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Abstract

Full Text

Chemistry

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NITRATION OF CERTAIN α,β-UNSATURATED ALDEHYDES AND KETONES OF THE FURAN SERIES

In our previous communications we presented the results of a study of the condensation reactions of 5-nitrofurfural with acetaldehyde ([1]) and the nitration of monofurfurylideneacetone (I) ([2]).

The second of the indicated methods for obtaining nitrofurans has a number of advantages over the method of condensing 5-nitrofurfural and its derivatives with carbonyl-containing compounds. It is therefore of definite interest to investigate the possibility of synthesizing substituted α,β-unsaturated aldehydes and ketones of the 5-nitrofuran series by nitration of the corresponding furan compounds.

Despite individual attempts to carry out such a route of synthesis, until recently it had not been successful. Thus, Sasaki ([3]) reports unsuccessful experiments on the nitration of β-(furyl-2)-acrolein (II) and monofurfurylideneacetone (I), while Saikachi et al. ([4]), in an attempt to nitrate α-methyl-β-(furyl-2)-acrolein (III) with acetyl nitrate, obtained only resinous condensation products of the starting substances.

We succeeded in carrying out the nitration of β-(furyl-2)-acrolein (II) and of several of its α-alkyl (III–VI) and α-alkoxymethyl derivatives (VII and VIII) (see Table 1), using nitration conditions different from those employed by the previous authors. These consist, first, in conducting the reaction at low temperature (from -25 to -30°) and, second, in adding small amounts of concentrated sulfuric acid as a catalyst. The presence of H_2SO_4 apparently so increases the concentration and the rate of formation of nitronium ions (NO_2^+) in the solution of acetic anhydride ([5–9]) that the nitration reaction predominates over side reactions.

Table 1 shows the yields and properties of the α,β-unsaturated aldehydes of the nitrofuran series (X–XXIII) synthesized by the indicated route.

The proposed mechanism of the nitration reaction of α,β-unsaturated aldehydes of the furan series is shown in the following scheme:

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$$\text{furyl-CH=CRCHO}$$

$$\xrightarrow[(CH_3CO)_2O]{H_2SO_4}$$

$$\text{furyl-CH=CRCH(OCOCH}_3)_2$$

$$NO_2^+ + CH_3COO^-$$

$$\text{at } 0 \text{ to } -5^\circ \qquad \text{at } -25 \text{ to } -30^\circ$$

$$[O_2N\text{-furyl-CHCRCH(OCOCH}_3)_2]^+ \; CH_3COO^- \longrightarrow \text{Polymers}$$

$$[O_2N\text{-furyl-CH=CRCH(OCOCH}_3)_2]^+ \; CH_3COO^-$$

$$\xrightarrow{\text{“B”}} \; +H_2O$$

$$[O_2N\text{-furyl-CH=CRCH(OCOCH}_3)_2]^+ \; OH^-$$

$$\longrightarrow -H_2O$$

$$O_2N\text{-furyl-CH=CRCH(OCOCH}_3)_2$$

$R = H;\ CH_3;\ C_2H_5;\ \text{iso-}C_3H_7;\ C_5H_{11};\ CH_2OCH_3;\ CH_2OC_2H_5,\ \text{etc.}$

Table 1

Nitration products and their derivatives

Starting compound	Structural formula of the product	M.p., °C	Yield, %	C, % found	C, % calcd.	H, % found	H, % calcd.	N, % found	N, % calcd.	Ultraviolet absorption spectra λ, mμ ($\varepsilon \cdot 10^{-3}$)
R_1=H, R_2=CH$_3$ (II)	(X)	97–98	25–30*	48,93	49,03	4,17	4,12	5,22	5,20	342 (13,00); 222 (13,10)
R_1=H, R_2=C$_2$H$_5$ (II)	(XI)	117–118	90	50,48	50,31	3,10	3,02	8,45	8,38	343 (16,20); 237 (11,80)
R_1=H, R_2=NHCOCH$_2$NH$_2$ (II)	(XII)	192 (decomp.)	92	–	–	–	–	25,01	24,99	392 (23,90); 292 (22,80)

