

$^5J_{\text{cis},\text{cis}}$ of the 1-H and 10-H protons does not show up in the spectra of II and III, i.e., this constant proves to be less than 0.2 Hz. This situation can be explained within the framework of the known concepts regarding transmission of long-range spin-spin coupling in unsaturated conjugated systems [3].

Thus the results of a detailed analysis of the PMR spectra of I-IV as compared with the spectra of V (Tables 1 and 2) constituted a complete confirmation of the structure of the new heterocyclic system.

EXPERIMENTAL

The PMR spectra were obtained with Bruker Physik WP-80 and WH-360 spectrometers under pulse conditions with Fourier transformation. The conditions for storage of the signals in the computer were selected in such a way as to ensure a resolution of no less than 0.05 Hz. A Lorentz-Gauss filter for contraction of the spectral lines was used prior to Fourier transformation. Iteration analysis of the spectra was carried out by means of the ITRCAL program with a BNC-28X computer equipped with a WP-80 spectrometer.

LITERATURE CITED

1. N. S. Prostakov, A. V. Varlamov, Navin Saksena, and A. A. Fomichev, Khim. Geterotsikl. Soedin., No. 1, 123 (1980).
2. N. S. Prostakov, N. Saxena, A. V. Varlamov, and A. A. Fomichev (Fomichov), J. Organomet. Chem., 218, 17 (1981).
3. H. Gunter, NMR Spectroscopy — An Introduction, Wiley, New York (1980), p. 116.

PYRROLES FROM KETOXIMES AND ACETYLENE.

23.* 2-(1-NAPHTHYL)- AND 2-(2-NAPHTHYL)PYRROLES

AND THEIR 1-VINYL DERIVATIVES

S. E. Korostova, B. A. Trofimov,
L. N. Sobenina, A. I. Mikhaleva,
and M. V. Sigalov

UDC 547.74/75.07

2-(1-Naphthyl)- and 2-(2-naphthyl)pyrroles and their 1-vinyl derivatives were synthesized in 22-64% yields by the reaction of 1- and 2-acetylnaphthalene oximes with acetylene at both atmospheric pressure and elevated pressures in an alkali metal hydroxide-dimethyl sulfoxide system.

The available information regarding naphthylpyrroles is limited [2-7], and their 1-vinyl derivatives are not known at all, although they are of great interest as monomers and starting substances for the production of biologically active compounds.

In a systematic study of the reaction of ketoximes with acetylene, which leads to pyrroles and 1-vinylpyrroles [8], we found that it can also be successfully extended to oximes of condensed aromatic ketones such as 1- and 2-acetylnaphthalenes Ia, b.

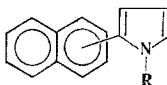
*See [1] for communication 22.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1351-1353, October, 1982. Original article submitted December 29, 1981.

TABLE 1. Effect of the Temperature on the Yields of the Products of the Reaction of Oxime Ib with Acetylene

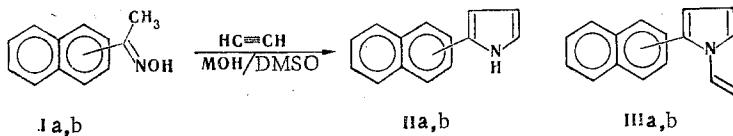
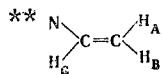
T, °C	Yields of pyrroles, %	
	IIb	IIIb
60	0	0
70	33	0
90	13	49
100	0	36

TABLE 2. PMR Spectra of Naphthylpyrroles*



Compound	R	δ , ppm						
		3-H	4-H	5-H	H^{**A}	H^{**B}	H^{**C}	H_{naphthyl}
IIa	H	6,20	6,31	6,70	—	—	—	7,2—7,6
IIIa	$\text{CH}=\text{CH}_2$	6,17	6,25	7,07	4,96	4,33	6,40	7,2—7,6
IIb	H	6,17	6,44	6,72	—	—	—	7,2—7,6
IIIb	$\text{CH}=\text{CH}_2$	6,17	6,17	6,95	4,99	4,49	6,90	7,2—7,6

*The SSCC of the pyrrole ring in all of the compounds were as follows: $^3J_{34} = 3.6$, $^3J_{45} = 3.2$, and $^4J_{35} = 1.8$ Hz.



