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A NEW GENERAL APPROACH TO 2-SUBSTITUTED METHYLENECYCLANES USING 1-(DIALKYLBORYLMETHYL)CYCLOALKENES

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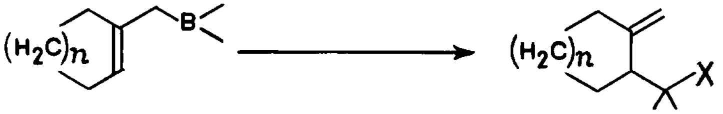
Summary: A novel method for the synthesis of 2-substituted methylenecyclopentanes and methylenecyclohexanes based on the allylboration of carbonyl compounds and alkoxyacetylenes with 1-(dialkylborylmethyl)cyclopentene and -cyclohexene is described.

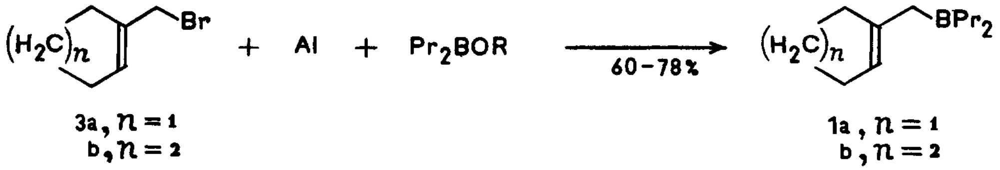
Methylenecycloalkanes are widely used as key compounds in the synthesis of various natural substances and their analogues, e.g. prostaglandins [1a], iridoids [1b,c], antibiotics [2] and as models in investigations of many addition reactions to the C=C bond. The known methods for the preparation of methylenecyclanes may be divided into three major classes: (1) elimination reactions, mainly pyrolytic [3a], (2) cyclisation and oligomerisation of some unsaturated compounds, e.g. allenes and α,ω-dienes [3a], (3) Wittig and related reactions [3a-d]. However, many of them have certain limitations. Therefore the search for new and effective ways to these compounds is still an important aim.

We have developed a new general approach to various 2-substituted methylenecyclanes 2 with the use of previously unknown cycloalkenylmethylboranes of the type 1:



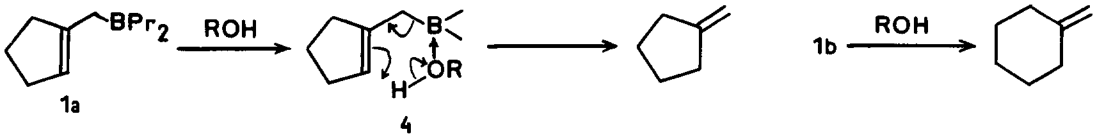
In this paper we describe the synthesis and some reactions of two first representatives of this class of compounds, 1-(dipropylborylmethyl)cyclopentene (1a) and 1-(dipropylborylmethyl)cyclohexene (1b).

Boranes 1a and 1b are easily obtained by interacting corresponding bromide (3a,b), boron ester Pr_2BOR and aluminum (Table).

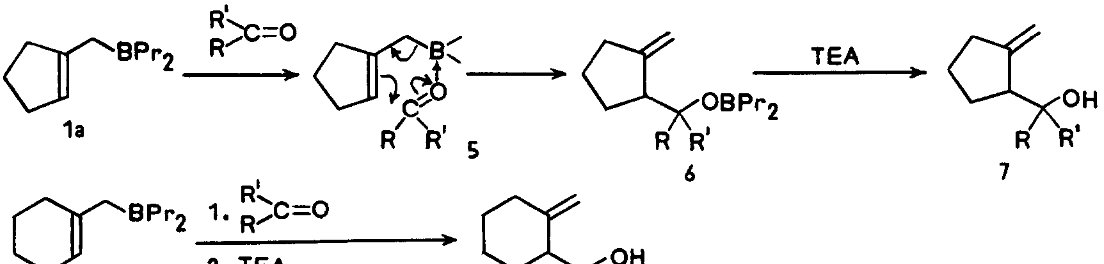


This method was previously used for the preparation of allyl-, metallyl-, crotyl- and prenyl(dialkyl)boranes [4] as well as a new isoprenylating reagent, 2-(dipropylborylmethyl)-1,3-butadiene [5].

1-(Dipropylborylmethyl)cycloalkenes 1a and 1b belong to allylic derivatives of boron and possess the high specific reactivity of this type of organoboranes [6]. They are cleaved by water and alcohols to form Pr_2BOR and methylenecyclopentane (b.p. 76-77°C, n_D^{22} 1.4332) or methylenecyclohexane (b.p. 99-101°C, n_D^{22} 1.4465), respectively (purity>97%), thus showing the protolysis to take place with the allylic rearrangement (4).



