Preparation of Oxepanes, Oxepenes, and Oxocanes by Iodoetherification using Bis(*sym*-collidine)iodine(I) Hexafluorophosphate as Electrophile

Yves Brunel and Gérard Rousseau*

Laboratoire des Carbocycles, URA CNRS 478, Institut de Chimie Moléculaire d'Orsay, Bât. 420, Université de Paris-Sud, 91405 Orsay, France

Received March 14, 1996[⊗]

Oxepanes have been obtained in good yields (40−95%) by iodoetherification of unsaturated alcohols using bis(*sym*-collidine)iodine(I) hexafluorophosphate **(1)** as electrophile, either by 7-*exo*-mode or 7-*endo*-mode cyclizations. 4-Oxepenes could also be formed from 4,6-heptadien-1-ols; the presence of a substituent on the carbon 6 appeared necessary, while for steric reasons the presence of a substituent on the carbon 7 was unfavorable. Oxocanes could be obtained in moderate yields (18−27%).

An increasing number of natural products of marine and terrestrial origin with an oxepane or an oxocane framework are being reported in the literature.[1,2] These compounds often have interesting biological activity, so efficient methods allowing their preparation appear necessary.[3] Access to these heterocycles from the corresponding lactones[4] (generally obtained from cyclanones or by Claisen rearrangement) was shown to be efficient.[5] Ring expansion of dihydropyrans,[6] Cope rearrangement of 2,3-divinyl epoxides,[7] and radical opening of bicyclic oxiranes[8] were also reported. Cyclization of linear precursors is an excellent route to heterocycles; however, for these ring sizes this reaction is disfavored by entropic and enthalpic factors.[9] Nevertheless, recent strategies show that the cyclization is possible in high yields, either by C−C[10] or by O−C[11] bond formation.

A simpler way to obtain these heterocycles should be an electrophilic cyclization (*exo*- or *endo*-mode in Scheme 1) starting from ethylenic alcohols or derivatives.[12]

The synthesis of oxepane derivatives by an *exo*-mode cyclization has been already reported using this approach with reagents such as lead tetraacetate,[13] *N*-(phenylthio)-morpholine,[14] (phenylseleno)phthalimide,[15] and mercuric[16] and palladium[17] salts. The formation of oxepane derivatives by an *endo*-mode cyclization is also possible with strong acids,[18] telluric derivatives,[19] and palladium salts.[20] While haloetherification has been intensively studied for the preparation of tetrahydrofuran and tetrahydropyran compounds,[12,21] only a few results are reported for larger ring sizes, and in general the yields are unsatisfactory.[22] However, the reaction of an unsaturated isoxazoline with iodine has been reported to give a 2-(iodomethyl)oxepane in good yield.[23]

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

(1) For reviews on marine products see: Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 251 and 551; **1986**, *3*, 1; **1987**, *4*, 539; **1988**, *5*, 613; **1990**, *7*, 269; **1991**, *8*, 97; **1992**, *9*, 323; **1993**, *10*, 497; **1994**, *11*, 355; **1995**, *12*, 223.

(2) For terrestrial products, see, for example: (a) Kawahara, N.; Nozawa, K.; Nakajima, S.; Kawai, K.-i.; Yamazaki, M. *J. Chem. Soc., Chem. Commun.* **1989**, 951. (b) Kawahara, N.; Nozawa, K.; Yamazaki, M.; Nakajima, S.; Kawai, K. *Chem. Pharm. Bull.* **1990**, *38*, 73. (c) Kanoja, R. M.; Wachter, M. P.; Levine, S. D.; Adams, R. E.; Chen, R.; Chin, E.; Cotter, M. L.; Hirsch, A. F.; Huettemann, R.; Kane, V. V.; Ostrowski, P.; Shaw, C. J.; Mateos, J. L.; Noriega, L.; Guzman, A.; Mijarez, A.; Tovar, L.; Shefter, E. *J. Org. Chem.* **1982**, *47*, 1310. (d) Aida, M.; Shinomiya, K.; Matsuzawa, Y.; Hano, Y.; Nomura, T. *Heterocycles* **1994**, *39*, 847. (e) Cimino, G.; Madaio, A.; Trivellone, E.; Uriz, M. *J. Nat. Prod.* **1994**, *57*, 784. (f) Escher, S.; Niclass, Y. *Helv. Chim. Acta* **1991**, *74*, 179. (g) Macias, F. A.; Molinillo, J. M. G.; Varela, R. M.; Torres, A.; Fronczek, F. R. *J. Org. Chem.* **1994**, *59*, 8261.

(3) For a review see: Moody, C. J.; Davies, M. J. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier Science Publishers B.V.: New York, 1992; Vol. 10, pp 201−239.

(4) For a review on medium ring lactones see: Rousseau, G. *Tetrahedron* **1995**, *43*, 2777.

(5) (a) Carling, R. W.; Curtis, N. R.; Holmes, A. B. *Tetrahedron Lett.* **1989**, *30*, 6081. (b) Robinson, R. A.; Clark, J. S.; Holmes, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 10400. (c) Paquette, L. A.; Sweeney, T. J. *Tetrahedron* **1990**, *46*, 4487.

(6) Nicolaou, K. C.; Hwang, C. K.; Duggan, M. E.; Bal Reddy, K. *Tetrahedron Lett.* **1987**, *28*, 1501.

(7) (a) Clark, D. L.; Chou, W.-N.; White, J. B. *J. Org. Chem.* **1990**, *55*, 3975. (b) Chou, W. N.; White, J. B.; Smith, W. B. *J. Am. Chem. Soc.* **1992**, *114*, 4658. (c) Boeckman, R. K.; Shair, M. D.; Vargas, J. R.; Stolz, L. A. *J. Org. Chem.* **1993**, *58*, 1295.

(8) Corser, D. A.; Marples, B. A.; Dart, R. K. *Synlett* **1992**, 987.

(9) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95.

(10) (a) Cockerill, G. S.; Kocienski, P.; Treadgold, R. *J. Chem. Soc., Perkin Trans. 1* **1985,** 2093. (b) Blumenkopf, T. A.; Overman, L. E. *Chem. Rev.* **1986**, *86*, 857. (c) Castañeda, A.; Kucera, D. J.; Overman, L. E. *J. Org. Chem.* **1989**, *54*, 5695. (d) Coppi, L.; Ricci, A.; Taddei, M. *J. Org. Chem.* **1988**, *53*, 913. (e) Guyot, B.; Pornet, J.; Miginiac, L. *J. Organomet. Chem.* **1989**, *373*, 279. (f) Yamamoto, Y.; Yamada, J.-i.; Kodota, I.*Tetrahedron Lett.* **1991**, *32*, 7069.

(11) (a) Nicolaou, K. C.; Hwang, C.-K.; Nugiel, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 4136. (b) Kocienski, P. J.; Love, C. J.; Whitby, E. J.; Costello, G.; Roberts, D.A. *Tetrahedron* **1989**, *45*, 3839. (c) Heslin, J. C.; Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1417. (d) Kotsuki, H.; Ushio, Y.; Kadota, I.; Ochi, M. *J. Org. Chem.* **1989**, *54*, 5153. (e) Nicolaou, K. C.; Hwang, C. K.; Duggan, M. E.; Nugiel, D. A.; Abe, Y.; Bal Reddy, K.; DeFrees, S. A.; Reddy, D. R.; Awartani, R. A.; Conley, S. R.; Rutjes, F.P. J. T.; Theodorakis, E. A. *J. Am. Chem. Soc.* **1995**, *117*, 10227.

(12) For a review, see: Harding, K. E.; Tiner, T. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 4, p 363.

(13) Cekovic, Z.; Saicic, R.; Mihailovic, M. L. *Res. Chem. Int.* **1989**, *11*, 257 and references cited therein.

(14) López-Tudanca, P. L.; Jones, K.; Brownbridge, P. *Tetrahedron Lett.* **1991**, *32*, 2261 and references cited therein.

(15) Jackson, W. P.; Ley, S. V.; Morton, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1028. See also: White, J. D.; Nishiguchi, T.; Skeean, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 3923.

(16) Hoye, T. R.; Caruso, A. J.; Dellaria, J. F.; Kurth, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 6704.

(17) Trost, B. M.; Tenaglia, A. *Tetrahedron Lett.* **1988,** *29*, 2927.

(18) Banthorpe, D. V.; Boullier, P. A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 114.

(19) Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1987**, *28*, 1281.

(20) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z.-i. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 735.

(21) Cardillo, G.; Orena, M. *Tetrahedron* **1990**, *46*, 3321. (b) Bartlett, P. A. In *Asymmetric Synthesis*; Morisson, J. D., Ed.; Academic Press: Orlando, FL, 1984; p 411.

(22) (a) Lasalle, F.; Grée, E. *C. R. Acad. Sci. Paris* **1990**, *310*, 907. (b) Evans, R. D.; Magee, J. W.; Schauble, J. H. *Synthesis* **1988**, 863. (c) Shieh, H.-M.; Prestwich, G. D. *Tetrahedron Lett.* **1982**, *23*, 4643.

(23) Kurth, M. J.; Rodriguez, M. J.; Olmstead, M. M. *J. Org. Chem.* **1990**, *55*, 283.

