transition metal powders and these studies will be reported shortly.

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(11) We had previously reported a procedure for preparing transition metal slurries via a reductive procedure.[9] This metal salt reduction involved the use of trialkyl- and triarylphosphines which resulted in a rather poorly defined mixture of black solids, soluble tris- and tetrakis(trialkylphosphine) metal(0) complexes, and possibly other soluble metal complexes. Moreover, these slurries were of little value in carrying out the chemistry described in this communication.

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(16) The slurries obtained are not pyrophoric; they do not flash on exposure to air nor when sprayed onto water. Addition of *N,N,N'N'*-tetramethylethylenediamine during and/or after reduction yields no coloration when the reduction is complete. These observations are strongly indicative that neither potassium metal nor nickel(II) exists after reduction is complete.

(17) E. O. Fischer and G. Bürger, *Z. Naturforsch., B*, **16,** 702 (1961).

(18) Typical quantities used are $NiCl_2$ (Cerac Inc., 0.710 g), Li (0.079 g), naphthalene (0.122 g), and alumina which was oven dried at 400-600 °C (0.94 g). The mixture in 10 mL of glyme was stirred at room temperature for 15 h yielding a thick black metal slurry.

(19) The ^{1}H NMR spectrum in $CDCl_3$ (internal Me_4Si) shows three singlets at δ 1.93 (2 H), 2.33 (3 H), and 2.85 (2 H) and is consistent with that obtained by M. Semmelhack, Ph.D. Thesis. In benzene (internal Me_4Si) the spectrum shows three singlets at δ 1.65 (2 H), 1.90 (3 H), and 2.64 (2 H). This spectrum is different from that reported in two conflicting citations, both of which are probably in error.[13,21]

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(22) The products were identified by comparison of gas chromatography retention times with those of authentic samples.

(23) It appears that a distribution of reactivity exists in the nickel powder of a given slurry. This is suggested by the change in product distribution as the crotyl coupling reaction proceeds. Initially the most reactive nickel particles within a slurry would couple the crotyl halides and the statistically major product, 3-methyl-1,5-heptadiene, would be predicted and is observed. As the less reactive yet more selective nickel particles couple the crotyl halide, an increase in the 2,6-octadiene concentration is expected for stereochemical reasons and this also is observed. Thus in the crotyl halide coupling reaction, the product distribution observed appears to be dependent on the reactivity of the activated nickel.

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Reuben D. Rieke,* Arunas V. Kavaliunas
Lee D. Rhyne
Department of Chemistry, University of Nebraska—Lincoln
Lincoln, Nebraska 68588

David J. J. Fraser
Department of Chemistry
University of North Carolina—Chapel Hill
Chapel Hill, North Carolina 27514

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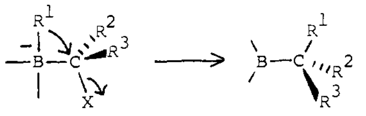
Stereochemistry at the Migration Terminus in the Base-Induced Rearrangement of α-Haloorganoboranes

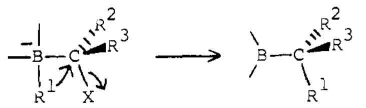
Sir:

Using a stereochemically defined α-iodo- or α-bromoorganoborane we have found that the base-induced migration of an alkyl group from boron to the α-halo carbon in the absence of solvent is stereospecific and occurs with essentially complete inversion at the migration terminus. Remarkably, in the presence of the normal hydroboration solvents, tetrahydrofuran (THF) or dimethyl sulfide, the α-halo carbon suffers complete loss of stereochemistry.

