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BF_3-induced cyclobutane-opening of verbenone and its deconjugate homolog. Efficient preparation of *o*-mentha-1,8-dien-3-one and *o*-menth-1-en-3-one in optically active forms

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Abstract

Starting with (+)-verbenone, readily obtainable from (+)-nopinone, enantioselective preparation of (*S*)-(+)-4-isopropenyl-, (*S*)-(−)-4-isopropyl- and (*R*)-(+)-4-(1-acetoxy-1-methylethyl)-3-methyl-2-cyclohexen-1-ones was accomplished with little loss of stereochemical integrity via BF_3-induced cyclobutane-opening of (+)-4-(methylene)nopinone. As we have developed an efficient chemical transformation of (+)-nopinone into (−)-verbenone, the present syntheses of the above cyclohexenones are formal syntheses of their enantiomers from (+)-nopinone.

1. Introduction

2-Cyclohexen-1-ones are potentially useful precursors for the synthesis of carbocycles. In fact, they have frequently been utilized as acceptors in the conjugate addition reaction with carbon nucleophiles and as dienophiles for the Diels–Alder reaction.[1,2]

During the course of our enantioselective synthesis of natural products from (+)-nopinone **1**, readily available in a large quantity by ozonolysis of (−)-β-pinene, a substantial quantity of *o*-mentha-1,8-diene-3-one (4-isopropenyl-3-methyl-2-cyclohexen-1-one) **2**, and *o*-menth-1-en-3-one (4-isopropyl-3-methyl-2-cyclohexen-1-one) **3**, in optically active forms were required as chiral starting materials (Fig. 1). A search of the literature showed a few racemic preparations of these useful compounds, in which transformation of the Hagemann's ester into **2** in five steps and ca. 40% overall yield[3] and $EtAlCl_2$-catalyzed cyclization of 8-methylnona-2,7-dien-4-one to give **3** in ca. 80% yield[4] may be synthetically reliable. Regarding optically active **2**, Lander et al. have isolated (*R*)-(−)-**2b** in ca. 7% yield from a complicated mixture produced on heating (−)-verbenone **4b** with *p*-toluenesulfonic acid in acetic acid

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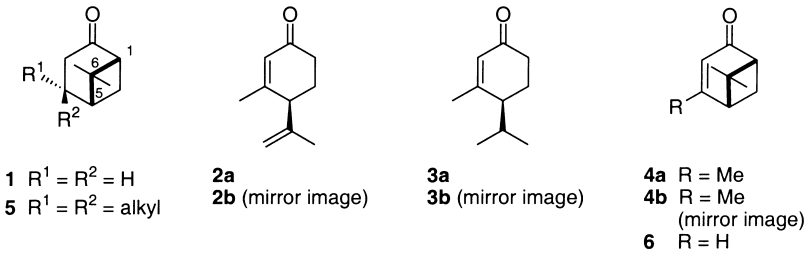
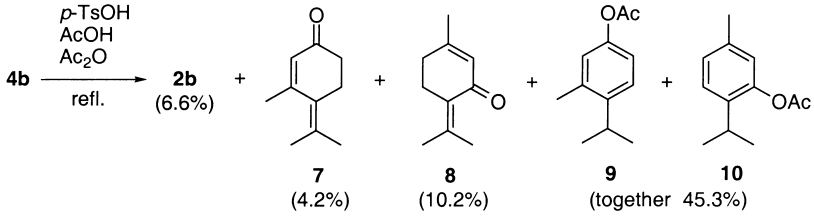


Figure 1.

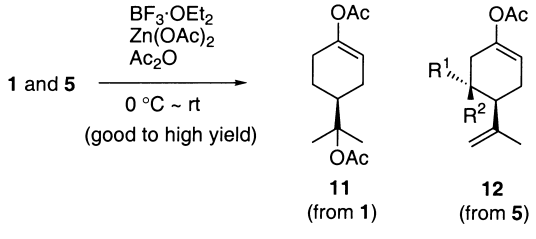
and acetic anhydride, along with a few ring-opened products **7**–**10** (Eq. 1).[5] On the other hand, (*S*)-(+)-**2a** was prepared by Fujisawa et al.,[6] in the synthesis of (+)-β-elemenone, from (*S*)-2-cyclohexen-1-ol in eight steps and ca. 15% overall yield. To the best of our knowledge, little is known about the preparation of **3** in optically active forms. These findings prompted us to study an efficient synthesis of the title compounds in optically active forms. We wish to report that, starting from (+)-verbenone **4a**, efficient preparations of (*S*)-**2a** and (*S*)-**3a** may be carried out in few steps and with synthetically satisfactory overall yields.



