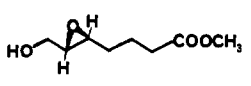

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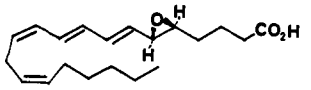
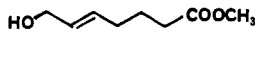


2

the earlier work the synthesis of **1** was effected expeditiously starting from D-(−)-ribose, a readily available chiral substance. In this paper we describe the synthesis of (−)-**1** from achiral precursors by asymmetric induction using the felicitous discovery of Katsuki and Sharpless that a reagent produced from optically active diethyl tartrate, *tert*-butyl hydroperoxide, and titanium tetraisopropoxide effects epoxidation of allylic alcohols with high enantioselectivity.[7]

In fact, reaction of methyl *trans*-7-hydroxy-5-heptenoate (**3**) with the Katsuki–Sharpless reagent (from L-(+)-tartaric acid diethyl ester) in methylene chloride under the prescribed[7] conditions afforded at best only traces of the desired epoxide **1** (by thin-layer chromatographic (TLC) and spectroscopic analysis), although the starting material was consumed at the expected[7] rate (within ca. 4 h at −20 °C). Since the crude reaction product(s)



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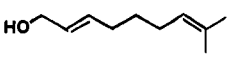

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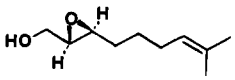

5

did not seem to contain epoxide or $COOCH_3$ units (^1H NMR analysis), it was evident that if the epoxy ester were being formed, it was subject to very rapid Lewis acid catalyzed decomposition involving the neighboring methoxycarbonyl group. Therefore a different substrate, *trans*-8-methyl-2,7-nonadien-1-ol (**4**), was chosen for the synthesis.

Reaction of 1-bromo-3-methyl-2-butene[9] with *tert*-butyl lithioacetate[10] in tetrahydrofuran (THF)–hexamethylphosphoric triamide (HMPA) from −78 to −10 °C over 1 h gave (80%) *tert*-butyl 5-methyl-4-hexenoate, bp 90–92 °C (8 torr), and this upon reduction with lithium aluminum hydride in ether afforded 5-methyl-4-hexen-1-ol, bp 78–79 °C (13 torr), in 81% yield. Transformation of this alcohol into the corresponding tosylate (*p*-toluenesulfonyl chloride in pyridine at −10 °C for 1 h, 94% yield) and coupling with the lithio derivative of propargyl tetrahydropyranyl ether[11] in 4:1 THF–HMPA at 55 °C for 5 h provided the tetrahydropyranyl ether of 8-methyl-non-2-yn-7-en-1-ol, bp 109–111 °C (0.15 torr), in 71% yield.[12] Cleavage of the tetrahydropyranyl group (1.5% *p*-toluenesulfonic acid in methanol at 23 °C for 1.5 h, 96% yield) and reduction[13] of the propargylic alcohol thus obtained (lithium aluminum hydrride in ether at reflux for 20 h) gave **4** in 95% yield.

Oxidation[7] of **4** using 3 equiv of anhydrous *tert*-butyl hydroperoxide (4 M in $ClCH_2CH_2Cl$) in the presence of 1 equiv of L-(+)-diethyl tartrate and 1 equiv of titanium isopropoxide in CH_2Cl_2 at −23 °C for 2.5 h produced after extractive workup and chromatography on silica gel (deactivated with 1% of triethylamine) the 2,3-epoxide of **4** (**5**), $[\alpha]^{23}_D$ −35.4° (*c* 2.1, $CHCl_3$), in 74% yield. Acetylation of **5** (Ac_2O–pyridine), ozonolysis of the acetate in ethyl acetate at −78 °C followed by oxidation of the resulting mixture with 2.5 equiv of Jones' reagent at −20 °C for 40 min, and esterification with diazomethane afforded (after column chromatography on silica gel) a 60% yield of the acetate of **1**, $[\alpha]^{23}_D$ −41.1° (*c* 2.38, $CHCl_3$). The optical purity of this product corresponds to 93% ee, since the rotation of optically pure acetate of **1**[1] was found to be $[\alpha]^{23}_D$ −44.3° (c 2.24, $CHCl_3$). Further, deacetylation of the $[\alpha]^{23}_D$ −41.1° acetate of **1** using 1.5 equiv of potassium carbonate in methanol at 23 °C for 15 min gave the alcohol **1** (93%) of rotation $[\alpha]^{23}_D$ −34.7° (c 2.16, $CHCl_3$), corresponding to 93% ee (the rotation of optically pure **1**[1] is $[\alpha]^{23}_D$ −37.4° (c 2.7, $CHCl_3$). The samples of **1** and its acetate prepared by the route outlined above were spectroscopically and chromatographically identical with authentic samples.[1] Clearly this synthesis is capable of providing leukotriene A of 93% optical purity. In addition, when L-amino acid derivatives for the further conversion of leukotrienes C, D, and E are used these substances can be obtained in pure form by reverse phase chromatography,[1] since the small amount (ca. 3.5%) of diastereomeric thiol conjugate is cleanly separable.[14,15]

