REACTION OF UNSATURATED ALDEHYDES WITH ACETONE CYANOHYDRIN IN THE PRESENCE OF DIETHYLAMINE

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As shown previously [1-3], the direction of the reaction of acetone cyanohydrin and secondary amines with α,β-unsaturated aldehydes depends on the structure of the reactants. The present work is a continuation of our investigation of the relationships in this reaction with diethylamine.

It has been shown that crotonaldehyde and 3,3-dimethylacrylaldehyde react smoothly with equimolar quantities of acetone cyanohydrin and diethylamine, giving the corresponding aminonitriles (I), while retaining the trans configuration for (Ia). The reaction with sorbaldehyde proceeds analogously

$$R^1R^2C{=}CH{-}CHO + (CH_3)_2C(OH)CN + Et_2NH \rightarrow R^1R^2C{=}CH{-}CH(CN)(NEt_2) \quad (I)$$

$R^1 = H,\ R^2 = CH_3$ (a); $R^1 = R^2 = CH_3$ (b); $R^1 = H,\ R^2 = CH{=}CH{-}CH_3$ (c).

Acrolein and 5,5)dichloro-2,4-pentadienal under the same reaction conditions, or even at 0-10°C, will polymerize. In the analogous reaction of trans-octatriene-2,4,6-al, there is a shift of the double bond to the position conjugated with the CN group, with the formation of the cyanenamine (II)

$$CH_3(CH{=}CH)_3CHO + (CH_3)_2C(OH)CN \rightarrow CH_3(CH{=}CH)_2CH_2CH{=}C(CN)(NEt_2) \quad (II)$$

Judging by the presence of two absorption bands of the CN group at 2210 and 2225 cm^{-1} in the IR spectrum of (II), and also by data on the stereochemistry of the analogous reaction of cinnamaldehyde [1], the product (II) that we obtained is a mixture of cis and trans isomers.

The structure of the aminonitriles (Ia-c) and the cyanenamine (II) was confirmed by IR, PMR, and mass spectra and by elemental analyses. The yields and characteristics of the compounds that were obtained are listed in Table 1.

A study of the interaction of α,β-unsaturated aldehydes with a fourfold excess of acetone cyanohydrin in the presence of a molar quantity of diethylamine showed that at elevated temperatures (80-90°C), crotonaldehyde and 3,3-dimethylacrylaldehyde form saturated derivatives of cyanamines (IIIa-b) as a result of addition of HCN at the double bond

$$R^1R^2C{=}CH{-}CHO + Me_2C(OH)CN \rightarrow R^1R^2C(CN){-}CH_2{-}CH(CN)(NEt_2) \quad (III)$$

$R^1 = H,\ R^2 = CH_3$ (a); $R^1 = R^2 = CH_3$ (b); $R^1 = H,\ R^2 = CH = CHPh$ (c); $R^1 = CH_3$, $R^2 = (CH_3)_2C = CHCH_2CH_2$ (d).

The products formed in the reaction with 5-phenyl-2,4-pentadiene decomposed when they were fractionated under vacuum (GLC). Separation of these products in a column with Al_2O_3 (elution with benzene) gave two fractions, designated A and B. According to GLC data, fraction A is a complex mixture of products with very similar retention times, whereas fraction B is an individual product (IIIc). In the IR spectrum of this product we find the following absorption bands: 2220 (nonconjugated CN group), 1635 (C=C stretching vibrations), and 970 cm^{-1} (trans CH=CH deformation vibrations). In the PMR spectrum (Table 1) we find signals of protons

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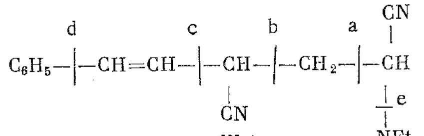
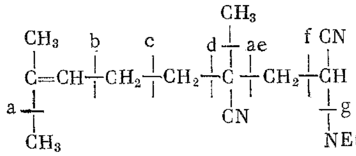
TABLE 1. Products from Reaction of Unsaturated Aldehydes with Acetone Cyanohydrin in the Presence of Diethylamine, and the Characteristics of These Products

