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REACTION OF ORGANOBORANES WITH METHOXYCARBENE, AND REACTION OF DICHLOROMETHYL METHYL ETHER WITH AT-COMPLEX OBTAINED FROM ORGANOBORANES AND METHYL LITHIUM

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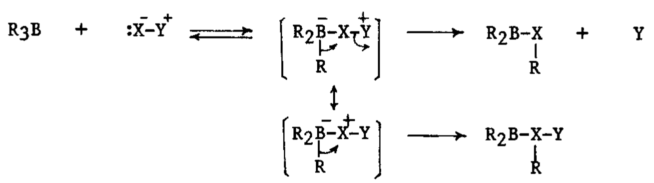
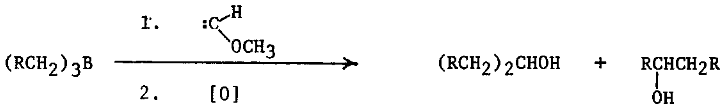
Recently, numerous papers describing new organic syntheses by means of organoboranes have been published (1). The majority of such reactions apparently arise from the fact that organoboranes exhibit a strong tendency to share an electron-pair with a nucleophile. The coordination should greatly increase the carbanion-like character of the alkyl groups and thereby facilitate reactions in which the alkyl group is transferred with its electron-pair to the near positive atom, as depicted in Scheme 1. Although carbenes usually behave as electrophiles, it has been reported that some of them have a nucleophilic character (2). In regard to the reaction of organoboranes with such carbenes, little work is seen to the present (3). It is our intent here to report that trialkylboranes undergo a remarkably facile reaction with methoxycarbene to form the corresponding two alcohols, I and II.

Scheme 1



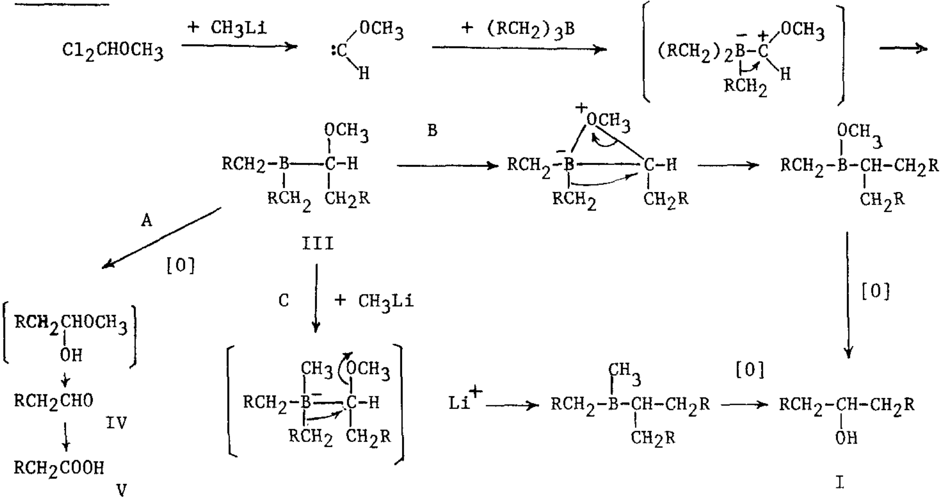


$$(RCH_2)_3B \xrightarrow[2.\quad [O]]{1.\quad :C(H)OCH_3} (RCH_2)_2CHOH + RCH(OH)CH_2R$$

I II

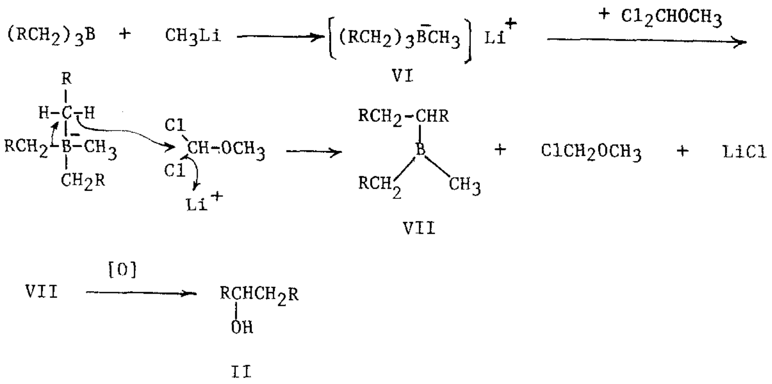
According to the reaction mechanism of organoboranes as described above, it is expected that an intermediate (III) formed converts into an aldehyde (IV) or an acid (V) by oxidation through path A in Scheme 2. Actually, we obtained two alcohols, I and II with a trace amount of acid (V). The result is summarized in Table 1. The former alcohol (I) seems to be formed through path B (4,5) and/or path C.

