SYNTHESIS OF FUNCTIONAL DERIVATIVES OF 2-METHYLENE-CYCLOPENTANE AND 2-METHYLENECYCLOHEXANE BASED ON THE ALLYLBORYLATION OF IMINES, NITRILES, ISOCYANATES, AND ISOTHIOCYANATES BY CYCLOALKENYLMETHYL(DIPROPYL)BORANES

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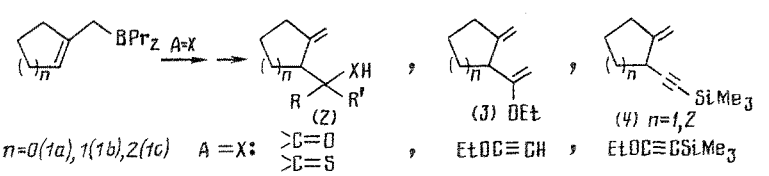
A study has been made of the allylborylation of imines, nitriles, isocyanates, and isothiocyanates by the action of cycloalkenylmethyl(dipropyl)boranes. Preparative methods have been developed for obtaining amines, phenylamides, and phenylthioamides of the 2-methylenecyclopentane and 2-methylenecyclohexane series.

Keywords: *allylborylation of imines, nitriles, isocyanates, and isothiocyanates; synthesis of derivatives of 2-methylenecyclohexane and 2-methylenecyclopentane; cyclohexenylmethyl(dipropyl)borane, cyclopentenylmethyl-(dipropyl)borane.*

Various methylenecyclanes are widely used in organic synthesis, for example, in revealing the relationships governing the addition of various reagents to a double bond, or as starting substances in the construction of natural compounds and their analogs (prostaglandins, antibiotics, terpenes, etc.). One of the most effective and simplest methods of obtaining derivatives of methylenecyclanes is the addition of cycloalkenylboranes of the allyl type **1a-c** [1] — which are derivatives of cyclobutene (**1a**, n = 0), cyclopentene (**1b**, n = 1), and cyclohexene (**1c**, n = 2) — to carbonyl compounds [2-4], thioketones [5], ethoxyacetylene [2-4], or trimethylsilylethoxyacetylene [6].

All such allylborylation reactions proceed entirely with an allyl rearrangement (of the type $2\pi + 2\pi + 2\sigma$) [1] and lead to boron adducts with an exocyclic double bond; the deborylation of these compounds yields unsaturated alcohols (**2**, X = O) [1-4], thiols (**2**, X = S) [5], dienes (**3**) [1-4], or enynes (**4**) [6]:



Substances commonly used as deborylating reagents are alcohols, triethanolamine, and hydrogen peroxide; both operations (allylborylation and deborylation) are carried out in the same flask. As a rule, these reactions are not complicated by side processes. Only in the case of boranes of the cyclobutene type (**1a**, n = 0), owing to structural features and the permanent allyl rearrangement [1], formation of the exomethylene compounds is sometimes accompanied by the formation of cyclobutene derivatives [1, 2]. Derivatives of cyclopentene (**1b**, n = 1) and cyclohexene (**1c**, n = 2) react regiospecifically, giving only the exomethylene products [3-6].

Continuing our studies along this line, we have investigated the reaction of the allylbornaes **1b, c** with imines, nitriles, phenyl isocyanate, and phenyl isothiocyanate. This work was aimed at expanding the sphere of application of the boranes **1b,**

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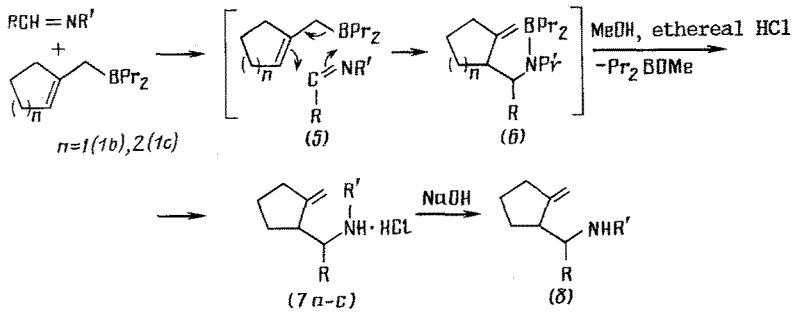
c in organic synthesis and at using these materials to obtain new types of compounds of the cyclopentane and cyclohexane series with an exocyclic double bond.

