then the ethereal layer was dried over anhydrous magnesium sulfate. After the solvent was removed, the residue was purified by column chromatography using a mixture of *n*-hexane–diethyl ether (5:1) as eluent (yield 46%).

3-Fluoro-5-heptan-2-one. A mixture of the compound (2.0 g, 10 mmol), prepared from the reaction of 4-chloro-3,4,4-trifluoro-2-butanone with sodium allyl alcoholate, and 1 N NaOH solution (20 mL) in ethanol (20 mL) was stirred at room temperature. After 1 h of stirring, the reaction mixture was acidified by 6 N HCl, and then the whole solution was stirred for 2 h at room temperature. The mixture was poured into water and oily materials were extracted with diethyl ether. The ethereal extract was dried over anhydrous magnesium sulfate. After removing the solvent, distillation gave 3-fluoro-5-heptan-2-one in 56% yield. The molecular ion (M^+, m/e 116) and other appropriate fragment peaks appeared in the mass spectrum.

4-Fluoro-5-hydroxy-1-heptene. A suspension of active fermenting bakers' yeast (Oriental Yeast Co. Ltd.) (50 g) and soluble starch (Wako's 1st grade, 75 g) in a buffer solution [600 mL, pH 7.3; prepared from $^1/_{15}$ M aqueous Na_2HPO_4 solution (460.8 mL) and $^1/_{15}$ M aqueous KH_2PO_4 solution (139.2 mL)] was stirred for 1 h at 35–36 °C in Jarfermentor (M-100, Tokyo Rikakikai Co. Ltd.). Into the mixture was added 3-fluoro-5-heptan-2-one (5 g), and then the whole mixture was stirred at 35–36 °C. After 3 days of stirring, the flocculant (200 ppm solution prepared from p-713, Dai-ichi Kogyo Seiyaku, 100 mL) was added into the stirring mixture for a few minutes. After standing for 1 h, the mixture was acidified with 1 N HCl solution, and then the precipitates were separated by filtration. The oily materials were extracted with diethyl ether. The ethereal extract was dried over anhydrous magnesium sulfate and the solvent was removed. Distillation gave 4-fluoro-5-hydroxy-1-heptene in 58% yield.

Registry No. 1 (R_1 = R^3 = Me, R_2 = H), 88100-62-3; 1 (R_1 = Me, R_2 = H, R_3 = Et), 88100-63-4; 1 (R_1 = Me, R_2 = H, R_3 = OEt), 2586-30-3; 1 (R_1 = Me, R_2 = H, R_3 = OMe), 88100-69-0; 1 (R_1 = Et, R_2 = H, R_3 = Me), 102283-24-9; 1 (R_1 = Et, R_2 = H, R_3 = Et), 102283-25-0; 1 (R_1 = Pr, R_2 = H, R_3 = Me), 102283-26-1; 1 (R_1 = Pr, R_2 = H, R_3 = Et), 102283-27-2; 1 (R_1 = Bu, R_2 = H, R_3 = Me), 102283-28-3; 1 (R_1 = Bu, R_2 = H, R_3 = Et), 102434-48-0; 2 (R_1 = Et, R_2 = H, R_3 = Me), 102283-30-7; 2 (R_1 = R_3 = Et, R_2 = H), 102283-31-8; 2 (R_1 = Pr, R_2 = H, R_3 = Me), 102283-32-9; 2 (R_1 = Pr, R_2 = H, R_3 = Et), 102283-33-0; 2 (R_1 = Bu, R_2 = H, R_3 = Me), 102283-34-1; 2 (R_1 = R^3 = Me, R_2 = H), 88100-72-5; 2 (R_1 = Me, R_2 = H, R_3 = Et), 88100-64-5; 4 (R_1 = Me, R_2 = R_3 = R_4 = R_5 = H), 102283-35-2; 4 (R_1 = R_2 = R_4 = Me, R_3 = R_5 = H), 102283-36-3; 4 (R_1 = R^3 = R_5 = Me, R_2 = R_4 = H), 102283-37-4; 4 (R_1 = Et, R_2 = R_3 = R_4 = R_5 = H), 102283-38-5; 4 (R_1 = Et, R_2 = Me, R_3 = R_4 = R_5 = H), 102283-39-6; 4 (R_1 = Et, R_2 = R_4 = H, R_3 = R_5 = Me), 102283-40-9; 4 (R_1 = Pr, R_2 = R_3 = R_4 = R_5 = H), 102283-41-0; 4 (R_1 = Bu, R_2 = R_3 = R_4 = R_5 = H), 102283-42-1; 7 (R_1 = Me, R_4 = R_5 = H), 2021-74-1; 7 (R_1 = R_5 = Me, R_4 = H), 102283-45-4; 7 (R_1 = R_4 = Me, R_5 = H), 102283-46-5; 7 (R_1 = Et, R_4 = R_5 = H), 102283-47-6; 7 (R_1 = Et, R_4 = H, R_5 = Me), 102283-48-7; 7 (R_1 = Et, R_4 = Me, R_5 = H), 102283-49-8; 7 (R_1 = Pr, R_4 = R_5 = H), 102283-50-1; 7 (R_1 = Bu, R_4 = R_5 = H), 102283-51-2; *threo*-8 (R_1 = Me, R_4 = H), 102283-52-3; *erythro*-8 (R_1 = Me, R_4 = H), 102283-53-4; *threo*-8 (R_1 = Et, R_4 = H), 102283-54-5; *erythro*-8 (R_1 = Et, R_4 = H), 102283-55-6; *threo*-8 (R_1 = Pr, R_4 = H), 102283-56-7; *erythro*-8 (R_1 = Pr, R_4 = H), 102283-57-8; *threo*-8 (R_1 = Bu, R_4 = H), 102283-58-9; *erythro*-8 (R_1 = Bu, R_4 = H), 102283-59-0; *threo*-9 (R_1 = R_3 = Me), 102283-60-3; *erythro*-9 (R_1 = R_3 = Me), 102283-74-9; *threo*-9 (R_1 = Me, R_3 = Et), 102283-62-5; *erythro*-9 (R_1 = Me, R_3 = Et), 102305-62-4; *threo*-9 (R_1 = Et, R_3 = Me), 102283-64-7; *erythro*-9 (R_1 = Et, R_3 = Me), 102283-75-0; *threo*-9 (R_1 = R_3 = Et), 102283-66-9; *erythro*-9 (R_1 = R_3 = Et), 102283-76-1; *threo*-9 (R_1 = Pr, R_3 = Me), 102283-68-1; *erythro*-9 (R_1 = Pr, R_3 = Me), 102283-77-2; *erythro*-9 (R_1 = Pr, R_3 = Et), 102283-70-5; *erytrho*-9 (R_1 = Pr, R_3 = Et), 102305-82-8; *threo*-9 (R_1 = Bu, R_3 = Me), 102283-72-7; *erythro*-9 (R_1 = Bu, R_3 = Me), 102283-78-3; 10 (R_1 = R_3 = Me), 102283-61-4; 10 (R_1 = Me, R_3 = Et), 102283-63-6; 10 (R_1 = Et, R_3 = Me), 102283-65-8; 10 (R_1 = R_3 = Et), 102283-67-0; 10 (R_1 = Pr, R_3 = Me), 102283-69-2; 10 (R_1 = Pr, R_3 = Et), 102283-71-6; 10 (R_1 = Bu, R_3 = Me), 102283-73-8; $MeC(O)CHFCO_2Et$, 1522-41-4; $EtC(O)CHFCO_2Et$, 759-67-1; *n*-$PrC(O)CHFCO_2Et$, 76435-44-4; *n*-$BuC(O)CHFCO_2Et$, 102283-29-4; $CH_2{=}C(O)CH_3$, 78-94-4; $CH_2{=}CHC(O)CH_2CH_3$, 1629-58-9; $CH_2{=}CHCO_2Et$, 140-88-5; (*E*)-$CH_3CH{=}CHCO_iMe$, 623-43-8; $MeC(O)CHFCF_2Cl$, 684-05-9; $EtC(O)CHFCF_2Cl$, 102283-43-2; *n*-$PrC(O)CHFCF_2Cl$, 76435-55-7; *n*-$BuC(O)CHFCF_2Cl$, 102283-44-3; $CH_2{=}CHCH_2OH$, 107-18-6; (*E*)-$CH_3CH{=}CHCH_2OH$, 504-61-0; $CH_2{=}CHCH(OH)CH_3$, 598-32-3; ethyl α-acetyl-α-fluoro-3-oxocyclohexaneacetate, 88100-70-3; 3-(1-fluoro-2-oxoprpyl)cyclohexanone, 102283-79-4; cyclohex-2-en-1-one, 930-68-7.

Synthesis of Polyether-Type Tetrahydrofurans via Hydroperoxide Cyclization

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Isomerization of an unsaturated hydroperoxy ester to the epoxy alcohol and thence to the tetrahydrofuran, as depicted in Scheme I, was investigated as a method for the stereocontrolled construction of ethers with a substitution pattern appropriate for polyether synthesis. This sequence is highly stereoselective in the case of the secondary hydroperoxides **11**, both with respect to the tetrahydrofuran stereochemistry as well as the acyclic relationship. With tertiary hydroperoxides (**18**, **21**, or **28**), little stereocontrol is seen over the ring stereochemistry. In the case of **28**, for example, the trans,cis and trans,trans bis ethers **29c** and **29t** are formed in a 1.4:1 ratio. Tertiary hydroperoxide **28** can be generated stereospecifically from **27mb** by a ring contraction process; however, when this method is applied in the related secondary system **27hi**, hydroperoxytetrahydropyran **31** is the major product. Cyclization of **31** affords a mixture of the fused bis ether isomers **32** and **33**.

