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SELECTIVE TRANSFORMATION OF ORGANOBORANES TO GRIGNARD REAGENTS BY USING PENTANE-1,5-DI(MAGNESIUM BROMIDE). SYNTHESES OF THE PHEROMONES OF SOUTHERN ARMYWORM MOTH AND DOUGLAS FIR TUSSOCK MOTH

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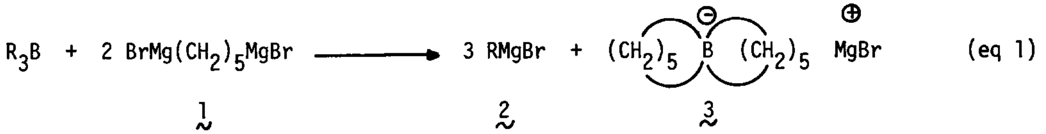
Summary: The selective transformation of trialkylboranes or B-alkyl-9-borabicyclo[3.3.1]-nonanes to alkylmagnesium bromides was accomplished upon treatment with pentane-1,5-di-(magnesium bromide) (**1**) in benzene.

The selective transformation of organoboranes to other organometallic compounds is synthetically efficient process, however, satisfactory procedures are limited to the transformation of alkenylboranes to alkenyl mercurys,[1] palladiums,[2] and coppers.[3] We herein report a novel selective transformation of trialkylboranes to alkylmagnesium compounds upon treatment with pentane-1,5-di(magnesium bromide) (**1**) as depicted in eq 1. The efficiency of the transformation is enhanced by the selective anti-Markovnikov-hydroboration and its tolerance for various common functional groups such as halogens and olefins. The transformation was verified by many successful synthetic examples, such as **4** and **5** which are known as insect pheromones of the southern armyworm moth, *Prodenia eridania* (Cramer) and Douglas fir tussock moth, *Orgyia pseudotugata*, respectively.



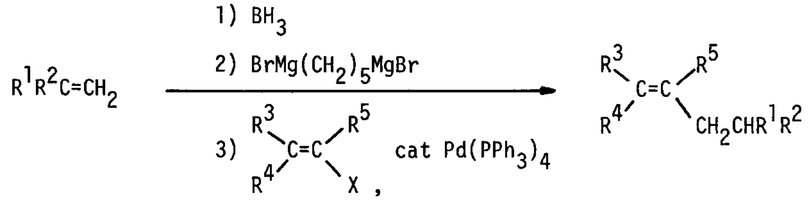
(eq 1)

An exchange of an alkyl group of trialkylboranes has been indicated to occur between a trialkylborane and a Grignard reagent[4] However, the alkyl-group exchange seems to be in equilibrium and hence hardly be used for organic syntheses. In fact, when a mixture of trihexylborane (1 mmol) and octylmagnesium bromide (3 mmol) in benzene was stirred at 25° for 1 hr, and then the resulting mixture was quenched with excess cyclohexanone (4 mmol), a mixture of 1-hexylcyclohexanol (1.25 mmol) and 1-octylcyclohexanol (1.50 mmol) was obtained.

As the result of the precise examination of the reactivity of various Grignard reagents toward a trialkylborane, we have found that when a trialkylborane is treated with **1**, the equilibrium lies to the right, and essentially three alkyl groups of a trialkylborane can be converted to three equiv of the corresponding alkylmagnesium bromide. The transformation proceeds fast in benzene and toluene, relatively fast in ether, but extremely slow in THF. The specific effect of the di-Grignard reagent may be attributed to the formation of a relatively stable bicyclic borate (**3**), although a definitive evidence has not yet been obtained. The Grignard reagents (**2**) thus formed were allowed to react in situ with various substrates without difficulty.

Typical synthetic examples of alcohols are listed in Table 1. In addition to trialkylboranes, B-alkyl-9-BBN can be converted into the corresponding Grignard reagent. In this case, however, the addition of THF as a co-solvent after the completion of transmetalation is necessary in order to avoid the contamination, due to the reduction of a carbonyl compound. Thus, 1-(4-cyclohexenyl)heptan-3-ol (**6**) was obtained from 9-BBN, 4-vinylcyclohexene, **1**, and pentanal in 62 % isolated yield.

