THE CHEMISTRY OF ETHYLENEIMINE

V. Derivatives of β-Hydroxyethylhydrazine Sulfate and Their Transformation under Conditions of the Wenker Synthesis*

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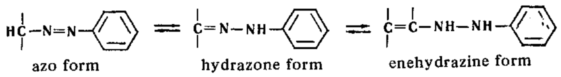
The structure of the products of the reaction of β-hydrazinoethyl hydrogen sulfate with aldehydes has been studied. In an alkaline media, the condensation products are converted into hydrazones of N-aminoethyleneimine or the corresponding azines. The structure of the cyclization products was shown by UV, IR, and PMR spectroscopy.

Preceding communications of this series have been devoted to the reactions of N-aminoethyleneimine with carbonyl compounds [1] and acid chlorides [2]. The present paper is devoted to a study of the structure and properties of compounds with the general formula $RCH=N-NHCH_2CH_2OSO_3H$ (I) obtained by the reaction of β-hydroxyethylhydrazine sulfate (II) with aromatic aldehydes.

The reaction of II with aldehydes was carried out at room temperature in aqueous ethanol. In view of the acid nature of II, it was unnecessary to use protolyzing catalysts to accelerate the condensation.

The characteristics of the compounds synthesized are given in Table 1. Ideas on the structure of I have undergone various changes in the course of the last few years. Fischer [3], Bieltz [4], and, comparatively recently, other workers [5-7], considered that the tautomeric transformation of the arylhydrazones in the following way



was likely.

Table 1. $RCH=N-NHCH_2CH_2-OSO_3H$

Compound	R	Color	Mp, °C	Empirical formula	Found, %				Calculated, %			
					C	H	N	S	C	H	N	S
III	C_6H_5—	White	150	$C_8H_{11}N_2SO_4$	44,30	4,90	11,60	13,30	44,26	4,93	11,50	13,10
IV	*m*-$O_2NC_6H_4$—	Yellow	190	$C_8H_{10}N_3SO_8$	37,27	3,52	14,50	11,20	37,37	3,81	14,53	11,07
V	*p*-$O_2NC_6H_4$—	Light yellow	204	$C_8H_{10}N_3SO_8$	37,50	3,92	14,56	11,24	37,37	3,81	14,53	11,07
VI	*p*-$(CH_3)_2NC_6H_4$—	Red	200	$C_{10}H_{16}N_3SO_4$	45,87	5,86	14,50	11,50	45,99	5,92	14,63	11,15
VII	3,4-$(CH_3O)_2C_6H_3$—	Yellow	196	$C_{10}H_{15}N_2O_6S$	43,99	4,17	9,31	10,65	44,30	3,36	8,40	10,74
VIII	2-C_9H_6N—*	Yellow	202	$C_{11}H_{12}N_3O_4S$	48,53	4,79	13,98	10,34	48,81	4,41	14,24	10,85
IX	4-HOOC-2-C_9H_5N—*	Yellow	207	$C_{12}H_{12}N_3SO_6$	44,21	4,07	12,02	8,76	43,70	4,20	11,76	8,96

*Quinoline derivatives.

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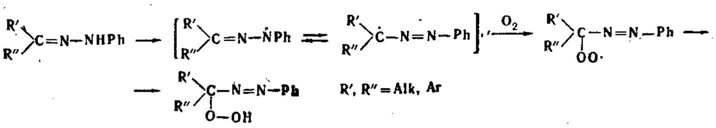
*For part IV, see [1].

At present, it has been shown that such a type of tautomeric equilibrium of the phenylhydrazones does not in fact exist. The observed transformations of the arylhydrazones are due not to their tautomerism but to the active intervention of atmospheric oxygen, leading to the formation of hydroperoxides with an azo structure [8, 9]:



The UV, IR, and PMR spectra of the compounds (I) synthesized show that they are true β-(hydroxysulfonyloxy)hydrazones. This is shown by the presence in the IR spectra of III-IX (see Table 2) of medium-intensity absorption bands in the 1630-1610 cm^{-1} region which must be ascribed to the stretching vibrations of the C =N bond.

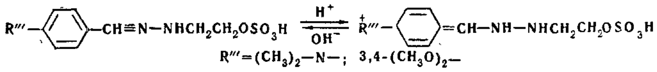
Table 2. Frequencies of the Stretching Vibrations of the Azomethine Bond in the IR Spectra of $RCH=N-NHCH_2 \cdot CH_2OSO_3H$

Compound	R	$\nu_{C=N}$, cm^{-1}
III	C_6H_5	1622
IV	m-$NO_2C_6H_4$	1617
V	p-$NO_2C_6H_4$	1620
VI	p-$(CH_3)_2NC_6H_4$	1610
VII	3,4-$(CH_3O)_2C_6H_3$	1615
VIII	2-C_9H_6N	1625
IX	4-HOOC-2-C_9H_5N	1627

It must be mentioned that the frequency of the stretching vibrations of the azomethine bond in III-IX is 10-30 cm^{-1} lower than in compounds in which the possibility of conjugation with the C =N is absent. Apparently, in the compounds considered conjugation takes place between the π-electrons of the azomethine bond and the unshared pair of electrons of the second nitrogen atom, and also with the π-electrons of the benzene ring (the orbitals of the π-electrons of the azomethine bond and of the p-electrons of the second nitrogen atom are parallel).

