

Allylic diboranes

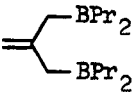
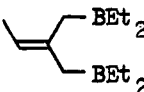
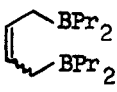
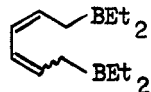
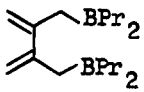
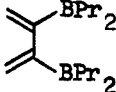
Yuri N. Bubnov

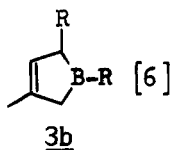
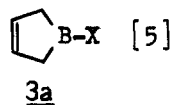
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Abstract -The synthesis and chemical properties of a series of novel unsaturated diboranes 1-6 with both boron atoms in allylic positions are described. Some new reactions of allylboranes, presented in the second section, proceed either with rearrangement ($2\pi+2\pi+2\sigma$) or with retention of configuration of the allylic fragment. Convenient methods for the preparation of allyl- and diallyloxiranes, homoallylic alcohols and thiols, as well as an approach for designing cyclic structures via allylboranes are suggested.

Allylboranes occupy an exceptional position among organoboron compounds. They differ essentially in properties and reactivity from aliphatic, vinylic and aromatic analogues due to their specific structure (β,γ -double bond) and, as a consequence, their ability to react with a ($2\pi+2\pi+2\sigma$)-type rearrangement [1-4]. Allylboranes readily add to compounds with multiple bonds (C=O, C=N, C≡N, C=C and C≡C) [2,3], that is quite nontypical for other classes of organoboranes [1,2,4]. Allylboration results in the creation of a new C-C bond. It proceeds chemo- and regioselectively and, with proper choice of reagents, stereo- and enantioselectively.

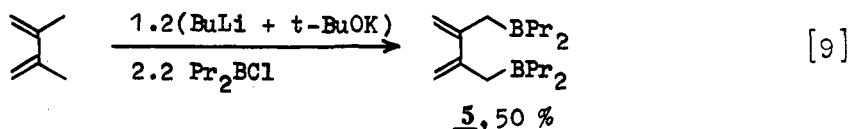
Used in organic chemistry hitherto were mainly allylboranes with one boron atom [2,3]. In this paper, the synthesis and some chemistry of novel β,γ -unsaturated diboranes 1-6 with both boron atoms in allylic positions are presented.

						
	<u>1</u>	<u>2</u>	<u>3</u> (E:Z≈4:1)	<u>4</u> (Z,Z:E,Z≈1:1)	<u>5</u>	<u>6</u>
$\delta(^{11}\text{B})$	88.75	87.0	84.5	84,5	86,5	80.0
Yield, %	41	40	45	75	50	37

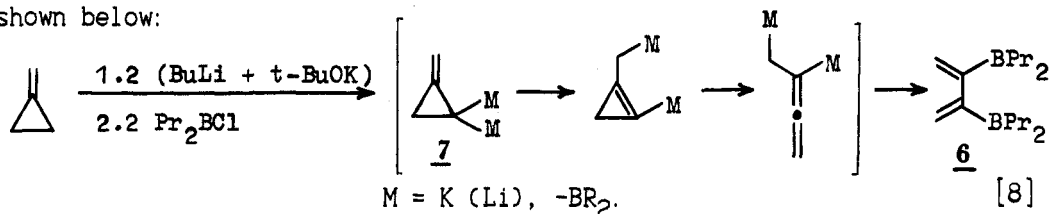


In principle, this group involves also 3-borolene 3a [5] and its derivatives 3b [6].

Synthesis. Diboranes 1-6 were synthesised in a two-step sequence (bis-metallation and transmetallation) from the corresponding olefins or dienes: isobutylene [3,7], trimethylethylene, 2-butene, 1,5-hexadiene [8], 2,3-dimethyl-1,3-butadiene [9] and methylenecyclopropane [8]. The metallation was performed by treatment of olefins and dienes with 2 equiv. of a 1:1 mixture of BuLi and *t*-BuOK. The reaction mixture was then treated with 2 equiv. of Pr₂BCl or Et₂BCl to give a corresponding diboranes 1-6 isolated by vacuum distillation.



