THE CHEMISTRY OF ETHYLENEIMINE

IV. Heterolysis of the Ring of N-Aminoethyleneimine Under the Action of Sulfonyl Halides*

S. A. Hiller, A. V. Eremeev, M. Yu. Lidak, and V. A. Pestunovich

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 1, pp. 8–11, 1970

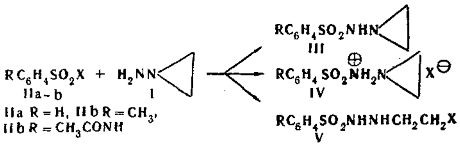
UDC 547.717:543.422.4.6:541.67

The reaction of N-aminoethyleneimine (I) with substituted benzenesulfonyl chlorides (II) has been studied. The main products of the heterolysis of the ring are substituted N'-(β-chloroethyl)benzenesulfonohydrazides (V). The structure of V has been shown by IR, UV, and PMR spectroscopy, and also by independent synthesis.

As is well known, with cyclic amines (piperidine, pyrrolidine, azetidine, aziridine) in the presence of alkaline agents binding hydrochloric acid, carboxylic acid chlorides form the corresponding amides [1–5]. Of the heterocycles mentioned only the amidinium cation of the last one, formed where proton-accepting agents are absent, possesses inadequate stability because of internal stress and undergoes ring opening with the formation of β-halogen-substituted ethylamides [6–8].

Continuing our investigations in the field of the chemistry of N-aminoaziridine [9, 10] it appeared of interest to study the behavior of the aziridine ring in this reaction, since the strength of its bond is increased somewhat through conjugation with the unshared electron pair of the nitrogen of the N-amino group.

In an attempt to carry out the reaction of N-aminoaziridine (I) with a representative of the most active group of acylating agents, sulfonyl halides, we unexpectedly obtained immediately well-crystallizing products, while numerous investigators before us, carrying out the similar reaction with ethyleneimine, have reported the formation of only resinous polymeric substances [11–15]. As can easily be seen from the scheme given here, the product of the reaction of N-aminoethyleneimine with arenesulfonyl halides may possess one of structures III–V:



So far as concerns their structure, judging from their electronic spectra which are extremely similar to those for the corresponding substituted benzenesulfonamides, it may be concluded, according to the literature [16], that the reaction products are substituted arenesulfonohydrazides possessing one of the proposed structures.

The choice between them can be made on the basis of an analysis of their PMR spectra, from which it can be seen that there are no signals characteristic for the protons of an aziridine ring in the PMR spectra of the products of the reaction of I with either benzenesulfonyl chloride (IIa) or with p-toluenesulfonyl chloride (IIb) (table).

The spectrum of each of the compounds studied has a multiplet of the AA'BB' type in the 6.1–6.6 ppm region a comparison of the intensity of which with the resonance of aromatic protons shows that these signals belong to the protons of two methylene groups. The chemical shifts of the protons of one of the methylene groups (weak field) in the spectrum of Va (6.27 ppm) and in that of Vb (6.25 ppm) are close to those in the PMR spectrum of 2-chloroethylamine (τ_{CH_2Cl} = 6.35 ppm) [17]. It follows from what has been said that the structure of the reaction products can correspond only to formula V. The considerable paramagnetic shift of the resonance of the N-methylene protons in the spectra of these compounds as compared with the corresponding signal in the spectrum of 2-chloroethylamine ($\tau_{N—CH_2}$ = 7.08 ppm) is due, in the first place, to the influence of the SO_2 group and to the contribution of the ring currents in the aromatic rings of these molecules. The position of the remaining lines in the PMR spectra of the products investigated

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*For part III, see [23].

(table) is also in good agreement with structure V.

Chemical Shifts of the Protons in the PMR Spectra (40 MHz, Internal Standard C_6H_{12}).

Compound	Solvent	Chemical shifts, τ ppm				
		NCH_2	CH_2Cl	CH_3	NH	aromatic proton
$C_6H_5SO_2NHNHCH_2CH_2Cl$	Dimethyl sulfoxide	6.67	6.27	—	5.16	2.25 (center)
p-$CH_3C_6H_4SO_2NHNHCH_2CH_2Cl$	Chloroform	6.70	6.25	7.54	—	2.27 (2.6-H) 2.61 (3.5-H) $J=8.5$ Hz

A further confirmation of the **structure** as that of an N'-(βchloroethyl)-benzenesulfonohydrazide is formed by the vibrational spectra of compounds Va–Vc, which were studied in the 400–3600 cm^{-1} region. They are characterized by the absence of C—H stretching vibrations in the 3010 and 3080 cm^{-1} regions and of ring deformation vibrations at 1210 and 857 cm^{-1}, which are characteristic for three-membered rings. These spectra contain characteristic frequencies of aromatic C—H bonds in the 3033 and 2986 cm^{-1} regions and of CH_2 groups at 1475 cm^{-1}. The symmetrical and antisymmetrical vibrations of the SO_2 group for these compounds appear in the form of high-intensity bands at 1336–1320 and 1150–1165 cm^{-1}, which is in agreement with literature data [18–21].