M=Li, K; I—III a 1-naphthyl, b 2-naphthyl

Under the conditions in [9] [100°C, 3 h, 30% KOH based on the weight of the ketoxime, dimethyl sulfoxide (DMSO)], which were previously found for alkyl aryl ketoximes, the reaction under acetylene pressure (12–16 atm absolute) proceeds with significant resinification and gives low yields of the pyrroles. Better results were obtained at 90°C. A mixture consisting of pyrrole IIa and 1-vinylpyrrole IIIa, the yields of which are 15 and 48%, respectively, is formed from oxime Ia at this temperature (2 h, KOH). The yields of pyrroles IIb and IIIb under the same conditions (except that the reaction time was 3 h) are 13 and 49%, respectively. 1-Acetylnaphthalene oxime condenses with acetylene under pressure at 60°C. It follows from the IR spectrum of the reaction mixture that it contains, in addition to pyrrole IIa [3440 cm^{-1} (N—H)], 1-vinylpyrrole IIIa [1640 cm^{-1} ($\text{CH}_2=\text{CH}-\text{N}$)]; however, it was difficult to isolate these products in this case because of their very low concentrations and the presence of starting oxime Ia [920, 3300 cm^{-1} ($\text{C}=\text{N}-\text{OH}$)], as well as the ketone [1680 cm^{-1} ($\text{C}=\text{O}$)], which is partially regenerable from the oxime under the reaction conditions. When the reaction temperature is raised to 80°C (3 h, KOH), the preponderant product becomes vinylpyrrole IIIa, the yield of which decreases not only as the temperature is raised but also as the reaction time is increased — 48% (90°C, 2 h) and 31% (90°C, 3 h) — as a consequence of resinification. Pyrrole IIa free of vinylpyrrole IIIa was isolated in 22% yield when the LiOH-DMSO catalytic pair was used (90°C, 3 h). The effect of the reaction temperature (3 h, 30% KOH, initial acetylene pressure 12 atm absolute) on the result of the reaction was followed in the case of the condensation of 2-acetylnaphthalene oxime with acetylene (Table 1).

As in other cases [8], the nature of the cation of the hydroxide has a substantial effect on the yields and ratios of the pyrroles. Thus, whereas the yield of pyrrole IIb is 33% in the presence of KOH (70°C, 3 h), LiOH has virtually no catalytic effect on the process at the same temperature. Pyrrole IIb can be obtained in good yield at atmospheric pressure in a flask equipped with a stirrer by passing acetylene through the heated (90-100°C) reaction mass. After 4.5 h, oxime Ib underwent ~70% conversion, and the yield of pyrrole IIb was 64%. The reaction proceeds further at 110-120°C (13 h): The reaction mixture consists of pyrrole IIb and vinylpyrrole IIIb in a ratio of 1:2. The pure reaction products were isolated in 18 and 31% yields, respectively, from this mixture by chromatography on Al_2O_3 [hexane-ether (3:1)]. The PMR spectra of pyrroles IIa, b and IIIa, b are presented in Table 2.

All of the synthesized pyrroles are crystalline substances that are soluble in ether, acetone, chloroform, and DMSO, only slightly soluble in alcohol and hexane, and insoluble in water.

EXPERIMENTAL

The IR spectra of KBr pellets of I-III were obtained with a UR-20 spectrometer. The PMR spectra of solutions in CCl_4 were recorded with a Tesla BS-487 C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

2-(1-Naphthyl)pyrrole (IIa). A mixture of 9.3 g (0.05 mole) of oxime Ia, 1.2 g (0.05 mole) of LiOH, and 100 ml of DMSO was heated at 90°C for 3 h in a 1-liter steel rotating autoclave under acetylene pressure (the initial pressure was 12 atm absolute), after which the reaction mixture was poured into 700 ml of cold water. The precipitate was removed by filtration and dried with filter paper to give 2.7 g of crude product. Recrystallization from petroleum ether gave 2.1 g (22%) of pyrrole IIa with mp 174-180°C. Found: C 86.8; H 5.7; N 7.3%. $\text{C}_{14}\text{H}_{11}\text{N}$. Calculated: C 87.0; H 5.8; N 7.2%.

