reflections, 14141 are independent, and these were used for the refinement of 650 parameters; maximal residual electron density: 402 e nm^{-3}, $R1(F>4\sigma(F))=0.054$ and $wR2=0.113$ (all data) with $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR2=(\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. Data were collected on a Siemens CCD platform diffractometer. The SMART program package was used for data collection. Raw frame data was processed by using SAINT and SADABS to yield the reflection data file. All subsequent calculations were performed using the SHELXTL program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis and hydrogen atoms were included by using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101403. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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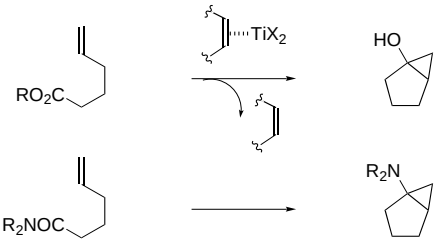
Highly Enantio- and Diastereoselective Synthesis of 2-Substituted 1-Bicyclo[3.1.0]hexanols**

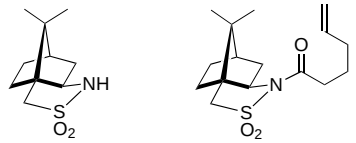
Ryo Mizojiri, Hirokazu Urabe, and Fumie Sato*

Bicyclic cyclopropanols and their derivatives, such as the trimethylsilyl ethers, have been utilized as useful intermediates in organic synthesis by the manipulation of their reactive cyclopropanol moiety.[1] However, the asymmetric preparation of these compounds has been quite limited so far,[2, 3] even though current developments in enantioselective synthesis should call for the use of optically active cyclopropanols as starting materials.

The reaction of unsaturated esters,[4] amides,[5] imides,[6] and related compounds[7] with an alkene–titanium complex[8] is a very convenient method to prepare bicyclic cyclopropanols[4] and cyclopropylamines[5] in one step [Eqs. (1) and (2); X = R′O, Cl, Br]. Extension of this transformation to an asymmetric version would clearly serve as a simple route to optically active cyclopropanols (or cyclopropylamines). To this end, the use of a chiral titanium complex was successful.[9] An alternative approach is to incorporate a chiral auxiliary in



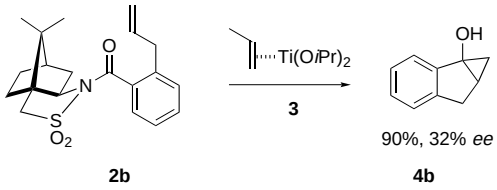
the substrate. Thus, an unsaturated carboxylic acid derivative having a chiral leaving group on its acyl group would afford the corresponding optically active bicyclic cyclopropanol; surprisingly, this method has not been reported yet. We chose Oppolzer's camphorsultam **1**[10] as the leaving group, because



1 **2a**

the known enantioselective α-alkylation of the *N*-acyl derivative **2a**[11] could be performed not only with activated halides (i.e., allyl or benzyl halides) but also with nonactivated counterparts (i.e., primary alkyl halides).[11] As we show here, this allowed the preparation of a variety of substituted bicyclic cyclopropanols.

The ability of acylsulfonamides to act as esters in reaction (1) to give cyclopropanols (rather than as amides in reaction (2) to yield cyclopropylamines) has not been demonstrated. This issue as well as the asymmetric induction in the nucleophilic addition to *N*-acylcamphorsultams[12] is addressed in the reaction of **2b** with [Ti(O*i*Pr)$_2$(η^2-propene)] (**3**) as shown in Equation (3).[4a] To our satisfaction, optically



2b **4b**

active cyclopropanol **4b** was obtained, while the possible byproduct, a *N*-cyclopropylsulfonamide, was not detected at all. Unfortunately, the enantiopurity of the product does not reach a satisfactory level.

