Journal of Organometallic Chemistry 694 (2009) 2106–2109

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

First allylboration of organic compounds with the N=N double bond. Synthesis of *N*-allylpyrazolidines and allyl-1,2-diphenylhydrazine

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ARTICLE INFO

Article history:
Received 18 September 2008
Received in revised form 9 February 2009
Accepted 13 February 2009
Available online 26 February 2009

Keywords:
Triallylborane
Allylboration
Azocompounds
Pyrazolines
N-Allylpyrazolidine
1-Allyl-1,2-diphenylhydrazine

ABSTRACT

Triallylborane adds to the N=N double bond of pyrazolines **1** and **2** at 0 °C giving after deboronation the corresponding *N*-allylpyrazolidines **4** and **5**. Further transformations of allylpyrazolidine **4** including the cyclopropane ring opening were studied. Allylboration of azobenzene with triallylborane gives rise to 1-allyl-1,2-diphenylhydrazine.

1. Introduction

The ability of β,γ-unsaturated (allylic) organoboron derivatives to add to organic compounds containing C=O, C=S, C=N, C=C, C≡C and N=O fragments is a unique property of this class of organoboranes [1]. These addition reactions proceed with allylic rearrangement via six-membered cyclic transition state ($2\pi + 2\pi + 2\sigma$ type) and present a novel and facile carbon–carbon/carbon–heteroatom bond formation pathway. These reactions proceed as easily as polarisation or strain of double bond increase [2]. Allylboration of carbonyl compounds, imines and acetylenes is widely explored in organic synthesis as a key step in synthesis of nature products and their analogues [3].

In this paper we describe the first allylboration of pyrazoline derivatives **1** or **2** and azobenzene, the compounds containing both cis and trans N=N double bonds. Further transformations of allylic pyrazolidine derivative **4** are also presented.

2. Results and discussion

2.1. Reaction of pyrazolines *1* and *2* with triallylborane

Addition of triallylborane to pyrazoline **1** synthesized by the interaction of *in situ* generated diazocyclopropane with 3,3-dimethylcyclopropene [4] was carried out at −5 to 0 °C in THF under dry argon. The reaction was completed in 0.5 h to furnish the product **3**, that was observed by ^{11}B NMR spectroscopy of reaction mixture, with only the Alk_2B–N fragment signal (broad singlet at 42.7 ppm) observed [5]. Subsequent deboration with MeOH (cleavage of B–N-bond) gave rise to allylpyrazolidine **4** in 76% yield (Scheme 1).

^{1}H NMR spectra of compound **4** shows signals at δ 5.99 ppm (1H), 5.11–5.17 (2H), and 3.22–3.39 (2H) which are characteristic for the allyl group, broad signal of NH-group at 3.83 ppm, two doublets at δ 2.90 and 1.69 ppm corresponding to H(1) and H(5), respectively, and signals of two methyl groups and 4 protons of spiro-fused cyclopropane ring at high field. A location of allyl group in the pyrazolidine **4** was assumed on the basis of 2D NOESY spectra where interaction of methylene protons of the allyl group at 3.22 ppm with one of the protons of spiro-fused cyclopropane ring at 0.74 ppm was observed. This data and an absence of NOE cross-peaks in pyrazolidine **4** between doublet signal corresponding to H(1) and any signals of $CH_2CH{=}CH_2$ fragment confirms that allyl group is attached to N atom adjacent to spirocyclopropane ring.

Pyrazolidine **4** is readily oxidized by air giving a mixture of unidentified products that is typical for pyrazolidines with unsubstituted NH-fragment [6].