(4) Hammarström, S.; Samuelsson, B.; Clark, D. A.; Goto, G.; Marfat, A.; Mioskowski, C.; Corey, E. J. *Ibid.* **1980**, *92*, 946.
(5) (a) Örning, L.; Widegran, D.; Hammarström, S.; Samuelsson, B. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 2014. (b) Lewis, R. A.; Austen, K. F.; Drazen, J. M.; Clark, D. A.; Marfat, A.; Corey, E. J. *Ibid.* **1980**, *77*, 3710.
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(7) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.
(8) The preparation of this substrate has recently been described; see: Corey, E. J.; Park, H.; Barton, A. E.; Nii, Y. *Tetrahedron Lett.* **1980**, *21*, 4243.
(9) Tanaka, J.; Katagiri, T.; Yamada, S. *J. Chem. Soc. Jpn.* **1966**, *87*, 877.
(10) Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* **1971**, *93*, 2318.
(11) Corey, E. J.; Sachdev, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 8483.
(12) Satisfactory infrared, ^1H NMR, and mass spectral data were obtained by using purified chromatographically homogeneous samples of each synthetic intermediate.
(13) Bates, E. B.; Jones, E. R. H.; Whiting, M. C. *J. Chem. Soc.* **1954**, 1854.
(14) Enantioselective allylic alcohol epoxidation has also been employed in the synthesis of leukotriene B and isomers; see: (a) Corey, E. J.; Hopkins, P. B.; Munroe, J. E.; Marfat, A.; Hashimoto, S. *J. Am. Chem. Soc.* **1980**, *102*, 7986. (b) Corey, E. J.; Marfat, A.; Munroe, J.; Kim, K. S.; Hopkins, P. B.; Brion, F. *Tetrahedron Lett.*, in press.
(15) This research was assisted financially by a grant from the National Science Foundation. We are grateful to Dr. Giichi Goto for reference samples.

Short, Stereospecific Total Syntheses of (±)-Modhephene and (±)-Epimodhephene

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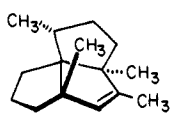
Received November 6, 1980

The toxic plant *Isocoma wrightii* (rayless goldenrod) has proven to be a rich source of structurally interesting sesquiterpenes.[1] In 1977, Zalkow and associates reported the isolation and characterization of isocomene (**1**), a novel tricyclo[6.3.0.0^{4,8}]undecane



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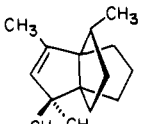

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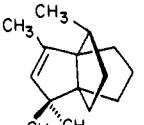


