2.158 (m, 1 H), 2.042–1.205 (c, 17 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.43, 67.49, 41.24, 37.31, 32.79, 30.96, 24.91, 24.18, 24.09, 22.74, 22.53, 22.23; exact mass calcd for $C_{12}H_{22}O_2$ 198.1621, found 198.1619 (1.8).

4-Acetoxycyclododecanone. Isomerization of (*E*)-4-acetoxy-2-cyclododecen-1-ol (**18**, 85.0 mg, 0.354 mmol) with **24** (13.7 mg, 17.7 μmol) and **33** (9.3 mg, 35.4 μmol) in dioxane (0.4 mL) for 3 h gave the product: 72.7 mg (86%); R_f = 0.34 (4:1 hexane–ether); IR 2935, 2866, 1732, 1712, 1470, 1442, 1365 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.831 (quint, J = 6.3 Hz, 1 H), 2.730–2.616 (m, 2 H), 2.359–2.261 (m, 2 H), 2.11–2.10 (m, 1 H), 2.037 (s, 3 H), 1.92–1.76 (m, 2 H), 1.70–1.20 (m, 13 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.24, 170.29, 71.49, 41.41, 37.01, 30.08, 27.15, 24.73, 24.68, 24.09, 23.36, 22.38, 21.91, 21.18.

8-Oxo-11-undecanolide. Isomerization of 8-hydroxy-9-undecen-11-olide (**20**, 63.6 mg, 0.321 mmol) with **24** (12.5 mg, 16.0 μmol) and **33** (8.5 mg, 32.1 μmol) in dioxane (0.4 mL) for 6.5 h gave the product: 18.0 mg (28%); R_f = 0.48 (2:1 hexane–ethyl acetate); IR (film) 2969, 2929, 2864, 1722, 1709, 1461, 1357 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.098 (m, 2 H), 2.518 (m, 2 H), 2.456 (m, 2 H), 2.325 (m, 2 H), 2.081 (quintet, J = 5.6 Hz, 2 H), 1.762 (quintet, J = 6.2 Hz, 2 H), 1.614 (quintet, J = 6.4 Hz, 2 H), 1.382 (quintet, J = 7.4 Hz, 2 H), 1.240 (quintet, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 210.73, 174.24, 64.64, 40.54, 40.41, 33.31, 24.72, 24.54, 23.04, 22.47, 20.89.

2-Methylundecanal. Isomerization of 2-methylene-1-undecanol (**21**, 152.7 mg, 0.829 mmol) with **22** (30.1 mg, 41.4 μmol) and **33** (21.9 mg, 82.8 μmol) in dioxane (0.6 mL) for 3.5 h gave the product:[21] 103.1 mg (68%); R_f = 0.63 (9:1 pentane–ether).

3-Phenylpropanal. Isomerization of cinnamyl alcohol (100.0 mg, 0.745 mmol) with **22** (27.1 mg, 37.3 μmol) and **33** (19.7 mg, 74.5 μmol) in dioxane (0.5 mL) for 8 h gave the product: 90.0 mg (90%); R_f = 0.59 (2:1 pentane–ether).

Synthesis of 3-Deuterio-5-phenyl-1-penten-3-ol. (a) 1,1-Dideuterio-3-phenyl-1-propanol. To a suspension of LAD (4.43 g, 105.5 mmol, >99% D) in ether (60 mL) at 0 °C was added a solution of hydrocinnamic acid (5.28 g, 35.2 mmol) in ether (40 mL) dropwise over 25 min. The resulting suspension was stirred at room temperature for 1 h and then heated at reflux for 8 h. After cooling to 0 °C, the mixture was quenched with aqueous $NaHSO_4$ (30 mL) and diluted with 2 M H_2SO_4 (ca. 70 mL) to dissolve the salts. The layers were washed with $NaHCO_3$ and brine, dried ($MgSO_4$), filtered, and evaporated to give the pure product: 4.558 g (94%); R_f = 0.50 (1:1 hexane–ether); IR (film) 3332, 3085, 3063, 3027, 2933, 2861, 2204, 2107, 1946, 1871, 1806, 1603, 1496, 1454, 1388 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.309–7.255 (m, 2 H), 7.212–7.174 (m, 3 H), 3.675–3.639 (m, <0.01 H), 2.709 (t, J = 7.8 Hz, 2 H), 1.884 (t, J = 7.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.69, 128.18, 128.14, 125.57, 60.85 (quint, $^1J_{CD}$ = 21.8 Hz), 33.72, 31.78.

