ORIENTATION IN THE NITRATION OF 3-PHENYL-4-SUBSTITUTED FURAZANS

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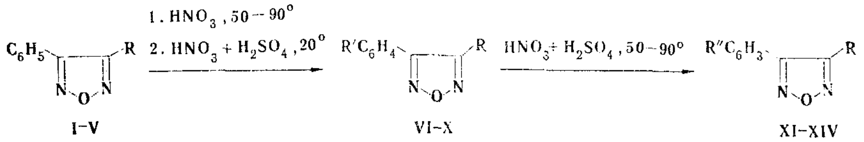
The nitration of 3-phenyl-4-substituted furazans with various nitrating agents was investigated. It is shown that the orientation of the nitro group that is incorporated in the phenyl ring is determined by the substituent in the 4 position of the furazan ring, whereas the introduction of a furazan substituent in the phenyl ring lowers the reactivity of the latter. The corresponding dinitro derivatives can be obtained by means of acid mixtures.

We have recently shown that the reason for the low nucleophilicity of aminofurazans as compared with anilines is the weaker positive inductive effect of the furazan ring as compared with the phenyl ring [1]. The literature contains several examples of the nitration of phenylfurazans to mononitro derivatives [2, 3]; however, it was demonstrated only recently in the case of 3-phenylfurazan (I) that the nitro group enters the phenyl ring in the para position with respect to the furazan ring [4, 5].

To ascertain the electronic effect of the furazan ring we investigated the nitration of a number of phenylfurazans with various nitrating agents. Thus only mononitro derivatives VI-X are formed in high yields in all cases when 3-phenylfurazans I-V are treated with concentrated nitric acid. The position of the nitro group in the phenyl ring was determined by means of the PMR spectra (Table 1). As a result of the investigation, we showed that the orientation of the entering nitro group is determined by the substituent in the 4 position of the furazan ring.



I R=H; II R=CH_3; III R=C_6H_5; IV R=NO_2; V R=COOH; VI R=H, R'=4'-NO_2; VII R=CH_3, R'=4'-NO_2; VIII R=4-$NO_2C_6H_4$, R'=4'-NO_2; IX R=NO_2, R'=3'-NO_2; X R=COOH, R'=3'-NO_2; XI R=H, R''=2',4'-NO_2; XII R=CH_3, R''=2',4'-NO_2; XIII R=2,4-$(NO_2)_2C_6H_3$, R''=2',4'-NO_2; XIV R=NO_2, R''=3',5'-NO_2

Similar results were obtained in the nitration of I-V with a mixture of sulfuric and nitric acids at 20°C. An increase in the temperature promotes further nitration to dinitro derivatives (XI-XIV). The introduction of a third nitro group in the phenyl ring was not observed in a single case. The use of nitronium tetrafluoroborate as the nitrating agent led to the formation of mononitro derivatives VI-X; the orientation of the entering nitro group is similar to the orientation observed in the case of nitration with acids. In contrast to diphenyl, stilbene, or azobenzene [6], 3,4-diphenylfurazan (III) does not form nitro derivative VIII when it is nitrated with a mixture of nitric acid and acetic anhydride, and this indicates a decrease in the reactivity of the phenyl ring whein a furazan substituent is present.

Thus the results obtained in this research show that a furazanyl substituent has a weak electron-donor effect that promotes orientation of the entering nitro group in the ortho and para positions. This effect can be disrupted by the introduction of electron-acceptor substituents in the 4 position of the furazan ring.

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TABLE 1. PMR Spectra of 3-Phenylfurazans and Their Nitro Derivatives

Compound	Chemical shifts of the protons, δ, ppm	
	phenyl ring*	substituent in the 4 position
I	8,05 m, 7,62 m	9,25
II	7,82 m, 7,58 m	2,52
III	7,52	
IV	7,9 m, 7,65 m	
VI	8,32 d., 8,55 d	9,45
VII	8,20 d, 8,55 d	2,65
VIII	7,96 d, 8,45 d	
IX	8,3 d, 7,95 t, 8,55 d, 8,8	
XI	9,1, 8,85 d, 8,29 d	9,18
XII	9,15, 8,9 d, 8,2 d	2,4
XIII	9,05, 8,9 d., 8,15 d	
XIV	9,15, 9,2	

*$J_o = 8$, $J_m = 2$ Hz.

TABLE 2. Conditions for the Preparation of Nitrophenylfurazans and Their Properties