For a definitive proof of the structure V deduced from an analysis of the PMR and vibrational spectra, we performed an independent synthesis of Va–Vc. For this purpose we first synthesized the hydrochlorides of β-chloro-, β-bromo-, and β-iodoethylhydrazines (VIa, VIb, and VIc) by the action of the corresponding hydrogen halides on N-aminoethyleneimine. Compounds VIa and VIb, in contrast to VIc, proved to be stable and nonhygroscopic products undergoing no change on storage.

The action on VIa of the substituted arenesulfonyl halides IIa and b gave substances completely identical with the products of the direct heterolysis of I by II:

$$\underset{\text{IIa, b}}{RC_6H_4SO_2Cl} + \underset{\text{VIa}}{ClCH_2CH_2NH\overset{\oplus}{N}H_3Cl^{\ominus}} \xrightarrow{NaOH} \underset{\text{V}}{RC_6H_4SO_2NHNHCH_2CH_2Cl}$$

$$\text{IIa } R=H,\ \text{IIb } R=CH_3$$

Products Va–Vc formed colorless crystalline compounds but in time (on prolonged storage under ordinary conditions) they decomposed with the formation of oily liquids. The vacuum distillation of the latter gave deeply-colored products. The IR spectra of these substances showed previously-lacking bands in the 1575 cm^{-1} region which are characteristic for the N=N bond. When the colored decomposition products were hydrolyzed, benzenesulfonic acid could be isolated from the reaction mixture. It is an interesting fact that the action of bromine on an ethanolic solution of N'-(β-chloroethyl)benzenesulfonohydrazide formed a similar deeply colored oily liquid.

From what has been said the preliminary conclusion can be drawn that in the air the N'-(β-chloroethyl)benzenesulfonohydrazides apparently undergo oxidation with the formation of azo compounds.

$$\underset{\text{V}}{C_6H_5SO_2NHNHCH_2CH_2Cl} \xrightarrow{O_2} C_6H_5SO_2N{=}N{-}CH_2CH_2Cl$$

This view is in harmony with the work of other authors who have reported the capacity of symmetrically substituted hydrazines for being converted into the corresponding azo compounds under comparatively mild oxidizing attack [22].

EXPERIMENTAL

N'-(β-Chloroethyl)benzenesulfonohydrazide (Va). With cooling to −10° C and vigorous stirring, a solution of 1.2 g (0.02 mole) of I in 15 ml of absolute ethanol was added to a solution of 3.52 g (0.02 mole) of benzulfonyl chloride in 10 ml of absolute ethanol. After 1 hr, the temperature of the reaction mixture was raised to 20–22° C and it was stirred at this temperature for another 2 hr. A crystalline product deposited, and this was separated off in an inert gas atmosphere and dried in a desiccator. It was recrystallized from ethanol, mp 103–105° C. Found, %: C 40.85; H 4.51; N 12.12; S 13.61; Cl 15.67. Calculated for $C_8H_{11}ClN_2O_2S$, %: C 40.91; H 4.68; N 11.93; S 13.63; Cl 15.13. Determination of Cl by the Volhard method: 15.29. Equivalent molecular weight 239.

N'-(β-Chloroethyl)-p-toluenesulfonohydrazide (Vb). With cooling to −10° C and vigorous stirring, 1.16 g (0.02 mole) of I in 10 ml of absolute ethanol was added to a solution of 3.82 g (0.02 mole) of p-toluenesulfonyl chloride in 15 ml of absolute ethanol. After the addition of the solution, the reaction mixture was kept at 20–22° C for 30 min. A crystalline precipitate deposited which was separated off in an inert gas atmosphere and dried in a desiccator. After recrystallization, a product with mp 200–201° C was obtained. Found, %: C 39.18; H 5.53; N 10.91; S 12.52; Cl 13.92. Calculated for $C_9H_{13}ClN_2O_2S$, %: C 39.26; H 5.61; N 11.21; S 12.82; Cl 14.26. Determination of Cl by the Volhard method: 14.8%. Equivalent molecular weight 250.91.

