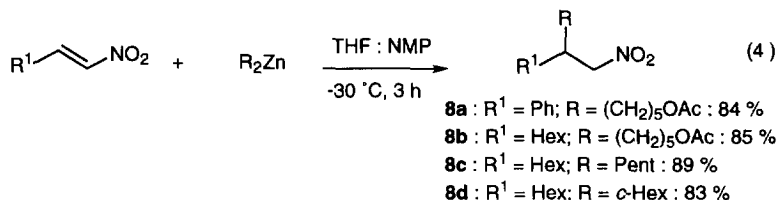


Interestingly, the amount of NMP used for these reactions can be considerably reduced and the addition of Pent₂Zn to cyclohexenone in the presence of only one equivalent of NMP affords **2a** in 84 % yield. Another polar solvent like DMSO is not suited for promoting these Michael additions and provide low yields of the 1,4-addition product. Remarkably, this procedure can be extended to other Michael acceptors and the reaction of (PivO(CH₂)₅)₂Zn (**1f**) with acrylonitrile in the presence of TMSCl provides the conjugate addition product **4** with incorporation of the TMS moiety at the α position in 82 % yield (eq 2).




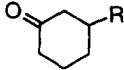
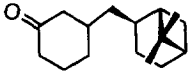

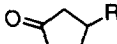
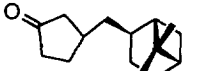
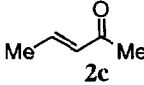
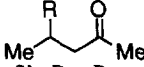
The substituted nitrile **5** adds the zinc reagents **1c** and **1e** giving the adducts **6** and **7** in respectively 84 % and 78 % yield (eq 3). The reaction of diorganozincs with aryl substituted nitroolefins can be complicated by an ipso-substitution of the nitro group in solvents like ether or THF.¹¹ By using a THF:NMP mixture, a smooth addition reaction occurs under mild conditions furnishing the expected nitroalkanes **8a-d** in 83-89 % isolated yield (eq 4). The origin of the reaction rate increase in NMP is not clear but may result from the ionization of the diorganozinc providing a more reactive organometallic system: RZn(NMP)⁺ R₃Zn⁻.¹²

In summary, we have shown that diorganozincs add efficiently to a range of Michael acceptors ¹³ in a solvent mixture of THF and NMP. Studies of the scope of this reaction, its mechanism and applications in asymmetric synthesis using chiral NMP derivatives are currently underway in our laboratory.

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Table 1. 1,4-Addition Products **3a-k** obtained by the Reaction of Diorganozincs **1a-e** to Enones **2a-c** in NMP (-30 °C, 1-3 h).

entry	enone	R ₂ Zn	product	yield (%) ^a
1		1a : R = Pent		83
2	2a	1b : R = PivO(CH ₂) ₃	3a : R = Pent	72
3	2a	1c : R = AcO(CH ₂) ₅	3b : R = (CH ₂) ₃ OPiv	74 ^b
4	2a	1d : R = <i>c</i> -Hex	3c : R = (CH ₂) ₅ OAc	82 (51) ^c
5	2a	1e : R = Myrt	3d : R = <i>c</i> -Hex	78
				
6		1d : R = <i>c</i> -Hex		82
7	2b	1c : R = (CH ₂) ₅ OAc	3f : R = <i>c</i> -Hex	83
8	2b	1e : R = Myrt	3g : R = (CH ₂) ₅ OAc	79
				
9		1a : R = Pent		81
10	2c	1c : R = (CH ₂) ₅ OAc	3i : R = Pent	82
11		1d : R = <i>c</i> -Hex	3j : R = (CH ₂) ₅ OAc	82
			3k : R = <i>c</i> -Hex	82

^a Isolated yield of analytically pure products. ^b By using the corresponding alkylzinc iodide, a yield of 20 % is obtained in the presence of TMSCl and 45 % in the presence of TMSBr. ^c Yield obtained by using *c*-HexZnI (1.0 equiv) and TMSBr (1.0 equiv).

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- (13) **Typical procedure : Preparation of 3-Myrtanlyclopentanone (3h).**

A 25 mL two-necked flask was charged with β -pinene (1.36 g, 10 mmol) and diethylborane (2.0 g, 10 mmol) in ether, was added at 0 °C. The resulting solution was stirred for 15 min, was allowed to warm to rt and was further stirred for 1 h. It was then cooled to 0 °C and the solvents were removed by applying high vacuum (0.1 mmHg) for 15 min at 0 °C, and for 30 min at rt. The reaction mixture was cooled to 0 °C and Et₂Zn (2 mL, 20 mmol) was added. The reaction mixture was stirred for 10 min at 0 °C and for 20 min at rt. It was again cooled to 0 °C and the solvents were removed as described above. The resulting zinc reagent (**1e**) was diluted in THF (3 mL) and was ready to use.

A 50 mL three-necked flask was charged with THF (2 mL) and NMP (3 mL) and was cooled to -30 °C. 2-Cyclopenten-1-one (410 mg, 5 mmol) and TMSCl (500 mg, 5 mmol) were added followed by *bis*(myrtanyl)zinc (**1e**) (3 mL of the above prepared solution, 5 mmol). The resulting reaction mixture was stirred for 3 h at -30 °C and was poured into an aqueous 10 % HCl solution (20 mL) in THF (20 mL), stirred for 15 min and was worked up as usually. After evaporation of the solvents, the crude residue was purified by flash chromatography (hexane:ether = 95:5) providing 3-myrtanlyclopentanone (**3h**; 869 mg, 79 %) as a colorless oil.

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