The stereocontrolled construction of α,α′-substituted tetrahydrofurans and -pyrans is a necessary element in synthetic approaches to polyether natural products such as nigericin (**1**) and septamycin (**2**). Whereas the cyclization of olefinic hydroxyl compounds is a straightforward way to generate cyclic ethers, in a number of instances more complex strategies must be employed to ensure the desired sense and degree of stereocontrol.[1] A goal of our

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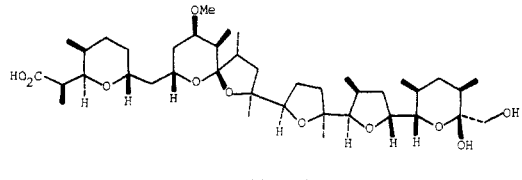
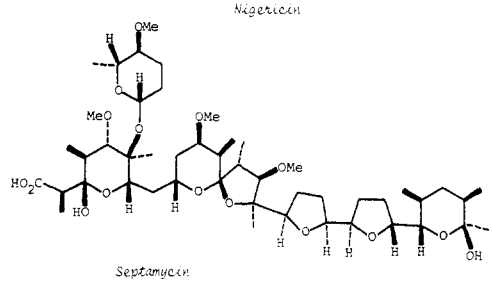


Nigericin



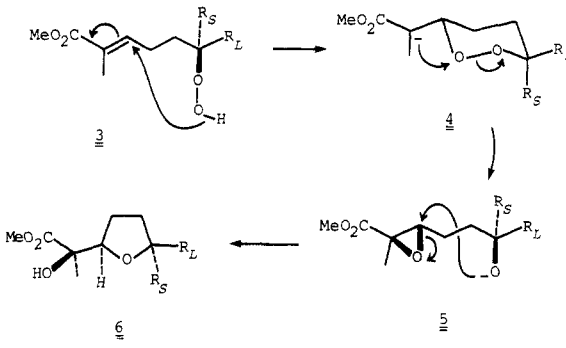
Septamycin

research in this area has been the development of a repertoire of reactions that allow the formation of polyether-type structures by sequential cyclization reactions with relative asymmetric induction or "linear stereocontrol".[2] We now describe an investigation of the intramolecular epoxidation and subsequent cyclization of ϵ-hydroperoxy-α,β-unsaturated esters as a method for synthesis of *cis*-α,α'-substituted tetrahydrofurans (Scheme I). We have also coupled this sequence with our previously reported method for the synthesis of *trans*-2,5-disubstituted tetrahydrofurans[2c] in order to prepare bis tetrahydrofurans with the nigericin- and septamycin-type substitution pattern.

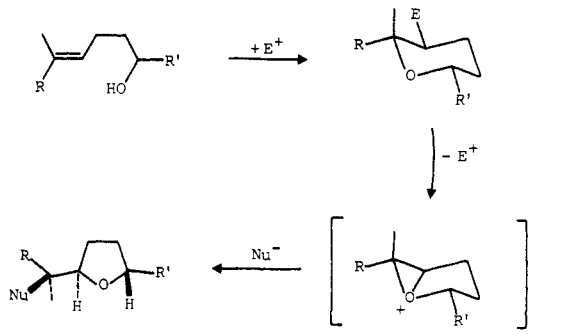
Three elements in the sequence depicted in Scheme I were important to ascertain. First was the degree of relative asymmetric induction that can be obtained in the intramolecular oxygen transfer. This epoxidation process determines the cis/trans stereochemistry of the resulting tetrahydrofuran ring. Second was the fidelity with which the stereochemistry of the double bond is preserved in the epoxidation, since this in turn controls the configuration of the side-chain stereocenter. Finally, a stereocontrolled method for introduction of the hydroperoxide itself was required in order to apply the strategy to the sequential elaboration of a polyether.

With respect to the first point, we envisaged that intramolecular delivery of the epoxide oxygen via a 1,2-dioxane intermediate would favor the syn stereochemistry and, thus, formation of the cis substituted tetrahydrofuran. The chair-like conformation of 3,6-*trans*-disubstituted-1,2-dioxanes has been confirmed by crystallography,[3] and Porter[4] and Bloodworth[5] and their co-workers have shown that the *trans*-diequatorial stereochemistry is favored in electrophilic cyclizations. The transformation of a 1,2-dioxane into an epoxy alcohol and thence to the (hydroxyalkyl)tetrahydrofuran is also precedented, either by radical[4] or ionic pathways. Indeed, base treatment of the

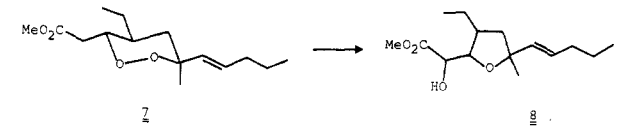
Scheme I



Scheme II



marine natural product plakortin (**7**) results in ring contraction analogous to that proposed in Scheme I.[6]



Cyclization of Secondary Hydroperoxides 11t and 11c. The secondary benzylic hydroperoxide **11t** is formed on solvolysis of the corresponding bromide **10t**[7] with silver trifluoroacetate and 90% hydrogen peroxide. This hydroperoxide can be isolated in 91% yield after chromatographic purification on silica gel. On treatment of **11t** with sodium hydride in THF, the desired sequence of transformations ensues, and a single product, **12ce**, is isolated in >98% yield. The 250-MHz ^{1}H NMR analysis of the crude product revealed less than 1% of isomeric material, indicating that both of the new stereocenters are generated with a high degree of fidelity. An authentic mixture of the cis and trans isomers, **12ce** and **12te**, both of which have the erythro relationship between the vicinal stereocenters, was prepared by peracid epoxidation of the alcohol **9t** and cyclization of the epoxide **13t**.[8] That one of the isomers from this transformation proved to be identical with the

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(2) For previously reported methods, see: (a) Rychnovsky, S. D.; Bartlett, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3963. (b) Bartlett, P. A.; Holmes, C. P. *Tetrahedron Lett.* **1983**, *24*, 1365. (c) Ting, P. C.; Bartlett, P. A. *J. Am. Chem. Soc.* **1984**, *106*, 2668. (d) Michael, J. P.; Ting, P. C.; Bartlett, P. A. *J. Org. Chem.* **1985**, *50*, 2416. (e) Bartlett, P. A.; Holm, K. H.; Morimoto, A. *J. Org. Chem.* **1985**, *50*, 5179. (f) Bartlett, P. A.; Ting, P. C. *J. Org. Chem.*, in press.

(3) Porter, N. A.; Roe, A. N.; McPhail, A. T. *J. Am. Chem. Soc.* **1980**, *102*, 7574–7576. Piccinni-Leopardi, C.; Germain, G.; Van Meerssche, M.; Albericci, M.; Braekman, J. C ; Daloze, D.; Tursch, B. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1523–1526.

(4) Porter, N. A.; Zuraw, P. J. *J. Org. Chem.* **1984**, *49*, 1345–1348; Nixon, J. R.; Cudd, M. A.; Porter, N. A. *Ibid.* **1978**, *43*, 4048–4052.

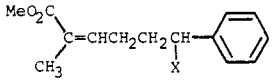
(5) Bloodworth, A. J.; Khan, Jamil A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2450–2457. Bloodworth, A. J.; Loveitt, M. E. *Ibid.* **1978**, 552–530.

(6) Higgs, M. D.; Faulkner, D. J. *J. Org. Chem.* **1978**, *43*, 3454. For reports of other marine natural products with 1,2-dioxane structures, see: Capon, R. J.; MacLeod, J. K. *Tetrahedron* **1985**, *41*, 3391–3404. Manes, L. V.; Bakus, G. J.; Crews, P. *Tetrahedron Lett.* **1984**, *25*, 931–934. Phillipson, D. W.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 7735–7736. Albericci, M.; Braekman, J. C.; Daloze, D.; Tursch, B. *Tetrahedron* **1982**, *38*, 1881–1890. Piccinni-Leopardi, C.; Germain, G.; Van Meersche, M.; Albericci, M.; Braekman, J. C.; Daloze, D.; Tursch, B. *J. Chem. Soc., Perkin Trans. 2*, **1982**, 1523–1526. Stierle, D. B.; Faulkner, D. J. *J. Org. Chem.* **1980**, *45*, 3396–3401. Albericci, M.; Collart-Lempereur, M.; Braekman, J. C.; Daloze, D.; Tursch, B.; DeClercq, J. P.; Germain, G.; Van Meersche, M. *Tetrahedron Lett.* **1979**, 2687–2690. Kashman, Y.; Rotem, M. *Ibid.* **1979**, 1707–1708.

(7) Preparation of this compound is described in the supplementary material.

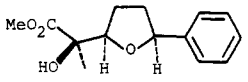
(8) House, H. O.; Ro, R. S. *J. Am. Chem. Soc.* **1958**, *80*, 2428. Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. *Ibid.* **1959**, *81*, 108. Keane, D. D.; O'Sullivan, W. I.; Philbin, E. M.; Simons, R. M.; Teague, P. C. *Tetrahedron* **1970**, *26*, 2533.

product from the hydroperoxide cyclization demonstrated that the trans geometry of the double bond is preserved during the intramolecular epoxidation sequence. Moreover, with both cis and trans isomers in hand, the ring stereochemistry could be assigned by NMR. Unambiguous evidence for the cis stereochemistry of **12ce** was provided by observation of an interaction between the two α-protons (H_A and H_B below) in a difference nuclear Overhauser enhancement experiment.

