Chemistry of Heterocyclic Compounds, Vol. 48, No. 5, August, 2012 (Russian Original Vol. 48, No. 5, May, 2012)

REARRANGEMENT OF CYCLOPROPYLBORANE INTO BORETANE

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Previously unknown boron-containing four-membered unsaturated heterocycle boretane was obtained via novel thermal rearrangement of cyclopropylborane and investigated by NMR and IR spectroscopy. Formation of boretane was also confirmed through its chemical transformation into more stable derivatives.

Keywords: boretane, cyclopropylborane, ConcIRT-spectra, ^{19}F NMR spectroscopy, real time IR spectroscopy, ring expansion.

Wagner-Meerwein rearrangement of cyclopropylmethyl cation **1** into cyclobutyl cation **2** [Eq. (1)], discovered by Demjanow at the beginning of the last century [1], has become a convenient synthetic tool for the preparation of four-membered carbocycles [2]. This 1,2-alkyl shift proceeds readily, as it is accompanied by significant strain release, and therefore is thermodynamically favored. However, the corresponding hetero-analogous reactions are scarce and essentially limited only to the rearrangement of cyclopropanone hemiaminals **3** into β-propiolactams **4** [Eq. (2)] [3, 4]. Herein we wish to report the first generation and spectroscopic identification of boretane **6** generated in the previously unknown strain-driven ring expansion of cyclopropylborane **5** [Eq. (3)].

Published computations reveal that in striking difference to organoboron heterocycles possessing two or more boron atoms, which tend to form non-classical aromatic structures [5, 6], boretane molecule was predicted to remain classical [7, 8]. This molecule has no unusual structural distortions besides a large puckering angle in the half-envelope conformation, which was explained by significant 1,3-transannular interaction [9]. Therefore, we were surprised to find that all four-membered boracycles reported to date were unsaturated, possessing at least one sp^2-hybridized carbon atom in the small ring [10-17]. Although intermediacy of boretane species **8** and **12** in the rearrangements of bicyclo[6.1.0]nonatrien-9-ylborane **7** and 9-borabarbaralane **10** was previously proposed [Eqs. (4) and (5)], to the best of our knowledge, no experimental evidence for the formation of saturated four-membered heterocycle with a single boron atom existed to date.

We pondered that the molecule of boretane could be obtained *via* ring expansion of cyclopropylborane. This hypothesis was based on the argument that such transformation would be isoelectronic to the above-mentioned rearrangement of cyclopropylmethyl cation [Eq. (1)]. In addition, it should be noticed that a

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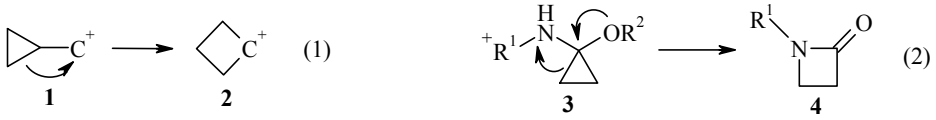
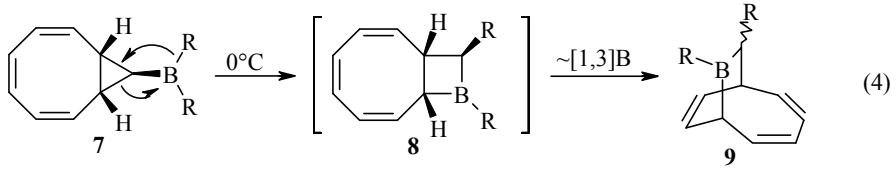
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, 867-882, May, 2012. Original article submitted June 06, 2011.

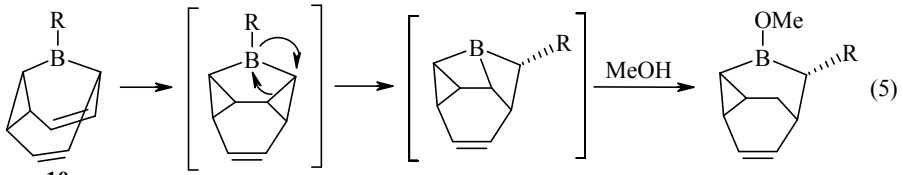
homologous stereospecific transformation of cyclobutylborane **14** into borolane **15** is known [Eq. (6)] [20] Thinking along these lines we subjected to thermal conditions a series of different di- and trisubstituted cyclopropylboranes **17**, generated *in situ via* noncatalytic hydroboration [21-24] of cyclopropenes **16** [Eq. (7)]. However, even prolonged heating at 100°C resulted in no reaction or thermal decomposition of cyclopropylboranes [Eq. (7)]. We rationalized that increasing steric bulk at the reaction site may potentially stimulate the desired rearrangement.



1 **2** **3** **4** **5** **6**

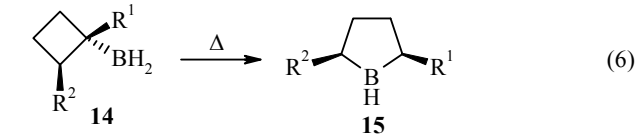


7 **8** **9**

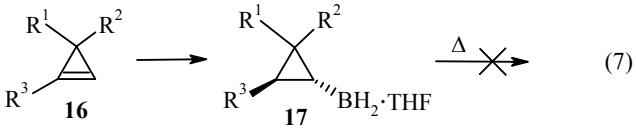


10 **11** **12** **13**

Accordingly, cyclopropene **18** bearing two phenyl substituents at atoms C-1 and C-2 was tested next in the reaction with BH_3·THF [Eq. (8)]. Monitoring the reaction course by ReactIR (Fig. 1)) revealed rapid formation of cyclopropylborane **19** upon addition of compound **18** to a BH_3·THF solution at room temperature (Fig. 1, event *1*). Gratifyingly, in contrast to all other cyclopropylboranes tested, heating of borane **19** at 100°C initiated its gradual conversion into a new component **C** (Fig. 1, event *2*). No visible changes in characteristic IR stretches were observed at this point, which was expected, as the anticipated rearrangement **19**→**20** should produce insignificant bond perturbations, detectable in the fingerprint region only. Thus, ConcIRT algorithm [25] was employed for detailed analysis of changes in the fingerprint region of IR spectra (Fig. 2).



14 **15**



16 **17**

R^1, R^2 = Alk, Ar, COR, R^3 = H, Ar

Despite significant similarity between the ConcIRT spectra of **B** and **C**, there are two distinct IR bands that differentiate these components (Fig. 2). Specifically, an absorption line at 1450-1480 cm^{-1} is attributed to C–H scissor vibrations of cyclopropyl ring in component **B**, while the broad band at 1250 cm^{-1} observed in the spectrum of component **C** according to our molecular modeling studies should correspond to rocking vibrations of methylene group in the boretane ring.

