## SYNTHESIS OF 2-SUBSTITUTED METHYLENECYCLOALKANES FROM 1-(DIALKYL-BORYLMETHYL)CYCLOALKENES

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UDC 542.91:547.1'127

Methylenecycloalkanes are used in the synthesis of natural products and their analogs, for example, prostaglandins and antibiotics, but also as model compounds in investigations of addition reactions to the C=C bond. Known methods for the preparation of methylenecyclo-alkanes may be divided into three types [1]: 1) elimination reactions; 2) cyclization and oligomerization of unsaturated compounds, for example,  $\alpha, \omega$ -dienes and allenes; 3) Wittig and related reactions of carbonyl compounds with ylides. However, each of these methods has certain limitations.

We have developed a novel general approach to 2-substituted methylenecycloalkanes (I), based on the alkylboration of carbonyl compounds and alkoxyacetylenes by means of hitherto unknown cycloalkenylmethylboranes (I, n = 1, 2).



This article deals with the synthesis and investigation of some reactions of l-(dipropylborylmethyl)cyclopentene (Ia) and l-(dipropylborylmethyl)cyclohexene (Ib), about which was published in [2].

Boranes (Ia) and (Ib) were prepared in yields of 78 and 61% by reaction of the corresponding organic bromides (IIIa, b), the boron ether  $Pr_2BOMe$ , and Al (turnings) activated by a small amount of mercuric chloride.



This method was used earlier for the preparation of allyl, methallyl, crotyl, prenyl [3], and isoprenyl(dialkyl) boranes. Compounds (Ia, b) are colorless liquids, stable under an inert gas atmosphere, and distillable under vacuum without decomposition and symmetrization. In the <sup>11</sup>B NMR spectra chemical shifts relative to  $BF_3 \cdot OEt_2$  have the values 85.3 and 86.3 ppm; in the IR spectra weak absorption bands of the trisubstituted double bond are found: 1649 and 3042 cm<sup>-1</sup> (Ia); 1667 and 3042 cm<sup>-1</sup> (Ib). According to IR and NMR spectral data, under normal conditions (20-40°C) both boranes exist mainly in the form with the intercyclic double bond and do not contain (with an accuracy of up to 2-3%) the corresponding isomer with an exo-methylene bond (the product of allylic isomerization).

l-(Dipropylborylmethyl)cycloalkenes (Ia) and (Ib) are allylic boron derivatives and display the high and specific chemical reactivity characteristic of this class of organoboranes. On reaction with water or alcohols they decompose with formation of  $R_2BOR'$  and methylene-cyclopentane (V) (yield 75%) and methylenecyclohexane (VI) (yield 60%), respectively, that is, the protolysis is accompanied by allylic rearrangement of (IV).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 420-425, February, 1988. Original article submitted September 16, 1986.



Similar to  $\beta,\gamma$ -unsaturated boron derivatives [5-7], (Ia) and (Ib) add to organic compounds containing the multiple bonds C=0, C=N-,  $-C\equiv N$ ,  $-C\equiv C-$ , etc. Reactions with aldehydes and ketones proceed at -60 to 0°C (with paraform at 40-50°C) and lead to ethers (VIII) or (X), by transetherification of which with higher alcohols the corresponding carbinols (IX) and (XI) were synthesized (Table 1).



Aliphatic and aromatic carbonyl compounds react according to this scheme. It is a fact that with methyl vinyl ketone and its homologs only the products of allylboration of the C=O group (IXd) and (XIc) are obtained, and that 1,4-addition products are not obtained at all. Reactions of (Ia) and (Ib) with RR'CO are conveniently carried out without solvent, but when necessary any inert solvent (CHCl<sub>3</sub>, CCl<sub>4</sub>, alkanes, benzene, toluene, ether, THF, etc.) can be used.

Another important reaction of  $\beta$ , $\gamma$ -unsaturated triorganoboranes is the cis-allylboration of acetylenic compounds [5, 7]. This reaction, which leads to 1,4-pentadienyl derivatives of boron, is the first step in the allylboron-acetylene condensation [5, 8]. We have found that boranes (Ia) and (Ib) add to ethoxyacetylene quantitatively at -60 to 0° C with practically instantaneous formation of adducts of type (XIII) with trans configuration of the boryl and EtO groups. The reaction proceeds instantly and is completed immediately after mix ing of the reagents.



