and washed with a small amount of EtOH, yielding compound (VIIId). An analytical product was prepared by recrystallization from EtOH.

Ketenaminals (VIIIf, g). A mixture containing 0.01 mole DKAs (VIIIc, d) and 0.01 mole MeONa in 20 ml MeOH was stirred at 20°C for 45 min, and 0.01 mole AcOH was added dropwise. The solvent was evaporated; $CHCl_3$ was added to the residue, which was filtered through SiO_2 (eluent, $CHCl_3$). The solvent was evaporated, and the crystalline residue was washed with hexane, yielding compounds (VIIIf, g). An analytical product was prepared by recrystallization from benzene. Compound (VIIIf) was obtained in a yield of 82% and was identical to the one synthesized earlier from acetylacetone and cyanamide [12].

The yields, elemental analysis data, and physicochemical characteristics of DKAs (VIIIa-d, g) and AKAs (IXa-d) are shown in Table 1; ^1H and ^{13}C NMR spectral data for these compounds are presented in Tables 2 and 3, respectively.

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N,N'-DIALKYL-N,N'-DINITROSULFODIAMIDES

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N,N'-dinitrosulfodiamides are formed in the nitration of sulfodiamides with concentrated nitric acid or nitronium borofluoride, and also on substitutional nitration of the corresponding N,N'-di-tert.-butyl derivatives with those reagents. Sulfuryl chloride reacts with the disodium salt of ethylene N,N'-dinitramine to produce 2,5-dinitro-1,2,5-thiadiazolidine-1,1-dioxide. The corresponding N-nitrosulfamides are formed when nitramine salts react with methane sulfochloride.

There is only scanty and conflicting published evidence on the preparation of N,N'-dinitrosulfodiamides (DNSDA). In [1], N,N'-dimethyl-DNSDA (IIa) was described as a solid substance, but in [2] it was considered to be a liquid. In [3], it was reported that a cyclic DNSDA had been made: 2,5-dinitro-1,2,5-thiadiazolidine-1,1-dioxide. It is doubtful whether that structure is correct however, since the compound claimed in [3] as 1,2,5-thiadiazolidine-1,1-dioxide has been shown [4] not to be such.

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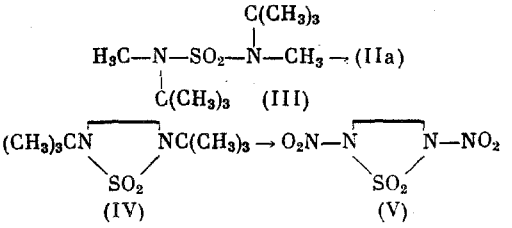
TABLE 1. DNSDA Synthesis by Sulfodiamide Nitration

Initial compound	Nitrating agent	DNSDA	Yield, %	Mp, °C
(Ia)	HNO_3	(IIa)	84	89–89.5 (benzene–hexane, 1:1)
	NO_2BF_4		58	
(III)	HNO_3		70	
(Ib)	HNO_3	(IIb)	74	58 (ethanol)
	NO_2BF_4		71	
(Ic)	NO_2BF_4	(IIc)	89	57 (ethanol)
(IV)	HNO_3	(V)	84	125–126 with decomposition (ethanol)

$$RNHSO_2NHR' \rightarrow RNSO_2NR'$$
$$\qquad\qquad\qquad\qquad\quad NO_2\ NO_2$$
(Ia–b) (IIa–c)

R = R′ = CH_3 (a); R = R′ = C_2H_5 (b); R = CH_3, R′ = C_2H_5 (c).



Here we examine two ways of making DNSDA: nitrating sulfamide derivatives and reacting nitramine salts with SO_2Cl_2. The compounds can be made by nitrating N,N'-dialkylsulfodiamides (Ia-c) directly with concentrated HNO_3 or NO_2BF_4, or by substitutional nitration based on the same reagents and the N,N'-di-tert.-butyl derivatives of sulfamides (III) and (IV) (Table 1).

Compound (IIa) was identical with that made in [1], while the parameters of (V) did not agree with those of the compound assigned that structure in [3], as would be expected.

The structures of (IIc) and (V) were confirmed by structure analysis. The thiadiazolidine ring in (V) has the twist conformation, with the C atoms diverging from the NSN plane to opposite sides by −0.28 and +0.35 Å. The nitramine groups are approximately parallel to the median plane of the heterocycle; the SNNO torsion angles are −19.8 and −21.3° (Fig. 1). The bond lengths and angles in (IIc) are close to the standard values (Fig. 2). The local symmetry in the molecule, apart from the terminal methyl group, is close to C_2, with the twofold rotation axis passing through the sulfur atom and the bisector of the OSO angle. In (IIc) and (V) crystals, the molecules are linked by Van der Waals forces.

