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Preliminary communication

IODINE INDUCED TRANSFER OF DIALKYLVINYLBORANES PRODUCED BY THE HYDRIDATION OF DIALKYLHALOBORANES IN THE PRESENCE OF 1-ALKYNES. GENERALIZATION OF THE ZWEIFEL *cis*-ALKENE SYNTHESIS*

SURENDRA U. KULKARNI, D. BASAVAIAH and HERBERT C. BROWN*
Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

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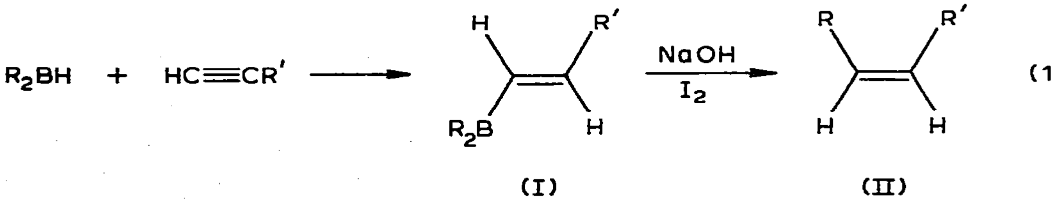
Summary

Dialkylvinylboranes, prepared conveniently via the hydridation of dialkylhaloboranes in the presence of terminal alkynes, react with iodine in the presence of a base at reduced temperatures to form the corresponding *cis*-disubstituted alkenes. This development greatly increases the generality of the elegant Zweifel *cis*-olefin synthesis.

The iodination of dialkylvinylboranes (I) in the presence of sodium hydroxide results in the transfer of one of the alkyl groups from boron to the adjacent carbon atom, followed by deboronoiodination, producing the corresponding *cis*-disubstituted alkenes (II, eq. 1) [1,2].



However, the utility of this elegant Zweifel synthesis was severely handicapped in the past by the limited availability of dialkylboranes. Direct hydroboration leads cleanly to the formation of dialkylboranes only in the case of relatively hindered alkenes (eq. 2).

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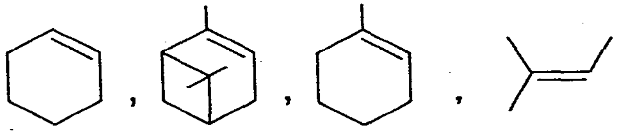
*In honor of Professor Henry Gilman for his exceptional pioneering contributions and many years of outstanding research and teaching in the field of organometallic chemistry.

$$2\ \text{alkene} + BH_3 \longrightarrow R_2BH$$

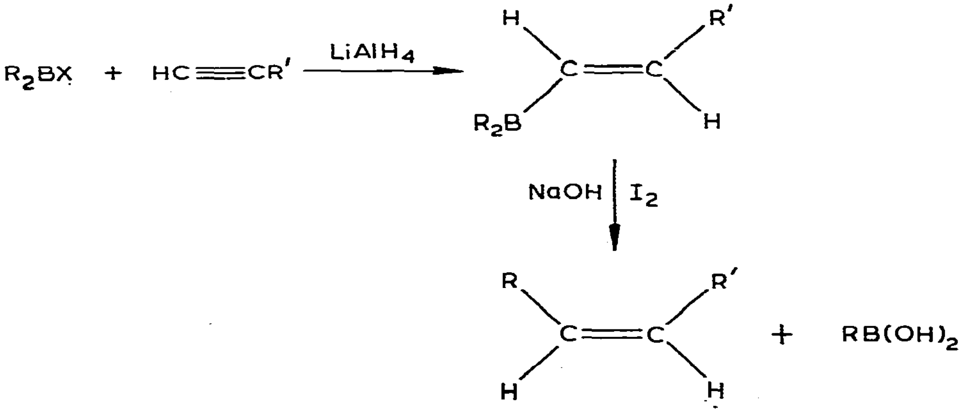
alkene =



(2)

More generally, the hydroboration fails to stop cleanly at the R_2BH stage [3]. Consequently, the hydroboration-ionation route has been severely limited by this limited availability of dialkylboranes.

Recent developments in this laboratory have provided a general preparation of a wide variety of dialkylboranes via the hydridation [4,5] of dialkylhaloboranes [6]. Consequently, we undertook to utilize such dialkylboranes for the synthesis of *cis*-alkenes by the Zweifel procedure (eq. 3).