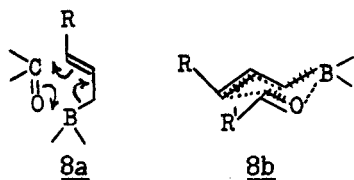
Dimetallation of methylenecyclopropane was expected to afford 2,3- or 2,2-diboron derivative 7 (M=BPr₂). However, a derivative of 1,3-butadiene 6 was obtained instead, boron atoms occupying both vinyl and allylic positions. A possible mechanism for its formation via a series of allylic rearrangements is shown below:



PROPERTIES

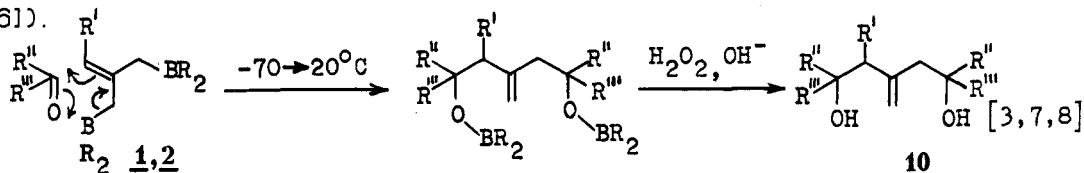
Diboranes 1-6 are stable in nitrogen atmosphere; exposure to air results in their oxidation and hydrolysis. Partial polymerisation occurs upon distillation of 5 and 6. In diboranes 1-5 permanent allylic rearrangement [2] takes place. As judged from NMR data, the standard free activation energy for 1 is 13.4±0.1 kcal/mol.

Reactions with carbonyl compounds.

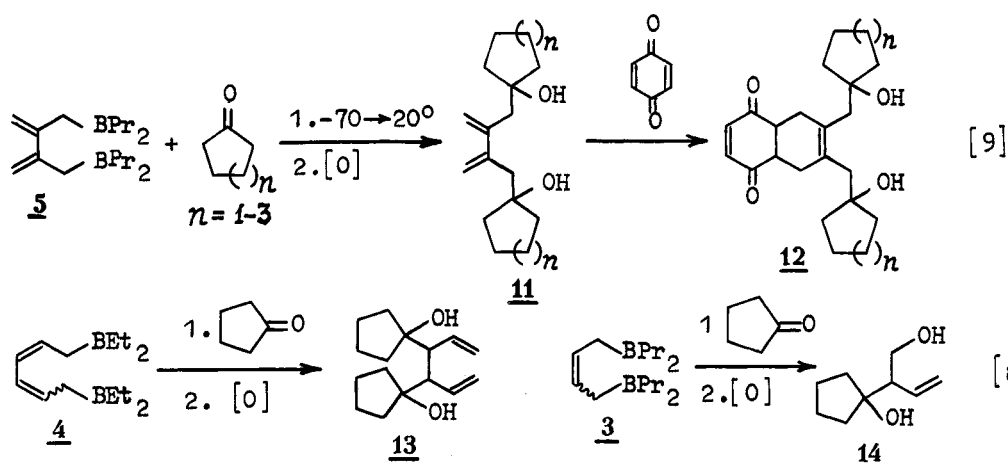


Diboranes 1-6 react with aldehydes and ketones at -70-20°C by addition to the carbonyl group, in all cases allylboration proceeding with a rearrangement via a six-membered transition state of the type 8a or 8b.

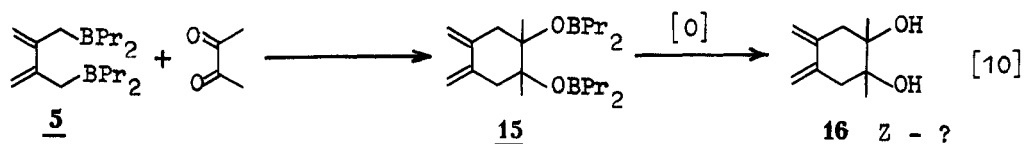
Synthesis of unsaturated diols. Allylboranes 1-6 were used as starting compounds for the synthesis of diols 10-14 with one or two double bonds [7-9]. Diene condensation of 1,6-diols 11 with *p*-quinone gives carbocyclic derivatives 12 [9]. Diborane 3 reacts with one molecule of a carbonyl compound to give a 3-butenylboron derivative which does not add to C=O group (cf. also [6]).