The B-C<sub>sp2</sub> bond in adducts of type (XIII) is easily (0-20°C) split under the action of alcohols; thereby 2-( $\alpha$ -ethoxyvinyl)-1-methylenecycloalkanes (XIV) and (XVI) are produced, by

TABLE	1
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Com- pound	Yield, %	Bp, °C (p, mm Hg	n <sub>D</sub> (°C)	<u>Found</u> Calc	<u>i_</u> , % 	IR spec- trum vC=C, cm <sup>-1</sup>	NMR spectrum, SC=CH <sub>2</sub> , ppm
(IXa)	50	58-60(7)	1,4764 (23,5)	75.23 74,95	<u>10,74</u> 10,79	1652	4,95 d
(IXÞ)	70 <b>a</b>	55–57(7)	1,4769 (20)	$\tfrac{76,05}{76,14}$	$\frac{11,28}{11,18}$	1650	4,87 m
(IXc)	87 <b>b</b>	61-62(7)	1,4711(21)	$\frac{76,87}{77,08}$	<u>11,59</u> 11,51	1650	4,90 m
(IXd)	75 <sup>b</sup>	68-69(1)	1,4862(21)	$\frac{78.94}{78,90}$	<u>10,63</u> 10,59	1650	5.05 m <sup>d</sup>
(IX e)	40,5 <sup>c</sup>	63-65(1)	1,5112(21)	$\frac{74.34}{74,13}$	8,09	1655	4,87 m
(XIA)	90,7	45-46(1)	1,4880(21)	$\frac{76.25}{76,14}$	$\frac{11,22}{11,18}$	1643	4.70 đ
(XIb)	74	69-71(7)	1.4812(22)	$\frac{76.92}{77,08}$	11.45 11,51	1648 <sup>д</sup>	4.57-4.80 m <sup>e</sup>
(XIc)	68,5	81-83(7)	1.4932(22)	$\frac{79.37}{79,46}$	<u>10.90</u> 10,91	1645	4,68 m <b>-f</b>
(XId)	52,5	64-65(1)	1,5051 (21)	79,66 79,94	<u>11,38</u> 11,18	1642	4,84 đ
(XIV)	84,5	49-50(7)	1,4625(20)	79.04 78,90	10.59 10,59	1600 1655	3,77; 3,84 4.85 m
(XV)	74	48-49(7)	1.4598(18)	77.16 77.38	<u>10,17</u> 9,74	1648	4,93 m
(XVI)	82	67-68(7)	1.4712(21)	79.60 79,46	10.81	1600 1653	3,83 .m 4,43-4.68 m
(XVII)	70	55(7)	1,4701 (23,5)	$\frac{78.27}{78.21}$	<u>10.29</u> 10,21	1648	4,64 m, 4.77 m
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<sup>a</sup>Purified over an SiO<sub>2</sub> column (CHCl<sub>3</sub>) and by distillation. <sup>b</sup>Purified by distillation. <sup>c</sup>Purified over an SiO<sub>2</sub> column (ether-hexane 1:1) and by distillation. <sup>d</sup> $\delta$ C=CH 5.95 m. <sup>e</sup>Cf. [13]. <sup>f</sup> $\delta$ C=CH 5.93 two dd (two diastereoisomers in the ratio of 1:1).

controlled hydrolysis of which (1% HCl) 2-acetyl-1-methylenecycloalkanes (XV) and (XVII) were synthesized.

In preparing dienes (XIV) and (XVI), and also carbinols (IX) and (XI), it is not necessary to isolate the adducts of type (XIII) or (VIII). After the addition of ethoxyacetylene, aldehyde, or ketone to (Ia) or (Ib), the mixture is warmed to room temperature, 1-2 moles of triethanolamine or other high-boiling alcohol is added, and the diene or alcohol is distilled from the mixture under vacuum.

The formation of only the addition products with an exo-methylene bond on allylboration of carbonyl compounds and ethoxyacetylene by means of boranes (Ia) and (Ib) shows unambiguously that these reactions completely run with an allyl-type rearrangement and probably are in agreement with processes of the  $2\pi + 2\pi + 2\sigma$  type.