S0022-3263(96)00506-3 CCC: $12.00

Scheme 1

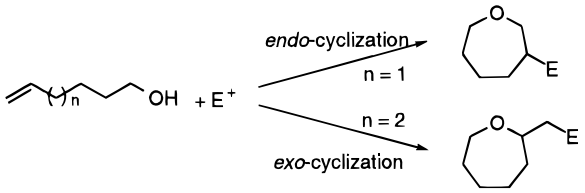
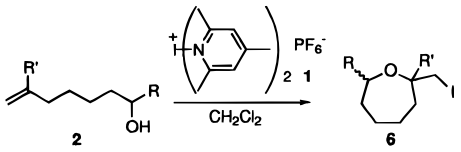
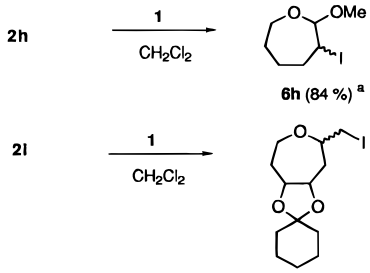


Table 1. Preparation of Oxepanes 6



R' = H; R = H:	**2a**	**6a**: (95%)
R' = H; R =Me:	**2b**	**6b**: (73%) [a]
R' = H; R = Pr:	**2c**	**6c**: (81%) [a]
R' = H; R = *i*Pr:	**2d**	**6d**: (80%) [a]
R' = H; R = Ph:	**2e**	**6e**: (65%) [a]
R' = H; R =CH_2OH:	**2f**	**6f**: (40%) [a]
R' =Me; R = H:	**2g**	**6g**: (71%)



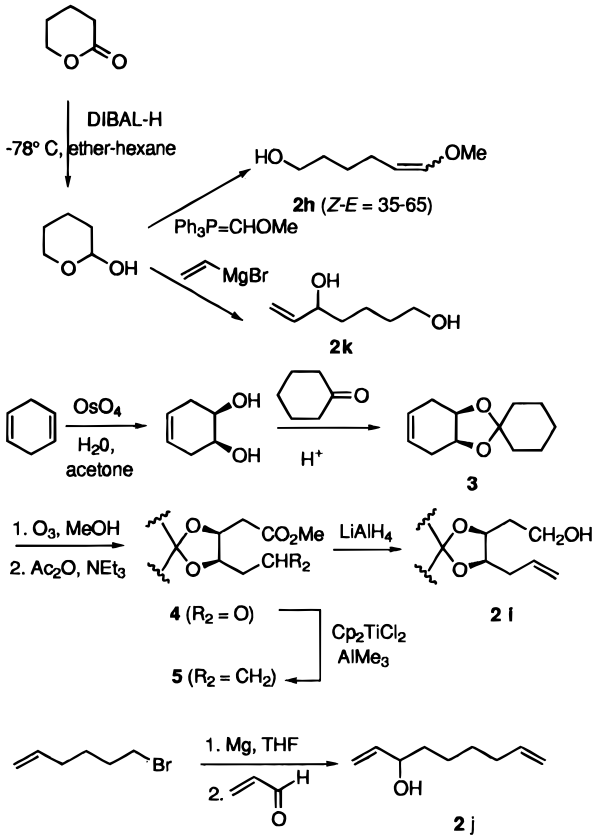
[a] Mixture (50:50) of diastereoisomers (except for **6h**: 35:35).

We recently reported that ϵ-caprolactones could be prepared in high yields by cyclization of 6-heptenoic acids using bis(collidine)iodine(I) hexafluorophosphate (**1**);[24] a reaction that was until then considered difficult. We thought it should be interesting to study the preparation of oxepanes and oxocanes from unsaturated alcohols under the same conditions. Our results are reported-here.[25]

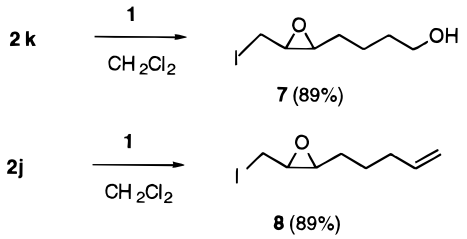
Preparation of Oxepanes

6-Hepten-1-ols **2a**−**g** necessary for this study (see Table 1) were either commercially available or prepared by conventional synthetic methods. Alcohols **2h**−**k** were obtained as depicted in Scheme 2. A special comment can be made about the preparation of alcohol **2i**. Selective mono-*cis*-dihydroxylation of 1,4-cyclohexadiene[25] followed by the acetal formation led to the unsaturated cyclohexanic compound **3** (38% yield for the two steps), which was transformed into keto ester **4** by ozonolysis and then reaction with acetic anhydride in the presence of triethylamine[25] (62% yield). The transformation of the aldehyde function into the olefin **5** was critical, and only the Tebbe reagent prepared *in situ*[28] was successful (55% yield). The subsequent reduction of the ester function into alcohol **2i** was accomplished in quantitative yield.

Scheme 2



Scheme 3



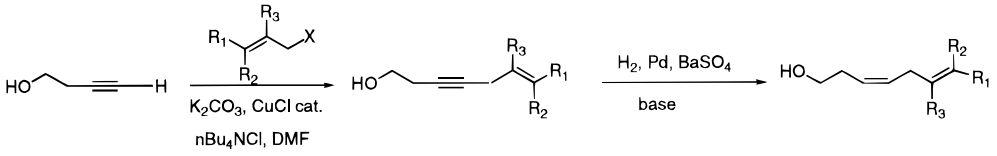
The iodoetherification were carried out in methylene chloride at room temperature in the presence of 1.1 equiv of bis(collidine)iodine(I) hexafluorophosphate (**1**) for 1 h. After completion of the reaction (checked by TLC), the solvent was removed under vacuum and the residue purified by liquid chromatography on silica gel. Oxepanes **6a**−**i** were obtained in good yields in the cases studies (Table 1).

Their structures were established by spectroscopic analysis (MS, ^{1}H NMR, ^{13}C-NMR). Particularly with MS (EI), compounds **6a**−**g**,**i** show an ion peak at M − CH_2I, and with ^{13}C-NMR the carbon bearing the iodide atom was found between 10 and 20 ppm. Oxocanes were not detected in these reactions. When a substituent was present at the α (alcohols **2b**−**f)** or γ,δ position (alcohol **2i**) of the alcohol function no diastereoselectivity was observed.

The reaction of alcohols **2j**,**k** with reagent **1** were used to study the chemioselectivity of the cyclization. In both cases, only the oxiranes were formed (Scheme 3). When the secondary alcohol of **2k** was protected as a dichlorobenzyl ether, no reaction with **1** was observed. In the same way, formation of oxepanes was not observed when

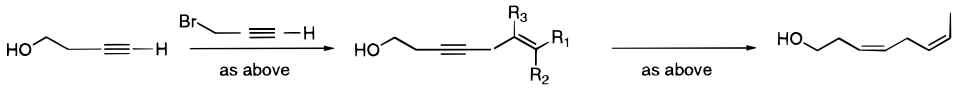
(24) Simonot, B.; Rousseau, G. *J. Org. Chem.* **1994**, *59*, 5912.
(25) For a preliminary report, see: Brunel, Y.; Rousseau, G. *Synlett* **1995**, 323.
(26) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.
(27) Schreiber, S. L.; Claus, R. E.; Reagen, J. *Tetrahedron Lett.* **1982**, *23*, 3867.
(28) Pine, S. H.; Shen, G. S.; Hoang, H. *Synthesis* **1991**, 165.

Table 2. Preparation of 3,6-Heptadien-1-ols 10a−f



		9a-e	10a-e
a	X = Br; $R_1 = R_2 = R_3 = H$	85 %	99 %
b	X = Cl; R_1 =Me; $R_2 = R_3 = H$	66 % [a]	82 % [a]
c	X = Cl; $R_1 = R_2$ = Me; R_3 =H	68 %	91 %
d	X = Cl; $R_1 = R_2$ = H; R_3 = Me	91 %	87 %
e	X = Br; $R_1 = R_2$ = H; R_3 = OMe	55 %	99 %

[a] as a 6-*Z*, *E* mixture: 10, 90



9f (47 %) **10f** (76 %)

the alcohol function of compounds **2a**−**e** was protected as the tetrahydropyranyl ether.[29]

Compounds **6a**−**g,i** were formed by an *exo*-mode cyclization. However, the reaction product obtained from alcohol **2h** shows that the formation of oxepane can also occur by an *endo*-mode cyclization. In this case, the reaction is probably diastereospecific, as we have previously demonstrated.[24]

Preparation of Oxepenes

The alcohols studied were prepared as shown in Table 2. A coupling reaction[30] between 3-butyn-1-ol and different allylic halides led to 6-hepten-3-yn-1-ols **9a**−**e**, which by catalytic hydrogenation (Pd over $BaSO_4$)[31] led to the 3(*Z*) alcohols **10a**−**e**. Compound **10f** was similarly obtained by catalytic hydrogenation of 3,5-heptadiyn-1-ol (**9f**).

The stereochemical purity of these compounds was checked by GC analysis, and no 3(*E*) isomer was detected. These unsaturated alcohols were reacted with reagent **1** in methylene chloride. Table 3 shows that a variety of products were formed, depending of the terminal double bond substitution.

With the unsubstituted alcohol **10a**, competition between the 7-*exo* and 5-*endo* mode cyclizations was observed with a low global yield (Table 3, entry a). Contrary to what was expected, introducing a *cis*-double bond did not favor the cyclization. We explain this result by the fact that introduction of the second double bond decreases the electronic density of the first double bond (and reciprocally) and, thus, lowers its reactivity toward the electrophilic reagent **1**. Monosubstitution of the terminal double bond did not increase the yield in 7-*exo* (or 8-*endo*)-mode cyclization products (Table 3, entries b and c). These results suggest that introduction of a methyl in this position induced a steric hindrance unfavorable to the 7- or 8-membered ring formation. This

Table 3. Iodoetherification of 3,6-Heptadien-1-ols 10a−f

entry	substrate	products (Yield, %)		
a	**10a**	**11** (36)	**12** (8)	
b	**10b**	**13** (3) cis-trans: 10-90	**14** (6) [a]	**15** (29)
c	**10c**	**16** (18)	**17** (6)	
d	**10d**	**18** (14)	**19** (9)[a]	
e	**10e**	**20** (70)		
f	**10f**	**21** (60)		

[a] Stereochemistry not determined.

is even more obvious with alcohol **10d** for which no oxepane or oxocane could be detected (Table 3, entry d). However, the presence of a substituent on the carbon in 6-position allows the formation of oxepenes in satisfactory yields (Table 3, entries e and f).