DNSDA could be made in the second way only from the disodium salt of ethylene-N,N'-dinitramine (VI). When (VI) reacts with SO_2Cl_2, one obtains (V) with a yield of about 40%. In reactions of SO_2Cl_2 with the sodium salts of methylnitramine and ethylnitramine, the corresponding DNSDA were not observed. At the same time, the reaction between (VI) or the Na salt of methylnitramine with methane sulfochloride gives the corresponding N-sulfonation products (VII and VIII) with yields of about 50%. At ∿20°C, the reaction occurs over a few days. If on the other hand the methane sulfochloride is reacted with the ethylene-N,N'-dinitramine or methylnitramine in the presence of NEt_3, one gets (VII) and (VIII) with higher yields after a few hours:

$$\underset{\text{(VII)}}{CH_3SO_2N(NO_2)CH_2CH_2N(NO_2)SO_2CH_3} \qquad \underset{\text{(VIII)}}{CH_3SO_2N(NO_2)CH_3}$$

It is suggested that the first stage in the reaction between SO_2Cl_2 and the nitramine salts occurs, but the resulting N-alkyl-N-nitrosulfochloride in each case reacts with a second molecule of the salt not on the amine nitrogen but on for example the nitro group oxygen, which prevents the formation of DNSDA. In (VI), the second stage is facilitated by the formation of a five-membered ring transition state.

EXPERIMENTAL

The PMR spectra were recorded with a Tesla BS-467, while the IR spectra were recorded with a Zeiss UR-20 on KBr disks.

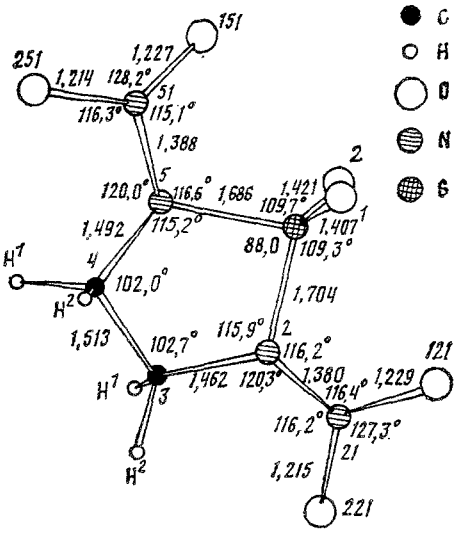


Fig. 1. Projection of the (V) molecule on the N^1SN^2 plane (N^5SO^1 113.8°, N^2SO^2 112.8°, O^1SO^2 119.0°).

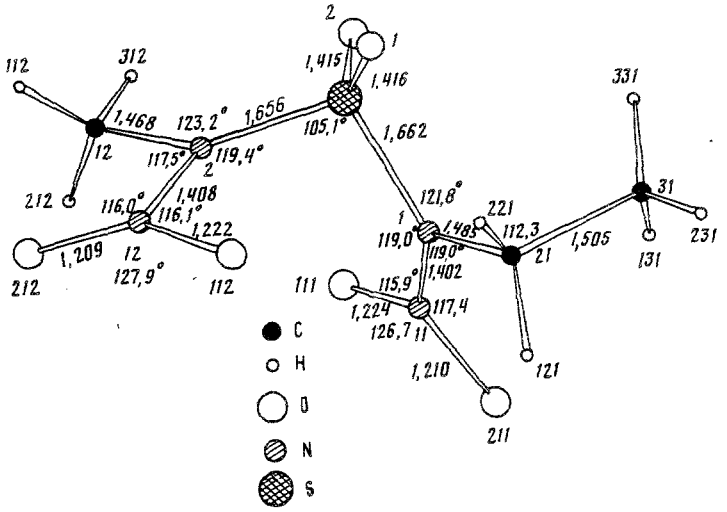


Fig. 2. Projection of the (IIc) molecule on the plane of the N^1SN^2 atoms (N^2SO^1 111.3°, N^2SO^2 104.9°, O^1SO^2 121.1°, N^1SO^1 103.7°, N^1SO^2 110.8°).

Crystals of (IIc) and (V) were examined by x-ray diffraction with a four-circle Syntex diffractometer (Mo radiation, graphite monochromator). We measured 1956 reflections for (IIc) and 1571 for (V), of which 1257 and 1399 correspondingly were observable. The structure was interpreted and the coordinates of the S, C, N, and O atoms were refined in the anisotropic approximation by means of a minicomputer on the EXTL software suite. The final R_f were 0.048 and 0.049. The accuracy in the bond lengths was ±0.003-0.005 Å and in the bond angles ±0.2-0.4°.