N'-(β-Chloroethyl)-p-acetamidobenzenesulfonohydrazide (Vc). This was obtained in a similar manner to the preceding compound from 4.68 g (0.02 mole) of p-acetamidobenzenesulfonohydrazide and 1.2 g (0.02 mole) of N-aminoethyleneimine. It was recrystallized from a mixture of ethanol and ether. White crystalline product with mp 145–147° C. Found, %: C 41.12; H 4.31; N 14.37; S 11.07; Cl 12.40. Calculated for $C_{10}H_{14}ClN_3O_3S$, %: C 41.00; H 4.42; N 14.35; S 10.93; Cl 12.13. Determination of Cl by the Volhard method: 12.16%.

Hydrochloride of β-chloroethylhydrazine (VIa). In an inert gas atmosphere, a solution of 5.8 g (0.1 mole) of I in 50 ml of absolute ethanol was saturated with dry hydrogen chloride. The temperature of the reaction mixture was raised in hourly steps from −30° C to room temperature. The precipitate that deposited was separated off and dried in a desiccator. It was recrystallized from a mixture of ethanol and ether, giving a white crystalline product with mp 34–36° C. Found, %: C 18.24; H 6.18; N 21.41; Cl 54.42. Calculated for $C_2H_7ClN_2 \cdot HCl$, %: C 18.32; H 6.11; N 20.3; Cl 54.19.

Oxidation of N'-(β-chloroethyl)benzenesulfonohydrazide (VIc). With stirring at the boiling point of the solvent, 2 g of bromine was added to a solution consisting of 0.5 g (0.002 mole) of N'-(β-chloroethyl)benzensulfonohydrazide (VIc) in 30 ml of absolute ethanol. After the addition of the bromine, the reaction mixture was kept for 2 hr. Then the cooled solution was evaporated in a rotary evaporator. An oily product was obtained the IR spectrum of which exhibited a band at 1575 cm^{-1} (N=N). On recrystallization from water, benzenesulfonic acid was obtained.

REFERENCES

1. G. Steinbrunn, West German patent no. 851196; C. A. **52**, 10200e, 1958.
2. P. Fleś and A. Markovac-Prpić, Arch. Kem., 27, 211, 1965; C. A., **50**, 11951a, 1956.
3. H. C. Brown and A. Tsukamoto, J. Am. Chem. Soc., 83, 2016, 1961.
4. H. C. Brown and A. Tsukamoto, J. Am. Chem. Soc., 83, 4549, 1961.
5. G. H. Coleman and G. P. Waugh, Proc. Iowa Acad. Sci., **40**, 115, 1933; C. A., **29**, 2527, 1935.
6. H. Bestian, Ann., **566**, 210, 1950.
7. K. Tanaka and T. Sugawa, Japanese patent no. 3489; C. A., **47**, 5963e, 1953.
8. K. Tanaka and T. Sugawa, J. Pharm. Soc. Japan., **72**, 1548, 1952; C. A., **47**, 86824, 1953.
9. S. A. Hiller, A. V. Eremeev, M. Yu. Lidak, and V. A. Pestunovich, KhGS [Chemistry of Heterocyclic Compounds], **4**, 815, 1968.
10. S. A. Hiller, A. V. Eremeev, M. Yu. Lidak, and V. A. Pestunovich, KhGS [Chemistry of Heterocyclic Compounds], **4**, 818, 1968.
11. E. Plötz and E. Weinharadt, West German patent no. 740723; C. A., **40**, 1170^5, 1946.
12. R. Lehmann and E. Grivsky, Bull. Soc. Chim. Belg., **55**, 52, 1946; C. A., **41**, 5475f, 1947.
13. I. L. Farbenind, Gelgian patent no. 449535; C. A., **42**, 208a, 1948.
14. E. Plötz and E. Weinhardt, West German patent no. 845802; C. A., 48, 7053d, 1954.
15. W. D. Stephens, L. R. Moffett, H. W. Vanghan, W. E. Hill, and S. P. Brown, Chem. Eng. Data, **8**, (4), 625, 1963; C. A., **60**, 485a, 1964.
16. P. G. Grammaticakis, Bull Soc. Chim. Fr., **9**, 93, 1953.
17. P. L. Levins and Z. B. Papanastassion, J. Am. Chem. Soc., **87**, 826, 1965.
18. S. Petoni, Spectrochim. Acta, **9**, 601, 1957.
19. E. A. Robinson, Can. J. Chem., **39**, 247, 1961.
20. N. S. Ham, A. N. Hambby, and R. H. Laby, Austral. J. Chem., **13**, 443, 1960.
21. L. Malewski and H. I. Weigmann, Spectrochim. Acta, **18**, 725, 1962.
22. D. M. Lemal, F. Menger, and Coata, J. Am. Chem. Soc., **86**, 2395, 1964.
23. S. A. Hiller, A. V. Eremeev, and M. Yu. Lidak, KhGS [Chemistry of Heterocyclic Compounds], **6**, 3, 1970.

1 March 1967

Institute of Organic Synthesis AS Latvian SSR, Riga