ELECTROPHILIC *ipso* SUBSTITUTIONS OF FURAN VINAMIDINIUM SALTS

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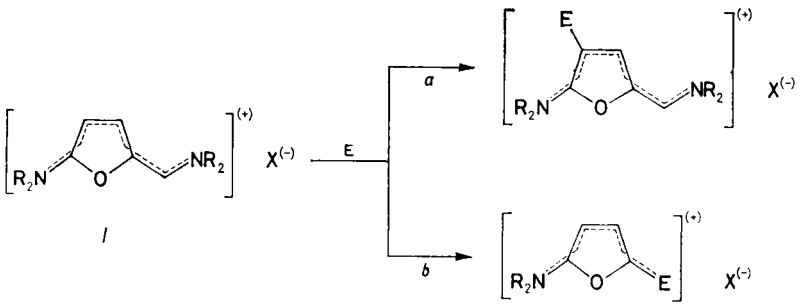
5-(N,N-Dialkylamino)-2-furfurylidene-N,N-dialkylimminium salts *I* (the vinamidinium salts of furan) react with arenediazonium salts to give products of *ipso* substitution in position 2 of the furan ring, i.e. 5-(N,N-dialkylamino)-2-azoarenefuran salts *II*. The structure of these products was evidenced by ^{1}H NMR and UV spectral data.

So far, the copulation of furan derivatives with arenediazonium salts has been only little studied[1-4] probably due to a low stability of the azoarenefuran derivatives. The 2,5-disubstituted derivatives of furan react with arenediazonium salts usually to afford the appropriate 3-azoarene derivatives.

Our preceding papers[5-7] referred to 5-(N,N-dialkylamino)-2-furfurylidene-N,N-dialkylimminium salts *I* as a pentamethinium system with an embodied furan ring. The enhanced electron density at even carbon atoms of the vinamidinium system[8-11] was utilized for the synthesis of β-substituted furan derivatives via the electrophilic



I

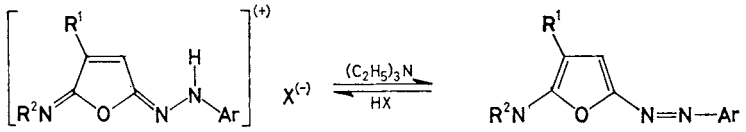
a, E = $[(CH_3)_2N{=}CR]^{(+)}$, $NO_2^{(+)}$, $Hal^{(+)}$, $[CH_3CO]^{(+)}$, $[ArCH{-}OH]^{(+)}$, $[ArCH{-}OCOCH_3]^{(+)}$

b, E = $[Ar{-}N_2]^{(+)}$

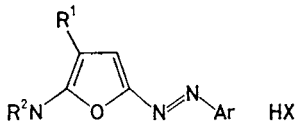
SCHEME 1

replacement reactions[5-7]. This paper deals with reactions of salts *I* with arenediazonium compounds.

Electrophilic replacement reactions of vinamidinium salts *I* with reagents of Vilsmeier–Haack type, halogenation, nitration[5,7], acetylation, and reactions with aromatic aldehydes in acidic medium[6] lead to substitution products in position 4 of the furan ring (Scheme 1, path *a*). Aiming to investigate reactions of *I* with further electrophilic reagents the behaviour with arenediazonium salts was examined. In contrast to the above-mentioned reactions, products of *ipso* substitution in position 2 of the furan ring were obtained (Scheme 1, path *b*).The resulting 5-(N,N-dialkylamino)-2-azoarenefurans were obtained under these raction conditions in form of