The structures of the compounds obtained were confirmed by elemental analyses and physicochemical data (IR and PMR). The IR spectra of all compounds [with the exclusion of boranes (Ia) and (Ib)] have absorption bands in the regions 880-895, 1645-1655, and 3070-3095  $\rm cm^{-1}$ , which characterize the exo-methylene bond. The valence vibration of the C=C bond in carbinols (IX) is found in the region 1650-1655  $\rm cm^{-1}$ , in carbinols (XI) in the region 1643-1648

 $cm^{-1}$ ; absorptions of the OH group in (IX) and (XI) are found at 3350-3480 cm<sup>-1</sup>. In addition to these bands, in the spectra of 2-( $\alpha$ -ethoxyviny1)-1-methylenecycloalkanes (XIV) and (XVI) absorptions in the regions 1600 and 3105 cm<sup>-1</sup> are found, and for 2-acety1-1-methylenecyclo-alkanes (XV) and (XVII) at 1710 cm<sup>-1</sup> (C=0). The chemical shifts of the protons of the methylene moiety (C=CH<sub>2</sub>) in the PMR spectra are listed in Table 1.

## EXPERIMENTAL

All operations with the organoboron compounds were carried out under a dry argon atmosphere. PMR spectra were recorded on Bruker WM-250 and Tesla BS-467 spectrometers; chemical shifts are listed relative to TMS. <sup>11</sup>B NMR spectra were recorded on a Bruker SXP/4-100 spectrometer; chemical shifts were measured relative to  $BF_3 \cdot Et_2O$ . IR spectra were taken on a UR-20 spectrometer. Bromides (IIIa, b) were synthesized according to [9].

<u>1-(Dipropylborylmethyl)cyclopentene (Ia)</u>. To 4 g of aluminum turnings, 0.1 g of mercuric chloride, and 30 ml of dry ether was added over 1 h with stirring and refluxing a mixture of 12.6 g (78.3 mmoles) of 1-bromomethylcyclopentene (IIIa) and 10 g (78.3 mmoles) of methoxy(dipropyl)borane, and the mixture was refluxed for 5 h. From the reaction mixture (Ia), bp 64-66°C (1 mm), was distilled under vacuum. Redistillation yielded 10.8 g (78%) of (Ia), bp 43°C (1 mm), np<sup>23.5</sup> 1.4542. Found, %: C 80.88; H 12.96; B 5.99. C<sub>12</sub>H<sub>23</sub>B. Calculated, %: C 80.91; H 13.01; B 6.08. PMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm): 5.10 m (CH=C).

<u>1-(Dipropylborylmethyl)cyclohexene (Ib)</u>. In the same way from 5 g of A1, 17 g (0.1 mole) of 1-bromomethylcyclohexene (IIIb), and 12.8 g (0.1 mole) of methoxy(dipropyl)borane in 50 ml of dry ether (12 h refluxing) was obtained 11.8 g (61%) of borane (Ib), bp 50°C (1 mm),  $n_D^{2^3.5}$  1.4583. Found, %: C 81.24; H 13.19; B 5.42. C<sub>13</sub>H<sub>25</sub>B. Calculated, %: C 81.26; H 13.11; B 5.63. PMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm): 5.10 m (CH=C).

<u>Methylenecyclopentane (V)</u>. A distillation flask was charged with 2.37 g (13.3 mmoles) of borane (Ia), cooled to -15°C, and 1.7 ml (13.4 mmoles) of n-hexanol was added dropwise. The mixture was gradually warmed up to ~20°C and distilled to yield 0.82 g (75%) of (V), bp 74-76°C,  $n_D^{22}$  1.4332 (cf. [10]).

<u>Methylenecyclohexane (VI)</u>. In the same way, from 0.98 g (5.1 mmoles) of borane (Ib) and 0.64 ml (5.1 mmoles) of n-hexanol was obtained 0.32 g (65%) of (VI), bp 99-101°C,  $n_D^{20}$  1.4445 (cf. [10]).

<u>2-Methylenecyclopentylmethylcarbinol (IXb)</u>. A distillation flask was charged with 2.06 g (11.5 mmoles) of borane (Ia), cooled to  $-5^{\circ}$ C, and with stirring 1 ml (16.6 mmoles) of MeCHO was added. The mixture was gradually warmed up to ~20°C, the excess of acetaldehyde was distilled off, and to the boron ether was added 3.2 ml of triethanolamine. After 30 min 1.38 g of (IXb) was distilled from the mixture. It was purified over a silica gel column (eluent CHCl<sub>3</sub>) and by distillation. Yield 1.0 g (70%) of (IXb).