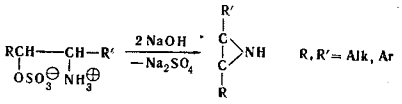
The existence of an intramolecular interaction of the π-p-π conjugation type is also shown by the electronic spectra of these substances. Characteristic maxima in the 260-360 nm region are observed in the spectra of all the compounds containing the >C =N−NH− grouping [10-18].

With a change in the pH of solutions of the hydrazones mentioned, the intensities and positions of the absorption bands in the UV spectra change sharply. Thus, in the spectra of VI and VII, containing electron-donating substituents in the aromatic ring, on passing from pH 11 to pH 1 a bathochromic shift is found (Fig. 1). This is obviously due to the fact that in acid solutions VI and VII have the quinoid structure:

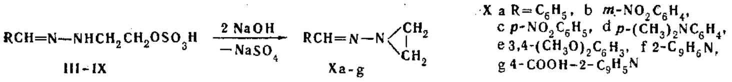


In the case of electron-accepting substituents, a similar shift is observed at pH 11 (Fig. 2).

In order to obtain ethylenimine derivatives, we have studied the behavior of III-IX under the conditions of the Wenker synthesis, i.e., the cyclization of β-aminoalkyl sulfate derivatives according to the equation:



Aqueous solutions of NaOH and Na_2CO_3 and triethylamine were used as the cyclizing agents. When a modified Wenker synthesis is performed, the main reaction leading to the formation of a three-membered nitrogen-containing heterocycle is the cleavage of the C−O bond under the action of caustic soda with the formation of sodium sulfate and subsequent intramolecular alkylation at the nitrogen atom, which is present in the state of sp^3 hybridization.



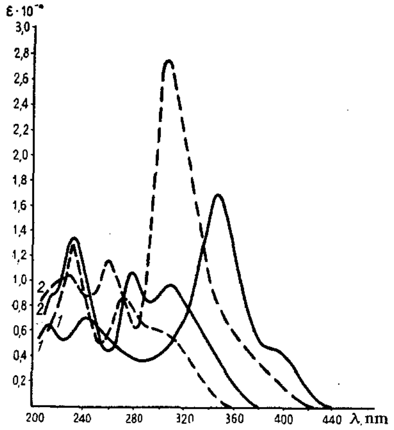


Fig. 1

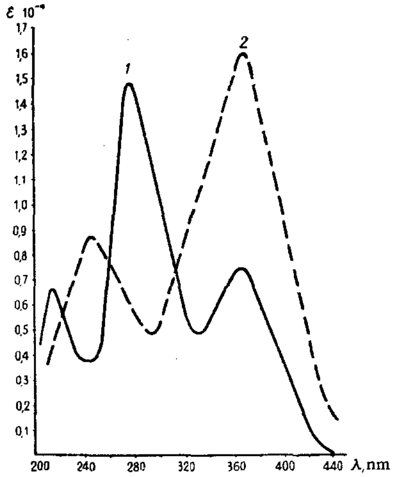
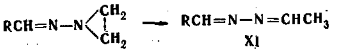


Fig. 2

Fig. 1. UV spectra of $RR'C_6H_3CH=N-NHCH_2CH_2OSO_3H$: 1) $R=p-(CH_3)_2N-$; $R'=H$. 2) $R=3-CH_3O-$; $R'=4-CH_3O$; -- pH 1; --- pH 11.

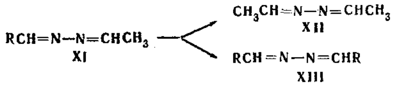
Fig. 2. UV spectrum of $p-O_2NC_6H_4CH=N-NHCH_2CH_2OSO_3H$: 1) pH 1; 2) pH 11.

