Pergamon

Tetrahedron Letters, Vol. 38, No. 37, pp. 6589-6590, 1997

0040-4039/97 $17.00 + 0.00

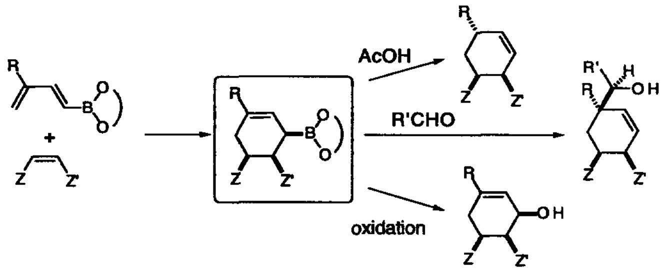
PII: S0040-4039(97)01507-4

1,3-Dienylboronates in Diels-Alder Reaction: Part III[1]

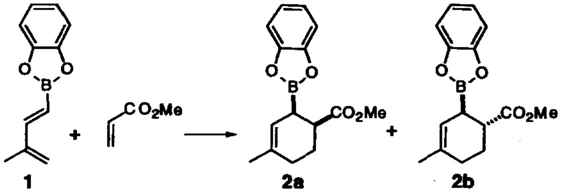
Pierre-Yves Renard[2] Yvan Six and Jean-Yves Lallemand*
DCSO, Ecole Polytechnique, F-91128 Palaiseau, France

Abstract: New examples of Diels-Alder reactions involving 1,3-disubstituted 1,3-dienylboronates are reported. Various dienophiles were tested. With methyl acrylate as the dienophile, lower reaction temperature, shorter reaction time and better stereocontrol have been reached with the use of a steochiometric amount of Lewis acid $EtAlCl_2$. © 1997 Elsevier Science Ltd.

When the Diels-Alder reaction is performed with 1,3-dienylboronates as the diene,[1,3] the resultant allylboronate offers a great number of possibilities for further stereocontrolled transformations.[4]



It has already been shown that the Diels-Alder adduct could be obtained with fairly good regio- and stereocontrol, and studies towards an enantiocontrolled reaction are currently under study.[1b,5a] However, the reaction conditions are rather harsh, require temperatures of at least 80°C or long reaction times, thus limiting the use of many potentially interesting functionalities. One elegant way of overcoming this problem is to activate the diene by reducing the electron-withdrawing power of the boron group, as achieved by Wang and Vaultier[5] by the use of a Lewis base to complex boron. But these reaction conditions are likely to raise problems in taking advantage of the Lewis acid properties born by the boron atom. We report here our results on the opposite strategy consisting in the activation of the dienophile by a Lewis acid,[6] in order to widen the scope of the reaction and to improve its stereocontrol. With this goal in mind, to allow comparison with previously published results,[1] easily available diene **1** and methyl acrylate were chosen to find the best reaction conditions.



Use of a stoechiometric amount of Lewis acid to activate the dienophile was first studied. As summarized in Table 1, $EtAlCl_2$ offered the best results. Stoechiometric amounts of Lewis acid are necessary to obtain higher yields. With Et_2AlCl, further aldehyde condensation was performed with good results as previously described.[1, 3c] In the case of $EtAlCl_2$, one equivalent of Et_3N had to be added before the aldehyde in order to obtain the expected condensation adduct.

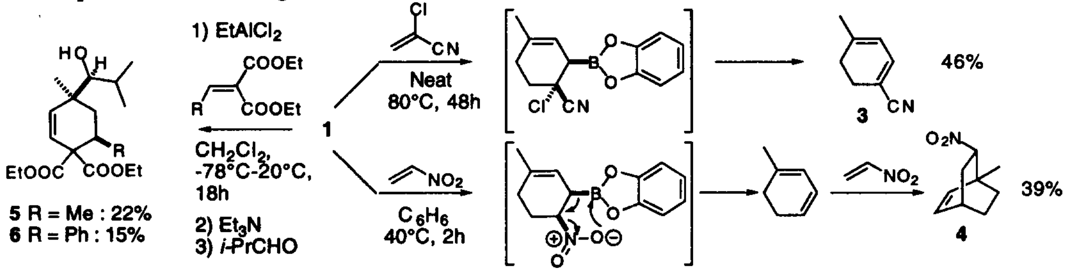
We also used other dienophiles in thermal conditions. As already described,[3c] N-phenyl maleimide and maleic anhydride react almost quantitatively with **1**, yielding exclusively the *endo* adducts. Acrylonitrile proved to be a far less useful dienophile, since polymerization and cycloaddition occured simultaneously under the various reaction conditions tested. Nevertheless, after 48 hours at 80°C, with acrylonitrile as the solvent, a 8/2 *endo/exo* mixture was obtained in 25% yield.

