

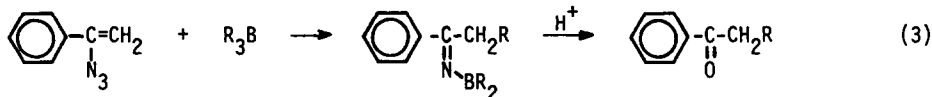
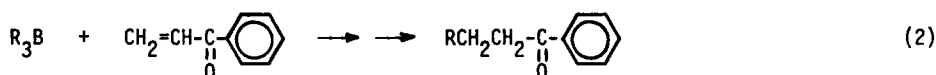
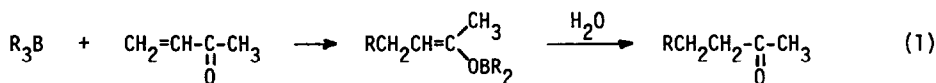
A FACILE REACTION OF TRIALKYLBORANES WITH α -AZIDOSTYRENE. A CONVENIENT AND GENERAL SYNTHESIS OF ALKYL ARYL KETONES VIA HYDROBORATION

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In recent years, many reports have been published dealing with the new syntheses of dialkyl ketones¹ and alkyl alkenyl ketones² from organoboranes. However, there are no reports on convenient synthetic procedures for alkyl aryl ketones³ via the reaction of organoboranes. Although we have previously reported that trialkylboranes undergo a remarkably fast 1,4-addition reaction to methyl vinyl ketone, and hydrolysis of the initially formed intermediate produces the corresponding alkyl methyl ketones (eq. 1),^{1d} the method is not applicable for aryl vinyl ketones for the synthesis of alkyl aryl ketones, because of the remarkable polymerization properties of such unsaturated ketones (eq. 2). For instance, treatment of tri-n-propylborane with phenyl vinyl ketone under the same reaction conditions conducted in the methyl vinyl ketone reaction, provided n-pentyl phenyl ketone in a yield of only 34% (glpc analysis).⁴

We wish to report here a convenient and general synthesis of alkyl aryl ketones by the reaction of trialkylboranes with α -azidostyrene under mild conditions in relatively good yields (eq. 3).



The following procedure for the preparation of n-propyl phenyl ketone is representative. A dry 25-ml flask equipped with a magnetic stirring bar, septum inlet and reflux condenser was flushed with nitrogen. The flask was charged under nitrogen with 3 ml (6 mmol) of triethylborane in tetrahydrofuran, and 0.625 g (5 mmol) of α -azidostyrene⁵ was gradually added at room

temperature to the organoborane solution. The mixture was maintained at the same temperature for 2 hr under stirring. Then 3 ml of 10% sulfuric acid was added and the solution was heated to 70°C and maintained for 0.5 hr to hydrolyze the intermediate. The reaction mixture was treated with 10 ml of 3N aqueous sodium hydroxide, followed by the dropwise addition of 5 ml of 30% hydrogen peroxide to oxidize the borinic acid by-product. Saturation of the aqueous phase with potassium carbonate yielded an organic phase in which glpc analysis revealed the presence of 4.75 mmol (95% yield) of n-propyl phenyl ketone.

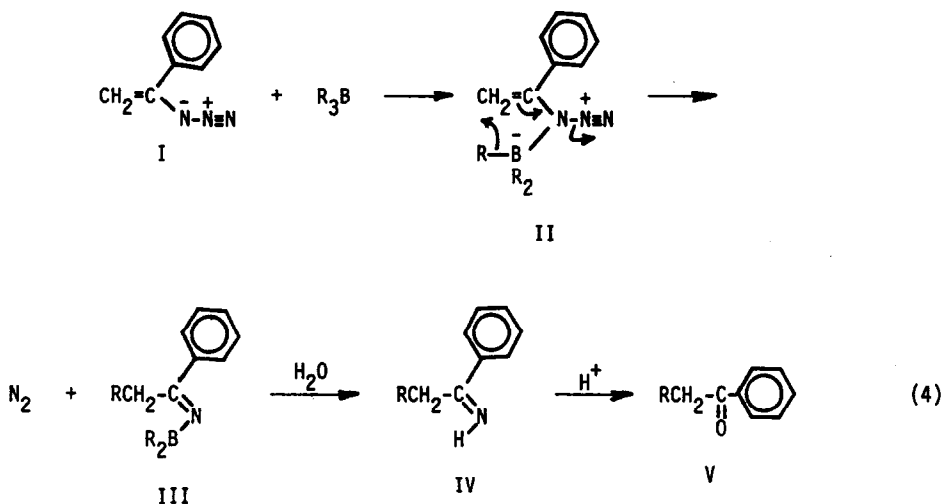
The results of representative reactions are summarized in Table 1.