(b) 1-Deuterio-3-phenylpropanal. To a suspension of PCC (7.02 g, 32.6 mmol) and Celite (7 g) in CH_2Cl_2 (30 mL) was added 1,1-dideuterio-3-phenyl-1-propanol (3.00 g, 21.7 mmol). The resulting suspension was stirred at room temperature for 2 h, diluted with ether (280 mL), filtered, evaporated, and chromatographed (4:1 hexane–ethyl acetate) to give the product; 771 mg (26%); R_f = 0.51; IR (film) 3087, 3063, 3029, 2928, 2080, 1713, 1604, 1497, 1454, 1403, 1358 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.318 (m, 5 H), 2.965 (t, J = 7.6 Hz, 2 H), 2.786 (t, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.04 (t, $^1J_{CD}$ = 26.4 Hz), 140.16, 128.34, 128.05, 126.023, 44.76 (t, $^2J_{CD}$ = 3.7 Hz), 27.77.

(c) 3-Deuterio-5-phenyl-1-penten-3-ol (31). A solution of vinylmagnesium bromide (10.0 mL, 10 mmol, 1 M in THF) was cooled to 0 °C and treated dropwise with a solution of 1-deuterio-3-phenylpropanal (770 mg, 5.70 mmol) in THF (5 mL). After stirring for 1 h, the mixture was quenched with aqueous $NaHSO_4$, diluted with ether, and separated; the organic layer was washed with $NaHCO_3$ and brine, dried ($MgSO_4$), evaporated, and chromatographed (1:1 hexane–ether) to yield 719 mg of the product (77%): R_f = 0.47; IR (film) 3363, 3085, 3063, 3027, 2926, 2859, 2115, 1641, 1604, 1496, 1455, 1417, 1062, 992, 924 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.308–7.271 (m, 2 H), 7.217–7.173 (m, 3 H), 5.907 (dd, J = 17.2, 10.4 Hz, 1 H), 5.252 (dd, J = 17.2, 1.5 Hz, 1 H), 5.145 (dd, J = 10.4, 1.5 Hz, 1 H), 2.789–2.654 (m, 2 H),

1.872-1.831 (m, 2 H), 1.508 (br, 1 H); ^{2}H NMR (61.4 MHz, $CHCl_3$) δ 4.085 (s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.79, 140.84, 128.34, 128.27, 125.71, 114.83, 71.84 (t, $^1J_{CD}$ = 21.8 Hz), 38.27, 31.49.

5-Deuterio-1-phenylpentan-3-one (32). Isomerization of **31** (110.4 mg, 0.676 mmol) with **22** (44.5 mg, 61.3 μmol) and **33** (32.4 mg, 123 μmol) in dioxane (0.7 mL) for 1 h gave the product: 69.6 mg (63%); R_f = 0.46 (4:1 hexane-ether); IR 3086, 3063, 3028, 2943, 2186, 1949, 1874, 1805, 1718, 1604, 1497, 1454, 1413, 1369 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.299-7.207 (m, 2 H), 7.193-7.173 (m, 3 H), 2.903 (t, J = 7.6 Hz, 2 H), 2.734 (t, J = 7.7 Hz, 2 H), 2.403 (t, J = 7.2 Hz, 2 H), 1.029 (tt, $^3J_{HH}$ = 7.3 Hz, $^2J_{HD}$ = 2.0 Hz, 2 H); ^{2}H NMR (61.4 MHz, $CHCl_3$) δ 1.056 (s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.59, 141.09, 128.38, 128.22, 125.99, 43.80, 35.96, 29.74, 7.41 (t, $^1J_{CD}$ = 19.4 Hz); exact mass calcd for $C_{11}H_{13}DO$ 163.1108, found 163.1096 (64.4).

Crossover Experiment. Isomerization of a mixture of 3-deuterio-5-phenyl-1-penten-3-ol (**29**, 60.0 mg, 0.368 mmol) and 1-tetradecen-3-ol (**2**, 78.1 mg, 0.368 mmol) with **22** (26.6 mg, 36.6 μmol) and **33** (19.2 mg, 73.4 μmol) in dioxane (0.75 mL) for 1.5 h gave 5-deuterio-1-phenylpentan-3-one (20.9 mg, 35%; R_f = 0.40, 6:1 hexane-ether) and 3-tetradecanone (71.2 mg, 91%; R_f = 0.61, 6:1 hexane-ether). These compounds were characterized as described above.