The (V) crystal is monoclinic, unit-cell parameters a = 5.9093(6), b = 12.184(1), c = 10.2053(7) Å; β = 93.266(7)°, V = 733.6(1) Å^3; Z = 4; ρ = 1.921(3) g/cm^3, space group P21/n.

The (IIc) crystal is orthorhombic, a = 9.7013(7), b = 12.617(9), c = 15.1380 Å; V = 1852.9(3) Å^3; Z = 8; ρ = 1.633 g/cm^3, space group Pb ca.

The initial sulfodiamides (Ia-c) and (IV) were made by standard methods [4-6].

General Method of Nitrating Sulfodiamides.* a) To 5.0 ml of concentrated HNO_3 at −15°C we added 0.002 mole of sulfodiamide in small batches and stirred the mixture for 10-20 min

*These DNSDA may decompose explosively on shock.

at −10 to −15°C, after which the mixture was poured into water containing ice and the precipitate was filtered off and washed on the filter with ice water to neutral reaction followed by drying in air and crystallization.

b) To 0.0025 mole of NO_2BF_4 in 15 ml of absolute CH_3CN at −20°C we added 0.001 mole of the sulfodiamide and stirred the mixture for 15 min at the same temperature, followed by pouring into water containing ice and filtering off the precipitate, which was washed with ice water to neutral reaction, dried in air, and crystallized.

The following are the DNSDA characteristics.

(IIa). Found C 11.25; H 2.90; N 26.38; S 15.01%. $C_2H_6N_4O_6S$. Calculated: C 11.21; H 2.80; N 26.17; S 14.95%. PMR spectrum ($CHCl_3$, δ, ppm): 3.73 s. IR spectrum (ν, cm^{-1}): 1200, 1405 (SO_2), 1300, 1605 (NO_2).

(IIb). Found: C 19.75; H 4.01; N 22.89; S 13.01%. $C_4H_{10}N_4O_6S$. Calculated: C 19.83; H 4.13; N 23.14; S 13.22%. PMR spectrum ($CHCl_3$, δ, ppm): 1.37 t (CH_3), 4.25 q (CH_2). IR spectrum (ν, cm^{-1}): 1200, 1405 (SO_2), 1305, 1585, (NO_2).

(IIc). Found: C 16.07; H 3.41; N 24.38; S 13.95%. $C_3H_8N_4O_6S$. Calculated: C 15.79; H 3.51; N 24.56; S 14.04%. PMR spectrum ($CHCl_3$, δ, ppm): 1.38 t (CH_3) 3.77 s (CH_3—N), 4.30 q (CH_2O). IR spectrum (ν, cm^{-1}): 1180, 1400 (SO_2), 1270, 1580 (NO_2).

(V). Found: C 11.57; H 2.03; N 26.27; S 14.95%. $C_2H_4N_4O_6S$. Calculated: C 11.32; H 1.88; N 26.41; S 15.05%. PMR spectrum (acetone-d_6, δ, ppm): 4.47 s. IR spectrum (ν, cm^{-1}): 1200, 1400 (SO_2), 1270, 1600 (NO_2).

Preparation of (V). We mixed 0.7 g of (VI) and 0.3 ml of SO_2Cl_2 in 10 ml of absolute CH_3CN for 5 h at about 20°C and left the mixture to stand overnight. The precipitate was filtered off and the filtrate was evaporated, with the resulting oil treated with 30 ml of $CHCl_3$ and the precipitated crystals filtered off, which were washed on the filter with water to give 0.32 g (42%) of (V). Extraction with ethyl acetate from the aqueous filtrate gave 0.2 g of ethylene-N,N'-dinitramine.

Preparation of (VII). To 0.3 g of ethylene-N,N'-dinitramine in 10 ml of absolute CH_3CN we added on cooling with ice water and stirring 0.56 ml of NEt_3 by drops, and then 0.3 ml of methanesulfochloride at about 20°C, with stirring for 4 h; the precipitate was filtered off and the filtrate was evaporated and treated with water. The precipitate was separated and dried in air, which gave 0.45 g (75%) of (VII), mp 153-157°C (from ethanol). Found: C 15.41; H 3.00; N 17.97; S 20.58%. $C_4H_{10}N_4O_8S_2$. Calculated: C 15.69; H 3.27; N 18.30; S 20.91%. PMR spectrum (δ, ppm, acetone-d_6): 3.58 s (CH_3), 4.45 s (CH_2). IR spectrum (ν, cm^{-1}): 1285, 1565 (NO_2), 1180, 1360 (SO_2).

