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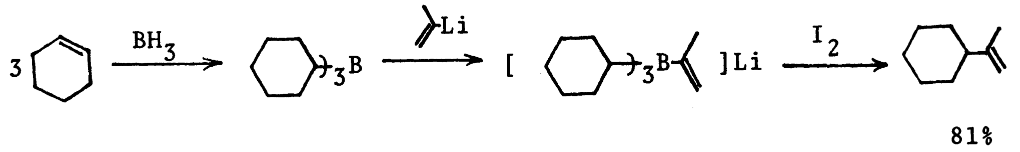
ISOPROPENYLATION OF OLEFINS VIA THE REACTION OF IODINE WITH LITHIUM TRIALKYLISOPROPENYLBORATES OBTAINABLE FROM TRIALKYLBORANES

Norio MIYAURA, Hiroyasu TAGAMI, Mitsuomi ITOH, and Akira SUZUKI*
Faculty of Engineering, Hokkaido University, Sapporo 060

Lithium trialkylisopropenylborates readily available from trialkylboranes and isopropenyllithium give the corresponding isopropenylalkanes in good yields by treatment with iodine. This procedure was applied to synthesize monoterpene derivatives such as limonene, diprene and an isomeric dihydrolinalool.

We previously reported that treatment of lithium 1-alkynyltriorganoborates with iodine produces internal alkynes in essentially quantitative yields,1) and the reaction is applicable to a wide variety of alkyl- and arylacetylenes and organoboranes. It was also reported that such ate-complexes give the corresponding alkenes by protonolysis with propionic acid.2) Recently, in addition to our work described above, many reports have appeared dealing with new applications of alkali metal trialkyl-1-alkynylborates to the synthesis of various kinds of organic compounds.3) On the other hand, there are a few reports on organic synthesis using 1-alkenyltriorganoborates obtained by the reaction of organoboranes with 1-alkenyllithium compounds.4)

We wish to report here on the isopropenylation of olefins via the reaction of iodine with lithium trialkylisopropenylborates. This procedure seems to be useful for the synthesis of natural products with isopropenyl group. In order to explore the possibility of utilizing the reaction, we first attempted to introduce the isopropenyl group into cyclohexane ring. It was found that addition of a solution of iodine in tetrahydrofuran (THF) to a solution of the ate-complex obtained from tricyclohexylborane and isopropenyllithium in ether at -78°C resulted in the immediate disappearance of the iodine color. After gradual warming the reaction mixture to room temperature, glpc analysis revealed the formation of isopropenylcyclohexane in a yield of 81% (eq. 1). The complex formed from tricyclopentylborane and isopropenyllithium also produced the expected isopropenylcyclopentane in a 77% yield (eq. 2). There appears to be no difficulty in introducing an isopropenyl group into aryl nuclei (eq. 3).



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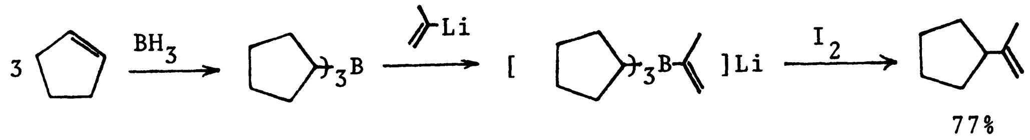

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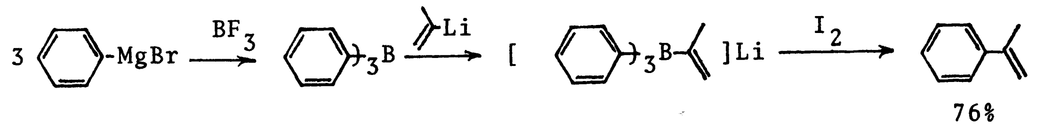
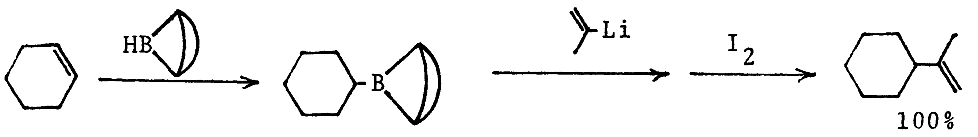


(3)

Although it was found that the present reaction provides a convenient new procedure for introducing the isopropenyl group, the reaction utilized only one of the alkyl groups in the trialkylborane molecule, as observed in many of the new reactions of organoboranes.[5)] We next examined the reaction using B-alkyl-9-borabicyclo[3.3.1]-nonane, available by hydroboration of olefin with 9-BBN,[6)] because the use of such a B-R-9-BBN derivative was known to solve the problem, namely only the 9-R group participates in organoborane reactions.

When a solution of the complex synthesized from B-cyclohexyl-9-BBN and isopropenyl lithium in ether was treated with iodine under the same reaction conditions mentioned above, the expected isopropenylcyclohexane was obtained quantitatively (eq. 4).

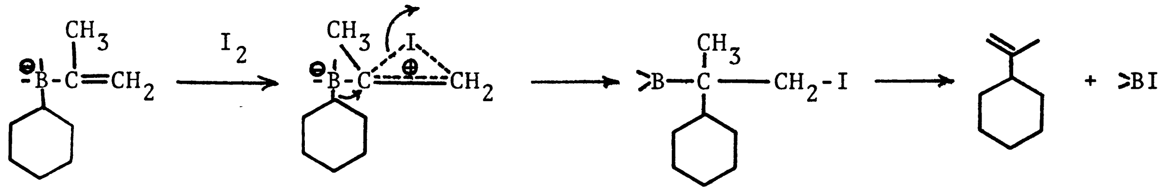


(4)

The following procedure for the preparation of isopropenylcyclohexane is representative. A dry 100 ml-flask, fitted with an inlet with a rubber septum cap, a magnetic stirring bar and a condenser, was flushed with nitrogen. Cyclohexene (1.52 ml, 15 mmol) was hydroborated with 20 ml (15 mmol) of 9-BBN in THF at 0°C for 1 hr. Then, 15 mmol (14 ml of 1.07M solution in ether) of isopropenyllithium was added at 0°C, and the reaction mixture was stirred for 2 hr at the same temperature. After cooling to -78°C, 3.8g (15 mmol) of iodine in THF was added to the solution under efficient stirring.