Preparations of Oxocanes

Alcohols **22a**−**f** were prepared by standard synthetic methods (see the Experimental Section). Their iodoetherifications are reported in Table 4.

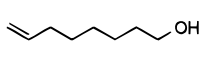
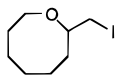
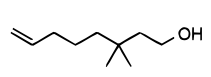
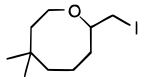
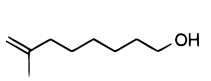
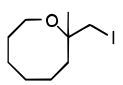
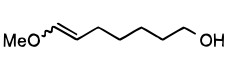
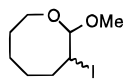
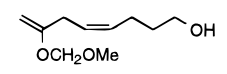
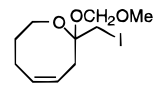
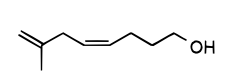
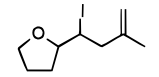
Oxocanes were generally formed, however, in low yields. Uncharacterized polar products (probably inter-

(29) The formation of oxepanes occurred in similar yields using the more electrophilic bis(collidine)bromine(I) hexafluorophosphate. In this case, the cyclization could be achieved with the tetrahydropyranyl ethers. For example: 66% yield in 2-(bromomethyl)-7-(2-methylethyl)-oxepane from **2d**-OTHP.

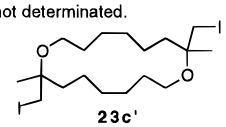
(30) (a) Jeffery, T.; Gueugnot, S.; Linstrumelle, G. *Tetrahedron Lett.* **1992**, *33*, 5757. (b) Jeffery, T. *Tetrahedron Lett.* **1989**, *30*, 2225.

(31) Sargent, M. V.; Wangchareontrakul, S. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1429.

Table 4. Preparation of Oxocanes by Iodoetherification

entry	substrate	product (Yield, %)
a	 **22a**	 **23a** (27)
b	 **22b**	 **23b** (24)
c	 **22c**	 **23c** (9) [a]
d	 **22d** [b]	 **23d** (23) [b]
e	 **22e**	 **23e** (18)
f	 **22f**	 **23f** (70) [c]

[a] 14 % of dimer **23c'** was also isolated. [b] *cis-trans* mixture (60-40). [c] streochemistry not determined.

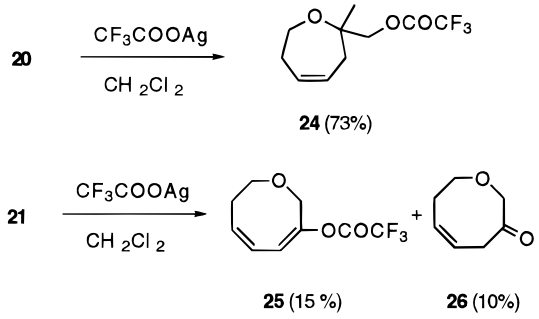


23c'

molecular reaction products) were mainly formed. The result obtained from alcohol **22a** (Table 4, entry a) was expected since we previously reported that 8-(iodomethyl)-2-oxocanone was obtained in only 5% yield by iodolactonization of the corresponding acid.[24] The other results were, however, unexpected. Entry b (Table 4) shows that the introduction of a *gem*-dimethyl group did not favor the cyclization, contrary to our report concerning the iodolactonization for this ring size.[32] We are unable to explain this discrepancy. In the same way, entries c and d (Table 4) show that the presence of an electron-donating substituent on the carbon double bond did not favor the cyclization as well by an *exo*-mode cyclization (Table 4, entry c) as by an *endo*-mode cyclization (Table 4, entry d). The presence of an enol ether on the terminal double bond allowed the obtainment, in low yield, of an oxocene (Table 4, entrie e) instead of the favored dihydrofuran as observed with a methyl (Table 4, entry f). However, in the cases examined the steric hindrance introduced by the substituent on carbons 7 or 8 disfavors the formation of oxocanes.

These results prompted us to investigate another route to oxocanes. It has been reported that the ring expansion of tetrahydropyrans to oxepanes was possible.[33] We wondered if we could similarly observe the ring expansion of oxepanes to oxocanes. Oxepanes **20** and **21** were treated with silver trifluoroacetate in methylene chloride (Scheme 4). Only the substitution product **24** was

Scheme 4



observed from **20**. With oxepene **21** the ring expansion did occur; however, the yield is too low to lead to a synthetically useful reaction.

In conclusion, we report for the first time that oxepanes can be obtained in good yields by iodoetherification either by 7-*exo*- or 7-*endo*-cyclizations using bis(collidine)iodine(I) hexafluorophosphate (**1**) as reagent. Formation of oxepenes is also possible if a substituent is present on the CC double bond in the 6-position in 3,6-heptadienols. However, oxocanes were obtained only in low yields. The reasons for such an improvement for the formation of 7-membered ethers compared to previous attempts[22] seem to be due to two factors: (1) the presence of a nonnucleophilic anion (PF_6^-) and (2) the presence of a collidine molecule probably[34] fixed to the iodine of the intermediate iodonium, which should increase the lifetime of this latter and so favor the intramolecular ring closure. Work is in progress to apply these results to the synthesis of polyether derivatives.

Experimental Section

General Remarks. All NMR spectra were measured in $CDCl_3$, and chemical shifts are expressed in ppm relation to internal $CHCl_3$. Mass spectra were obtained at an ionization voltage of 70 eV. All solvents were purified by known standard procedures; in particular, methylene chloride was distilled from CaH_2. Alcohol **2f** is commercially available. The iodoetherifications were conducted in the dark; however, the iodo ethers are enough stable to be manipulated without special care.

6-Hepten-1-ol (2a) was prepared by $LiAlH_4$ reduction of 6-heptanoic acid in ether (84% yield): bp 80 °C/11 mmHg (lit.[35] bp 76 °C/12 mmHg); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.29 (s, 1H), 1.32−1.50 (m, 4H), 1.57 (q, J = 6.5 Hz, 2H), 2.06 (q, J = 6.5 Hz, 2H), 3.65 (t, J = 6.5 Hz, 2H), 4.95 (dd, J = 10.5, 2.0 Hz, 1H), 5.01 (dd, J = 17.0, 2.0 Hz, 1H), 5.83 (ddt, J = 6.5, 10.5, 17.0 Hz, 1H).

7-Octen-2-ol (2b). Previously reported.[22a]

9-Decen-4-ol (2c). Reaction of propanal with ethyl diazoacetate in the presence of tin(II) chloride[36] led to ethyl 3-oxoheptanoate (62% yield), which was alkylated with 1-bromo-4-pentene (66% yield). Decarboxylation and reduction ($LiAlH_4$−ether) led to to alcohol **2c** (50% yield): bp 100 °C/10 mmHg; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, J = 7.0 Hz, 3H), 1.33−1.48 (m, 2H), 1.48−1.74 (m, 4H), 2.08 (q, J = 6.5 Hz, 2H), 2.39 (t, J = 7.0 Hz, 2H), 2.42 (t, J = 7.0 Hz, 2H), 4.95 (dd, J = 2.0, 10.5 Hz, 1H), 5.02 (dd, J = 2.0, 17 Hz, 1H), 5.81 (ddt, J = 6.5, 10.5, 17.0 Hz). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.90; H, 13.02.

(32) Simonot, B.; Rousseau, G. *Tetrahedron Lett.* **1993**, *34*, 4527.

(33) Colonge, J.; Corbet, P. *Bull. Soc. Chim. Fr.* **1960**, 287. (b) Bartlett, P. A.; Ting, P. C. *J. Org. Chem.* **1986**, *51*, 2230.

(34) We previously reported[24] results that show that bis(pyridine)-iodine(I) hexafluorophosphate was less efficient than the corresponding collidine reagent in iodolactonizations. This seems to imply that the base is fixed on the iodonium in the intermediate.

(35) Bohlmann, F.; Grenz, M.; Niedballa, U. *Chem. Ber.* **1986**, *101*, 532.

(36) Holmquist, C. R.; Roskamp, E. J. *J. Org. Chem.* **1989**, *54*, 3258.

2-Methyl-8-nonen-3-ol (2d). Obtained by $LiAlH_4$ reduction in ether of 2-methyl-8-nonen-3-one[37] (89% yield): bp 90 °C/10 mmHg; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (d, J = 7 Hz, 3H), 0.94 (d, J = 7 Hz, 3H), 1.18−1.57 (m, 6H), 1.57−1.75 (m, 1H), 2.01−2.20 (m, 2H), 3.28−3.48 (m, 1H), 3.62−3.74 (m, 1H), 4.96 (dd, J = 2.0, 10.5 Hz, 1H), 5.03 (dd, J = 2.0, 17.0 Hz, 1H), 5.83 (ddt, J = 6.5, 10.5, 17.0 Hz, 1H). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.99; H, 12.75.

1-Phenyl-6-hepten-1-ol (2e). Obtained by $LiAlH_4$ reduction in ether of 1-phenyl-6-hepten-1-one[38] (66% yield): bp 74 °C/0.1 mmHg; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22−1.50 (m, 4H), 1.58 (s, 1H), 1.62−1.88 (m, 2H), 2.05 (q, J = 6.5 Hz, 2H), 4.62−4.72 (m, 1H), 4.95 (dd, J = 2.0, 10.5 Hz, 1H), 5.01 (dd, J = 2.0, 17.0 Hz, 1H), 5.80 (ddt, J = 6.5, 10.5, 17.0 Hz, 1H), 7.28−7.42 (m, 5H). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.25; H, 9.59.