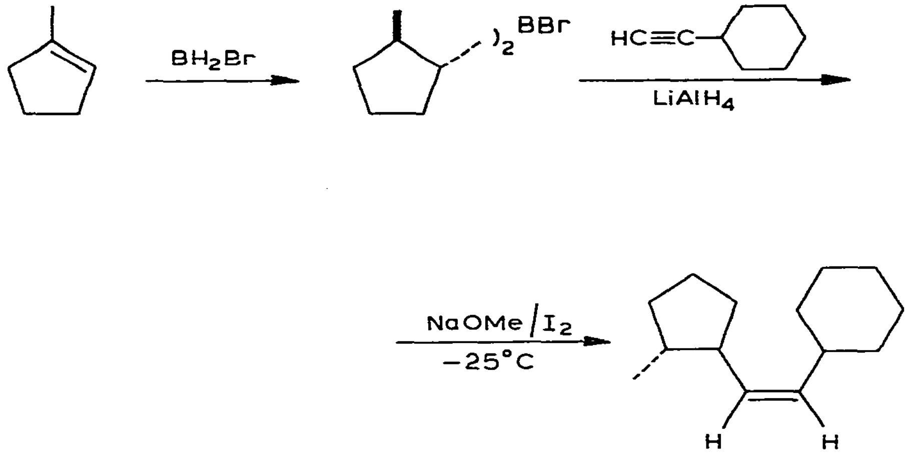
(3)

Unfortunately, we encountered two difficulties. The monohydroboration of terminal alkynes with relatively unhindered dialkylboranes is accompanied by a competing dihydroboration [5]. The iodination of such dialkylvinylboranes containing groups of low steric requirements and appreciable amounts of 1,1-dibora derivatives as side-products produced considerable amounts of alkyl iodides along with the desired *cis*-alkenes. The formation of such alkyl iodides presumably arises from a reaction similar to that involved in converting trialkylboranes into the corresponding iodides [7,8]. The formation of such iodides is undesirable. They both decrease the yield and decrease the purity of the *cis*-alkene product.

We circumvented these difficulties in the following manner. First, the amount of dihydroboration can be decreased by carrying out the hydroboration of the 1-alkyne with the dialkylborane at a lower temperature, generally −25°C [5]. Unfortunately, at this temperature the rate of hydroboration is often inconveniently slow. Use of an excess of the 1-alkyne, generally 100%, reduces the amount of dihydroboration to an insignificant factor. If desired, the excess 1-alkyne can be readily recovered by distillation from the hydroboration product.

Finally, we established that the second difficulty, the concurrent formation of alkyl iodides, can be circumvented by carrying out the treatment of the dialkylvinylborane with sodium methoxide and iodine at lower temperatures (−25°C when R = secondary alkyl; −50°C when R = primary alkyl group, eq. 3). In fact, a temperature of −78°C proved to be generally satisfactory for all dialkylvinylboranes to form the desired *cis*-alkene with negligible formation of alkyl iodides.

Consequently, the present procedure greatly extends the range of applicability of the elegant Zweifel synthesis of *cis*-olefins [1]. At the present time, we have encountered no case of an alkene which cannot be utilized to form the corresponding *cis*-disubstituted alkene (eq. 3). We have demonstrated the applicability of this procedure to the utilization of relatively hindered alkenes, such as 1-methylcyclopentene, as in the synthesis of *cis*-1-cyclohexyl-2-(*trans*-2-methylcyclopentyl)ethylene, in > 97% isomeric purity (eq. 4). Similarly, alkenes with intermediate steric requirements, such as cyclopentene, are readily utilized as in the synthesis of *cis*-1-cyclopentyl-1-octene (eq. 5).



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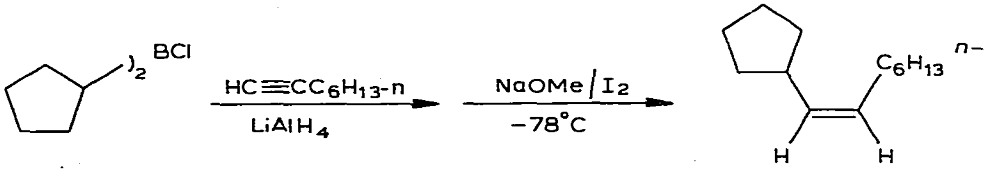
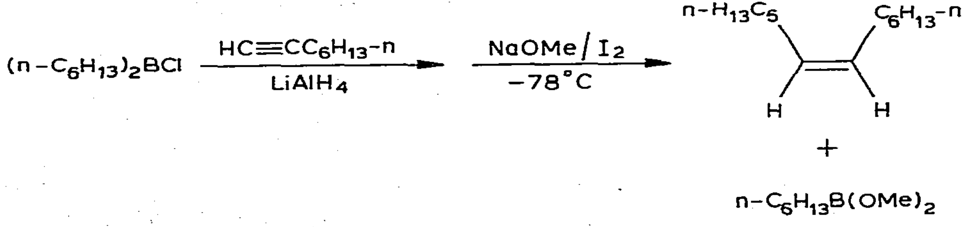


(5)

Finally, even alkenes of low steric requirements, such as 1-hexene, are readily utilized, making possible the synthesis of *cis*-alkenes carrying two unhindered primary alkyl groups (eq. 6). This particular class of alkenes had previously been inaccessible via the iodination reaction.