Compound	Nitrating agent	Reaction temp., °C	Reaction time, h	mp, °C	Found				Empirical formula	Calc.				Yield, %
					C, %	H, %	N, %	M		C, %	H, %	N, %	M	
VI	HNO_3	20—25	2,0	145[a]	49,9	2,9	21,7	187	$C_8H_5N_3O_3$	50,3	2,6	22,0	191	50
VII	HNO_3	50	0,5	75[b]	52,4	3,5	20,6	200	$C_9H_7N_3O_3$	52,7	3,4	20,5	205	85
VIII	HNO_3	50	0,5	218[c]	54,1	2,6	18,2	308	$C_{14}H_8N_4O_5$	53,9	2,6	18,0	312	77
	NO_2BF_4	25	12,0											77
IX	HNO_3—H_2SO_4 (1 : 1)	20—50	0,3	—	40,4	1,7	23,7	240	$C_8H_4N_4O_5$	40,7	1,7	23,7	236	97
X	HNO_3—H_2SO_4 (1 : 1)	20	4,0	117—118[c]	45,8	2,1	18,0	237	$C_9H_5N_3O_5$	46,0	2,1	17,9	235	80
XI	HNO_3—H_2SO_4 (1 : 1)	20—25	12,0	112[a]	40,4	1,8	24,0	230	$C_8H_4N_4O_5$	40,7	1,7	23,7	236	40
XII	HNO_3—H_2SO_4 (1 : 1)	90	1,0	73[a]	43,2	2,3	22,5	253	$C_9H_6N_4O_5$	43,2	2,4	22,4	250	97
XIII	HNO_3—H_2SO_4 (1 : 1)[d]	90	2,0	232[c]	41,8	1,6	20,7	400	$C_{14}H_6N_6O_9$	41,8	1,5	20,9	409	80
XIV	HNO_3—H_2SO_4 (1 : 1)	70—95	2,0	170[a]	34,1	1,1	25,3	275	$C_8H_3N_5O_7$	34,2	1,1	24,9	281	90

[a] From ethanol. [b] From CCl_4. [c] From acetic acid. [d] In this case 62% oleum was used.

EXPERIMENTAL

The IR spectra of thin films of the compounds on an NaCl support were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in D_6-acetone were recorded with a Perkin-Elmer R-12 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The molecular masses were determined by inverse ebullioscopy by means of thermistors.

3-Phenylfurazan (I). A mixture of 5.0 g (0.03 mole) of phenylglyoxime and 3.5 g (0.035 mole) of succinic anhydride was fused at 105-110°C, after which it was cooled and extracted with ether (four 100-ml portions). The ether extract was washed with 10% Na_2CO_3 and water, and the solvent was evaporated. Furazan I was recrystallized from CCl_4 or pentane to give 1.5 g (33%) of a product with mp 36°C (mp 36°C [7]).

3-Phenyl-4-methylfurazan (II). A mixture of 31.0 g (0.173 mole) of phenylmethylglyoxime diacetate and 620 ml of 30% NaOH was refluxed for 1.5-2 h, after which it was cooled and extracted with ether. The extract was dried with anhydrous $MgSO_4$, and the solvent was removed by distillation. The residual liquid was distilled *in vacuo* to give 5.8 g of a product with bp 98°C (2.7 hPa), n_D^{20} 1.5450, and d_4^{20} 1.13. IR spectrum: 1475, 1280, 1090 (furazan ring); 720, 790 cm^{-1} (C_6H_5). Found: C 60.7; H 5.6; N 15.5%; M 158; MR_D 44.0.

3,4-Diphenylfurazan (III). The reaction of 7.5 g (0.031 mole) of diphenylglyoxime and 3.2 g (0.032 mole) of succinic anhydride at 170-180°C under the conditions for the preparation of I gave 3.5 g (50%) of a product with mp 98°C (from ethanol) (mp 98°C [8]).

3-Phenyl-4-nitrofurazan (IV). A 5-g (0.031 mole) sample of 3-phenyl-4-aminofurazan was oxidized with trifluoroperacetic acid (from 10 ml of 90% H_2O_2 and 66 ml of trifluoroacetic anhydride) in 30 ml of methylene chloride at 20-25°C for 12 h. The mixture was then poured into

100 ml of water, the organic layer was separated, and the mother liquor was extracted with 30 ml of methylene chloride. The extracts were combined, washed with water (four 50-ml portions), dried, and evaporated to give 3.5 g (60%) of IV with mp 40°C (from pentane). IR spectrum: 1580, 1355 (NO_2); 1465, 1230, 1020 cm^{-1} (furazan ring). Found: C 50.3; H 2.6; N 21.8%; M 181. $C_8H_5N_3O_3$. Calculated: C 50.3; H 2.6; N 22.0%; M 191.

3-Phenylfurazancarboxylic Acid (V). A mixture of 3 g (0.018 mole) of 3-phenyl-4-methylfurazan, 6 g (0.04 mole) of $KMnO_4$, and 100 g of 20% H_2SO_4 was heated at 80-85°C, after which the contents of the flask were cooled, treated with oxalic acid until the MnO_2 vanished completely, and extracted with ether. The solvent was removed, and the 3-phenylfurazancarboxylic acid was purified by sublimation to give 1.0 g (30%) of a product with mp 109°C (mp 109°C [9]).

General Method for the Acidic Nitration of 3-Phenylfurazans. A 1-g sample of the phenylfurazan was added with vigorous stirring at 20-25°C to 20 ml of 96% HNO_3 (or a mixture of 20 ml of 96% HNO_3 and 20 ml of 96% H_2SO_4), and the mixture was heated to the necessary temperature and maintained at this temperature for the required time. It was then cooled and poured over ice, and the resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from a suitable solvent (see Table 2).

General Method for Nitration with Nitronium Tetrafluoroborate. A 4-g (0.03 mole) sample of NO_2BF_4 was added at 20-25°C to 0.004 mole of 3-phenylfurazan I-IV in 20 ml of acetonitrile, and the mixture was allowed to stand for 12 h, after which it was poured into water, and the resulting precipitate was removed by filtration, dried, and recrystallized from a suitable solvent. The structures of the resulting VI-IX were confirmed by means of the PMR spectra and by the absence of melting-point depressions for mixtures of the products with mononitro derivatives VI-IX obtained by acidic nitration.

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