6-Methyl-6-hepten-1-ol (2g). Prepared as reported in ref 39.

6-Methoxy-5-hexen-1-ol (2h). Prepared by DIBAL (in hexane) reduction in CH_2Cl_2 of δ-valerolactone (93% yield) followed by reaction with (methoxymethylene)triphenylphosphorane in ether[40] (50% yield) (*Z*/*E* mixture: 35/65): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.20−1.66 (m, 5H), 1.96 (q, J = 6.3 Hz, 1.3H), 2.10 (q, J = 6.3 Hz, 0.7 H), 3.51 (s, 1.95H), 3.60 (s, 1.05H), 3.66 (m, 2H), 4.34 (q, J = 6.3 Hz, 0.35H), 4.72 (dt, J = 6.3, 12.0 Hz, 0.65H), 5.90 (d, J = 6.3 Hz, 0.35H), 6.30 (d, J = 12 Hz, 0.65H). Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.72; H, 10.98.

(1*R,2*R**)-4-Cyclohexene-1,2-diol.**[41] Prepared according to ref 26.

(4*R,5*R**)-4,5-(1,1-Cyclohexylidenedioxy)-1-cyclohexene (3).** A mixture of 1,2-diol (1.326 g, 11.6 mmol), cyclohexanone (12 mL), and *p*-toluenesulfonic acid (0.3 g) was heated at 50 °C for 12 h. The excess of cyclohexanone was distilled under vacuum, and the residue was purified by liquid chromatography over silica gel (ether/hexane: 40/60) to give 1.885 g of acetal **3** (83% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32−1.70 (m, 10H), 2.29 (dd, J = 2.0, 3.0 Hz, 4H), 4.34 (dt, J = 1.0, 3.0 Hz, 2H), 5.78 (t, J = 2.0 Hz, 2H).

(3*R,4*R**)-Methyl 6-Oxo-3,4-(1,1-cyclohexylidenedioxy)hexanoate (4).** In a mixture of acetal **3** (1.88 g, 9.67 mmol), CH_2Cl_2 (40 mL), methanol (10 mL), and $NaHCO_3$ (0.35 g) cooled at −78 °C was bubbled ozone until a persistent blue color appeared. After 15 min at −78 °C, the excess of ozone was removed with argon. The reaction mixture was then warmed to room temperature, filtered, and concentrated to ∼10 mL. CH_2Cl_2 (50 mL) was added, and after the mixture was cooled to 0 °C, triethylamine (2 mL) and acetic anhydride (2.7 mL) were added. The solution was stirred 12 h at rt and concentrated under vacuum, and the residue was purified by liquid chromatography over silica gel (ether/hexane: 30/70) to give 1.54 g of ester **4** (62% yield): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.30−1.70 (m, 10H), 2.39−2.81 (m, 4H), 3.72 (s, 3H), 4.59−4.76 (m, 2H), 9.81 (t, J = 2.0 Hz, 1H); MS EI *m*/*z* (rel inten) 256 (10), 213 (8), 141 (61), 109 (21), 99 (15), 81 (100), 71 (20), 55 (30), 42 (17), 41 (24).

(3*R,4*R**)-Methyl 3,4-(1,1-Cyclohexylidenedioxy)-6-heptanoate (5).** The unsaturated ester **5** was obtained following the procedure reported in ref 28. A mixture of bis(cyclopentadienyl)titanium dichloride (1.013 g, 4.07 mmol) and trimethylaluminum (4.07 mL of a 2 M solution in toluene) was stirred for 72 h at room temperature and then cooled to −78 °C. A solution of oxo ester **4** (1.04 g, 4.07 mmol) in THF (10 mL) was added. The cooled bath was removed, and the solution was stirred for 30 min at room temperature. Ether (10 mL) and 1 M aqueous NaOH solution were added slowly. After separation, the organic phase was dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by liquid chromatography over silica gel (ether/hexane: 30/70) to give 0.571 g of ester **5** (55% yield): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.32−1.75 (m, 10H), 2.08−2.69 (m, 4H), 3.73 (s, 3H), 4.24 (dt, J = 5.0, 7.5 Hz, 1H), 4.55 (dt, J = 5.0, 7.5 Hz, 1H), 5.06−5.20 (m, 2H), 5.84 (m, 1H); MS EI *m*/*z* (rel inten) 254 (20), 211 (24), 139 (72), 125 (11), 115 (27), 107 (51), 97 (43), 79 (100), 69 (19), 55 (67), 41 (51).

(3*R,4*R**)-3,4-(1,1-Cyclohexylidenedioxy)-6-hepten-1-ol (2i).** To a solution of $LiAlH_4$ (94 mg, 2.47 mmol) in ether (20 mL) was added ester **5** (0.571 g, 2.2 mmol). After 30 min at room temperature, hydrated sodium sulfate was added, and the mixture was stirred 2 h. After filtration, the filtrate was concentrated under vacuum to 0.508 g of alcohol **2i** (100% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26 (m, 1H), 1.32−1.92 (m, 12H), 2.12, 2.48 (m, 2H), 3.86 (m, 2H), 4.12−4.35 (m, 2H), 5.06−5.21 (m, 2H), 5.85 (m, 1H); MS EI *m*/*z* (rel inten) 226 (10), 183 (19), 111 (100), 99 (34), 93 (20), 81 (37), 79 (17), 69 (41), 67 (23), 55 (56), 41 (78). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.80; H, 9.66.

1,8-Nonadien-3-ol (2j). Acrolein (0.98 g, 17.5 mmol) in solution in THF (2 mL) was added dropwise to a cooled solution (−40 °C) of the Grignard reagent prepared from magnesium (0.387 g, 15.9 mmol) and 5-bromo-1-hexene (2.6 g, 16 mmol) in THF (18 mL). The temperature was slowly warmed to 0 °C, and a saturated solution of ammonium chloride was added (20 mL). The aqueous phase was extracted with ether (3 × 30 mL) and the organic phase dried (Na_2SO_4) and evaporated. The residue was distilled under vacuum (bp 44−46 °C/0.1 mmHg) to give 0.786 g of alcohol **2j** (36% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28−1.58 (m, 7H), 2.08 (q, J = 6.5 Hz, 2H), 4.10 (dt, J = 2.0, 6.5 Hz, 1H), 4.94 (dd, J = 2.0, 10.5 Hz, 1H), 5.01 (dd, J = 2.0, 17 Hz, 1H), 5.12 (dd, J = 2.0, 10.5 Hz, 1H), 5.23 (dd, J = 2.0, 17.0 Hz, 1H), 5.71−5.96 (m, 2H); ^{13}C NMR δ 24.8, 28.8, 33.7, 36.8, 73.0, 114.3, 114.4, 138.8, 141.3; MS EI *m*/*z* (rel inten) 83 (10), 81 (12), 90 (11), 79 (10), 68 (12), 67 (14), 57 (100), 55 (18), 41 (22).

6-Heptene-1,5-diol (2k). DIBAL (33 mL, 1 M in hexane) was added dropwise to a stirred and cooled (−78 °C) solution of δ-valerolactone (3 g, 30 mmol) in a mixture of hexane−ether (50 mL, 1:1). After 2 h at −78 °C vinylmagnesium chloride (15% in THF; 15.2 mL, 26 mmol) was added. The solution was warmed to rt and stirred for 12 h. Ammonium chloride solution was added (50 mL), and after separation, the aqueous phase was extracted with CH_2Cl_2 (10 × 50 mL). The organic phases were dried (Na_2SO_4) and concentrated. Chromatography of the residue over silica gel (ether) gave 0.738 g of diol **2k** (19% yield): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.35−1.78 (m, 8H), 3.66 (t, J = 6.5 Hz, 2H), 4.13 (q, J = 6.5 Hz, 1H), 5.12 (dd, J = 2.0, 10.5 Hz, 1H), 5.24 (dd, J = 2.0, 17.0 Hz, 1H), 5.87 (ddt, J = 6.5, 10.5, 17.0 Hz, 1H). Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.38; H, 11.03.

General Procedure for the Iodoetherification Reactions. To a solution of the alcohol (2 mmol) in CH_2Cl_2 (40 mL) was added bis(collidine)iodine(I) hexafluorophosphate[24] (1.13 g; 2.2 mmol). After the reaction mixture was stirred for 1 h at rt, 1 g of silica gel was added, and the solvent was removed under vacuum. The solid residue was deposited on the top of a silica gel column and purified (elution ether/hexane) to give an yellow oil.

2-(Iodomethyl)oxepane (6a). Previously reported:[22a] ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.45−2.03 (m, 8H), 3.20 (d, J = 5.7 Hz, 2H), 3.55−3.68 (m, 2H), 3.84−3.95 (m, 1H); ^{13}C NMR δ 11.2, 25.6, 26.1, 30.6, 35.0, 68.7, 78.7

2-(Iodomethyl)-7-methyloxepane (6b). The two diastereoisomers were separated by liquid chromatography. A isomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (d, J = 6.0 Hz, 3H), 1.35−1.95 (m, 8H), 3.17 (m, 2H), 3.58−3.69 (m, 2H); ^{13}C NMR δ 11.3, 22.3, 24.1, 27.0, 35.3, 37.5, 71.0, 76.8. Anal. Calcd for $C_8H_{15}IO$: C, 37.81; H, 5.95. Found: C, 38.05; H, 6.03. B isomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.24 (d, J = 6.0 Hz, 3H), 1.30−2.10 (m, 8H), 3.20 (m, 2H), 3.62−4.05 (m, 2H); ^{13}C NMR δ 11.5, 22.5, 25.7, 27.1, 35.4, 37.9, 74.0, 79.6. Anal. Calcd for $C_8H_{15}IO$: C, 37.81; H, 5.95. Found: C, 38.11; H, 6.07.