Allylboration of pyrazoline **2** available by the cycloaddition of diazocyclopropane to styrene [7] was performed in THF at 0 °C. After the treatment with methanol, pyrazolidine **5** was isolated in 45% yield as colorless oil (Scheme 2). This compound is also

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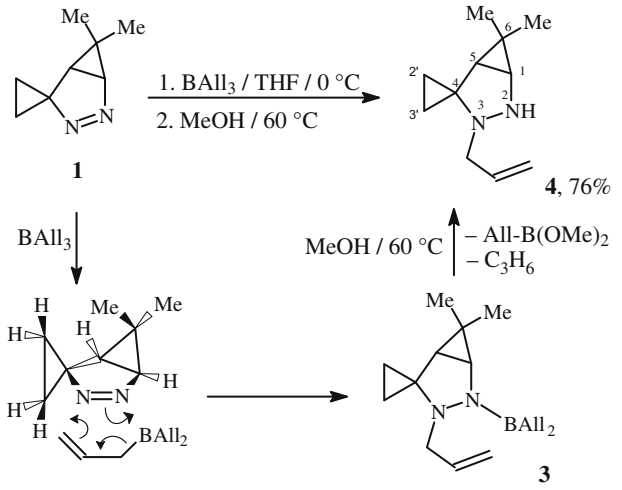
doi:10.1016/j.jorganchem.2009.02.012



Scheme 1. Reaction of pyrazoline **1** with triallylborane.

easily oxidized in air. Storing a solution of pyrazolidine **5** in $CDCl_3$ (0 °C, 6 days) results in the formation of allylpyrazoline **6** which was isolated in 35% yield by TLC on silica gel (Scheme 2). A small amount of colorless precipitate was also formed, but it was not identified.

The main differences in ^{1}H NMR spectra of compounds **5** and **6** are in the observed chemical shifts of the protons for heterocyclic fragments. Thus in pyrazolidine **5** the three-spin system of H(6) and two H(7) protons is observed as three doublet of doublets at δ 4.64, 2.56 and 2.00 ppm, while in pyrazoline **6** two protons at C(7) give the singlet at δ 3.16 ppm. In ^{13}C NMR spectra signals of C(6) atoms of pyrazolidine **5** and pyrazoline **6** show at 62.9 and 148.4 ppm, respectively.

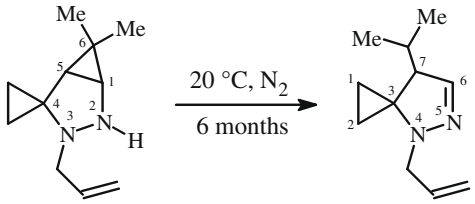
A location of allyl group in the pyrazolidine **5** was also assumed on the basis of 2D NOESY spectra where interaction of methylene protons of the allyl groups at 3.33 ppm with one of the protons of spiro-fused cyclopropyl ring at 0.98 ppm was observed. NOE cross-peak was also observed in pyrazoline **6** between signal of allyl CH_2 group at 3.48 ppm and multiplet of cyclopropyl protons at 1.08 ppm.

Excellent regioselectivity of the triallylborane addition to pyrazolines **1** and **2** requires some comments. The most interesting is the addition of All–B fragment to N=N bond of the compound **1**, which is substituted with cyclopropane rings of different nature – one ring is spiro-fused, while another is presented as a part of bicyclic system.

Regioselectivity of this reaction can be explained by the ability of the electron density of spiro-fused cyclopropane ring, that is perpendicular to the plane of pyrazoline ring to interact with N=N double bond increasing electron density on nitrogen atom remote from spiro-fused cyclopropane ring (i.e. on the N(2) atom in the compound **1** or N(5) atom in the compound **2**). This remote nitrogen forms an initial complex with the boron atom of triallylborane molecule. It should be noted that other electrophiles also attack pyrazoline **1** and other pyrazolines with spiro-fused cyclopropane ring at N atom remote from the ring [8]. In addition this nitrogen atom is less sterically hindered, which may also play an auxiliary role.

2.2. Spontaneous isomerisation of allylpyrazolidine **4**

Compound **4** was believed to be stable in the absence of oxygen, however after 6 months the compound appeared to have decomposed, as proton signals associated with this compound were not observed in solution. The main product was identified as substituted 4,5-diazaspiro[2.4]hept-5-ene **7**, that formed in a ~70% yield by a cleavage of C–C bond of condensed cyclopropane ring following by hydrogen shift:



Interestingly, in this case the cleavage of the C(1)–C(6) bond of bicyclic system, but not the bridge the C(1)–C(5) bond takes place.