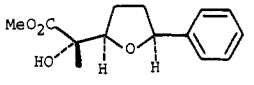


9: X = OH
10: X = Br
11: X = OOH

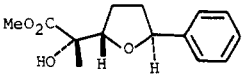
t: E-isomer c: Z-isomer



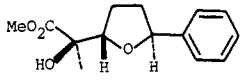
12ce



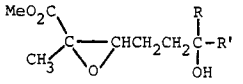
12ct



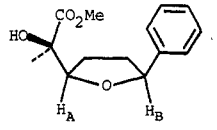
12te



12tt



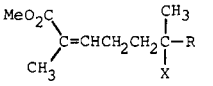
13: R = H, R' = Ph
14: R = Me, R' = Ph
15: R = Me, R' = iBu



12ce

We considered two explanations for the high selectivity seen in generation of the erythro vicinal stereochemistry: (1) oxygen transfer from the hydroperoxide is stereospecific and there is no rotation around the C_α–C_β bond in enolate **4** before closure to the epoxide or (2) strong thermodynamic preference for formation of the trans epoxide is manifested even in the presence of such rotation. To settle this question, we prepared and cyclized the corresponding cis olefinic hydroperoxide, **11c**. Again, a single product was obtained in nearly quantitative yield, and it proved to be the threo diastereomer **12ct**. Thus, closure of enolate **4** to form the epoxide **5** must be considerably faster than rotation about the C_α–C_β bond. This is in contrast to intermolecular alkaline epoxidation of acyclic unsaturated carbonyl compounds, which is not stereospecific.[8] As in the case of the erythro isomer **12ce**, the stereochemistry of **12ct** was proven by synthesis and NMR analysis of the mixture **12ct**/**12tt**.

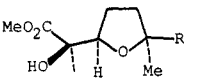
Cyclization of Tertiary Hydroperoxides. Having demonstrated the basic elements of the sequence, we were interested in applying it to the cyclization of a tertiary hydroperoxide, with the hope that it would be useful for generating *cis*-2,2,5-trisubstituted-tetrahydrofurans with the substitution pattern of the nigericin C-ring. Accordingly, we prepared the tertiary benzylic and tertiary alkyl bromides **17t**[8] and **20t**[8] and converted them into the corresponding hydroperoxides **18t** and **21t** in 73% and 90% yield, respectively. In contrast to the results observed with the secondary hydroperoxides **11**, cyclization of **18t** and **21t** with sodium hydride in THF shows poor selectivity, affording a 1.4/1 mixture of stereoisomers in each instance. That **22** and **23** are produced as cis/trans as opposed to erythro/threo isomers was demonstrated in these cases by cyclization of the epoxides **14t**[8] and **15t**.[8] The cis isomers **18c** and **21c** were also prepared and cyclized, giving mixtures of **22ct**/**22tt** and **23ct**/**23tt** in similar ratios.



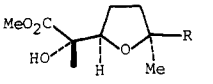
R = Ph R = iBu

16 X = OH 19
17 X = Br 20
18 X = OOH 21

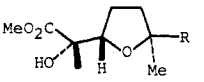
t: E-isomer c: Z-isomer



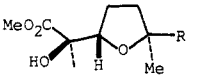
ce



ct



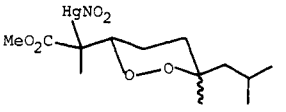
te



tt

22: R = Ph 23: R = iBu

We explored a variety of conditions and alternative methods in an attempt to improve the selectivity of these cyclizations. Initiating the reaction of hydroperoxide **21** with sodium hydride in THF at −78 °C with slow warming to room temperature increased the ratio of product isomers only to 1.7/1; variation in cation (Li or K) or solvent (ether, ethanol) offered no improvement. The transformation can be carried out in a stepwise fashion by generating the dioxane intermediate **24** with mercuric nitrate in aceto-



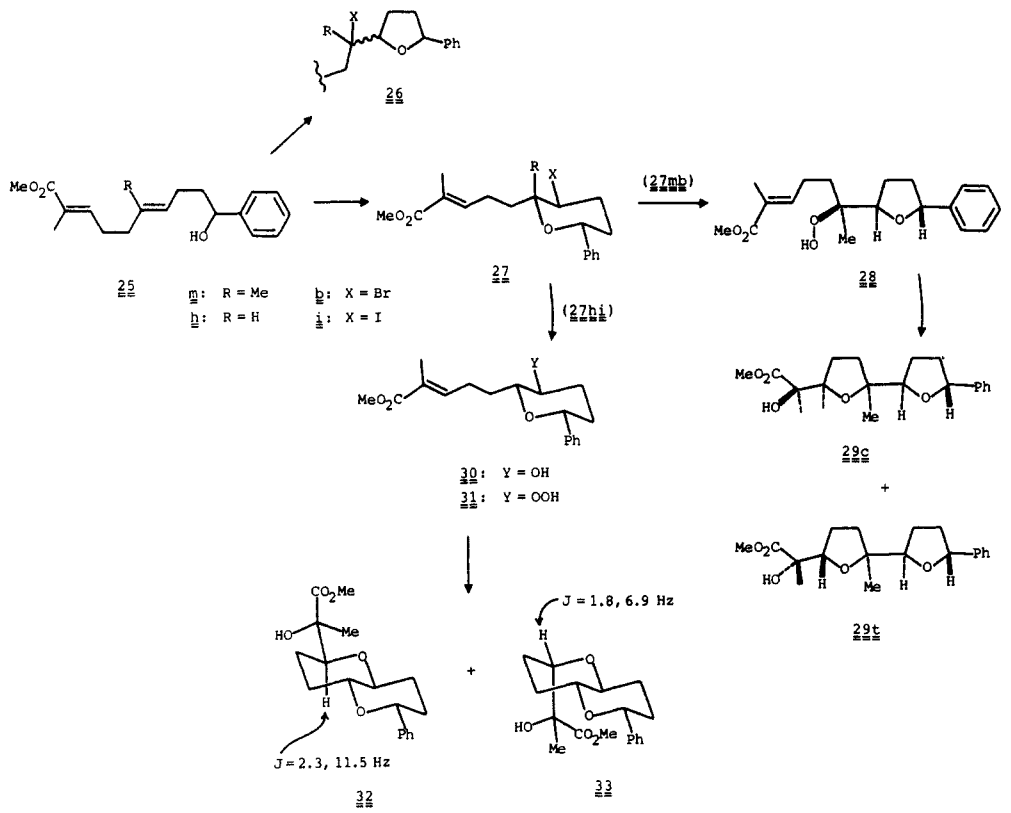
24

nitrile (97% crude yield) and subsequently reducing the organomercurial with sodium sulfide (46% overall yield). No improvement in selectivity results, however. The modest selectivity in the cyclization of these tertiary hydroperoxides is not unexpected in view of the special interplay between geminal alkyl and phenyl substituents in cyclohexyl systems[9] and of the small difference in *A*-values for methyl and isobutyl groups.[10] Although differences in the high field ^1H and ^{13}C NMR spectra can be discerned for the stereoisomers of **22** and **23**, we were not able to interpret them unambiguously and assign the cis and trans stereochemistry with confidence. Generation of a hydroperoxide with a substitution pattern more relevant to the polyether targets was therefore required.

Synthesis of Bis Tetrahydrofurans by Sequential Cyclization/Ring Contraction and Intramolecular Epoxidation/Cyclization. We recently reported a method for stereospecific formation of *trans*-2,5-disubstituted-tetrahydrofurans via an electrophilic cyclization/ring contraction sequence (Scheme II).[2c,d] To couple the hydroperoxide cyclization with this transformation requires

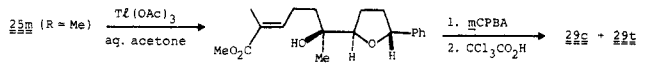
(9) Allinger, N. L.; Tribble, M. T. *Tetrahedron Lett.* **1971**, 3259. Shea, K. J.; Dougherty, T. K. *J. Org. Chem.* **1985**, *50*, 4439. Hodgson, D. J.; Rychlewska, U.; Eliel, E. L.; Manoharan, M.; Knox, D. E.; Olefirowicz, E. M. *Ibid.* **1985**, *50*, 4838.

(10) Gordon, A. J.; Ford, R. A. *The Chemists Companion*; Wiley-Interscience, New York, 1972; p 156.



(1)

Scheme III

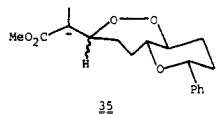


only that the oxiranium ion (or carbocation) intermediate in the ring contraction step be trapped stereospecifically with hydrogen peroxide.

Accordingly, the dienol **25m**[8] was prepared and cyclized with 2,4,4,6-tetrabromocyclohexadienone (TBCO)[2c] to give the tetrahydropyran **27mb** in 56% yield, accompanied by 14% of a mixture of equal amounts of the cis and trans tetrahydrofurans **26mb** (eq 1). Ring contraction of **27mb** with silver trifluoroacetate in the presence of 90% hydrogen peroxide proceeds in the desired manner, affording the tertiary hydroperoxide **28** in 68% yield after chromatographic purification. Unfortunately, cyclization of this material under the standard conditions (NaH/THF/0 °C) affords only a 1.4/1 mixture of cis and trans isomers **29c** and **29t**. To confirm our stereochemical assignment and to demonstrate that the loss of stereocontrol had indeed occurred during the second cyclization step, we synthesized an authentic sample of **29c** and **29t** by the route shown in Scheme III. Nevertheless, our assignment of the cis structure **29c** to the major isomer from the hydroperoxide cyclization remains tentative in the absence of unambiguous spectral differences.