2-(Iodomethyl)-7-propyloxepane (6c). The two diastereoisomers could not be separated by liquid chromatography:

(37) Drouin J.; Leyendecker, Y.; Conia, J. M. *Tetrahedron* **1980**, *36*, 1195.
(38) Paquette, L. A.; Gilday, J. P.; Maynard, G. D. *J. Org. Chem.* **1989**, *54*, 5044.
(39) Brunel, Y.; Rousseau, G. *Tetrahedron Lett.* **1996**, in press.
(40) Anderson, C. L.; Soderquist, J. A.; Kabalka, G. W. *Tetrahedron Lett.* **1992**, *33*, 6915.
(41) Tschamber, T.; Backenstrass, F.; Fritz, H.; Streith, J. *Helv. Chim. Acta* **1992**, **72**, 1052.

^{1}H NMR (200 MHz, $CDCl_3$) δ (A−B mixture) 0.92 (t, J = 7.0 Hz, 3H, B isomer), 0.93 (t, J = 7.0 Hz, 3H (A isomer), 1.25−2.15 (m, 12H), 3.14−3.21 (m, 2H), 3.44−3.85 (m, 2H); ^{13}C NMR δ (A−B mixture) 10.9/11.0, 13.9/14.1, 19.4/19.7, 24.6/25.4, 27.0/27.1, 35.2/35.6, 36.0/36.6, 38.4/39.3, 74.4/74.8, 79.5/80.1. Anal. Calcd for $C_{10}H_{19}IO$: C, 42.57; H, 6.79. Found (mixture): C, 42.80; H, 6.87.

2-(Iodomethyl)-7-(2-methylethyl)oxepane (6d). The two diastereoisomers could not be separated by liquid chromatography: ^{1}H NMR (200 MHz, $CDCl_3$) δ (A−B mixture) 0.85−1.06 (m, 6H), 1.24−2.02 (m, 8H), 2.10−2.27 (m, 1H), 3.09−3.30 (m, 2H), 3.53−3.68 (m, 1H), 3.75−3.92 (m, 1H); ^{13}C NMR δ (A−B mixture) 10.6/10.7, 18.6/18.9, 19.1/19.3, 24.7/25.3, 26.6/27.6, 32.9/33.2, 33.4/34.0, 34.7/35.6, 75.2/79.2, 79.7/85.3. Anal. Calcd for $C_{10}H_{19}IO$: C, 42.57; H, 6.79. Found (mixture): C, 42.39; H, 6.68.

2-(Iodomethyl)-7-phenyloxepane (6e). The two diastereoisomers were separated by liquid chromatography. A isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.60−2.20 (m, 8H), 3.25−3.35 (m, 2H), 3.81−3.93 (m, 1H), 4.69 (dd, J = 7.8, 4.7 Hz, 1H), 7.24−7.51 (m, 5H); ^{13}C NMR δ 11.2, 24.8, 25.2, 35.5, 38.3, 79.4, 81.5, 125.8, 126.7, 128.0, 144.3. Anal. Calcd for $C_{13}H_{17}IO$: C, 49.38; H, 5.42. Found: C, 49.21; H, 5.49. B isomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.46−2.29 (m, 8H), 3.18−3.28 (m, 2H), 3.84−3.97 (m, 1H), 4.76 (dd, J = 2.0, 10.5 Hz, 1H), 7.24−7.66 (m, 5H); ^{13}C NMR δ 10.7, 26.5, 27.9, 34.9, 36.9, 75.4, 76.1, 126.1, 127.0, 128.1, 143.6. Anal. Calcd for $C_{13}H_{17}IO$: C, 49.38; H, 5.42. Found: C, 49.50; H, 5.66.

7-(Hydroxymethyl)-2-(iodomethyl)oxepane (6f). The two diastereoisomers were separated by liquid chromatography. A isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.32−2.01 (m, 8H), 2.57−2.77 (m, 1H), 3.13−3.29 (m, 2H), 3.44−3.57 (m, 2H), 3.57−3.78 (m, 2H); ^{13}C NMR δ 11.5, 24.7, 25.1, 31.6, 66.7, 80.8, 81.9. Anal. Calcd for $C_8H_{15}IO_2$: C, 35.57; H, 5.60. Found: C, 35.84; H, 5.84. B isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.40−2.18 (m, 8H), 3.60−3.70 (m, 2H), 3.88−4.36 (m, 4H), 4.82−4.89 (m, 1H); ^{13}C NMR δ 11.3, 26.4, 26.9, 35.2, 35.8, 64.7, 80.4, 81.5. Anal. Calcd for $C_8H_{15}IO_2$: C, 35.57; H, 5.60. Found: C, 35.71; H, 5.70.

2-(Iodomethyl)-2-methyloxepane (6g). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.25 (s, 3H), 1.30−1.92 (m, 8H), 2.23 (d, J = 10.5 Hz, 1H), 3.27 (d, J = 10.5 Hz, 1H), 3.38−3.68 (m, 2H); ^{13}C NMR δ 17.8, 23.2, 26.6, 29.5, 31.5, 37.8, 63.4, 75.3. Anal. Calcd for $C_8H_{15}IO$: C, 37.81; H, 5.95. Found: C, 38.04; H, 5.99.

3-Iodo-2-methoxyoxepane (6h). The two diastereoisomers were separated by liquid chromatography. *Trans* isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.35−1.80 (m, 4H), 2.06−2.37 (m, 2H), 3.37 (s, 3H), 3.54 (ddt, J = 1.0, 2.6, 12.0 Hz, 1H), 3.82 (m, 1H), 4.08 (ddd, J = 2.6, 7.8, 10.5 Hz, 1H), 4.85 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 28.9, 29.6, 32.5, 37.4, 55.6, 63.2, 109.5. Anal. Calcd for $C_7H_{13}IO_2$: C, 32.83; H, 5.12. Found: C, 32.49; H, 5.06. *Cis* isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.47−1.95 (m, 4H), 2.02−2.35 (m, 2H), 3.45 (s, 3H), 3.72 (m, 1H), 3.94 (m, 1H), 4.19 (d, J = 2.0 Hz, 1H), 4.33 (ddd, J = 1.4, 2.0, 5.2 Hz, 1H); ^{13}C NMR δ 24.7, 29.5, 31.8, 35.8, 55.9, 64.8, 103.3. Anal. Calcd for $C_7H_{13}IO_2$: C, 32.83; H, 5.12. Found: C, 32.58; H, 5.12.

Oxepane 6i. The two diastereoisomers could not be separated by liquid chromatograghy: ^{1}H NMR (200 MHz, $CDCl_3$) δ (A−B mixture) 1.25−1.78 (m, 10H), 1.80−2.25 (m, 4H), 3.25 (m, 2H), 3.28−4.08 (m, 3H), 4.32−4.52 (m, 2H); ^{13}C NMR δ (A−Bmixture) 10.6/12.5, 23.4/23.5, 23.8/23.9, 25.0/25.1, 32.7/33.3, 33.9/34.0, 35.5/37.2, 38.6/40.0, 64.5/65.8, 73.6/74.1, 74.9/75.7, 75.8/76.9, 107.0/109.2. Anal. Calcd for $C_{13}H_{21}IO_3$: C, 44.33; H, 6.01. Found (mixture): C, 44.48; H, 6.16.

5,6-Epoxy-7-iodoheptan-1-ol (7). Only one diastereoisomer of unassigned stereochemistry was isolated (checked by GC using a 25 m CPSIL 5 column): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.40−1.70 (m, 7H), 2.82 (td, J = 2.0, 5.2 Hz, 1H), 2.98−3.07 (m, 2H), 3.21−3.30 (m, 1H), 3.68 (t, J = 5.5 Hz, 2H); ^{13}C NMR δ 12.0, 22.8, 25.9, 26.9, 68.6, 73.5, 79.3. Anal. Calcd for $C_7H_{13}IO_2$: C, 32.83; H, 5.12. Found: C, 32.98; H, 5.33.

7,8-Epoxy-9-iodo-1-nonene (8). Only one diastereoisomer of unassigned stereochemistry was isolated (checked by GC using a 25 m CPSIL 5 column): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.38−1.65 (m, 6H), 2.08 (q, J = 6.5 Hz, 2H), 2.81−2.98 (m, 1H), 3.05 (m, 2H), 3.20−3.30 (m, 1H), 4.97 (dd, J = 2.0, 10.5 Hz, 1H), 5.03 (dd, J = 2.0, 17.0 Hz, 1H), 5.81 (ddt, J = 6.5, 10.5, 17.0 Hz, 1H); ^{13}C NMR δ 4.9, 25.2, 28.4, 31.4, 33.4, 58.2, 62.4, 114.5, 139.7. Anal. Calcd for $C_9H_{15}IO$: C, 40.62; H, 5.68. Found: C, 40.88; H, 5.51.

Preparation of 6-Hepten-3-yn-1-ols 9a−d. Prepared according to ref 30. Under argon, a mixture of potassium carbonate (5.14 g, 37 mmol), Cu(I)Cl (0.123 g, 0.12 mmol), tetrabutylammonium chloride (0.734 g, 2.5 mmol), DMF (50 mL), 3-butyn-1-ol (2 mL, 27 mmol), and the desired allylic bromide was stirred for 48 h at rt. After filtration over Celite and a careful washing of the solid with ether, the filtrate was washed with brine. The aqueous phase was extracted with ether (50 mL), and the combined organic phases were dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by liquid chromatography over silica gel (hexane/ether: 70/30). The alcohols **9a−d** were obtained in the yields reported in Table 2.