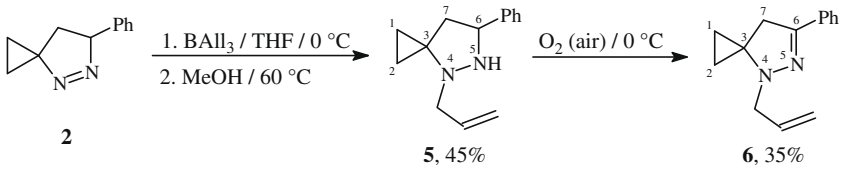
2.3. Isomerization of allylpyrazolidine **4** under the action of $Hg(OCOCF_3)_2$

The structure of pyrazolidine **4** having several chemically active centers provides an interesting possibilities for its further transformations involving, for example, the opening of one or both cyclopropane fragments. In this connection, a mercuration of pyrazolidine **4** was studied to compare a reactivity of double bound of the allyl group and cyclopropane rings [9]. Moreover, in the case of anti-Markovnikov addition of $Hg(OCOCF_3)_2$ to double bond as it was previously observed for some other systems [10] it could hope to prepare a tricyclic molecule by a following interaction of NH-fragment with organo-mercury intermediate formed.

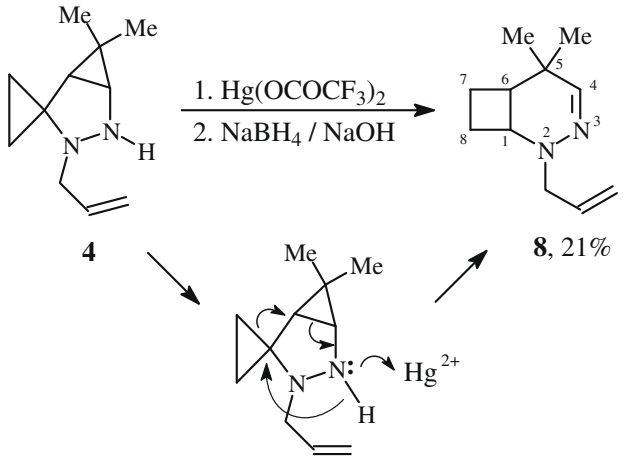
Reaction of pyrazolidine **4** with $Hg(OCOCF_3)_2$ was performed under argon in dry acetonitrile at 0 °C for 2 h followed by treatment with basic $NaBH_4$ solution and organic compounds were extracted with Et_2O. Spectral data of the reaction mixture show that at least four products were formed in this reaction, but we were able to isolate by column chromatography on silica gel and fully identify only one of them, namely tetrahydropyridazine derivative **8** (21%, Scheme 3). According to ^{1}H NMR spectra of **8**, allyl group was not involved in the reaction, while signals of both cyclopropane rings disappeared.

The initial step of isomerisation of strained pyrazolidine **4** to tetrahydropyridazine **8** is, probably, formation of complex of $Hg(OCOCF_3)_2$ with less substituted nitrogen atom of pyrazolidine followed by bonds reorganization and hydrogen migration (Scheme 3).

^{1}H NMR spectra of compound **8** shows narrow doublet ($J_{4,6}$ = 2.0 Hz) at 6.81 ppm relating to CH=N fragment and five



Scheme 2. Allylboration of pyrazoline **2**.

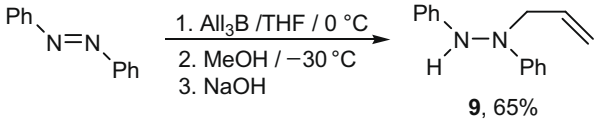


Scheme 3. Isomerization of allylpyrazolidine **4** under the action of $Hg(OCOCF_3)_2$.

well-resolved signals of allyl group. Deshielding influence of nitrogen atom leads to down-field shift of the multiplet of H(1) at 3.52 ppm. Other multipletes of cyclobutane system occupy a region from 1.50 to 2.28 ppm. Using a C_6D_6 instead of $CDCl_3$ as a solvent for NMR spectroscopy provides to avoid overlapping of multipletes of cyclobutane protons and effectively employ 2D NMR experiments – NOESY, COSY and {C,H}-correlation – for analysis of spectral data. Structure of compound **8** is also confirmed by ^{13}C NMR spectra in which 10 signals are observed.