Scheme 2



In addition to these two alcohols, the formation of methyl alkyl carbinol was also observed. Accordingly, it was confirmed that the reaction proceeds, at least, partially through path C. Further, a crossover experiment revealled that the migration of alkyl group in organoborane is intramolecular.

Scheme 3



On the other hand, the formation of the second alcohol (II) is explained as follows: organoborane reacts with methyl lithium, instead of methoxycarbene to form an at-complex (VI) (6), which is converted into a new organoborane (VII) by migration of the alkylgroup, as shown in Scheme 3. It has been already pointed out that in the at-complex such as VI α-hydrogen of the alkyl group tends to migrate as a hydride (7). If the alcohol (II) is yielded by such a reaction mechanism, only II could be obtained by using the condition in which the at-complex (VI) is prepared alone. In order to determine whether this anticipation is correct, the reaction was run, and it was shown that an addition of dichloromethyl ether into the at-complex solution gives the alcohol (II) alone as expected, and the alkyl migration also proceeds intramolecularly. The result is listed in Table 2.

The following procedure is representative of the reaction with methoxycarbene. A dry 25 ml flask equipped with septum inlet, nitrogen inlet, reflux condenser and magnetic stirrer was flushed with nitrogen. The flask was charged with 1.28 ml of 1.98 M borane (2.54 mmole) in tetrahydrofuran and placed in an ice bath. Hydroboration was carried out by dropwise addition of 0.67 ml (7.62 mmole) of cyclopentene and then the reaction mixture was stirred for 2 hr at room temperature. The tricyclopentyl borane - THF solution thus obtained was treated with 0.203 ml (2.54 mmole) of dichloromethyl methyl ether and 2.4 ml of 1.59 M methyl lithium (3.81 mmole) in ether. The reaction mixture was maintained under stirring at room temperature. After 2 hr, the product was oxidized with 2 ml of 3 N-sodium hydroxide and 2 ml of 30 % hydrogen peroxide. The aqueous phase was saturated with potassium carbonate, extracted with ether, and the combined extracts were analyzed. Glpc. analysis indicated the presence of 0.66 mmole (26 % based on boron) of 1-cyclopentyl cyclopentanol and 0.30 mmole (12 %) of dicyclopentyl carbinol. For experiment of the reaction of at-complex with dichloromethyl methyl ether, the organoborane was subjected to react with methyl lithium at room temperature first and then with dichloromethyl ether. Finally, the product was oxidized as previously described.

The present results are highly promising for an extention of the reaction of organoboranes with carbenes.

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Table 1

Reaction of Organoboranes with Methoxy Carbene

Organoborane	Product[a]	Product yield (%)[b]		
		$MeLi/R_3B=1$	3	10
Triethylborane	2-Butanol	22	35	39
	3-Pentanol	3	14	24
Tripropylborane	3-Hexanol	18	21	33
	4-Heptanol	6	15	40
Tripentylborane	5-Decanol	17	20	28
	6-Undecanol	8	15	21
Tricyclopentylborane	1-Cyclopentyl cyclopentanol	26	34	25
	Dicyclopentyl carbinol	12	37	50

[a] The compound gave satisfactory elemental analyses and spectral data in agreement with the assigned structure.

[b] Based on the organoborane used.

Table 2

Reaction of At-complex Obtained from Organoborane and Methyllithium with Dichloromethyl Methyl Ether

Organoborane	Product[a]	Product yield (%)[b]		
		$MeLi/R_3B=1$	3	10
Triethylborane	2-Butanol	33	50	50
Tripropylborane	3-Hexanol	22	36	45
Tripentylborane	5-Decanol	33	43	54
Tricyclopentyl borane	1-Cyclopentyl cyclopentanol	49	51	47

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