Reaction with Imines

The allylborylation of imines (Schiff bases) with various compounds has been described in a number of reports: with triallylborane [7]; isoprenyl(dipropyl)borane [8]; allyl(dimethoxy)borane [9]; 9-allyl-, 9-methallyl-, and 9-crotyl-9-borabicyclo[3.3.1]nonane [10]; and 9-(3,3-trimethyleneallyl)-, 9-(3,3-tetramethyleneallyl)-, and 9(3,3-pentamethyleneallyl)-9-borabicyclo[3.3.1]nonane [8, 11]. In all cases, butenylamines were obtained.

We have found that reactions of the boranes **1b, c** with imines proceed at ~20°C in an ether or hydrocarbon medium, leading to unsaturated borylated amines of the type of **6**.



n=2, R=Ph, R'=Me (**7a**); 2, Ph, n-C_6H_{13} (**7b**); 1, Ph, Me (**7c**); 2, Ph, Me (**8**).

As should be expected, addition at the C=N bond goes forward with rearrangement — through the transition state **5**. The aminoboranes **6** that were formed were treated successively with methanol and an ether solution of HCl. This gave 50-90% yields of the crystalline hydrochlorides of the 1-[α-(alkylamino)benzyl]-2-methlenecycloalkanes **7a-c**, the structure of which was confirmed by spectroscopic methods (IR, PMR) and elemental analysis. The IR spectra of all of the hydrochlorides exhibited absorption bands in the intervals 890-915, 1650-1655, and 3075-3090 cm^{-1}, characteristic for the exomethylene bond ($C=CH_2$), and broad bands of the ammonium group in the 2400-2830 cm^{-1} region.

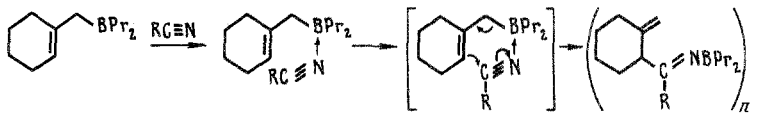
The salts readily yield the free bases upon treatment with a 10% NaOH solution. Thus, from **7a**, the amine **8** is recovered in the form of a yellow oil with a yield of 76.6%. According to the PMR data, the amine **8** is a mixture of two isomers in an 85:15 ratio. If we assume that the addition of the borane **1c** proceeds with a chairlike transition state with an axial position of the substituents of the imine fragment, then the main product of the reaction is the *threo* isomer, the minor product the *erythro* isomer. However, additional studies will be needed to establish their structures exactly (these studies are currently being pursued).

Reaction with Nitriles

The allylborylation of nitriles by triallylborane proceeds in stages [12, 13]. Initially, the crystal complex $All_3B \leftarrow N{\equiv}CR$ is formed; this is followed by intramolecular allylborylation with the formation of iminoboranes, which are dimerized to cyclodiborazanes.

Analogous reactions of allyl(dialkyl)boranes with acetonitrile, acrylonitrile, benzonitrile, α-cyanothiophene, and α-cyanofuran, depending on the nature of the radicals in the $RC{\equiv}N$ and in the organoborane, lead to monomeric or dimeric iminoboranes [14]. Both forms are readily identified on the basis of their IR spectra (C=N band for the monomer at 1790-1810 cm^{-1}, for the dimer at 1670-1690 cm^{-1}) and on the basis of their ^{11}B NMR spectra (signal at 35-40 ppm relative to $BF_3 \cdot OEt_2$ for the monomers and at 3-10 ppm for the dimers.

We have established that the reactions of the borane **1c** with acetonitrile and benzonitrile lead to final products that differ in structure, even though the reactions proceed identically in the first stages.

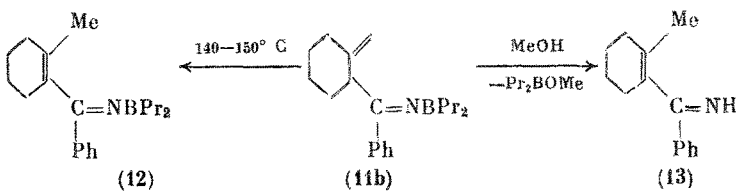


(1c) (9) (10) (11a,b)

R=CH_3, n=2 (**11a**); C_6H_5, 1 (**11b**).