IIA *III*



IIB

IIa, R^1 = H; R^2 = $(CH_3)_2N$; Ar = C_6H_5; X = BF_4
IIb, R^1 = H; R^2 = $(CH_3)_2N$; Ar = 4-C_2H_5OCO—C_6H_4; X = BF_4
IIc, R^1 = H; R^2 = $(CH_3)_2N$; Ar = 4-NO_2—C_6H_4; X = BF_4
IId, R^1 = H; R^2 = $(CH_3)_2N$; Ar = 3-NO_2—C_6H_4; X = Br
IIe, R^1 = H; R^2 = $(CH_3)_2N$; Ar = 2-NO_2—C_6H_4; X = Br
IIf, R^1 = H; R^2 = $(CH_3)_2N$; Ar = 3-Br—C_6H_4; X = ClO_4
IIg, R^1 = H; R^2 = $(CH_3)_2N$; Ar = 4-CH_3CONH—C_6H_4; X = Br
IIh, R^1 = H; R^2 = $(CH_3)_2N$; Ar = 4-CH_3—C_6H_4; X = BF_4
IIi, R^1 = H; R^2 = $(CH_3)_2N$; Ar = 4-CH_3-3-NO_2—C_6H_3; X = ClO_4
IIj, R^1 = Br; R^2 = $(CH_3)_2N$; Ar = 4-NO_2—C_6H_4; X = BF_4
IIk, R^1 = $CH(OCH_3)C_6H_5$; R^2 = $(CH_3)_2N$; Ar = 4-NO_2—C_6H_4; X = ClO_4
IIl, R^1 = $CH(N^{(+)}\bigcirc)C_6H_5$; R^2 = $(CH_3)_2N$; Ar = 4-NO_2—C_6H_4; X = ClO_4
IIm, R^1 = H; R^2 = O⌒N; Ar = 4-NO_2—C_6H_4; X = Br
IIn, R^1 = H; R^2 = O⌒N; Ar = 3-NO_2—C_6H_4; X = ClO_4
IIo, R^1 = H; R^2 = O⌒N; Ar = 2-NO_2—C_6H_4; X = ClO_4
IIp, R^1 = H; R^2 = O⌒N; Ar = 3-Br—C_6H_4; X = ClO_4

SCHEME 2

TABLE I

5-(N,N-Dialkylamino)-2-azoarenefuran compounds *II*

Compound	Formula (M_r)	M.p., °C (yield, %)	Calculated/found			
			% C	% H	% N	% Hal
IIa	$C_{12}H_{14}BF_4N_3O$	235–238	47·55	4·65	13·86	—
	(303·1)	(64)	47·11	4·62	13·34	—
IIb	$C_{15}H_{18}BF_4N_3O_3$	232–236	48·02	4·83	11·20	—
	(375·1)	(42)	48·66	4·78	11·16	—
IIc	$C_{12}H_{13}BF_4N_4O_3$	229–231	41·40	3·76	16·09	—
	(348·1)	(84)	40·93	3·77	16·05	—
IId	$C_{12}H_{13}BrN_4O_3$	243–247	42·24	3·84	16·42	23·44
	(341·2)	(93)	42·71	3·87	16·02	23·31
IIe	$C_{12}H_{13}BrN_4O_3$	110–113	42·24	3·84	16·42	23·44
	(341·2)	(70)	42·86	3·89	16·01	23·25
IIf	$C_{12}H_{13}BrN_3ClO_5$	240–243	36·52	3·32	10·65	29·24
	(394·6)	(88)	36·41	3·47	11·09	29·06
IIg	$C_{14}H_{17}BrN_4O_2$	239–243	47·59	4·85	15·86	22·64
	(353·3)	(45)	48·02	4·91	15·43	22·24
IIh	$C_{13}H_{16}BF_4N_3O$	195–202	49·24	5·09	13·25	—
	(317·1)	(44)	50·10	5·12	12·94	—
IIi	$C_{13}H_{15}ClN_4O_7$	223–226	41·67	4·03	14·95	9·46
	(374·7)	(76)	42·38	4·46	15·48	9·10
IIj	$C_{12}H_{12}BBrF_4N_4O_3$	205–208	33·45	2·83	13·12	18·71
	(426·9)	(72)	33·69	2·89	13·25	19·02
IIk	$C_{20}H_{21}ClN_4O_8$	190–195	49·95	4·40	11·65	7·37
	(480·9)	(94)	49·78	4·51	11·77	7·40
IIl	$C_{24}H_{23}Cl_2N_5O_{11}$	133–137	45·87	3·69	11·14	11·28
	(628·4)	(69)	46·02	3·60	10·92	11·57
IIm	$C_{14}H_{15}BrN_4O_4$	205–209	43·87	3·94	14·82	20·86
	(383·3)	(46)	43·85	3·96	14·52	20·73
IIn	$C_{14}H_{15}ClN_4O_8$	170–173	41·75	3·75	13·91	8·80
	(402·7)	(91)	41·16	4·87	14·25	8·71
IIo	$C_{14}H_{15}ClNgO_8$	65–67	41·75	3·75	13·91	8·80
	(402·7)	(39)	42·76	3·99	13·32	9·06
IIp	$C_{14}H_{15}BrClN_3O_6$	165–169	38·51	3·46	9·62	26·40
	(436·6)	(60)	39·50	4·06	10·12	26·07