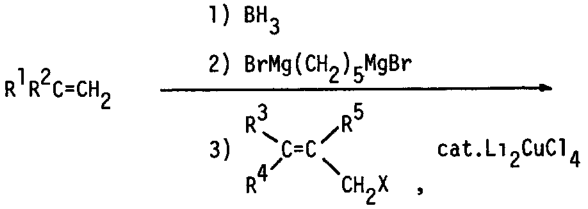
The stereospecific one-pot synthesis of alkenes from alkenyl halides and the Grignard reagents thus formed is accomplished conveniently by using the palladium catalyzed cross-coupling reaction[5] as depicted in eq 2. The efficiency of this method is argumented by the ease with



(eq 2)

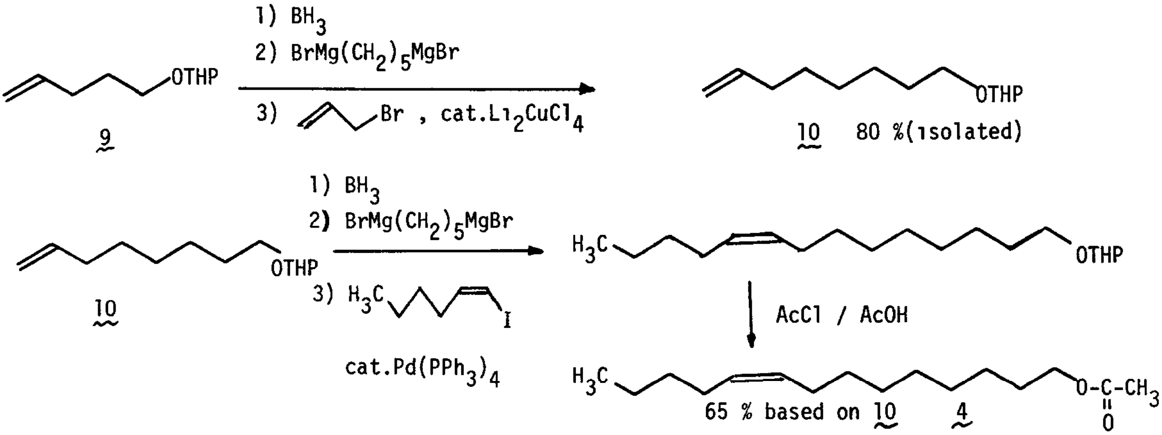
which it is performed as typified in the following procedure for the preparation of **7** from (-)-β-pinene and (E)-β-bromostyrene. All operations were carried out under argon. Hydroboration of (-)-β-pinene (4.1 g, 30 mmol) was accomplished by dropwise addition of BH_3 (10 mmol) in THF at 0° and continuous stirring for 1 hr at room temperature. After the removal of THF under reduced pressure, the borane was dissolved in toluene (40 ml) and treated with the ether-toluene solution of **1** (20 mmol) at 25° for 1 hr. Tetrakis(triphenylphosphine)palladium (0.98 g, 0.85 mmol) and a THF solution of (E)-β-bromostyrene (6.2 g, 34 mmol, 10 ml) was added at room temperature. The mixture was stirred for additional 6 hr and treated with a 1N-HCl solution (40 ml). The organic phase was washed with water, dried over $MgSO_4$, concentrated at reduced pressure. The crude product was dissolved in pentane and subjected to a dry silica column. Elution with pentane gave **7** (5.6 g, 23 mmol) in 78 % yield, n_D^{20}, 1.5532. Other examples are shown in Table 1.

Three carbon homologation of alkenes can be performed efficiently when allyl bromides are allowed to react with **2** as shown in eq 3. For example, 11-chloro-1-undecene can be converted into 14-chloro-1-tetradecene (**8**) by a one-pot reaction. When to an ether-toluene solution of the Grignard reagent, prepared by the hydroboration-transmetalation, was added a THF solution



(eq 3)

of 0.03 equiv of Li_2CuCl_4,[7] and then allyl bromide at 0°, 8 was obtained in 88 % yield, bp 96°/2 mmHg. The transformation was practically used for the three-step synthesis of 4, a sex pheromone of the southern armyworm moth.[6, 8] The synthetic procedure, based on the $C_5 + C_3 + C_6$ principle, was shown in the following Scheme.