Similarly to simple β,γ-unsaturated boron derivatives [6,7], 1a and 1b add to organic compounds with multiple bonds. Thus reactions with aliphatic and aromatic aldehydes and ketones as well as with conjugated enones at -30 ÷ 0°C lead to esters 6, reesterification of which with higher alcohols furnishes corresponding carbinols 7 and 8.

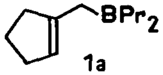
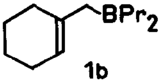
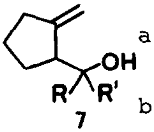
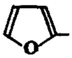
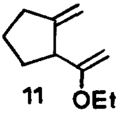
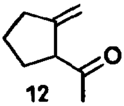
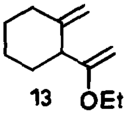
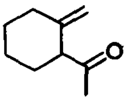


TEA = triethanolamine

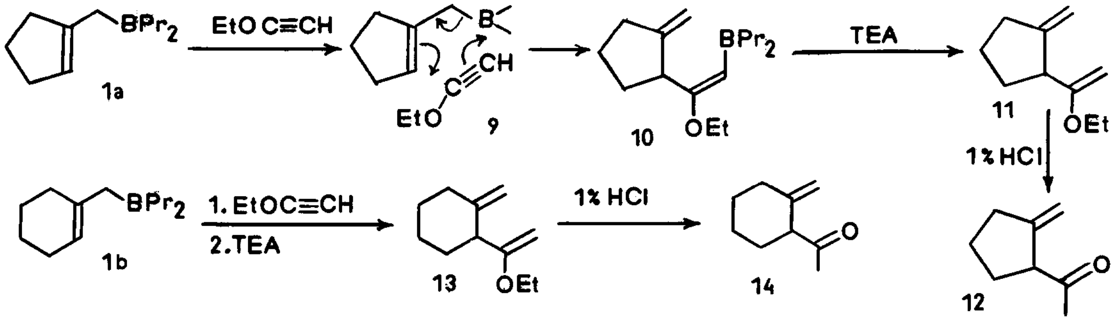
Cis-allylboration of acetylene compounds [6,8] represents one more significant reaction of β,γ-unsaturated triorganoboranes. This reaction is the first stage of the allylboron-acetylene condensation [6,9] and leads to 1,4-pentadienyl boron compounds.

We have established that boranes 1a and 1b add to ethoxyacetylene quantitatively at -30 ÷ 0°C to form cis-addition products of the type 10.

Table

Compound [1]	R	R′	Yield [2] %	B.P. °C/mmHg	n_D (°C)	IR $\nu_{C=C}$ cm^{-1}	^1H NMR (δ, ppm) C=CH	^1H NMR (δ, ppm) $C=CH_2$
 **1a**	–	–	78	43/1	1.4542 (23.5)	1649	5.10 [3]	
 **1b**	–	–	61	50/1	1.4583 (23.5)	1667	5.10 [4]	
 **7** a	Me	H	70	55-57/7	1.4769 (20)	1650		4.87 m
b	Me	Me	87	61-62/7	1.4711 (21)	1650		4.90 m
c	Me	$CH=CH_2$	75	68-69/1	1.4862 (21)	1650	(5.95 m)	5.05 m
d		H	40.5	63-65/1	1.5112 (21)	1655		4.87 m
 **8** a	Me	H	74	69-71/7	1.4812 (22)	1648		4.57-4.80
b	Me	$CH=CH_2$	68.5	81-83/7	1.4932 (22)	1645	5.93 (two dd)	4.68 m
 **11**	–	–	84.5	49-50/7	1.4625 (20)	1600 1655		3.77, 3.84 4.85 m
 **12**	–	–	74	48-49/7	1.4598 (18)	1648		4.93 m [5]
 **13**	–	–	82	67-68/7	1.4712 (21)	1600 1653		3.83 m 4.43-4.68
 **14**	–	–	70	55/7	1.4701 (23.5)	1648		4.64 m [6] 4.77 m

1) Satisfactory elemental analysis was obtained; 2) Product was isolated by distillation; 3) δ_{B-CH_2} = 2.12 ppm; 4) δ_{B-CH_2} = 1.93 ppm; 5) δ_{CH_3}=2.08 ppm; 6) δ_{CH_3}= 2.0 ppm.



The B-C_{sp^2} bond in adducts 10 is easily split (0 → 20°C) by alcohols to give 2-(α-ethoxyvinyl)-1-methylenecycloalkanes 11 and 13. These are hydrolysed with 1% HCl to produce 2-acetyl-1-methylenecycloalkanes 12 and 14(Table).

The exclusive formation of the exo-methylene products (Table) in the allylboration of carbonyl compounds and ethoxyacetylene with boranes 1a and 1b confirms unambigously that these reactions occur totally with allylic rearrangement (5 or 9) apparently in concerted processes.

A cyclic allylborane of another type, cyclohex-2-enyl(diisopinocampheyl)borane, has been used by Brown in the reaction with MeCHO [10].

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