Compound	Yield, %	T, °C (time, h)	bp, °C (p, mm Hg)	n_D^{20}	Empirical formula	Found/Calculated, %: C	H	N	PMR spectrum (δ, ppm; J, Hz)	IR spectrum (νCN, cm⁻¹)
(Ia)	44	20(24)	60–65(0,3)	1,4470	$C_9H_{16}N_2$	71,00 / 71,05	10,48 / 10,52	18,78 / 18,42	1,06 t (6H, 2CH₃ amine, J=7), 1,79 d (3H, CH₃, J=7), 2,20–2,86 m(4H, 2CH₂ amine), 4,23 m (1H, CH(CN)NEt₂), 5,33 m (1H, CH=), 6,00 m (1H, CH=)	2230
(Ib)	67	20(24)	60 (0,3)	1,4565	$C_{10}H_{18}N_2$	71,96 / 72,24	10,92 / 10,91	16,90 / 16,85	1,02 t (6H, 2CH₃ amine., J=7), 1,67 s, 1,73 s (6H, 2CH₃), 2,03–3,01 m (4H, 2CH₂ amine.), 4,20 d (1H, CH(CN)NEt₂, J=7), 5,12–5,17 m (1H, CH=)	2230
(Ic)	61	20(24)	78,5–81 (0,45)	1,4895	$C_{11}H_{18}N_2$	73,80 / 74,17	9,98 / 10,11	15,80 / 15,72	1,00 t (6H, 2CH₃ amine, J=7), 1,73 d (3H, CH₃, J=7), 2,10–2,82 m (4H, 2CH₂ amine), 4,13–4,30 m (1H, CH(CN)NEt₂), 5,20–6,80 m (4H, CH=CHCH=CH)	2230
(II)	60	20(24)	99–102 (0,4)	1,5160	$C_{13}H_{20}N_2$	76,42 / 76,42	9,92 / 9,87	13,78 / 13,71	1,04 t (6H, 2CH₃ amine., J=7), 1,68 d (3H, CH₃, J=7), 2,58–3,35 m (6H, 2CH₂ amine, CH₂), 4,88 t (1H, CH=C, J=7), 5,14–6,36 m (4H, CH=CHCH=CH)	2210 w 2225 s
(IIIa)	50	80(1)	100–102 (0,4)	1,4480	$C_{10}H_{17}N_3$	66,89 / 66,96	9,74 / 9,57	23,45 / 23,44	1,10 t (6H, 2CH₃ amine, J=7), 1,33 d (3H, CH₃, J=7); 1,80–2,22 m (2H, CH₂), 2,33–3,17 m (5H, 2CH₂ amine, CH(CN)), 3,62–4,00 m (1H, CH(CN)NEt₂)	2250
(IIIb)	65	80(1)	84–86 (0,3)	1,4530	$C_{11}H_{19}N_3$	68,10 / 68,35	10,05 / 9,91	21,72 / 21,74	1,07 t (6H, 2CH₃ amine J=7), 1,32 s, 1,37 s (6H, 2CH₃), 1,80–2,00 m (2H, CH₂), 2,12–2,90 m (4H, 2CH₂ amine.), 3,72–3,95 m (1H, CH(CN)NEt₂)	2245
(IIIc)	19	95(2)			$C_{17}H_{21}N_3$	76,50 / 76,37	7,89 / 7,92	15,54 / 15,72	1,03 t (6H, 2CH₃ amine J=7), 2,60–3,14 m (6H, 2CH₂ amine CH₂), 3,44–3,96 m (2H, CH(CN), CH(CN)NEt₂), 5,75–7,02 m (2H, CH=CH), 7,15 s (5H, C₆H₅)	2220
(IIId)	90	80(4)		1,4680	$C_{16}H_{27}N_3$	73,14 / 73,51	10,34 / 10,41	16,00 / 16,08	1,10 t (6H, 2CH₃ amine J=7), 1,39 s, 1,43 s (3H, CH₃), 1,61 s, 1,66 s (6H, (CH₃)₂C=), 1,66–2,64 m (10H, CH₂CH₂, 2CH₂ amine CH₂), 3,70–4,00 m (1H, CH(CN)NEt₂), 4,98–5,13 m (1H, CH=)	2240
(IV)		90(1,5)			$C_{11}H_{18}N_2$	73,18 / 74,11	10,43 / 10,18	14,30 / 15,71	0,95–1,00 m (6H, 2CH₃ amine; 1,54–1,60 m (3H, CH₃), 2,02–3,42 m (6H, 2CH₂ amine CH₂), 4,74–6,36 m (3H, CH=CH, CH=C)	2215 m 2230 w