hydrogen salts *II* (Table I), which, when reacted with triethylamine furnished the corresponding 5-(N,N-dialkylamino)-2-azoarenefurans *III*. Compounds *III* are very unstable and therefore, they were identified directly in the reaction mixture by ^{1}H NMR spectroscopy (Table II). The attempt to isolate them resulted in failure. Treatment with acids makes it possible to transform them into the original salts *II* (Scheme 2).

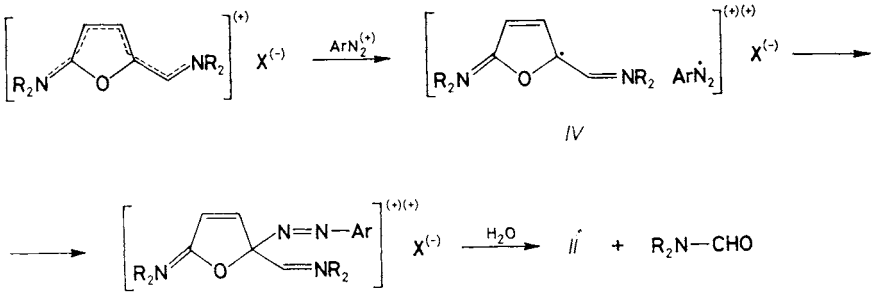
Salts *II* can be considered as aza analogues of vinamidium salts *I* with possible structures *IIA* or *IIB*. Structure *IIA* is preferred on the basis of ^{1}H NMR spectra. The high coupling constants of protons $J(3, 4) = 5{\cdot}4$ Hz in compounds *IIa*–*IIi*, *IIm*–*IIp* are comparable with those ($J(3, 4) = 5{\cdot}2$ Hz) of vinamidinium salts[12] *I* in contrast to coupling constants $J(3, 4) = 4$ Hz in like furan compounds[5,6]. Another argument for the structure *IIA* provide two resonance signals of methyl groups of the dimethylamino grouping of compounds *IIa*–*IIj* measured even at 80°C.

The different orientation of replacement reaction of *I* with arenediazonium cation with respect to other electrophilic reagents can be rationalized by the reaction course associated with an electron transfer. Vinamidinium salts are electron-rich π-systems with a low oxidation potential[8–11]. In general, these systems can transfer electron to some ionic electrophiles as e.g. arenediazonium cations[13–15]. This way is followed when reacting 4-(N,N-dimethylamino)benzaldehyde[16,17], 4-(N,N-dimethylamino)-1-alkenyl substituted benzene derivatives[13,14], and analogous indole derivatives[14] with diazonium salts. The reaction proceeds through the so-called Wehland intermediate[14,16] *IV*, which is interpreted as an interaction of cation-radical and aryldiimino radical formed by an electron transfer (Scheme 3). The

TABLE II

UV spectra of compounds *II* and *III*

Compound	λ_{max} (log ε)	Compound	λ_{max} (log ε)
IIa	455 (3·33)	*IIIa*	478 (3·56)
IIb	464 (3·43)	*IIIb*	508 (3·54)
IIc	460 (3·40)	*IIIc*	543 (3·54)
IId	432 (3·05)	*IIId*	500 (3·70)
IIg	483 (3·44)	*IIIg*	487 (3·52)
IIh	462 (3·36)	*IIIh*	464 (3·38)
IIj	340 (3·15)	*IIIj*	380 (3·16)
	425 (3·17)		420 (3·26)
IIm	352 (3·15)	*IIIm*	475 (3·38)



SCHEME 3

following elimination of the methylenimminium group in water furnished products of *ipso* substitution. 5-(N,N-Dialkylamino)-2-azoarenefuran hydrogen salts *II* enable preparation and investigation of little stable furan derivatives.