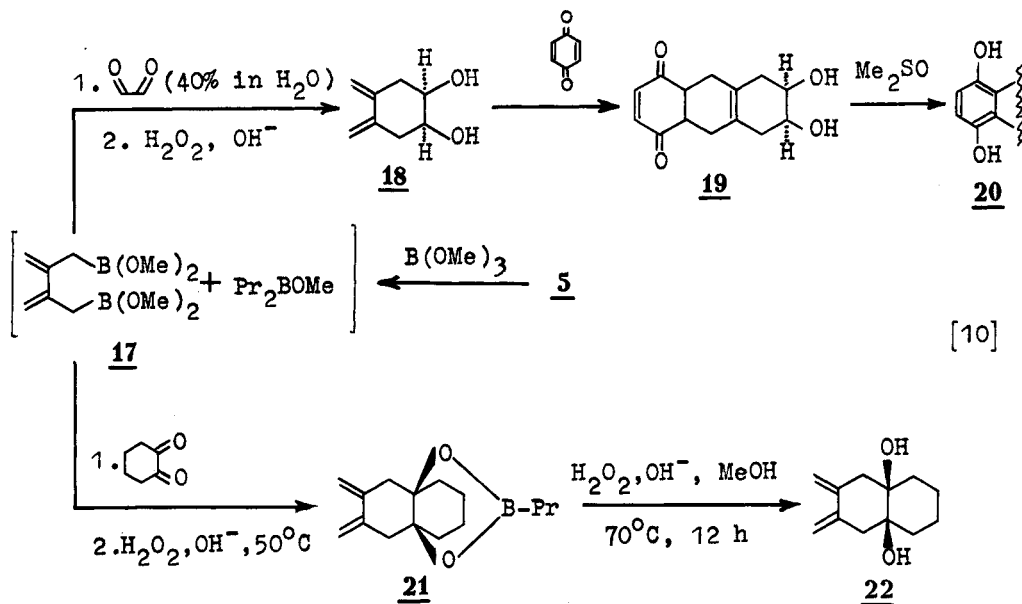
1, R' = H; 2, R' = Me; R'' R''' CO = MeCHO, PhCHO, Me₂CO, (CH₂)_nCO (n=4-6).



Synthesis of carbocycles. The bifunctional character of allylic diboranes allows them to be used for the synthesis of cyclic and polycyclic systems. Thus, reaction of 5 with 2,3-butanedione gives diboron compound 15, deboronation of which (H_2O_2 , OH^-) affords diol 16.