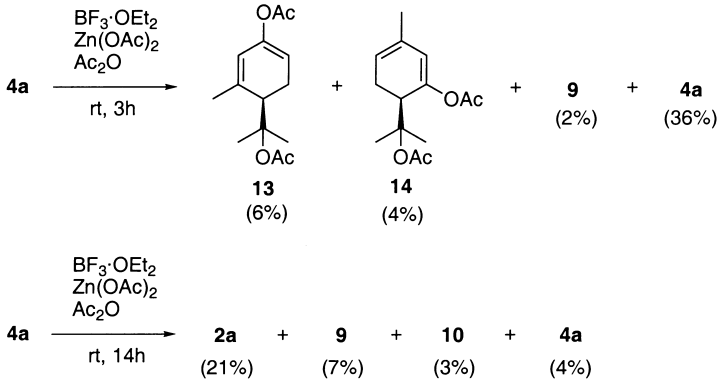
(1)

2. Results and discussion

We have established that cyclobutane ring opening of **1** and its substituted nopinones **5** with a combined reagent, $BF_3 \cdot OEt_2/Zn(OAc)_2/Ac_2O$, proceeded smoothly by a regioselective cleavage of the C(1)–C(6) bond at 0°C–room temperature to give enol acetates of cyclohexanones, **11**[7] and **12**,[8] respectively, in good to high yields with little loss of optical integrity (Eq. 2). First, as part of a study on cyclobutane opening of nopinone and its related compounds, we examined the reaction of verbenone **4a** with our combined reagent, because our reaction conditions are milder than those in Lander's case.[5] More effective production of the cyclobutane-opened product **13**, which would serve as a precursor of **2a**, could therefore be expected (Scheme 1). Optically active verbenone **4a** is a natural product which is available commercially. However, this substrate with high optical purity is expensive. Efficient synthesis of **4a** has been achieved by the allylic oxidation of (*S*)-(−)-α-pinene,[9] and by chemical transformation of **1** via (+)-apoverbenone **6** which we have recently reported.[10]



(2)

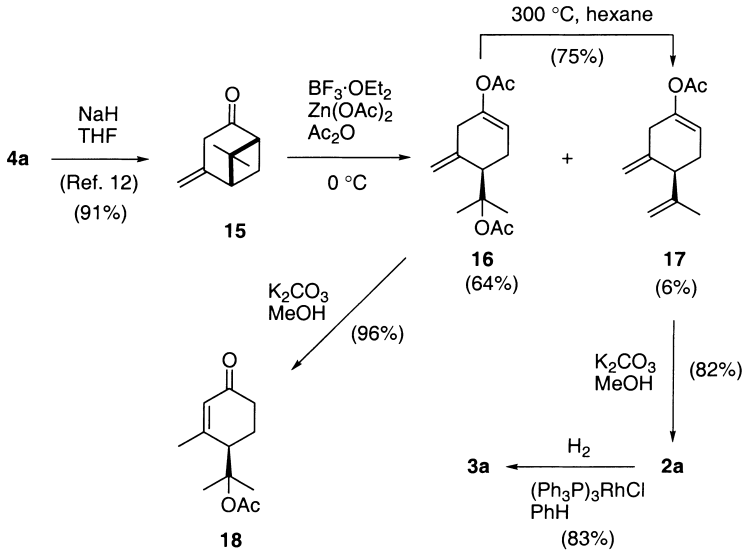


Scheme 1.

BF_3-induced cyclobutane ring opening of **4a** was carried out under our reaction conditions; stirring **4a** with $BF_3 \cdot OEt_2$ (0.5–1.0 equiv.) in the presence of $Zn(OAc)_2$ (1.0 equiv.) in Ac_2O[7,8] (Scheme 1). The reaction was very sluggish at 0°C, and the substrate **4a** was recovered unchanged in a short reaction time. On treating at room temperature for 3 h, enol acetates, **13** and **14**, and aromatized compound **9** were obtained, albeit in 6, 4 and 2% yields, respectively, along with unreacted **4a**. Enol acetate **13** is the expected product arising from the C(1)–C(6) bond cleavage, whereas formation of enol acetate **14** would be characteristic of verbenone **4a**, and could be accounted for by cleavage of the C(5)–C(6) bond attached to an enone function. On prolonged reaction (14 h) at room temperature, gradual disappearance of the products **13** and **14** (TLC analyses) led to a mixture of complicated products, from which enone **2a** in 21% yields and aromatized compounds **9** and **10** in 7 and 3% yields, respectively, were obtained. Structural elucidation of these products was carried out by comparison of their ^1H NMR spectra with those of the authentic samples. Treatment of **13** and **14** with $BF_3 \cdot OEt_2$ under the same reaction conditions produced **9** and **10**, respectively. These findings indicate that enol acetates **13** and **14** are the initial products in the ring-opening reaction, and compounds **9** and **10** could be derived from **13** and **14**, respectively, by elimination of an acetoxy group on the side chain followed by aromatization with the aid of acetic acid. In addition, the enone **2a** may act as a precursor for the formation of **9**.

