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VINYLOXYBORANE PROMOTED 1,4-ADDITION OF TRIETHYL(1-METHYLINDOL-2-YL)BORATE TO 2-CYCLOALKENONES

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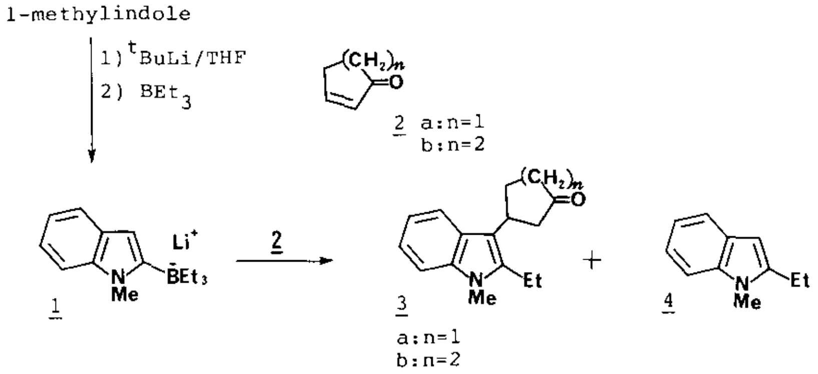
Abstract - The conjugate addition reaction of triethyl(1-methylindol-2-yl)borate to 2-cycloalkenone could be effected with a catalytic amount of vinyloxyborane.

Vinyloxyborane has been amply established as a versatile enolate species for regio- and diastereoselective aldol condensation so far.[1] In connection with our recent investigation on the potential synthetic application of trialkylindolylborates,[2] the present study demonstrates that vinyloxyborane could catalyze the Michael type addition reaction of triethyl(1-methylindol-2-yl)borate (1) to 2-cycloalkenone (2). The sole example of such conjugate addition reported was the reaction of borate (1) with chalcone through the agency of $TiCl_4$ to afford the adduct in 50% yield.[3]

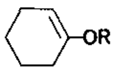


The reaction of borate (1)[2] (derived from 1-methylindole and tert-BuLi, followed by treatment with triethylborane) with enone (2) (1.5 equiv.) in tetrahydrofuran (THF) under an argon atmosphere provided a small amount of the expected adduct (3)[4] together with a significant amount of 2-ethylindole (4). However, it was found that the addition of vinyloxyborane (0.25 equiv.) to a reaction mixture of borate (1) and enone (2) (1.5 equiv.) provided the adduct (3) in satisfactory yield (Table 1).

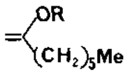
Table 1 Reaction of 1 with 2 in the presence of vinyloxyborane[a]

Vinyloxyborane	enone (2)	Yield (%)[b] 3	Yield (%)[b] 4
—	2a	20 (3a)	55
—	2b	19 (3b)	53
5a[c]	2a	75 (3a)	10
	2b	77 (3b)	10
5b[c]	2b	75 (3b)	10
5c[d]	2b	55 (3b)	28
5d[c]	2b	78 (3b)	9
5e[c]	2b	53 (3b)	20

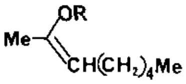
a) The reaction was carried out with 1, 2 (1.5 equiv.) and vinyloxyborane (5) (0.25 equiv.) in THF under an argon atmosphere at -20°C, then at room temperature for 2 h. b) Isolated yields based on 1-methylindole. c) Generated from the corresponding carbonyl compound and lithium diisopropylamide, followed by treatment with 9-BBN triflate in THF at -78°C under an argon atmosphere.[1] d) Generated from 2-octanone, diisopropylethylamine and 9-BBN triflate in THF at -78°C under an argon atmosphere.[1]



5a



5b



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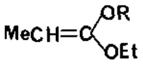
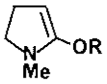


5d



5e

R=9-borabicyclo[3.3.1]nonanyl (9-BBN)

It turned out that treatment of borate (1) with enone (2) (1.5 equiv.) in the presence of trialkylborane (0.25 equiv.) under an argon atmosphere also gave the adduct (3) in high yield, and tri(sec-butyl)borane gave the best result among trialkylboranes examined (Table 2). The latter procedure involves that a catalytic amount of vinyloxyborane arose in situ from trialkylborane and enone (2) through the known path[5,6] and promoted likewise the addition reaction. In conclusion, a novel utilization of vinyloxyborane could be shown for the first time as a catalyst for the Michael addition of borate (1) to enone (2). It seems to be possible in this case that vinyloxyborane initially activated enone (2) through the coordination to the carbonyl function and promoted the addition reaction. Additional experiments designated to probe these results in greater detail, including mechanistic investigation and further application of the present procedure to other conjugate addition reactions, are in order.

Table 2 Reaction of 1 with 2 in the presence of trialkylborane (BR_3)[a]

		Yield (%)[b]	
BR_3	enone (2)	3	4
BEt_3	2a	50 (3a)	20
	2b	48 (3b)	20
B(sec-Bu)$_3$	2a	75 (3a)	10
	2b	78 (3b)	10
B-Bu-9-BBN[c]	2b	60 (3b)	20
$B(CH_2SiMe_3)_3$	2b	50 (3b)	25

a) A mixture of 1, 2 (1.5 equiv.) and trialkylborane (0.25 equiv.) was treated in THF at -20°C under an argon atmosphere for 1 h, then at room temperature for 2 h.
b) Isolated yields based on 1-methylindole. c) 9-BBN = 9-borabicyclo[3.3.1]nonanyl.

ACKNOWLEDGEMENT

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2. M. Terashima and M. Ishikura, Advances in Heterocyclic Chem., 1989, 46, 143; M. Ishikura and M. Terashima, J. Chem. Soc., Chem. Commun., 1989, 135 and references cited therein.
3. A. B. Levy, Tetrahedron Lett., 1979, 4021.
4. Compounds (3) have been characterized by ^{1}H nmr, ^{13}C nmr, ir and ms spectral data, and elemental analysis; nmr spectral data for 3 are as follows: 3a: ^{1}H Nmr (CDCl$_3$) δ 1.21(t, J=8Hz, 3H), 2.83(q, J=8Hz, 2H), 2.1-3.1(m, 7H), 3.67(s, 3H), 6.9-7.8(m, 4H). ^{13}C Nmr (CDCl$_3$) δ 15.1 (q), 17.8(t), 29.3(q), 30.2(t), 34.8(t), 39.5(t), 44.8(d), 109.8(d), *110.5(s), 118.8(d), 118.9(d), 120.6(d), 125.6(s), 137.2(s), 138.8(s),* 219.2(s). 3b: ^{1}H Nmr (CDCl$_3$) δ 1.16(t, J=8Hz, 3H), 2.80(q, J=8Hz, 2H), 1.6-3.8(m, 9H), 3.68(s, 3H), 7.0-7.5(m, 3H), 7.69(dd, J=2,7Hz, 1H). ^{13}C Nmr (CDCl$_3$) δ 15.0(q), 17.7(t), 26.1(t), 29.2(q), 31.9(t), 37.6(t), 41.3(t), 48.5(d), 109.1(d), 112.6(s), 118.6(d), 119.0(d), 120.5(d), 125.8(d), 137.0(s), 137.9(s), 211.3(s).
5. The addition of galvinoxyl (0.5 equiv.) to a reaction mixture of 1, 2b and tri(sec-butyl)borane (0.25 equiv.) gave the adduct (3b) in 20% yield; c.f., G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, J. Am. Chem. Soc., 1970, 92, 710.
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