To determine whether, finally, the hydroperoxide cyclization could be employed to advantage in the synthesis of a *cis*-2,5-disubstituted-tetrahydrofuran in a polyether-type environment, we prepared the dienol **25h**[8] as a model for the septamycin BC-rings. The intended cyclization/ring contraction in this instance represents a departure from our previous study,[2c] since the disubstituted double bond of **25h** has no orientational effects to control the regiochemistry of either the cyclization or the solvolysis. Indeed, the major product from treatment of **25h** with TBCO is the mixture of tetrahydrofurans **26hb**. However, the desired tetrahydropyran **27hi** can be obtained in 44% yield with iodine in acetonitrile;[11] a 1:1 mixture of the tetrahydrofurans **26hi** constitutes 32% of the product in this case. However, solvolysis of **27hi** with silver trifluoroacetate does not proceed with ring contraction as required, rather the hydroxy- and hydroperoxytetrahydropyrans **30** and **31** are formed as the major products under aqueous conditions or in the presence of 90% hydrogen peroxide, respectively. Distinction between the five- and six-membered ether structures is readily made on the basis of their appearance in the ^{1}H NMR and mass spectra and comparison with the halotetrahydropyrans and -furans **26h** and **27h**.

Cyclization of **31** via the intramolecular epoxidation process or of **30** via conventional epoxidation affords a 1:1 mixture of the fused bicyclic diethers **32** and **33**. The lack of stereoselectivity in the former case may be attributed to the lack of discrimination in cyclization to the seven-membered intermediate **35**. The stereochemistry of the



two isomers was readily assigned on the basis of the different coupling constants observed for the designated hydrogens. This assignment was corroborated by the different rates at which the diastereomeric epoxides of **30** undergo acid-catalyzed cyclization; that leading to the congested axial isomer **33** is consumed much more slowly that its diastereomer.

Conclusion

The intramolecular epoxidation process described above can be highly stereoselective with certain substrates. However, it would not appear to have a straightforward

(11) Bartlett, P. A.; Myerson, J. *J. Am. Chem. Soc.* **1978**, *100*, 3950–3952.

application to polyether natural products of the type indicated in the introduction.

Experimental Section

General Methods. IR and NMR spectra were obtained in $CDCl_3$ solution; NMR spectral data are presented as follows: chemical shift (relative to internal tetramethylsilane as 0 ppm) (multiplicity, number of protons, coupling constants in hertz). Unless otherwise indicated, all NMR spectra were recorded at 250 MHz for ^1H NMR and 51 MHz for ^{13}C NMR. All reaction workups culminated in washing the organic layer with brine, drying over $MgSO_4$, and evaporation under reduced pressure on a rotary evaporator. Chromatography was performed on silica gel according to the method of Still.[12]

Note: Synthesis and characterization of many of the starting materials is described in the supplementary material.

General Procedure for Preparation of Hydroperoxides. Methyl 6-Hydroperoxy-2-methyl-6-phenyl-2(*E*)-hexenoate (11t). Silver trifluoroacetate (345 mg, 1.16 mmol) was added in small portions to a solution of 310 mg (1.04 mmol) of bromide **10t** and 410 mg (10.8 mmol) of 90% hydrogen peroxide in 5 mL of THF at 0 °C. After 2 h, the mixture was filtered through Celite, and the filtrate was washed with aqueous $NaHCO_3$ to remove the excess HOOH. After extraction with ether, workup gave a colorless oil; this material had a peroxide content of 88% by iodometric titration, performed according to the method of Siggia.[13] Final purification by chromatography (30% EtOAc/hexane) afforded 239 mg (91% yield) of the pure hydroperoxide **11t**: IR 1260, 1720, 2960, 3410 cm^{-1}; ^1H NMR (250 MHz) δ 1.78 (s, 3), 1.9–2.3 (m, 4), 3.72 (s, 3), 4.9 (t, 1, J = 6.9), 6.73 (t, 1, J = 7), 7.3–7.4 (m, 5), 8.05 (s, 1). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.86; H, 7.31.

The following compounds were prepared in a similar manner.

Methyl 6-hydroperoxy-2-methyl-6-phenyl-2(*Z*)-hexenoate (11c): 97% yield from **10c** after purification; peroxide content of 88% by iodometric titration; IR 1260, 1720, 2960, 3410 cm^{-1}; ^1H NMR δ 1.8–2.1 (m, 2), 1.89 (s, 3), 2.5 (q, 2, J = 6.8), 3.7 (s, 3), 4.92 (t, 1, J = 6.8), 5.92 (t, 1, J = 8.1), 7.3–7.4 (m, 5), 8.25 (br s, 1). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.99; H, 7.25.

Methyl 2,6-dimethyl-6-hydroperoxy-6-phenyl-2(*E*)-hexenoate (18t): reaction time of 30 min; 88% yield from **17t** after chromatography (20% EtOAc/hexane); 83% peroxide content by titration; IR 910, 1265, 1720, 2960, 3460 cm^{-1}; ^1H NMR δ 1.65 (s, 3), 1.74 (s, 3), 1.8–2.2 (m, 4), 3.7 (s, 3), 6.69 (t, 1, J = 7.2), 7.2–7.5 (m, 5), 7.81 (br s, 1). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.45; H, 7.66.

Methyl 2,6-dimethyl-6-hydroperoxy-6-phenyl-2(*Z*)-hexenoate (18c): 99% yield from **17c** after chromatography (20% EtOAc/hexane); 77% peroxide content by titration; IR 910, 1265, 1720, 2960, 3460 cm^{-1}; ^1H NMR δ 1.57 (s, 3), 1.86 (s, 3), 1.9–2.2 (m, 2), 2.42 (q, 2, J = 7.6), 3.69 (s, 3), 6.02 (t, 1, J = 8.9), 7.2–7.6 (m, 5), 8.74 (br s, 1). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.93; H, 7.75.

Methyl 6-hydroperoxy-2,6,8-trimethyl-2(*E*)-nonenoate (21t): 98% crude yield from **20t**, used in the next step without purification; 92% peroxide content by iodometric titration; IR 910, 1285, 1440, 1650, 1720, 2960, 3420 cm^{-1}; ^1H NMR δ 0.925 (d, 3, J = 6.6), 0.94 (d, 3, J = 6.6), 1.19 (s, 3), 1.4–1.8 (m, 5), 1.82 (s, 3), 2.2 (m, 2), 3.7 (s, 3), 6.75 (t, 1, J = 7.5), 7.62 (br s, 1). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.88; H, 9.90. Found: C, 61.32; H, 9.78.

Methyl 6-Hydroperoxy-2,6,8-trimethyl-2(*Z*)-nonenoate (21c). The crude hydroperoxide **21c** (90% yield) was purified on silica gel (30% EtOAc/hexane) (48% yield) and tritrated (95% peroxide content): IR 910, 1285, 1440, 1650, 1720, 2960, 3420 cm^{-1}; ^1H NMR δ 0.94 (d, 3, J = 6.6), 0.99 (d, 3, J = 6.6), 1.19 (s, 3), 1.3–1.9 (m, 5), 1.90 (s, 3), 2.45 (m, 2), 3.74 (s, 3), 6.11 (t, 1, J = 8.3), 8.9 (br s, 1). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 64.26; H, 9.77.

General Cyclization Procedure. Methyl (α*RS*,2*RS*,5*SR*)-α-Hydroxy-α-methyl-5-phenyl-2-tetrahydrofuranacetate (12ce) and the α*RS*,2*RS*,5*RS* Diastereomer (12te). Via Epoxide Cyclization. A 0.02 M solution of trichloroacetic acid in CH_2Cl_2 (3.84 mL, 0.077 mmol) was added to 64 mg (0.26 mmol) of the mixture of epoxides **13t**. After 6 h at 21 °C, 10 mL of CH_2Cl_2 was added and the mixture was washed with 10% NaOH and worked up to give 62 mg (97%) of a 1:1 mixture of **12ce** and **12te** as a colorless oil.

Via Hydroperoxide Cyclization. The hydroperoxide **11t** (175 mg, 0.7 mmol) in 1.5 mL of THF was slowly added at 0 °C to a suspension of NaH (34 mg, 50%, 0.71 mmol) in 2 mL of THF. After 5 min, only the epoxide was discernible by TLC; this material cyclized at 0 °C over a 4-h period. The solution was diluted with 10 mL of ether and extracted with 10% NaOH. The basic aqueous layer was washed with ether, acidified with concentrated HCl, and extracted with CH_2Cl_2. Workup afforded an acid which was esterified with excess diazomethane to give 149 mg (85% crude yield) of **12ce** as an oil which proved to be a single diastereomer (>99%) according to high field NMR analysis. Purification of this material on silica gel (10% EtOAc/hexane) provided an analytical sample (110 mg, 63% purified yield): IR 910, 1740, 2960, 3540 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.97; H, 7.34.

12ce: ^1H NMR (500 MHz) δ 1.515 (s, 3), 1.8 (m, 1), 2.05 (m, 2), 2.25 (m, 1), 3.1 (br s, 1, D_2O-exchangeable), 3.774 (s, 3), 4.2 (dd, 1, J = 6.1, 8.05), 4.86 (dd, 1, J = 6.32, 8.86), 7.2–7.4 (m, 5); ^{13}C NMR (125.8 MHz) δ 22.57, 26.85, 34.48, 52.56, 76.48, 81.53, 83.80, 125.76, 127.30, 128.3, 129.66, 141.96, 175.05.

12te: ^1H NMR δ 1.528 (s, 3), 1.85 (m, 1), 2.05 (m, 2), 2.35 (m, 1), 3.1 (br s, 1, D_2O-exchangeable), 3.8 (s, 3), 4.36 (t, 1, J = 7.4), 5.00 (dd, 1, J = 5.95, 8.56), 7.2–7.4 (m, 5); ^{13}C NMR (50.8 MHz) δ 23.04, 26.96, 35.37, 52.70, 76.61, 81.73, 83.95, 125.90, 126.13, 127.44, 128.55, 142.80, 175.17.

