5-NITROPHENYL-2-FURFURYL-N-ONIUM BROMIDES*

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Received July 30th, 1979

The title compounds were prepared by reaction of 5-nitrophenyl-2-furfuryl bromides with tertiary amines as pyridine, α, β-picolines, trimethylamine, triethylamine and tripropylamine. Their IR, UV and ^{1}N-NMR spectra are interpreted.

Our preceding papers dealt with 5-nitrophenyl-2-furfurylalcohols[1] which, upon reaction with phosphorous bromide, gave a relatively highly reactive 5-nitrophenyl-2--furfuryl bromides[2]. The compounds can also be used for preparation of ethers, acetates, and 5-nitrophenyl-2-furfuryl sulfones[3,4]. This paper concerns the preparation of 5-nitrophenyl-2-furfuryl-N-onium bromides (*I – XVIII*) obtained from the corresponding alcohols and phosphorous bromide and a consecutive reaction of these bromides with tertiary amines (Scheme 1).

Scheme 1

Compound	X	Y		X	Y
I	2-NO_2	pyridine	*X*	2-NO_2	trimethylamine
II	3-NO_2	pyridine	*XI*	3-NO_2	trimethylamine
III	4-NO_2	pyridine	*XII*	4-NO_2	trimethylamine
IV	2-NO_2	α-picoline	*XIII*	2-NO_2	triethylamine
V	3-NO_2	α-picoline	*XIV*	3-NO_2	triethylamine
VI	4-NO_2	α-picoline	*XV*	4-NO_2	triethylamine
VII	2-NO_2	β-picoline	*XVI*	2-NO_2	tripropylamine
VIII	3-NO_2	β-picoline	*XVIII*	3-NO_2	tripropylamine
IX	4-NO_2	β-picoline	*XVIII*	4-NO_2	tripropylamine

* Part CXLVIII in the series Furan Derivatives; Part CXLVII: This Journal *45*, 910 (1980).

TABLE I

5-Nitrophenyl-2-furfuryl-N-onium Bromides *I*—*XVIII*

Compound	Formula (mol. weight)	M.p., °C[a] (yield, %)	Calculated/Found			
			% C	% H	% N	% Br
I	$C_{16}H_{13}BrN_2O_3$ (361·2)	156—157 (79)	53·20 53·02	3·62 3·58	7·75 7·83	22·12 21·92
II	$C_{16}H_{13}BrN_2O_3$ (361·2)	198—200 (67)	53·20 53·28	3·62 3·72	7·75 7·77	22·12 21·96
III	$C_{16}H_{13}BrN_2O_3$ (361·2)	221—223 (66)	53·20 53·32	3·62 3·72	7·75 7·82	22·12 22·03
IV	$C_{17}H_{15}BrN_2O_3$ (375·2)	206—208 (69)	54·42 54·58	4·02 4·10	7·46 7·62	21·29 21·48
V	$C_{17}H_{15}BrN_2O_3$ (375·2)	193—195 (68)	54·42 54·60	4·02 4·16	7·46 7·58	21·29 21·27
VI	$C_{17}H_{15}BrN_2O_3$ (375·2)	234—235 (71)	54·42 54·62	4·02 4·00	7·46 7·50	21·29 21·39
VII	$C_{17}H_{15}BrN_2O_3$ (375·2)	178—180 (77)	54·42 54·48	4·02 3·98	7·46 7·52	21·29 21·43
VIII	$C_{17}H_{15}BrN_2O_3$ (375·2)	179—182 (70)	54·42 54·48	4·02 3·82	7·46 7·54	21·29 21·47
IX	$C_{17}H_{15}BrN_2O_3$ (375·2)	253—255 (74)	54·42 54·52	4·02 4·16	7·46 7·50	21·29 21·52
X	$C_{14}H_{17}BrN_2O_3$ (341·2)	227—228 (73)	49·28 49·42	5·02 5·08	8·21 8·27	23·42 23·36
XI	$C_{14}H_{17}BrN_2O_3$ (341·2)	238—239 (68)	49·28 49·38	5·02 5·10	8·21 8·32	23·42 23·24
XII	$C_{14}H_{17}BrN_2O_3$ (341·2)	246—248 (80)	49·28 49·48	5·02 5·12	8·21 8·39	23·42 23·33
XIII	$C_{17}H_{23}BrN_2O_3$ (383·3)	189—190 (81)	53·27 53·47	6·05 6·11	7·31 7·57	20·84 20·53
XIV	$C_{17}H_{23}BrN_2O_3$ (383·3)	196—198 (80)	53·27 53·37	6·05 5·85	7·31 7·61	20·84 20·81
XV	$C_{17}H_{23}BrN_2O_3$ (383·3)	201—202 (82)	53·27 53·40	6·05 5·97	7·31 7·58	20·84 20·74
XVI	$C_{20}H_{29}BrN_2O_3$ (425·4)	110—114 (71)	56·47 56·52	6·87 6·90	6·58 6·68	18·78 18·65
XVII	$C_{20}H_{29}BrN_2O_3$ (425·4)	— (76)	56·47 56·54	6·87 7·00	6·58 6·72	18·78 18·63
XVIII	$C_{20}H_{29}BrN_2O_3$ (425·4)	197—199 (79)	56·47 56·60	6·87 7·12	6·58 6·64	18·78 18·60

[a] Crystallized from ethanol.

The above-mentioned compounds were especially prepared for studying their biological properties, since it is known that [5-(4-nitrophenyl)-2-furoylmethyl]pyridinium bromide[5] is pharmacologically active and reveals anti-inflammatory properties. The prepared compounds are analogous substances to that one without carbonyl group between the furan ring and methylene group.

