Russian Journal of Organic Chemistry, Vol. 41, No. 5, 2005, pp. 739–741. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 5, 2005, pp. 753–755.

Uncommon Heterocyclization into a Pyrazole System of *Z*-3-(2-Naphthyl)-3-chloro-2-propenal Semicarbazone and Thiosemicarbazone

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Received October 29, 2004

Abstract—By reaction of *Z*-3-(2-naphthyl)-3-chloro-2-propenal with semicarbazide hydrochloride and thiosemicarbazide the corresponding semicarbazone and thiosemicarbazone were obtained that underwent a heterocyclization into a pyrazole system with elimination of amide moieties and with migration of the naphthyl fragment into the position *4* of the pyrazole ring. The alkylation of 4-(2-naphthyl)pyrazole synthesized with 2-nitropentachloro-1,3-butadiene afforded 1,1-bis[4-(2-naphthyl)-pyrazol-1-yl]-2-nitrotrichloro-1,3- butadiene.

Z-3-(2-Naphthyl)-3-chloro-2-propen-1-al (**I**) easily prepared from 2-acetonaphthone by Vilsmeier–Haack reaction [1] contains two reactive sites (C=O and =CCl) that permits an effective application of the compound to building up versatile heterocyclic systems including a naphthalene fragment: benzodiazepine, isoxazole, pyrimidine [2], and quinoline [3]. We formerly demonstrated that the reaction between chloropropenal **I** and hydrazine hydrate was a convenient procedure for preparation of 5-(2-naphthyl)pyrazole [2].

The goal of this study was preparation of chloropropenal **I** semicarbazone and thiosemicarbazone and the attempt at their heterocyclization into a pyrazole system containing a naphthalene fragment and amide or thioamide groups respectively.

Semicarbazone **II** and thiosemicarbazone **III** of chloropropenal we obtained in 80–82% yield by reacting chloropropenal **I** with semicarbazide hydrochloride and thiosemicarbazide respectively. The IR spectra of compounds **II** and **III** obtained lacked the absorption bands of the aldehyde group and contained the bands from C=N bonds vibrations at 1563 (compound **II**) and 1597 cm^{-1} (compound **III**). Vibrations of the NH_2 groups of compounds **II** and **III** are characterized by absorption bands at 3473 and 3432 cm^{-1} respectively, and vibrations of the NH groups appeared as broadened bands in the region 3206–3283 cm^{-1}. In the ^1H NMR spectra of compounds **II** and **III** alongside the resonances from the protons of the naphthyl groups and exocyclic =CH broadened singlets were observed with the chemical shifts δ 9.4–10.5 and 6.35–6.45 ppm belonging to the protons of the NH and NH_2 groups respectively.

The heterocyclization of compounds **II** and **III** into a pyrazole system was effected by boiling in the glacial acetic acid. We expected to obtain pyrazole with a naphthyl fragment attached to position *5* of the ring and amide or thioamide group in position *1*. However the process occurred differently and involved a loss of amide groups and a migration of the naphthyl fragment into position *4* of the pyrazole ring. Thus in both cases the same product was obtained that based on elemental analysis, ^1H NMR, IR, and mass spectra was assigned a structure of 4-(2-naphthyl)pyrazole (**IV**).

In the mass spectrum of compound **IV** the molecular ion peak is present with *m/z* 194 and relative abundance 100%, and the elemental analysis corresponds to an empirical formula $C_{13}H_{10}N_2$. The IR and ^1H NMR spectra of compound **IV** essentially differ from the spectra of 5-(2-naphthyl)-pyrazole (**V**) we have synthesized previously [2]. In the ^1H NMR spectrum of compound **IV** alongside the multiplet belonging to the protons of the naphthyl fragment two doublets were identified located at δ 6.85 and 7.77 ppm with a coupling constant *J* 2.2 Hz corresponding to the =CH groups of the pyrazole ring, whereas in the spectrum of 5-(2-naphthyl)pyrazole (**V**) the protons of the heterocycle appeared as doublets at δ 7.0 and 7.95 ppm, ^3J 6 Hz [2]. The relatively small value of the coupling constant observed for compound **IV** suggests by analogy with the published data on the spectra of related substances [4, 5] that it is ^4J, and thus