The following compounds were prepared in a similar manner.

Methyl (α*RS*,2*SR*,5*RS*)-α-Hydroxy-α-methyl-5-phenyl-2-tetrahydrofuranacetate (12ct) and the α*RS*,2*SR*,5*SR* Diastereomer (12tt). Epoxide cyclization: as a 1:1 mixture of **12ct** and **12tt** (98% yield) in 8 h from the diastereomeric mixture of epoxides **13c**. **Hydroperoxide cyclization**: as a single isomer (**12ct**, high field NMR analysis) in 72% yield after purification by chromatography (10% EtOAc/hexane): IR 910, 1740, 2960, 3540 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.11; H, 7.25.

12ct: mp 62–65 °C; ^1H NMR (500 MHz) δ 1.386 (s, 3), 1.85 (m, 1), 2.05 (m, 1), 2.15 (m, 1), 2.25 (m, 1), 3.2 (br s, 1, D_2O-exchangeable), 3.811 (s, 3), 4.286 (dd, 1, J = 8.0, 5.95), 4.866 (dd, 1, J = 8.7, 6.44), 7.2–7.4 (m, 5); ^{13}C NMR (50.8 MHz) δ 21.99, 25.80, 34.48, 52.90, 75.95, 76.28, 81.60, 83.53, 125.68, 127.33, 128.34, 142.34, 176.11.

12tt: ^1H NMR δ 1.35 (s, 3), 1.85 (m, 1), 2.05 (m, 1), 2.15 (m, 1), 2.4 (m, 1), 3.824 (s, 3), 4.438 (dd, 1, J = 8.2, 6.73), 5.05 (dd, 1, J = 8.25, 6.0), 7.2–7.4 (m, 5); ^{13}C NMR (125.8 MHz) δ 21.43, 25.74, 35.36, 52.89, 75.95, 76.28, 81.56, 83.48, 125.47, 127.16, 128.24, 142.36, 176.4.

Methyl (α*RS*,2*RS*,5*SR*)-α-Hydroxy-α,5-dimethyl-5-phenyl-2-tetrahydrofuranacetate (22ce) and the α*RS*,2*RS*,5*RS* Diastereomer (22te). Epoxide cyclization: 92% yield as a 1:1 mixture of **22ce** and **22te** from the diastereomeric epoxides **14t**. **Hydroperoxide cyclization**: as a 1.3:1 mixture of isomers in 73% yield from **18t**: IR 1070, 1265, 1455, 1740, 2965, 3550 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.14; H, 7.33.

Major isomer: ^1H NMR (500 MHz) δ 1.49 (s, 3), 1.50 (s, 3), 1.75 (m, 1), 2.0 (m, 2), 2.1 (m, 1), 3.1 (br s, 1, D_2O-exchangeable), 3.645 (s, 3), 4.28 (t, 1, J = 7.2), 7.2–7.45 (m, 5); ^{13}C NMR δ 21.74, 25.76, 28.09, 38.21, 51.51, 75.51, 82.66, 84.13, 123.57, 125.45, 127.03, 127.03, 127.32, 146.84, 173.90.

Minor isomer: ^1H NMR (500 MHz) δ 1.49 (s, 3), 1.50 (s, 3), 1.75 (m, 1), 2.0 (m, 2), 2.2 (m, 1), 3.2 (br s, 1, D_2O-exchangeable), 3.78 (s, 3), 4.14 (dd, 1, J = 6.05, 7.7), 7.2–7.45 (m, 5); ^{13}C NMR δ 21.74, 25.54, 29.08, 38.21, 51.51, 75.65, 82.47, 84.41, 123.51, 125.45, 127.17, 127.59, 146.59, 174.98.

Methyl (α*RS*,2*SR*,5*RS*)-α-Hydroxy-α,5-dimethyl-5-phenyl-2-tetrahydrofuranacetate (22ct) and the α*RS*,2*SR*,5*SR* Diastereomer (22tt). Epoxide cyclization: as a mixture of **22ct** and **22tt** in 91% yield from the 1:1 diastereomeric mixture of epoxides **14c**. **Hydroperoxide cyclization**: as

(12) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(13) Siggia, S. *Quantitative Analysis via Functional Groups*; Wiley: New York, 1949; p 100.

a 1.1:1 mixture of isomers in 57% yield from **18c** after chromatography (10% EtOAc/hexane): IR 1265, 1455, 1740, 2965, 3550 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.90; H, 7.63.

Major isomer: ^1H NMR (500 MHz) δ 1.34 (s, 3), 1.49 (s, 3), 1.8 (m, 1), 2.07 (m, 2), 2.11 (m, 1), 3.0 (br s, 1, D_2O-exchangeable), 3.86 (s, 3), 4.225 (t, 1, J = 6.9), 7.2–7.4 (m, 5); ^{13}C NMR δ 21.39, 25.40, 29.38, 30.36, 39.28, 52.76, 76.04, 83.06, 85.31, 124.42, 126.46, 128.15, 128.31, 176.1.

Minor isomer: ^1H NMR (500 MHz) δ 1.33 (s, 3), 1.44 (s, 3), 1.8 (m, 1), 2.07 (m, 2), 2.11 (m, 1), 3.0 (br s, 1, D_2O-exchangeable), 3.86 (s, 3), 4.225 (t, 1, J = 6.9), 7.2–7.4 (m, 5); ^{13}C NMR δ 21.39, 25.36, 29.38, 30.27, 38.75, 52.76, 75.40, 82.96, 85.31, 124.5, 126.42, 128.23, 128.31, 176.1.

Methyl (α*RS*,2*RS*,5*SR*)-α-Hydroxy-α,5-dimethyl-5-(2-methylpropyl)-2-tetrahydrofuranacetate (23ce) and the α*RS*,2*RS*,5*RS* Diastereomer (23te). Epoxide cyclization: as a 1:1 mixture of **23ce** and **23te** in 94% yield (after chromatography) from the 1:1 diasteromeric mixture of epoxides **15t**. **Hydroperoxide cyclization**: 82% yield from **21t** as a 1.4:1 mixture of diastereomers by high field ^1H NMR: IR 1260, 1740, 2970, 3550 cm^{-1}. Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 63.55; H, 10.04.

Major isomer: ^1H NMR (500 MHz) δ 0.908 (d, 3, J = 6.65), 0.955 (d, 3, J = 6.65), 1.175 (s, 3), 1.43 (s, 3), 1.35–2.0 (m, 7), 3.11 (s, 1, D_2O-exchangeable), 3.77 (s, 3), 4.075 (t, 1, J = 7.1); ^{13}C NMR (125.8 MHz) 23.00, 24.06, 24.35, 24.63, 24.76, 26.47, 37.77, 50.21, 52.36, 76.075, 82.41, 84.39, 174.87.

Minor isomer: ^1H NMR (500 MHz) δ 0.916 (d, 3, J = 6.6), 0.952 (d, 3, J = 6.6), 1.168 (s, 3), 1.434 (s, 3), 1.35–2.0 (m, 7), 3.13 (s, 1, D_2O-exchangeable), 3.77 (s, 3), 4.01 (dd, 1, J = 6.2, 8.5); ^{13}C NMR δ 22.89, 24.19, 24.34, 24.41, 24.64, 24.73, 38.14, 49.40, 52.42, 76.45, 83.28, 84.18, 174.67.

Methyl (α*RS*,2*SR*,5*RS*)-α-Hydroxy-α,5-dimethyl-5-(2-methylpropyl)-2-tetrahydrofuranacetate (23ct) and the α*RS*,2*SR*,5*SR* Diastereomer (23tt). Epoxide cyclization: as a 1:1 mixture of **23ct** and **23tt** (86% yield) from the mixture of epoxides of **15c**. **Hydroperoxide cyclization**: as a 1.4:1 mixture of isomers (81% yield) from hydroperoxide **21c**: IR 1738, 2960, 3550 cm^{-1}. Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 63.71; H, 9.97.

Major isomer: ^1H NMR (500 MHz) δ 0.883 (d, 3, J = 6.6), 0.922 (d, 3, J = 6.6), 1.179 (s, 3), 1.308 (s, 3), 1.3–2.0 (m, 7), 3.131 (br s, 1, D_2O-exchangeable), 3.748 (s, 3), 4.156 (t, 1, J = 7.2); ^{13}C NMR (125.8 MHz) δ 21.24, 24.00, 24.50, 24.81, 25.08, 26.38, 38.13, 49.45, 52.58, 76.73, 82.14, 84.00, 174.78.

Minor isomer: ^1H NMR (500 MHz) δ 0.891 (d, 3, J = 4.9), 0.901 (d, 3, J = 4.9), 1.136 (s, 3), 1.308 (s, 3), 1.3–2.0 (m, 7), 3.089 (br s, 1, D_2O-exchangeable), 3.769 (s, 3), 4.102 (dd, 1, J = 6.1, 9.25); ^{13}C NMR δ 20.94, 23.73, 24.50, 24.81, 25.08, 26.385, 38.33, 50.21, 52.585, 76.74, 82.79, 84.25, 174.72.

Synthesis of Bis Ethers. Methyl 2-Methyl-5-[(2*RS*,3*SR*,6*RS*)-3-bromo-2-methyl-6-phenyl-2-tetrahydropyranyl]-2(*E*)-pentenoate (27mb). 2,4,4,6-Tetrabromo-2,5-cyclohexadienone (991 mg, 2.42 mmol) was added to a solution of alcohol **25m** (730 mg, 2.42 mmol) in 24 mL of dry CH_2Cl_2. After being stirred in the dark for 24 h at 21 °C, the solution was washed with 10% NaOH and worked up. The crude product was purified by chromatography (4% ether/hexane) to give 518 mg (56%) of **27mb**, 70 mg (7.6%) of *cis*-**26mb**, and 58 mg (6.3%) of *trans*-**26mb**.

