

PYRIDINE-INDUCED REACTION OF TRICYCLOALKYLBORANES
WITH CROTONALDEHYDE

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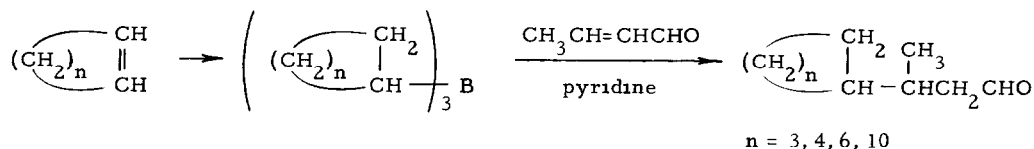
The 1,4-addition of trialkylborane to crotonaldehyde is recorded to proceed under irradiation or in the presence of free radical initiators^{1,2,3} This paper describes the reaction of tricycloalkylboranes with this aldehyde in the presence of an excess of pyridine⁴ at room temperature under a nitrogen atmosphere

A toluene solution of tricyclohexylborane, prepared from cyclohexene and borane, crotonaldehyde, and pyridine (1:1:3) was stirred at room temperature under a nitrogen atmosphere and the reaction was monitored by glc After 8 days the analysis indicated the completion of the reaction affording 97% yield of the product, 3-cyclohexylbutanal The yields were dependent on the borane/pyridine ratios 10% for 1:0, 27% for 1:1, and 97% for 1:3 after 8 days at room temperature In the presence of equimolar pyridine, the yield reached to 27% after 4 days and remained practically unchanged on further stirring When an additional 2 molar equivalent pyridine was added, the yield was increased again to nearly 50% after 8 days⁶

The promoting action of other tertiary amines has been checked by using a mixture of tricyclohexylborane, crotonaldehyde, and the amine (1:1:3) at room temperature for 8 days The yields of 3-cyclohexylbutanal are given against the respective tertiary amine triethylamine 48%, α,α -dipyridyl 16%, 2-picoline 47%, 3-picoline 48%, 4-picoline 96%, 2,6-lutidine 83% Thus some methyl-substituted pyridines were nearly as effective as pyridine itself, but bidentate α,α -dipyridyl was less satisfactory Toluene was the most effective solvent for this reaction within the examined ones such as benzene, toluene, cumene, and THF

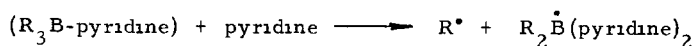
The reaction in excess, neat pyridine gave unsatisfactory result

The pyridine-assisted reaction of tricycloalkylboranes and crotonaldehyde proceeded smoothly under similar condition with such starting olefins as follows to afford products in parentheses cyclopentene (3-cyclopentylbutanal, 99%), cyclooctene (3-cyclooctylbutanal, 20%) and cyclododecene (3-cyclododecylbutanal, 81%) In contrast, however, the reaction of tributylborane with crotonaldehyde in the presence of pyridine gave only 20% yield of 3-methylbutanal⁷



REFERENCES AND REMARKS

- 1 H C Brown and G W Kabalka, J Am Chem Soc, 92, 712, 714 (1970)
- 2 M M Midland and H C Brown, ibid, 93, 1506 (1971), A Suzuki, S Nozawa, M Harada, M Itoh, H C Brown, and M M Midland, ibid, 93, 1508 (1971)
- 3 H C Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N Y, 1972
- 4 Pyridine-assisted reaction of trialkylborane was reported to induced polymerization of methyl methacrylate⁵
- 5 K Kojima, Y Iwata, M Nagayama, and S Iwabuchi, J Polym Sci B, 8, 541 (1970)
- 6 All yields are based on R₃B not on each R-B bond When the initial mixture consisted of tricyclohexylborane, crotonaldehyde and pyridine (1 3 1), the yield reached to 40% after 5 days When the ratio was changed to 1 3 3 at this point, the yield was increased again to reach finally to nearly 99% after 15 days
- 7 Kojima et al⁵ suggested the existence of radical species in pyridine-tributylborane complex The origin of the radicals may be ascribed to the following scheme



The attempted detection of R[•] in the present system by means of galvinoxyl failed due to the reactivity towards the toluene solvent The experimental results so-far obtained however, do not exclude the alternative ionic mechanism