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SYNTHESIS OF α,β-UNSATURATED METHYL ESTERS BY BH_3-HYDROGENOLYSIS OF THE CORRESPONDING β-ENAMINE ESTERS

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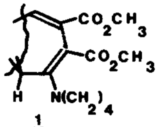
In the course of synthetic work on sesquiterpenes we required a method to convert an enamine diester in a seven-membered ring compound into the corresponding diene diester (e.g. 1→2) without epimerisation at the allylic carbons.



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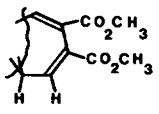

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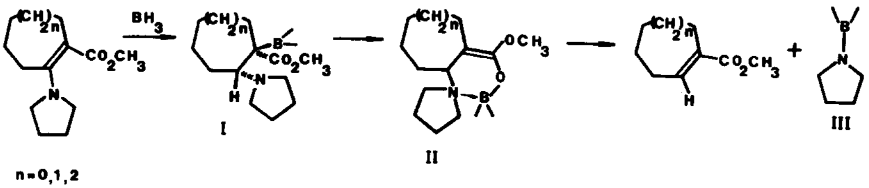
Hydrogenolysis of enamines by hydroboration and decomposition of the borane-enamine adduct in refluxing propionic acid gives olefins in good yield[1] but no report has been made of the application of this reaction to more complicated systems for instance with the enamine in conjugation with a carbonyl group. We now wish to report the hydrogenolysis of some β-enamine methyl esters using diborane. The results are shown in Table 1.

The borane complexes formed with compounds 3, 4, 5 and 6 decomposed spontaneously at r.t. giving the α,β-unsaturated ester, as shown in Scheme 1.

Scheme 1.



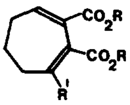
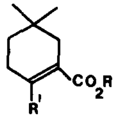
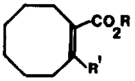
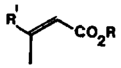
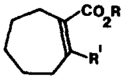
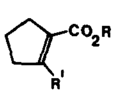
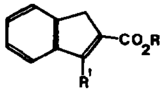
The reaction probably proceeds by 1,2-addition of diborane to the carbon-carbon double bond (I), followed by enolisation-migration (cf. ref.2) to a six-membered chelate (II) suitably arranged for a concerted elimination process. The products did not react further with the organoborane complex[3,4] (II) or with the aminoborane[5] (III).

The molar ratio borane:enamine ester is important. Thus 3 reacted with different molar ratios of the reagent giving the following yields (nmr): 100% (1:1), 70% (2:3) and 40% (1:3).

Enamine esters in a five-membered ring system (8, 9) did not react. This is presumably due to the rigidity of the five-membered ring preventing any accommodation to strain in the transition state.

The open-chain enamine ester 7 gives a stable borane complex, probably the 1,2-addition product (nmr). This could be decomposed by refluxing with propionic acid.

Table 1. Hydrogenolysis of enamine methyl esters using diborane
Starting mtrl: R=CH_3 ; R'=$N(CH_2)_4$ Product: R=CH_3 ; R'=H

	Starting mtrl$^{a)}$	Yield(%)		Starting mtrl$^{a)}$	Yield(%)
3		88	6		72
4		62	7		35^b
5		70	8		c
			9		c

a) The enamine esters contained less than 5% of the non-conjugated isomer except for 5 (20%). b) Propionic acid reflux. c) No reaction

Attempts to alkylate 6 in the γ-position[6,7] were unsuccessful.

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Experimental

The enamine esters were prepared according to the literature. All compounds have been fully characterized(combustion analyses, IR, NMR and MS).

Hydrogenolysis of enamine methyl esters; general procedure: BH$_3$/THF reagent solution(4 mmol; 0°; N$_2$) was added dropwise to the enamine ester(4 mmol) dissolved in 15 ml dry THF and the solution was stirred for a further 18 h. The oily residue obtained on evaporation was taken up in ethyl acetate-hexane (1:1) and the solution was filtered and evaporated. Chromatography on silica (50 g) with ethyl acetate-hexane as eluent gave a small forerun of aminoborane complex, followed by the desired α,β-unsaturated ester in high purity.

References

1. J.W. Lewis and A.A. Pearce, J. Chem. Soc. (B) 1969 863
2. H.C. Brown and K.A. Kelbys, J. Amer. Chem. Soc. 86 1795 (1964)
3. H.C. Brown and R.L. Sharp, ibid. 90 2915 (1968)
4. D.N. Butler and A.H. Soloway, ibid. 88 484 (1966)
5. R.J. Brotherton and H. Steinberg, Progress in Boron Chemistry Vol.3, Pergamon Press Inc., London 1970 p. 249
6. T.A. Bryson and R.B. Gammill, Tetrahedron Lett. 3963 (1974)
7. M. Yoshimoto, N. Ishida and T. Hiraoka, ibid. 39 (1973)