27mb: IR 1090, 1290, 1440, 1650, 1720, 2960, 3000, 3040 cm^{-1}; ^1H NMR δ 1.49 (s, 3), 1.6–1.8 (m, 2), 1.86 (s, 3), 1.8–2.0 (m, 2), 2.3–2.5 (m, 4), 3.72 (s, 3), 4.12 (dd, 1, J = 5.4, 11.6), 4.7 (dd, 1, J = 11.6, 2.5), 6.83 (t, 1, J = 7), 7.3–7.4 (m, 5); ^{13}C NMR δ 12.38, 17.12, 22.15, 31.68, 36.79, 39.97, 51.66, 54.60, 71.96, 77.11, 125.58, 127.37, 127.53, 128.31, 142.48, 142.53, 168.58. Anal. Calcd for $C_{19}H_{25}BrO_3$: C, 59.85; H, 6.61; Br, 20.96. Found: C, 59.40; H, 6.49; Br, 21.41.

***cis*-26mb**: IR 1060, 1090, 1130, 1200, 1290, 1440, 1725, 2970, 3000, 3040 cm^{-1}; ^1H NMR δ 1.78 (s, 3), 1.88 (s, 3), 1.9–2.3 (m, 5), 2.35–2.6 (m, 3), 3.72 (s, 3), 4.27 (dd, 1, J = 8.26, 6.7), 5.07 (dd, 1, J = 9.0, 5.7), 6.79 (t, 1, J = 8.1), 7.2–7.4 (m, 5); ^{13}C NMR δ 12.41, 24.99, 25.79, 29.59, 35.61, 41.16, 51.71, 73.09, 82.13, 85.45, 125.47, 127.28, 128.13, 128.30, 141.15, 142.80, 168.47. Anal. Calcd for $C_{19}H_{25}BrO_3$: C, 59.85; H, 6.61; Br, 20.96. Found: C, 59.30; H, 6.36; Br, 21.82.

***trans*-26mb**: IR 910, 1050, 1260, 1435, 1650, 1715, 2955, 3040 cm^{-1}; ^1H NMR δ 1.77 (s, 3), 1.88 (s, 3), 1.8–2.3 (m, 6), 2.4–2.6 (m, 2), 3.72 (s, 3), 4.13 (t, 1, J = 6.8), 4.86 (dd, 1, J = 8.8, 5.8), 6.78 (t, 1, J = 7), 7.2–7.4 (m, 5); ^{13}C NMR δ 12.43, 25.0, 25.73, 28.93, 34.44, 41.30, 51.68, 72.30, 81.93, 84.59, 125.79, 127.43, 128.16, 128.28, 141.17, 141.82, 168.45; MS, m/z (relative intensity) 380 (M^+, 1.8), 273, 227, 199, 173, 171, 161, 147, 145, 143, 133, 127, 117, 107, 106, 105 (100), 99.

Methyl 5-[(2*RS*,3*SR*,6*RS*)-3-Iodo-6-phenyl-2-tetrahydropyranyl]-2(*E*)-pentenoate (27hi). Iodine (529 mg, 2.08 mmol) was added to a solution of alcohol **25h** (200 mg, 0.69 mmol) in 4.8 mL of dry acetonitrile at 0 °C. The resulting purple solution was allowed to stir in the dark at 0 °C for 18 h, then was quenched with 10 mL of saturated aqueous $Na_2S_2O_3$. The aqueous solution was extracted with EtOAc (5 × 10 mL) and worked up to give 370 mg of a crude yellow oil which was purified by chromatography (3–9% ether/hexane) to afford 22 mg (7.7%) of the 2*Z* isomer of **27hi**, 126 mg (44%) of **27hi**, 46 mg (16%) of *trans*-**26hi**, and 46 mg (16%) of *cis*-**26hi**.

27hi: IR 1270, 1440, 1720, 2960, 3040 cm^{-1}; ^1H NMR δ 1.6–1.9 (m, 4), 1.81 (s, 3), 2.2–2.5 (m, 3), 2.6–2.7 (m, 1), 3.67 (td, 1, J = 8.7, 2.0), 3.73 (s, 3), 3.99 (td, 1, J = 12.1, 4.4), 4.5 (dd, 1, J = 10.6, 2.7), 6.8 (t, 1, J = 7.3), 7.3–7.4 (m, 5); ^{13}C NMR δ 12.40, 24.48, 31.81, 34.20, 37.44, 38.88, 51.71, 79.81, 81.98, 125.55, 127.47, 127.97, 128.32, 141.87, 142.11, 168.66. Anal. Calcd for $C_{18}H_{23}IO_3$: C, 52.19; H, 5.6; I, 30.63. Found: C, 51.97; H, 5.67; I, 30.9.

2*Z* isomer of 27hi: IR 910, 1120, 1205, 1440, 1460, 1720, 2870, 2960, 3040 cm^{-1}; ^1H NMR δ 1.7–1.9 (m, 4), 2.1–2.3 (m, 1), 2.3–2.5 (m, 1), 2.6–2.7 (m, 2), 3.67 (s, 3), 3.7 (td, 1, J = 8.4, 2.3), 4.01 (td, 1, J = 10.3, 4.5), 4.49 (dd, 1, J = 10.8, 2.7), 5.98 (t, 1, J = 7.4), 7.2–7.4 (m, 5); ^{13}C NMR (125 MHz) δ 20.66, 25.52, 32.08, 34.96, 37.32, 38.92, 51.22, 79.60, 82.30, 125.57, 127.3, 127.38, 128.24, 142.0, 142.5, 171.57.

***trans*-26hi**: IR 1040, 1080, 1130, 1200, 1260, 1430, 1650, 1715, 2950, 3030 cm^{-1}; ^1H NMR δ 1.9–2.1 (m, 4), 1.90 (s, 3), 2.2–2.3 (m, 2), 2.3–2.6 (m, 2), 3.73 (s, 3), 3.95 (q, 1, J = 6), 4.18 (td, 1, J = 7.4, 3.4), 4.95 (t, 1, J = 8.1), 6.75 (t, 1, J = 8), 7.2–7.4 (m, 5); ^{13}C NMR δ 12.67, 28.61, 33.66, 35.34, 35.38, 42.62, 51.72, 81.61, 82.85, 125.53, 127.35, 128.33, 128.72, 140.30, 142.66, 168.42. Anal. Calcd for $C_{18}H_{23}IO_3$: C, 52.19; H, 5.6; I, 30.63. Found: C, 51.93; H, 5.64; I, 30.40.

***cis*-26hi**: IR 1050, 1200, 1260, 1435, 1650, 1715, 2960, 3040 cm^{-1}; ^1H NMR δ 1.8–2.2 (m, 4), 1.9 (s, 3), 2.3–2.6 (m, 4), 3.73 (s, 3), 4.13 (m, 2), 5.10 (dd, 1, J = 8.6, 5.7), 6.73 (t, 1, J = 7.9), 7.2–7.4 (m, 5); ^{13}C NMR δ 12.71, 28.50, 32.17, 34.01, 35.30, 41.50, 51.76, 82.27, 82.51, 125.88, 127.46, 128.33, 128.86, 140.29, 142.19, 168.43. Anal. Calcd for $C_{18}H_{23}IO_3$: C, 52.19; H, 5.6; I, 30.63. Found: C, 51.97; H, 5.68; I, 30.39.

Methyl (6*RS*)-6-Hydroperoxy-2-methyl-6-[(2*SR*,5*SR*,6*RS*)-2-phenyl-5-tetrahydrofuranyl]-2(*E*)-heptenoate (28). Silver trifluoroacetate (174 mg, 0.79 mmol) was added in small portions at 0 °C to a solution of bromide **26mb** (150 mg, 0.39 mmol) and 90% hydrogen peroxide (1 g, 26.5 mmol) in 3.9 mL THF. After 8 h the solution was filtered through Celite and partitioned between saturated aqueous $NaHCO_3$ and ether. The destruction of excess H_2O_2 proceeded by a vigorous evolution of gas. The resulting solution was extracted with ether and worked up to give 123 mg of a crude oil which was purified by chromatography (20–30% EtOAc/hexane) to provide 88 mg (68%) of the hydroperoxide **28** (containing 93% of peroxide by titration): IR 1060, 1200, 1290, 1445, 1725, 2960, 3000, 3040, 3580 cm^{-1}; ^1H NMR δ 1.25 (s, 3), 1.4–1.7 (m, 1), 1.87 (s, 3), 1.9–2.1 (m, 4), 2.2–2.5 (m, 3), 3.73 (s, 3), 4.38 (dd, 1, J = 8.9, 6.2), 5.04 (dd, 1, J = 8.52, 6.2), 6.8 (t, 1, J = 7), 7.2–7.5 (m, 6); ^{13}C NMR δ 12.38, 18.32, 22.41, 28.10, 31.11, 35.24, 51.74, 81.82, 84.58, 85.88, 125.50, 127.46, 127.79, 128.41, 142.38, 142.63, 168.75. Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 65.76; H, 7.52.

Methyl (α*RS*,2*RS*,5*SR*)-α-Hydroxy-α,5-dimethyl-5-[(2*RS*,5*RS*)-5-phenyl-2-tetrahydrofuranyl]-2-tetrahydrofuranacetate (29c) and the α*RS*,2*RS*,5*RS* (2*SR*,5*SR*) Isomer (29t). Via Epoxide Cyclization. Trichloroacetic acid (21 mg, 0.13 mmol) was added to a solution of the epoxides of **34** (145 mg, 0.43 mmol) in 0.43 mL of CH_2Cl_2. After 18 h at 23 °C, 10 mL of CH_2Cl_2 was added and the solution was extracted with 10% NaOH and worked up to give a 1:1 mixture of tetrahydrofurans **29c** and **29t** (142 mg, 98%). These isomers were separated by

chromatography (10–20% EtOAc/hexane) to give 48 mg (33%) of **29c** and 56 mg (39%) of **29t** (assignments tentative).

