UDC 547.722 + 543.544

RESEARCHES ON FURANS

XLVI. Furethylation of Primary Amines*

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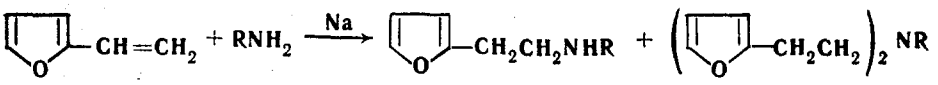
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 6, pp. 839–842, 1966

Reaction of 2-vinylfuran with primary amines gives mono- and di-[β-(2-furyl) amines, along with nitrogen compounds of undetermined structure.

We previously showed that it was possible to furylethylate secondary amines with 2-vinylfuran in the presence of sodium metal, high yields of [β-(2-furyl) ethyl] dialkylamines being obtained [1].

The present paper studies the reaction of 2-vinylfuran (I) with primary amines (methyl-, ethyl-, isopropyl-, and n-butylamine, also aniline) (IIa-e), and it is shown that the products are mixtures of secondary (IIIa-e) and tertiary (IVa-d) [β-(2-furyl) ethyl] amines:



I IIa-e IIIa-e IVa-d

R = a CH_3—; b C_2H_5—; c *i*-C_3H_7—; d *n*-C_4H_9—; e C_6H_5—

The amines were isolated from the reaction products by careful fractional distillation, followed by column chromatography with alumina using benzene. The homogeneities of the amines obtained were proved by preparing crystalline derivatives, as well as by thin-layer chromatography on alumina.

The sole product of reaction of 2-vinylfuran with aniline is N-[β-(2-furyl) ethyl] aniline, obtained in high (85%) yield. Reaction of 2-vinylfuran with methylamine gives, in addition to secondary and tertiary amines (IIIa and IVa), high-boiling amines of undetermined structure, the analytical data corresponding to compounds formed by addition of 1 mole methylamine to 3 moles of vinylfuran. High-boiling amine is also formed in the reaction of 2-vinylfuran with isopropylamine. At present we are investigating the structures of these compounds.

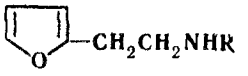
Experimental

Reaction of 2-vinylfuran with methylamine. A mixture of 30 ml $MeNH_2$ (IIa), 10 ml dry ether, 1 g finely-sliced sodium was cooled to −15° C, stirred, and 5 g 2-vinylfuran (I) added dropwise. The reaction mixture turned dark-red. The cooling bath was removed, so that the products warmed up to room temperature, when they were left for 12 hr. 10 ml MeOH was added to destroy unchanged sodium, then 50 ml water was added, the mixture saturated with solid KOH, and extracted with ether. The extract was dried over KOH, the ether and unreacted 2-vinyl furan distilled off, when there was obtained 0.4 g (3%) methyl [β-(2-furyl) ethyl] amine (IIIa), bp 69–70° C (20 mm), n_D^{25} 1.4740 (the literature gives bp 69–70°C (20 mm), n_D^{26} 1.4720). The derivative formed with phenylisothiocyanate has mp 69° C (ex EtOH) (the literature gives mp 69–70° C). Further distillation gives 1.4 g (24%) methyldi [β-(2-furyl) ethyl]- amine (IVa), and 0.5 g high-boiling fraction (bp 169–170° C (3 mm)).

The other amines were reacted similarly, using mole ratios 2-vinylfuran: amine: Na = 2.5:5:1. Temperatures and reaction times were: ethylamine 20° C, 16 hr; isopropylamine 35° C, 2 hr; n-butylamine 80° C, 4 hr. When the heating of the reaction mixture was finished, the latter was kept at room temperature for 12 hr.

Tables 1 and 2 give the properties of the amines and their derivatives.

* For Part XLV see [3].

