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A Short Synthesis of (±)-3-Oxosilphinene

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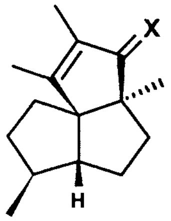
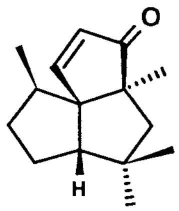
A total synthesis of (±)-3-oxosilphinene was achieved stereoselectively in five steps from the known enone.

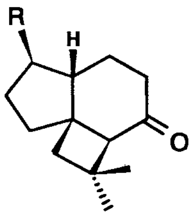
Much attention has been paid to synthetic studies of angularly-fused triquinane sesquiterpenes because of their intriguing structures.[1] We have developed a novel method for constructing the fused 5-5-5 ring systems through the novel rearrangement of the fused 5-6-4 ketones and have achieved total syntheses of (±)-silphiperfol-6-ene (1) and (±)-5-oxosilphiperfol-6-ene (2) by utilizing the rearrangement as the pivotal step.[2] As a further extension of our work, we disclose here a total synthesis of (±)-3-oxosilphinene (3)[3,4] in short steps.



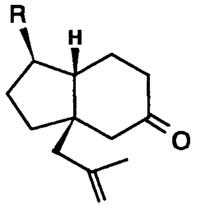
1 X = H_2
2 X = O



3



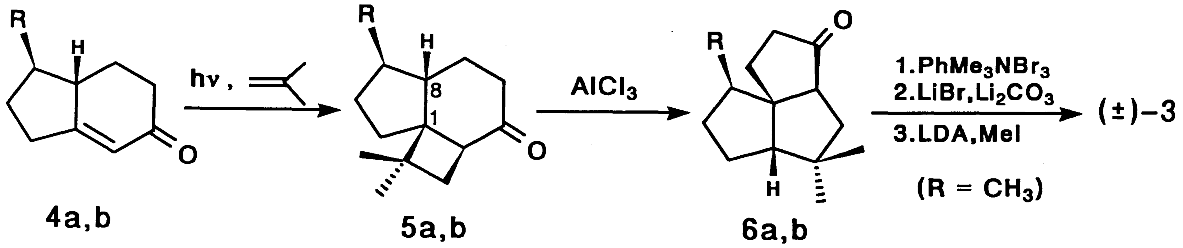
7a R = CH_3
7b R = H



8a R = CH_3
8b R = H

We planned to prepare the angular ketone **6a**, which could be readily transformed to (±)-3, by rearrangement of the ketone **5a** as outlined in Scheme 1. Since it was anticipated that preparation of **5a** by photocycloaddition of the enone **4a**[5] to isobutylene would be difficult in view of the poor regioselectivity observed in enone-isobutylene photoreaction,[6] we first investigated, as a model study, photoreaction of the enone **4b**.[7] Indeed, irradiation of **4b** and isobutylene in various solvents (n-C_5H_{12}, CH_2Cl_2, $CHCl_3$, C_2H_5Br, $(CH_3)_2CO$, $CH_3CO_2C_2H_5$, and CH_3CN) at 0 °C gave the head to head cycloadduct **7b**[8] as major product (20-40% yields) along with the adduct **8b** (18-24%) and the desired head to tail adduct **5b** was obtained only in minor amount (3-18% yields).[9] However, reversal of the selectivity was achieved by using the surface photochemistry technique.[10] Thus, irradiation of **4b** and isobutylene (ca. 10 equiv.) on silica gel (Nacarai Tesque, Silica Gel, 35-70 mesh) at room temperature for 9 h gave **5b** in 32% yield along with **7b** and **8b** in 16% and 10% yields, respectively. As expected, reaction of **5b** with $AlCl_3$ (2 equiv.) [CH_2Cl_2, rt, 3 h] gave the angular ketone **6b** in 86% yield.

With successful results on the model study, we attempted the total synthesis of (±)-**3**. Irradiation of the enone **4a** on silica gel for 8 h as described above gave the head to tail cycloadduct **5a** in 31% yield together with the by-products **7a** and **8a** in 8% and 7% yields, respectively.[9] Treatment of **5a** with $AlCl_3$ for 1 h afforded the desired ketone **6b** in 55% yield. α-Bromination of **6b** [$PhMe_3NBr_3$, THF, 0 °C, 1 h] followed by dehydrobromination [LiBr, Li_2CO_3, DMF, ca. 110 °C, 2 h] and α′-methylation [LDA, THF, -78 °C, then MeI, -78 °C, 5 h] gave (±)-**3** in 34% yield for three steps. The ^1H and ^{13}C-NMR spectra of **3** were consistent with that of an authentic sample synthesized[4] and that reported for natural product,[3] respectively. Thus, the total synthesis of (±)-**3** was accomplished in a stereoselective manner in five steps from the known enone **4a**.



4a,b **5a,b** **6a,b**

a R = CH_3 , **b** R = H

Scheme 1.

We would like to thank Professor K. Fukumoto of Tohoku University for generous supply of the copy of the ^1H-NMR spectrum of (±)-3.

References

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8) All new compounds gave satisfactory spectral and analytical data.
9) The stereochemistry of the new stereogenic center (C-1 and C-4) relative to C-8 of the photoadducts **5a,b**, **7a,b**, and **8a,b** was assumed based on the previous results of the photocycloaddition of the enones **4a,b** to olefins,[2] and that of **5a** was finally confirmed by transformation to **3**. Their regiochemistry was unambiguously elucidated from the spectral properties.
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