Via Hydroperoxide Cyclization. Sodium hydride (2 mg, 50%, 0.045 mmol) was added at 0 °C to a solution of hydroperoxide **28** (15 mg, 0.045 mmol) in 0.45 mL of dry THF. After 6 h at 0 °C, 2 mL of 10% aqueous HCl was added and the mixture was extracted with ether (5 × 5 mL). Workup provided a colorless oil which was esterified with excess CH_2N_2 in ether and filtered through a plug of silica gel (20% EtOAc/hexane) to give 8.7 mg (58%) of the cyclized material as a 1.4/1 mixture of **29c**/**29t** by ^1H NMR.

29c (tentative): IR 970, 1275, 1460, 1740, 2900, 2980, 3000, 3060, 3080, 3550 cm^{-1}; ^1H NMR (500 MHz) δ 1.2 (s, 3), 1.47 (s, 3), 1.55–1.75 (m, 2), 1.85–2.0 (m, 2), 2.07–2.15 (m, 2), 2.2–2.25 (m, 1), 2.35–2.45 (m, 1), 3.73 (s, 3), 4.36 (m, 2), 5.05 (dd, 1, J = 9.3, 5.8), 7.2–7.4 (m, 5); ^{13}C NMR δ 24.26, 24.71, 27.36, 29.62, 30.68, 35.73, 52.21, 78.11, 81.64, 82.82, 85.18, 87.08, 125.29, 127.23, 128.35, 142.65, 174.36. Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.40; H, 7.80.

29t (tentative): IR 1070, 1180, 1270, 1380, 1460, 1740, 2900, 3000, 3040, 3540 cm^{-1}; ^1H NMR (500 MHz) δ 1.19 (s, 3), 1.44 (s, 3), 1.65–1.75 (m, 1), 1.8–1.85 (m, 2), 1.88–1.92 (m, 1), 1.95–2.1 (m, 4), 2.3–2.4 (m, 1), 3.77 (s, 3), 4.16 (dd, 2, J = 8.5, 6.7), 4.986 (dd, 1, J = 8.35, 6.2); ^{13}C NMR δ 23.03, 23.35, 26.66, 28.41, 33.72, 35.62, 52.44, 76.28, 81.36, 85.04, 85.43, 86.06, 125.56, 127.09, 128.26, 143.56, 174.80. Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.19; H, 7.84.

Methyl 5-[(2*RS*,3*SR*,6*RS*)-3-Hydroxy-6-phenyl-2-tetrahydropyranyl]-2(*E*)-pentenoate (30). Silver tetrafluoroborate (14 mg, 0.072 mmol) was added to a solution of iodide **27hi** (30 mg, 0.072 mmol) in 0.2 mL of acetone and 0.02 mL of water. After 2 h, the mixture was filtered and evaporated under vacuum. The crude product was dissolved in CH_2Cl_2 and worked up to give an oil which was chromatographed (10–30% EtOAc/hexane) to furnish 21 mg (96%) of **30** as a colorless oil: IR 990, 1270, 1450, 1720, 2960, 3020, 3650 cm^{-1}; ^1H NMR δ 1.6–1.8 (m, 5), 1.81 (s, 3), 2.0–2.1 (m, 1), 2.15–2.3 (m, 1), 2.39 (q, 2, J = 7.5), 3.25 (td, 1, J = 9.1, 2.6), 3.43 (dt, 1, J = 4.7, 10), 3.72 (s, 3), 4.34 (dd, 1, J = 10.7, 2.2), 6.82 (t, 1, J = 7.2), 7.2–7.4 (m, 5); ^{13}C NMR δ 12.35, 24.50, 30.85, 33.23, 33.52, 51.72, 70.20, 78.93, 81.44, 125.67, 127.29, 127.73, 128.23, 142.33, 142.60, 168.86; MS, m/z (relative intensity) 304 (M^+, 2), 157, 147, 124, 116, 105, 104 (100), 91.

One milligram (4% yield) of a minor isomer (presumed to be the tetrahydrofuran) was also isolated: IR 1060, 1260, 1440, 1715, 2960, 3040, 3600 cm^{-1}; ^1H NMR δ 1.5–1.6 (m, 2), 1.6–1.8 (m, 2), 1.87 (s, 3), 1.9–2.1 (m, 2), 2.3–2.5 (m, 3), 3.74 (s, 3), 3.90 (td, 1, J = 6.5, 3.4), 4.14 (td, 1, J = 6.1, 3.6), 5.02 (dd, 1, J = 7.8, 5.8), 6.78 (t, 1, J = 7.8), 7.2–7.4 (m, 5); ^{13}C NMR (125 MHz) δ 12.38, 25.19, 25.74, 31.22, 35.60, 51.69, 71.46, 81.51, 82.86, 125.49, 127.33, 128.15, 128.40, 141.68, 143.16, 168.61; MS, m/z (relative intensity) 304 (M^+, 8.5), 157, 148, 147, 129, 125, 117, 105, 104, 91 (100).

Methyl 5-[(2*RS*,3*SR*,6*RS*)-3-Hydroperoxy-6-phenyl-2-tetrahydropyranyl]-2(*E*)-pentenoate (31). Silver trifluoroacetate (13 mg, 0.06 mmol) was added at 0 °C to a solution of iodide **27hi** (25 mg, 0.06 mmol) and 90% hydrogen peroxide (0.25 g, 6.6 mmol) in 0.25 mL of THF. After 1 h at 0 °C, the mixture was filtered through Celite and the excess H_2O_2 was destroyed with saturated aqueous $NaHCO_3$. Extraction with ether (4 × 10 mL) followed by workup and chromatographic purification (20% EtOAc/hexane) afforded 11 mg (57%) of the hydroperoxide **27hi** as a colorless oil. This material was used without titration for the cyclization: IR 1090, 1280, 1440, 1710, 2860, 2960, 3040, 3400, 3560 cm^{-1}; ^1H NMR δ 1.5–1.9 (m, 4), 1.82 (s, 3), 2.0–2.2 (m, 2), 2.3–2.5 (m, 2), 3.44 (td, 1, J = 8.9, 2.8), 3.73 (s, 3), 3.8 (td, 1, J = 9.3, 4.3), 4.35 (dd, 1, J = 11.0, 2.3), 6.82 (t, 1, J = 7.6), 7.2–7.4 (m, 5), 8.02 (br s, 1). Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 64.47; H, 7.38.

Methyl (2*RS*,3*SR*)-2,3-Epoxy-5-[(2*RS*,3*SR*,6*RS*)-3-hydroxy-6-phenyl-2-tetrahydropyranyl]-2-methylpentanoate and the 2*SR*,3*RS* Diastereomer (Epoxides of 30). *m*-Chloroperoxybenzoic acid (28 mg, 0.164 mmol) was added at 0 °C to a solution of ester **30** (10 mg, 0.033 mmol) in 0.35 mL of CH_2Cl_2. After 18 h at 23 °C, 1 mL of saturated aqueous $Na_2S_2O_3$ was added, followed by 15 mL of CH_2Cl_2. The resulting solution was washed with 10% NaOH and worked up to give 10 mg (95%) of the crude epoxide mixture as a colorless oil: IR 910, 1100, 1180, 1210, 1225, 1310, 1445, 1460, 1745, 2870, 2960, 3040, 3640 cm^{-1}. Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.48; H, 7.62.

2*RS*,3*SR*: ^1H NMR δ 1.52 (s, 3), 1.6–1.8 (m, 5), 1.8–2.0 (m, 1), 2.0–2.1 (m, 1), 2.1–2.3 (m, 2), 3.3–3.35 (m, 2), 3.42 (td, 1, J = 9.1, 4.8), 3.67 (s, 3), 4.37 (dd, 1, J = 6.3, 2.2), 7.2–7.4 (m, 5); ^{13}C NMR δ 13.52, 24.35, 28.78, 33.31, 33.55, 52.54, 57.59, 62.60, 70.25, 78.87, 81.85, 125.63, 127.28, 128.22, 142.35, 172.07.

2*SR*,3*RS*: ^1H NMR δ 1.51 (s, 3), 1.6–1.8 (m, 5), 1.8–2.0 (m, 1), 2.0–2.1 (m, 1), 2.1–2.3 (m, 2), 3.2–3.35 (m, 2), 3.35–3.45 (m, 1), 3.72 (s, 3), 4.37 (m, 1), 7.2–7.4 (m, 5); ^{13}C NMR δ 13.51, 23.71, 28.54, 33.38, 33.55, 48.03, 57.88, 62.32, 70.11, 78.96, 81.84, 125.63, 127.31, 128.23, 142.33, 172.0.

Methyl (α*RS*,1*SR*,3*SR*,6*RS*,8*RS*)-α-Hydroxy-α-methyl-8-phenyl-2,7-dioxabicyclo[4.4.0]decane-3-acetate (32) and the α*RS*,1*RS*,3*SR*,6*SR*,8*SR* Isomer (33). Via Epoxide Cyclization. Trichloroacetic acid (4.6 mg, 0.03 mmol) was added to a solution of the epoxides above (30 mg, 0.09 mmol) in 1 mL of CH_2Cl_2. After 4 h the reaction was partitioned between CH_2Cl_2 and 10% NaOH; workup gave a crude oil which was purified by chromatography (10–30% EtOAc/hexane) to provide 14 mg (47% yield) of **32** and 15 mg (50%) of the starting epoxide (single diastereomer by ^1H NMR). The recovered starting material was treated as above for 18 h at 23 °C to give 11 mg (37% overall yield) of **33**.