Physical constants, IR, UV and ^{1}H-NMR spectral data are listed in Tables I – III. Stretching vibrations of methylene group attached to the furan ring are shifted to about 1400 cm^{-1} due to the quaternary nitrogen. Similarly, the chemical shift of protons is considerably influenced by the character of the embodied ammonium group. Attempts to measure the pK_a values of the synthesized compounds by a spectroscopic method failed. The low acidity of methylene group hydrogens is associated with a low stability of the formed C-anion; this fact can be rationalized by the inability to create a quinoid structure through the benzene–furan system. The pK_a values

TABLE II
IR and UV Spectra of 5-Nitrophenyl-2-furfuryl-N-onium Bromides (λ_{max} in nm, ν in cm^{-1})

Compound	ν(C=C)	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$	ν(Fu)[a]	λ_{max}(log ε)
I	1 633	1 534	1 357	1 035	259 (4·53)
II	1 630	1 526	1 350	1 030	266 (4·47)
					283 (4·42)
III	1 632	1 515	1 340	1 028	339 (4·31)
IV	1 630	1 535	1 365	1 033	265 (4·35)
V	1 622	1 530	1 350	1 027	269 (4·54)
VI	1 630	1 517	1 338	1 030	339 (4·37)
VII	1 632	1 530	1 365	1 020	262 (4·33)
VIII	1 626	1 526	1 356	1 027	270 (4·45)
IX	1 622	1 514	1 332	1 028	339 (4·37)
X	1 615	1 538	1 360	1 038	255 (4·36)
XI	1 608	1 533	1 350	1 040	272 (4·50)
					283 (4·50)
XII	1 608	1 520	1 340	1 030	336 (4·34)
XIII	1 615	1 542	1 368	1 032	255 (4·31)
XIV	1 620	1 530	1 350	1 015	275 (4·41)
XV	1 608	1 518	1 335	1 033	336 (4·33)
XVI	1 620	1 528	1 366	1 030	250 (4·30)
XVII	1 620	1 526	1 350	1 025	274 (4·41)
XVIII	1 605	1 516	1 334	1 035	336 (4·30)

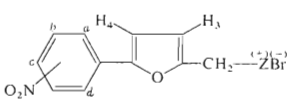
[a] Furan ring.

of analogous substances possessing the nitro group directly on the furan ring have already been reported[6]. This type of compounds[6] evidently forms a C-anion more easily due to the negative charge stabilization at nitro group through a quinoid structure.

The investigation of reactivity of the synthesized substances showed that the reaction with alkoxides and phenolates resulted in a replacement of anions, nevertheless the nucleophilic substitution of $-N(CH_3)_3$ group did not take place. The condensation reaction of 5-(4-nitrophenyl-2-furfuryl)pyridinium bromide with aromatic aldehydes in acetic anhydride under catalysis of sodium acetate did not proceed at temperatures up to 140°C.

TABLE III

^{1}H-NMR Spectra of Compounds *I*—*XVIII* (Chemical shifts, δ, ppm)



Compound[a]	CH_2	H_3	H_4	H_a	H_b	H_c	H_d
I	6·08	7·09	6·95		(7·55—8·00) m		
II	6·13	7·06	7·33	8·30	7·77	8·20	8·49
III	6·13	7·08	7·38	7·99	8·28		
IV	6·00	7·01	7·01		(7·55—8·00) m		
V	6·10	7·04	7·32	8·15	7·73	8·15	8·41
VI	6·09	7·36	7·36	7·93	8·27	—	—
VII	5·99	7·00	7·00		(7·55—8·00) m		
VIII	6·05	7·06	7·31	8·17	7·72	8·17	8·46
IX	6·03	7·05	7·34	7·96	8·28	—	—
X	4·75	7·08	7·01		(7·55—8·00) m		
XI	4·82	7·03	7·39	8·20	7·77	8·20	8·49
XII	4·82	7·05	7·41	7·97	8·30	—	—
XIII	4·64	7·07	7·11		(7·55—8·00) m		
XIV	4·71	7·07	7·38	8·20	7·77	8·20	8·48
XV	4·73	7·09	7·43	8·00	8·30	—	—
XVI	4·69	7·09	7·07		(7·55—8·00) m		
XVII	4·78	7·07	7·38	8·20	7·77	8·20	8·49
XVIII	4·78	7·10	7·44	7·98	8·32	—	—

[a] Compounds *I*—*IX* show signals of protons of the pyridine moiety. The spectra of other compounds reveal signals of alkyl group protons. The chemical shifts are not given.

EXPERIMENTAL

Infrared spectra of the respective substances (1 mg) in KBr (300 mg) were measured with a UR-20 (Zeiss, Jena) spectrophotometer calibrated against the polystyrene foil. Electron absorption spectra were taken with a UV-VIS (Zeiss, Jena) apparatus at a $2 \cdot 10^{-5}$M concentration in 1-cm cells in methanol at room temperature. ^{1}H-NMR spectra were recorded with a Tesla BS 487-C instrument operating at 80 MHz in hexadeuteriodimethyl sulfoxide with tetramethylsilane as an internal standard at 25°C.

5-Nitrophenyl-2-furfuryl-N-onium bromides I–XVIII: To a stirred solution of 5-nitrophenyl-2-furfuryl bromide (2·82 g, 10 mmol) in ether (25 ml) the respective tertiary amine (15 mmol) in ether (15 ml) was added at room temperature. The mixture was stirred for 12 h during which time the raw products separated; they were crystallized from ethanol.

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Translated by Z. Votický.