2.4. Reaction of triallylborane with azobenzene

Contrary to pyrazolines **1** and **2**, azobenzene exists predominantly in *trans*-configuration. Its reaction with triallylborane proceeds at 0 °C. Further deboronation with aqueous NaOH and distillation in vacuo gives rise to 1-allyl-1,2-diphenylhydrazine (**9**) [11] in 65% yield.



3. Conclusion

Triallylborane allyborates the N=N double bond of pyrazolines and azobenzene under mild conditions (−5 to 0 °C) to give after deboronation *N*-allylpyrazolidines and allylhydrazine, respectively. Rearrangement of allylpyrazolidine **4** into tetrahydropyridazine derivative **8** in the presence of $Hg(OCOCF_3)_2$ proceeding via cleavage of both cyclopropane rings was observed. Compounds **4** and **5** are transformed spontaneously or under the action of O_2 to 4,5-diazaspiro[2.4]hept-5-enes (**7**) and (**6**), respectively.

4. Experimental

4.1. Materials and instrumentation

All reactions were carried out under argon atmosphere. All the reagents used were chemically pure and are of analytical reagent grade. Triallylborane [3a] and pyrazolines **1** [4] and **2** [7] were prepared as described previously. All solvents used in the reactions were dried and freshly distilled. The ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer (^1H – 300.13 MHz), ^{11}B and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer (^{11}B – 64.21 MHz, ^{13}C – 50.32 MHz). The proton chemical shifts were referenced to Me_4Si, which was added to solvent as the internal standard. Carbon resonances were referenced to $CDCl_3$ (δ = 77.1 ppm) and the ^{11}B NMR spectra to $Et_2O \cdot BF_3$ (δ = 0 ppm). 2D NMR spectra were obtained on a Bruker DRX-500 instrument. The mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet probe). Elemental analyses were done with a Perkin–Elmer 2400 series II CHN analyzer. For chromatography, silica gel 60 (0.040–0.063 mm; Merck) was used.

4.2. Synthesis of 3-allyl-6,6-dimethylspiro{2,3-diazabicyclo[3.1.0]hexan-4,1′-cyclopropane} (*4*)

Triallylborane (1.02 g, 7.6 mmol) was added dropwise at −5 to 0 °C over a period of 30 min to a stirred solution of 6,6-dimethylspiro{2,3-diazabicyclo[3.1.0]hex-2-en-4,1′-cyclopropane} (**1**) (1.04 g, 7.6 mmol) in 5 mL of THF. Then reaction mixture was allowed to warm up to room temperature and aliquote for ^{11}B NMR spectra was taken. The only signal of ^{11}B at 42.7 ppm was observed indicating the formation of the compound **3** with B–N-bond [5]. Then 2 mL of MeOH was added at 0 °C and a mixture was refluxed for 1 h. Pyrazolidine **4** was isolated as colorless oil (1.030 g, 76% yield), b.p. 33–34 °C/0.01 Torr.

Elemental Anal. Calc. for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 73.81; H, 10.07; N, 15.63%. The partial mass spectrum, *m*/*z* (I_{rel} (%)): 177 $[M-H]^+$ (46), 163 $[M-NH]^+$ (27), 41 $[C_3H_5]$ (100). ^1H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 0.55 (d.d.d, ^2J = 4.3, ^3J = 6.7, ^3J = 10.0, 1H, H(3')), 0.74 (d.d.d, ^2J = 5.7, ^3J = 6.7, ^3J = 10.7, 1H, H(2')), 0.84 (d.d.d, ^2J = 5.7, ^3J = 6.6, ^3J = 10.0, 1H, H(7)), 0.94 (m, 4H, H(8) + CH_3), 1.31 (s, 3H, CH_3), 1.69 (d, ^3J = 7.3, 1H, H(5)), 2.90 (d, ^3J = 7.3, 1H, H(1)), 3.22 (d.d.t, $^4J \approx 1.5$, ^3J = 5.7, ^2J = 13.7, 1H, one of NCH_2), 3.39 (d.d.t, $^4J \approx 1.5$, ^3J = 6.9, ^2J = 13.7, 1H, one of NCH_2), 3.83 (br.s, 1H, NH), 5.11 (br.d, ^3J = 10.2, 1H, one of $=CH_2$), 5.17 (br.d, ^3J = 17.2, 1H, one of $=CH_2$), 5.99 (d.d.d.d, ^3J = 5.7, ^3J = 6.9, ^3J = 10.2, ^3J = 17.2, 1H, =CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 8.10 (C(2')), 14.50 (CH_3), 14.63 (C(3')), 25.17 (CH_3), 31.12 (C(6)), 39.39 (C(5)), 49.62 (C(4)), 51.50 (C(1)), 59.16 (NCH_2), 116.27 ($=CH_2$), 136.82 (=CH).