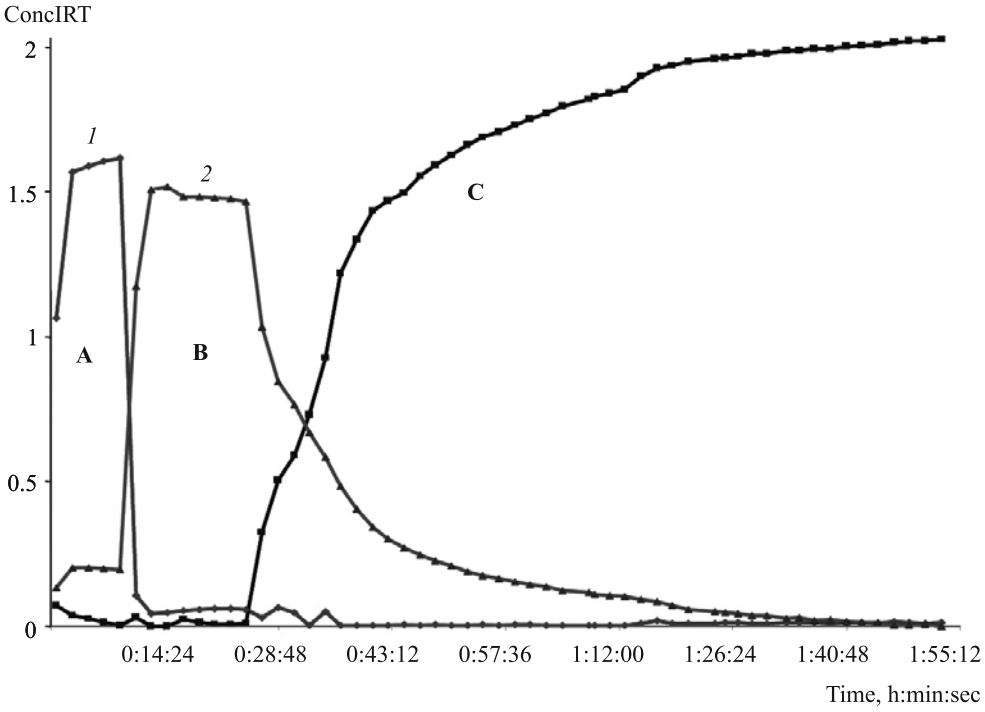
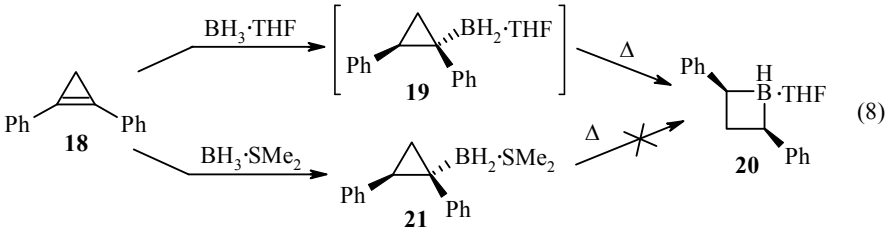


Fig. 1. ConcIRT kinetic plot of hydroboration/rearrangement reaction. Event *1* – addition of cyclopropene **18**; event *2* – heating of the mixture at 100°C. Components: **A** – BH_3·THF complex; **B** – cyclopropylborane **19**; **C** –boretane **20**.

Surprisingly, when analogous reaction was carried out in the presence of BH_3·SMe_2 complex [Eq. (8)], no rearrangement of the corresponding cyclopropylborane **21** was observed even upon prolonged heating at 100°C. DFT computations (B3LYP/6-31G*) of Mulliken charges revealed significant difference in electronic density on boron atoms between structures **19** (+0.338) and **21** (+0.075), suggesting the rearrangement is strongly dependent on the "cationic" character of the reactive center, and can be completely suppressed by strong Lewis bases.

Scheme 1



(8)

To gain additional support for the boretane formation, we treated the reaction mixture with KHF_2 hoping to stabilize the four-membered ring in the form of more stable fluoroborate derivatives (Scheme 1). Analysis of ^{19}F NMR spectrum of the obtained mixture revealed that, along with peaks of cyclopropyltrifluoroborate **23** and BF_4^-, the spectrum contained a resonance at -155 ppm (AB system, $^2J_{FBF}$ = 76 Hz), which was assigned to C_s-symmetric difluoroborate **25** (Fig. 3, spectrum A). A resonance at -153 ppm was attributed to a C_2-symmetric difluoroborate **27**, a putative thermodynamically favored rearrangement product of the isomerization of compound **25** *via* acyclic intermediate **26** (Scheme 1). It is important to mention that, potentially, another *meso* compound **24**, resulting from dicyclopropylborane **22**, can be present in the mixture,

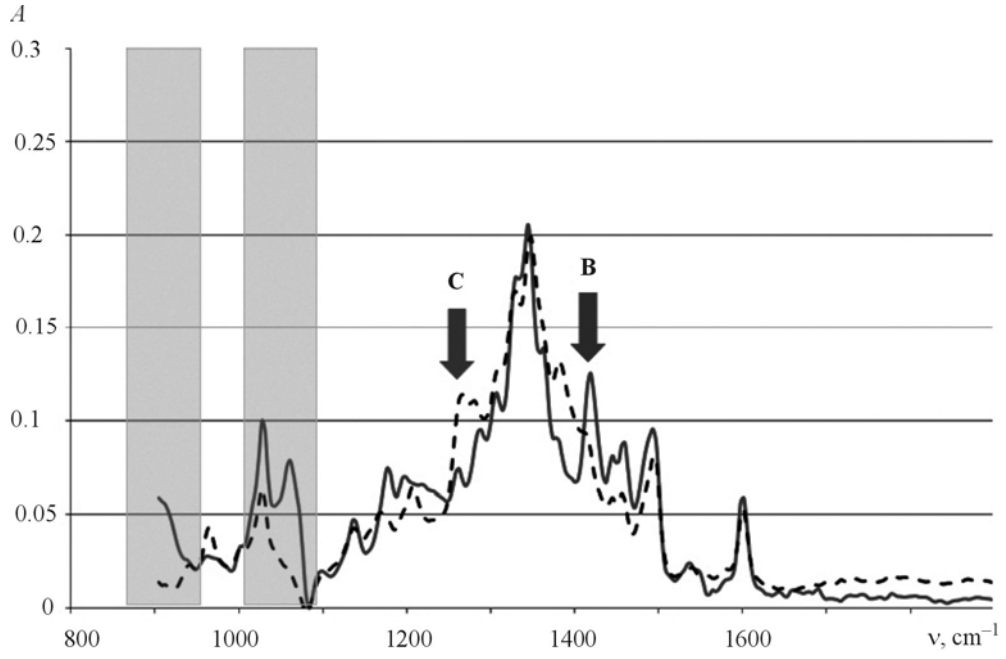
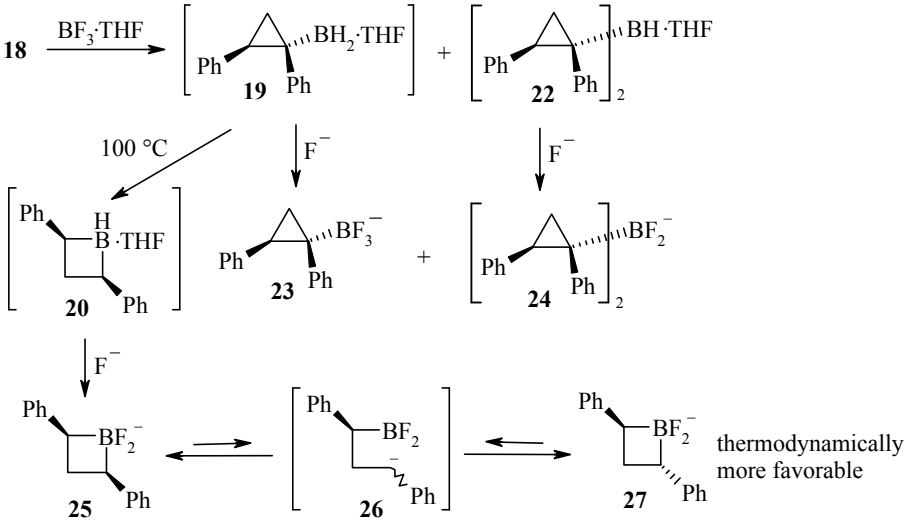