At −70°C (in hexane or pentane), a solid complex is formed; at temperatures above −40°C, this is converted to a monomeric or dimeric iminoborane (**11a, b**). The final product of the reaction of **1c** with acetonitrile is the crystalline dimer **11a**, which is stable when exposed to oxygen and atmospheric moisture and remains unchanged upon boiling in MeOH. In the IR spectrum of this compound there are intense bands in the 1670 cm^{-1} region (C=N); in the ^{11}B NMR spectrum, one signal is observed, at 5.28 ppm.

In contrast, the reaction of **1c** with benzonitrile leads to the monomeric iminoborane **11b** (in the IR spectrum there is an intense band of C=N at 1810 cm^{-1}); this compound is readily hydrolyzed and oxidized in air. It is a colorless oily liquid that can be vacuum-distilled without decomposition. However, under the conditions of distillation (140-143°C, 1 mm Hg), the borane **11b** is isomerized to the thermodynamically more stable compound **12** with an intracyclic double bond. In the IR spectrum of the distilled product **12** there are no bands for the exomethylene bond (896, 1650, 3088 cm^{-1}), and a weak band is observed at 1670 cm^{-1} (intracyclic C=C bond).

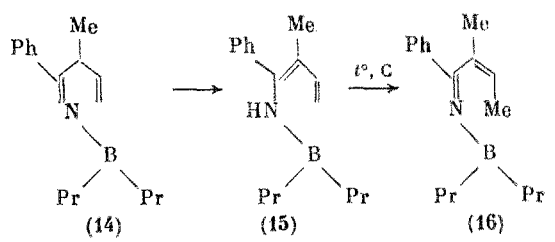


(12) (11b) (13)

Upon treatment of the iminoborane **11b** with methanol under various conditions (1-h refluxing, or at −20°C), the B−N bond is cleaved, and the imine **13** is formed as the main product.

Conversion of the iminoborane **11b** to **12** upon heating, and also formation of the cyclohexene compound **13** by deborylation through the action of MeOH, have been confirmed by spectroscopic data.

This sort of isomerization of iminoboranes under the influence of traces of moisture, alcohols, or amines has been studied in detail in [15]. Thus, the iminoborane **14**, obtained from crotyl(dipropyl)borane and benzonitrile, is isomerized in the presence of traces of alcohol or water to give the dienamine form **15**,

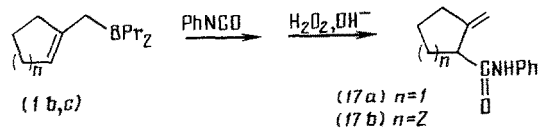


(14) (15) (16)

and upon distillation is converted to the iminoborane **16** with a system of conjugated bonds.

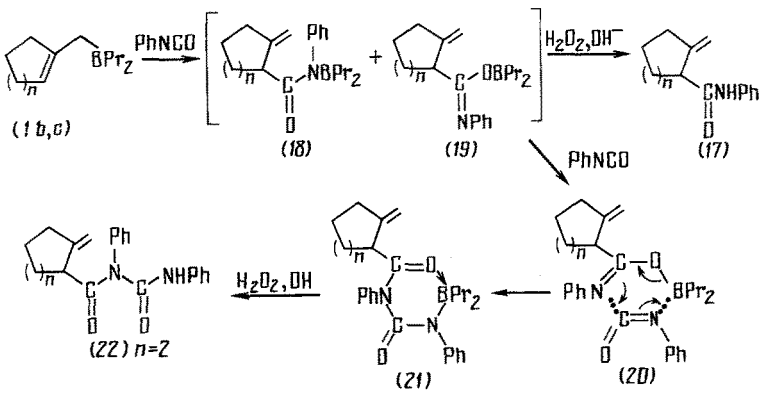
Reactions with Phenyl Isocyanate and Phenyl Isothiocyanate. Synthesis of Phenylamides of 2-Methylenecyclopentane- and 2-Methylenecyclohexanecarboxylic Acids

The allylborylation of PhNCO and PhNCS had not been studied previously. We have established that the reactions of the boranes **1b** and **1c** with phenyl isocyanate in a 2:1 ratio (−60°C in pentane) leads (after oxidative deborylation) to phenylamides of (respectively) 2-methylenecyclopentane- or 2-methylenecyclohexanecarboxylic acid (**17a, b**) with 50 and 75% yields.