Nonetheless, the α-branched acylsultams, readily prepared by diastereoselective alkylation of the *N*-acylcamphorsultam **2a** according to the literature method,[11] showed nearly complete stereocontrol in the cyclopropanol cyclization. Thus, treatment of **2c** with **3** afforded **4c** virtually as a single product and in high yield [Eq. (4)]. The diastereoselectivity was determined by ^{1}H NMR spectroscopy in comparison with an authentic mixture of the diastereoisomers, and the relative configuration shown for **4c** was established by NOE experi-

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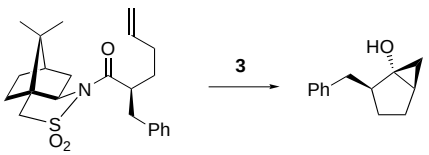
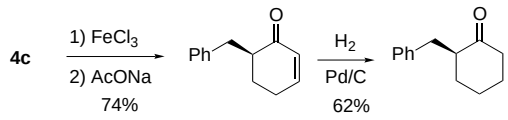


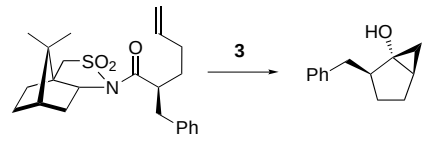
2c *ds* > 99: 1 **4c** 86% *ds* > 99: 1 >98% *ee* (4)

ments. That the enatiopurity of **4c** maintains the original value of **2c** was verified by a ^{1}H NMR chiral shift study ([Eu(hfc)$_3$], hfc = 3-(heptafluoropropylhydroxymethylene)-D-camphorate). The absolute structure of **4c** was determined by derivatization to the known (−)-2-(phenylmethyl)cyclohexanone[13] through ring expansion with $FeCl_3$[14] followed by hydrogenation of the resultant cyclohexenone [Eq. (5)].

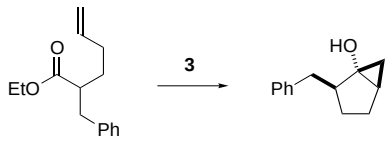


(5)

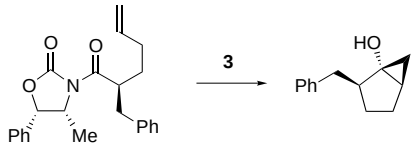
The highly stereoselective construction of the bicyclic cyclopropanol moiety (which, at the same time, leads to the high diastereoselectivity) seems to arise from a cooperative effect of the chiral auxiliary used and the neighboring alkyl substituent that results in the second chiral center (R in Table 1). If instead of the acylsultam **2c**, its diastereoisomer **2j** [Eq. (6)], a simple ethyl ester **5** [Eq. (7)],[4b] or the *N*-acyloxazolidinone **7** from Evans et al.[15] [Eq. (8)] is used, there is a considerable decrease in the diastereoselectivity. This supports the above rationalization.



2j *ds* > 99:1 **6** 78% *ds* = 92: 8 (6)



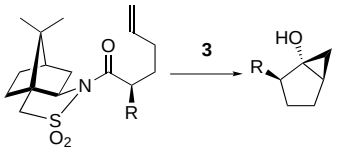
5 **6** 77% *ds* = 66:34 (7)



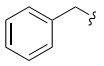
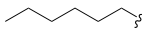
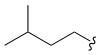
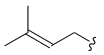
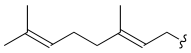
7 **6** 38% *ds* = 74:26 (8)

Table 1 shows that a variety of bicyclic cyclopropanols can be obtained in good yields and with high diastereoselectivities. Another important feature of this reaction is the compatibility of a variety of functional groups. For instance, the reaction of **2f** and **2g** afforded the desired products with their internal olefins intact. In addition, oxygen functionalities such as a silyl ether and even a *tert*-butyl ester group in substrates **2h** and **2i** survived the reaction conditions. The parent camphorsultam **1** was recovered after the reaction (80–90% for entries 1 and 2) and could be recycled for other runs.

Table 1. Diastereoselective synthesis of optically active cyclopropanols by the following reaction:[a]



2 *ds* > 99: 1 **4** >98% *ee*

Entry	R	Derivative	Yield of **4** [%][b]	*ds*[c]
1		**c**	86	> 99:1[d]
2		**d**	58	> 95:5
3		**e**	80	> 95:5
4		**f**	87	> 95:5
5		**g**	74	> 95:5
6	*t*BuMe$_2$SiO 	**h**	84	> 95:5
7	*t*BuO$_2$C	**i**	56	92:8[d]

[a] For details, see the Experimental Section. [b] Yield of isolated product. [c] Determined by ^{1}H and ^{13}C NMR spectroscopy of the crude and purified samples, unless otherwise noted. [d] Determined by ^{1}H NMR spectroscopy in comparison with an authentic mixture of the diastereomers.