2-(2-Naphthyl)pyrrole (IIb). A 2.8-g (0.05 mole) sample of KOH and 120 ml of DMSO were placed in a flask equipped with a stirrer, a reflux condenser, and a bubbler, the flask was heated to 95°C, 9.3 g (0.05 mole) of oxime Ib was added, and acetylene was bubbled into the mixture for 4.5 h (until traces of vinylpyrrole IIIb appeared). The reaction was monitored by chromatography on Silufol [hexane-ether (3:1)]. The reaction mass was cooled to room temperature and poured into 700 ml of cold water. The precipitate was removed by filtration, dried, and recrystallized repeatedly from hexane to give 6.2 g (64%) of pyrrole IIb with mp 154-155°C [4]. Found: C 86.4; H 5.9; N 7.2%. $\text{C}_{14}\text{H}_{11}\text{N}$. Calculated: C 87.0; H 5.7; N 7.2%.

1-Vinyl-2-(1-naphthyl)pyrrole (IIIa). A mixture of 3.6 g (0.019 mole) of oxime Ia, 1.02 g (0.019 mole) of KOH, and 46 ml of DMSO was heated at 90°C for 2 h with acetylene under pressure (the initial pressure was 12 atm absolute), after which the reaction mass was diluted with water (500 ml), and the reaction product was extracted with ether. The ether extracts were washed with water and dried with potassium carbonate. The ether was removed, and the residue was distilled *in vacuo* to give 2.6 g (49%) of a substance with bp 130-170°C (1.3 hPa) that crystallized in the receiver. Recrystallization from ethanol gave pure vinylpyrrole IIIa with mp 51-52°C. Found: C 87.8; H 6.2; N 6.0%. $\text{C}_{16}\text{H}_{13}\text{N}$. Calculated: C 87.6; H 6.0; N 6.4%.

1-Vinyl-2-(2-naphthyl)pyrrole (IIIb). A total of 3.4 g (62%) of vinylpyrrole IIIb, with mp 50-51°C, was obtained from 4.65 g (0.025 mole) of oxime Ib in the presence of 1.4 g (0.025 mole) of KOH and 60 ml of DMSO by heating at 90°C for 3 h by the method used to prepare vinyl pyrrole IIIa. Found: C 87.5; H 5.9; N 6.4%. $\text{C}_{16}\text{H}_{13}\text{N}$. Calculated: C 87.6; H 6.0; N 6.4%.

LITERATURE CITED

1. A. I. Mikhaleva, B. A. Trofimov, A. N. Vasil'ev, G. A. Komarova, and V. I. Skorobogatova, Khim. Geterotsikl. Soedin., No. 9, 1202 (1982).
2. West German Patent No. 1105714; Chem. Abstr., 56, 8215 (1962).
3. French Patent No. 1549829; Ref. Zh. Khim., 23N619P (1969).
4. A. Pictet and C. Long, Ber., 37, 2792 (1904).
5. T. K. Inakov, N. Madikhanov, and A. G. Makhsumov, Deposited Paper No. 2713-74, All-Union Institute of Scientific and Technical Information; Ref. Zh. Khim., 6Zh349 (1975).
6. M. J. Haddadin, B. J. Agha, and R. F. Tabri, J. Org. Chem., 44, 494 (1979).
7. A. R. Katritzky, C. A. Ramsden, and Z. Zakaria, J. Chem. Soc., Chem. Commun., 363 (1979).
8. B. A. Trofimov and A. I. Mikhaleva, Khim. Geterotsikl. Soedin., No. 10, 1299 (1980).
9. B. A. Trofimov, S. E. Korostova, L. N. Balabanova, and A. I. Mikhaleva, Zh. Org. Khim., 14, 1733 (1978).