Tetrahedron Letters, Vol. 31, No. 12, pp 1739-1740, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

CONJUGATE ADDITION REACTION OF ORGANOLITHIUMS TO NAPHTHALENECARBOXYLATES

Kiyoshi Tomioka,* Mitsuru Shindo, and Kenji Koga
Faculty of Pharmaceutical Sciences, University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

Summary: Reaction of 2,6-di-tert-butyl-4-methoxyphenyl naphthalenecarboxylates with organolithiums provided the addition products to naphthalene nucleus in quantitative yield.

Addition of organometallics to naphthalene nucleus in forming a carbon-carbon bond has been a challenge in synthetic organic chemistry. Recent progresses in the field have been achieved by Meyers based on the oxazoline and imine chemistry.[1] Contrary to these successes, no practical procedure of using naphthalene derivatives having carbonyl or carboxyl function as electron withdrawing group has been developed. We describe here for the first time that 2,6-di-*tert*-butyl-4-methoxyphenyl naphthalenecarboxylate (BHA ester) serves as an acceptor in the reaction of organolithiums.

General idea under consideration for realizing addition of organometallics to naphthalene nucleus relies on steric control, allowing conjugate-type addition by sterically inhibiting nucleophilic attack to carbonyl carbon. Reports by Seebach[2] and Cook[3] have also demonstrated that sterically hindered α,β-unsaturated trityl ketones and BHA esters serve as the Michael acceptors to afford 1,4-conjugate addition products.

Trityl ketone (**1**), *tert*-butyl (**2**), and BHA (**3**) esters were prepared from 1-naphthalenecarbonyl chloride according to the procedure reported for unsaturated carbonyl compounds.[2~4] Although **1** and **2** in reaction with butyllithium provided, respectively, a mixture of complex products[5] and 5-(1-naphthyl)nonan-5-ol (73%) arising from 1,2-addition, BHA ester (**3**) served as an excellent acceptor providing expected product (**4b**: R^1=OBHA, R^2=Bu) in quantitative yield.

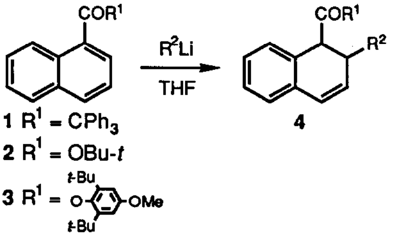


Table I. Synthesis of 4 (R^1=OBHA) from 3

R^2Li	Temp / deg	4	*cis / trans*	Yield / %
Ph	-45	**4a**	2.3	>99
Bu	-78	**4b**	3.5	>99
Me	-23	**4c**	2.2	>99

Typical procedure is exemplified by synthesis of **4b**: A solution of butyllithium (R^2Li) in hexane (1.59 M, 1.3 equiv) was added at -78 °C to a solution of **3** in THF (0.1 M), and the whole was stirred at -78 °C for 1 h and was quenched with CF_3CO_2H. The mixture was diluted with ether and washed successively with satd. $NaHCO_3$ and brine, and dried over $MgSO_4$. Concentration and column chromatography (SiO_2, hexane-ether) provided separable *cis*- and *trans*-**4b** in quantitative yield[1,6]

As summarized in Table I and II, 2-substituted and 1-substituted dihydronaphthalenecarboxylates (**4** and **6**) were obtained from **3** and **5**, respectively, in quantitative yields. It is noteworthy that steric control in protonation of intermediate enolates provided *cis*-**4** as a major product.[1,6]

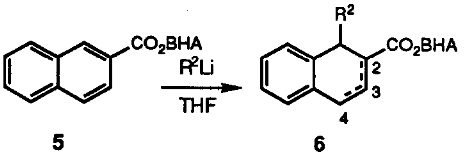
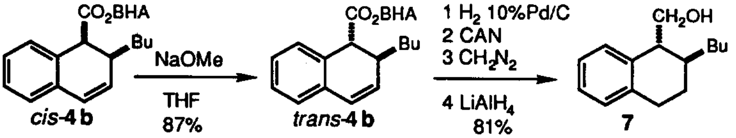


Table II. Synthesis of **6** from **5**

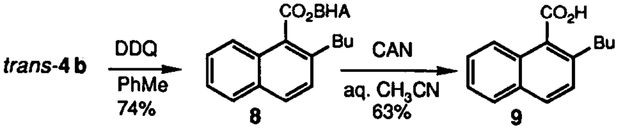
R^2Li	Temp / deg	**6**	Δ2,3 / 3,4	Yield / %
Ph	-45	**6a**	2	>99
Bu	-78	**6b**	4	>99
Me	-23	**6c**	4	>99

Other nucleophiles, butylmagnesium bromide and lithiated ethyl acetate, were found to be unreactive toward **3**.

Epimerization of *cis*-**4b** into *trans*-**4b** was carried out in 87% yield by treating with NaOMe in THF at room temperature. Further elaborations of *trans*-**4b** as shown below provided 2-butyl-1,2,3,4-tetrahydro-1-naphthalenemethanol (**7**) in 81% overall yield.



Aromatization of *trans*-**4b** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing toluene followed by oxidative hydrolysis of **8** with ceric ammonium nitrate (CAN)[3,7] in aqueous acetonitrile at room temperature afforded 2-butyl-1-naphthalenecarboxylic acid (**9**) in good yield.



Further studies including application of the present reaction to an enantioselective process[6] are in progress in our laboratories.[8]

References and Notes

1. A. I. Meyers, G. P.Roth, D. Hoyer, B. A. Barner, and D. Laucher, *J. Am. Chem. Soc.*, **110**, 4611 (1988), and references cited therein.
2. D. Seebach, M. Ertas, R. Locher, and W. B. Schweizer, *Helv. Chim. Acta*, **68**, 264 (1985).
3. M. P. Cook, Jr., *J. Org. Chem.*, **51**, 1637 (1986).
4. New compounds described are racemic and gave satisfactory spectroscopic and analytical data.
5. Reaction of **1** with PhLi provided naphthyldiphenylmethanol in 13% yield, arising from 1,2-addition of PhLi followed by detritylation and further 1,2-addition of PhLi.
6. K. Tomioka, M. Shindo, and K. Koga, *J. Am. Chem. Soc.*, **111**, 8266 (1989).
7. C. H. Heathcock, M. C. Pirrung, S. H. Montgomery, and J. Lampe, *Tetrahedron*, **37**, 4087 (1981).
8. Authors are grateful to Japan Foundation for Optically Active Compounds and Grant-in-Aid for Scientific Research, Ministry of Education, Science and Culture, Japan, for partial financial support.

(Received in Japan 11 January 1990)