The amides **7a, b** are colorless crystalline substances; their structures have been confirmed by elemental analyses and spectroscopic data (IR and PMR; see Experimental section).

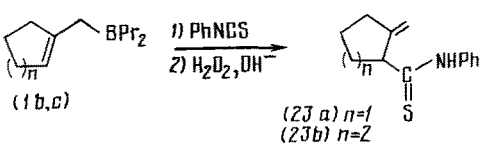
This means that the addition of **1b, c** to PhNCO is also accomplished with an allyl rearrangement. For now, it is difficult to identify the bond in the isocyanate molecule (C=N or C=O) at which the borallyl fragment is added, or to say which of the two tautomeric products is formed as a result of the reaction (**18** or **19**). It is more likely that the compound **19** is obtained, since the B–O bond (120-130 kcal/mole) is far stronger than the B–N bond (106 kcal/mole) [16]. It is not at all impossible that an equilibrium exists in the solution (**18** ⇄ **19**). At the same time, all of this is not really important in the present case, since both adducts **18** and **19**, when exposed to hydrogen peroxide in an alkaline medium (deborylation) give exactly the same anilide **17**.



The analogous reaction of **1c** with phenyl isocyanate in a 1:1 ratio (in pentane, 0 → 20°C) leads (after oxidative deborylation) to a mixture of the phenylamide **17b** and a substituted acylurea (**22**, n = 2) in a 1:1 ratio. By column chromatography on SiO_2, both of the compounds were isolated in the individual state with a yield of ~25%. One of the possible paths to the formation of the acylurea is shown in the above reaction scheme. The initially formed carbimidoyloxyborane **19** adds to a second molecule of PhNCO, giving an inner-complex boron adduct **21**, which upon desorption gives the urea **22**.

The structure of **22** has been confirmed by IR and PMR spectroscopic data. Thus, in the PMR spectrum in $CHCl_3$ there are the following signals: 11.6 br.s (NH); 6.95-8.15 m (10H, $2C_6H_5$); 4.82 m and 4.65 m (2H, CH_2=C); 2.85 m (1H, CH–CO); 0.95-2.45 m (8H, protons of cyclohexane ring).

Analogously from **1b, c** the phenyl isothiocyanate, we obtained the phenylthioamides (**23a, b**) in the form of yellow crystals with respective yields of 48.8% and 58.9%.



Thus, in the course of these studies we have been successful in expanding quite considerably the field of application of the boranes **1b** and **1c** in organic synthesis. Their reactions with imines, nitriles, isocyanates, and isothiocyanates, which proceed entirely with an allyl type rearrangement, can be used successfully in obtaining various nitrogen-containing derivatives of cyclopentane and cyclohexane with an exocyclic double bond.

EXPERIMENTAL

All operations with the organoboron compounds were performed in a dry argon atmosphere.

The PMR spectra were taken in Bruker WM-250, Bruker AC-200 P, and Tesla BS-467 spectrometers; the chemical shifts were referred to TMS. The ^{11}B spectra were taken in a Bruker SXP/4-100 spectrometer; the chemical shifts were referred to $BF_3 \cdot OEt_2$. The IR spectra were taken in a UR-20 instrument.

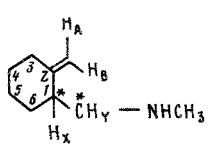
The benzalmethylamine and benzal-*n*-hexylamine were synthesized by procedures given in [17].