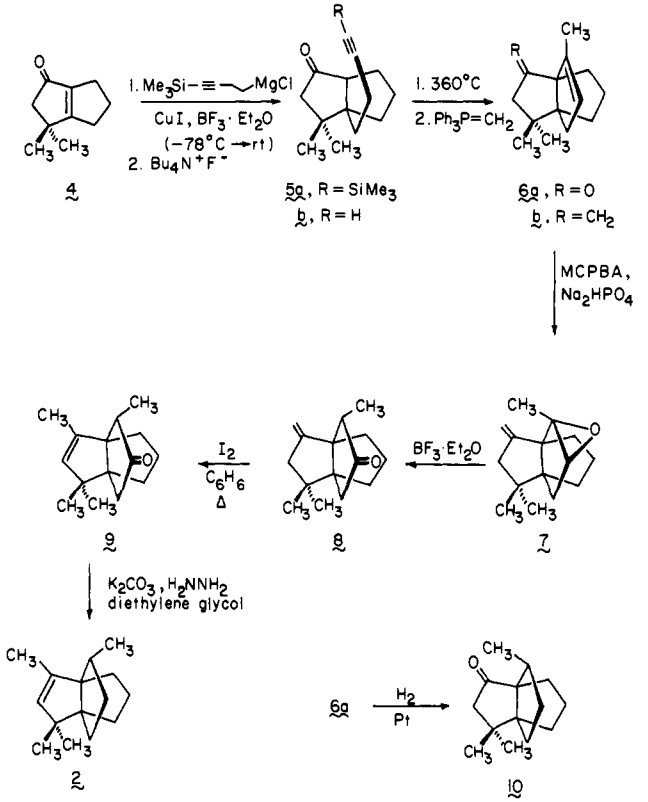
3

featuring a bridged spirane arrangement of three cyclopentane rings.[2] This unusual hydrocarbon immediately became a synthetic target for several research groups including our own,[3] and several imaginative routes to **1** have been completed at this time.[3-6]

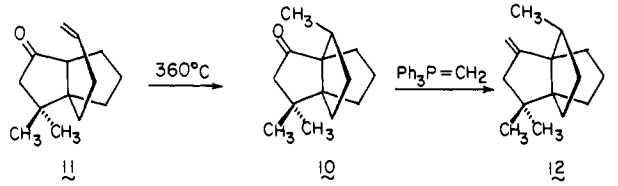
(1) Zalkow, L. H.; Harris, R. N., III; Burke, N. I. *J. Nat. Prod.* **1979**, *42*, 96.
(2) Zalkow, L. H.; Harris, R. N., III; Van Derveer, D.; Bertrand, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 456.
(3) Paquette, L. A.; Han, Y. K. *J. Org. Chem.* **1979**, *44*, 4014.
(4) Oppolzer, W.; Battig, K.; Hudlicky, T. *Helv. Chim. Acta* **1979**, *62*, 1493.
(5) Pirrung, M. *J. Am. Chem. Soc.* **1979**, *101*, 7130.
(6) Dauben, W. G.; Walker, D., private communication.

0002-7863/81/1503-722$01.00/0

Scheme I



Scheme II



Cooccurring with isocomene is modhephene (**2**), the first carbocyclic [3.3.3]propellane to be identified from natural sources. The structural features and stereochemistry of **2** were established by X-ray analysis of a *cis*-diol derivative.[7] The uniqueness of **2** among sesquiterpenes aroused our interest in its total synthesis, and we report herein efficient and fully stereocontrolled approaches to both **2** and epimodhephene (**3**).[8]

Our synthetic planning was based on the ready availability of bicyclic enone **4** from cyclopentene and β,β-dimethylacrylic acid[9] in conjunction with intramolecular ene chemistry[10] for elaboration of the third cyclopentane ring. On reaction with the Grignard reagent of 4-chloro-1-(trimethylsilyl)-1-butyne,[11] cuprous iodide, and boron trifluoride etherate in tetrahydrofuran (−78 °C → room temperature),[12] **4** was transformed by conjugate addition to **5a** (52%).[13] Following deprotection of the triple bond in **5a** ($Bu_4N^+F^-$, THF, H_2O, 25 °C, 81%), terminal acetylene **5b** was directly subjected to thermal activation (decalin, sealed tube, 360 °C, 100 min). Under the conditions employed, the initially formed exocyclic methylene derivative experienced isomerization to **6a** which was isolated in 56% yield.[14] Wittig olefination of this unsaturated ketone with methyltriphenylphosphonium bromide and potassium *tert*-butoxide in diisopropyl ether[15] (68 °C, 12 h) proceeded smoothly to give diene **6b** (81%, Scheme I).