4.3. Synthesis of 4-allyl-6-phenyl-4,5-diazaspiroheptane (*5*)

N-Allylpyrazolidine **5** was synthesized and isolated in the same manner as described above for compound **4** starting from pyrazoline **2** (0.41 g, 2.4 mmol) and triallylborane (0.32 g, 2.4 mmol). For initial adduct with B–N-bond a broad singlet at 43.3 ppm was observed in ^{11}B NMR spectra. Pyrazolidine **5** was obtained by distillation as colorless oil (0.23 g, 45% yield), b.p. 61–63 °C/0.01 Torr.

^1H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 0.64 (m, 1H, H(1)), 0.77 (m, 1H, H(2)), 0.98 (m, 2H, H(1) + H(2)), 2.00 (d.d, ^3J = 6.2, ^2J = 12.7, 1H, H(7)), 2.56 (d.d, ^3J = 9.4, ^2J = 12.7, 1H, H(7)), 3.29 (d.d.t, $^4J \approx 1.5$, ^3J = 6.1, ^2J = 13.8, 1H, one of NCH_2), 3.33 (d.d.t, $^4J \approx 1.4$, ^3J = 6.3, ^2J = 13.8, 1H, one of NCH_2), 4.12 (br.s, 1H, NH), 4.64 (d.d, ^3J = 6.2, ^3J = 9.4, 1H, H(6)), 5.11 (br.d, ^3J = 10.2, 1H, one of $=CH_2$), 5.19 (d.q, $^2J \approx {}^4J \approx 1.7$, ^3J = 17.2, 1H, one of $=CH_2$), 5.99 (d.d.t, ^3J = 6.2, ^3J = 10.2, ^3J = 17.2, 1H, =CH), 7.27 (m, 3H, Ph), 7.41 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): 10.28 (C(2)), 13.96 (C(1)), 41.57 (C(7)), 50.76 (C(3)), 57.60 (NCH_2), 62.94 (C(6)), 116.29 ($=CH_2$), 126.98 (2 × C-*ortho*), 127.11 (C-*para*), 128.52 (2 × C-*metha*), 136.59 (=CH), 143.46 (C-*ipso*).

4.4. Isolation of 4-allyl-6-phenyl-4,5-diazospirohept-5-ene (*6*)

Solution of *N*-allylpyrazolidine **5** (43 mg, 0.2 mmol) in 0.4 ml of $CDCl_3$ was stored at 0 °C. Monitoring with ^1H NMR spectroscopy indicated gradual disappearance of compound **5** and growing of signals of pyrazoline **6**. The reaction was complete after 6 days. Small amount of colorless precipitate was also formed, but its

structure was not determined. Reaction mixture was filtered, solution concentrated in vacuo and the residue was purified by preparative TLC on silica gel using toluene–MeOH (30:1) as eluent to give compound **6** (15 mg, 35% yield) as pale yellow oil.