Starting compound	Structural formula of the product (Y = [illegible])	M.p., °C	Yield, %	C, % found	C, % calcd.	H, % found	H, % calcd.	N, % found	N, % calcd.	Ultraviolet absorption spectra λ, mμ (ε · 10⁻³)
$R_1=CH_3$; $R_2=H$ (III)	$YCH(OCOCH_3)_2$ (XIII)	113–114	42*	50,81	50,87	4,45	4,63	5,21	4,95	350 (16,86); 231 (19,60)
$R_1=CH_3$; $R_2=H$ (III)	$YCHO$ (XIV)	94,5–95,5	94	53,23	53,04	4,10	3,90	7,69	7,73	347 (24,40); 284 (8,30); 244 (22,66)
$R_1=CH_3$; $R_2=H$ (III)	$YCH=NNHCONH_2$ (XV)	240 decomp.	93	45,46	45,38	4,37	4,23	23,31	23,52	395 (24,00); 292 (19,60)
$R_1=C_2H_5$; $R_2=H$ (IV)	$YCH(OCOCH_3)_2$ (XVI)	100–101	21*	52,70	52,52	4,93	5,09	4,97	5,71	350 (16,50); 232 (18,80)
$R_1=C_2H_5$; $R_2=H$ (IV)	$YCHO$ (XVII)	74–75	92	55,51	55,38	4,57	4,65	7,38	7,18	350 (16,50); 285 (5,80); 245 (9,20)
$R_1=C_2H_5$; $R_2=H$ (IV)	$YCH=NNHCONH_2$ (XVIII)	219–220 (decomp.)	91	–	–	–	–	22,21	22,56	
R_1-iso-C_3H_7; $R_2=H$ (V)	$YCH=NNHCONH_2$ (XIX)	214 (decomp.)	17*	49,40	49,62	5,32	5,30	21,43	21,04	390 (16,70); 292 (16,20); 224 (9,56)

Starting compound $HC=C(R_1)-O-C(R_2)=CH-CH=O$ (?)	Structural formula of the product $HC=C(-O-C(NO_2)=CH-)...CH=Y$ (?)	M.p., °C	Yield, %	C, % found	C, % calcd.	H, % found	H, % calcd.	N, % found	N, % calcd.	Ultraviolet absorption spectra λ, mμ ($\varepsilon \cdot 10^{-3}$)
$R_1=C_5H_{11}$, $R_2=H$ (VI)	$Y=NNHCOCH_2CN$ (XX)	162–163	37*	–	–	-	–	17,96	17,60	385 (24,00); 284 (29,40)
$R_1=CH_3$, $R_2=H$ (VII)	[illegible] (XXI)	118–119	17*	51,54	51,19	4,36	4,30	6,50	6,63	345 (14,10); 243 (7,80)
$R_1=CH_3$, $R_2=H$ (VII)	$Y=NNHCONH_2$ (XXII)	222–223 (decomp.)	95	44,89	44,78	4,60	4,51	21,24	20,89	393 (21,40); 292 (18,70)
$R_1=CH_3$, $R_2=CH_3$ (VIII)	$Y=NNHCONH_2$ (XXIII)	219–220 (decomp.)	17*	-	–	–	–	19,62	12,85	388 (20,60); 293 (20,00);247 (10,04); 224 (11,72)
$R_1=H$, $R_2=C(CH_3)_3$ (IX)	[illegible] (XXIV)	108–109	34*	59,10	59,19	5,80	5,87	6,33	6,28	347 (21,10); 243 (12,00)

* Yield at the nitration stage.

The initial elementary act is evidently the formation of the oxonium cation B, which exists in the acetic anhydride solution.

When the reaction mixture is poured, after completion of nitration, into ice water, an oily intermediate product first separates; upon further stirring with water it is converted into the final solid nitro product.