EXPERIMENTAL

The melting points were measured on a Kofler micro hot-stage, the UV spectra of $3 . 10^{-5}$ to $5 . 10^{-5}$ mol l^{-1} (ε in m^2 mol^{-1}) acetone solutions were recorded with a UV-VIS spectrophotometer (Zeiss, Jena), the ^{1}H NMR spectra of deuteriodimethyl sulfoxide solutions containing tetramethylenesilane as an internal reference were run with a BS 487C (Tesla, Czechoslovakia) spectrometer operating at 80 MHz.

5-(N,N-Dialkylamino)-2-azoarenefuran Hydrogen Tetrafluoroborates, Perchlorates, and Bromides *II*

The respective diazonium salt (6 mmol) was added to a stirred solution of *I* (6 mmol) in water (15 ml) at 0—5°C and then stirred at room temperature for another 2—5 h. The precipitated substance was filtered off and washed with water. If *II* failed to precipitate (*IIa*), the solution was left to stand in a refrigerator overnight. The product was crystallized from acetic acid–water (95 : 5). The diazonium salts can be utilized in form of tetrafluoroborates, sulfates, chlorides, or bromides preparated by diazotization of the corresponding anilines in situ in water. Compounds *II* can be obtained as perchlorates by addition of $NaClO_4$ (5 mmol) in water (15 ml) (compounds *IIf*—*IIi*, *IIn*—*IIp*).

^{1}H NMR *spectra of* 5-(N,N-*dialkylamino*)-2-*azoarenefuran compounds II*: *IIa*: 3·53 s, 3 H, (CH_3); 3·61 s, 3 H (CH_3); 7·40 s, 5 H, (H-arom.); 7·55 d, 1 H, (H-4, J(3, 4) = 5·3); 7·85 d, 1 H (H-3); 11·30 s, 1 H (NH).

IIb: 1·32 t, 3 H (CH_3, J = 7); 3·52 s, 3 H (CH_3); 3·58 s, 3 H (CH_3); 4·28 q, 2 H (CH_2); 7·40 d, 2 H (H-arom., J = 8); 7·62 d, 1 H (H-4, J(3, 4) = 5·4); 8·05 d, 1 H (H-3); 7·96 d, 2 H (H-arom.); 11·28 s, 1 H (NH).

IIc: 3·41 s, 3 H (CH_3); 3·52 s, 3 H (CH_3); 7·38 d, 1 H (H-4, J(3, 4) = 5·6); 7·65 d, 2 H (H-arom., J = 9·5); 8·01 d, 1 H (H-3); 8·18 d, 2 H (H-arom.).

IId: 3·50 s, 3 H (CH_3); 3·60 s, 3 H (CH_3); 7·65 d, 1 H (H-4, J(3, 4) = 5·3); 7·88 m, 4 H (H-arom).; 8·05 d, 1 H (H-3).

IIe: 3·32 s, 3 H (CH_3); 3·37 s, 3 H (CH_3); 6·85 d, 1 H (H-4, $J(3, 4) = 5·1$); 7·93 d, 1 H (H-3); 8·00 m, 4 H (H-arom).

IIf: 3·48 d, 3 H (CH_3); 3·60 s, 3 H (CH_3); 7·26 m, 3 H (H-arom); 7·47 s, 1 H (H-arom.); 7·53 d, 1 H (H-4, $J(3, 4) = 5·4$); 7·98 d, 1 H (H-3).

IIg: 1·97 s, 3 H (CH_3); 3·45 s, 3 H (CH_3); 3·52 s, 3 H, (CH_3); 7·28 d, 2 H (H-arom., $J = 9$); 7·48 d, 1 H (H-4, $J(3, 4) = 5·2$); 7·57 d, 2 H, (H-arom.); 7·95 d, 1 H (H-3); 9·98 s, 1 H (NH); 11·52 s, 1 H (NH).

IIh: 2·27 s, 3 H (CH_3); 3·42 s, 3 H (CH_3); 3·52 s, 3 H (CH_3); 7·35 s, 4 H (H-arom.); 7·43 d, 1 H (H-4, $J(3, 4) = 5·2$); 7·76 d, 1 H (H-3).