Fig. 2. ConcIRT spectra for components **B** (solid line) and **C** (dashed line), fingerprint region. Bands at 1470 and 1250 cm^{-1} are discussed in text. Regions highlighted are obscured by solvent (THF).

which is expected to have a similar to compound **25** splitting pattern in ^{19}F NMR spectrum. However, independently generated compound **22** (Fig. 3, spectrum B) was observed in higher field at -165 ppm, which allowed us to exclude the possible erroneous assignment.

Having obtained spectroscopic evidences for the formation of boretane species, we attempted to isolate complexes **25** and **27**, albeit as yet unsuccessfully. However, oxidative treatment of the reaction [Eq. (8)] afforded a mixture of 1,3-diphenylpropan-1-one (**29**), a product of base-catalyzed ring opening of cyclopropanol **28**, and *meso*-1,3-diphenylpropane-1,3-diol (**30**). The latter was evidently obtained upon oxidative cleavage of C–B bonds in boretane **20**, thus indirectly confirming formation of the four-membered ring under the reaction conditions. Oxidation with hydrogen peroxide–urea complex afforded *syn* diastereomer **30** as sole



product, while notable amounts of *anti* isomer were obtained when the reaction was carried out in the presence of NaOH. This result can be explained by the ability of strong base to induce epimerization of C_S-boretane **20** into C_2-epimer, analogous to the epimerization **25**→**27** discussed above (Scheme 1).

Since boretane **20** exists in dynamic equilibrium with diastereomeric dimers **31** and **32**, it could be argued that the latter may undergo the following expansion of the strained four-membered cycles to form the corresponding 1,5-diboracyclooctanes **33** and **34** (Scheme 2). An alternative mechanism that could be realized in the presence of excess BH_3·THF would involve hydroboration of the boretane cycle affording (3-boryl-1,3-diphenylpropyl)borane (**35**). Provided both ring expansions proceed stereospecifically, subsequent oxidation of the obtained products would also lead to the exclusive formation of *syn*-diol **30** (Scheme 2). Below we critically analyze both these hypotheses from the mechanistic standpoint with respect to the obtained experimental data.

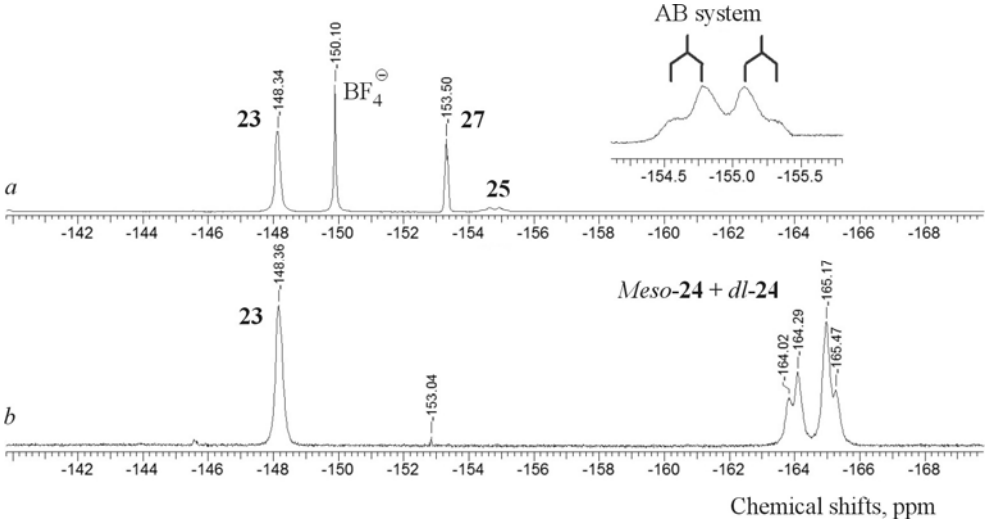
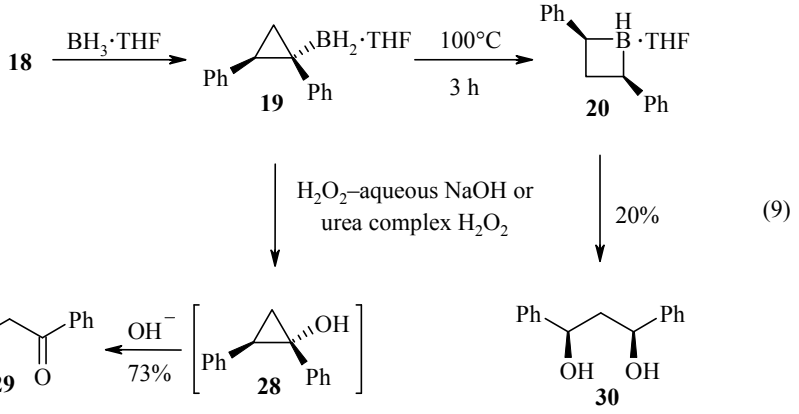
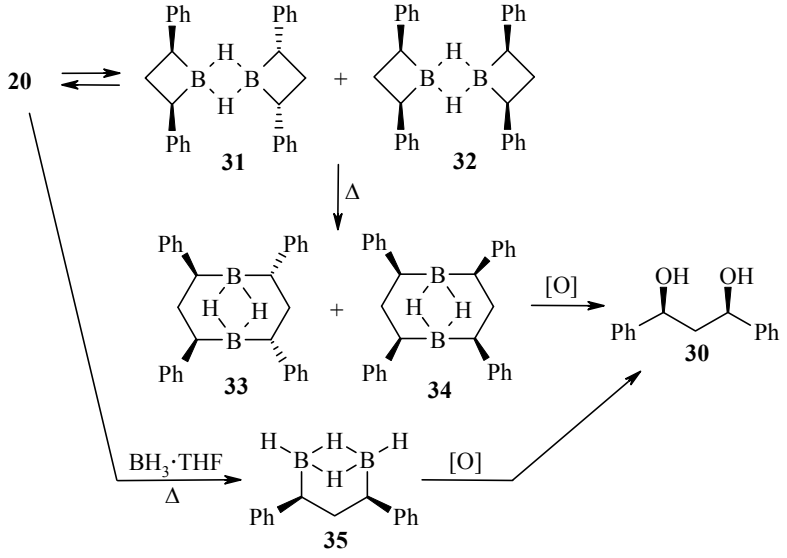


Fig. 3. ^{19}F NMR spectra of the reaction mixture quenched with KHF_2. (*a*) reaction mixture heated at 100°C for 3 h prior to quench; (*b*) mixture of compound **16** and BH_3·THF in a ratio of 2:1, quenched at room temperature.



