SYNTHESES BASED ON 5-ARYL-2-BROMOACETYLFURANS

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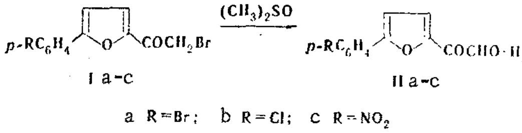
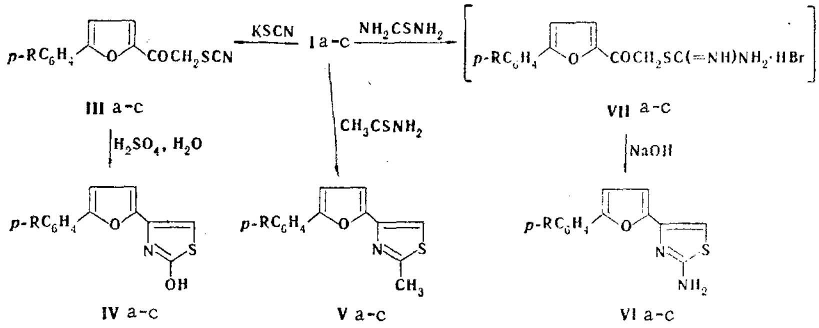
(5-Aryl-2-furyl)glyoxals and 4-(5-aryl-2-furyl)thiazoles were synthesized from 5-aryl-2-bromoacetylfurans.

Continuing our research on arylfurans, we have studied the possibility of using the 5-aryl-2-bromoacetylfurans (Ia-c) that we previously [1] synthesized for the synthesis of (5-aryl-2-furyl)glyoxals. (5-Aryl-2-furyl)glyoxal hydrates (IIa-c) were obtained in 60-90% yields by the action of dimethyl sulfoxide (DMSO) on I.



We also studied the possibility of using I in the synthesis of thiazole systems containing a 5-arylfuryl group in the 4 position of the thiazole ring. The reaction of alcohol solutions of bromo ketones (Ia-c) with potassium thiocyanate, thioacetamide, or thiourea gave, respectively, 2-hydroxy- (IVa-c), 2-methyl-(Va-c), or 2-aminothiazoles (VIa-c). 2-Amino-4-[5-(p-nitrophenyl)-2-furyl]thiazole (VIc) was obtained in acetone with preliminary isolation of isothiuronium hydrobromide VIIc.



EXPERIMENTAL

[5-(p-Bromophenyl)-2-furyl]glyoxal Hydrate (IIa). A solution of 1.7 g (3 mmole) of Ia in 7 ml of DMSO was heated at 50 deg for 4 h and allowed to stand overnight. The next day, 50 ml of water was added to the mixture, and the precipitated IIa was removed by filtration. Glyoxals IIb,c were similarly obtained (Table 1).

5-(p-Bromophenyl)-2-(thiocyanatoacetyl)furan (IIIa). A solution of 3.53 g (10 mmole) of Ia in 40 ml of alcohol was added to a solution of 1.54 g (14 mmole) of potassium thiocyanate in 5 ml of alcohol, and the mixture was heated for 1 h with stirring on a boiling-water bath, after which the precipitate was removed by

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TABLE 1. (5-Aryl-2-furyl)glyoxals (IIa-c)

Compound	R	mp, °C	R_f[a]	Empirical formula	Found %					Calc., %					IR spectrum		UV spectrum[b]		Yield, %
					C	H	halogen	N	S	C	H	halogen	N	S	$\nu_{C=O}$, cm^{-1}	ν_{OH}, cm^{-1}	λ_{max}, nm	lg ε	
IIa	Br	131—135		$C_{12}H_7BrO_3 \cdot H_2O$	48,5	3,0	26,5			48,5	3,0	26,9			1655 m 1680	3380—3420	330; 226	4,47; 4,13	65
Thiosemicarbazone		225—226		$C_{13}H_{10}BrN_3O_2S$	44,2	2,7		11,8	9,0	44,3	2,8		11,9	9,1					
IIb	Cl	126—127,5[c]	0,64[e]	$C_{12}H_7ClO_3 \cdot H_2O$	57,1	3,8	13,8			57,1	3,6	14,0			1643 m 1685	3380—3418	330; 228	4,41; 4,14	69
Thiosemicarbazone		229—230	0,66[f]	$C_{13}H_{10}ClN_3O_2S$	50,6	3,2	11,3		10,7	50,9	3,3	11,5		10,4					
IIc	NO_2	84—86[g]	0,35[h]	$C_{12}H_7NO_5 \cdot H_2O$	54,5	3,5		5,2		54,7	3,4		5,3		1600—1680 v.br	3280—3400	352; 222	4,58; 4,22	58
Dihydrate		146—148[d]		$C_{12}H_7NO_5 \cdot 2H_2O$	51,5	4,1		4,9		51,2	3,9		5,0						
Thiosemicarbazone		230—231		$C_{13}H_{10}N_4O_4S$	48,9	3,1		17,8	10,3	49,0	3,2		17,6	10,1					

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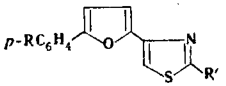
[a] Silufol, development in UV light. [b] In ethanol. [c] With decomposition. [d] From water. [e] Ether. [f] Ether–ethyl acetate (5 : 1). [g] From alcohol. [h] Ether–petroleum ether (4 : 1).