Table 1. Conversion of Olefins into 1-Phenyl-2-alkyl-1-ethanones by Reaction of the Corresponding Organoboranes with α -Azidostyrene

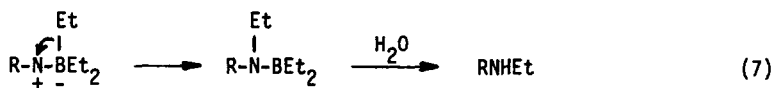
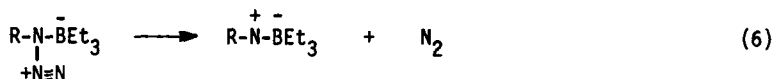
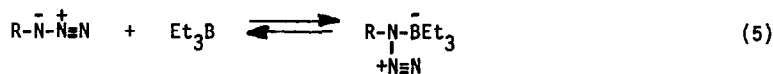
Olefin	Product, ^a %	Yield, ^b %
Ethylene	1-Phenyl-1-butanone	95
1-Butene	1-Phenyl-1-hexanone, 97 1-Phenyl-3-methyl-1-pentanone, 3	85
Isobutene	1-Phenyl-4-methyl-1-pentanone	83
2-Butene	1-Phenyl-3-methyl-1-pentanone	79
1-Hexene	1-Phenyl-1-octanone, 89 1-Phenyl-3-methyl-1-heptanone, 11	68
Cyclopentene	1-Phenyl-2-cyclopentyl-1-ethanone	80

^aAll products were either compared with authentic samples or exhibited analytical data and spectra in accordance with the assigned structures. ^bBy glpc analysis, based on the azide used.

Since our efforts were mainly directed toward the practical application of this novel reaction, we have not undertaken a mechanistic investigation of the reaction. The formation of alkyl aryl ketone, however, may be rationalized in terms of (a) attack of the negative azido nitrogen to the boron atom to form a complex (II), (b) alkyl group migration in II from boron to the methylene carbon through a five-membered cyclic transition with elimination of nitrogen molecule, and (c) hydrolysis of the intermediate (III) to the expected ketone (V) through the corresponding imine (IV) (eq. 4). The formation of the imine intermediate was confirmed by methanolysis instead of hydrolysis with 10% sulfuric acid.



The present novel reaction is in contrast with the reaction of triethylborane with alkyl azides. We previously reported that a wide variety of organic azides react readily with triethylborane in refluxing xylene to give corresponding secondary amines, and proposed that the reaction mechanism involves reversible coordination of the azide with triethylborane (eq. 5), followed by a loss of the nitrogen molecule from the intermediate (eq. 6), with subsequent migration of the ethyl group from boron to nitrogen (eq. 7).⁶ Solvolysis produces the corresponding secondary amine (eq. 7). The same type of reaction of dialkylchloroboranes with organic azides was also reported.⁷ In the present experiment, such a formation of vinylic secondary amine was not observed.



In the present reaction, there appears to be no difficulty in introducing alkyl groups including primary, highly branched, secondary, and alicyclic groups in the organoboranes. Consequently, this synthesis appears to be one of a wide generality, providing alkyl aryl ketones from a wide variety of structural types of alkenes.

References

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