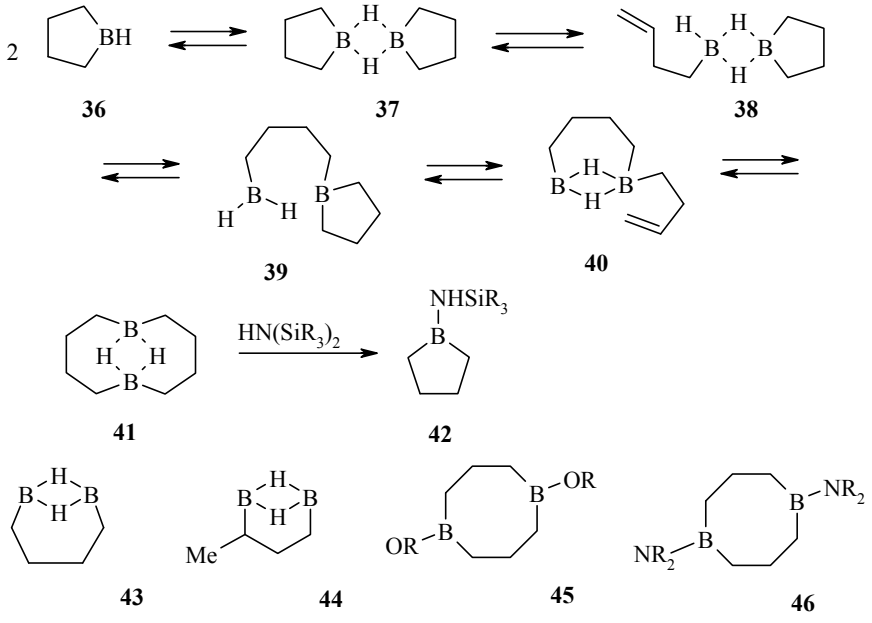
Discussion on Putative Routes for Boretane Ring Expansion. Potential reactivity of boretane can be assessed by analogy with the known higher homolog, borolane **36** (Scheme 3). The dimeric structure of bisborolane (**32**) was originally assigned by Köster to a compound obtained by reduction of *B*-chloroborolane with lithium aluminum hydride [26]. However, later Brown proposed for the same product an alternative 1,6-diboracyclodecane (**41**), which is stabilized by transannular hydride bridging [27, 28] (Scheme 3). The unstable structure of unsubstituted bisborolane **37** remained elusive for a long time before Brown finally

Scheme 2



Brown finally prepared it at low temperatures and intercepted it in reactions with MeOH and 1-octene [29]. However, at ambient temperatures bisborolane **37** was shown to rapidly convert into a thermodynamically more stable compound **41** and some polymeric products. Product **41** could also be obtained upon hydroboration of 1,3-butadiene with various hydroborating agents at elevated temperatures [30], while at lower temperatures this reaction provided tetramethylene diborane **43** as a major product along with small quantities of isomeric trimethylene diborane **44** (Scheme 3) [31]. The rearrangement of bisborolane **37** into diboracyle **41** was

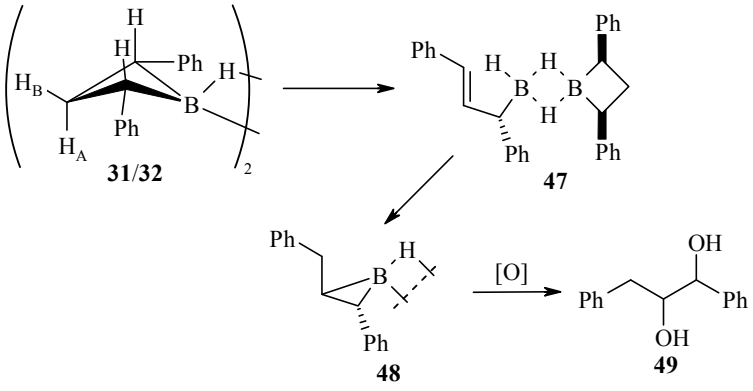
Scheme 3



referred to as "redistribution", and no detailed mechanism was provided [30]. However, the mechanism for thermal isomerization of organoboranes, proposed by Brown later and now commonly accepted [32-34], involves the following iterations of dehydroboration-hydroboration steps and presumes unavoidable formation of intermediate alkene species **38** and **40** (Scheme 3) [35-40].

Notably, the presence of the B–H bond in the borolane is crucial for successful rearrangement **36→41**. Thus, no ring expansion was observed with *B*-alkyl- [41-45], *B*-halo- [46-48], *B*-amino- [49, 50], and *B*-alkoxy-substituted [46, 51-53] borolanes. Furthermore, a reverse reaction takes place upon treatment of compound **41** with some amines to form *B*-aminoborolane derivatives **42** [54-55].

Scheme 4



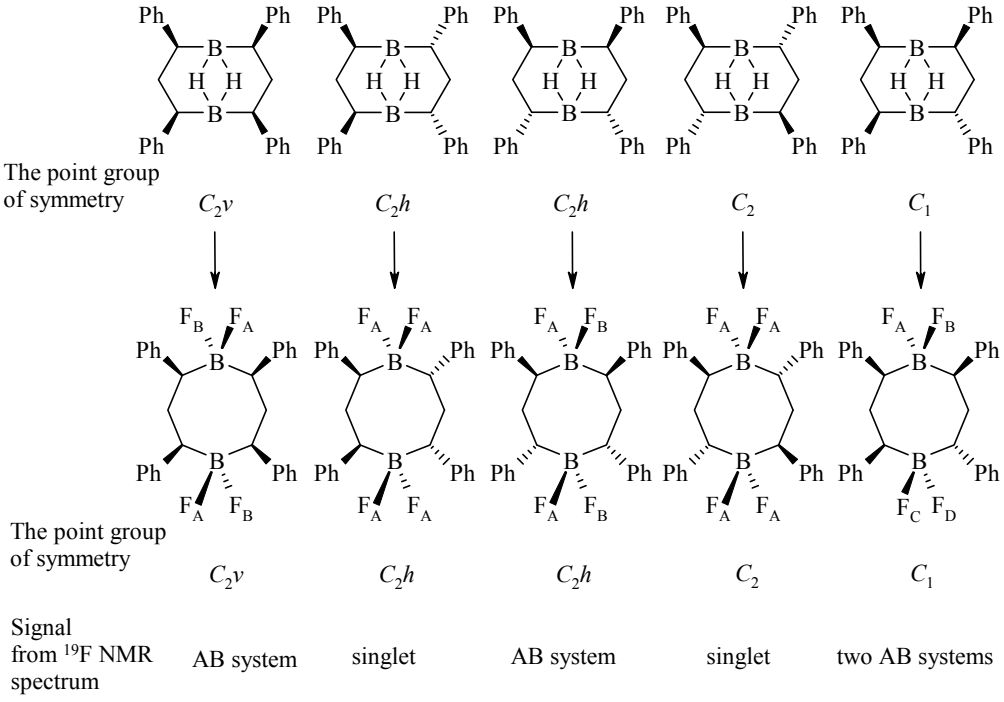
It should also be pointed out that the described transformation **36→41** is both thermodynamically and kinetically favored only in the case of 2,5-unsubstituted borolanes, since only in the absence of steric hindrance could species **41** be efficiently stabilized by transannular hydride bridging. In contrast, the presence of substitutions at the carbon atoms adjacent to boron impedes dehydroboration/re-hydroboration processes, making 2,5-disubstituted borolanes significantly more stable compounds, which do not undergo the described rearrangement into 1,6-diboracyclodecanes even at elevated temperatures [51-53].