Preparation of (VIII). To 0.3 g of methylnitramine and 0.6 ml of NEt_3 in 10 ml of absolute CH_3CN at about 20°C we added by drops 0.33 ml of methane sulfochloride in 2 ml of absolute CH_3CN and stirred the mixture for 4 h; the precipitate was filtered off and the filtrate was evaporated, with the residue taken up in ether and the ether solution washed with water and dried with $MgSO_4$. When the ether was evaporated off, we obtained 0.56 g (92%) of (VIII), mp 41-42°C [7]. PMR spectrum (δ, ppm, $CHCl_3$): 3.46 s (SO_2CH_3), 3.52 br.s (CH_3N).

Preparation of (III). We mixed 20 ml of a 50% aqueous solution of NaOH, 20 ml of benzene, 0.5 g of triethylbenzylammonium bromide, 2.08 g of N,N'-di-tert.-butylsulfamide, and 4 ml of dimethyl sulfate for 1.5 h at about 20°C and then added 50 ml of water and stirred for a further 1.5 h. The benzene layer was separated off and the water layer was extracted with 3 × 20 ml of benzene, with the combined benzene extracts washed with water to a neutral reaction and dried over $MgSO_4$. When the benzene was evaporated off, we obtained 2.07 g (88%) of (III), mp 42-43°C (freezing from pentane). PMR spectrum: (δ, ppm, $CHCl_3$): 1.31 s (CH_3C), 2.66 s (CH_3—N). Found: C 50.72; H 10.00; N 12.03; S 13.75%. $C_{10}H_{24}N_2O_2S$. Calculated: C 50.85; H 10.17; N 11.86; S 13.56%.

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ASYMMETRIC NITROGEN. 73.*
GEMINAL SYSTEMS. 47.*
CONFIGURATION STABILITY AND MECHANISM FOR INVERSION OF N-CHLOROXAZIRIDINES

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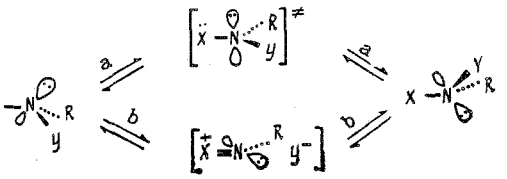
We have studied the kinetics of racemization and thermolysis of (+)-2-chloro-3,3-pentamethyleneoxaziridine (I). The activation energy determined for inversion of the nitrogen atom in (I) in n-heptane is 28.9 kcal/mole lower than the value calculated (ab initio, 3-21G) for 2-chloroxaziridine (II). Based on this and also on the increase in the inversion rate of (I) with an increase in the polarity of the solvent and the entropy of activation (–43.5 cal/mole·K, n-heptane), we conclude that the mechanism for inversion of N-chloroxaziridines is "nonclassical," by means of reversible ionization of the N–Cl bond through a solvate-unseparated ion pair.

N-chloroxaziridines are a new system for studying pyramidal stability of the N atom bonded to two heteroatomic ligands. On the one hand, for these compounds we can expect an extremely high barrier to "classical" inversion through a planar transition state (PTS) (Scheme 1, Route (a)), since upon introduction of a Cl atom to the nitrogen, the already significant enthalpy of activation for inversion of oxaziridines ($\Delta H^{\neq} \sim 34$ kcal/mole [2]) should increase. On the other hand, inversion of nitrogen gem-systems X—N—Y, including N-chloroxaziridines,

can be accomplished according to a "nonclassical" dissociative mechanism, i.e., by means of reversible ionization of the N–Y bond (Scheme 1, Route (b)) [3]. As shown for the example of N-chlorodiaziridines in [4], such a process is characterized by a low value of $\Delta H^{\neq}$ and a large negative entropy of activation ($\Delta S^{\neq}$). The reason for the preferential occurrence of dissociative inversion is weakening of the N–Y bond as a result of n_X–σ_{NY}*-hyperconjugation and its related easy heterolysis in solution [3, 4]



(1)

Hindered inversion of the pyramid of the N atom in N-chloroxaziridines has been observed previously from the ^1H and ^{13}C NMR spectra [5], but the activation parameters were not measured.

In this work, the configurational stability of N-chloroxaziridines has been studied using data on the kinetics of racemization of (+)-2-chloro-3,3-pentamethyleneoxaziridine (I) (Table 1) and a nonempirical quantum-chemical calculation for 2-chloroxaziridine (II). The pyramidal ground state of (II) [5] and the planar transition state PTS-(II) were calculated in the 3-21G basis.

*For the previous communication, see [1].

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