In summary, the cyclization of unsaturated acylsulfonamides derived from Oppolzer's camphorsultam with low-valent titanium complex **3** affords optically active bicyclic cyclopropanols, which are difficult to prepare by existing methods. The synthetic utility of the products **4**, an example for which is illustrated by the preparation of an optically active 6-substituted-2-cyclohexenone [Eq. (5)], will be reported in due course.

Experimental Section

The following procedure for the preparation of **4c** is representative: To a solution of **2c** (80 mg, 0.20 mmol) and Ti(O*i*Pr)$_4$ (0.12 mL, 0.40 mmol) in Et$_2$O (2.0 mL) was added *i*PrMgCl (0.57 mL of a 1.40 M solution in Et$_2$O, 0.80 mmol) at −50 °C under argon. After the reaction mixture was stirred

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at low temperature (ca. −45 to −40 °C) for 1 h, it was stirred at 0 °C for another hour. After the addition of water (0.20 mL) in THF (0.40 mL), the solution was stirred for 0.5 h at room temperature. The resultant suspension was filtered through celite, which was subsequently washed with Et_2O. The filtrate and Et_2O fractions were concentrated in vacuo to afford a crude oil. Purification by column chromatography (silica gel, hexane/ether 5/1) afforded **4c** (32 mg, 86 % yield) as a colorless oil. $[\alpha]_D^{27} = -0.65$ ($c = 0.46$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 3404, 3062, 2929, 1948, 1876, 1602, 1495, 1452, 976, 756, 701\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.15-7.32$ (m, 5H), 2.87 (dd, $J = 6.0$, 13 Hz, 1H), 2.43–2.66 (m, 2H), 1.82 (ddt, $J = 4.2$, 7.8, 12 Hz, 1H), 1.61–1.70 (m, 1H), 1.69 (s, 1H), 1.48 (dd, $J = 7.8$, 12 Hz, 1H), 1.37 (dt, $J = 9.0$, 4.2 Hz, 1H), 0.86–0.91 (m, 1H), 0.76 (dd, $J = 5.4$, 9.0 Hz, 1H), 0.67 (t, $J = 5.4$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.8$, 24.3, 25.3, 28.3, 37.9, 46.8, 67.1, 126.1, 128.6, 128.9, 141.7.

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Two New Isopolyoxotungstates(VI) with the Empirical Composition $Cs_2W_2O_7 \cdot 2H_2O$ and $Na_2W_2O_7 \cdot H_2O$: An Icosatetratungstate and a Polymeric Compound**

Irene Brüdgam, Joachim Fuchs, Hans Hartl,* and Rosemarie Palm

Dedicated to Professor Hartmut Bärnighausen on the occasion of his 65th birthday

Owing to their structural and electronic diversity, iso- and heteropolyoxometalates with different metal centers and varying oxidation states undergo an exceptionally wide variety of reactions, which have applications in many fields of chemistry (synthesis, analytical chemistry, catalysis, biochemistry).[1] The number of dissimilar polyoxometalates is enormous; however, certain structural units appear repeatedly, depending on the metal counterion and the synthesis conditions. These can serve as structural components of large, in some cases huge, polyoxometalates formed by conservative self-organizing processes.[2, 3] Examples of isopolytungstates (VI) include the dodecatungstates $H_2W_{12}O_{40}^{6-}$ (Keggin-type)[4] and $H_2W_{12}O_{42}^{10-}$ (paratungstate-Z),[5] the heptatungstate $W_7O_{24}^{6-}$,[6] and the hexatungstate $W_6O_{19}^{2-}$[7] as well as fragments of these anions, which act as isolated units or as components of high molecular aggregates. These groups are linked to each other either directly or through cations and heteroatoms.

Isopolyoxotungstates are produced in a similar manner as other polyoxometalates by acidification of aqueous solutions of monotungstates. In the present case, we used the oxide WO_3, which reacts in water like the hypothetical diprotic acid H_2WO_4, for the acidification. The molar ratio of H^+ introduced to WO_4^{2-} is defined as the degree of acidification of the metalate solution, the molar ratio of H^+ that reacted per WO_4^{2-} is the degree of protonation.[8] The title compounds $Cs_2W_2O_7 \cdot 2H_2O$ (**1**) and $Na_2W_2O_7 \cdot H_2O$ (**2**), which are formally prepared according to Equation (1), display a degree

$$2\,WO_4^{2-} + 2\,H^+ \rightleftharpoons W_2O_7^{2-} + H_2O \qquad (1)$$

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