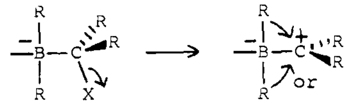
The ability to form carbon–carbon bonds is one of the outstanding features of organoborane chemistry. Many of these carbon–carbon (and carbon–heteroatom) bond-forming reactions are believed to proceed through an organoborate anion which undergoes a facile 1,2 migration of an alkyl group from boron to an adjacent atom containing an appropriate leaving group.[1] Particularly important in this process is that the stereochemistry of the boron–carbon bond is maintained in the final product.[2] However, despite the wide number and utility of these reactions, very little is known about the stereochemistry of the carbon containing the leaving group.[3] The rearrangement could occur by three distinct pathways. In a concerted process (S_N2 like) the alkyl group could displace the leaving group from the back side giving inversion of configuration on carbon (eq 1). Also in a concerted process the migration could lead to retention of configuration on carbon (eq 2). Finally in a stepwise process (S_N1 like) the intermediate could first ionize with a consequent loss of stereochemistry at the migration terminus (eq 3). To test the stereochemistry of the reaction we have investigated the base-induced alkyl-transfer reaction of a stereochemically defined α-iodo- and α-bromoorganoborane.



(1)

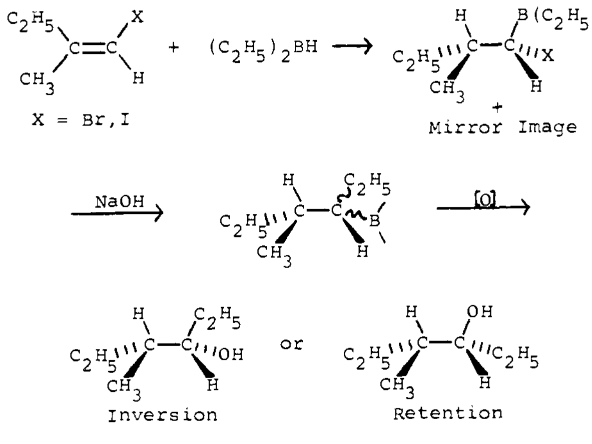


(2)



(3)

Cis hydroboration[4] from the top or bottom of (*Z*)-1-iodo-[5] or (*Z*)-1-bromo-2-methyl-1-butene[6] with diethylborane[7] produces two enantiomeric α-haloorganoboranes. A migration



with retention of configuration at the α-halo carbon followed by oxidation[8] would produce the *RR,SS* pair of alcohols. Migration with inversion of configuration on the other hand would produce the *RS,SR* pair of alcohols.[9]

Diethylborane was prepared in THF and added to the (*Z*)-vinyl iodide. After 1 h, base was added, the mixture oxidized and the alcohol isolated in 80% yield. Both VPC[10] and NMR[11] analysis indicated that a nearly 1:1 mixture of the diasteriomers had formed. In view of the stereoselectivity normally associated with organoborane reactions, this was a very surprising result. The reaction was then performed using diethylborane prepared from triethylborane and borane–methyl sulfide. An ~3:1 mixture was formed with the product of inversion of configuration predominating. Since the diethylborane contained only 0.3 mol of Me_2S, the reaction was repeated using 1 mol of Me_2S. Again a nearly 1:1 mixture of alcohols was obtained. The Me_2S was evidently causing loss of stereochemistry. Finally, when the vinyl iodide and diethylborane were carefully distilled to remove traces of THF or Me_2S and the reaction was run in the absence of solvent, a >99% selectivity for the product of inversion of configuration was obtained. The organoborane from the (*Z*)-vinyl bromide behaved in a similar manner.

To confirm that there was no stereochemical bias in the system (*E*)-1-iodo-2-methyl-1-butene[12] was subjected to the transfer reaction. Once again THF caused epimerization while the pure material gave >99% *RR,SS* product.