Accordingly, the resistance of boretane species **20** toward ring expansion into 1,5-diboracyclooctanes (1,5-diborocanes) **33** or **34** can be rationalized as follows. Firstly, stabilization of 1,5-diborocane molecule by transannular hydride bridging is expected to be far less efficient due to the angular strain associated with this interaction. Indeed, while *B*-alkoxy [41-59] and *B*-amino [60, 61] derivatives of 1,5-diborocane **45** and **46**, in which no transannular bridging can be realized, are well known, the parent organoborane remains elusive. Secondly, two bulky substituents at the atoms C-2 and C-4 contribute into stabilization of compound **20** or the corresponding dimers **30** and **31**. Thirdly, dehydroboration of boretane molecule necessary for ring expansion seems problematic from the following standpoint. According to the principle of microscopic reversibility, the dehydroboration reaction should proceed *via* the same transition step as the hydroboration reaction, i.e., a tetracentered two-electron concerted transition state. This presumes that C(2)–B and C(3)–^{A}H (or C(3)–^{B}H) bonds should be aligned in the same plane in mandatory *syn* fashion (Scheme 4). However, such orientation can hardly be realized in a conformationally restricted four-membered ring, in which the indicated bonds are locked in a practically orthogonal arrangement (Scheme 4).

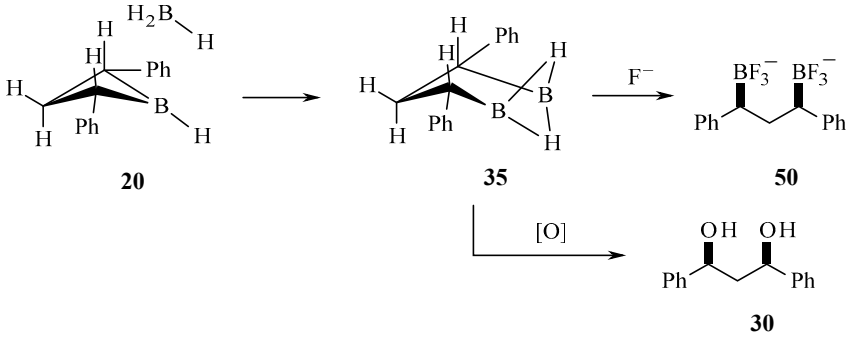
Furthermore, our experimental data do not agree with the hypothesis of 1,5-diborocane formation. Thus, in the unlikely event species **47** is obtained in thermal dehydroboration of boretane dimer **31** (or **32**), the issue of the alternative regioselectivity of the subsequent hydroboration of the newly formed double bond should be addressed. Although the Baldwin rules were originally formulated for nucleophilic cyclizations, the same geometric reasons should be generally acceptable for determining the selectivity of synchronous electrophilic attack as well; i.e., 3-*exo*-*trig* direction of the attack should be somewhat preferred over 4-*endo*-*trig* cyclization. Therefore, formation of certain amounts of borirane **48** [62-64] should be unavoidable, and the subsequent oxidation of this compound should afford 1,2-diol **49** (Scheme 4). The latter product, however, has never been detected in crude reaction mixtures. Moreover, non-stereoselective re-hydroboration of species **47** would produce a mixture of five diastereomeric 1,5-diborocanes with different relative arrangements of the phenyl substituents, which would subsequently give five different difluoroborate species after treatment with fluoride (Scheme 5). The corresponding ^{19}F NMR spectrum of this mixture would consist of two singlets (corresponding

to the molecules with C_2h and C_2 symmetries), two independent AB systems (corresponding to the molecules with C_2h and C_2v symmetries), and two sets of AB systems, belonging to the same C_1-symmetric species (Scheme 5). However, the experimentally obtained spectrum was significantly simpler, consisting of only one singlet and one AB system (Fig. 3, spectrum A), which rules out the hypothetic formation of 1,5-borocane-type dimeric structures, at least *via* the classical dehydroboration–hydroboration mechanism.

Scheme 5



Scheme 6



An alternative potential route for the boretane ring expansion should also be mentioned, which involves hydroboration of the initially formed strained boretane ring [53, 54] to give trimethylenediborane entities **42** (Scheme 6), analogous to the known species **44** described above (Scheme 3) this case, due to a significant puckering angle in boretane **20**, a substrate envelope conformation with two pseudo-equatorial phenyl substituents would be thermodynamically more stable, which would result in the borane addition from the convex face, leading to the formation of *cis*-diphenyltrimethylenediborane **35**. This transformation is expected

to proceed with retention of configuration at the reacting carbon atoms due to a synchronous *syn*-selective hydroboration mechanism (Scheme 6). After oxidation, trimethylenediborane **35** would selectively provide *syn*-diol **28**, which is consistent with experimental observations [Scheme 2, Eq. (9)]. This putative route, however, does not agree with the obtained spectroscopic data. Indeed, treatment of diborane **35** with fluoride should provide C_S-symmetric *syn*-bis(trifluoroborate) anion **50**, which should appear in ^{19}F NMR as a singlet. At most one more singlet could be observed in this spectrum, corresponding to the C_2-symmetric *anti* diastereomer. Formation of the latter species in this transformation, however, is highly unlikely. Nontheless, the AB system observed in our experiments (Fig. 3) clearly indicates the presence of diorganyl-substituted boron atom, and the symmetry analysis provided above allowed for elimination of all other possible topologies and geometries monocyclic besides structure of boretane **20**.

In conclusion, we investigated the possibility of cyclopropylborane ring expansion reaction, an isoelectronic heteroanalog of the known rearrangement of cyclopropylmethyl cation. It was demonstrated that this process can proceed for sterically hindered substrates at elevated temperatures affording previously unknown saturated four-membered boron-containing heterocycle (boretane), which was confirmed by spectral data (IR and NMR). Formation of boretane was also confirmed through transformation of this unstable compound into 1,3-diol.

EXPERIMENTAL

NMR spectra were recorded on a 400.13 MHz instrument, equipped with quadruple-band gradient probe (H/C/P/F QNP). ^{13}C and ^{19}F spectra were registered with broad-band decoupling. (+) and (-) Signs represent positive and negative intensities, respectively, of signals in ^{13}C DEPT-135 experiments. *In situ* FTIR spectra were recorded using Mettler Toledo ReactIR iC10 spectrometer with 6 mm silicon probe. Column chromatography was carried out employing silica gel (Selecto Scientific, 63-200 μm). Pre-coated silica gel plates (Merck Kieselgel 60 F-254) were used for thin-layer chromatography.