Alkyl (aryl)- [β-(2-furyl) ethyl] amines 

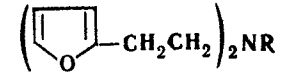
Compound No.	R	Bp, °C (pressure mm)	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calculated	Mp, °C	Formula	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N	Yield, %
IIIb*	C_2H_5	60 (7)	1.4700	0.9476	40.99	41.25		$C_8H_{13}NO$	69.04 68.89	9.51 9.39	9.81 9.75	69.03	9.41	10.06	19
Hydrochloride							154	$C_8H_{14}ClNO$	54.63 54.77	7.97 8.27		54.70	8.03		
Derivative with C_6H_5NCO							95	$C_{15}H_{18}N_2O_2$	70.13 70.36	7.30 7.24		69.74	7.02		
IIIc	i-C_3H_7	62—63 (6)	1.4655	0.9240	45.85	45.86		$C_9H_{15}NO$	70.32 70.30	10.13 10.26	8.79 8.70	70.54	9.87	9.14	13
Derivative with C_6H_5NCO							105	$C_{16}H_{20}N_2O_2$	70.84 70.69	7.56 7.52		70.56	7.40		
Methiodide**							234	$C_{11}H_{20}JNO$	42.81 42.88	6.68 6.90	4.69	42.73	6.52	4.53	
IIId***	n-C_4H_9	89 (6)	1.4670	0.9238	50.24	50.49		$C_{10}H_{17}NO$	71.51 71.52	10.24 10.41	7.73 7.87	71.81	10.24	8.37	10
Hydrochloride							246—247	$C_{10}H_{18}ClNO$	58.79 59.00	8.92 9.01		58.95	8.90		
IIIe	C_6H_5	123 (1)	1.5732	1.0788	57.13	56.13		$C_{12}H_{13}NO$	76.99 77.13	7.30 7.18		76.98	7.00		85****
Derivative with C_6H_5NCO							97	$C_{19}H_{18}N_2O_2$	74.39 74.47	5.66 5.85	8.95 8.81	74.49	5.92	9.14	

* Purified by recrystallizing the hydrochloride, followed by recovery of the base.

** Dimethylisopropyl [β-(2-furyl) ethyl] ammonium iodide.

*** Purified by chromatographing on an alumina column.

**** On the aniline reacted.

Alkyldi[β-(2-furyl) ethyl] amines 

Compound No.	R	Bp, °C (pressure mm)	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calculated	Mp, °C	Formula	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N	Yield, %
IVa	CH_3*	122—123 (2—3)	1.5030	1.0373	62.49	63.19		$C_{13}H_{17}NO_2$	70.89 70.99	7.75 7.76	6.07 6.09	71,20	7.81	6.38	24
Picrate							103,5	$C_{19}H_{20}N_4O_9$	51.01	4.47	11.96 12.13	50.89	4.49	12.48	
Methiodide							110	$C_{14}H_{20}JNO_2$	46.45 46.49	5.55 5.41	4.55 4.26	46.55	5.58	3.88	
IVb	C_2H_5**	116—117 (2)	1.5015	1.0219	67.32	67.81		$C_{14}H_{19}NO_2$	71.95 72.10	8.29 8.14	6.36 6.46	72.07	8.21	5.99	40
Picrate							114	$C_{20}H_{22}N_4O_9$	52.01 51.99	4.90 4.97		51.95	4.80		
IVc	*i*-C_3H_7***	114—115 (1)	1.4983	1.0149	71.48	72.43		$C_{15}H_{21}NO_2$	72.41 72.26	8.79 8.74	5.93 6.02	72.85	8.56	5.66	24
Picrate							102	$C_{21}H_{24}N_4O_9$			12.02 11.88			11.76	
IVd	*n*-C_4H_9**	140—142 (3)	1.5008	0.9832	78.17	77.04		$C_{16}H_{23}NO_2$	73.12 73.11	9.51 9.29		73.52	8.87		38
Picrolonate							110	$C_{26}H_{31}N_5O$			13.45 13.61			13.32	

*In addition to IIIa and IVa, there was obtained a fraction bp 169°–170° C (3 mm), n_D^{20} 1.5182; d_4^{20} 1.0733. Found: C 72.81, 72.61; H 7.44, 7.41; N 4.15, 4.37%. Calculated for $3C_6H_6O + CH_3NH_2$. C 72.82; H 7.39; N 4.47%.

**Purified by column chromatography on alumina.

***In addition to IIIc and IVc, there is obtained a fraction Vc, bp 147°–152° C (1 mm), mp 32.5° C (ex dry ether + heptane).

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3 May 1966

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