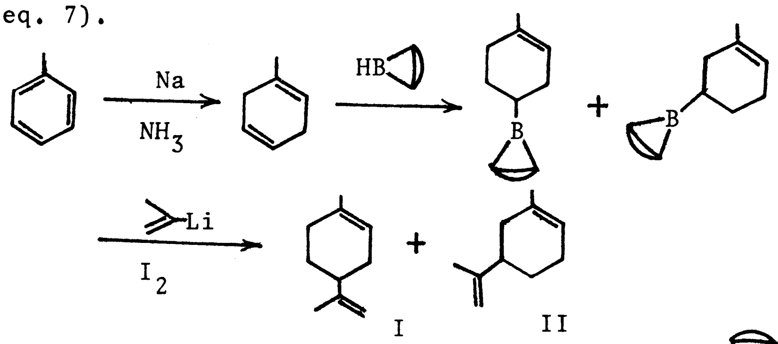
The mixture was allowed to warm to room temperature, and finally was oxidized with 4 ml of 3N-NaOH and 4 ml of 30% hydrogen peroxide under the usual conditions. Analysis of the organic layer by glpc revealed that isopropenylcyclohexane had been formed in a yield of 100%.

The reaction may be rationalized in terms of (a) electrophilic addition of iodine to form a cyclic iodonium ion species, (b) alkyl group migration from boron to the adjacent carbon, and (c) elimination of iodine and the boron moiety (eq. 5).



(5)

Next, we applied the reaction to the synthesis of some kinds of terpene derivatives. 1-Methylcyclohexa-1,4-diene, obtained by Birch's reduction of toluene,[7] was hydroborated with 9-BBN, followed by treatment with iodine, in situ. A mixture of limonene (I) and diprene (II) was obtained in a 63% yield in a ratio of 43:57 (eq. 6). An isomeric dihydrolinalool (III) was also prepared by the same procedure. 3-Methyl-5-hexen-3-ol was hydroborated with two moles of 9-BBN, one mole of which was employed for the reaction with the hydroxyl group, and the mixture was then treated with iodine in the same manner. The expected 3,7-dimethyl-7-octen-3-ol (III) was produced in a yield of 73% (eq. 7).



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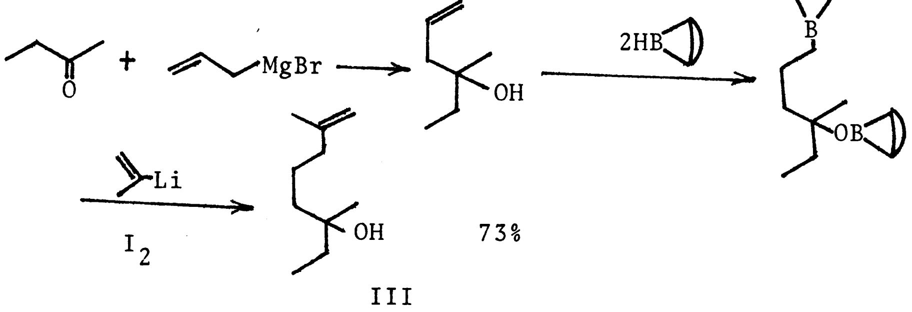

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References

* To whom correspondence should be addressed.

1) A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair, and M. M. Midland, J. Amer. Chem. Soc., 95, 3080 (1973).

2) N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, Tetrahedron Lett., 2961 (1974).

3) (a) P. Binger, Angew. Chem., 79, 57 (1967). (b) P. Binger and R. Koster, Synthesis, 309 (1973). (c) M. Naruse, T. Tomita, K. Utimoto, and H. Nozaki, Tetrahedron Lett., 795 (1973), (d) A. Suzuki, N. Miyaura, S. Abiko, and M. Itoh, Abstracts of the 2nd International Meeting on Boron Chemistry, p.77, Leeds, England, March 25-29, 1974. (e) M. M. Midland, J. A. Sinclair, and H. C. Brown, J. Org, Chem., 39, 731 (1974). (f) M. Naruse, K. Utimoto, and H. Nozaki, Tetrahedron Lett., 1847 (1973). (g) Idem, ibid., 2741 (1973). (h) A. Pelter, C. R. Harrison, and D. Kirkpatrick, Chem. Commun., 544 (1974). (i) Idem, Tetrahedron Lett., 4491 (1973). (j) A. Pelter and K. J. Gould, Chem. Commun., 347 (1974).

4) K. Utimoto, K. Uchida, and H. Nozaki, ibid., 4527 (1973).

5) For example, see, H. C. Brown, "Boranes in Organic Chemistry", Cornell Univ. Press, Ithaca, 1972.

6) E. F. Knights and H. C. Brown, J. Amer. Chem. Soc., 90, 5280, 5281, 5283 (1968); H. C. Brown et al., ibid., 91, 2144, 2146, 2147, 2149, 2150, 4304, 4306 (1969).

7) A. J. Birch, J. Chem. Soc., 1642 (1947).

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