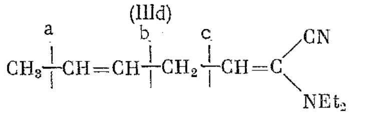
TABLE 2. Mass Spectra of Cyanamines (IIIc, d) and Cyanenamine (IV)



(IIIc)



(IIId)



(IV)

(IIIc)			(IIId)			(IV)		
m/z	I, %	Rupture or ion	m/z	I, %	Rupture or ion	m/z	I, %	Rupture or ion
267	2,0	M^+	261	3,4	M^+	178	21,6	M^+
240	13,3	M^+–HCN	246	3,0	a	169	26,0	
225	11,1		178	1,5	d	163	70,5	a
176	11,1		151	15,0	m/z 178 – HCN	149	21,6	
149	17,8		136	3,8	e	136	12,3	m/z 163 – HCN
131	35,5		125	10,8	e	123	37,0	c
111	100,0	a	112	30,0		121	40,0	
104	17,8		111	100,0	f	109	27,7	
103	22,5	c	109	18,4		108	24,6	
98	8,9		98	25,5	$Et_2\overset{+}{N}C_2H_2$	107	24,6	
91	28,9		84	25,0		100	40,0	
89	35,5		83	29,3	d	94	27,7	
77	22,2	d	81	18,0		82	30,8	
72	11,1	e	73	3,0		81	40,0	
71	13,3		72	16,0	g	79	27,7	
70	13,3		70	18,4		72	52,0	
69	15,5		69	30,0	c	69	35,4	
59	40,0		58	20,0	$Et\overset{+}{N}H{=}CH_2$	68	32,3	
58	40,0		56	81,0		67	38,5	
57	24,4		55	51,0	b	58	100,0	
56	40,0		51	40,5		56	43,0	
55	26,7		41	97,0		55	77,0	c
125	4,5	b				54	34,0	
						42	34,0	
						41	49,0	b

belonging to the fragments Et_2N, C_6H_5, and CH=CH, and also signals in the 2.6–3.14 ppm region (probably CH_2CH_3 and CH_2) and in the 3.44–3.96 ppm region (probably CHCN). According to the results from elemental analysis, this product has the empirical formula $C_{17}H_{21}N_3$. On the basis of these data, we have assigned to this product the structure 5-phenyl-1-diethylamino-1,3-dicyano-4-pentene (IIIc); this structure does not contradict the mass spectrum of the product (Table 2).

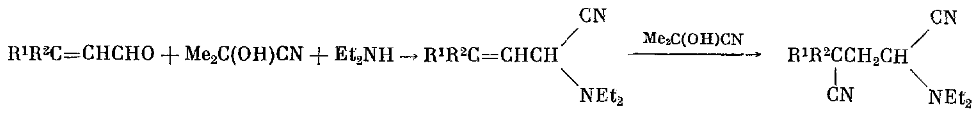
Citral reacts with an equimolar quantity of diethylamine and excess acetone cyanohydrin at 80°C, giving an oily, dark brown product. In the IR spectrum of this product there is an absorption band at 2240 cm^{-1} (nonconjugated CN group), and in its PMR spectrum (in $CDCl_3$) there are signals with chemical shifts that are characteristic for NEt_2, CH_3, $(CH_3)_2C=$, $(CH_3)_2C=CH$, and CH(CN)NEt_2 (Table 1). The elemental analysis of the product corresponds to the empirical formula $C_{16}H_{27}N_3$. On the basis of these data, the product can be assigned the structure of 1-diethylamino-3,7-dimethyl-1,3-dicyano-6-octene (IIId). Its mass spectrum does not contradict the structure (IIId) (Table 2).