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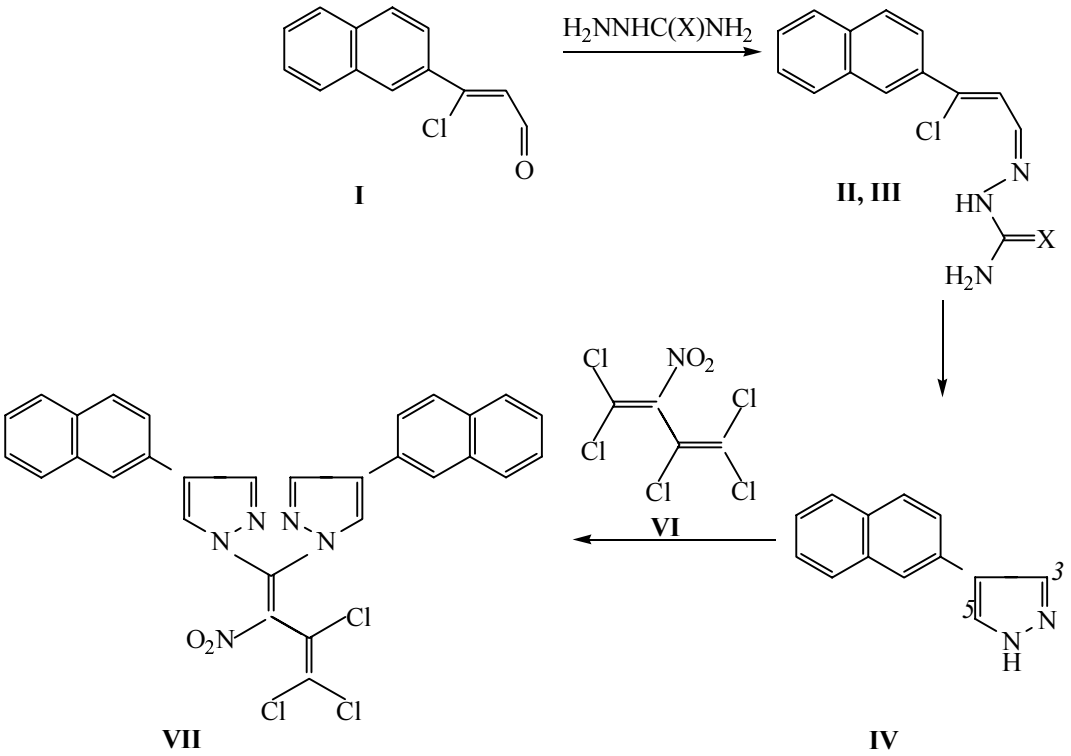

X = O (**II**), S (**III**).

the compound obtained may be regarded as 4-(2-naphthyl)pyrazole.

In the IR spectrum of compound **IV** the vibrations of C=N bond are characterized by a strong absorption band at 1536 cm^{-1}, whereas in the IR spectrum of the isomeric pyrazole **V** the absorption band corresponding to the C=N bond appears at 1556 cm^{-1}. The NH group gave rise to a broadened band at 3134 cm^{-1}. The absorption bands of the bonds C=O and/or C=S are lacking in the spectra.

4-(2-Naphthyl)pyrazole (**IV**) synthesized was brought into reaction with an active electrophile, 2-nitropentachloro-1,3-butadiene (**VI**), highly reactive in the processes of nucleophilic vinyl chlorine substitution [6]. It turned out that pyrazole **IV** was less active in the reaction with nitrodiene **VI** than its isomer **V** which readily reacted with the nitrodiene at room temperature [2]. With pyrazole **IV** a boiling of reagents in benzene for 15 h was required to obtain the reaction product 1,1-bis[4-(2-naphthyl)pyrazol-1-yl]-2-nitrotrichloro-1,3-butadiene (**VII**). Thus two terminal chlorine atoms in α-nitro-β,β-dichlorovinyl group of the nitrodiene system suffered substitution forming a bridge between two pyrazole molecules. The composition and structure of the compound obtained were proved by elemental analysis, IR, ^{1}H NMR, and mass spectrum. In the IR spectrum of compound **VII** the absorption bands of the N–H bond are lacking, and strong absorption bands appear at 1379 and 1542 cm^{-1} corresponding to symmetric and asymmetrical vibrations of the NO_2 group respectively. In the ^{1}H NMR spectrum of compound **VII** the multiplets from the naphthyl fragments of the molecule are observed and doublets from the =CH groups of the pyrazole heterocycles; therewith the signal of the N=CH group is considerably shifted downfield compared to the similar signal in the spectrum of pyrazole **IV** due to the electron-withdrawing effect of the conjugated trichloronitrodiene system. In the mass spectrum of compound **VII** a group of peaks corresponding to the molecular ion and of products of its fragmentation under the electron impact was observed. The fragmentation occurred with the loss of naphthyl fragments, chlorine atoms, and nitro group. The intensity ratio of the main isotope components $^{35}Cl/^{37}Cl$ in the group of the molecular ion peaks was equal to 100:98:32 corresponding to the presence in the molecule of three chlorine atoms [7, 8].

EXPERIMENTAL

IR spectra were measured on a Fourier spectrometer Nicolet Protege-460 from samples pelletized with KBr. ^{1}H NMR spectra were registered on spectrometer Tesla BS-567A (100 MHz) from solutions in DMSO-d_6

(compound **III**) and $CDCl_3$ (compounds **II**, **IV**, and **VII**), internal reference TMS. Mass spectra were obtained on a GC-MS instrument Hewlett-Packard HP 5890/5972 in an electron impact mode at the electrons energy 70 eV equipped with a capillary column HP-5MS 30 m long, internal diameter 0.25 mm, stationary phase (5% PhMe Silicone) 0.25 μm thick, vaporizer temperature 250°C. The identification of the components was performed using the computer Database of mass spectra NBS75k.