We established that the main cyclization reaction is accompanied by a number of side reactions complicating the preparation of individual substances. Thus, for example, we observed the intramolecular rearrangement of compounds Xa-g with opening of the ethylenimine ring and the formation of a mixed azine, which is in harmony with the results given in our previous papers [19].



$$RCH=N-N{<}\begin{smallmatrix}CH_2\\|\\CH_2\end{smallmatrix} \rightarrow \underset{XI}{RCH=N-N=CHCH_3}$$

In view of the capacity of such azines with structure XI for further conversions, it may be expected that the disproportionation of XI could form the symmetrical azines XII and XIII in the following way:



$$\underset{XI}{RCH=N-N=CHCH_3} \begin{smallmatrix}\nearrow \underset{XII}{CH_3CH=N-N=CHCH_3}\\ \searrow \underset{XIII}{RCH=N-N=CHR}\end{smallmatrix}$$

A study of the structure of the substances formed together with X in the cyclization of III-IX by means of modern physical methods confirms the correctness of this scheme.

Thus, when an aqueous solution of the initial N-benzylidene-N'-(hydroxysulfonyloxyethyl)hydrazine (III) was added to a boiling solution of caustic soda with the simultaneous distillation of water, the distillate contained a water-immiscible liquid. Its IR spectrum had the characteristic frequencies of the ν_{CH_2} stretching vibrations of $N{<}\begin{smallmatrix}CH_2\\|\\CH_2\end{smallmatrix}$ at 3007 and 3080 cm^{-1} and the δ_{sCH_2} deformation vibrations of $N{<}\begin{smallmatrix}CH_2\\|\\CH_2\end{smallmatrix}$ at 1295 cm^{-1}, which may indicate the structure of benzaldehyde ethylenehydrazone (Xa).

However, after a study of the PMR spectrum of the liquid under analysis, the conclusion that it was an individual compound with the structure Xa proved to be erroneous. The PMR spectrum contains signals showing not only the presence of methylene protons of an aziridine ring (multiplet with $\tau=8.0$ ppm) but also a doublet with $\tau=8.03$ ppm due to the protons of a methyl group (Fig. 3). This shows that the liquid analyzed is a mixture of compounds with structures Xa and XIa.

A particular feature of the PMR spectrum of this sample is the increase in the absorption of the azine XIa with time, while the proportion of absorption due to the hydrazone Xa falls. This rise, monitored from the change in the ratio

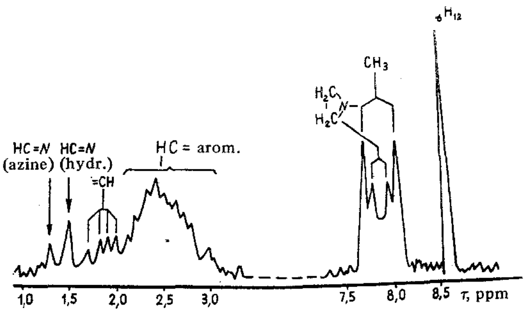


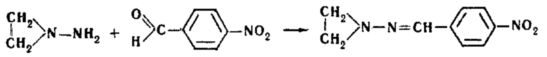
Fig. 3. PMR spectrum of $C_6H_5CH{=}N{-}N\begin{smallmatrix}CH_2\\ |\\ CH_2\end{smallmatrix}$.

of the intensities of absorption of the corresponding singlets at $\tau = 1.38$ ppm and $\tau = 1.55$ ppm is characterized by a change in the hydrazone–azine ratio, equal at first to 1 : 1, to 1 : 3 after the mixture had been heated for 1.5 hr at 80°C. This is a good illustration of the ease of isomerization of benzaldehyde ethylenehydrazone Xa.

The preparative isolation of the main cyclization product Xa encounters great difficulties because of its thermal instability. It proved to be possible only when using a high vacuum (0.01 mm).

The bulk of the distillate collected proved to be benzaldehyde ethylenehydrazone (Xa), as was shown by determining its elementary composition and by the physical methods mentioned above. Compound XIIIa was isolated from the still residue by crystallization. Its UV and IR spectra proved to be identical with the spectra of benzaldehyde azine obtained by independent synthesis. The lightest fraction consisted of acetaldehyde, the formation of which we envisage by the isomerization of Xa in the manner shown on p. 431. The identity of this fraction with XII was shown by gas-liquid chromatography and by spectroscopy.

The cyclization of p-nitrobenzaldehyde hydroxysulfonyloxyethylhydrazone (V) gave a red-brown substance with a high melting point having the composition $C_9H_9N_3O$. However, its physicochemical constants differed sharply from those of p-nitrobenzaldehyde ethylenehydrazone, which has the same composition, obtained by independent synthesis in the following way:



The IR spectra of Xc showed that its molecule does not contain an aziridine ring. The compound underwent no change on prolonged boiling in hydrochloric acid. These results permit the assumption that the end-product of the conversion of V under the conditions of the Wenker reaction is a product of the further condensation of Xc. The extremely low solubility of this compound in organic solvents does not permit its structure to be established definitively.