1-[α-(Methylamino)benzyl]-2-methylenecyclohexane Hydrochloride (7a). A three-necked flask equipped with a magnetic stirrer, thermometer, dropping funnel, and reflux condenser was charged with 1.54 g (8 mmoles) of the borane **1c** in 5 ml of ether. At 20°C, 0.9 g (7.6 mmoles) of benzalmethylamine was added slowly (dropwise) while the reaction mixture warmed up to 30°C. Then the ether was driven off, and 0.45 ml of absolute MeOH, 15 ml of ether, and 2.5 ml of an ether solution of HCl were added to the reaction mixture. The resulting precipitate was transferred to a filter funnel and washed with acetone and ether, then vacuum-dried. Obtained 1.54 g (81%) of the hydrochloride of **7a**, mp 257°C (decomp). Found, %: C 71.29; H 8.98; Cl 14.33; N 5.94. $C_{15}H_{22}ClN$. Calculated, %: C 71.55; H 8.81; Cl 14.08; N 5.56. IR spectrum ($CHCl_3$, ν, cm^{-1}): 915, 1655, 3075 ($C=CH_2$); 2400-2830 (NH_2^+). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 10.0 br.s (1H, HCl) and 8.45 br.s (1H, $\rangle N-H$, $-\overset{\oplus}{N}H_2\cdots\overset{\ominus}{Cl}$); 7.6 m (2H, H-*ortho* from C_6C_5); 7.4 m (3H, H-*meta* and H-*para* from C_6H_5); 5.35 m and 5.07 m (2H, $C=CH_2$); 4.20 d (1H, $\rangle CH-N$, J = 11.3); 3.13 m (1H, cyclohexane ring); 2.43 s (3H, $\rangle N-CH_3$); 1.2-2.4 w.m (8H, cyclohexane ring).

1-[α-(n-Hexylamino)benzyl]-2-methylenecyclohexane Hydrochloride (7b). Analogously, to the aminoborane obtained from 1.2 g (6.2 mmoles) of the borane **1c** and 1.0 g (5.3 mmoles) of benzalhexaylamine, there was added 1 ml of CH_3OH, 10 ml of ether, and 3 ml of 2.45 *N* ether solution of HCl. Obtained 0.85 g (50%) of **7b**, mp 167-168°C. Found, %: C 74.47; H 9.89; Cl 10.87; N 4.50. $C_{20}H_{32}ClN$. Calculated, %: C 74.62; H 10.02; Cl 11.01; N 4.35. IR spectrum (CCl_4, ν, cm^{-1}): 895, 1649, 3091 ($C=CH_2$); 2500-2800 w (NH_2^+). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 9.97 br.s (1H, HCl); 9.37 br.s (1H, $\rangle NH$); 7.55 m (2H, H-*ortho* from C_6H_5); 7.35 m (3H, H-*meta* and H-*para* from C_6H_5); 4.42 m and 4.30 m (2H, $C=CH_2$); 4.33 d (1H, $\rangle CH-N$); 3.27 m (1H, cyclohexane ring); 2.80 t (2H, $\rangle N-CH_2$, J = 7.5); 2.60 m (1H, cyclohexane ring); 1.80 w.m (8H, cyclohexane ring and β-CH_2 from C_6H_{13}); 1.40 m (1H, cyclohexane ring); 1.10 m (6H, $-(CH_2)_3-Me$); 0.87 t (3H, $-CH_3$, J = 7.0).

1-[α-(Methylamino)benzyl]-2-methylenecyclopentane Hydrochloride (7c). The aminoborane obtained from 1.12 g (6.3 mmoles) of the borane **1b** in 5 ml of pentane in 0.75 g (6.3 mmoles) of benzalmethylamine was treated with 0.5 ml of MeOH, 10 ml of ether, and 1.8 ml of a 3.88 *N* solution of HCl in ether. The resulting precipitate was filtered off, washed with acetone and ether, and dried. Obtained 1.35 g (90%) of the hydrochloride of **7c**, mp 206°C (decomp.). Found, %: C 70.49; H 8.54; Cl 14.90; N 5.90. $C_{14}H_{20}ClN$. Calculated, %: C 70.72; H 8.48; Cl 14.91; N 5.89. IR spectrum ($CHCl_3$, ν, cm^{-1}): 890, 1652, 3075 ($C=CH_2$); 2440-2800 (NH_2^+). PMR spectrum ($CDCl_3$, δ, ppm); 9.95 br.s (1H, HCl); 9.45 br.s (1H, $\rangle N-H$); 7.6 m (2H, H-*ortho* from C_6H_5); 7.4 m (3H, H-*meta* and H-*para* from C_6H_5); 4.84 m and 4.20 m (2H, $C=CH_2$); 3.87 d (1H, $\rangle CH-N$); 3.32 m (1H, cyclopentane ring); 2.48 s (3H, $\rangle NCH_3$); 1.4-2.4 w.m (6H, cyclohexane ring).