6-Hepten-3-yn-1-ol (9a): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.76 (t, J = 6.0 Hz, 1H), 2.48 (tt, J = 1.0, 6.0 Hz, 2H), 2.98 (dt, J = 1.0, 6.0 Hz, 2H), 3.72 (q, J = 6.0 Hz, 2H), 5.13 (ddt, J = 2.0, 2.0, 10.5 Hz, 1H), 5.32 (ddt, J = 2.0, 2.0, 18.0 Hz, 1H), 5.84 (ddt, J = 6.0, 10.5, 18 Hz, 1H).

(*E*)-6-Octen-3-yn-1-ol (9b): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.70 (dd, J = 0.5, 6.5 Hz, 3H), 1.79 (t, J = 6.5 Hz, 1H), 2.42−2.54 (tt, J = 0.5, 6.5 Hz, 2H), 2.85−2.96 (m, 2H), 3.71 (q, J = 6.5 Hz, 2H), 5.32−5.51 (m, 1), 5.58−5.72 (m, 1H).

7-Methyl-6-octen-3-yn-1-ol (9c): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.63 (s, 3H), 1.74 (d, J = 0.5 Hz, 3H), 1.80 (t, J = 6.0 Hz, 1H), 2.46 (tt, J = 2.0, 6.0 Hz, 2H), 2.89 (dt, J = 2.0, 6.0 Hz, 2H), 3.70 (q, J = 6.0 Hz, 2H), 5.18 (tq, J = 0.5, 6.0 Hz, 1H).

6-Methyl-6-hepten-3-yn-1-ol (9d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.79 (s, 3H), 1.86 (t, J = 6 Hz, 1H), 2.50 (tt, J = 2.0, 6.0 Hz, 2H), 2.89 (m, 2H), 3.73 (q, J = 6.0 Hz, 2H), 4.82 (m, 1H), 4.99 (m, 1H).

6-Methoxy-6-hepten-3-yn-1-ol (9e). The coupling reaction between 3-butyn-1-ol and 1-bromo-2-methoxypropene[42] was conducted as reported for the preparation of alcohols **9a−d**, except than the amount of Cu(I)Cl was 1.2 mmol and the reaction time was 72 h: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.81 (t, J = 6.5 Hz, 1H), 2.49 (tt, J = 2.0, 6.5 Hz, 2H), 3.02 (m, 2H), 3.59 (s, 3H), 3.72 (q, J = 6.5 Hz, 2H), 4.0 (d, J = 2.0 Hz, 1H), 4.22 (d, J = 2.0 Hz, 1H).

3,6-Octadieyn-1-ol (9f). The coupling reaction between 3-butyn-1-ol and 1-bromo-3-butyne[43] was conducted as reported for the preparation of alcohols **9a−d** (12 h of reaction: 47% yield): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.93 (s, 1H), 1.80 (t, J = 2.5 Hz, 3H), 2.47 (tt, J = 2.5, 6.5 Hz, 2H), 3.14 (sex, J = 2.5 Hz, 2H), 3.71 (t, J = 6.5 Hz, 2H).

General Procedure for the Preparation of Dienols 10a−d,f. A suspension of 25 mg of Pd over $BaSO_4$[28] in 15 mL of pyridine was stirred under H_2 for 30 min at rt. The acetylenic alcohol (4.5 mmol) was introduced, and the mixture was stirred until 1 equiv of H_2 was absorbed. After filtration over Celite, the filtrate was neutralized with 6 N aqueous HCl. The aqueous phase was extracted with ether (3 × 20 mL), and the combined organic phases were dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by liquid chromatography over silica gel. The stereochemical purity of these compounds was checked by GC (25 m CPSIL 5 column). In all cases the stereochemistry of the 3-CC double bond was exclusively *Z*.

(3*Z*)-3,6-Heptadien-1-ol (10a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.05 (m, 1H), 2.37 (qd, J = 1.0, 6.5 Hz, 2H), 2.85 (t, J = 6.5 Hz, 2H), 3.61−3.71 (m, 2H), 5.00 (dd, J = 2.0, 8.5 Hz, 1H), 5.06 (dd, J = 2.0, 17.0 Hz, 1H), 5.38−5.71 (m, 2H), 5.85 (ddt, J = 6.5, 8.5, 17.0 Hz, 1H); MS EI *m*/*z* (rel inten) 94 (6), 79 (100), 77 (16), 67 (28), 53 (15). Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.17; H, 10.95.

(42) Jacobson, R. M.; Raths, R. A.; McDonald, J. H. *J. Org. Chem.* **1977**, *42*, 2545.

(43) Brandsma, L. *Preparation Acetylenic Chemistry*; 2nd ed.; Elsevier: Amsterdam, 1988; p 248.

(3*Z*,6*E*)-3,6-Octadien-1-ol (10b). Ten percent of the (3*Z*,6*Z*)-isomer was present, due to the isomeric purity of the commercial crotonyl chloride: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.67 (dd, J = 0.5, 6.5 Hz, 3H), 2.20 (s, 1H), 2.36 (q, J = 6.5 Hz, 2H), 2.79 (t, J = 6.5 Hz, 2H), 3.66 (t, J = 6.5 Hz, 2H), 5.32−5.66 (m, 4H); MS EI m/z (rel inten) 108 (7), 98 (21), 97 (11), 95 (23), 93 (85), 83 (13), 82 (41), 81 (38), 80 (26), 79 (37), 77 (61), 67 (100), 66 (17), 65 (17), 55 (89), 53 (44), 41 (62). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.37; H, 11.21.

(3*Z*)-7-Methyl-3,6-octadien-1-ol (10c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.38 (t, J = 6.5 Hz, 1H (OH)), 1.67 (s, 3H), 1.73 (d, J = 0.5 Hz, 3H), 2.38 (q, J = 6.5 Hz, 2H), 2.78 (t, J = 6.5 Hz, 2H), 3.68 (q, J = 6.5 Hz, 2H), 5.10 (tq, J = 0.5, 6.5 Hz, 1H), 5.30−5.65 (m, 2H); MS EI m/z (rel inten) 140 (7), 122 (5), 107 (36), 97 (14), 95 (11), 93 (18), 91 (25), 83 (14), 81 (13), 79 (39), 77 (22), 69 (34), 67 (100), 55 (66), 53 (36), 41 (66). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.91; H, 11.70.

(3*Z*)-6-Methyl-3,6-heptadien-1-ol (10d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43 (s, 1H), 1.74 (s, 3H), 2.36 (q, J = 6.5 Hz, 2H), 2.79 (d, J = 6.5 Hz, 2H), 3.66 (t, J = 6.5 Hz, 2H), 4.73 (m, 2H), 5.43−5.72 (m, 2H); MS EI m/z (rel inten) 126 (6), 111 (17), 108 (4), 95 (51), 93 (80), 91 (36), 83 (11), 82 (38), 81 (35), 80 (28), 79 (60), 77 (48), 67 (100), 55 (65), 53 (46), 41 (61). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.01; H, 11.38.

(3*Z*,6*Z*)-3,6-Octadien-1-ol (10f): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.58 (s, 1H), 1.64 (d, J = 6 Hz, 3H), 2.49 (q, J = 6.5 Hz, 2H), 2.85 (t, J = 6.5 Hz, 2H), 3.66 (t, J = 6.5 Hz, 2H), 5.28−5.67 (m, 4H); MS EI m/z (rel inten) 126 (0.5), 108 (5), 95 (15), 93 (88), 91 (40), 82 (25), 81 (25), 79 (64), 77 (51), 67 (100), 65 (20), 55 (47), 53 (26), 41 (22). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.29; H, 11.36.

(3*Z*)-6-Methoxy-3,6-heptadien-1-ol (10e). A suspension of 25 mg of Pd over $BaSO_4$ in 10 mL of hexane was stirred under H_2 for 30 min at rt. Then 4 μL of quinoline and 200 mg (1.4 mmol) of alcohol **9e** were added, and the mixture was stirred until 1 equiv of H_2 was absorbed. After filtration on a Büchner funnel, the filtrate was concentrated under vacuum, and the sensitive alcohol **10e** was used without further purification for the iodoetherification: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.77 (m, 1H), 2.38 (q, J = 6.5 Hz, 2H), 2.90 (d, J = 7.5 Hz, 2H), 3.54 (s, 3H), 3.62−3.71 (m, 2H), 3.91 (d, J = 2 Hz, 1H), 4.34 (d, J = 2 Hz, 1H), 5.46−5.72 (m, 2H).

2-(Iodomethyl)-4-oxepenene (11): ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.15−2.59 (m, 4H), 3.25 (d, J = 6 Hz, 2H), 3.40−3.56 (m, 2H), 4.11 (ddd, J = 4.0, 4.0, 12.5 Hz, 1H), 5.68−5.90 (m, 2H); ^{13}C NMR δ 10.7, 32.0, 36.6, 69.7, 79.2, 127.9, 131.1; MS EI m/z (rel inten) 238 (8), 111 (24), 97 (12), 79(21), 68 (80), 67 (100), 55 (31), 43 (41). Anal. Calcd for $C_7H_{11}IO$: C, 35.32; H, 4.66. Found: C, 35.43; H, 4.71.

(2*R,3*R**)-3-Iodo-2-(2-propenyl)tetrahydrofuran (12):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.05−1.80 (m, 2H), 2.22−3.06 (m, 2H), 3.85−3.99 (m, 2H), 4.04−4.22 (m, 1H), 4.45−4.50 (m, 1H), 5.08−5.30 (m, 2H), 5.82 (ddt, J = 6.5, 10.5, 17.0 Hz, 1H); ^{13}C NMR δ 14.1, 31.8, 39.0, 65.8, 80.8, 124.3, 133.5; MS EI m/z (rel inten) 238 (6), 197 (19), 168 (13), 111 (100), 71 (83), 70 (88), 69 (21), 55 (31). Anal. Calcd for $C_7H_{11}IO$: C, 35.32; H, 4.66. Found: C, 35.51; H, 4.80.