In contrast to III-V, the other initial hydrazones listed in Table 2 do not give compounds of the type of benzaldehyde ethylenehydrazone under the conditions of the Wenker reaction but the corresponding symmetrical azines. The structures of XIIId-g were shown by the agreement of their physical and spectroscopic characteristics with those of the products of independent syntheses.

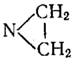
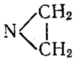
The formation of these compounds apparently takes place through the intermediate stage of the initial formation of X. In favor of this statement is the detection of acetaldehyde azine in the products of cyclization of V-IX under the conditions of the Wenker synthesis. It can be formed only if the isomerization of X into a mixture of symmetrical azines takes place.

EXPERIMENTAL

Aromatic aldehyde (hydroxysulfonyloxy)ethylhydrazones. With stirring, 0.1 mole of the appropriate aromatic aldehyde was added to a solution of 16 g (0.1 mole) of β-hydroxyethylhydrazine sulfate in 50 ml of water and 10 ml of ethanol. After some time, a precipitate separated out which was filtered off. Compounds III-IX were recrystallized from ethanol.

The physicochemical constants of the compounds synthesized are given in Table 2.

Benzaldehyde ethylenehydrazone. An aqueous solution of 12 g (0.05 mole) of III was added to a boiling solution of caustic soda. The rate of addition of the solution of III was determined by the rate of collection of distillate. The organic layer formed in the aqueous solution was separated off and dried over sodium sulfate. The purity of the reaction product was determined by gas-liquid chromatography ("Tsvet-1" chromatograph) with a katharometer as the detector and 10% of PEG-1500 and 0.1% of KOH on Chromosorb W as the stationary phase with a column 6 m long, a thermostat temperature of 180°C and an evaporator temperature of 220°C, J =150 mA and helium as the carrier gas at a rate of feed of 46.6 cm^3/min. Bp 172-173°C; n_D^{20} 1.5920; d_4^{20} 0.9648. Found %: C 73.90; H 6.79; N 19.19. $C_9H_{10}N_2$. Calculated %: C 73.97; H 6.37; N 19.16.

m-Nitrobenzaldehyde ethylenehydrazone. To 14 g (0.05 mole) of IV dissolved in 100 ml of water was added 50 ml of 14% caustic soda solution and the mixture was heated at 60°C for 2 hr. The precipitate was filtered off and recrystallized from ethanol. Mp 194-196°C. IR spectrum: νCH_2  $N\Big\langle\begin{array}{l}CH_2\\ |\\ CH_2\end{array}$ 3040 cm^{-1}, $\delta_S CH_2$  $N\Big\langle\begin{array}{l}CH_2\\ |\\ CH_2\end{array}$ 1295 cm^{-1}. Found %: C 56.30; H 5.04; N 21.89. $C_9H_9N_3O$. Calculated %: C 56.51; H 4.70; N 22.04.

The cyclization of p-nitrobenzaldehyde (hydroxysulfonyloxy)ethylhydrazone was carried out under similar conditions. Mp 420°C (decomp.).

The end-products obtained in the analogous reactions of the hydrazones VI-IX were the symmetrical azines of the corresponding aldehydes and acetaldehyde azine (Table 3).

Table 3. RCH =N−N =CHR

Compound	R	Mp, °C	Empirical formula	Found, %			Calculated, %		
				C	H	N	C	H	N
XIIId	p-$(CH_3)_2NC_6H_4$	264—266	$C_{18}H_{22}N_4$	73.71	7.71	19.21	73.50	7.50	19.00
XIII e	3,4-$(CH_3O)_2C_6H_3$	221	$C_{18}H_{20}N_2$	65.40	6.34	8.48	66 00	6.10	8.40
XIII f	2-C_9H_6N	273—275	$C_{20}H_{14}N_4$	77.96	5.58	18.32	77.41	9.51	18.08
XIII g	4-$HOOC_9H_5N$	249—250	$C_{22}H_{14}N_4O_2$	64.24	3.64	14.21	64.37	3.52	14.07

p-Nitrobenzaldehyde ethylenehydrazone. With stirring, 3 g (0.05 mole) of N-aminoethyleneimine was added to a solution of 7.6 g (0.05 mole) of p-nitrobenzaldehyde in 50 ml of ethanol. The mixture was kept at 80°C for 4 hr. The crystals that separated out when it was cooled were recrystallized from ethanol. Mp 152-154°C. PMR spectrum: CH_2, 7.78 ppm (broadened singlet); CH =N, 1.50 ppm; C_6H_4, 3,5-H, 2.21 ppm, 2,6-H 1.81 ppm (AA'BB' multiplet). Found %: C 56.42; H 4.86; N 21.88. $C_9H_9N_3O_2$. Calculated %: C 56.52; H 4.70; N 22.04.

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