Lewis Acid	Solvant	Temperature (°C)	Time (h)	**2a/2b**
none	C_6H_6	80	24	80/20
none	neat	80	12	85/15
none	neat	60	12	90/10
Et_2AlCl	C_6H_6	80	4.5	85/15[a]
$EtAlCl_2$	**CH_2Cl_2**	**20**	**6**	**>95/5[b]**
$EtAlCl_2$	CH_2Cl_2	0	50	>95/5
$AlCl_3$	CH_2Cl_2	0	diene polymerizes ; some product was detected after 4h	
$TiCl_4$	CH_2Cl_2	0	diene polymerizes ; traces of product were observed after 3h	
$BF_3•Et_2O$	CH_2Cl_2	0	no reaction after 6h	
$BF_3•Et_2O$	CH_2Cl_2	20	slow degradation of the diene	

Table 1

Subsequent allylboration led with propanal yielded 67% (a) and 40% (b) isolated condensation products.

In the case of chloroacrylonitrile, a potential vinyl alkoxide equivalent, the adduct undergoes a deboronochlorination as previouly described,[7] and probably via a mecanism similar to that proposed by Matteson,[8] yielding compound **3**. Similarly, the reaction of diene **1** with nitroethylene affords compound **4** as a single diastereomer. This structure results of the Diels-Alder reaction between an elimination product and excess nitroethylene. When treated with diethyl ethylidene malonate or diethyl benzalmalonate in the presence of Lewis acid, diene **1** gave only *endo* cycloaddition product. Subsequent allylboration with isobutyraldehyde afforded compounds **5** and **6** in moderate yield, which stereochemistry could be easily confirmed. The following dienophiles failed to react with diene **1** : phenylvinyl sulfone, cyclohexenone, methyl vinylketone, acroleine, trimethylsilyl ethylene, 1-nitro 2-trimethylsilyl ethylene, 3-acetyl ethyl acrylate, ethyl vinyl ether and vinyl acetate both in thermal conditions (80°C), and when a Lewis acid is added ($EtAlCl_2$, -78 to 20°C overnight).



Activation of the dienophile with the Lewis acid $EtAlCl_2$ allowed us to perform Diels-Alder cycloaddition reaction of 1,3-dienylboronate **1** with methyl acrylate at lower temperature, increasing the yield and the stereocontrol of the reaction. This improvement is of great interest, since it is obtained with a moderately electron deficient dienophile, and is compatible with a further aldehyde condensation. Further studies on more substituted dienes are currently in progress[3a].

Acknowlegements : We thank Dr I. Hanna and Dr S.Z. Zard for useful discussions.

REFERENCES AND NOTES

1. a) Part I : Renard, P.Y. and Lallemand, J.Y. *Bull. Soc. Chim. Fr.* **1996**, *133*, 143-149.
   b) Part II : Renard, P.Y. and Lallemand, J.Y *Tetrahedron : Asymmetry* **1996**, *7*, 2523-2524
2. Present address : SMM, DBCM/DSV CEA Saclay F-91191 Gif sur Yvette Cedex, France.
3. a) Six, Y.; Ohannessian, G. and Lallemand, J.Y. *Bull. Soc. Chim. Fr.* **1996**, *133*, 1143-1148 and unpublished results.
   b) Mikhailov; B.M. and Chekasova, K.L. *Zh. Obshch. Khim.* **1972**, *42*, 138-146 and 1744-1747.
   c) Vaultier, M.; Truchet, F. and Carboni, B. *Tetrahedron Lett.* **1987**, *28*, 4169-4172.
4. Recent general reviews : a)Yamamoto, Y. and Asao, N. *Chem. Rev.* **1993**, *93*, 2207-2293.
   b) Brown, H.C. and Ramachandran, P.V. *Pure Appl. Chem.* **1994**, *66*, 201-212.
5. a) Wang, K. *J. Chem. Soc., Chem. Commun.* **1991**, 1515-1517.
   b) Garnier, L.; Plunian, B.; Mortier, J. and Vaultier, M. *Tetrahedron Lett.* **1996**, *37*, 6699-6700.
6. Recent review : Pindur, U.; Lutz, G. and Otto, C. *Chem .Reviews* **1993**, *113*, 1663-1920.
7. Hawthorne, M.F. *J. Am. Chem. Soc.*, **1960**, *82* , 1886-1888.
8. Matteson, D.S. and Liedtke, J.D. *J. Am. Chem. Soc.* **1965**, *87*, 1526-1531.

(*Received in France* 12 *March* 1997; *accepted* 20 *July* 1997)