1-[α-(Methylamino)benzyl]-2-methylenecyclohexane (8). To a suspension of 1.3 g (5.1 mmoles) of the hydrochloride of **7a** in 10 ml of ether, 2 ml of a 15% solution of NaOH was added. After dissolving the original insoluble material, the ether layer was removed, the ether was driven off, and the residue (1.0 g of a yellow oil) was distilled. Obtained 0.84 g (84%) of the amine **8**, bp 106-107°C (1 mm Hg), n_D^{20} 1.5387. Found, %: C 83.32; H 9.66. $C_{15}H_{21}N$. Calculated, %: C 83.67; H 9.83. IR spectrum (no solvent, ν, cm^{-1}): 892, 1645, 3085 ($C=CH_2$); 3350 (NH). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): In the spectrum, signals from two stereoisomers were observed, with a mole ratio approximately 85:15. For the major isomer: 7.30 m (5H, C_6H_5); 4.88 m (2H, $C=CH_2$); 3.58 d (1H, H_Y, J_{XY} = 10.5); 2.38 d.t (1H, H_X, J_{YX} = 10.5); $J_{6a,X} = J_{6e,X}$ = 4.6); 2.20 s (3H, $\rangle N-CH_3$); 2.20 m (2H, 3-CH_2); 1.1-1.9 w.m (6H, 4,5,6-CH_2).



For the minor isomer: 4.62 m (1H, H_A); 4.43 m (1H, H_B); 3.83 d (1H, H_Y, J_{YX} = 6.3); 2.23 s (3H, $\diagdown N-CH_3$). The spectrum of the other protons overlaps the spectrum of the major isomer. The assignment of isomers was based on the SSCC J_{XY} = 10.5 (apparently, the *threo* isomer), J_{XY} = 6.3 (the *erythro* isomer).

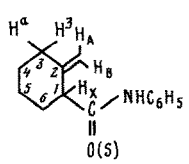
Dimer of [Methyl(2-methylenecyclohexyl)ketimino]di(*n*-propyl)borane (11a). A three-necked flask equipped with a magnetic stirrer, dropping funnel, thermometer, and stopcock for the introduction of argon was charged with 1.6 g (8.1 mmoles) of the borane **1c** in 5 ml of hexane. At −70°C, 0.38 g (9.2 mmoles) of a solution of acetonitrile in 2 ml of hexane was added, and the reaction mixture was gradually warmed to ~20°C. The white crystalline precipitate was filtered off, washed with hexane, and dried. Obtained 0.89 g (48%) of the iminoborane **11a**, mp 142-143°C. Found, %: C 77.00; H 12.01; B 4.53. $C_{15}H_{28}BN$. Calculated, %: C 77.25; H 12.10; B 4.64. IR spectrum (CCl_4, ν, cm^{-1}): 1670 (C=N); 898, 1650, 3086 (C=CH_2). PMR spectrum ($CDCl_3$, δ, ppm): 4.76 m and 4.38 m (2H, C=CH_2); 3.17 m (1H, cyclohexane ring); 2.37 m (1H, cyclohexane ring); 1.95 s (3H, $CH_3-\underset{|}{C}=N-$); 0.7-2.10 w.m (21H, cyclohexane ring and $2C_3H_7$).

[(2-Methylenecyclohexyl)phenylketimino]di(*n*-propyl)borane (11b) and [(2-Methylcyclohexen-1-yl)phenylketimino]-di(*n*-propyl)borane (12). Analogously, from 1.56 g (8.2 mmoles) of the borane **1c** in 5 ml of pentane and 0.84 g (8.2 mmoles) of benzonitrile, obtained, after removing the solvent, crude **11b** in the form of a yellow oil. IR spectrum (no solvent, ν, cm^{-1}): 1810 (C=N); 895, 1650, 3089 (C=CH_2). After distillation, obtained 1.57 g (65.7%) of the iminoborane **12**, bp 140-143°C (1 mm Hg). Found, %: C 81.11; H 10.01; B 3.30. $C_{20}H_{30}BN$. Calculated, %: C 81.35; H 10.24; B 3.66. IR spectrum (CCl_4, ν, cm^{-1}): 1803 (C=N); 1670 (C=C). PMR spectrum (CCl_4,, δ, ppm): 7.70 m (5H, C_6H_5); 2.40 m (4H, α-CH_2 propyl groups); 1.83 s (3H, CH_3-); 0.8-2.2 w.m (18H, 3,4,5,6-CH_2 cyclohexane ring and $2C_2H_5$).