After all, BF_3-induced cyclobutane-opening reaction of **4a** provided directly **2a** albeit in 21% yield.[11] However, in spite of the careful optimization of reaction conditions, this reaction always produced a complicated mixture of products. It was assumed that this disappointing result could be attributed not only to the competing cleavage of the C(5)–C(6) bond of verbenone **4a**, but also to elimination of an acetoxy group at the homoallylic position in the products with formation of aromatized compounds **9** and **10**. We thus turned our attention to cyclobutane-opening of enone **15**, followed by reconstruction of a conjugate enone function in the product (Scheme 2), because compound **15** is a deconjugate analog of **4a**, and would react in a similar manner as **1** and **5**, as seen in Eq. 2.

Enone **15** was prepared from **4a** in high yield according to the procedure published by Ohloff et al.[12] As expected, the cyclobutane-opening of **15** under our reaction conditions proceeded smoothly even at 0°C to give diacetate **16** and monoacetate **17** in 64 and 6% yields, respectively,[13] which were readily separable by silica gel column chromatography. Judging from the fact that the deconjugate enone **15** itself is easily isomerized to its thermodynamically stable precursor **4a** by a base or an acid, it is worth mentioning that, under our reaction conditions, the ring-opening reaction smoothly proceeds in a regioselective fashion prior to isomerization of a double bond. In fact, on prolonged reaction, formation of **4a** was detected in a complicated mixture of products.



Scheme 2.

Regioselective elimination of an acetoxy group in the side chain of **16** was examined next. After various attempts at the pyrolysis of **16**, it was found that passing a solution of **16** in hexane through a quartz tube packed with quartz beads at 300°C with the aid of an N_2 stream gave **17** in 75% yield as the sole product.[14] The desired enone (+)-**2a** was prepared from **17** in 82% yield by methanolysis with K_2CO_3 in methanol and concomitant isomerization of a double bond. Regioselective hydrogenation of **2a** was successfully carried out under the homogeneous conditions employing tris(triphenylphosphine)rhodium chloride [$(PPh_3)_3RhCl$] to give **3a** in 83% yield.[14] The compounds **2a**, **3a**, **16**, and **17** thus obtained are stable, and can be stored in a refrigerator.

The enantiomeric purity of **2a** and **3a** were established by HPLC analysis employing a Chiral Pak AD column with hexane–isopropyl alcohol as eluant, indicating the enantiomeric purities (ees) of both **2a** and **3a** to be 98.9%. When the ee (99%) of the starting material **4a** is taken into account, it was confirmed that there is almost no loss of enantiomeric purity in the chemical transformations of **4a** into **2a** and **3a**.

Finally, methanolysis of **16** in the presence of K_2CO_3 was carried out. When the reaction was conducted at 0°C for 30 min, enone **18** was obtained in a nearly quantitative yield, whereas prolonged exposure resulted in the unfavorable elimination of acetic acid to produce the dienone **7** as the major product along with **18**.

3. Conclusion

In summary, BF_3-induced cyclobutane-opening of verbenone **4a** provided a complicated mixture of products, from which two initial products, **13** and **14**, in a short reaction time, and enone **2a**, on prolonged exposure, were isolated along with aromatized compounds **9** and **10**. On the other hand, the reaction of **15**, a deconjugate homolog of **4a**, with $BF_3 \cdot OEt_2$ proceeded smoothly via an expected ring-opening to give **16** and **17** in good combined yield. On pyrolysis, compound **16** led to **17** in good yield. Enantioselective preparation of enones (*S*)-**2a** and (*S*)-**3a** were accomplished by treatment of **17** with a base for the former, and by regioselective hydrogenation of **2a** for the latter. Ultimately, (*S*)-**2a** and (*S*)-**3a** were prepared in four and five steps, and ca. 45 and ca. 40% overall yields from (+)-verbenone **4a**, respectively. As we have developed a general and efficient chemical transformation of **1** into (−)-verbenone **4b**,[15] the

present synthesis of (*S*)-**2** and (*S*)-**3** is formal synthesis of their enantiomers, (*R*)-**2** and (*R*)-**3**. The present methodology is useful for the laboratory-scale preparation of **2** and **3** in optically active forms on account of the availability of starting materials, simplicity of operations, and good overall yields.