Previously [3], by distillation of the mixture obtained in the reaction of citral with equimolar quantities of diethylamine and acetone cyanohydrin, we recovered a mixture of various nitriles, among which there was no (IIId); this means that (IIId) is not obtained in the reaction with equimolar quantities.

Sorbaldehyde reacts with an equimolar quantity of diethylamine and excess acetone cyanohydrin; however, judging by TLC and GLC data, it gives a complex mixture of products that cannot be separated by fractional distillation. However, on a plate with Al_2O_3 (elution with a 3/2 mixture of ether and hexane), we were able to recover from the reaction mixture a fraction in which the main product is apparently 1-diethylamino-1-cyano-1,4-hexadiene (IV). The structure (IV) has been assigned to this product on the basis of spectral data. In its IR spectrum there are the following absorption bands: 2215 (nonconjugated CN group), 1610 and 1650 (C=C stretching vibrations), and 970 cm^{-1} (trans-CH=CH deformation vibrations). An analysis of the mass spectrum of this product does not contradict the structure (IV) (Table 2).

We should note that 2,4,6-octatrienal under analogous conditions forms only the cyanenamine (II).

Starting from the set of data we have obtained, we have attempted to elucidate the course of the reaction of α,β-unsaturated aldehydes with diethylamine and excess acetone cyanohydrin. For this purpose, we added molar quantities of diethylamine and acetone cyanohydrin to the aminonitrile (Ia) at room temperature, then heated the reaction mixture for 1 h, and left it for 1 day at ≈20°C. After treatment and vacuum distillation, a product was obtained that was identical to (IIIa) according to GLC and the PMR spectrum. This same product is also obtained without heating, but much more slowly (reaction course monitored by GLC). Thus, on the basis of the data obtained previously [1, 2] and the data that we have obtained in the example of crotonaldehyde, we can postulate the following scheme for the reaction of α,β-unsaturated aldehydes with diethylamine and excess acetone cyanohydrin:



EXPERIMENTAL

The GLC analysis of the products was performed in an LKhM-8MD-5 chromatograph with a 1.4-m glass column with SE-30, carrier gas nitrogen. The PMR spectra were taken in CCl_4 in a Varian 60-IL instrument relative to HMDS; the IR spectra were taken in CCl_4 in a UR-20 instrument; the UV spectra were taken in alcohol in a Specord spectrophotometer; the mass spectra were taken in a Varian MAT CH-6 mass spectrometer and Varian MAT-111 chromatograph/mass spectrometer.

Reaction of α-β-Unsaturated Aldehydes with Acetone Cyanohydrin and Diethylamine. a) To a mixture of the aldehyde with an equimolar quantity of acetone cyanohydrin, an equimolar quantity of diethylamine was added with stirring at ≈20°C. A moderately exothermic reaction was observed. After a certain time (see Table 1), the mixture was treated with water and extracted with ether; the extract was dried with $MgSO_4$, the solvent was driven off, and the residue was distilled.

b) To a mixture of the aldehyde and a fourfold excess of acetone cyanohydrin, an equimolar quantity of diethylamine was added dropwise with stirring. The mixture was heated at a certain temperature for a certain length of time (see Table 1). The reaction mixture was treated as described above. The yields and characteristics of the products are listed in Table 1.

CONCLUSIONS

1. Conjugated monoene and diene aldehydes react with equimolar quantities of acetone cyanohydrin and diethylamine, giving β,γ-unsaturated cyanamines. With excess acetone cyanohydrin, these cyanamines are subsequently hydrogenated, forming 3,3-substituted 3-cyanoaminonitriles.

The analogous reaction of a triene aldehyde does not depend on the quantity of acetone cyanohydrin; the reaction leads to the cyanenamine.

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