Due to the different substitution plans of the olefinic bonds in **6b**, it was possible to discriminate completely in favor of the endocyclic site of unsaturation upon treatment with *m*-chloroperbenzoic acid (CH_2Cl_2, 0 °C, 91%). To the best of our knowledge, the formation of **7** was highly regio- and stereoselective. The stereocontrol presumably arises because of steric shielding provided by the β-methyl group of the geminate pair. Substantiation of the stereochemical assignment was accomplished in the following manner. Controlled isomerization of **7** with boron trifluoride etherate (CH_2Cl_2, 0 °C, 5 min) proceeds with in-plane 1,2-hydrogen shift[16] to give epimerically homogeneous **8** [^{13}C NMR ($CDCl_3$, ppm) 221.02, 162.09, 104.14, 63.11, 61.66, 53.77, 49.03, 46.24, 40.42, 38.90, 36.05, 26.46, 26.22, 24.09, and 11.77]. This product proved to be in the series isomeric to that in which **10** finds itself. The latter ketone, initially obtained by the catalytic hydrogenation of **6a**, was later synthesized in a stereochemically definitive manner (Scheme II).

With these results in hand, our strategy required that the integrity of the single chiral center be maintained. Molecular models suggested that the configuration present in **8** would be better guaranteed during the projected Wolff–Kishner reduction if allylic isomerization of the double bond were first implemented. To this end, **8** was exposed to iodine in benzene[17] to give isomerically pure **9** in 73% yield. Reduction of **9** with potassium carbonate and hydrazine hydrate in hot diethylene glycol[18] followed by VPC purification (15% SE-30 on Chromosorb G, 150 °C) afforded epimerically pure modhephene (84%) as a colorless oil, the IR and ^1H NMR spectra of which were superimposable upon those of the authentic sample.[19]

Having achieved this eight-step synthesis of **2**, we proceeded to elaborate epimodhephene (**3**) in yet more expedient fashion. As before, boron trifluoride etherate catalysis proved most efficacious in promoting cuprate addition to the hindered enone β carbon atom in **4**. Thus, with 3-butenylmagnesium bromide and cuprous iodide, **11** was isolated in 81% yield. When heated in decalin solution at 360 °C for 4 h, **11** was efficiently converted to **10** (85%) [^{13}C NMR ($CDCl_3$, ppm) 220.29, 80.71, 70.27, 66.82, 55.89, 46.42, 38.78, 35.80, 35.68, 26.70, 26.16, 25.00, and 16.02]. The requirement that ene reactions of this type proceed via the appropriate enol tautomer serves to lock the newly formed methyl group syn to the ketone carbonyl. Ketone **10** reacted with methylenetriphenylphosphorane (68 °C, 12 h) somewhat more sluggishly than **6a**. Nonetheless, **12** was obtained in quite acceptable yield (67%). The isomerization of **12** with iodine in benzene (reflux, 10 h) furnished **3** (92%). Interestingly, whereas exocyclic olefin **12** displays well-separated signals for its geminate methyl groups (δ 0.99 and 0.90), those in **3** are tightly spaced at 90 MHz (δ 1.02 and 1.00), more reminiscent of the situation in modhephene (singlet at δ 0.92 in CCl_4).

(7) Zalkow, L. H.; Harris, R. N., III; Van Derveer, D. *J. Chem. Soc., Chem. Commun.* **1978**, 420.

(8) (a) An earlier disclosure has been made of a synthesis of **2**: Smith, A. B., III; Jervis, P. J. "Abstracts of Papers", 179th National Meeting of the American Chemical Society, Houston, TX; American Chemical Society, Washington, DC, 1980; ORGN 63. (b) **Note added in proof**: An alternative approach to modhephene has recently been reported by: Karpf, M.; Dreiding, A. S. *Tetrahedron Lett.* **1980**, 4569.

(9) Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 1971. Compare: Dev, S. *Ind. J. Chem.* **1957**, *34*, 169. Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017.

(10) Conia, J. M.; LePerchec, P. *Synthesis* **1975**, 1.

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(12) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1978**, *100*, 3240.

(13) All new compounds exhibited compatible infrared, proton magnetic resonance, and mass spectroscopic data which may be found in the supplementary material. In addition, the elemental composition of all key intermediates has been substantiated by combustion analysis. Yields refer to isolated chromatographically homogeneous materials.

(14) The exocyclic olefin could be obtained under very strictly controlled conditions, but this was difficult to achieve reproducibly because of the ease of isomerization to **6a**.

(15) Drouin, J. Thèse, Université de Paris-Sud, Orsay, France, 1976, p 120. Also see: Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron Lett.* **1975**, 4053.

(16) See, for example: Henbest, H. B.; Wrigley, T. I. *J. Chem. Soc.* **1957**, 4596. Shoppee, C. W.; Howden, M. E. H.; Killick, R. W.; Summers, G. H. R. *Ibid.* **1959**, 63.