Glassware employed in moisture-free syntheses was additionally flash-dried in vacuum and cooled in a stream of dry nitrogen prior to use. Water was purified by dual-stage deionization, followed by dual-stage reverse osmosis. Commercially available anhydrous THF was additionally purified by passing consecutively through two columns with activated alumina. Anhydrous diisopropylamine was obtained by distillation of a commercially available material (ACS reagent grade) over calcium hydride and stored in Schlenk vessels under inert atmosphere. Anhydrous methanol and THF-d_8 were obtained by double distillation of commercially available materials (ACS reagent grade) over sodium metal. All other reagents and solvents used were purchased from commercial sources and used as received without additional purification.

1,2-Diphenylcyclopropene (**18**). A solution of $BH_3 \cdot Me_2NH$ complex (300 mg, 5.1 mmol) in MeOH (1.5 ml), followed by a solution of Me_3SiCl (630 μl, 5 mmol) in MeOH (1.5 ml) was added to a solution of 2,3-diphenylcycloprop-2-enone (500 mg, 2.4 mmol) in MeOH stirred at 0^{o}C . The mixture was stirred for 1 h at 0^{o}C and then concentrated in vacuum. The residue was dissolved in a hexane–THF (30:1) mixture, washed with ice-cold water, and evaporated. Flash column chromatography on silica gel (hexane–CH_2Cl_2 5:1 as eluent) afforded cyclopropene **16** as a colorless crystalline material, with properties identical to those previously published [67]. Yield 354 mg (1.8 mmol, 77%).

A. **Typical Procedure for Hydroboration of 1,2-Diphenylcyclopropene (18) with $BH_3 \cdot$THF Complex without Rearrangement (General Method).** An oven-dried 3 ml Wheaton V-vial equipped with a magnetic spin vane and a screw cup with a PTFE faced silicon septum was charged with 1,2-diphenyl-cyclopropene **18** (124 mg, 0.65 mmol). A solution of $BH_3 \cdot$THF complex in THF (1 M, 2.0 equiv., 1.3 ml) was added at room temperature. The mixture was stirred for 20 min and then quenched according to Procedures C or D.

B. **Typical Procedure for Hydroboration of 1,2-Diphenylcyclopropene (18) with BH_3·THF Complex and Rearrangement (General Method).** An oven-dried 3 ml Wheaton V-vial equipped with a magnetic spin vane and Mininert valve was charged with 1,2-diphenylcyclopropene **18** (124 mg, 0.65 mmol). A solution of BH_3·THF complex in THF (1 M, 2 equiv., 1.3 ml) was added at room temperature. The mixture was heated at 100°C for 3 h, then cooled down and quenched according to Procedures C or D.

C. **Typical Procedure for Oxidative Quench with NaOH/H_2O_2 Mixture (General Method)**.The reaction mixture was poured into a mixture of 3 N aqueous NaOH (1.5 ml), and a 30% aqueous H_2O_2 solution (1.5 ml) was added, followed by methanol (1.5 ml). The mixture was stirred for 2 h at room temperature and then extracted with EtOAc (2×10 ml). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by preparative column chromatography on silica gel, eluent hexane–EtOAc 2:1.

D. **Typical Procedure for Oxidative Quench with Urea–H_2O_2 Complex (General Method)**. Urea–H_2O_2 complex (3.5-4 equiv.) was added by portions to a reaction mixture at 0°C. The resulting mixture was stirred overnight and then worked up as described in procedure C.

Combination of procedure A with oxidative quench C afforded 1,3-diphenylpropan-1-one (**29**) as a sole product in 90% yield. ^{1}H NMR ($CDCl_3$), δ 7.98, ppm (*J,* Hz): (2H, d, *J* = 7.3, *ortho*-CH); 7.57 (1H, t, *J* = 7.7, *para*-CH); 7.47 (2H, t, *J* = 7.8, *meta*-CH); 7.34-7.21 (5H, m, arom.); 3.32 (2H, t, *J* = 7.7, PhC$\underline{H}_2$); 3.09 (2H, t, *J* = 7.7, COC$\underline{H}_2$). ^{13}C NMR ($CDCl_3$), δ, ppm: 199.7; 141.7; 137.2; 133.5 (+); 129.05 (+, 2C); 128.97 (+, 2C); 128.9 (+, 2C); 128.5 (+, 2C); 126.6 (+); 40.9 (-); 30.5 (-).

Combination of procedure B and oxidative quench C afforded 1,3-diphenylpropan-1-one **29** (73%) with a mixture of *meso*- and *dl*-1,3-diphenylpropane-1,3-diols **30** in a ratio of 5:1 to 2:1 (20%).

Combination of procedure A and oxidative quench D produced 1,2-diphenylcyclopropanol **26** as a sole product in 55% yield (compound notably decomposes on column and upon storage). ^{1}H NMR (acetone-d_6), δ, ppm (*J*, Hz): 7.25 (2H, d, *J* = 7.8, *ortho*-CH); 7.12 (2H, t, *J* = 7.2, *meta*-CH); 7.07-7.04 (3H, m, *para*- and *meta*-CH); 6.98 (1H, t, *J* = 7.1, *para*-CH); 6.94 (2H, d, *J* = 7.6, *ortho*-CH); 2.69 (1H, dd, *J* = 10.0, *J* = 7.3, C$\underline{H}$–OH); 1.76 (1H, dd, *J* = 7.3, *J* = 6.1, cyclopropane); 1.56 (1H, dd, *J* = 10.0, *J* = 6.1, cyclopropane). ^{13}C NMR (acetone-d_6), δ, ppm: 141.2; 139.2; 129.0 (+, 2C); 128.8 (+, 2C); 128.3 (+, 2C); 128.2 (+, 2C); 127.2 (+); 126.1 (+); 62.9; 33.7 (+); 19.5 (-).

Combination of procedure B and oxidative quench D afforded a mixture of cyclopropanol **28** (50%) and *meso*-1,3-diphenylpropane-1,3-diol **30** (16%), identical to the independently prepared sample (see procedure E).

