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Preliminary communication

OXIDATION OF ORGANOBORANES WITH PYRIDINIUM CHLOROCHROMATE: A FACILE SYNTHESIS OF KETONES FROM ALKENES

V.V. RAMANA RAO, D. DEVAPRABHAKARA* and S. CHANDRASEKARAN** Department of Chemistry, Indian Institute of Technology, Kanpur-208016, U.P. (India) (Received August 31st, 1978)

Summary

Organoboranes from cyclic alkenes on oxidation with an excess of pyridinium chlorochromate provide ketones in high yield.

Oxidation of organoboranes with aqueous chromic acid is known to give ketones in moderate to good yields and the reaction has been used in the synthesis of a variety of ketones from alkenes or dienes [1,6]. The tedious extractive work-up and strong acidic conditions employed limit the utility of these reactions. Our interest in the chemistry of medium ring compounds prompted us to examine the oxidation of organoboranes from these alkenes with pyridinium chlorochromate [7]. The corresponding ketones were obtained in excellent yields (Table 1) and the anhydrous reaction conditions and easy work-up procedure make this a convenient one step procedure for the oxidation of alkenes to ketones in high yield.

TABLE 1

Alkene	Product ^a	Yield (%)
Cyclohexene	Cyclohexanone	81
Cycloheptene	Cycloheptanone	83
(Z)-Cyclooctene	Cyclooctanone	88
(Z)-Cyclononene	Cyclononanone	92
(Z)-Cyclodecene	Cyclodecanone	92
(Z)-Cyclododecene	Cyclododecanone	92
(E)-4-Octene	Octan-4-one	88

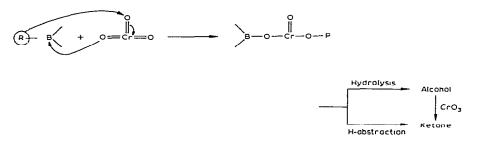
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^aThe ketones were identified by comparison of the IR spectra. GLC retention times with those of authentic samples and by the m.p.'s of the semicarbazones.

*Deceased 12th January, 1978.

**To whom correspondence should be addressed.

The oxidation of organoboranes with pyridinium chlorochromate probably proceeds via the formation of alcohols which are subsequently oxidised to ketones. Analysis of an incomplete reaction by IR and GLC showed the presence of alcohol and ketone:



The alkenes were hydroborated by Brown's procedure [1], then the THF was removed under reduced pressure. The resulting organoborane was dissolved in dichloromethane and cooled to 0° C. Pyridinium chlorochromate (3 mol excess) was added during 5 min and the mixture was brought to room temperature and stirred for 10 h. It was then treated with anhydrous ether and the solution was filtered through a pad of anhydrous magnesium sulphate and neutral alumina. The filtrate was evaporated to leave the ketones as colourless oils.

Work is in progress with other monocyclic, bicyclic and tricyclic organoboranes.

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