(17) Bell, R. A.; Ireland, R. E.; Mander, L. N. *J. Org. Chem.* **1966**, *31*, 2536.

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(19) We are particularly grateful to Professor Leon Zalkow for his generosity in making copies of these spectra available to us.

A key feature of this pair of syntheses is the unambiguous manner in which stereochemistry has been introduced at a chiral center in one of three bridges of a [3.3.3]propellane relative to the other two (differently substituted) members. The sequences of reactions provide independent proof of both the structure and configuration of the natural product. Finally, it seems likely that the basic approaches outlined herein will prove applicable to other areas of propellane chemistry where stereochemical issues have been given scant attention.[20,21]

Acknowledgment. This research was made possible by the generous financial support of the National Institutes of Health (Grants AI-11490 and GM-28468) and the Eli Lilly Co.

Supplementary Material Available: IR, ^{1}H NMR, and MS data of compounds **2**, **3**, and **5**–**12** (3 pages). Ordering information is given on any current masthead page.

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(21) Ginsburg, D. "Propellanes. Structure and Reactions"; Verlag Chemie: Weinheim/Bergstr., West Germany, 1975.

A Total Synthesis of a Racemic Eriolanin

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Received October 10, 1980

The lactones eriolanin (**1**) and eriolangin (**2**) are members of the rare 1,10-secoeudesmanolide class of sesquiterpenes. Isolated by Kupchan and co-workers from the chloroform extract of the plant *Eirophgllum lanatum* Forbes (Composite), these natural products were found to possess significant in vivo activity against P-388 leukemia in mice as well as in vitro activity against cell cultures derived from human carcinoma of the nasopharynx (KB).[1] The biological activity exhibited by **1** and **2** clearly reflects the presence of two α,β-unsaturated carbonyl residues in each molecule.[2] However, of much greater interest to the synthetic chemist is the stereochemistry of **1** and **2** which consists of three contiguous chiral centers within a cyclohexene ring along with an additional chiral center allylic and exocyclic to the ring—the entire array posing a provocative problem. In meeting this challenge, Grieco and co-workers have crafted an elegant solution ultimately resulting in total syntheses of both **1** and **2** as well as the third member of this class of natural products, ivangulin (**3**).[3] Herein, we describe the result of quite different synthetic reasoning demonstrated by the construction of eriolanin.

It occurred to us that base-induced ring opening of the bicyclooctenol **4** ought to afford the cyclohexenone **5** possessing the indicated stereochemistry.[4] Either stereoselective reduction or epoxidation of **5** would result in procurement of an intermediate readily convertible into the synthetic target. Our initial efforts to secure **4** utilized the obvious [4 + 2] cycloaddition reaction which unfortunately led to a low-yield production of all possible isomers of the corresponding adduct.[5] We were able, however, to stereoselectively secure **4** by using the sequence shown in Scheme I.

Treatment of the hydroxymethyl residue of the vinylogous ester **6** with chloromethyl methyl ether followed by hydrolysis with aqueous KOH at 50 °C gave the corresponding alcohol-protected vinylogous acid.[6] Refluxing this substance in a mixture of toluene and hexamethyldisilazane afforded the air-sensitive vinylogous silyl ester **7** [bp 110 °C (10^{-3} mm Hg)] in 70% overall yield from **6**.[7] A stereoselective tandem conjugate addition reaction of this substance to methyl crotonate was then carried out. Kinetic deprotonation of **7** with lithium diisopropylamide (LDA) in THF at −78 °C followed by addition of methyl crotonate gave the bicyclooctanone **8** as a single substance (mp 39.5–41 °C) in 74% yield.[8] A variety of methods for the conversion of **8** into **4** were examined, and by far the best route commenced with deprotonation of **8** with LDA followed by bromination of the enolate with elemental bromine. The bromo ketone was reduced with sodium borohydride to give a mixture of bromohydrins which were then treated with zinc in ethanol to afford **4** (oil); desilylation of the bridgehead alcohol occurs in the last reaction workup. The olefin alcohol was treated with a catalytic amount of potassium *tert*-butoxide in *tert*-butyl alcohol at 22 °C for 3 min to afford a single substance **5** (oil) in 74% overall yield from **8**.[9] Lithium tri-*tert*-butoxyaluminum hydride reduction of **5** gave a 92% yield of the β-allylic alcohol **9** contaminated with small amounts of the undesired α isomer.[10] Derivatization of **9** with *tert*-butylchlorodimethylsilane (TBSCl) followed by epoxidation with *N*-bromosuccinimide (NBS) in acetone/water/Na_2CO_3 afforded the *trans*-α-oxy epoxide **10** in 77% yield from **5**.[11] The fully decoupled ^{1}H spectrum of this substance at 400 MHz confirmed its relative stereochemistry.