4. Experimental section

4.1. General remarks

(+)-Verbenone **4a** was obtained by oxidation of (*S*)-(−)-α-pinene (99% ee) according to the published procedure by Lajunen et al.[9] The deconjugate enone **15** was prepared from (+)-**4a** according to the published procedure by Ohloff et al.[11] ^{1}H NMR spectra were recorded at 400 MHz. *J* Values are given in hertz. [α] Values are given in units of 10^{-1} deg cm^2 g^{-1}. All reactions were carried out under a dry N_2 or Ar atmosphere. Extracts obtained on aqueous work-up of the reaction mixtures were washed successively with water and brine, unless otherwise stated, and Na_2SO_4 was used for drying of extracts. Column chromatography was performed on 70–230 mesh silica gel (Merck). Medium-pressure chromatography (MPLC) utilized a 22∅×300 mm silica gel (10 μm) column. Solvents for elution are shown in parentheses. Ether refers to diethyl ether.

*4.2. (*R*)-(−)-3-Acetoxy-6-(1-acetoxy-1-methylethyl)-1-methyl-1,3-cyclohexadiene **13**, 1-acetoxy-6-(1-acetoxy-1-methylethyl)-3-methyl-1,3-cyclohexadiene **14** and 1-acetoxy-4-isopropyl-3-methylbenzene **9***

To a stirred mixture of **4a** (1.0 g, 6.16 mmol) and zinc acetate (1.24 g, 6.16 mmol) in acetic anhydride (12 ml) at 0°C was added $BF_3 \cdot OEt_2$ (0.86 ml, 6.16 mmol). After being stirred briefly, the cooling bath was removed, and stirring was continued at room temperature for 3 h. The reaction mixture was diluted with water (15 ml), and stirring was continued for an additional 2 h. The product was extracted with ether:hexane (1:1), and the combined extracts were washed successively with aqueous $NaHCO_3$, water and brine, and dried. Evaporation of the solvent left a residue which was filtered through a short silica gel column (hexane:EtOAc, 6:1). Concentration of the filtrate followed by purification of the residue by MPLC (hexane:EtOAc, 10:1) gave **13** (88 mg, 6%), **14** (60 mg, 4%), **9** (24 mg, 2%) and unreacted **4a** (360 mg, 36%).

13: oil, $[\alpha]_D^{20}$ −194.5 (*c* 0.34, $CHCl_3$). IR (film) 1763, 1732, 1670, 1618, 1247, 1218, 1183, 1124, 1023, 912, 869, 817 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.52 and 1.54 (3H, s each), 1.92 (3H, s), 1.99 and 2.13 (3H, s each), 2.42 (1H, ddd, *J*=18.3, 6.6, 1.5), 2.62 (1H, ddd, *J*=18.3, 10.2, 2.0), 2.89 (1H, d, *J*=10.2), 5.16 (1H, d, *J*=6.6, 2.0), 5.66 (1H, s). HRMS *m/z* calcd for $C_{12}H_{16}O_2$ [M−OAc]$^+$ 192.1149, found 192.1151.

14: oil, $[\alpha]_D^{20}$ +89.8 (*c* 0.24, $CHCl_3$). IR (film) 1763, 1732, 1682, 1617, 1584, 1250, 1212, 1182, 1132, 1078, 1044, 1019, 952, 982, 884 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.41 and 1.47 (3H, s each), 1.70 (3H, s), 1.98 and 2.13 (3H, s each), 2.35 (1H, ddd, *J*=18.6, 6.1, 1.3), 2.71 (1H, ddd, *J*=18.6, 10.8, 2.9), 3.16 (1H, dd, *J*=10.8, 1.3), 5.27 (1H, dd, *J*=6.1, 2.9), 5.68 (1H, s). HRMS *m/z* calcd for $C_{12}H_{16}0_2$ [M−OAc]$^+$ 192.1149, found 192.1151.