(6)

TABLE 1

SYNTHESIS OF *cis*-DISUBSTITUTED ALKENES FROM DIALKYLHALOBORANES AND TERMINAL ALKYNES [a]

Alkene for R_2BX	X	Alkyne (mmol)	Iodination temperature (°C)	Product [b,c]	Yield [d] (%)	B.p. (°C/mmHg)	n_D^{20}
Cyclopentene	Cl	1-Hexyne (100)	–5	*cis*-1-Cyclopentyl-1-hexene	76	55–57(2.0)	1.4555
Cyclopentene	Cl	1-Octyne (50)	–78	*cis*-1-Cyclopentyl-1-octene	62	80–81(1.6)	1.4580
1-Methylcyclopentene	Br	1-Cyclohexylethyne (50)	–25	*cis*-1-Cyclohexyl-2-(*trans*-2-methyl-cyclopentyl)-ethylene [e]	67	58–60(0.6)	1.4803
cis-2-Butene	Br	1-Octyne (100)	–5	*cis*-3-Methylundec-4-ene	72	58–59(1.5)	1.4310
cis-3-Hexene	Cl	1-Octyne (50)	–25	*cis*-4-Ethyldodec-5-ene	70	78–79(1.8)	1.4384
1-Hexene	Cl	1-Octyne (100)	–78	*cis*-7-Tetradecene [f]	66	75–76(0.8)	1.4399

[a] All reactions were carried out with 50 mmol of R_2BX. [b] Structures were confirmed by ^1H and ^{13}C NMR spectral analyses; chemical purities of all products were > 97% by GC analysis on 6 ft SE-30 column (impurities are the dienes corresponding to the alkynes, < 3%). [c] Isomeric purities are ~99% unless mentioned otherwise (determined by ^{13}C NMR analysis [9]). [d] Yields of pure products, isolated by distillation; based on R_2BX. [e] Contains 2–3% of *trans* isomer (by ^{13}C NMR). [f] Distilled R_2BCl was utilized in order to minimize the formation of diene, which presumably arises from $RBCl_2$.

In summary, the present modification permits a general synthesis of *cis*-disubstituted alkenes of different steric requirements under mild reaction conditions. A variety of alkenes prepared by this method are listed in Table 1.

The following procedure for the synthesis of *cis*-1-cyclopentyl-1-octene is representative. To a solution of 5.5 ml $BH_2Cl \cdot SMe_2$ (50 mmol) in 35 ml of CH_2Cl_2 taken in a 500-ml round-bottom flask was added 9.7 ml of cyclopentene (110 mmol) at 0°C under nitrogen. The mixture was stirred at room temperature for 2 h, and the solvent was removed under reduced pressure. The residue was dissolved by adding 40 ml of THF at 0°C, and 7.4 ml of 1-octyne (50 mmol) was added, followed by a dropwise addition of 6.0 ml of a 2.2 *M* solution of $LiAlH_4$ (13.2 mmol, 5% excess) in THF, with vigorous stirring. The reaction was allowed to proceed for 2 h at 0°C, followed by 0.5 h at room temperature, then cooled to −78°C, and 45 ml of a 4.4 *M* solution of NaOMe in MeOH (200 mmol) and 12.7 g of I_2 (50 mmol) in 50 ml of THF, were added sequentially with vigorous stirring. Stirring was continued at −78°C for 3.0 h. Any excess iodine present was decolorized by adding an aqueous solution of $Na_2S_2O_3$. The flask was then brought to room temperature and the reaction mixture was extracted with pentane (3 × 75 ml). The organic layer was washed with 3 *N* NaOH solution (50 ml), and water (100 ml), dried over anhydrous K_2CO_3, and the solvents were removed under vacuum. Distillation afforded 5.6 g (62% yield) of *cis*-1-cyclopentyl-1-octene, b.p. 80—81°C/1.6 mmHg, n_D^{20} 1.4580. GC analysis indicated 99% chemical purity, and ^{13}C NMR showed 99% isomeric purity [9].

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References

1 G. Zweifel, H. Arzoumanian and C.C. Whitney, J. Amer. Chem. Soc., 89 (1967) 3652.
2 G. Zweifel, R.P. Fisher, J.T. Snow and C.C. Whitney, J. Amer. Chem. Soc., 93 (1971) 6309.
3 H.C. Brown, G.W. Kramer, A.B. Levy and M.M. Midland, Organic Syntheses via Boranes, Wiley-Interscience, New York, 1975.
4 H.C. Brown and S.U. Kulkarni, J. Organometal. Chem., 218 (1981) 299.
5 H.C. Brown, D. Basavaiah and S.U. Kulkarni, J. Organometal. Chem., 225 (1982) 63.
6 H.C. Brown, N. Ravindran and S.U. Kulkarni, J. Org. Chem., 44 (1979) 2417.
7 H.C. Brown, M.W. Rathke and M.M. Rogić, J. Amer. Chem. Soc., 90 (1968) 5038.
8 H.C. Brown and C.F. Lane, J. Amer. Chem. Soc., 92 (1970) 6660.
9 In a mixture of isomers, the vinylic carbons of *cis*-alkenes appear upfield relative to the corresponding carbons of the trans isomers: D.E. Dorman, M. Jautelat and J.D. Roberts, J. Org. Chem., 36 (1971) 2757.