3-(2-Naphthyl)-3-chloro-2-propenal semicarbazone (II). A mixture of 2 g (9.2 mmol) of 3-(2-naphthyl)-3-chloro-2-propenal (**I**) and 1.04 g (9.2 mmol) of semicarbazide hydrochloride was heated at reflux in ethanol for 3 h. On cooling the reaction mixture the separated precipitate was filtered off, washed with water, with ethanol, and dried in a vacuum. Yield 2.4 g (82%), mp 231–233°C. IR spectrum, ν, cm^{-1}: 1492, 1583, 1603 (C=C), 1563 (C=N), 1739 (C=O). ^1H NMR spectrum, δ, ppm: 6.45 br.s (2H, NH_2), 7.20 d (1H, ClC=CH, ^3J 9 Hz), 7.50–8.0 m (6H naphth.), 8.10 d (1H, CH=N, ^3J 9 Hz), 8.30 s (1H, C^{1}H naphth.), 10.50 br.s (1H, NH). Found, %: C 61.64; H 4.73; Cl 12.65; N 15.70. $[M]^+$ 273. $C_{14}H_{12}ClN_3O$. Calculated, %: C 61.43; H 4.22; Cl 12.95; N 15.35. *M* 273.71.

3-(2-Naphthyl)-3-chloro-2-propenal thiosemicarbazone (III). A mixture of 2 g (9.2 mmol) of 3-(2-naphthyl)-3-chloro-2-propenal (**I**) and 0.84 g (9.2 mmol) of thiosemicarbazide in ethanol was stirred at 70°C for 15 min. On cooling the reaction mixture the separated precipitate was filtered off, washed with water, with ethanol, and dried in a vacuum. Yield 2.28 g (80%), mp 178–180°C. IR spectrum, ν, cm^{-1}: 1500, 1563 (C=C), 1507 (C=S), 1597 (C=N). ^1H NMR spectrum, δ, ppm: 6.35 br.s (2H, NH_2), 7.0 d (1H, ClC=CH, ^3J 9 Hz), 7.50–8.0 m (6H naphth.), 8.10 d (1H, CH=N, ^3J 9 Hz), 8.24 s (1H, C^{1}H naphth.), 9.40 br.s (1H, NH). Found, %: C 58.23; H 4.63; Cl 11.85; N 14.48; S 10.81. $[M]^+$ 289. $C_{14}H_{12}ClN_3S$. Calculated, %: C 58.00; H 4.18; Cl 12.23; N 14.53; S 11.06. *M* 289.78.

4-(2-Naphthyl)pyrazole (IV). A mixture of 1 g (3.5 mmol) of semicarbazone **II** and 15 ml of glacial acetic acid was boiled for 3 h, then on cooling it was poured into 100 ml of water, neutralized with a solution of KOH, the separated precipitate was filtered off, washed with water, with hexane, and dried in a vacuum. Yield 0.3 g (86%), mp 148–150°C. IR spectrum, ν, cm^{-1}: 1519, 1600, 1628 (C=C), 1536 (C=N), 3049 (=C–H), 3134 (N–H). ^1H NMR spectrum, δ, ppm: 5.7 br.s (1H, NH), 6.85 d (1H, C^{5}H pyrazole, ^4J 2.2 Hz), 7.4–7.6 m (2H naphth.), 7.77 d (1H, C^{3}H pyrazole, ^4J 2.2 Hz), 7.85–7.97 m (4H naphth.), 8.32 c (1H, C^{1}H naphth.). Found, %: C 80.35; H 5.34; N 14.14. $[M]^+$ 194. $C_{13}H_{10}N_2$. Calculated, %: C 80.38; H 5.20; N 14.42. *M* 194.25.

1,1-Bis[4-(2-naphthyl)pyrazol-1-yl]-2-nitrotrichloro-1,3-butadiene (VII). A solution of 0.78 g (4 mmol) of naphthylpyrazole **IV** and 0.27 g (1 mmol) of 2-nitropentachloro-1,3-butadiene (**V**) in 40 ml of benzene was heated at reflux for 15 h. The separated precipitate was filtered off, washed with ethyl ether, and dried in a vacuum. We obtained 0.6 g (82%) of bispyrazole product **VII** mp 198–199°C. IR spectrum, ν, cm^{-1}: 1379, 1542 (NO_2), 1509, 1573 (C=C), 1621 (C=N), 3045 (=C–H). ^1H NMR spectrum, δ, ppm: 7.08 d (2H, 2C^{5}H pyrazole, ^4J 2.8 Hz), 7.45–7.60 m (4H naphth.), 7.70 d (2H, 2C^{3}H pyrazole, ^4J 2.8 Hz), 7.8–8.0 m (8H naphth.), 8.30 br.s (2H, 2C^{1}H naphth.). Found, %: C 61.18; H 3.40; Cl 17.94; N 11.84. $[M]^+$ 585. $C_{30}H_{18}Cl_3N_5O_2$. Calculated, %: C 61.50; H 2.93; Cl 18.16; N 11.96. *M* 586.85.

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