9: oil, IR (film) 1762, 1211, 1016, 902 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (6H, δ, *J*=6.8), 2.27 (3H, s), 2.32 (3H, s), 3.09 (1H, h, *J*=6.8), 6.84 (1H, d, *J*=2.6), 6.88 (1H, dd, *J*=8.3, 2.6), 7.23 (1H, d, *J*=8.3). The IR and ^{1}H NMR spectral data were identical with those of the authentic sample.[4]

4.3. (S)-(+)-4-Isopropenyl-3-methyl-2-cyclohexen-1-one **2a** and 2-acetoxy-1-isopropyl-4-methylbenzene **10**

To a stirred mixture of **4a** (162 mg, 1.0 mmol) and zinc acetate (183 mg, 1.0 mmol) in acetic anhydride (2 ml) at 0°C was added $BF_3 \cdot OEt_2$ (0.13 ml, 1.0 mmol). After being stirred briefly, the cooling bath was removed, and stirring continued at room temperature for 14 h. Aqueous work-up according to the procedure described above followed by purification of the residue by MPLC gave **2a** (31 mg, 21%), **9** (14 mg, 7%), **10** (6 mg, 3%) and unreacted **4a** (15 mg, 9%).

2a: oil, $[\alpha]_D^{20}$ +167.6 (*c* 0.34, $CHCl_3$), {lit.[5] $[\alpha]_D^{22}$ +171.9 (*c* 1.01, $CHCl_3$)}. IR (film) 1670, 1645, 1625, 1248, 1191, 898, 877 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (3H, s), 1.90 (3H, s), 1.96–2.13 (2H, m), 2.26 (1H, ddd, *J*=16.6, 5.8, 4.8), 2.41 (1H, ddd, *J*=16.6, 11.2, 4.8), 2.89 (1H, t, *J*=4.6), 4.74 (1H, s), 4.96 (1H, s), 5.97 (1H, s). The IR and ^1H NMR spectral data were identical with those of the authentic sample.[3,5]

10: oil, IR (film) 1763, 1368, 1209, 1120, 899 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (6H, δ, *J*=6.8), 2.31 (6H, s), 2.97 (1H, h, *J*=6.8), 6.80 (1H, d, *J*=1.0), 7.03 (1H, dd, *J*=8.1, 1.0), 7.19 (1H, d, *J*=8.1). The ^1H NMR spectrum was identical with that of the authentic sample (thymol acetate).

4.4. (R)-(−)-1-Acetoxy-4-(1-acetoxy-1-methylethyl)-5-(methylene)cyclohexene **16** and (R)-(−)-1-acetoxy-4-isopropenyl-5-(methylene)cyclohexene **17**

To a stirred mixture of **15** (150 mg, 1.00 mmol) and zinc acetate (183 mg, 1.00 mmol) in acetic anhydride (3 ml) at 0°C was added $BF_3 \cdot OEt_2$ (0.06 ml, 0.50 mmol), and stirring was continued for 3 h. To the reaction mixture, water (7 ml) was added and stirring was continued for an additional 2 h. The product was extracted with ether, and combined extracts were washed successively with aqueous $NaHCO_3$, water, and brine, and dried. Removal of the solvent left a residue which was chromatographed on silica gel (hexane:ether, 9:1) to give **16** (162 mg, 64%) and **17** (11 mg, 6%) along with unreacted **15** (6 mg, 4%).

16: oil, $[\alpha]_D^{24}$ −11.8 (*c* 0.15, $CHCl_3$). IR (film) 1760, 1732, 1646, 1252, 1220, 1118, 1020, 944; ^1H NMR ($CDCl_3$) δ 1.50 and 1.53 (3H, s each), 1.97 and 2.12 (3H, s each), 2.34 (2H, s with fine splittings), 2.79 (1H, d, *J*=18.8), 2.82–2.85 (1H, m), 3.04 (1H, d with fine splittings, *J*=18.8), 4.94 (1H, s), 4.99 (1H, s), 5.40 (1H, s). Anal. calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.35; H, 7.87.

17: oil, $[\alpha]_D^{24}$ −82.5 (*c* 1.04, $CHCl_3$). IR (film) 1759, 1695, 1646, 1216, 1119, 1080, 1011, 895; ^1H NMR ($CDCl_3$) δ 1.75 (3H, s), 2.12 (3H, s each), 2.32–2.37 (2H, m), 2.86–2.96 (3H, m), 4.84 (2H, s), 4.88 (1H, s), 4.95 (1H, s), 5.44 (1H, s). Anal. calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.65; H, 8.24.