Elemental Anal. Calc. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.36; H, 7.75; N, 12.94%. The partial mass spectrum, m/z (I_{rel} (%)): 212 $[M]^+$ (14), 211 $[M-H]^+$ (13), 197 $[M-NH]^+$ (15), 183 $[M-H-N_2]^+$, 157 $[M-C_3H_5N]^+$ (20), 51 (63), 41 $[C_3H_5]$ (92), 39 (100). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 0.62 (m, 2H, H(1) + H(2)), 1.08 (m, 2H, H(1) + H(2)), 3.16 (s, 2H, H(7)), 3.48 (d.t, $^4J \approx 1.5$, $^3J = 6.1$, 2H, NCH_2), 5.14 (d.q, $^2J \approx {}^4J \approx 1.5$, $^3J = 10.3$, 1H, one of $=CH_2$), 5.24 (d.q, $^2J \approx {}^4J \approx 1.6$, $^3J = 17.3$, 1H, one of $=CH_2$), 6.05 (d.d.t, $^3J = 6.1$, $^3J = 10.3$, $^3J = 17.3$, 1H, =CH), 7.32 (m, 3H, Ph), 7.61 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): 8.65 (C(1) + C(2)), 41.91 (C(7)), 47.91 (C(3)), 52.13 (NCH_2), 116.62 ($=CH_2$), 125.52 (2 × C-*ortho*), 128.31 (2 × C-*metha*), 128.46 (C-*para*), 133.16 (C-*ipso*), 135.59 (=CH), 148.43 (C(6)).

4.5. Isolation of 4-allyl-7-iso-propyl-4,5-diazospirohept-5-ene (7)

Pyrazolidine **4** (287 mg, 1.6 mmol) was kept under Ar at room temperature for 6 months; ^{1}H NMR spectra showed that it had decomposed almost completely with formation of several products. The yield of main product – pyrazoline **7** – was estimated as 60–70% based on data of ^{1}H NMR spectra. It was isolated as pale yellow oil (111 mg, 39% yield) by column chromatography on silica gel using petrol ether–AcOEt (10:1) as eluent.

Elemental Anal. Calc. for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 73.96; H, 10.11; N, 15.58%. The partial mass spectrum, m/z (I_{rel} (%)): 177 $[M-H]^+$ (16), 135 $[M-C_3H_7]^+$ (22), 41 $[C_3H_5]$ (100). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 0.24 (d.d.d, $^2J = 5.5$, $^3J = 7.3$, $^3J = 10.0$, 1H, H(1)), 0.86 (m, 2H, H(2) + H(2)), 0.95 (d, $^3J = 6.9$, 3H, CH_3), 0.97 (d, $^3J = 6.9$, 3H, CH_3), 1.07 (d.d.d, $^2J = 5.5$, $^3J = 6.7$, $^3J = 10.5$, 1H, H(1)), 1.67 (d.sept, $^3J = 4.1$, $^3J = 6.9$, 1H, CH), 2.77 (d.d, $^3J = 1.7$, $^3J = 4.1$, 1H, H(7)), 3.29 (d.d.t, $^4J \approx 1.6$, $^3J = 5.9$, $^2J = 14.4$, 1H, one of NCH_2), 3.33 (d.d.t, $^4J \approx 1.6$, $^3J = 6.1$, $^2J = 14.4$, 1H, one of NCH_2), 5.12 (d.q, $^2J \approx {}^4J \approx 1.6$, $^3J = 10.2$, 1H, one of $=CH_2$), 5.22 (d.q, $^2J \approx {}^4J \approx 1.6$, $^3J = 17.2$, 1H, one of $=CH_2$), 5.96 (d.d.t, $^3J \approx 6.0$, $^3J = 10.2$, $^3J = 17.2$, 1H, =CH), 6.71 (d, $^3J = 1.7$, 1H, (H(6)). ^{13}C NMR ($CDCl_3$, δ, ppm): 3.80 (C(2)), 9.62 (C(1)), 17.93 (CH_3), 21.10 (CH_3), 28.89 (CH), 49.02 (C(3)), 51.95 (NCH_2), 58.57 (C(7)), 116.41 ($=CH_2$), 135.73 (=CH), 141.65 (C(6)).