(2-Methylcyclohexen-1-yl)phenylimine (13). To the iminoborane **11b** obtained from 1.47 g (7.7 mmoles) of the borane **1c** and 0.78 g (7.7 mmoles) of benzonitrile, 10 ml of absolute MeOH was added at −20°C, and the mixture was allowed to stand for 12 h. The excess MeOH and the methyl ester of di(*n*-propyl)boric acid were removed under vacuum, and the residue was distilled. Obtained 0.87 g (58%) of the imine **13**, bp 113-115°C (1 mm Hg), $n_D^{22.5}$ 1.5652. Found, %: C 84.38; H 8.68; N 7.03. $C_{14}H_{17}N$. Calculated, %: C 84.37; H 8.60; N 7.03. IR spectrum (CCl_4, ν, cm^{-1}): 1670 (C=C); 1600, 1580 (C=N, C_6H_5); 3265 (NH). PMR spectrum ($CDCl_3$, δ, ppm): 8.85 br.s (1H, NH); 7.75 m (2H, H-*ortho* from C_6H_5); 7.40 m (3H, H-*meta* and H-*para* from C_6H_5); 2.10 m and 1.70 m (8H, cyclohexane ring); 1.57 s (3H, $-CH_3$).

N-Phenyl-2-methylenecyclopentanamide (17a). To a solution of 1.6 g (9 mmoles) of the borane **1b** in 15 ml of pentane, chilled to −60°C, 0.53 ml (4.5 mmoles) of phenyl isocyanate was added dropwise. The reaction mixture was gradually warmed to 20°C, the pentane was driven off, and 15 ml of ether and 3.6 ml of a 10% NaOH solution were added. At 0-5°C, 4 ml of 30% H_2O_2 was added slowly in drops. The resulting precipitate was filtered off. The ether layer was removed, and the aqueous layer was extracted with ether (4 × 8 ml). The ether was removed from the ether solution, and the 0.55 g of the crystalline substance that remained in the residue was purified in a column with SiO_2 (eluent 1:1 ether−hexane). Obtained 0.45 g (50%) of the amide **17a**, mp 109-110°C. Found, %: C 77.69; H 7.55; N 6.66. $C_{13}H_{15}NO$. Calculated, %: C 77.58; H 7.51; N 6.93. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1682 (C=O), 903, 3075 (the 1650 band is masked by the intense absorption band of C=O) (C=CH_2); 3396, 3440 (NH). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 7.8 br.s (1H, NH); 7.54 d (2H, H-*ortho*, $J_{m,o}$ = 7.5); 7.32 d.d (2H, H-*meta*, $J_{o,m} = J_{p,m}$ = 7.5); 7.11 t (1H, H-*para*, $J_{m,p}$ = 7.5); 5.23 and 5.18 m (2H, C=CH_2); 3.38 m (1H, cyclopentane ring); 1.6-2.6 w.m (6H, cyclopentane ring).

N-Phenyl-2-methylenecyclohexanamide (17b). Analogously, from 2.57 g (13.4 mmoles) of the borane **1c** and 0.79 g (6.7 mmoles) of PhNCO, we obtained a boron adduct that was then treated with 4 ml of 15% NaOH solution and 5 ml of 30% H_2O_2 in ether solution. A crystalline substance (1 g) was recovered and then purified within a column with SiO_2 (eluent 1:1 ether−hexane). Obtained 0.82 g (57%) of the amide **17b**, mp 102-104°C. Found, %: C 78.14; H 8.09; N 6.85. $C_{14}H_{17}NO$. Calculated, %: C 78.10; H 7.97; N 6.50. IR spectrum ($CHCl_3$, ν, cm^{-1}): 905, 1650, 3080 (C=CH_2); 1690 (C=O); 3405, 3440 w (NH). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 7.65 br.s (1H, NH); 7.53 d (2H, H-*ortho*, $J_{m,o}$ = 7.5); 7.30 d.d (2H, H-*meta*, $J_{o,m} = J_{p,m}$ = 7.5); 7.08 t (1H, H-*para*, $J_{m,p}$ = 7.5); 5.05 and 4.95 m (2H, H_A and H_B, C=CH_2); 3.22 m (1H, H_X); 2.5-2.1 w.m (3H, 3-CH_2 and 6H^e); 1.8-1.3 w.m (5H, 4,5-CH_2, and 6-H^a).