4.5. Pyrolysis of **16**

A solution of **16** (1.20 g, 4.76 mmol) in hexane (10 ml) was passed through a quartz tube (21×1.5 cm) packed with quartz beads at 300°C with the aid of an N_2 stream, and the vapor was condensed in a dry ice–acetone bath. The condensate was passed through a silica gel column (hexane:ether, 9:1) to give **17** (688 mg, 75%) and unreacted **16** (95 mg, 8%). The IR and ^1H NMR spectral data of **17** were identical with those of the authentic sample prepared above.

4.6. Methanolysis of **17** with formation of **2a**

A mixture of **17** (688 mg, 3.58 mmol) and K_2CO_3 (990 mg, 7.16 mmol) in methanol (5 ml) was stirred at 0°C for 30 min, and then at room temperature for 1.5 h. Water was added to the reaction mixture, and the product was extracted with ether. Concentration of the extracts followed by chromatography of the residue on silica gel (hexane:ether, 4:1) gave **2a** (439 mg, 82%), $[\alpha]_D^{15}$ +187.1 (*c* 1.06, $CHCl_3$), whose IR and ^1H NMR spectral data were identical with those of an authentic sample prepared from **4a**. HPLC analysis employing a Chiral Pak AD column with hexane–isopropyl alcohol (49:1) as eluant demonstrated the ee to be 98.9%.

4.7. (S)-(−)-4-Isopropyl-3-methyl-2-cyclohexen-1-one **3a**

The compound **2a** (150 mg, 1.0 mmol) and $(Ph_3P)_3RhCl$ (46 mg, 0.05 mmol) were dissolved in degassed benzene (2 ml), and the resulting solution was hydrogenated at atmospheric pressure for 6 h. The reaction mixture was added to a silica gel column, and the benzene was removed by use of hexane as eluant, then the product was eluted with hexane:ether (4:1) to give **3a** (127 mg, 83%) as an oil, $[\alpha]_D^{19}$ −20.8 (*c* 0.53, $CHCl_3$). IR (film) 1678, 1619, 1253, 1191, 947, 872 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 and 1.04 (3H, d, *J*=6.8 each), 1.86 (1H, m), 1.96 (1H, m), 1.99 (3H, s), 2.17–2.26 (2H, m), 2.28 (1H, ddd, *J*=17.0, 10.0, 5.4), 2.46 (1H, ddd, *J*=17.0, 7.1, 4.7), 5.92 (1H, s). Anal. calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.61; H, 10.56. HPLC analysis employing a Chiral Pak AD column with hexane:isopropyl alcohol (99:1) as eluant demonstrated the ee to be 98.9%.

4.8. (R)-(+)-4-(1-Acetoxy-1-methylethyl)-3-methyl-2-cyclohexen-1-one **18**

A mixture of **16** (154 mg, 0.61 mmol) and K_2CO_3 (337 mg, 2.44 mmol) in methanol (1 ml) was stirred at 0°C for 30 min. The reaction mixture was quenched by addition of water and extracted with ether. Removal of the solvent followed by chromatography of the residue on silica gel (hexane:ether, 4:1) gave **18** (89 mg, 96%) as an oil, $[\alpha]_D^{24}$ +78.1 (*c* 0.92, $CHCl_3$). IR (film) 1732, 1671, 1623, 1251, 1116, 1019, 951, 870; ^1H NMR ($CDCl_3$) δ 1.47 and 1.64 (3H, s each), 1.99 (3H, s), 2.07 (3H, 3), 2.02–2.15 (2H, m), 2.31 (1H, dt, *J*=17.8, 5.8), 2.36 (1H, ddd, *J*=17.8, 10.5, 5.8), 3.04 (1H, t, *J*=5.8), 6.01 (1H, s). HRMS *m/z* calcd for $C_{10}H_{15}O$ $[M-OAc]^+$: 151.1122; found 151.1122.

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11. Comparison of the optical rotation, $[\alpha]_D$ +167.6 ($CHCl_3$), of **2a** directly derived from **4a** with that, $[\alpha]_D$ +187.1 ($CHCl_3$), of **2a** obtained via **15** revealed that the former **2a** may be somewhat racemized in the course of the ring-opening reaction (see Experimental).
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13. On a large scale preparation, a tendency to decrease the combined yield of the ring-opened products **16** and **17** was observed. We have, at present, no reasonable explanation for this observation.
14. For analogous reaction, see Kato, M.; Watanabe, M.; Tooyama, Y.; Vogler, B.; Yoshikoshi, A. *Synthesis* **1992**, 1055.
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