9

10 80 %(isolated)

10

65 % based on 10 4

Next, as an example of reductive acylation of an alkene, the synthesis of Douglas fir tussock moth pheromone, 5 from (Z)-1,4-decadiene (11) is shown below. When the Grignard reagent, prepared from hydroboration of 11 with 9-BBN, followed by treatment with 1, was allowed to react with CuI at -45° and then undecanoyl chloride at -45°, compound 5[6, 9] was obtained in 78 % yield, bp 175°/0.35 mmHg, n_D^{20}; 1.4575.

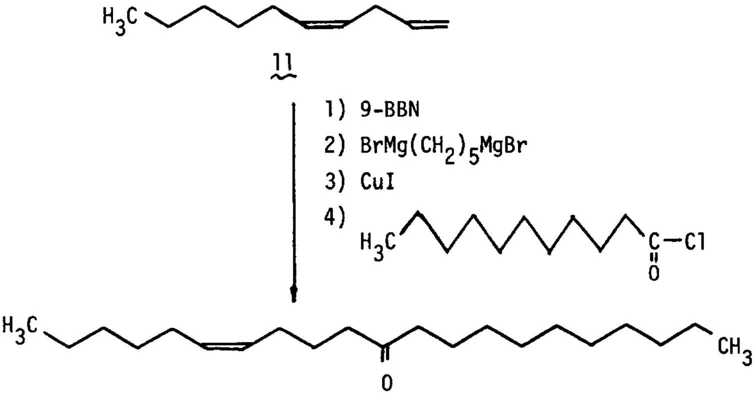


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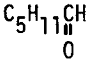
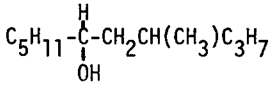
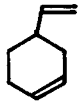
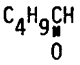
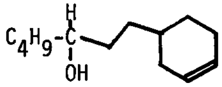
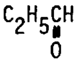
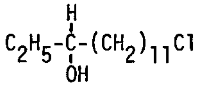
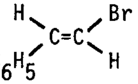
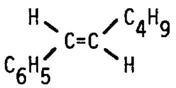
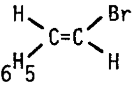
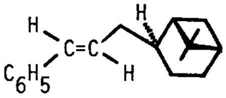
Table 1. Reactions of the Grignard reagents derived from alkenes.

Alkene	Substrate	Catalyst	Product^6	Yield$^{a)}$ %
$CH_2=C(CH_3)C_3H_7$	 $C_5H_{11}\underset{\overset{\|}{O}}{C}H$	–	 $C_5H_{11}-\overset{H}{\underset{OH}{C}}-CH_2CH(CH_3)C_3H_7$	94
 b)	 $C_4H_9\underset{\overset{\|}{O}}{C}H$	–	 6	(62)
$CH_2=CH(CH_2)_9Cl$	 $C_2H_5\underset{\overset{\|}{O}}{C}H$	–	 $C_2H_5-\overset{H}{\underset{OH}{C}}-(CH_2)_{11}Cl$	(92)
$CH_2=CHCH_2CH_3$		$Pd(PPh_3)_4$ c)	 e)	77
		$Pd(PPh_3)_4$ c)	 e) 7	(78)
$CH_2=CH(CH_2)_7CH_3$	$CH_2=CHCH_2Br$	Li_2CuCl_4 d)	$CH_2=CH(CH_2)_{10}CH_3$	(90)
$CH_2=CH(CH_2)_9Cl$	$CH_2=CHCH_2Br$	Li_2CuCl_4 d)	$CH_2=CH(CH_2)_{12}Cl$ 8	(88)

a) Yield by glc based on alkene (numbers in parentheses are isolated yields). b) 9-BBN was used as a hydroborating reagent. c) 5 % $Pd(PPh_3)_4$. d) 3 % Li_2CuCl_4. e) Isomeric purity was above 99 %.

References and Notes

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