As is known, in accordance with the view of Freer and Johnson ([10]), Clauson-Kaas and Fakstorp ([11]), and others ([12,13]), analogous intermediate products formed in the nitration of acidophobic furans are assigned the structure of 2-

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acetoxy-5-nitro-2,5-dihydrofurans (A). Under the action of alkaline agents, the latter readily eliminate acetic acid. However, such a structure (A) is unable to explain the ease, observed in our case, with which the so-called "intermediate" is converted into the final nitro product by the action of water alone.

In the nitration of the α,β-unsaturated aldehydes II–VIII mentioned in Table 1, the structure of the oily intermediate products formed apparently corresponds more closely to the structure of the oxonium compound $B^{+}CH_3COO^{-}$ in the scheme given. Thus, in the present case it is possible once again to demonstrate the existence of labile intermediate oxonium

Table 2

Compound *	m.p., °C	N, % found	N, % calc.
$RCH=C(CH_3)CH=NNHCO{-}C_5H_4N$ ** (XXV)	236–7 (decomp.)	19.02	18.66
$RCH=C(CH_3)CH=NNHCOCH_2CN$ (XXVI)	243–4 (decomp.)	21.54	21.37
$RCH=C(CH_3)CH=NZ$ (XXVII)	244–6 (decomp.)	15.55	15.84
$RCH=C(C_2H_5)CH=NNHCOCH_2CN$ (XXVIII)	219 (decomp.)	20.40	20.28
$RCH=C(C_2H_5)CH=NZ$ (XXIX)	220–221 (decomp.)	15.01	15.05
$RCH=C(\text{iso-}C_3H_7)CH=NNHCSNH_2$ (XXX)	185–4 (decomp.)	19.66	19.85
$RCH=C(\text{iso-}C_3H_7)CH=NNHCOCH_2CN$ (XXXI)	185–6 (decomp.)	18.94	19.30
$RCH=C(\text{iso-}C_3H_7)CH=NX$ (XXXII)	229–230 (decomp.)	18.29	18.29

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Compound *	m.p., °C	N, % found	N, % calc.
$RCH=C(C_5H_{11})CH=NNH{-}C_6H_3(NO_2)_2$ (XXXIII)	159–160	16.84	16.78
$RCH=C(CH_2OCH_3)CH=NNHCSNH_2$ (XXXIV)	186 (decomp.)	19.66	19.71
$RCH=C(CH_2OCH_3)CH=NNHCO{-}C_5H_4N$ ** (XXXV)	190 (decomp.)	17.18	16.96
$RCH=C(CH_2OCH_3)CH=NNHCOCH_2CN$ (XXXVI)	188 (decomp.)	18.89	19.17
$RCH=C(CH_2OCH_3)CH=NOH$ (XXXVII)	139–140	12.48	12.39
$RCH=C(CH_2OCH_3)CH=NX$ (XXXVIII)	decomp. >250	17.90	18.18
$RCH=C(CH_2OCH_3)CH=NZ$ (XXXIX)	175–7 (decomp.)	14.29	14.24
$RCH=C(CH_2OC_2H_5)CH=NNHCOCH_2CN$ (XL)	192–4 (decomp.)	18.33	18.30
$RCH=C(CH_2OC_2H_5)CH=NX$ (XLI)	232–5 (decomp.)	17.11	17.39
$RCH=C(CH_2OC_2H_5)CH=NZ$ (XLII)	176–7 (decomp.)	13.50	13.59
$RCH=CHC(CH_3)=NNHCSNH_2$ (XLIII)	210 (decomp.)	22.20	22.04