N-Phenyl-2-methylenecyclopentanethioamide (23a). To a solution of 1.93 g (10.8 mmoles) of the borane **1b** in 15 ml of pentane, chilled to −40°C, 1.09 g (8.1 mmoles) of PhNCS in 2 ml of pentane was added. The mixture was stirred for 0.5 h at −30°C and then gradually warmed to 20°C. The pentane was driven off, and 15 ml of ether and 2.9 ml of a 15% NaOH solution were added. Next, at 0°C, 4.2 ml of 30% H_2O_2 was added slowly by drops and then stirred for 1 h at 20°C. The ether layer was separated, and the aqueous layer was extracted with ether (3 × 10 ml). From the combined ether solution, the ether was driven off, and the residue of 1.57 g of crude **23a** was purified in a column with SiO_2 (eluent $CHCl_3$, repeated with 2:1 pentane−ether). Obtained 0.86 g (48.8%) of **23a** in the form of yellow crystals, mp 70-71°C. Found, %: C 71.59; H 7.14; N 6.34; S 14.56. $C_{13}H_{15}NS$. Calculated, %: C 71.85; H 6.96; N 6.45; S 14.74. IR spectrum (CH_2Cl_2, ν, cm^{-1}): 890, 1648, 3080 (C=CH_2), 3315, 3377 (NH). PMR spectrum ($CDCl_3$, δ, ppm): 9.20 br.s (1H, NH); 7.75 d (2H, H-*ortho* from C_6H_5); 7.40 t (2H, H-*meta* from C_6H_5); 7.20 t (1H, H-*para* from C_6H_5); 5.36 q (1H, H_A, $J_{AB} = J_{AX} = J_{Aa} = 2.2$); 5.17 q (1H, H_B, $J_{BA} = J_{BX} = J_{Be} = 2.2$); 3.90 br.t (1H, H_X, $J_{1,5} = 8.0$); 3.0-1.5 w.m (6H, 3,4,5-CH_2).

N-Phenyl-2-methylenecyclohexanethioamide (23b). Analogously, from 2.28 g (11.8 mmoles) of the borane **1c** and 1.08 g (8 mmoles) of PhNCS in pentane solution, obtained a boron adduct that was then treated with 3.1 ml of a 15% NaOH solution and (at 0°C) with 4.6 ml of 30% H_2O_2. Recovered 1.8 g of crude **23b**, which was purified in a column with SiO_2 (eluent $CHCl_3$ and 2:1 hexane−ether). Obtained 1.09 g (58.9%) of the amide **23b**, mp 107-108°C. Found, %: C 72.59; H 7.29; N 5.92; S 13.69. $C_{14}H_{17}NS$. Calculated, %: C 72.68; H 7.41; N 6.05; S 13.86. IR spectrum (CH_2Cl_2, ν, cm^{-1}): 915, 1648, 3090 (C=CH_2); 3325, 3379 (NH). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 9.05 br.s (1H, NH); 7.70 d (2H, H-*ortho*, C_6H_5); 7.40 t (2H, H-*meta*, C_6H_5); 7.25 t (1H, H-*para*, C_6H_5); 5.13 q (1H, H_A, $J_{AB} = J_{AX} = J_{Aa} = 2.10$); 4.98 q (1H, H_B, $J_{BA} = J_{BX} = J_{Be} = 2.10$); 3.43 br.t (1H, H_X, $J_{1,6} = 7.8$); 2.65 m (1H, 3-H^e); 2.25 m (2H; 3-H^a and 6-H^e); 2.0-1.5 w.m (5H, 6-H^a and 4,5-CH_2).

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