Via Hydroperoxide Cyclization. Sodium hydride (2 mg, 50%, 0.045 mmol) was added at 0 °C to a solution of hydroperoxide **31** (11 mg, 0.034 mmol) in 0.3 mL of THF. After 6 h at 0 °C, the mixture was partitioned between ether and 10% NaOH; the aqueous phase was washed with ether (3 × 5 mL), acidified to pH 2 with concentrated HCl, and extracted with CH_2Cl_2. Workup gave 7 mg (64%) of the cyclized material as a 1:1 mixture of **32** and **33** by ^1H NMR. The crude product was chromatographed (10–20% EtOAc/hexane) to furnish 3 mg (27%) of **32** and 2.5 mg (23%) of **33**.

32: IR 1010, 1240, 1460, 1745, 2890, 2950, 2980, 3560 cm^{-1}; ^1H NMR (500 MHz) δ 1.46 (s, 3), 1.55–1.65 (m, 2), 1.65–1.8 (m, 3), 1.9–2.0 (m, 1), 2.05–2.15 (m, 2), 3.18 (m, 2), 3.3 (br s, 1, D_2O-exchangeable), 3.52 (dd, 1, J = 11.5, 2.3), 3.8 (s, 3), 4.41 (dd, 1, J = 10.8, 2.2), 7.2–7.4 (m, 5); ^{13}C NMR δ 22.32, 25.12, 29.25, 29.84, 33.33, 52.66, 78.02, 78.37, 79.73, 81.93, 81.94, 125.95, 127.52, 128.36, 142.12, 174.84; MS, m/z (relative intensity) 320 (M^+), 217 (100), 173, 171, 131, 117, 105, 104, 99, 91; HRMS calcd for $C_{18}H_{24}O_5$ m/z 320.1623, found m/z 320.1616.

33: IR 1100, 1175, 1230, 1270, 1460, 1730, 2880, 2950, 3040, 3540 cm^{-1}; ^1H NMR (500 MHz) δ 1.51 (s, 3), 1.55–1.65 (m, 2), 1.7–1.8 (m, 2), 1.85–2.0 (m, 2), 2.0–2.15 (m, 2), 3.29 (td, 1, J = 9.2, 4.5), 3.45 (br s, 1, D_2O-exchangeable), 3.81 (s, 3), 3.86 (td, 1, J = 9.2, 4.5), 3.93 (dd, 1, J = 6.9, 1.8), 4.42 (dd, 1, J = 11.4, 2.2), 7.2–7.4 (m, 5); ^{13}C NMR δ 23.64, 24.46, 26.33, 30.59, 33.58, 53.26, 71.76, 74.72, 78.45, 79.91, 80.33, 126.02, 127.46, 128.35, 142.36, 177.0; MS, m/z (relative intensity) 320 (M^+), 218, 217 (100), 173, 131, 117, 105, 104, 99, 91; HRMS calcd for $C_{18}H_{24}O_5$ m/z 320.1623, found m/z 320.1610.

Methyl (6*RS*)-6-Hydroxy-2-methyl-6-[(2*SR*,5*SR*)-5-phenyl-2-tetrahydrofuranyl]-2(*E*)-heptenoate (34). Thallium triacetate sesquihydrate (347 mg, 0.85 mmol) was added to a stirred solution of alcohol **25m** (228 mg, 0.75 mmol) in a mixture of 2.8 mL of acetone, 0.7 mL of water, and 0.42 mL of 48% aqueous HBF_4 at 0 °C. After 1 h, 1 mL of brine and some solid K_2CO_3 were added and the mixture was evaporated. Extraction with CH_2Cl_2 (4 × 10 mL) followed by workup and chromatography (20% EtOAc/hexane) provided 158 mg (66%) of the cyclized alcohol **34** as a colorless oil: IR 910, 1065, 1290, 1440, 1660, 1720, 2900, 2960, 2995, 3040, 3600 cm^{-1}; ^1H NMR δ 1.27 (s, 3), 1.4–1.7 (m, 2), 1.85 (s, 3), 1.9–2.0 (m, 2), 2.2–2.4 (m, 3), 3.72 (s, 3), 4.05 (t, 1, J = 7.7), 4.95 (dd, 1, J = 5.6, 8.1), 6.79 (t, 1, J = 7.2), 7.2–7.4 (m, 5); ^{13}C NMR (300 MHz) δ 12.18, 22.66, 23.41, 26.88, 35.46, 35.84, 51.51, 73.07, 81.23, 86.04, 125.30, 127.05, 127.32, 128.15, 142.46, 143.14, 168.44. Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 69.77; H, 8.11.

Methyl (2*RS*,3*SR*,6*SR*)-2,3-Epoxy-6-hydroxy-2-methyl-6-[(2*RS*,5*RS*)-5-phenyl-2-tetrahydrofuranyl]heptanoate and the 2*RS*,3*SR*,6*RS*[2*SR*,5*SR*] Diastereomer (Epoxides of 34). MCPBA (143 mg, 0.71 mmol) was added at 0 °C to a solution of ester **34** (150 mg, 0.47 mmol) in 5 mL of CH_2Cl_2. After 4 h at

23 °C, the mixture was partitioned between 1 mL of saturated Na_2CO_3 and 15 mL of CH_2Cl_2. The organic phase was washed with 10% aqueous NaOH and worked up to give a 1:1 mixture of epoxides (151 mg, 96%) as a colorless oil: IR 1070, 1200, 1310, 1460, 1745, 2965, 3000, 3040, 3600 cm^{-1}; ^1H NMR δ 1.25 (s, 1.5), 1.26 (s, 1.5), 1.55 (s, 1.5), 1.56 (s, 1.5), 1.4–2.1 (m, 8), 2.4 (m, 1), 3.22 (t, 1, J = 5.9), 3.75 (s, 3), 4.06 (t, 1, J = 8.3), 4.98 (t, 1, J = 8.55), 7.2–7.4 (m, 5). Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 67.89; H, 7.87.

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Supplementary Material Available: Experimental details and characterization of the synthetic intermediates not described above (12 pages). Ordering information is given on any current masthead page.

Notes

Evidence for Hydrogen Transfer in the Photochemistry of 2,2,6,6-Tetramethylpiperidine-*N*-oxyl[1]

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There have been several reports on the photochemistry of stable nitroxide free radicals.[3-9] Two types of reactivity have been observed: (i) cleavage of one of the C–N bonds and (ii) hydrogen abstraction by an excited nitroxide. The former is the mechanism in the case of di-*tert*-butyl nitroxide[7] which yields 2-methyl-2-nitrosopropane and *tert*-butyl radical which is then scavenged by a second nitroxide molecule. In the case of cyclic nitroxide, 3-carbamoyl-2,2,5,5-tetramethylpyrroline-1-oxyl, α-cleavage is followed by loss of nitric oxide to yield a diene as product.[3] The abstraction mechanism (ii) has been observed in systems such as 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl[6] and a steroid nitroxide.[4]

Recent work from this laboratory[10] on the reaction of nitroxides such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (Tempo) with diphenylcarbene showed that some nitroxide decomposition occurred on direct photolysis of Tempo in both acetonitrile and isooctane. The products (GC–MS) indicated the addition of a solvent moiety (e.g., $-CH_2CN$ from acetonitrile) to the nitroxide; mechanisms i and ii were suggested as possible reaction paths, with the former followed by addition of the radical resulting from α-cleavage to the solvent being favored. This reaction has now been examined in detail by product studies and quantum yield measurements. The results, which indicate that excited Tempo is an efficient hydrogen abstractor, may be compared with recent data for hydrogen abstraction by excited states of transient radicals.

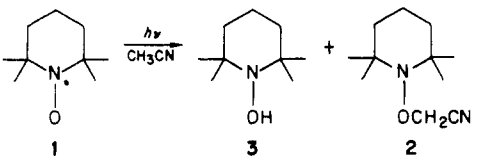
Table I. Quantum Yields for Product Formation for the Photolysis of Tempo in Various Solvents at 310 K

solvent	product	quantum yield[a]
acetonitrile	2	0.14
acetonitrile-d_3	2-d_2	0.16
toluene	4	0.022
toluene-d_8	4-d_7	0.021

[a] Average of two measurements.

Results and Discussion

Prolonged irradiation of a deaerated acetonitrile solution of Tempo (1) led almost exclusively to a single product, which GC–MS showed to correspond to the addition of $-CH_2CN$ to Tempo. The material was isolated and identified as **2** on the basis of its IR, NMR, MS, and elemental analysis. Examination of the photolysis mixture by capillary GC after short irradiation times (i.e., conversions $\leq$20%) indicated the formation, in addition to **2**, of a second primary photoproduct and that the two were formed in equal yields at low conversion. However, the second product readily reverted to starting material upon standing. This material was identified as **3** on the basis of its GC–MS spectrum and its ready oxidation to **1** and by analogy with earlier work.[9] These results indicate that excited Tempo abstracts hydrogen from the solvent to produce **3** plus a $\dot{C}H_2CN$ radical which then couples with a second Tempo molecule to produce **2**. This is a somewhat surprising result as hydrogen abstraction from acetonitrile is not normally a facile process. For example, the combined data from competitive reactions indicate that even at 408 K hydrogen abstraction from acetonitrile by *tert*-butoxyl radicals is ~20 times slower than that from cyclohexane.[11]



1 3 2 (1)

Photolysis of Tempo in toluene resulted in a similar hydrogen abstraction reaction to yield the expected

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