IIi: 2·32 s, 3 H (CH_3); 3·52 s, 3 H (CH_3); 3·56 s, 3 H (CH_3); 7·77 d, 1 H (H-4, $J(3, 4) = 5·6$); 7·86 d, 1 H (H-3); 7·90 m, 3 H (H-arom.); 11·17 s, 1 H (NH).

IIj: 2·73 s, 3 H (CH_3); 2·76 s, 3 H (CH_3); 6·55 s, 1 H (H-3); 6·70 d, 2 H (H-arom., $J = 9$); 8·00 d, 2 H (H-arom.); 11·30 s, 1 H (NH).

IIk: 2·48 s, 3 H (CH_3); 2·63 s, 3 H (CH_3); 3·21 s, 3 H (OCH_3); 5·25 s, 1 H (CH); 6·65 d, 2 H (H-arom., $J = 9$); 7·24 s, 5 H (H-arom.); 7·62 s, 1 H (H-3); 7·91 d, 2 H (H-arom.); 11·26 s, 1 H (NH).

III: 3·73 s, 3 H (CH_3); 3·79 s, 3 H (CH_3); 6·16 s, 1 H (CH); 7·32 s, 1 H (H-3); 7·45 m, 5 H (H-pyridine); 7·49 d, 2 H (H-arom., $J = 9$); 7·50 s, 5 H (H-arom.); 8·97 d, 2 H (H-arom.); 11·02 s, 1 H (NH).

IIm: 4·04 m, 8 H ($4 \times CH_2$); 6·68 d, 1 H (H-4, $J(3, 4) = 5·4$); 7·40 d, 2 H (H-arom., $J = 9$); 7·66 d, 1 H (H-3); 7·83 s, 2 H (H-arom.); 11·27 s, 1 H (NH).

IIn: 3·42 m, 8 H ($4 \times CH_2$); 7·15 m, 3 H (H-arom.); 7·25 d, 1 H (H-4, $J(3, 4) = 5$); 7·50 d, 1 H (H-3); 8·25 s, 1 H (H-arom.); 11·90 s, 1 H (NH).

IIo: 3·51 m, 8 H ($4 \times CH_2$); 6·97 d, 1 H (H-4, $J(3, 4) = 5·1$); 7·82 d, 1 H (H-3); 8·50 m, 4 H (H-arom.); 10·47 s, 1 H (NH).

IIp: 3·72 m, 8 H ($4 \times CH_2$); 6·82 d, 1 H (H-4, $J(3, 4) = 5$); 7·65 s, 1 H (H-arom.); 7·12 m, 3 H (H-arom.); 7·86 d, 1 H (H-3); 11·45 s, 1 H (NH).

5-(N,N-Dialkylamino)-2-azoarenefurans *III*

Triethylamine (1·5 mmol) was added to a suspension of *II* (1 mmol) in ethanol (10 ml) or hexadeuteriodimethyl sulfoxide for an NMR experiment. The mixture got an intense colouration. This solution was used for NMR and UV measurements of compounds *III*. Addition of perchloric acid (1·5 mmol) resulted in separation of compound *II*.

^{1}H NMR *spectra of* 5-(N,N-*dialkylamino*)-2-*azofurans III*: *IIIa*: 3·15 s, 6 H (CH_3); 5·96 d, 1 H (H-4, $J(3, 4) = 4·2$); 7·32 d, 1 H (H-3); 7·46 m, 5 H (H-arom.).

IIIb: 1·32 t, 3 H (CH_3, $J = 7$); 3·12 s, 6 H (CH_3); 4·27 q, 2 H (CH_2); 7·40 d, 2 H (H-arom., $J = 9$); 7·42 d, 1 H (H-4, $J(3, 4) = 4·2$); 8·05 d, 1 H (H-3); 7·96 d, 2 H (H-arom.).

IIIc: 3·44 s, 6 H (CH_3); 7·40 d, 1 H (H-4, $J(3, 4) = 4·2$); 7·52 d, 2 H (H-arom., $J = 9$); 7·97 d, 2 H (H-arom.); 8·16 d, 1 H (H-3).

IIId: 2·92 s, 6 H (CH_3); 5·90 d, 1 H (H-4, $J(3, 4) = 4$); 7·32 d, 1 H (H-3); 7·80 m, 3 H (H-arom.); 8·35 s, 1 H (H-arom.).