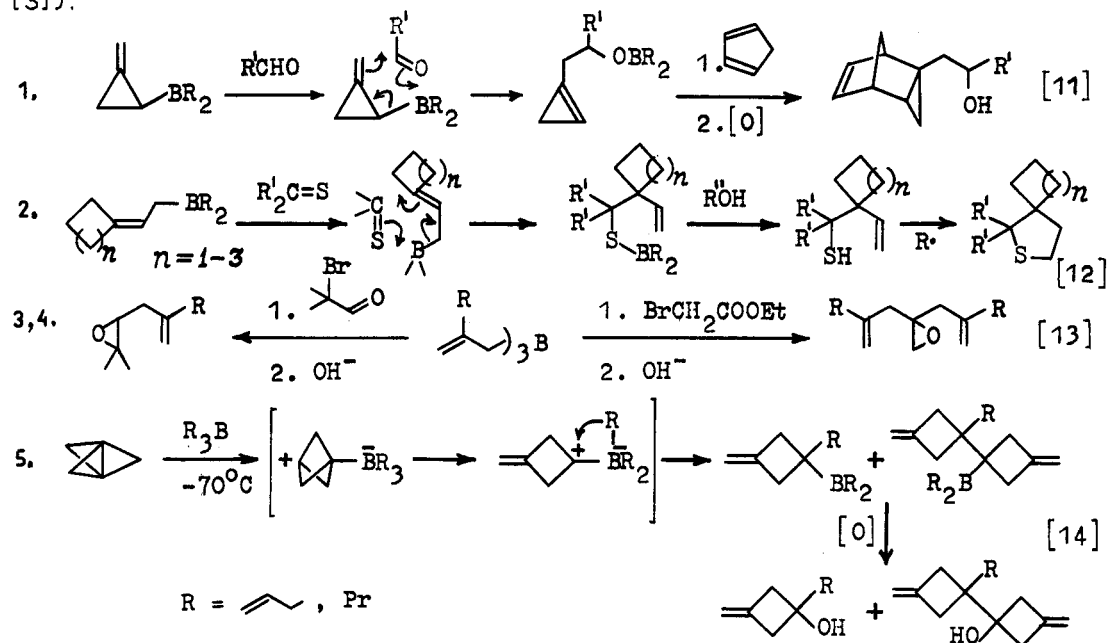


Interaction of glyoxal (40% aqueous solution) with ester 17 (prepared *in situ* from 5 and $\text{B}(\text{OMe})_3$, 20°C , 10 days, $\delta(^{11}\text{B})$ 31.7 ppm) gives rise to *cis*-diol 18. Condensation of 18 with *p*-benzoquinone produces tricyclic compound 19, which converts spontaneously into hydroquinone 20 when dissolved in Me_2SO .



Condensation of 1,2-cyclohexanedione with 17 in the presence of Pr_2BOMe (see above), followed by conventional oxidation at $20 - 50^\circ\text{C}$ in methanol, results in formation of air-stable boron-containing propellane 21, which could be deboronated only by boiling in H_2O_2 for 12 h.

Novel synthetic applications of allylboranes. Apart from investigation of new allylic diboranes 1-6, studies of β,γ -unsaturated monoboranes was continued. Shown below are four new allylboronation reactions (with aldehydes, thioketones, α -bromaldehydes and ethyl bromoacetate) and a reaction with [1.1.1]-propellane which proceeds with retention of configuration of the allylic fragment (similarly to the reaction of allylboranes with bicyclo[1.1.0]butane [3]).



Acknowledgements The author expresses his deep gratitude to Drs M. E. Gursky, L. I. Lavrinovich, I. D. Gridnev and also to A. V. Geiderikh, A. Yu. Zykov, V. I. Zheludeva and S. B. Golovin for their enthusiasm while carrying out certain parts of this work and for stimulating discussions. Also I thank Professor J. J. Eisch for reading the manuscript before publication.

REFERENCES

1. R. Koster, Houben-Weyl Methoden der Organischen Chemie, XIII/3a, 3b, 3c, Thieme, Stuttgart, 1982-1984.
2. B. M. Mikhailov, Yu. N. Bubnov, Organoboron compounds in Organic Synthesis, Harwood Acad. Sci. Publ., Chur, London, N-Y, 1984.
3. Yu. N. Bubnov, Pure Appl. Chem., **59**, 895 (1987).
4. A. Peter, K. Smith, H. C. Brown, Borane Reagents, Academic Press, London, 1988.
5. G. E. Herberich, B. Hessner, D. Sohnen, J. Organometal. Chem., **233**, C35, (1982). W. Hubbard, K. Stanzl, J. Organometal. Chem., **174**, 141 (1979).
6. G. Zweifel, T. M. Soup, J. Am. Chem. Soc., **110**, 5578 (1988) and refs. therein.
7. Yu. N. Bubnov, M. E. Gursky, D. G. Pershin, Izv. AN SSSR, Ser. Khim., 1987, 1193.
8. Yu. N. Bubnov, M. E. Gursky, A. V. Geiderikh, Russ. J. Organometal. Chem., **2**, 1433 (1989).
9. M. E. Gursky, S. B. Golovin, Yu. N. Bubnov, Izv. AN SSSR Ser. Khim., 1990, 495.
10. Yu. N. Bubnov, M. E. Gursky, S. B. Golovin, A. V. Ignatenko, Izv. AN SSSR, Ser. Khim., 1990, in press.
11. Yu. N. Bubnov, M. E. Gursky, A. V. Ignatenko, ibid., 1988, 2184.
12. Yu. N. Bubnov, V. I. Zheludeva, A. V. Ignatenko, ibid., 1989, 1210. G. I. Nikishin, V. I. Zheludeva, L. I. Lavrinovich, D. V. Demchuk, E. I. Troyansky, Yu. N. Bubnov, ibid., 1989, 2155.
13. Yu. N. Bubnov, A. Yu. Zykov, N. A. Donskaya, ibid., 1988, 1199.
14. Yu. N. Bubnov, L. I. Lavrinovich, A. V. Ignatenko, N. K. Sadovaya, L. S. Surmina, A. S. Kozmin, N. S. Zefirov, ibid., 1989, 210.