22. R. G. Kostyanovsky, V. F. Rudchenko, V. G. Shtamburg, I. I. Chervin, and Sh. S. Nasibov, *Tetrahedron*, **37**, 4245 (1981).
23. R. V. Hoffman and N. B. Christophe, *J. Org. Chem.*, **53**, 4769 (1988).
24. S. A. Glover, A. Goosen, G. W. MacCleland, and J. L. Schoonrad, *Tetrahedron*, **43**, 2577 (1987).
25. V. F. Rudchenko, S. M. Ignatov, I. I. Chervin, and R. G. Kostyanovsky, *Tetrahedron*, **44**, 2233 (1988).
26. R. A. Abramovitch and R. Jeyaraman, *Azides and Nitrenes, Reactivity and Utility*, E. F. V. Scriven (ed.), Academic Press, Orlando (1984), p. 297.
27. U. Svanholm and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 1234 (1974).
28. D. Serve, *J. Am. Chem. Soc.*, **97**, 432 (1975).
29. G. K. MacLean, J. Passmore, M. N. S. Rao, M. J. Shriver, P. S. White, D. Bethell, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Dalton Trans.*, No. 6, 1405 (1985).
30. N. Burford, J. P. Johnson, J. Passmore, M. J. Shriver, and P. S. White, *J. Chem. Soc., Chem. Commun.*, No. 12, 966 (1986).
31. I. E. Chlenov, L. N. Kolymagina, and V. A. Tartakovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 1893 (1972).
32. J. M. Domagala and R. D. Bach, *J. Am. Chem. Soc.*, **98**, 1975 (1976).
33. V. A. Tartakovskii, I. A. Savostyanova, and S. S. Novikov, *Zh. Org. Khim.*, **4**, 240 (1968).
34. M. V. Kashutina, S. L. Ioffe, V. M. Shitkin, N. O. Cherskaya, V. A. Korenevskii, and V. A. Tartakovskii, *Zh. Obshch. Khim.*, **43**, 1715 (1973).

REARRANGEMENTS OF 1-OXA-2-AZOLES.

2.* STRUCTURE AND ISOMERIZATION OF PENTAMETHYLENE-AMIDOXIMES OF 4-AMINOFURAZAN-3-CARBOXYLIC ACID

V. G. Andrianov, V. G. Semenikhina, and A. V. Eremeev

UDC 547.793.2

The Z-oxime of the pentamethyleneamide of 4-aminofurazan-3-carboxylic acid isomerizes – rapidly in acid media, slowly in the absence of acid – to the E-oxime which at 120-140°C undergoes alkali-catalyzed rearrangement to 4-piperidinofurazan-3-carboxyamidoxime.

The amidoxime of 4-aminofurazan-3-carboxylic acid (I), at 120-140°C in the presence of alkali, undergoes a degenerative rearrangement [1]:

Ia Ib

*For Communication 1 see [1].

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 122-123, January, 1991. Original article submitted January 30, 1989; revision submitted January 8, 1990.

 0009-3122/91/2701-0102$12.50

TABLE 1. Amidoximes IIa-c

Compound	Empirical formula	Mp, °C	PMR spectrum, δ, ppm				Yield %
			C—CH_2, m	N—CH_2, m	NH_2, s	OH, s	
IIa	$C_8H_{13}N_5O_2$	106 ... 109	1,51	3,20	6,09	10,67	
IIb	$C_8H_{13}N_5O_2$	131 ... 133	1,51	2,98	5,89	9,93	88
IIc	$C_8H_{13}N_5O_2$	116 ... 118	1,53	3,22	6,13	10,07	75

The reaction comprises three stages – Z to E isomerization of the oxime group, recyclization, and E to Z isomerization of the oxime group. Similar transformations of derivatives of 1,2,4-oxadiazole proceed much more readily, often even at room temperature [2, 3], the rate-determining step being the isomerization of the oxime group [3]. The difficulty in bringing about the rearrangement of derivatives of the furazan I prompts the question: What is the limiting stage in this reaction? Since the E oximes of unsubstituted amidoximes are thermodynamically less stable than the Z oximes, one can hardly point to an E oxime intermediate in the rearrangement of furazan I. In this connection, we have studied Z–E isomerization and rearrangement for the example of an N,N-disubstituted derivative – the oxime of the pentamethyleneamide of 4-aminofurazan-3-carboxylic acid (IIa). As we have shown previously [4], the Z oxime IIa which we prepared is readily transformed in an acid medium into the E oxime IIb:

IIa IIb

Isomerization also occurs slowly on keeping the Z oxime IIa at room temperature. In the PMR spectrum of the E oxime IIb there is observed a very characteristic shift of the signal of the hydroxyl proton of the oxime group upfield relative to that of the Z oxime [5]. In addition, x-ray analysis of compounds IIa and IIb confirms that the assignment of configuration of the oxime groups is correct [4].

