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ADDITION OF ALKYNYL ANIONS TO ALDIMINES CONTAINING α-HYDROGENS : A NOVEL SYNTHESIS OF β-AMINOACETYLENES

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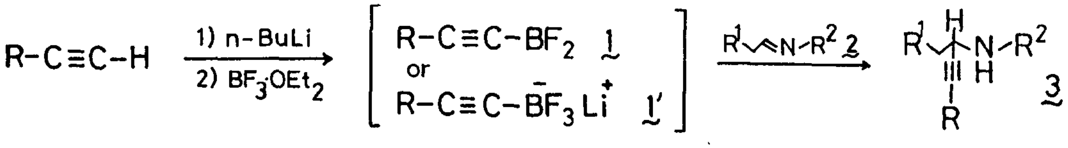
Abstract : Alkynylboranes (or alkynylborates), prepared <u>in situ</u> from lithium acetylide and $BF_3 \cdot Et_2O$, added to aldimines containing α-hydrogens to afford β-aminoacetylenes in good yields.

Poor reactivity of imines to nucleophilic addition of organometallic reagents is widely known,[1,8] and actually deprotonation of α-hydrogen of aldimines and ketimines by alkyl Grignard reagents is well documented.[2] Alkyl- and aryllithiums add to aldimines in low to moderate yields[3] and it is also reported recently that sec-butyllithium deprotonates α-hydrogen of ketimines.[4]

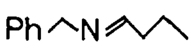
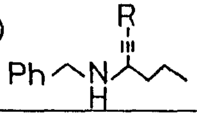
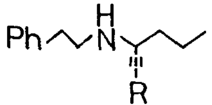
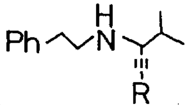
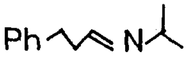
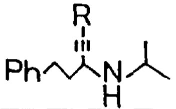
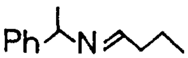
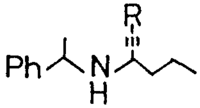
During an attempt to activate imines for nucleophilic addition of organometallic reagents, we recently found that boron trifluoride complexes of organocopper reagents added successfully to aldimines containing α-hydrogens due to activation of the imine by coordination of Lewis acid part of the reagent.[5] As a further extention of this project, now we report a novel synthesis of β-aminoacetylenes by alkylation of aldimines. When alkynylboranes(**1**) [or alkynylborates(**1'**)] prepared from lithium acetylides and boron trifluoride etherate[6] were reacted with aldimines(**2**) at -78° C, the corresponding addition products(**3**), <u>i.e.</u>, β-aminoacetylenes, were obtained in good yields and the results are summarized in the Table.[7] It should be noted here that simple lithium acetylide, <u>i.e.</u>, 1-pentynyllithium, did not add to **2b** or **2c** at all and the starting aldimines were recovered.



A typical procedure of the reaction is as follows: To a solution of 1-pentyne(0.60ml, 6.2mmol)in THF(15ml), n-butyllithium in hexane(1.5M, 6.2mmol) was slowly added at -78° C under argon with stirring. After stirring for 30 min, $BF_3 \cdot OEt_2$(0.76ml, 6.2mmol) was added to the solution and the mixture was stirred for 10 min to prepare 1-pentynylborane(**1-i**) [or 1-pentynylborate (**1'-i**)]. N-Isobutylidenephenethylamine(**2c**:0.58ml, 3.1mmol)was then added and the reaction mixture was stirred for 1 hr at -78°C and for 1 hr at room temperature. The resulting mixture was treated with aq. 10% NaOH(10ml) and then the product was extracted with ether(20ml×3) and dried($MgSO_4$). The crude product was purified by preparative TLC on silica gel with isopropylamine : hexane(1:30) as an eluent to afford the addition product(3c-i: 0.51g, 2.1mmol) in 68% yield.

β-Aminoacetylenes(3) are useful precursors in synthesis, because it can be transformed into a variety of functionalized compounds and such an attempt is now in progress. Quite recent papers by Volkmann *et al.*[8] prompted us to publish the present results.

Table The Synthesis of β-Aminoacetylenes(3)

Imine(2)	Alkynylborane or borate(1)$^{1)}$, R	Product(3)$^{2)}$		Yield(%)
 (2a)	$CH_3(CH_2)_2$ (1-i)		3a-i	57
	Ph (1-ii)		3a-ii	60
 (2b)	$CH_3(CH_2)_2$		3b-i	69
	Ph		3b-ii	57
 (2c)	$CH_3(CH_2)_2$		3c-i	68
	Ph		3c-ii	75
 (2d)	$CH_3(CH_2)_2$		3d-i	82
	Ph		3d-ii	79
 (2e)	$CH_3(CH_2)_2$		3e-i	67
	Ph		3e-ii	62

1) Two equivalents of 1 were used. 2) These compounds have been fully characterized by IR, ^{1}HNMR, MS,and elemental analyses data.

References and Notes

1. R. W. Layer, Chem. Rev., 63, 489(1963). 2. a)G. Stork and S. Dowd, J. Am. Chem. Soc., 85, 2178(1963); b)A. I. Meyers, D. R. Williams, and M. Druelinger, ibid., 98, 3032(1976); c)J. K. Whitesell and M. A. Whitesell, J. Org. Chem., 42, 377(1977). 3. a)J. Huet, Bull. Soc. Chim. Fr., 1964, 952; b)F. E. Scully, Jr., J. Org. Chem., 45, 1515(1980). 4. A. Hosomi, Y. Araki, and H. Sakurai, J. Am. Chem. Soc., 104, 2081(1982). 5. M. Wada, Y. Sakurai, and K. Akiba, the preceding paper 6. M. Yamaguchi, T. Waseda, and I. Hirao, Chem. Lett., 1983, 35. 7. Ketimines did not react with 1 under the present conditions. 8. a)R.A. Volkmann, J. T. Davis, and C. N. Meltz, J. Am. Chem. Soc., 105, 5946(1983); b)C. N. Meltz and R. A. Volkmann, Tetrahedron Lett., 24, 4503(1983). 9. Partial support of this work was provided by Grant-in-Aid for Scientific Research (No.58540317)and Special Project Research(No.57218017)administered by Ministry of Education, Culture, and Science.

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