4.6. Isomerization of pyrazolidine 4 into 8 with $Hg(OCOCF_3)_2$

To a stirred solution of pyrazolidine **4** (178 mg, 1.0 mmol) in 20 mL of dry CH_3CN at −5 °C was added dropwise solution of $Hg(OCOCF_3)_2$ (640 mg, 1.5 mmol) in 4 mL of dry CH_3CN and stirring was continued for 2 h at 0 °C, then a solution of $NaBH_4$ (76 mg, 2 mmol) in 2 mL of 3 N aqueous NaOH was added. After 40 min at 0 °C, 50 ml of saturated aqueous $NaHCO_3$ was added and products was extracted with Et_2O (4 × 20 mL). Organic layers was combined, dried over Na_2SO_4, then Et_2O was evaporated in vacuo and residue was separated by column chromatography on silica gel using gradient elution with petrol ether–EtOAc (40:1 to 5:1).

2-Allyl-5,5-dimethyl-2,3-diaza-bicyclo[4.2.0]oct-3-ene (**8**) was isolated as colorless oil (36 mg, 21%).

Elemental Anal. Calc. for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 73.96; H, 10.38; N, 15.60%. The partial mass spectrum, m/z (I_{rel} (%)): 178 $[M]^+$ (11), 149 $[M-C_2H_5]^+$ (13), 135 $[M-C_3H_7]^+$ (100), 41 $[C_3H_5]$ (84). ^{1}H NMR (C_6D_6, δ, ppm, J/Hz): 0.73 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.50 (m, 1H, H(7)), 1.65 (m, 1H, H(7)), 1.72 (m, 1H, H(8)), 1.87 (m, 1H, H(8)), 2.28 (m, 1H, H(6)), 3.44 (d.d.t, $^4J \approx 1.1$, $^3J = 7.2$, $^2J = 14.3$, 1H, one of NCH_2), 3.52 (m, 1H, H(1)), 3.98 (d.d.t, $^4J \approx 1.7$, $^3J = 5.1$, $^2J = 14.3$, 1H, one of NCH_2), 5.09 (br.d, $^3J = 10.2$, 1H, one of $=CH_2$), 5.17 (br.d, $^3J = 17.2$, 1H, one of $=CH_2$), 6.06 (d.d.d.d, $^3J = 5.1$, $^3J = 7.2$, $^3J = 10.2$, $^3J = 17.2$, 1H, =CH), 6.81 (d, $^4J = 2.0$, H(4)). ^{13}C NMR ($CDCl_3$, δ, ppm): 21.24 (C(7)), 22.09 (C(8)), 23.25 (2×CH_3), 31.67 (C(5)), 45.70 (C(6)), 53.94 (C(1)), 57.36 (NCH_2), 116.74 ($=CH_2$), 135.57 (=CH), 149.81 (C(4)).

4.7. Synthesis of 4-allyl-1,2-diphenylhydrazine (9)

Triallylborane (2.42 g, 18 mmol) was added to azobenzene (3.28 g, 18 mmol) at 0 °C and the reaction was warmed to room temperature; a clean solution was formed in several minutes. Methanol (3 ml) was added dropwise at 30 °C. Further treatment with aqueous NaOH (10%, 7 ml), extraction with ether, drying and distillation gave rise to 1-allyl-1,2-diphenylhydrazine (**9**) in 65% yield, b.p. 98–100 °C/0.03 Torr. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 4.10 (br.s, 2H, NCH_2), 5.20 (d.q, $^2J \approx {}^4J \approx 1.5$, $^3J = 17.0$, 1H, one of $=CH_2$), 5.24 (d.q, $^2J \approx {}^4J \approx 1.4$, $^3J = 10.4$, 1H, one of $=CH_2$), 5.65 (br.s, 1H, NH), 5.87 (d.d.t, $^3J \approx 5.9$, $^3J = 10.4$, $^3J = 17.0$, 1H, =CH), 6.80 (m, 4H, Ph), 6.97 (m, 2H, Ph), 7.20 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): 53.46 (NCH_2), 112.82 and 113.15 (4C-*ortho*), 118.87 and 119.91 (2C-*para*), 118.91 ($=CH_2$), 129.24 and 129.42 (4C-*metha*), 131.89 (=CH), 147.43 and 149.77 (2C-*ipso*). Lit. [11].

Acknowledgements

This work was supported by the President of Russian Federation (Sci. School No. 3834.2008.3), Russian Foundation for Basic Research (grant No 08-03-00790), and Presidium of RAS (No. 18, coordinator – V.A. Tartakovsky).

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