Pergamon

Tetrahedron Letters, Vol. 38, No. 10, pp. 1851-1852, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00222-0

The Peterson Olefination of Benzyl Carbamates[1]

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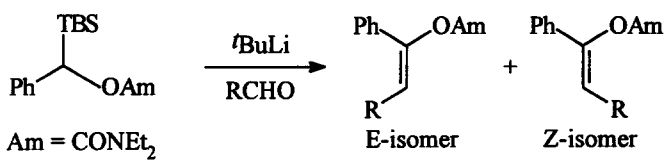
Abstract: An efficient synthesis of substituted vinyl carbamates, from benzyl carbamates *via* the Peterson olefination is described.

The Peterson olefination is a useful carbon-carbon double bond forming reaction analogous to the Wittig reaction. The two major drawbacks of this reaction are considered to be the difficulty in obtaining the α-silyl carbanion and its low stereoselectivity.[2] As a consequence of this, the Peterson olefination has found limited application in synthesis.

Our continued investigation of the reactivity of benzyl carbamates[3] has included the investigation of its application in the Peterson olefination. The olefin products were isolated directly on reaction of the α-silylated benzyl carbamate[4] with carbonyl compounds. The inherent stability of the benzylic anion, which is enhanced by the silyl moiety, simplifies the anion formation in benzylsilane as opposed to alkylsilane substrates.[5] The added advantage of the α-silylated benzyl carbamate is the additional stabilisation of this α-silylbenzyl carbanion by the carbamate functionality. We are therefore able to isolate the vinyl carbamates (Scheme) in moderate to good yields with relatively high stereoselectivity (Table).[6] Although the preparation of vinyl carbamates[7] *via* the Peterson olefination is novel, similar methodology has been employed for the synthesis of the related vinyl ethers.[8]



Scheme

This reaction (Scheme) gives good Z-selectivity (Table, entries 1, 3, 4, 5, 6 and 9), when the ^{t}butyldimethylsilyl carbamate is used, in comparison to the near 1:1 ratios obtained previously for the

'butyldimethylsilyl benzyl substrate.[2] This Z-selectivity is in accordance with the stepwise mechanistic model proposed by Bassindale and co-workers.[9] Optimisation of the reaction conditions using piperonal as the electrophile, indicates that better stereoselectivity is obtained in ether than in THF (Table, entries 1 and 2).

Table: Results of the Peterson olefination.

	Electrophile[a]	solvent	time/hrs	yield[b]/%	E:Z[c]
1	piperonal	Et_2O	5	76[d,e]	7:93
2	piperonal	THF	3	79[e]	39:61
3	2-quinolinecarboxaldehyde	Et_2O	5	80[d]	20:80
4	2-thiophenecarboxaldehyde	Et_2O	5	78[d]	11:89
5	2-pyridinecarboxaldehyde	Et_2O	5	65[d,f]	23:77
6	furfural	Et_2O	5	70[d]	17:83
7	benzophenone	Et_2O	5	42[e]	n/a
8	benzophenone	Et_2O	5	82[d]	n/a
9	benzaldehyde	Et_2O	5	82[d]	9:91

a 2 eq. were used, except for the quinoline aldehydes, when 1.5 eq. were found to give the same yield. **b** Isolated yields. **c** Ratios determined by NMR rather than GC since some of the isomers were found to interconvert in the injection port (220°C). **d** Reaction was allowed to proceed at room temperature after the base and electrophile had been added at -78°C. **e** Reaction carried out at -78°C. **f** 1.0 eq. 'BuLi used.

Allowing the reaction to warm to room temperature does not adversely affect the selectivity (Table, entry 1), but enhances the yield of the reaction (Table, entries 7 and 8).

Acknowledgements: The Authors wish to thank the University of Natal and The Foundation for Research Development (FRD) for financial assistance.

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(*Received in UK* 20 *December* 1996; *revised* 27 *January* 1997; *accepted* 31 *January* 1997)