We then turned our attention to the C_1 homologation of the side chain of **10** and found that several standard methods of accomplishing this were unsatisfactory. By recourse to reduction of the ester with diisobutylaluminum hydride and conversion of the resulting alcohol into its corresponding iodide (via the mesylate), we were able to add a C_2 unit employing (divinylcopper)lithium, thereby obtining the olefin **11** in 85% yield from **10**. The lactone residue was then appended onto **11** by removal of the silyl residue with triethylamine hydrofluoride, reaction of the epoxy alcohol with dilithioacetate, and lactonization mediated by *p*-toluenesulfonic acid.[12] The lactone **12** (mp 75–76 °C) was obtained in 72% yield from **11**.

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(3) For total syntheses of **1** and **2**, see P. A. Grieco, T. Oguri, S. Gilman, and G. T. DeTitta, *J. Am. Chem. Soc.*, **100**, 1616 (1978); P. A. Grieco, T. Oguri, and S. Gilman, *ibid.*, **102**, 5886 (1980). For the isolation of **3**, see W. Herz, Y. Sumi, V. Sudarsanam, and D. Raulais, *J. Org. Chem.*, **32**, 3658 (1967). For a total synthesis of **3**, see P. A. Grieco, T. Oguri, C.-L. J. Wang, and E. Williams, *J. Org. Chem.*, **42**, 4113 (1977).

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(5) For some examples of similar difficulties with the Diels–Alder reaction, see A. J. Birch, P. L. MacDonald, and V. H. Powell, *Tetrahedron Lett.*, **5**, 351 (1969); T. Ibuka, Y. Mori, and Y. Isubushi, *ibid.*, **36**, 3169 (1976); T. Ibuka, Y. Mori, T. Aoyama, Y. Isubushi, *Chem. Pharm. Bull.*, **26**, 456 (1978).

(6) Compound **6** is readily prepared from trimethylgallic acid. Yields much higher than that reported in the literature can be realized by rapid reaction workup: O. L. Chapman and P. Fitton, *J. Am. Chem. Soc.*, **85**, 41 (1963), and references cited therein. Also see W. Nagata, S. Hirai, T. Okumura, and K. Kawata, *ibid.*, **90**, 1650 (1968).

(7) S. Torkelson and C. Ainsworth; [*Synthesis*, 722 (1976)] describe the use of hexamethyldisilane with imidazole for silylation of 1,3-dicarbonyl compounds. The use of bis(trimethylsilyl)acetamide has been described for this type of reaction by J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Am. Chem. Soc.*, **88**, 3390 (1966).

(8) Tandem conjugate addition reactions starting from the kinetic enolates of unsaturated cyclic ketones have been described in detail by K. B. White and W. Reusch, *Tetrahedron*, **24**, 2439 (1978). A single reaction of this kind starting from the kinetic enolate derived from a cyclic vinylogous ester has been reported by M. L. Quesada, R. H. Schlessinger, and W. H. Parsons, *J. Org. Chem.*, **43**, 3968 (1978).

(9) The singularity of this material was demonstrated by the ^{1}H spectrum of this substance at 400 MHz together with its ^{13}C spectrum.

(10) The stereochemical course of this reaction was anticipated on the basis of literature precedence summarized by E. Toromanoff, *Top. Stereochem.*, *2*, 157 (1967).

(11) While a varity of methods to secure *trans*-α-oxy epoxides are available, the method described therein proved considerably superior in this instance. For other examples, see C. G. Chavdarian and C. H. Heathcock, *Synth. Commun.*, **6**, 277 (1976).

(12) For several examples of the reaction of dilithio acetate with α-oxy expoxides, see S. Danishefsky, M.-Y. Tsai, and T. Kitahara, *J. Org. Chem.*, **42**, 396 (1977).

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