

THE REACTION OF IODINE WITH VINYLTRIALKYLBORATES DERIVED FROM TRIALKYLBORANES AND TRISYLHYDRAZONES OF METHYL KETONES. A NEW METHOD FOR SYNTHESIS OF 1,1-DIALKYLETHENES

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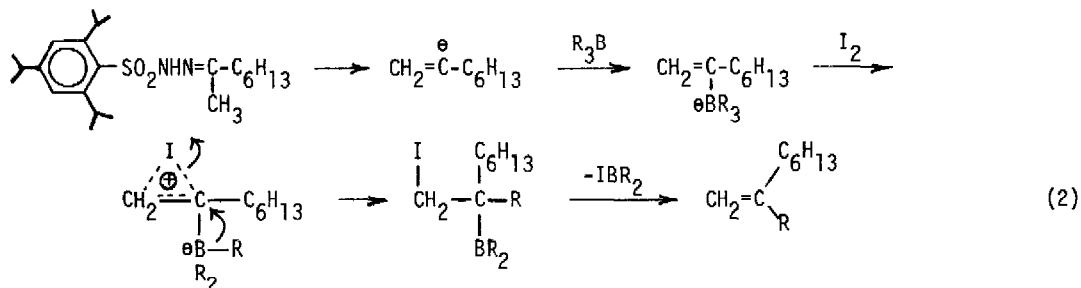
Summary: 1,1-Dialkylethenes are readily prepared in good yields from vinyltrialkylborates derived from trialkylboranes and trisylhydrazones of methyl ketones by treatment with iodine.

Organoborates have become increasingly important in the formation of carbon-carbon bonds.¹⁻⁶ Tosylhydrazones constitute novel intermediates in the conversion of ketones to alkenes (Bamford-Stevens reaction and the related reactions, eq. 1).⁷ Though such a method already enjoys widespread use as a powerful synthetic route to alkenes of a vast variety of structures, it suffers



from the unavoidable disadvantage that only parent olefins can be synthesized. Recently reported highly convenient synthesis⁸ of vinylolithium derivatives from 2,4,6-triisopropylbenzenesulfonylhydrazones (trisylhydrazones) of ketones prompted us to see their utility in the formation of carbon-carbon bonds via organoborates. The overall reaction would mean formation of alkenes from ketones with various alkyl substituents easily available by means of hydroboration.

In this communication we wish to report a new versatile method for the synthesis of 1,1-dialkylethenes from methyl ketone trisylhydrazones by the use of trialkylboranes as alkylating agents. Thus, trialkylboranes were treated with the carbanion derived from 2-octanone trisylhydrazone⁸ to give vinyltrialkylborates. Treatment of such ate-complexes with iodine results in an alkyl migration from boron to carbon followed by spontaneous deiodoboration of the intermediate to provide a highly convenient synthesis of 1,1-dialkylethenes (eq. 2).



The following procedure for the preparation of 2-cyclopentyl-1-octene is representative. A dry 100 ml-flask equipped with a magnetic stirring bar, a septum inlet, and a reflux condenser was flushed with argon. The flask was charged under argon with 1.12 g (2.275 mmol) of 2-octa-

none trisylhydrazone, m.p. 87°C (dec.) and 10 ml of a 20% TMEDA in hexane, and stirring started. The solution was cooled to -78°C and butyllithium in hexane (5.52 mmol, 4.60 ml of 1.2 M solution) was added dropwise. After stirring at the temperature for 20 min, the mixture was allowed to warm to 0°C. The flask was held at 0°C for 15 min to ensure the completion of nitrogen evolution. To the reaction mixture again cooled to -78°C, tricyclopentylborane (1.75 mmol, 1.17 ml of a 1.5 M solution in THF) was added. The mixture was stirred below -70°C for 1 h followed by 1 h stirring at room temperature. The flask was again cooled to -60°C and iodine (1.80 mmol) in 5 ml of ether was added. The reaction mixture was stirred around -60°C for 30 min followed by 1 h stirring at room temperature, and a few drops of alkaline aqueous sodium thiosulfate was added to remove an excess of iodine. After the usual alkaline hydrogen peroxide oxidation, the solution was saturated with potassium carbonate. The glpc analysis of separated organic phase indicated formation of 2-cyclopentyl-1-octene in a 95% yield. Representative results are summarized in Table 1.

The present synthesis would increase the potential usefulness of its synthetic utility by employing readily available trialkylboranes with a wide variety of structures as alkylating agents. Currently, extensive work is under investigation to establish the generality of this procedure.

Table 1. Synthesis of 1,1-Dialkylethenes

Methyl ketone R'-CO-CH ₃ , R' (M.p. of trisyl hydrazone)	Organoborane R ₃ B, R	Product ^{a)} yield, ^{b)} % R'-C=CH ₂ R
Hexyl (87°C, dec.)	Propyl	69
	Butyl	77
	Isobutyl	94
	sec-Butyl	73
	Cyclopentyl	95
Phenyl (151°C, dec.)	Propyl	84
	Butyl	93
	Isobutyl	97
	sec-Butyl	82
	Cyclopentyl	83
Isopropyl (118°C, dec.)	Hexyl	63
	Cyclopentyl	78
	Hexyl	79

a) Satisfactory IR and ¹H-NMR spectra and elemental analyses were obtained for all compounds. b) Based on organoboranes.

References and Notes

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