Thus the E oxime IIb, in contrast to the E oxime of the pentamethyleneamide of 1,2,4-oxadiazole-3-carboxylic acid [6], appears to be a stable product with no tendency to spontaneous recyclization. Rearrangement of the E oxime IIb takes place under the same conditions as the rearrangement of the unsubstituted amidoxime Ia – at a temperature of 120-140°C in the presence of alkali:

II b II c

The reaction proceeds to completion and the starting material IIb is not detected in the reaction mixture, i.e., equilibrium is completely shifted in the direction of the formation of the furazan IIc. The furazan IIc is also formed from the Z oxime IIa under similar conditions.

Thus it has been shown that, for the example of the oxime of the pentamethyleneamide of 4-aminofurazan-3-carboxylic acid, the rate-determining step in the rearrangement of carboxyamidoximes of aminofurazan is the recyclization stage, and not the isomerization of the oxime group. In this respect they differ from the carboxyamidoximes of 1,2,4-oxadiazole.

EXPERIMENTAL

PMR spectra were run on a Bruker WH-90 in DMSO-D_6, with TMS as internal standard. The characteristics of the compounds are set out in Table 1. The results of elemental analysis for C, H, and N corresponded to those calculated.

E-Oxime of Pentamethyleneamide of 4-Aminofurazan-3-carboxylic Acid (IIb). The Z-oxime of the pentamethylene amide of 4-aminofurazan-3-carboxylic acid (IIa) (2.11 g, 10 mmoles) was dissolved in a mixture of 3 ml concentrated HCl and 7 ml water. After 8 h the acid was neutralized with saturated sodium bicarbonate solution. The residue was filtered off and recrystallized from chloroform to yield 1.86 g of product.

Amidoxime of 4-Piperidinofurazan-3-carboxylic Acid (IIc). A solution of 1.27 g (6 mmoles) Z or E oxime II and 1.12 g (20 mmoles) KOH in 5 ml ethylene glycol was heated at 120-140°C for 7 h. The reaction mixture was cooled, diluted with 8 ml of water, and neutralized with hydrochloric acid. The residue was filtered off and recrystallized from water to yield 0.95 g of product.

LITERATURE CITED

1. V. G. Andrianov, V. G. Semenikhina, A. V. Eremeev, and A. P. Gaukhman, *Khim. Geterotsikl. Soedin.*, No. 12, 1701 (1988).
2. V. G. Andrianov, A. V. Eremeev, and Yu. B. Sheremet, *Khim. Geterotsikl. Soedin.*, No. 6, 856 (1988).
3. N. Vivona, V. Frenna, S. Buscemi, and M. Ruccia, *J. Heterocycl. Chem.*, **22**, 97 (1985).
4. A. F. Mishnev, V. G. Andrianov, V. G. Semenikhina, and A. V. Eremeev, *Zh. Strukt. Khim.*, **32** (1991).
5. V. G. Andrianov and A. V. Eremeev, *Zh. Org. Khim.*, **20**, 150 (1984).
6. V. G. Andrianov, V. G. Semenikhina, and A. V. Eremeev, *Khim. Geterotsikl. Soedin.* (1991).

SYNTHESIS OF PYRIDO[1,2-c][1,3]BENZOXAZINES BASED ON 1-BENZYL-3-HYDROXY-3-METHYL-6-(2-BENZYLOXYPHENYL)-4-PIPERIDONES

G. V. Pshenichnii, Samekh Khamo, V. A. Mashenkov, and L. S. Stanishevskii

UDC 547.867.2'823.07: 543.422.25:541.63

The stereomeric 1-benzyl-3-hydroxy-3-methyl-6e-(2-benzyloxyphenyl)-4-piperidones on debenzylation and subsequent reaction with formaldehyde are converted into cis- and trans-1,3,4-10b-tetrahydro-3-hydroxy-3-methyl-2-oxopyrido-[1,2-c][1,3]benzoxazines.

Arising out of the growing interest in recent years in the chemistry of cannabinoids (certain derivatives of 9H-dibenzo[b,d]pyrans, isolated from *Cannabis sativa Linn.* and possessing high biological activity [1]), published work has appeared on the synthesis of their heterocyclic analogs, in particular pyrido[1,2-c][1,3]benzoxazines [2, 3].

We have developed a new approach to the synthesis of these compounds based on the stereoisomeric piperidones III and IV and involving catalytic debenzylation over palladium and subsequent treatment with formaldehyde, it being possible thus to prepare benzoxazines V and VI without isolating the intermediate NH-piperidones. The piperidones III and IV are prepared by the known route [4] of crotonic condensation of the epoxy ketone I with 2-benzyloxybenzaldehyde and further reaction of the cinnamoyloxirane II with benzylamine.

The composition and structure of the compounds synthesized were confirmed by elemental analysis, and their IR, PMR, and ^{13}C NMR spectra. Thus, the configuration of the piperidones III and IV follows from the values of the chemical shifts of the methyl groups in the PMR spectra (Table 1) [4]. In the IR spectrum of compound V, the so-called Bohlmann bands [5] are observed in the 2700-2850 cm^{-1} region, these being associated with trans-hydrogen bonding. The absence of these bands from the IR spectrum of compound VI is evidence of cis-hydrogen bonding (see scheme below).

V. I. Lenin Belorussian State University, Minsk 220080.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 124-127, January, 1991. Original article submitted May 22, 1989.

0009-3122/91/2701-0104$12.50