(2*R,3*S**)-3-Iodo-2-methyl-4-oxocene (13):** ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.88 (d, J = 7.8 Hz, 3H), 2.16−2.61 (m, 4H), 3.12 (m, 1H), 3.50 (td, J = 1.0, 10.5 Hz, 1H), 4.06−4.15 (m, 1H), 4.26 (td, J = 4.7, 8.0 Hz, 1H), 5.70−5.90 (m, 1H). A small d (J = 7.8 Hz) was detected at 1.94 for the (2*R**,3*R**) diastereoisomer; ^{13}C NMR δ 23.9, 32.0, 32.5, 34.8, 69.7, 84.0, 128.2, 130.9; MS EI m/z (rel inten) 252 (5), 125 (66), 97 (15), 82 (17), 81 (11), 68 (100), 67 (93), 57 (31), 41 (23). Anal. Calcd for $C_8H_{13}IO$: C, 38.12; H, 5.20. Found: C, 38.31; H, 5.33.

2-(1-Iodoethyl)-4-oxepene (14): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.39 (d, J = 6.0 Hz, 3H), 2.00−2.62 (m, 4H), 3.54−4.18 (m, 4H), 5.38−5.66 (m, 2H); ^{13}C NMR δ 10.7, 30.2, 32.8, 44.6, 69.7, 79.3, 126.9, 131.8; MS EI m/z (rel inten) 252 (2), 125 (9), 97 (54), 79 (21), 68 (80), 67 (100), 55 (31), 41 (29). Anal. Calcd for $C_8H_{13}IO$: C, 38.12; H, 5.20. Found: C, 37.98; H, 5.43.

(2*R,3*R**)-2-[2(*E*)-Butenyl]-3-iodotetrahydrofuran (15):** ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.68 (dd, J = 1.0, 6.3 Hz, 3H), 2.15−2.30 (m, 1H), 2.36−2.54 (m, 2H), 2.68 (ddt, J = 5.2, 8.5, 15.0 Hz, 1H), 2.93 (dt, J = 3.8, 6.3 Hz, 1H), 3.92 (dt, J = 2.5, 8.5 Hz, 1H), 4.18 (q, J = 8.5 Hz, 1H), 4.48 (m, 1H), 5.40 (dtq, J = 1.0, 6.3, 15.0 Hz, 1H), 5.67 (dq, J = 6.3, 15 Hz, 1H); ^{13}C NMR δ 18.0, 33.9, 39.0, 40.6, 66.1, 81.8, 125.9, 128.5; MS EI m/z (rel inten) 252 (1), 197 (28), 70 (100), 55 (22). Anal. Calcd for $C_8H_{13}IO$: C, 38.12; H, 5.20. Found: C, 38.28; H, 5.40.

(2*R,3*R**)-3-Iodo-2-methyl-4-oxocene (16):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.94 (d, J = 7.8 Hz, 3H), 2.10−2.60 (m, 4H), 2.92 (m, 1H), 3.50 (td, J = 1.0, 10.5 Hz, 1H), 4.05−4.20 (m, 2H), 5.78 (m, 2H); ^{13}C NMR δ 12.5, 24.9, 32.0, 36.4, 69.8, 84.0, 128.1, 130.7. Anal. Calcd for $C_8H_{13}IO$: C, 38.12; H, 5.20. Found: C, 38.51; H, 5.41.

(2*R,3*R**)-2-[2(*Z*)-Butenyl]-3-iodotetrahydrofuran (17):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.65 (d, J = 6.5 Hz, 3H), 2.10−2.75 (m, 4H), 2.88 (dt, J = 3.5, 6.5 Hz, 1H), 3.88 (m, 1H), 4.14 (m, 1H), 4.43 (m, 1H), 5.26−5.68 (m, 2H); ^{13}C NMR δ 18.2, 37.1, 39.1, 40.2, 66.1, 81.9, 125.2, 129.1; MS EI m/z (rel inten) 252 (2), 197 (30), 125 (5), 70 (100), 55 (21). Anal. Calcd for $C_8H_{13}IO$: C, 38.12; H, 5.20. Found: C, 38.42; H, 5.33.

(2*R,3*R**)-3-Iodo-2-(3-methyl-2-butenyl)tetrahydrofuran (18):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.67 (s, 3H), 1.71 (d, J = 0.5 Hz, 3H), 2.10−2.28 (m, 1H), 2.40−2.80 (m, 3H), 2.91 (dt, J = 4.0, 6.3 Hz, 1H), 3.94 (dt, J = 4.0, 8.5 Hz, 1H), 4.18 (q, J = 8.5 Hz, 1H), 4.49 (m, 1H), 5.10 (m, 1H); ^{13}C NMR δ 18.4, 25.8, 34.1, 36.3, 39.0, 66.1, 82.1, 118.8, 134.6; MS EI m/z (rel inten) 266 (4), 197 (48), 139 (5), 70 (91), 69 (100), 41 (50). Anal. Calcd for $C_9H_{15}IO$: C, 40.62; H, 5.68. Found: C, 40.51; H, 5.79.

2-(1-Iodo-4-methyl-3-pentenyl)oxetane (19): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.67 (s, 3H), 1.74 (d, J = 0.5 Hz, 3H), 2.16−2.63 (m, 4H), 3.75−4.00 (m, 3H), 4.09 (dt, J = 1.0, 6.3 Hz, 1H), 5.18 (m, 1H); ^{13}C NMR δ 18.1, 23.1, 26.0, 31.2, 38.5, 67.2, 88.3, 119.2, 134.9; MS EI m/z (rel inten) 266 (3), 197 (70), 139 (5), 69 (100), 57 (10), 41 (52). Anal. Calcd for $C_9H_{15}IO$: C, 40.62; H, 5.68. Found: C, 40.63; H, 5.82.

2-(Iodomethyl)-2-methyl-4-oxepene (20): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.36 (s, 3H), 2.38 (m, 2H), 2.57 (dq, J = 6.0, 15.0 Hz, 2H), 3.45 (AB pattern, $\Delta\nu$ = 8.5 Hz, J = 10 Hz, 2H), 3.84 (t, J = 6 Hz, 2H), 5.53−5.68 (m, 1H), 5.72−5.85 (m, 1H); ^{13}C NMR δ 17.6, 26.4, 32.9, 36.2, 62.3, 76.5, 125.3, 131.0; MS EI m/z (rel inten) 252 (1), 125 (25), 111 (4), 68 (100), 67 (38), 53 (20). Anal. Calcd for $C_8H_{13}IO$: C, 38.12; H, 5.20. Found: C, 38.30; H, 5.28.

2-(Iodomethyl)-2-methoxy-4-oxepene (21): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.16−2.90 (m, 4H), 3.24 (s, 3H), 3.36 (s, 2H), 3.76 (dt, J = 3.5, 12.5 Hz, 1H), 4.15 (ddd, J = 3.5, 11.8, 12.5 Hz, 1H), 5.43−5.74 (m, 2H); ^{13}C NMR δ 9.2, 32.5, 34.0, 47.8, 62.0, 102.9, 122.6, 130.5. Anal. Calcd for $C_8H_{13}IO_2$: C, 35.84; H, 4.89. Found: C, 35.65; H, 4.70.

7-Octen-1-ol (22a).[44] This alcohol was obtained by $LiAlH_4$ reduction in ether of 7-octenoic acid.[45]

3,3-Dimethyl-7-octen-1-ol (22b). This alcohol was obtained by $LiAlH_4$ reduction in ether of ethyl 3,3-dimethyl-7-octenoate, prepared according to ref 46 by addition of 4-penten-1-yl magnesium bromide to ethyl 3,3-dimethylacrylate in the presence of Cu(I)Cl: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (s, 6H), 1.06−1.45 (m, 4H), 1.48−1.58 (m, 3H), 2.05 (q, J = 6.5 Hz, 2H), 3.62−3.74 (m, 2H), 4.92 (dd, J = 2.0, 10.5 Hz, 1H), 5.00 (dd, J = 2.0, 17.0 Hz, 1H), 5.81 (ddt, J = 6.5, 10.5, 17.0 Hz, 1H).

7-Methyl-7-octen-1-ol (22c). Prepared as reported in ref 36: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.80−1.60 (m, 9H), 1.70 (s, 3H), 2.01 (t, J = 7.5 Hz, 2H), 3.65 (t, J = 7.5 Hz, 2H), 4.70 (m, 2H).

7-Methoxy-6-hepten-1-ol (22d). The experimental protocol reported for the preparation compound **2h** was used (similar yields): Z/E mixture 40/60; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.21−1.70 (m, 7H), 1.95 (q, J = 6.5 Hz, 12H (*E* isomer)), 2.08 (q, J = 6.5 Hz, 0.8 H (*Z* isomer)), 3.51 (s, 1.8H (*E* isomer)), 3.59 (s, 1.2H (*Z* isomer)), 4.35 (q, J = 6.5 Hz, 0.4H

(44) Cope, A. C.; Hecht, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 4872.
(45) Colonge, J.; Lasfargues, P. *Bull. Soc. Chim. Fr.* **1962**, 177.
(46) Cahiez, G.; Alami, M. *Tetrahedron Lett.* **1990**, *31*, 7425.

(*Z* isomer)), 4.71 (dt, J = 6.5, 11.0 Hz, 0.6H (*E* isomer)), 5.88 (d, J = 6.5 Hz, 0.4H (*Z* isomer)), 6.30 (d, J = 11.0 Hz, 0.6H (*E* isomer)).