E**. Independent Synthesis of *meso*-1,3-Diphenylpropane-1,3-diol** (**30**) [68, 69]. A solution of *n*-BuLi in hexane (2.5 M, 4.8 ml, 12.0 mmol) was added dropwise to a stirred at -78°C solution of dry *i*-Pr_2NH (1.72 ml, 12.2 mmol) in anhydrous THF (20 ml). The resulting mixture was stirred for 10 min, and a solution of acetophenone (1.22 g, 10 mmol) in THF (5 ml) was added dropwise. The mixture was stirred for 10 min at -78°C. Neat benzaldehyde (1.28 ml, 12 mmol) was added, and stirring was continued for 30 min at -78°C. The cold reaction mixture was poured into a separatory funnel with EtOAc and saturated aqueous NH_4Cl. The organic layer was separated; the aqueous layer was extracted with EtOAc. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Preparative column chromatography on silica gel (hexane–EtOAc 5:1 as eluent) afforded 3-hydroxy-1,3-diphenylpropan-1-one as a yellowish oil. Yield 1.96 g (8.7 mmol, 87%). A solution of $TiCl_4$ in CH_2Cl_2 (1 M, 2.8 ml, 2.8 mmol) was added to a solution of the obtained aldol (530 mg, 2.34 mmol) stirred at -78°C in anhydrous CH_2Cl_2 (5 ml) . The mixture was stirred at -78°C for 10 min. BH_3-Py complex (0.7 ml, 7 mmol) was added dropwise, and stirring was continued for 2 h. The cold mixture was quenched by addition of aqueous HCl (1 M) and extracted with CH_2Cl_2. The combined organic phases were washed with brine and concentrated. The residue was dissolved in MeOH–Et_2O (1:1) and treated with aqueous NaOH (3 N) and 30% H_2O_2 overnight. The resulting mixture was extracted with EtOAc, washed with brine, dried with $MgSO_4$, and concentrated. Preparative column chromatography on silica gel (hexane–EtOAc 3:2 as eluent) afforded *meso*-1,3-diphenylpropane-1,3-diol **28** as a white solid. Yield 0.34 g

(1.5 mmol, 64%). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 7.39-7.31 (8H, m, arom.); 7.28-7.26 (2H, m, arom.); 4.98 (2H, dd, *J* = 10.1, *J* = 2.8, PhC<u>H</u>OH); 3.71 (2H, br. s, OH); 2.17 (1H, dt, *J* = 14.6, *J* = 10.1, CH_2); 1.95 (1H, dt, *J* = 14.6, *J* = 2.8, CH_2). ^{13}C NMR (100.65 MHz, $CDCl_3$), δ, ppm: 144.1 (2C); 128.4 (+, 4C); 127.6 (+, 2C); 125.7 (+, 4C); 74.9 (+, 2C); 47.6 (-).

PREPARATION OF FLUOROBORATES FOR ^{19}F NMR STUDIES

F**. Procedure for Generation of Fluoroborates 25 and 27.** The reaction mixture obtained according to procedure B was treated with anhydrous MeOH (4 equiv.) and the solvents were removed in vacuum. A solution of KHF_2 in MeOH–water (30:1) was added to the dry residue, and the mixture was stirred for 30 min. The solvents were evaporated, and the residue was dissolved in dry THF-d_8. ^{19}F NMR spectrum showed four major components: *cis*-(1,2-diphenylcyclopropyl)trifluoroborate **27**: ^{19}F NMR (THF-d_8) δ -148.3 (3F, s); tetrafluoroborate (KBF_4) resulting from excess BH_3-THF: ^{19}F NMR (THF-d_8), δ, ppm: -150.1 (4F, s) (used as chemical shift secondary internal standard); C_2-symmetric difluoroborate **27**: ^{19}F NMR (THF-d_8), δ, ppm: -153.5 (2F, s); C_S-symmetric difluoroborate **25**: ^{19}F NMR (THF-d_8), δ, ppm (*J*, Hz): -154.6 (1F, d, $^2J_{FF}$ = 76); -155.2 (1F, d, $^2J_{FF}$ = 76).

Procedure for Generation of Difluoroborate 24. A solution of BH_3·THF complex in THF (1 M, 0.50 equiv., 125 μl) was added at room temperature to a solution of 1,2-diphenylcyclo-propene **18** (48 mg, 0.25 mmol) in THF (500 μl). The mixture was stirred for 2 h, and then quenched with MeOH (40 μl). The solvents were removed in vacuum, and a solution of KHF_2 in MeOH–water (30:1) was added to the dry residue. The mixture was stirred for 30 min; then the solvent was evaporated and the residue dissolved in dry THF-d_8. ^{19}F NMR spectrum showed three major components: *cis*-(1,2-diphenylcyclopropyl)trifluoroborate **23**: ^{19}F NMR (THF-d_8), δ, ppm: -148.3 (3F, s); C_2-symmetric difluoroborate *dl*-**24**: ^{19}F NMR (THF-d_8), δ, ppm: -165.2 (2F, s); C_S-symmetric difluoroborate *meso*-**24**: ^{19}F NMR (THF-d_8), δ, ppm (*J*, Hz): -164.2 (1F, d, $^2J_{FF}$ = 101); -65.3 (1F, d, $^2J_{FF}$ = 101).

ReactIR STUDIES AND IR SPECTRA INTERPRETATION

Procedure for ReactIR Monitored Reactions. The pressure tube (102 mm L×13 mm OD) with a Teflon stopcock side arm and magnetic bar was equipped with a 6 mm Silicon ReactIR probe using #7 Ace-Thread polypropylene adaptor. BH_3·THF solution (1 M in THF, 0.5 ml) was added *via* syringe using a bore of the stopcock opened for a short time, and the spectra acquisition sequence was initiated (256 scans per spectrum, one spectrum every 2 min). After 10 min a solution of cyclopropene **18** (48 mg, 0.25 mmol) in anhydrous THF (0.5 ml) was added (Fig. 1, event *1*), and acquisition was continued for 16 min. Then the reaction tube was placed in a pre-heated to 100°C oil bath (Fig. 1, event *2*)) and the reaction was monitored for another 1.5 h. Acquired spectra were processed using ConcIRT (Concentration in Real Time) [25] algorithm. Three components were identified (A, B, and C, Fig. 1). A linear kinetic plot $\ln(C_{compB})$/Time revealed first-order kinetics in the rearrangement of B (Fig. 4). An analogous experiment performed in the presence of BH_3·SMe_2 complex showed rapid formation of cyclopropylborane **21**, which remained unchanged when heated for 1 h at 100°C.

Theoretical modeling was performed using Gaussian 03 software [70]. Geometries of both cyclopropylborane **19** and boretane **20** were optimized and the corresponding vibrational spectra were DFT-modeled (B3LYP/6-31G). The spectra were simulated for the gaseous phase (Fig. 5) without taking into account temperature and solvation effects and possible conformational changes. Nevertheless, both experimental ConcIRT (Fig. 2) and simulated spectra (Fig. 5) contain a set of characteristic bands in the fingerprint area, based on which the structure of cyclopropyl borane **17** was assigned to component B (Fig. 5, group of bands B)

and the structure of boretane **18** to component **C** (Fig. 5, group of bands C), respectively. Analysis of computed vibration modes revealed that band B corresponds to C–H scissor vibrations of the cyclopropyl ring in structure **19** (Fig. 5), while band C can be interpreted as a combination of symmetric and nonsymmetric rocking vibrations of the boretane ring (Fig. 7).