TABLE 2



Compound	R	R′	mp, °C	Empirical formula	Found, %					Calc., %					UV spectrum[a]		Yield, %
					C	H	halogen	N	S	C	H	halogen	N	S	λ_{max}, nm	lg ε	
IVa	Br	OH	248—249[b]	$C_{13}H_8BrNO_2S$	48,1	2,6	24,4	4,6	9,8	48,5	2,5	24,8	4,3	9,9	333; 261	4,46; 4,19	90
IVb	Cl	OH	249—252[b]	$C_{13}H_8ClNO_2S$	55,8	2,8	12,6		11,4	56,2	2,9	12,8		11,5	330; 256	4,42; 4,11	60
IVc	NO_2	OH	266—269[b]	$C_{13}H_8N_2O_4S$	53,8	2.8		9,8	11,1	54,2	2,8		9,7	11,1			75
Va	Br	CH_3	139—140[c]	$C_{14}H_{10}BrNOS$	52,1	3,2	25,2	4,4	9,8	52,5	3,1	24,9	4,4	10,0	328; 233	4,54; 4,11	70
Vb	Cl	CH_3	135,5—137[c]	$C_{14}H_{10}ClNOS$	60,7	3,5	12,9		11,7	61,0	3,6	12,9		11,6	324; 230	4,54; 4,23	68
Vc	NO_2	CH_3	174,5—177[c]	$C_{14}H_{10}N_2O_3S$	59,0	3,5		10,1	10,8	58,7	3,5		9,8	11,2	386; 272	4,37; 4,08	65
VIa	Br	NH_2	192,5—193,5[c]	$C_{13}H_9BrN_2OS$	48,6	2,8	24,5	8,6	9,6	48,6	2,8	8,7	24,9	10,0	335; 272	4,41; 4,27	90
VIb	Cl	NH_2	172—173[c]	$C_{13}H_9ClN_2OS$	56,2	3,3	12,9	9,9	11,8	56,4	3,3	12,8	10,1	11,6	334; 272	4,49; 4,41	65
VIc	NO_2	NH_2	228—230[c]	$C_{13}H_9N_3O_3S$	54,3	3,1		14,6	11,1	54,3	3,2		14,6	11,2	256; 300; 406	4,13; 4,12; 4,30	83

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[a] In ethanol. [b] From acetic acid. [c] From alcohol.

filtration to give 3.2 g (98%) of IIIa with mp 141-142 deg (from alcohol). Found: N 4.6; S 9.6%. $C_{13}H_8BrNO_2S$. Calculated: N 4.3; S 9.9%.

5-(p-Chlorophenyl)-2-(thiocyanatoacetyl)furan (IIIb). This compound was similarly obtained in 90% yield and had mp 134-135.5° (from alcohol) and R_f 0.6 (Al_2O_3, benzene, development with iodine). Found: C 56.1; H 2.9; Cl 12.4; S 11.8%. $C_{13}H_8ClNO_2S$. Calculated: C 56.2; H 2.9; Cl 12.8; S 11.6%.

5-(p-Nitrophenyl)-2-(thiocyanatoacetyl)furan (IIIc). This compound was similarly obtained in 75% yield and had mp 151.5-153° (from alcohol). Found: C 53.8; H 2.7; N 9.8; S 10.8%. $C_{13}H_8N_2O_4S$. Calculated: C 54.2; H 2.8; N 9.7; S 11.1%.

2-Hydroxy-4-[5-(p-bromophenyl)-2-furyl]thiazole (IVa). A mixture of 2.42 g (7 mmole of IIIa in 40 ml of glacial acetic acid, 1 ml of water, and 0.3 ml of concentrated sulfuric acid was heated with stirring for 30 min on a boiling-water bath, after which it was cooled, and IVa was removed by filtration. Hydroxythiazoles IVb,c (Table 2) were similarly obtained.

2-Methyl-4-[5-(p-bromophenyl)-2-furyl]thiazole (Va). A solution of 1 g (3 mmole of Ia and 0.18 g (3 mmole) of thioacetamide in 20 ml of alcohol was heated with stirring on a boiling-water bath for 1 h, after which it was cooled, and Va was removed by filtration. 2-Methylthiazoles Vb,c (Table 2) were similarly obtained.

2-Amino-4-[5-(p-bromophenyl)-2-furyl]thiazole (VIa). A mixture of 1 g (13 mmole) of thiourea in 3 ml of water and 4.34 g (13 mmole) of Ia in 50 ml of alcohol was heated for 2 h with stirring on a boiling-water bath, after which it was cooled and treated with 2.5 g of sodium hydroxide. The mixture was then poured into 100 ml of water, and the precipitated VIa was removed by filtration. 2-Aminothiazole VIb (Table 2) was similarly obtained.

S-{2-[5-(p-Nitrophenyl)-2-furyl]-1-oxoethyl}isothiuronium Hydrobromide (VIIc). A solution of 0.25 g (4 mmole) of thiourea in 15 ml of acetone was added to a solution of 1 g (3 mmole) of Ic in 4 ml of acetone, and the mixture was refluxed for 30 min. It was then cooled and filtered to give 1.1 g (89%) of hydrobromide VIIc, which had mp 308-310° (dec.) after washing with acetone. Found: C 40.3; H 2.9; Br 20.5; S 8.1%. $C_{13}H_{11}N_3O_4S \cdot HBr$. Calculated: C 40.4; H 3.1; Br 20.7; S 8.3%.

2-Amino-4-[5-(p-nitrophenyl)-2-furyl]thiazole (VIc). Ammonium hydroxide (20%) was added to a suspension of 1 g (2 mmole) of hydrobromide VIIc in 5 ml of water until the mixture was alkaline, and the precipitated VIc was removed by filtration (Table 2).

LITERATURE CITED

1. A. F. Oleinik, T. I. Vozyakova, G. A. Modnikova, and K. Yu. Novitskii, Khim. Geterotsikl. Soedin., 1448 (1972).