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Communications to the Editor

A Convergent Synthetic Route to the Tunicamycin Antibiotics. Synthesis of (+)-Tunicamycin V

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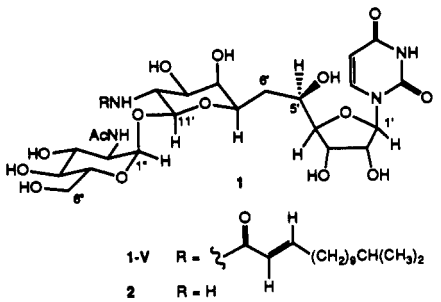
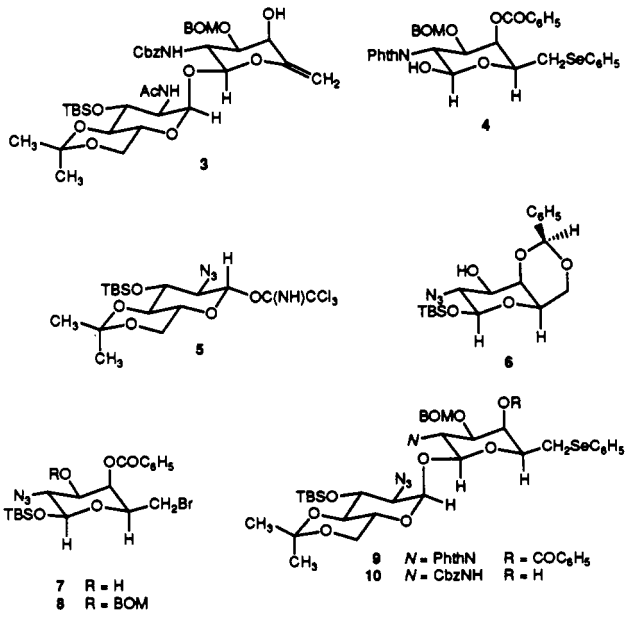
The tunicamycins are a family of natural products represented generally by structure **1**, wherein R indicates one of several long-chain branched, linear, saturated or unsaturated acyl substituents. They elicit a considerable range of biological responses including antimicrobial, antifungal, antiviral, and antitumor activities. Their ability to function as potent inhibitors of oligosaccharide synthesis in eukaryotic cells has established them as unique biochemical probes of the role of glycosylation on protein structure and function.[1] In this work, we describe a concise synthetic route to the tunicamycins, illustrated by the preparation of (+)-tunicamycin V (**1-V**).[2]



Previous studies directed toward a synthesis of the undecose core of **1**, tunicaminyluracil (C1′-C11′),[2h] suggested that the complete antibiotic structure might be assembled in a highly convergent manner by the coupling of an allylic alcohol such as **3** with a suitably protected uridine 5′-aldehyde derivative to form the C5′-C6′ bond (vide infra). In the implementation of this strategy, it was first necessary to address the problem of formation of the "trehalose" glycosidic linkage within **3**. Prior work had established this to be a difficult bond formation;[2f,g] in a single reported success, Koenigs-Knorr methodology was found to produce the desired β,α-linkage, albeit in poor yield (18%).[2f] After an extensive investigation of the variables critical for successful coupling, we have developed an efficient synthesis of the desired trehalose linkage employing the galactosamine derivative **4** as nucleophile and the glucosamine derivative **5** as electrophile. Both



coupling partners were prepared in multigram quantities from simple carbohydrate precursors. Galactosamine derivative **4** was synthesized in six steps from the readily available precursor **6**.[3] Oxidative cleavage of the benzylidene acetal within **6** was achieved, without protection of the hydroxyl group, by irradiation of a solution of **6** in bromotrichloromethane (0.08 M, 0 °C, 2.5 h, 275-W sun lamp), providing the bromo alcohol **7** in 87% yield.[4] Bromo alcohol **7** was protected as its benzyloxymethyl (BOM) ether **8** with BOM chloride (5.0 equiv) and diisopropylethylamine

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