(4*Z*)-(Methoxymethoxy)-4,7-octadien-1-ol (22e). Prepared in two steps from 4-pentyn-1-ol by a coupling reaction with 1-chloro-2-(methoxymethoxy)propene[47] as reported for the preparation of alcohol **9e** (28% yield) followed by a catalytic hydrogenation: under H_2 a suspension of 5% palladium over calcium carbonate (30 mg) in ethyl acetate was stirred for 20 min, and then acetylenic alcohol (0.3 g, 1.6 mmol) was added. The mixture was stirred until 1 equiv of H_2 was absorbed, and then the resulting mixture was filtered on paper. The filtrate was concentrated under vacuum and used immediately for the iodoetherification: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.67 (q, J = 6.5 Hz, 2H), 2.14−2.26 (m, 3H), 2.89 (d, J = 5.0 Hz, 2H), 3.45 (s, 3H), 3.67 (t, J = 6.5 Hz, 2H), 4.04−4.12 (m, 2H), 4.96 (s, 2H), 5.45−5.60 (m, 2H).

(*Z*)-7-Methyl-4,7-octadien-1-ol (22f). Prepared by the coupling reaction of 4-pentyn-1-ol with methallyl chloride (51% yield) as reported for the preparation of compounds **9a**−**d** followed by a catalytic hydrogenation as reported for the preparation of dienols **10a**−**d** (97% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.45 (m, 1H), 1.67 (q, J = 6.5 Hz, 2H), 1.75 (s, 3H), 2.16 (q, J = 6.5 Hz, 2H), 2.76 (d, J = 5.0 Hz, 2H), 3.67 (t, J = 6.5 Hz, 2H), 4.72 (m, 2H), 5.40−5.58 (m, 2H).

2-(Iodomethyl)oxocane (23a): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.15−1.81 (m, 10H), 3.16 (d, J = 6.0 Hz, 2H), 3.56−3.75 (m, 2H), 3.87−4.00 (m, 1H); ^{13}C NMR δ 12.3, 24.2, 26.5, 30.6, 34.2, 35.1, 69.3, 79.0; MS EI *m*/*z* (rel inten) 254 (14), 127 (25), 113 (100), 95 (35). Anal. Calcd for $C_8H_{15}IO$: C, 37.81; H, 5.95. Found: C, 37.96; H, 6.12.

6,6-Dimethyl-2-(iodomethyl)oxocane (23b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.82 (s, 3H), 0.96 (s, 3H), 1.15−2.05 (m, 8H), 3.21 (d, J = 6.3 Hz, 2H), 3.28−4.22 (m, 3H); ^{13}C NMR δ 11.5, 27.5, 28.0, 31.2, 31.8, 32.1, 39.3, 39.7, 67.7, 83.1; MS EI *m*/*z* (rel inten) 282 (8), 155 (33), 141 (100), 123 (27), 95 (23), 81 (40), 69 (83), 55 (38), 41 (67). Anal. Calcd for $C_{10}H_{19}IO$: C, 42.57; H, 6.79. Found: C, 42.72; H, 6.91.

2-(Iodomethyl)-2-methyloxocane (23c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (s, 3H), 1.40−1.96 (m, 10H), 3.25 (AB pattern, $\Delta\nu$ = 34 Hz, J = 10.5 Hz), 3.48−3.58 (m, 1H), 3.62−3.74 (m, 1H); ^{13}C NMR δ 18.1, 25.0, 25.2, 25.7, 25.9, 30.8, 30.9, 62.8, 75.5. Anal. Calcd for $C_9H_{17}IO$: C, 40.31; H, 6.39 Found: C, 40.11; H, 6.52.

2,10-Bis(iodomethyl)-2,10-dimethyl-1,9-dioxacyclohexadecane (23c′): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12−1.77 (m, 20H), 1.24 (s, 3H), 1.26 (s, 3H), 3.11−3.38 (m, 8H); ^{13}C NMR δ 17.0, 17.1, 22.9, 23.0, 24.9, 25.0, 25.4 (2C), 28.2 (2C), 28.3, 28.5, 33.9, 34.0, 59.8, 60.0, 74.1, 74.2. Anal. Calcd for $C_{18}H_{34}I_2O_2$: C, 40.31; H, 6.39 Found: C, 40.44; H, 6.58.

3-Iodo-2-methoxyoxocane (23d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28−2.10 (m, 6H), 2.10−2.45 (m, 2H), 3.40 (s, 1.8H (2*R**,3*S** isomer)), 3.45 (s, 12H (2*R**,3*R** isomer)), 3.69 (d, J = 1 Hz, 0.4H (2*R**,3*R** isomer)), 3.70−4.50 (m, 3H), 4.69 (d, J = 10.0 Hz, 0.6H (2*R**,3*S** isomer)); ^{13}C NMR δ (2*R**,3*R**/2*R**,3*S**isomers) 24.7/25.3, 26.5/27.3, 28.6/29.3, 34.7/35.1, 35.3/38.0, 54.8/55.5, 72.9/77.2, 104.6/108.5. Anal. Calcd for $C_8H_{15}IO_2$: C, 35.57; H, 5.60. Found (mixture): C, 35.72; H, 5.80.

2-(Iodomethyl)-2-[(methoxymethyl)oxy]-4-oxocene (23e): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.56−1.87 (m, 2H), 2.21 (m, 2H), 2.57 (ddd, J = 0.5, 7.6, 13.0 Hz, 1H), 2.74 (dd, J = 7.6, 13.0 Hz, 1H), 3.20 (d, J = 12.0 Hz, 1H), 3.36 (dd, J = 0.5, 12.0 Hz, 1H), 3.52 (s, 3H), 3.71 (dt, J = 3.5, 12.5 Hz, 1H), 3.90 (ddd, J = 3.5, 10.5, 12.5 Hz, 1H), 4.57 (d, J = 7.5 Hz, 1H), 4.90 (d, J = 7.5 Hz, 1H), 5.61 (dt, J = 7.6, 10.0 Hz, 1H), 5.96 (dt, J = 8.8, 10.0 Hz, 1H); ^{13}C NMR δ 9.6, 26.0, 31.5, 33.4, 57.1, 64.7, 89.6, 103.0, 124.8, 134.4; MS EI *m*/*z* (rel inten) 251 (2), 94 (16), 45 (100). Anal. Calcd for $C_{10}H_{17}IO_3$: C, 38.48; H, 5.49. Found: C, 38.78; H, 5.58.

2-(1-Iodo-3-methyl-3-butenyl)tetrahydrofuran (23f): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.76 (s, 3H), 1.87−2.18 (m, 4H), 2.56−2.76 (m, 2H), 3.69 (dt, J = 4.0, 6.5 Hz, 1H), 3.86 (dt, J = 6.3, 7.8 Hz, 1H), 4.00 (dt, J = 6.3, 7.8 Hz, 1H), 4.28 (ddd, J = 4.0, 5.5, 8.5 Hz, 1H), 4.81 (s, 1H), 4.92 (s, 1H); ^{13}C NMR δ 21.4, 25.8, 30.9, 38.8, 44.6, 68.6, 81.0, 113.2, 142.2; MS EI *m*/*z* (rel inten) 139 (30), 92 (22), 79 (21), 77 (11), 71 (100), 69 (19), 67 (16), 55 (39), 53 (13), 43 (38), 41 (45). Anal. Calcd for $C_9H_{15}IO$: C, 40.62; H, 5.68. Found: C, 40.81; H, 5.79.

Reaction of Oxepenes with Silver Trifluoroacetate. To a solution of oxepene (1.48 mmol) in methylene chloride (10 mL) was added silver trifluoroacetate (0.327 mg, 1.48 mmol). Silver iodide was immediately formed. The solid was filtered over Celite and the filtrate concentrated under vacuum. The residue was purified by liquid chromatography over silica gel.

2-Methyl-2-[[(trifluoroacetyl)oxy]methyl]-4-oxopene (24): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.53 (s, 3H), 2.10−2.51 (m, 2H), 2.65 (dd, J = 8.3, 12.5 Hz, 1H), 2.88 (dd, J = 8.3, 12.5 Hz, 1H), 3.43−3.66 (m, 2H), 3.72−4.08 (m, 2H), 5.67 (dt, J = 8.3, 10.5 Hz, 1H), 5.94 (dt, J = 7.6, 10.5 Hz, 1H); ^{13}C NMR δ 20.4, 29.5, 33.3, 61.8, 73.0, 75.4, 114.2 (q, J = 350 Hz), 127.4, 132.0, 156.6 (q, J = 50 Hz). Anal. Calcd for $C_{10}H_{13}F_3O_3$: C, 50.42; H, 5.50. Found: C, 50.61; H, 5.67.

3,5-Oxacyclooctadienyl) trifluoroacetate (25): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.61 (q, J = 0.5, 4.2 Hz, 2H), 4.21 (t, J = 4.2 Hz, 2H), 4.78 (s, 2H), 5.20 (d, J = 8.5 Hz, 1H), 5.72 (ddt, J = 0.5, 8.5, 11.0 Hz, 1H), 5.92 (dt, J = 4.2, 11.0 Hz, 1H); ^{13}C NMR δ 34.3, 68.8, 69.7, 104.5, 114.4 (q, J = 315 Hz), 122.9, 132.3, 152.1, 157.2 (q, J = 44 Hz).

5-Oxocen-3-one (26): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.40 (m, 2H), 3.41 (d, J = 7.6 Hz, 2H), 3.82 (m, 2H), 4.05 (s, 2H), 5.15 (dt, J = 7.6, 10.5 Hz, 1H), 5.94 (dt, J = 7.6, 10.5 Hz, 1H); ^{13}C NMR δ 34.2, 51.5, 67.2, 70.5, 123.9, 132.6, 158.2. Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.82; H, 8.14.

Supporting Information Available: Experimental procedures for **2a**−**k**, **3**−**5**, **9a**−**f**, and **22a**−**e** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960506T

(47) Ping Gu, X.; Ikeda, I.; Okahara, M. *Bull. Chim. Soc. Jpn* **1987**, *60*, 397.