The hydroxide-induced transfer reaction of α-iodo- or α-bromoorganoboranes in the absence of THF or Me_2S thus proceeds in a stereospecific manner to give inversion at the migration terminus (eq 1). The situation is less clear when THF or Me_2S are present. It is reported that α-bromoethyldiethylborane undergoes a THF-induced rearrangement with a half-life of 120 min.[13] Addition of THF to the α-iodoorganoborane gives no apparent loss in the NMR signal for the proton geminal to the iodide (doublet, δ 4.01, J = 10 Hz) even after 48 h. This signal disappears only after the addition of a sodium hydroxide solution. However, the addition of 10 mol excess of THF to the α-iodoorganoborane followed by sodium hydroxide 1 min later causes nearly complete epimerization. (The addition of 3 M sodium hydroxide saturated with THF gives virtually no epimerization.) Even small amounts of THF in the vinyl iodide cause considerable loss of configuration over a period of time.

The THF appears to be causing the epimerization of the borane without causing migration. To test this possibility the ^{13}C spectra of the diastereomeric α-iodoorganoboranes were examined. The organoborane from the (*Z*)- vinyl iodide gave resonances (from Me_4Si) at δ 36.3, 31.5, 18.1, 10.6, and 10.3 (2) ppm, while the organoborane from the (*E*)-vinyl iodide gave resonances at 37.1, 29.5, 22.5, 12.1, and 10.3 (2) ppm. Excess THF was then added to the organoborane from the (*E*)-vinyl iodide. After 1 h the ^{13}C spectrum indicated that a mixture of the two diastereomeric α-haloorganoboranes was present. Oxidation of the NMR sample produced a 1:1 mixture of the diastereomeric alcohols. The α-haloorganoborane thus appears to be configurationally labile in the presence of THF.

The alkyl-transfer reaction of α-iodo- and α-bromoorganoboranes can be controlled to give a stereospecific synthesis at the halogen-bearing carbon. This fact combined with the ready availability of configurationally defined vinyl halides[5,6,12] now makes it possible to stereoselectively prepare a variety of organic products. We are continuing to explore these possibilities.

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(8) Oxidation of organoboranes with basic hydrogen peroxide proceeds with retention of configuration.[2c,d]

(9) The authentic *RR,SS* and *RS,SR* alcohols were prepared by hydroboration–oxidation of (*Z*)- and (*E*)-3-methyl-3-hexene, respectively.

(10) A 10 ft × 1/8 in. 10% TCP column was used for VPC analysis.

(11) The two diasteriomeric alcohols could be differentiated by the CHOH ^1H NMR (90 MHz), although the two signals were not completely resolved after decoupling NMR: *RR,SS*, δ 3.39 (m); *RS,SR*, δ 3.33 (m).

(12) Prepared by iodination of the organometallic obtained from the reaction of 1-butyne with methylmagnesium bromide–cuprous bromide (A. Marfat, P. F. McGuirk, and P. Helquist, *Tetrahedron Lett.*, 1363 (1978)).

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(15) National Science Foundation Undergraduate Research Participant, 1978.

M. Mark Midland,*[14] Andrew R. Zolopa
Ronald L. Halterman[15]
Department of Chemistry, University of California
Riverside, California 92521

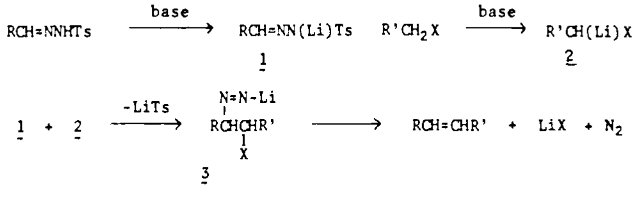
Received August 17, 1978

A New Olefin Synthesis: Condensation of Aldehyde Tosylhydrazones with Stabilized Carbanions

Sir:

We report a synthesis of alkenes from aldehyde tosylhydrazones which provides a simple and inexpensive alternative to the Wittig reaction. In the new reaction, anionic species **1** and **2** undergo an unusual condensation-fragmentation process as illustrated in Scheme I. The intimate mechanistic details are unknown, but formation of intermediate **3** seems essential to explain the overall results.[1,2]

Scheme I



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