Alcohols (IXc-d) and XIb-d) were prepared in the same way (Table 1). The temperature at which the reagents were mixed varied from -10 to -60°C in these cases.

<u>2-Methylenecyclopentyl-1-methanol (IXa)</u>. A mixture of 2.85 g (16 mmoles) of borane (Ia) and 0.48 g (16 mmoles) of paraform, previously dried over  $P_2O_5$  under vacuum, was heated at 40-50°C for 5 h, unreacted paraform was filtered off, washed with pentane, and the solvent was evaporated. To the residue was added 3 ml of triethanolamine and alcohol (IXa), bp 64-67°C (7 mm), was distilled off. It was purified over a silica gel (100/160  $\mu$ ) column with hexane-ether 9:1 as eluent (Table 1) (cf. [11]).

<u>l-Methylene-2-(dipropylboryloxymethyl)cyclohexane (X, R = R' = H)</u>. In the same way as in the foregoing example, to 2.67 g (13.9 mmoles) of (Ib) was added 0.42 g (13.9 mmoles) of paraform, the suspension was heated at 40-50°C for 1 h, and allowed to stand overnight. Unreacted paraform was filtered off and washed with pentane. After evaporation of the pentane, distillation of the residue yielded 1.72 g (57.3%) of (X, R = R' = H), bp 70-74°C (1 mm). Found, %: C 76.06; H 12.12; B 4.56.  $C_{14}H_{27}OB$ . Calculated, %: C 75.68; H 12.25; B 4.87. IK spectrum (CCl<sub>4</sub>,  $\nu$ , cm<sup>-1</sup>): 882 (C-H), 1652 (C=C), 3080 (C-H), 1320-1350 (B-O).

<u>2-Methylenecyclohexyl-l-methanol (XIa)</u>. To 1.7 g (7.7 mmoles) of boron ether (X, R = R' = H) was added 2 ml of triethanolamine; distillation yielded 0.88 g (90.7%) of (XIa), bp 45-46°C (1 mm),  $n_D^{21}$  1.4880 (cf. [12]).  $\frac{2-(\alpha-\text{Ethoxyvinyl})-1-\text{methylenecyclopentane (XIV)}}{2.14 \text{ g} (12 \text{ mmoles}) \text{ of borane (Ia), with cooling (-5°C) 1.1 ml of ethoxyacetylene in 1 ml of pentane was added dropwise, the mixture was warmed to ~20°C, and the pentane was distilled off. To the residue was added 3.5 ml of triethanolamine; vacuum distillation yielded 1.5 g (84%) of diene (XIV), bp 49-50°C (7 mm).$ 

 $2-(\alpha-\text{Ethoxyviny1})-1-\text{methylenecyclohexane (XVI)}$ . In the same way, from 1.7 g (8.84 mmoles) of borane (Ib) and 0.82 ml (8.85 mmoles) of ethoxyacetylene (-30°C) was obtained 1.32 g (90%) of diene (XVI). A second distillation yielded 1.2 g (82.6%).

<u>1-Acetyl-1-methylenecyclopentane (XV)</u>. To 10 ml of a 1% HCl solution was added at 0°C a solution of 0.87 g (5.72 mmoles) of diene (XIV) in 10 ml of ether. The reaction was monitored by means of IR spectra (appearance of a band at 1710 (C=O) and disappearance of the band at 1600 cm<sup>-1</sup>). The ethereal layer was separated, washed with water, and dried over  $Na_2SO_4$ . The ether was evaporated and distillation of the residue yielded 0.35 g (50%) of ketone (XV).

<u>1-Acetyl-1-methylenecyclohexane (XVII)</u>. In the same way, from 0.88 g (5.29 mmoles) of  $2-(\alpha-\text{ethoxyvinyl})-1-\text{methylenecyclohexane (XVI)}$  was obtained 0.52 g (70%) of ketone (XVII).

## CONCLUSIONS

We have developed a novel general method for the preparation of 2-substituted methylene cycloalkanes, which is based upon the allylboration of carbonyl compounds and alkoxyacetylenes by means of hitherto unknown cycloalkenylmethyl(dialkyl)boranes.

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