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Compound *	m.p., °C	N, % found	N, % calc.
$RCH=CHC(CH_3)=NNHCOCH_2CN$ (XLIV)	225 (decomp.)	21.53	21.37
$RCH=CHC(CH_3)=NOH$ (XLV)	175–7 (decomp.)	14.43	14.28
$RCH=CHC(CH_3)=NNHCO–C_5H_4N$ ** (XLVI)	225 (decomp.)	18.74	18.66
$RCH=CHC(CH_3)=NNHCOR$ (XLVII)	235–6 (decomp.)	16.62	16.77
$RCH=CHC(CH_3)=NNHCO–C=CH–O–CH=CBr$ (XLVIII)	215–7 (decomp.)	11.75	11.42
$RCH=CHC(CH_3)=N–N=C(CH_3)CH=CHR$ (XLIX)	188–9	15.65	15.64
$RCH=CHC(CH_3)=NN(CH_2CH_2OH)COCONH_2$ (L)	181–5 (decomp.)	18.15	18.06
$RCH=CHC(CH_3)=NNH–C_6H_3(NO_2)_2$ (LI)	257 (decomp.)	19.06	19.38

* $R = O_2N$-furyl-, X = a cyclic residue containing $–N–CH_2$, $–CO$, and $–NH$; Z = a cyclic residue containing $–N–CO–O$ and $–CH_2$, as shown in the original structural formulas.

** C_5H_4N = pyridyl-4.

compounds upon nitration of acidophobic furans, the possible existence of which had previously led one of us to express certain assumptions ([5],[6]).

In conclusion it should be noted that it was not possible to carry out, by the indicated route, an equally successful nitration of aldehydes and ketones of the furan series containing two or more conjugated double bonds in the side chain, for

example, 5-(furyl-2)-pentadien-2,4-al-1; 1-(furyl-2)-hexadien-1,3-one-5; 1,5-bis-(furyl-2)-pentadien-1,4-one-3 and 1,9-bis-(furyl-2)-nonatetraen-1,3,6,8-one-5.

On the other hand, the nitration of 4,4-dimethyl-1-(furyl-2)-penten-1-one-3 proceeds comparatively smoothly; this has been carried out by us for the first time (see Table 1, IX).

Table 2 gives data on synthesized polynuclear derivatives of α,β-unsaturated nitrofuran aldehydes and ketones at the carbonyl group (XXV–LI).

The antibacterial, antitubercular and fungistatic properties of these compounds will be described in more detail in one of the following communications.

Experimental Part

Nitration of α,β-unsaturated aldehydes (see Table 1). To the nitrating mixture, prepared from 266 g of acetic anhydride, 9.4 g of purified nitric acid (^{14}) (sp. gr. 1.51) and 0.5 g of sulfuric acid (sp. gr. 1.84), a solution of 0.1 mole of (furyl-2)-alkenal II–VIII in 40 ml of acetic anhydride was added dropwise with stirring over the course of an hour at −30°. Thereafter the nitration product was isolated by pouring the reaction mixture into 500 g of ice with 500 ml of water and stirring for 3-4 h. The final crystalline diacetates of α,β-unsaturated 5-nitrofuryl-2-alkenals X, XIII and XVI were purified by recrystallization from alcohol or tetrahydrofuran. Conversion of the diacetates X, XIII and XVI into the corresponding aldehydes XI, XIV and XVII was carried out by heating with 20% H_2SO_4 at 90-95° for 10 min.

In the nitration of α,β-unsaturated furan aldehydes V–VIII, the corresponding final nitro products could not be isolated as crystalline compounds. Hydrolysis of these substances with 20% H_2SO_4 at 90-95° for 10 min gave, in the case of VII, the crystalline aldehyde XXI, while for the others the corresponding hydrazones XIX, XX, XXII and XXIII were obtained; their structures were proved by elemental analysis and by determination of the ultraviolet absorption spectra. The absorption maxima of the latter completely coincide with the maxima of analogous derivatives of known α,β-unsaturated 5-nitrofuryl-2-alkenals (^{6}).

Nitration of 4,4-dimethyl-1-(furyl-2)-penten-1-one-3 (XI) was carried out by the method described by us previously for the nitration of monofurfurylideneacetone (I) (^{2}).

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