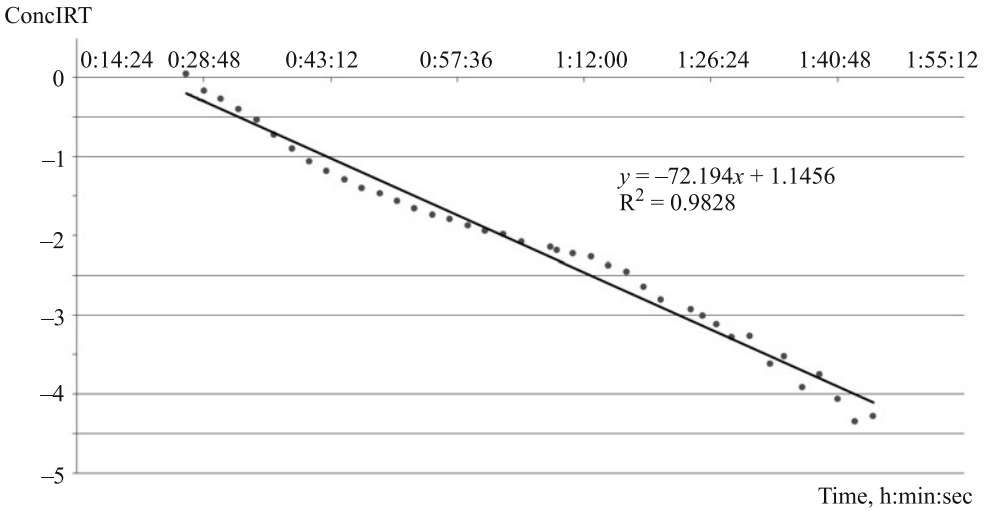


Fig. 4. Kinetic plot of the rearrangement of cyclopropylborane **18** (component B) at 100°C, obtained from ConcIRT spectra of the reaction mixture.

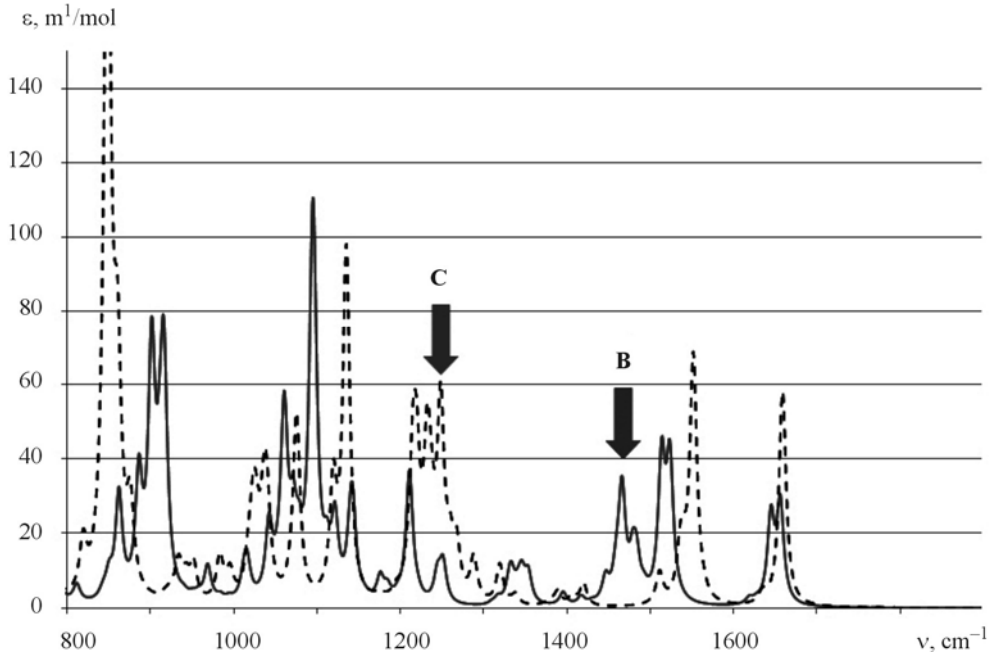


Fig. 5. Theoretical IR spectra of compounds **19** (dashed) and **20** (solid line): fingerprint region calculated for gas phase. Specific absorption bands discussed in text are marked with arrows.

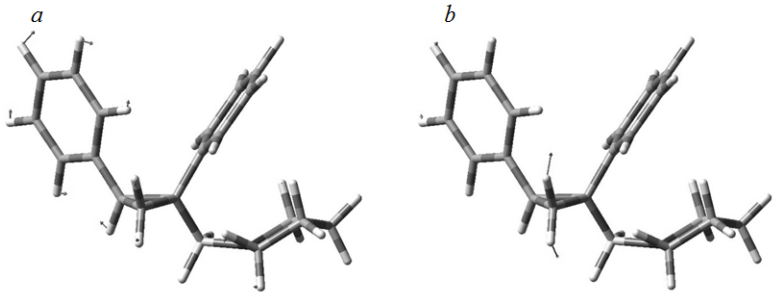


Fig. 6. Displacement vectors and vibrational frequencies corresponding to the absorptions at 1479 cm^{-1} (left) and 1447 cm^{-1} (right) in theoretically modelled IR spectrum of compound **19**. These frequencies belong to the group of absorption bands marked with letter **B** in Fig 5.

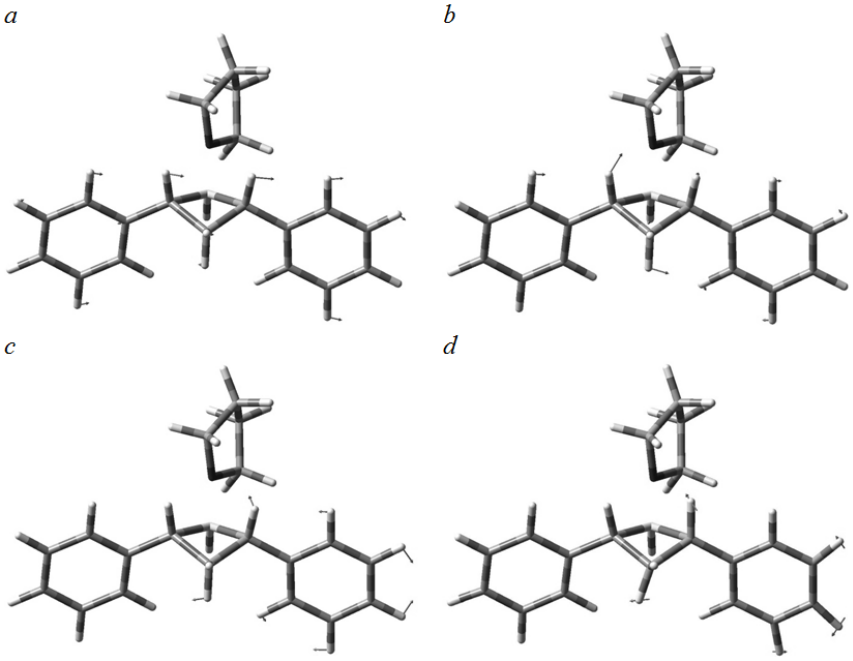


Fig. 7. Displacement vectors and vibrational frequencies corresponding to the absorptions at 1249 (top left), 1233 (top right), 1220 (bottom left), and 1216 cm^{-1} (bottom right) in theoretically modelled IR spectrum of compound **20**. These frequencies belong to the group of absorption bands marked with letter **C** in Fig. 5.

This work was supported by the University of Kansas (KU) and the Center for Environmentally Beneficial Catalysis (CEBC).

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