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CYCLIC β-ENAMINOESTERS DECARBOXYLATION WITH BORIC ACID : A CONVENIENT SYNTHESIS OF CYCLIC IMINES

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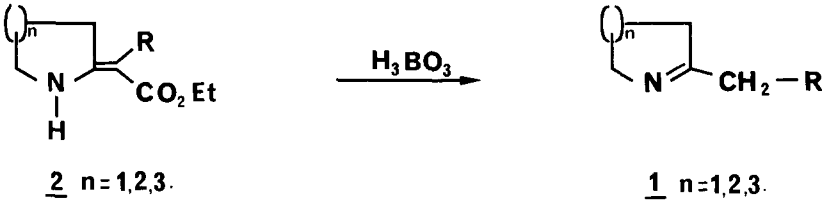
Summary : Δ^1-pyrrolines, Δ^1-piperideines and 1-aza 1-cycloheptenes are formed in good yields from the decarboxylation of alkylated cyclic β-enaminoesters with boric acid.

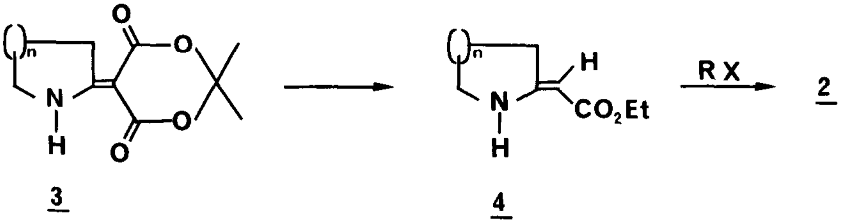
Cyclic 2-alkyl imines (1) are useful synthons for indolizidine and quinolizidine alkaloids synthesis[1]. Numerous methods are available for the preparation of 2-alkyl pyrrolines (1, n = 1)[2-7] but these do not give 2-alkyl piperideines or 1-aza 1-cycloheptenes (1, n = 2 or 3) in useful amounts[8,9]. The litterature also shows that cyclic imines containing a long chain are not easily prepared.

In this letter, we report that 2-alkyl cyclic imines (1 n = 1,2,3) can be readily obtained from cyclic β-enaminoesters precursors (2 n = 1,2,3) which are heated at 180°C during 45 minutes with two equivalents of boric acid (scheme 1). Direct hydrolysis or saponification did not give good yields.



scheme 1

In previous papers, we described a monodecarboxylating transesterification reaction[11,12] of β-enaminoesters (3 n = 1,2,3)[13] in basic or neutral medium and the alkylation[14] of β-enaminoesters 4 which need a basic (4 n = 1,2) or a neutral medium (4 n = 3) (scheme 2).



scheme 2

Table. Cyclic imines 1.

n	R	Yield %	b.p. (°C)/Torr	n	R	Yield %	b.p.(°C)/Torr
1	H[a]	80	94/760[2,3]	2	CH_2-CH_3	65	60/15[3,8]
1	CH_3	95	128/760[2]	2	CH_2-Ph	70	85/0.01
1	CH_2-CH_3	70	135/760[2,3]	2	$(CH_2)_8$//	70	110/0.01
1	CH_2-Ph	80	110/0.01	2	$(CH_2)_9$-CH_3	80	115/0.01
1	$(CH_2)_8$//	50	105/0.01	3	H	40	110/760[3,9]
1	$(CH_2)_9$-CH_3	90	100/0.01	3	CH_3	35	60/20[9]
2	H[a]	70	120/769[3,8]	3	CH_2-CH_3	30	78/20[3,9]
2	CH_3	65	70/60	3	CH_2-Ph	40	105/0.05

a. In same conditions the cyclic imines 1 (n = 1), 1 (n = 2) are directly prepared from 3 (n = 1,2) with respectively 80, 47 % yields.

All the ^1H-NMR spectra of the cyclic 2-alkyl imines present a multiplet at $\delta = 3.40$-4.00 ppm, corresponding to the $-CH_2-$ bearing by the nitrogen atom.

The synthetic patway in this work provides a useful method for preparation for cyclic 2-alkyl imines from a very available starting material through easy transformations of functionnal groups.

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