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A Convenient Method for the Radical Cyclization of the Aldol Products to Fused Bicyclic Carbocycles

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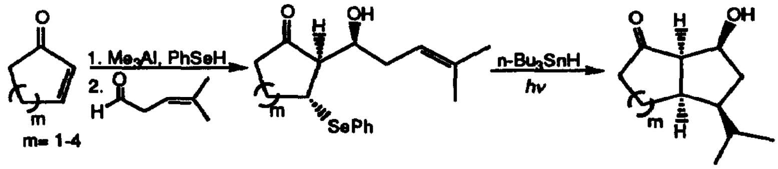
***Abstract:** Photochemical initiation of radical cyclization of aldol condensation products employing simple flood lamp gave various bicyclic carbocycles.*

Radical cyclization is an efficient way to carbocyclic realm of cyclopentenoids. Michael-aldol tandem followed by radical cyclization was reported as a new and highly convergent method for annulation of bicyclic[3.3.0]octanes.[1,2] Frequently thermal initiation in combination with a syringe pump has been used for radical cyclization. However, we found this method cannot be generally applied to the radical cyclization stage for radical cyclization of aldol products to various fused bicyclic carbocycles. This limitation was resulted from decomposition of thermally labile products over prolonged reaction period. Herein, we report simple photo initiation for the cyclization, which circumvents this limitation, and its successful application to the synthesis of various fused carbocycles.

In the sequence of the Michael-aldol tandem-radical cyclization, the treatment of α,β–unsaturated cyclic ketones with (phenylseleno)dimethylalane followed by the addition of 4-methylpent-3-ene-1-al provided the corresponding aldol products and consequent radical cyclization of these species in the presence of n-Bu_3SnH in ether or THF afforded fused carbocycles as shown below.[1,2] Although photochemical initiation generally requires UV light,[3] we found common household flood lamp (250 Watts) is quite suitable for the cyclization toward the fused bicycles. Furthermore, the reaction time for this cyclization requires only 5 to 10 min.[4] Results of our experiments were summarized in Table 1.



Each entry of Table 1 showed the product with β stereochemisty at the side chain. This observed stereoselectivity of radical cyclization in our experiments can be rationalized by Beckwith model[5,6] for the conformation A as shown below. It is very interesting that when 4,4-dimethylcyclopentenone was subjected to our reaction condition, the ratio between α and β of the side chains was found to be 3:1 rather than the value of 1:1 previously reported in the literature.[1]This selectivity can be elucidated by the favorable conformation B.

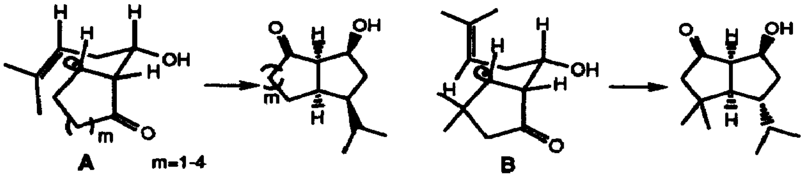
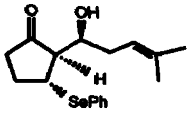
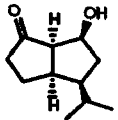
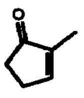
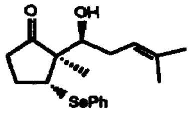
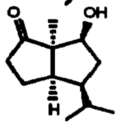
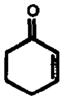
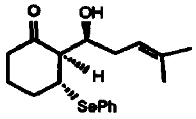
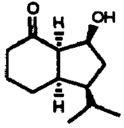
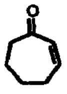
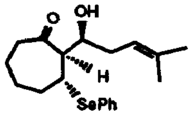
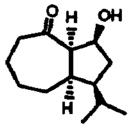
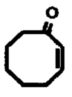
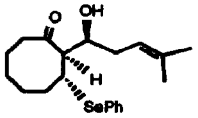
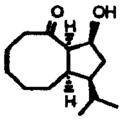


Table 1. Radical Cyclization of Aldol Products

Entry	Substrates	Aldol Products (% yield)	Cyclization Products (% yield)
1		 (92)	 (62)
2		 (40)	 (45)
3		 (84)	 (45)
4		 (61)	 (93)
5		 (55)	 (73)

References and notes

1. Leonard, W. R.; Livinghouse, T. *Tetrahedron Lett.* **1985**, *26*, 6431.
2. Itoh, A.; Ozawa, S.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 274.
3. Sakai, S.; Murata, M.; Wada, N.; Fujinami, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1873.
4. A typical procedure is as follows: to a stirred solution of selenophenyl alcohol (2 mmol) in ether (2 mL) was added. n-Bu_3SnH (4 mmol) under nitrogen atomosphere. The solution was irradiated by a flood lamp. After 5 to 10 min, the solvent was removed *in vacuo* to give the crude product, which was purified by column chromatography (SiO_2, hexane:ethyl acetate=4:1) to provide the pure bicyclic compound.
5. Beckwith, A. L. J.; Easton, C. J., Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1983**, *36*, 545.
6. (a) RajanBabu, T. V.; Fukunaga, T. *J. Am. Chem. Soc.* **1989**, *111*, 296. (b) RajanBabu, T. V.; Fukunaga, T.; Reddy, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1759.

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