IIIf: 3·50 s, 6 H (CH_3); 7·10 m, 4 H (H-arom.); 7·51 d, 1 H (H-4, $J(3, 4) = 4·2$); 7·97 d, 1 H (H-3).

IIIg: 2·00 s, 3 H (CH_3); 3·01 s, 6 H (CH_3); 5·87 d, 1 H (H-4, $J(3, 4) = 4$); 7·21 d, 1 H (H-3); 7·42 d, 2 H (H-arom., $J = 9$); 7·62 d, 2 H (H-arom.); 10·11 s, 1 H (NH).

IIIh: 2·26 s, 3 H (CH_3); 3·23 s, 6 H (CH_3); 5·92 d, 1 H (H-4, $J(3, 4) = 4$); 7·30 d, 2 H (H-3); 7·32 s, 4 H (H-arom.).

IIIi: 2·70 s, 6 H (CH_3); 6·55 s, 1 H (H-3); 6·70 d, 2 H (H-arom., $J = 9$); 8·00 d, 2 H (H-arom.).

IIIk: 2·50 s, 6 H (CH_3); 3·18 s, 3 H (CH_3); 5·23 s, 1 H (CH); 7·00 d, 2 H (H-arom., $J = 9$); 7·35 s, 5 H (H-arom.); 7·62 s, 1 H (H-3); 7·90 d, 2 H (H-arom.).

IIIm: 3·47 m, 8 H ($4 \times CH_2$); 6·68 d, 1H (H-4, $J(3, 4) = 4·2$); 7·42 d, 2 H (H-arom., $J = 9$); 7·80 d, 1 H (H-3); 8·10 d, 2 H (H-arom.).

IIIp: 3·58 m, 8 H ($4 \times CH_2$); 6·28 d, 1 H (H-4, $J(3, 4) = 4$); 7·12 m, 3 H (H-arom.); 7·87 d, 1 H (H-3); 8·12 s, 1 H (H-arom).

REFERENCES

1. Barle M. G., Gore S. T., Mackie R. K., Mhatre S., Tedder J. M.: J. Chem. Soc., Perkin Trans. 1, *1978*, 401.
2. Boyd G. V., Heatherington K.: J. Chem. Soc., Perkin Trans. 1, *1973*, 2523.
3. Iten P. X., Eugster H. C., Helv. Chim. Acta *61*, 1033 (1978).
4. Mikhailenko F. A., Shevchuk L. I.: Khim. Geterotsikl. Soedin. *1974*, 1325.
5. Gracza T., Arnold Z., Kováč J.: Collect. Czech. Chem. Commun. *49*, 1600 (1984).
6. Gracza T., Arnold Z., Kováč J.: Collect. Czech. Commun. *50*, 675 (1985).
7. Kováč J., Gracza T., Arnold Z.: Heterocycles *21*, 448 (1984).
8. Lloyd D., McNab H.: Angew. Chem. *88*, 496 (1976).
9. Radeglia R., Eugalhardt G., Lipmaa E., Pehle T., Nothe K. P., Pähne B.: Org. Magn. Reson. *4*, 571 (1972).
10. Lloyd D., Mackie R. K., McNab H., Marshall D. R., Tucker K.: Tetrahedron *32*, 2339 (1976).
11. Fabian J., Hartman H.: J. Mol. Struct. *27*, 67 (1975).
12. Gracza T.: *Thesis*. Slovak Institute of Technology, Bratislava 1985.
13. Colonna M., Greci L., Poloni M.: J. Chem. Soc., Perkin Trans. 2, *1982*, 455.
14. Colonna M., Poloni M.: Gazz. Chim. Ital. *114*, 495 (1984).
15. Jackson A. H., Shannon P. V. R., Tinker A. C.: J. Chem. Soc. Chem. Commun. *1976*, 196.
16. Clems A. H., Helsby P., Ridd J. H., Alornran I., Sondall J. P. B.: J. Chem. Soc., Perkin Trans. 2, *1985*, 1217.
17. Perekalin V. V., Popova L. P., Abramovich I. I.: Zh. Org. Khim. *24*, 1653 (1975).

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